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A Study on the 15 years (2003~2017) Trends of Carbon species in $PM_{2.5}$ in Seoul

서울의 대기 중 초미세먼지 내 탄소화학종의 15년간 농도 변화에 관한 연구

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Abstract

A Study on the 15 years(2003~2017) Trends of Carbon species in $PM_{2.5}$ in Seoul

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This study focuses on the long-term trend of $PM_{2.5}$ and carbon species (Organic Carbon(OC), Elemental Carbon (EC)), one of the major components of $PM_{2.5}$, in Seoul, Korea, with aim of assessing the main correlated factors and potential sources. Ambient $PM_{2.5}$ were collected every third day over a 24-h period in Seoul, Korea using two-channel system from March 2003 to December 2017. The trends of $PM_{2.5}$, OC, EC, POC, SOC and OC/EC ratio were observed at rate of -1.91%/year, -3.02%/year, -6.35%/year, -3.20%/year, -2.62 %/year and -12.56%/year respectively ($p < 0.001$) during the study period. The increasing or decreasing tendency of $PM_{2.5}$ and carbon species was statistically significant from a minimum of 4 years to a maximum of 13 years. It is estimated that the fundamental decrease in $PM_{2.5}$ and its carbon species was more influenced by the reduction of air pollutant emissions than the short-term changes in meteorological factors. As a result of estimating local sources using Conditional Probability Function (CPF), potential sources of $PM_{2.5}$, SOC were estimated to be in the southwest and northwest of the receptor, respectively, while other carbon species were observed to high

probabilities of high concentration events at low velocities (less than 3 m/s) in all directions. As a result of estimating potential sources for long-range-transportation using Potential Source Contribution Function (PSCF), Concentration Weighted Trajectory (CWT), high concentration loading of $PM_{2.5}$ and carbon species were observed mainly in Middle left of the Korean peninsula, Northeast China, Shandong peninsula, Hebei province, Beijing, upper area of east China.

Also, high concentration loading of $PM_{2.5}$ only was observed in Southeast China, which could be a source of secondary inorganic aerosol that contribute significantly to $PM_{2.5}$. Take these aspects into assessing the long-term trends of $PM_{2.5}$ and carbon species in Seoul, it is estimated that the declining tendency has been mainly affected by the combined effect of reducing air pollutant emissions in Korea and whole East Asia. These results are consistent with the concentration levels and periods of the $PM_{2.5}$ and its carbon species of previous short-term study.

This is the first study that statistically evaluate the long-term trends in $PM_{2.5}$ and carbon species on ground-monitoring in Seoul. In order to effective air quality management, it is necessary to continual understand of air pollutant and verifying the achievement of the NAAQS through long-term observation as well as the review of the previous studies results.

Keywords: Fine particulate matter ($PM_{2.5}$), Carbon species, Long term trends analysis, potential source, Conditional Probability Function (CPF), Potential Source Contribution Function (PSCF), Concentration Weighted Trajectory (CWT)

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I. Introduction

Since reported that ambient particulate matter ($PM_{2.5}$, aerodynamic meter < 2.5 μm) has significant impact on the human health effects, visibility reduction, and climate change in various studies, understanding of $PM_{2.5}$ has become an important issue globally. Recent studies have shown that that exposure to ambient particulate matter was the fifth-ranking mortality risk factor in 2015, causing 4.2 million deaths and loss of 103.1 million disability-adjusted life-years world-wide (Cohen et al., 2017).

The major constituents of $PM_{2.5}$ are carbon species, contributing 20–80% to the total mass: Organic Carbon (OC), which contains less volatile and more reflective species, and Elemental Carbon (EC; alternatively referred to as black carbon, BC), which is the less reflective and more light-absorbing component (Poschl, 2005). Also, among other species of $PM_{2.5}$, carbon species have been reported to have a significant impact on human health impact (Baumgartner et al., 2014; Heo et al., 2014; Wagner et al., 2014). Therefore, in order to effective air quality management, it is necessary to understand the air pollutant in terms of chemical constituent and to verify the achievement of the atmospheric environment standard through long-term observation. Several studies on long-term ground observations have reported decreasing trends of $PM_{2.5}$ over long periods in New York, Europe and the Indian Himalayas with different reduction rates since 2000. (Cusack, Alastuey, Perez, Pey, & Querol, 2012; Querol et al., 2014; Rattigan, Civerolo, Felton, Schwab, & Demerjian, 2016; Sarkar, Roy, Chatterjee, Ghosh, & Raha, 2019) On the other hands, Asia is one of the most serious continents with air pollution problems, the number of reported studies for verification of air quality control strategy have been limited by the absence of long-term ground observation. In Korea, there are only one review paper about short term studies to reanalysis the long-term trend, but the consistency of the results data is limited because of the confusion of different sampling location and analysis methods. No studies have been reported to analyze long-term changes in PM2.5 and carbon species based on ground observation. This study focus on long-term trends for $PM_{2.5}$ and its carbon species at major city, Seoul of South Korea, with aim of tracking the main correlated factors and potential sources of long-term period.

II. Experimental Methods

1. Sample collection and analysis

The monitoring site is located on the rooftop of the student hall (37.5◦ N, 127.00◦ E) of Seoul National University Yeongeon campus, residential complex in Jongno-gu, Seoul, Korea. Air samples were collected every third day over a 24-h period using 2-channel system from March 2003 to December 2017. Each channel consists of cyclone (URG-2000-30EH, URG Corp., USA), vacuum pump (WOB-L Pump series, Welch-Gardner Denver Inc., USA) and dry gas meter and filter packs (URG-2000-30FG, URG Corp., USA). The flow rate was monitored for each channel by dry gas meters to provide a particle size cutoff of 2.5μm. The $PM_{2.5}$ mass was measured by weighing the Teflon filter (R2PL047, 47mm diameter, 1μm pore size, Pall Corp., USA) using a microbalance (CPA225D, Sartorius, Japan) with sensitivity ± 0.01 mg. The sampling for carbon species in $PM_{2.5}$ was collected in Quartz microfiber filters (7202, 47mm diameter, TISSUE QUARTZ 2500 QAT-UP, Pall Corp., USA) which were pre-baked at 450℃ for 12 hours to minimize background carbon. The analysis of carbon species was quantitatively analyzed with OC and EC using the carbon analyzer (Lab OC-EC Aerosol Analyzer model4L, Sunset Lab. Inc., USA) and quantitatively analyzed with OC and EC based on the NIOSH 5040 protocol TOT (Thermal Optical Transmittance) method.

The accuracy of the $PM_{2.5}$ mass concentration, for the period 2003-2007, QA/QC procedures such as verification of measurement recovery rate and blank filter correction were applied. Also, the accuracy for this period was cross-verified through several comparative-analysis with other studies. However, in the period of 2008-2017, the interval of data was sporadic and comparative verification with other studies was relatively insufficient. In order to correct the $PM_{2.5}$ mass concentration accuracy in this period, the mass concentration was calibrated with a correction factor (= 1.282) derived from a comparison of the $PM_{2.5}$ mass concentration with the $PM_{2.5}$ values of national air pollutant observation network (β-ray measurement, located 1 km from the sampling site) for the period 2003-2007.

2. Synoptic meteorological data, Ambient Gaseous materials data

Automatic Weather Station (AWS) for monitoring the synoptic meteorological data is located in Jongno-gu, Seoul, 2.3 km southeast of the ambient $PM_{2.5}$ sampling site. Hourly meteorological data was monitored by using different sensors over the study period. Hourly data of ambient gaseous materials (CO, O_3, NO_2, SO_2) and ambient PM_{10} was monitored at 24 national air pollutant monitoring networks in Seoul during the study period. In order to estimate the trend of concentration change in the whole city of Seoul, the hourly measurements at 24 stations were arithmetically averaged (Air korea, http://www.airkorea.or.kr/realSearch). Hourly data of ambient Volatile organic compounds (VOCs) was monitored at only Bulgwang-dong station, one of the national air monitoring networks in Seoul from 2006 to 2016.

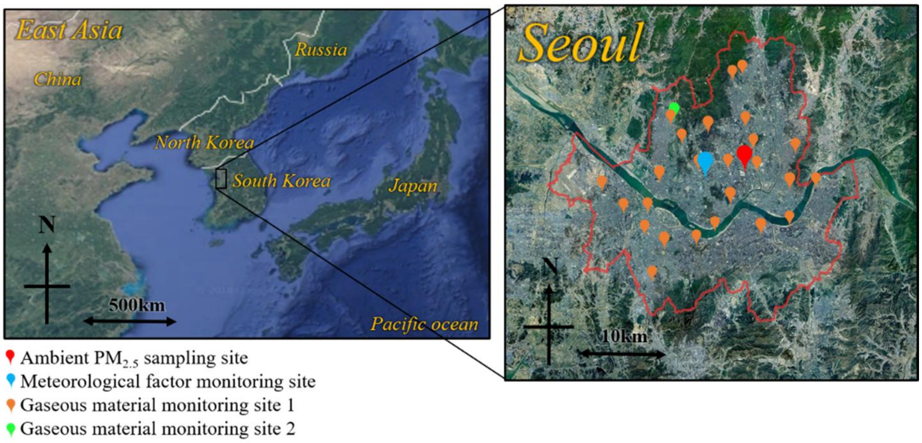

Figure 1. Location of the monitoring sites considered in this study: ambient $PM_{2.5}$monitoring station (red), meteorological factor monitoring station (sky blue), urban monitoring station for ambient gaseous material data (orange; CO, O_3, SO_2, NO_2, PM_{10}, green; VOCs).

Table 1. Details of the gaseous monitoring sites in Seoul.

Station			Location		Measure					
Name	Code	Type	Lat. (dgr.)	Long. (dgr.)	SO_2	O_3	NO_2	CO	PM_{10}	VOCs
Gangnam-gu	111261	Urban background	37.57	126.97	o	o	o	o	o	x
Gangdong-gu	111274	Urban background	37.55	127.14	o	o	o	o	o	x
Gangbuk-gu	111291	Urban background	37.65	127.01	o	o	o	o	o	x
Gangseo-gu	111212	Urban background	37.54	126.84	o	o	o	o	o	x
Gwanak-gu	111251	Urban background	37.49	126.93	o	o	o	o	o	x
Gwangjin-gu	111141	Urban background	37.55	127.09	o	o	o	o	o	x
Guro-gu	111221	Urban background	37.50	126.89	o	o	o	o	o	x
Geumcheon-gu	111281	Urban background	37.45	126.91	o	o	o	o	o	x
Nowon-gu	111311	Urban background	37.66	127.07	o	o	o	o	o	x
Dobong-gu	111171	Urban background	37.65	127.03	o	o	o	o	o	x
Dongdaemun-gu	111152	Urban background	37.58	127.03	o	o	o	o	o	x
Dongjak-gu	111241	Urban background	37.48	126.97	o	o	o	o	o	x
Mapo-gu	111201	Urban background	37.56	126.91	o	o	o	o	o	x
Seodaemun-gu	111191	Urban background	37.59	126.95	o	o	o	o	o	x
Seocho-gu	111262	Urban background	37.50	126.99	o	o	o	o	o	x
Seongdong-gu	111142	Urban background	37.54	127.05	o	o	o	o	o	x
Seongbuk-gu	111161	Urban background	37.61	127.03	o	o	o	o	o	x
Songpa-gu	111273	Urban background	37.50	127.09	o	o	o	o	o	x
Yangcheon-gu	111301	Urban background	37.53	126.86	o	o	o	o	o	x
Yeongdeungpo-gu	111231	Urban background	37.53	126.90	o	o	o	o	o	x
Yongsan-gu	111131	Urban background	37.54	127.00	o	o	o	o	o	x
Eunpyeong-gu	111181	Urban background	37.61	126.93	o	o	o	o	o	o
Jongno-gu	111123	Urban background	37.57	127.01	o	o	o	o	o	x
Jung-gu	111121	Urban background	37.56	126.97	o	o	o	o	o	x

3. Model description

3.1 EC tracer Model

The EC tracer method was applied to estimate the carbon species as primary and secondary organic carbon. Primary Organic Carbon (POC) is generally emitted directly from combustion activities such as burning of fossil fuels or biomass, biogenic source including plant spores, pollen, vegetation debris and soil organics. Secondary Organic Carbon (SOC) is generally formed by the Secondary chemical reaction of POC or VOCs (Day, Zhang, & Pandis, 2015). EC tracer Method uses following equation to calculate POC at a given receptor.

$$\mathrm{SOC} = \mathrm{OC} - \left(\left[\frac{\mathrm{OC}}{\mathrm{EC}}\right]_{pri} \times \mathrm{EC}\right) + \mathrm{OC}_{non-comb}$$

EC tracer method has been applied in previous studies and this technique is based on the following two assumptions. 1) OC and EC have a common combustion source, which has a specific primary ratio of OC/EC (here after referred to as $[\mathrm{OC/EC}]_{prim}$). 2) The ratio of OC/EC increases as the secondary formation of OC progresses. The most common approach is a linear regression of a subset of data in which $[\mathrm{OC/EC}]_{prim}$ is determined as the slope and as $\mathrm{OC}_{non\text{-}comb}$ as the y-intercept (Snyder, Rutter, Collins, Worley, & Schauer, 2009). In fact, it is difficult to measure the $[\mathrm{OC/EC}]_{prim}$, which has a high uncertainty due to unidentified chemical reactions and yield of precursors (Kroll & Seinfeld, 2008). In addition, due to wide range OC/EC ratio by source type, emission control, diurnal or seasonal pattern and meteorological factors, the ratio values should be derived very carefully. Previous studies have suggested the ratio values as lowest 5% ratio of OC/EC or value of slope in the correlation between OC and EC within a certain period such as one season. In the preprocessing of the model input data, the cases that $PM_{2.5}$ or carbon species were not analyzed or carbon faction was larger than the mass concentration of $PM_{2.5}$ were excluded from the modeling input data. In this study, the four methods to derive $[OC/EC]_{prim}$ were applied and compared. Through this process, the lowest 5% of each season was applied as the most reasonable $[OC/EC]_{prim}$ of this long-term study.

3.2 The wind rose model and Conditional Probability Function (CPF)

The wind rose model was applied to estimate and plot wind data by specific period. The CPF was used to show the wind directions that dominate a specific concentration of various pollutants; showing the occurring probability of specific events higher than some concentration criteria by direction and speed of wind(Ashbaugh, Malm, & Sadeh, 1985). The CPF is calculated as follows

$$CPF = \frac{m_{\theta j}}{n_{\theta j}}$$

where $m_{\theta j}$ is the number of samples in the wind sector θ and wind speed interval j with mixing ratios greater than specific 'high' concentration criteria, and $n_{\theta j}$ is the total number of samples in the same wind speed-direction interval. In the preprocessing of model input data, the hourly meteorological data were daily averaged on the basis of vector for direction and velocity of wind. Then, daily meteorological data was merged with the pollutant concentrations of the same day to make the model input data. The models calculation was performed using Open-air package of R-studio ver. 1.1.463.

3.3 Back-trajectory analysis, Potential Source Contribution Function (PSCF), Concentration Weighted Trajectory (CWT)

Back-trajectory analysis is a method for estimating the air mass origin by tracking past back-trajectories at the given receptor. In this work, to make trajectories practicable to run for 15 years, the National Oceanic and Atmospheric Administration- National Centers for Environmental Prediction/National Center for Atmospheric Research (NOAA-NCEP/NCAR) reanalysis data was used, and Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model calculated trajectories based on archive data (http: //ready.arl.noaa.gov/HYSPLIT_agreement.php), which are on a latitude-longitude grid (2.5 degree). The HYSPLIT model tracks the latitude and longitude of 3 hours before the air mass entering the receptor site from elsewhere. Also, the air mass was tracked up to 72 hours, with a starting altitude of 500 meters. The PSCF calculates the probability that a source is located at latitude i and longitude j (Fleming, Monks, & Manning, 2012). The PSCF approach has been widely used in the analysis of air mass back trajectories. The basis of PSCF is that if a source is located at (i, j), an air parcel back trajectory passing through that location indicates that material from the source can be collected and transported along the trajectory to the receptor site. PSCF solves

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}}$$

where n_{ij} is the number of times that the trajectories passed through the cell (i, j) and m_{ij} is the number of times that a source concentration was high when the

trajectories passed through the cell (i, j). The criterion for determining m_{ij} is controlled by percentile value. A limitation of the PSCF method is that grid cells can have the same PSCF value when sample concentrations are either only slightly higher or much higher than the criterion (Hsu, Holsen, & Hopke, 2003). As a result, it can be difficult to distinguish moderate sources from strong ones. Seibert et al. (1994) computed concentration fields to identify source areas of pollutants (Seibert, Kromp-Kolb, Baltensperger, Jost, & Schwikowski, 1994). This approach is referred to as the CWT (Concentration Weighted Trajectory). A grid domain was used as in the PSCF method. For each grid cell, the mean(CWT) concentration of a pollutant species was calculated as follows:

$$\ln(\bar{C}_{ij}) = \frac{1}{\sum_{k=1}^{N} \tau_{ij}} \sum_{k=1}^{n} \ln(\bar{C}_k)\tau_{ijk}$$

where i and j are the indices of grid, k the index of trajectory, N the total number of trajectories used in analysis, c_k the pollutant concentration measured upon arrival of trajectory k, and τ_{ijk} the residence time of trajectory k in grid cell (i, j). A high value of $\bar{C}_{ij}$ means that, air parcels passing over cell (i, j) would, on average, cause high concentrations at the receptor site. In the preprocessing of the model input data, the back-trajectories for 15 years were selected only on the day when $PM_{2.5}$ and carbon species concentration data were available. Then, based on the date of the back-trajectories, model input data was made by merging $PM_{2.5}$ and carbon species concentrations into back-trajectories data frame. The models calculation was performed using Open-air package of R-studio ver. 1.1.463.

3.4 Trend analysis: Theil-Sen method

Long-term trends of $PM_{2.5}$ and carbon species were estimated by using the Theil-Sen method. The basic idea of Theil-Sen method plots the n monthly mean concentration of each air pollutant and calculates the slopes between all pairs in a given a set of n. The number of slopes is increased by $\approx n^2$, and the Theil-Sen method derives the median of all slopes to the final slope. In addition, Theil-Sen method uses the bootstrap function to yield confidence intervals even in the case of non-normal data and heteroscedasticity (non-constant error variance). Therefore, this technique is resistant to outliers or missing values which can be important in data set of air pollutant. The computation of Theil-Sen method was performed using 'Open-air package' of R-studio ver. 1.1.463.

III. Results

1. Long-term trends and general features of Carbon species in $PM_{2.5}$

Long-term trends of $PM_{2.5}$ and carbon species is shown in figure 2. One point on the graph represents the monthly mean concentration value for each pollutant. The smooth line was added to visualize the change over the long-term period, which represents the 95% confidence intervals of the fit. The smooth line is essentially determined using generalized additive modelling between time and pollutant concentration. The monthly mean concentrations of $PM_{2.5}$ ranged from 11.00 μg/m^3 to 131.75 μg/m^3(average ± standard deviation: 36.93 ± 13.55 μg/m^3), showing decreasing trends of −1.78%/year with statistical significance ($p < 0.001$) since 2003. In the sub-period (5-years) trend analysis of $PM_{2.5}$, no increase or decrease of concentration was estimated at a statistically significant level ($p < 0.1$). The monthly mean concentrations of OC ranged from 2.24 μg/m^3 to 19.24 μg/m^3 (average ± standard deviation: 7.36 ± 2.80 μg/m^3, showing decreasing trends of −3.02%/year with statistical significance ($p < 0.001$). In the sub-period trend analysis of OC, statistically significant decrease was estimated during the period of 2008-2012 ($p < 0.01$). The monthly mean concentrations of EC ranged from 0.34 μg/m^3 to 6.28 μg/m^3 (1.97 ± 1.27 μg/m^3), showing decreasing trends of −6.23%/year with statistical significance ($p < 0.001$). In the sub-period trend analysis of EC, statistically significant decrease was estimated during the period of 2003-2007 ($p < 0.001$) and 2013-2017 ($p < 0.1$). The monthly mean ratio of $OC/PM_{2.5}$ and $EC/PM_{2.5}$ ranged from 0.11 to 0.48 with average ± standard of 0.23 ± 0.064, 0.014 to 0.23 with average ± standard of 0.064 ± 0.040, respectively. The trends of $OC/PM_{2.5}$, $EC/PM_{2.5}$ showed statistically significant decrease (−1.52%/year; $p < 0.001$, −5.2%/year; $p < 0.001$, respectively). In the sub-period trend analysis of $OC/PM_{2.5}$, statistically significant decrease was estimated during the period of 2008-2012 ($p < 0.005$). In the sub-period trend analysis of $EC/PM_{2.5}$, statistically significant decrease was estimated during the period of 2003-2007 ($p < 0.1$) and 2013-2017 ($p < 0.05$). The monthly mean concentrations of POC and SOC ranged from 0.28 μg/m^3 to 12.95 μg/m^3, from 0.011 μg/m^3 to 18.82 μg/m^3 respectively. Overall trend of monthly mean concentrations of POC and SOC showed a continuously decrease (−3.20%/year, −2.65% /year respectively) for 15 years with statistical significance ($p < 0.001$). In the sub-period trend analysis of POC and SOC, statistically significant decrease in SOC was estimated during the period of 2008-2012 ($p < 0.05$). On the other hand, the monthly mean ratio of OC/EC showed increasing trend (−1.52%/year; $p < 0.001$) and ranged from 1.08 μg/m^3 to 14.72 μg/m^3

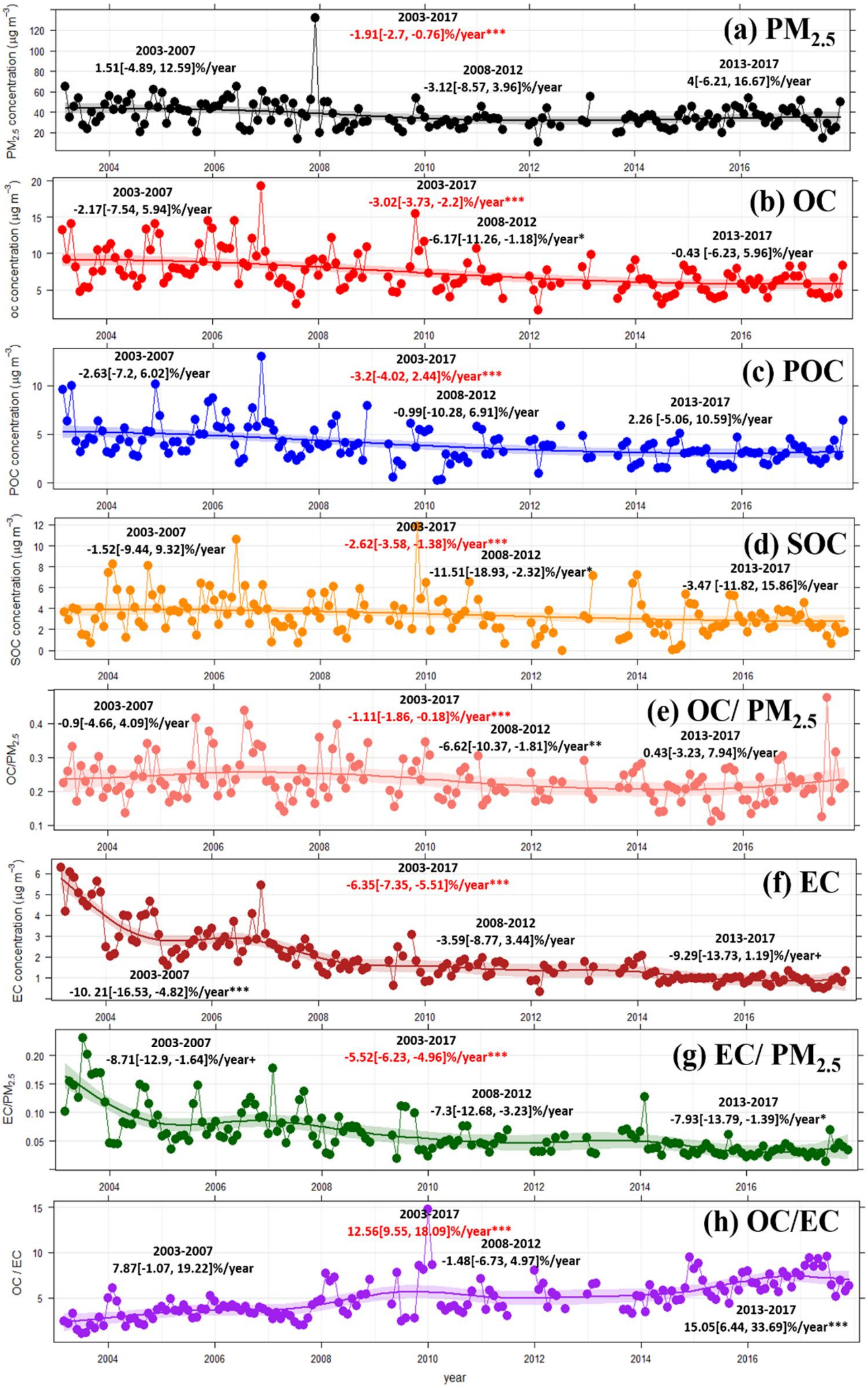

Figure 2. Long-term trend of carbon species in $PM_{2.5}$ in Seoul 2003-2017.

Table 2. Annual concentrations of carbon species in $PM_{2.5}$ in Seoul 2003-2017. (unit: $\mu g/m^3$)

YEAR	$PM_{2.5}$	Concentrations: arithmetic mean ± standard deviation (mass fractions, %)				
		OC	EC	POC	SOC	OC/EC
2003	44.6 ± 24.9	14.4 ± 5.7 (32.2)	5.5 ± 2.9 (12.3)	5.8 ± 4.4 (16.6)	2.8 ± 3.0 (8.0)	2.0 ± 2.1
2004	48.3 ± 25.1	16.2 ± 5.5 (33.6)	3.3 ± 1.6 (6.8)	4.6 ± 3.0 (12.1)	5.1 ± 4.0 (12.3)	3.4 ± 1.9
2005	45.4 ± 24.7	14.4 ± 5.2 (31.7)	2.5 ± 1.1 (5.5)	4.8 ± 3.1 (13.5)	4.2 ± 3.7 (10.5)	3.8 ± 1.6
2006	48.3 ± 26.1	18 ± 5.6 (37.3)	3.2 ± 1.5 (6.6)	6.2 ± 4.6 (16.1)	5.0 ± 4.1 (14.0)	3.9 ± 1.9
2007	45.7 ± 42.9	11.4 ± 4.6 (24.9)	2.5 ± 1.0 (5.4)	4.1 ± 2.5 (12.7)	2.7 ± 2.5 (7.0)	3.0 ± 1.3
2008	30.6 ± 16.2	11.2 ± 4.5 (36.5)	1.4 ± 0.6 (4.6)	4.5 ± 2.5 (16.8)	3.7 ± 3.3 (11.1)	5.5 ± 2.5
2009	27.4 ± 15.8	11.2 ± 4.6 (40.9)	2.3 ± 0.8 (8.4)	3.6 ± 2.4 (11.7)	4.0 ± 3.5 (11.9)	4.6 ± 3.2
2010	26.9 ± 11.9	9.4 ± 4.6 (34.8)	1.6 ± 0.9 (5.8)	2.6 ± 1.9 (9.5)	3.9 ± 2.3 (13.9)	5.4 ± 3.7
2011	37.6 ± 17.4	12.4 ± 3.3 (32.9)	1.5 ± 0.6 (3.9)	4.2 ± 2.1 (13.0)	2.8 ± 2.0 (8.0)	4.8 ± 1.9
2012	28.4 ± 15.5	7.9 ± 1.9 (27.7)	1.4 ± 0.7 (4.8)	3.9 ± 1.8 (14.3)	1.7 ± 1.2 (6.0)	5.1 ± 1.6
2013	30.9 ± 16.9	10.1 ± 3.6 (32.7)	1.4 ± 0.7 (4.5)	3.1 ± 1.9 (12.7)	3.0 ± 3.1 (10.9)	4.4 ± 1.7
2014	31.8 ± 16.4	8.5 ± 3.3 (26.8)	1.0 ± 0.7 (3.1)	3.1 ± 1.6 (11.5)	2.7 ± 3.0 (8.5)	5.6 ± 2.6
2015	34.5 ± 15.7	8.5 ± 3.2 (24.8)	0.9 ± 0.5 (2.7)	2.9 ± 1.3 (10.7)	2.9 ± 2.5 (10.1)	6.3 ± 2.7
2016	45.5 ± 20.2	9.4 ± 2.7 (20.5)	0.9 ± 0.4 (2.1)	2.9 ± 1.3 (9.3)	3.0 ± 2.1 (9.6)	6.6 ± 2.4
2017	37.6 ± 19.8	9.3 ± 3.3 (24.6)	0.8 ± 0.4 (2.1)	3.3 ± 1.9 (12.6)	2.7 ± 2.1 (10.0)	8.2 ± 3.2
Total	37.5 ± 21.9	7.2 ± 4.3 (19.0)	1.8 ± 1.6 (4.8)	3.8 ± 2.7 (10.2)	3.3 ± 3.0 (8.8)	5.3 ± 2.7

In order to provide a reference to the long-term trends in the establishment of future atmospheric environmental policies, the first occurrence period in which the trends of changing air pollutants are observed to statistically significant ($p < 0.1$) is analyzed. The concentrations of POC and SOC were excluded from the sensitivity analysis because it was indirectly predicted values by using carbon species and higher level of uncertainty compared to other carbon species in each sub-period. The statistical significance of trend changes in $PM_{2.5}$, OC, and EC was yielded from data sets of at least 13 years, 10 years, and 5 years, respectively (Figure 3-5).

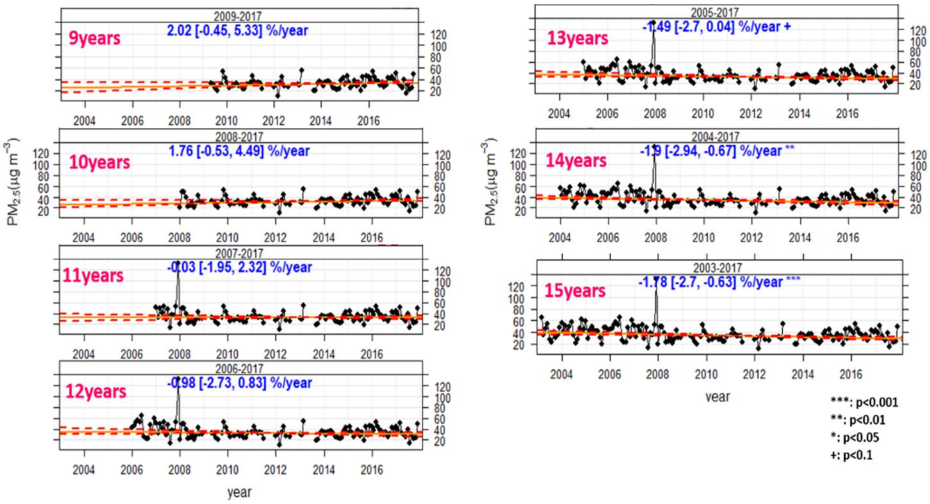

Figure 3. Statistical sensitivity analysis of $PM_{2.5}$ trend change.

The statistical significance of trend changes in OC/EC ratio was observed from data sets of at least 5 years. Considering the time length of data required to verify the statistical change of the trend, the period of establishing the atmospheric environmental policy, and the its application time, the 5-year unit was considered to be the most reasonable sub-period for the analysis for long-term trend analysis.

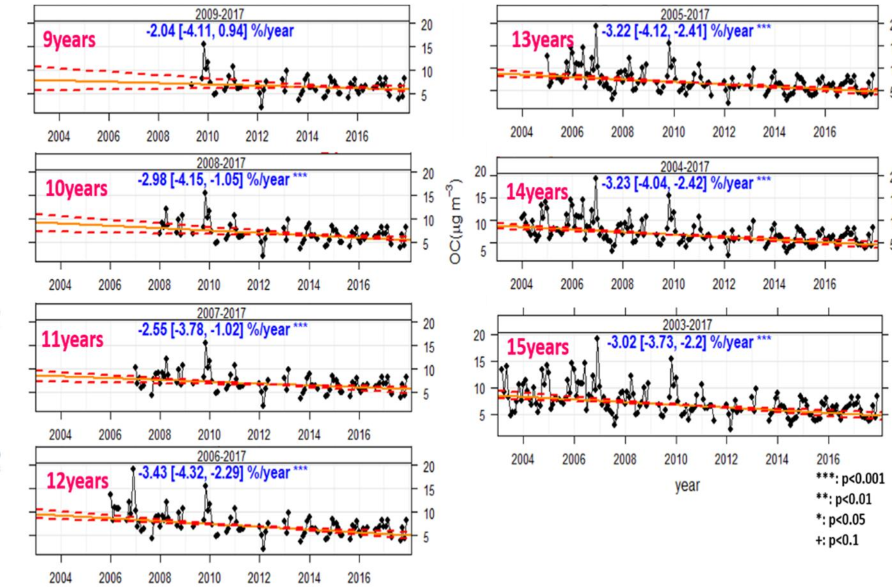

Figure 4. Statistical sensitivity analysis of OC trend change.

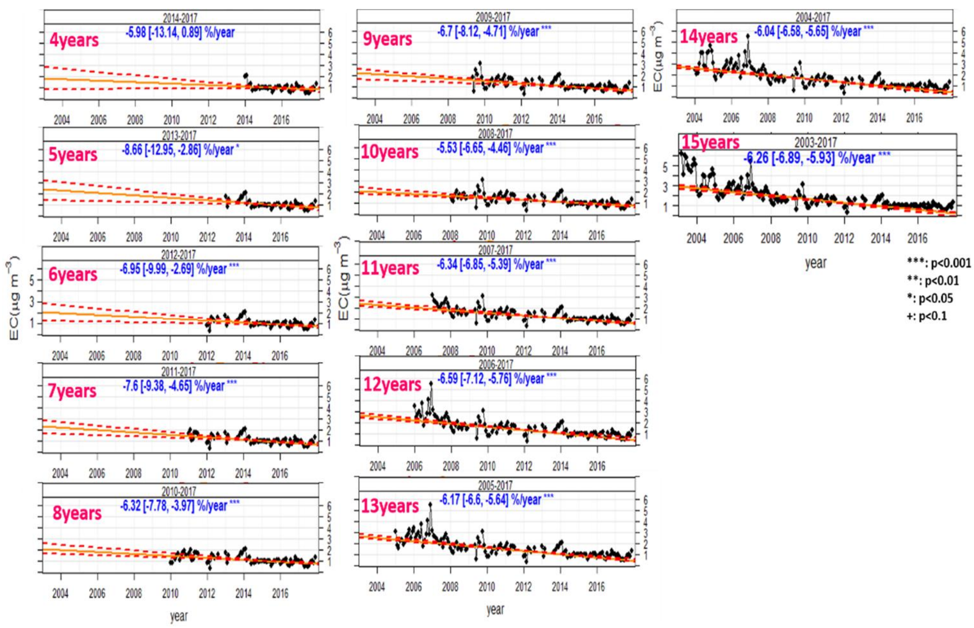

Figure 5. Statistical sensitivity analysis of EC trend change.

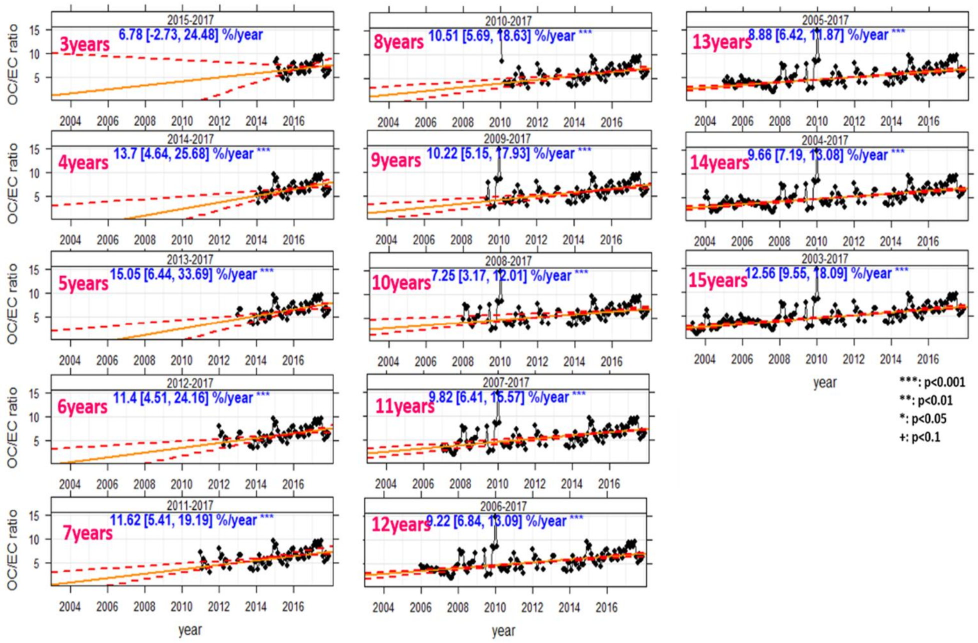

Figure 6. Statistical sensitivity analysis of OC/EC ratio trend change.

To assess the seasonal effects on the long-term trends of $PM_{2.5}$ and carbon species, trend analysis split by season was performed and was shown Figure 6. Seasonal trend analysis of OC, EC, POC, OC/EC ratio showed that the tendency of increase or decrease in all seasons was the same and statistically significant, but the rate of changes in trends was different. In the case of $PM_{2.5}$, statistical significance of long-term decrease was shown only in spring and autumn. In the case of SOC, statistical significance of long-term decrease was shown only in spring and summer.

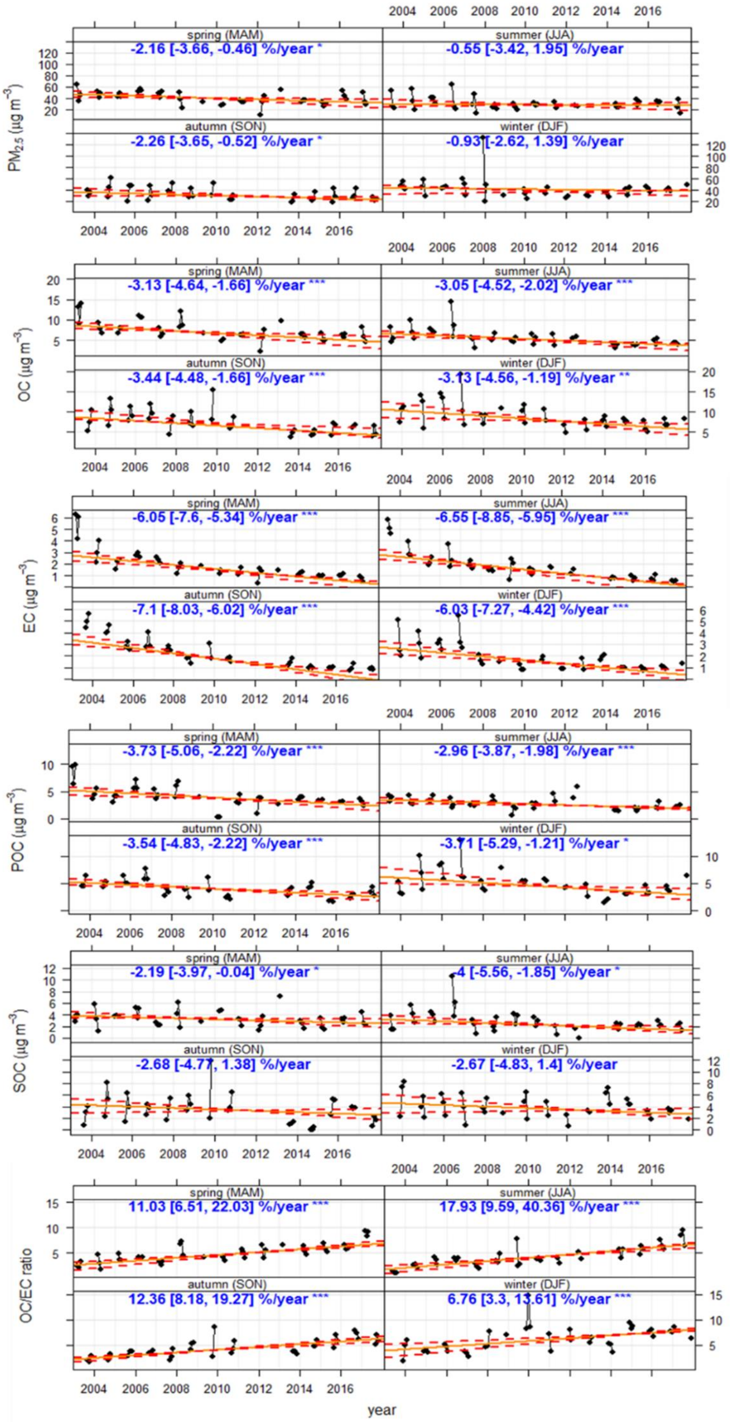

Figure 7. Long-term trend of $PM_{2.5}$ and carbon species in Seoul for each season.

In order to analyze the seasonal effects of long-term changes, sensitivity analysis of $PM_{2.5}$ were performed according to the inclusion and exclusion of summer. As a result of the analysis, the long-term decrease of $PM_{2.5}$ was more rapid in the case of excluding the summer, but in both cases, the statistical significance of the decrease was shown in the data set over the past 13 years based on 2017. Based on these results, it is estimated that the steady decline over several years has a more dominant influence on the long-term change than the seasonal fluctuation. Therefore, in the following analysis, long-term trend analysis including all seasons was performed.

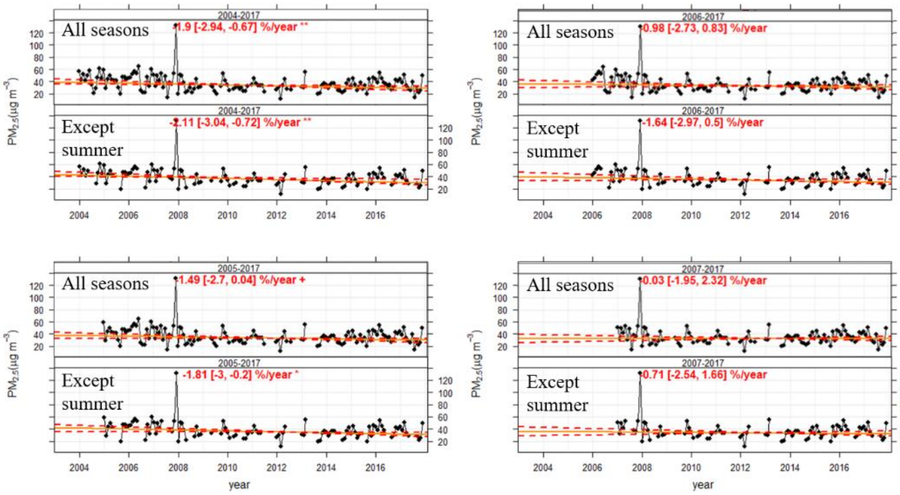

Figure 8. Long-term trend sensitivity analysis of $PM_{2.5}$ according to the inclusion and exclusion of summer.

Correlation analysis was performed to estimate the common source and relevance of $PM_{2.5}$ and carbon species for each period in long-term period, and was shown in the Figure 9. Positive correlation between $PM_{2.5}$, OC and EC was observed for each study period. (2003-2007; N= 459, 2008-2012; N= 179, 2013-2017; N= 712). This result suggest that specific common sources have an effect on $PM_{2.5}$ and carbon species. The slopes of the linear regression in the correlation was the lowest in 2003-2007 (y=0.18x+1.64), but remarkably increased 2008-2012 (y=0.06x+1.09), and the highest value during 2013-2017 (y=0.04x+0.80). This is due to the more rapid decline in EC concentration compared to the decreasing trend in OC concentration, which suggest that carbon emissions characteristics are changed very evidently over long-term period.

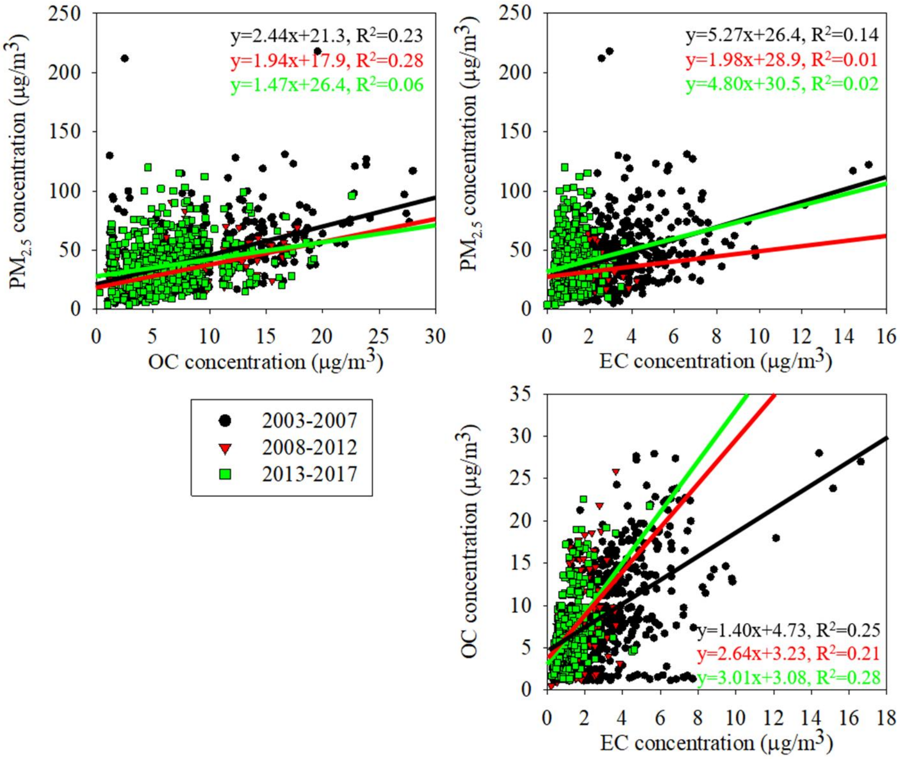

Figure 9. Correlation analysis of Carbon species in $PM_{2.5}$ in Seoul 2003-2017.

2. Effects of meteorological factors and gaseous materials over long-term periods

In order to assess the key correlated factors of long-term trend of $PM_{2.5}$ and carbon species, the synoptic meteorological data, national air pollutant emission data (Clean Air Policy Support System, CAPSS) and air pollutant data of national observation network in Seoul were compared with the trends. The synoptic meteorological data of Seoul during the study period is shown at the top of Figure10.

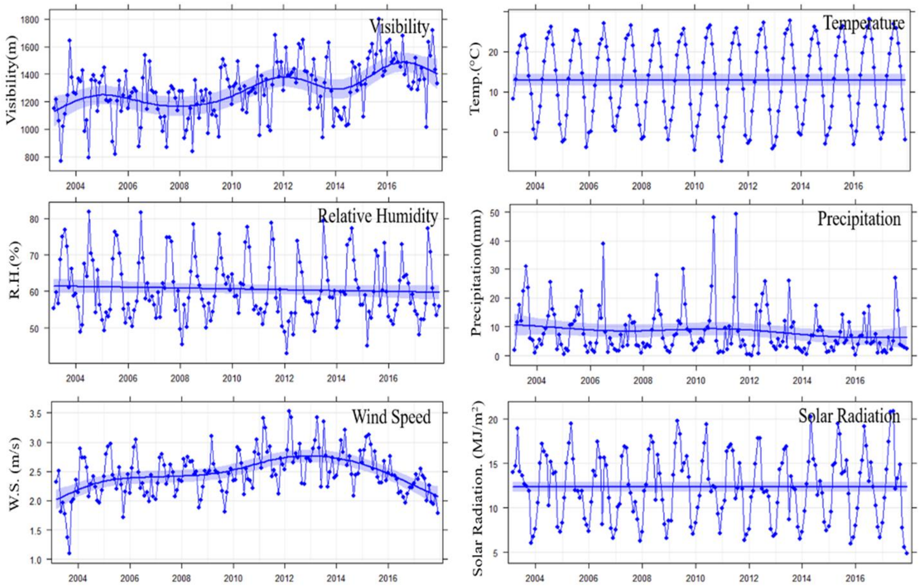

Figure 10. Long-term trends of synoptic meteorological data in Seoul, Korea.

Marked annual variation were observed in precipitation, wind speed, while relative humidity and solar radiation remained relatively constant level. In terms of long-term period precipitation, small decreasing tendencies were observed in 2006 and 2014, and then increases tendency was shown in 2011 but the overall trend declined. Precipitation is closely related to the removal of air pollutants, but it does not clearly correspond to the overall trend of $PM_{2.5}$ and PM_{10} (Figure 11). In the case of temperature, relative humidity, solar radiation, there were no significant variation over long-term period. Interestingly, long-term trend of visibility increased markedly for 15 years, suggesting that the concentration of air pollutants has declined during the study period. Such estimation based on visibility distance are consistent with previous long-term trend review study, which shows a notable decrease of PM during 2006–2013 (Han & Kim, 2015). The period of 2010-2015 was characterized by the tendency of highest wind speed, which usually favor the dispersion of the locally generated pollutants and appear to be cause drastic decrease of PM in 2012. Comprehensively, the meteorological conditions of precipitation and wind speed during the period of 2008-2012 were also estimated to have affected the reduction of $PM_{2.5}$ and its carbon species. Also, relatively low precipitation and wind speeds during 2013-2017 are considered to have influenced the high concentrations loadings. In order to estimate the long-term trends of air pollutant emissions, the changes in ambient gaseous air pollutant and CAPSS data in Seoul were analyzed and shown in Figures 11 and 12, respectively. Ambient TVOCs is well known as one of the largest contributors to organic carbon production. Also CO, SO_2, NO_2 could be emitted from combustion source, and O_3 could be indicator of active level of secondary photochemical reaction. The NO_2 concentrations was observed to decrease by -0.62%/year during the study period, with the statistical significance ($p < 0.005$).

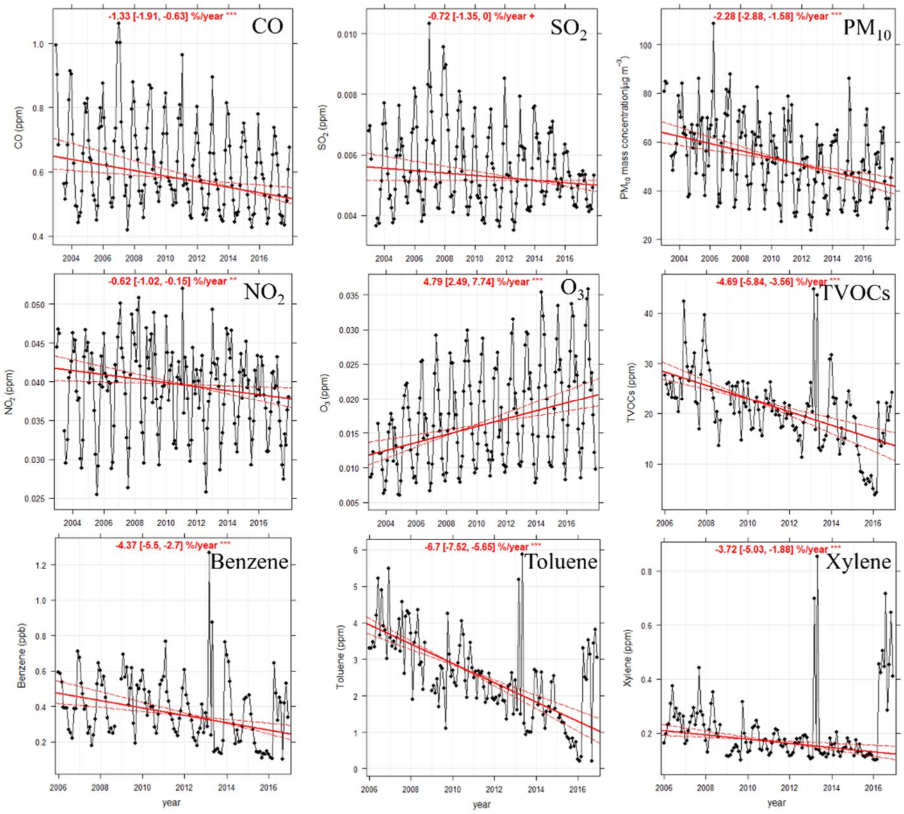

Figure 11. Long-term trends of gaseous materials and PM_{10} in Seoul, Korea.

In case of CO concentrations, the statistically significant decreasing trends were found as -1.33%/year ($p < 0.001$). The concentration of PM_{10} shows the decreasing trends which are characterized by a drastic 2010 decrease, remaining then almost constant during 2012–2017. Also, two tendencies appeared to be characterized as a common feature in indicator materials (CO, SO_2, NO_2) of combustion activities, which show relatively stable variation before 2008 and relatively marked decreasing since 2008. Trend of O_3 concentration increased with statistical significance of 4.79%/year in the study period ($p < 0.001$). These patterns are attributed probably to a decrease of NO_x emissions (Figure 11). Decreasing trend of NO_2 concentration imply less consumption of O_3 to oxidize NO pollutant into NO_2. Also, an increased urban formation of O_3 could be result of a possible VOCs/NO_x disequilibrium induced by decreased NO_x concentrations (Camredon, Aumont, Lee-Taylor, & Madronich, 2007). Overall, the decline trend for PM_{10} is -2.28% / year, consistent with $PM_{2.5}$, but trends are more pronounced than trends for $PM_{2.5}$ concentration (-1.71%/year, $p < 0.001$). As a whole, TVOCs trends are characterized by a gradual decrease, with a marked variation in 2010 and 2015-2016. Since VOCs were measured at one measuring station, it seems that the influence of the abrupt concentration increase was reflected locally. The concentration of TVOCs shows a statistically significant decrease of −4.69%/year, −6.7%/year, −4.37%/year and –3.72%/year for TVOCs, toluene, benzene and xylene respectively ($p < 0.001$). Ambient VOCs have been applied as a major indicator of organic carbon emission sources in many studies. In particular, aromatics are a major contributor to the yield of organic carbon production and the mass concentration of TVOCs. These decreasing trend of all VOCs is also consistent with the trend of OC and SOC in $PM_{2.5}$ in study period. Air pollutant emission data of CAPSS were accessible only at the annual time resolution, and the changes in emissions for each air pollutant in Seoul was shown in the figure 11. The emissions trends of gaseous air pollutants suggesting combustion activity and VOCs decreased overall. This tendency is consistent with the trends of ambient air pollutant, gaseous indicators of combustion activity, measured in the atmosphere.

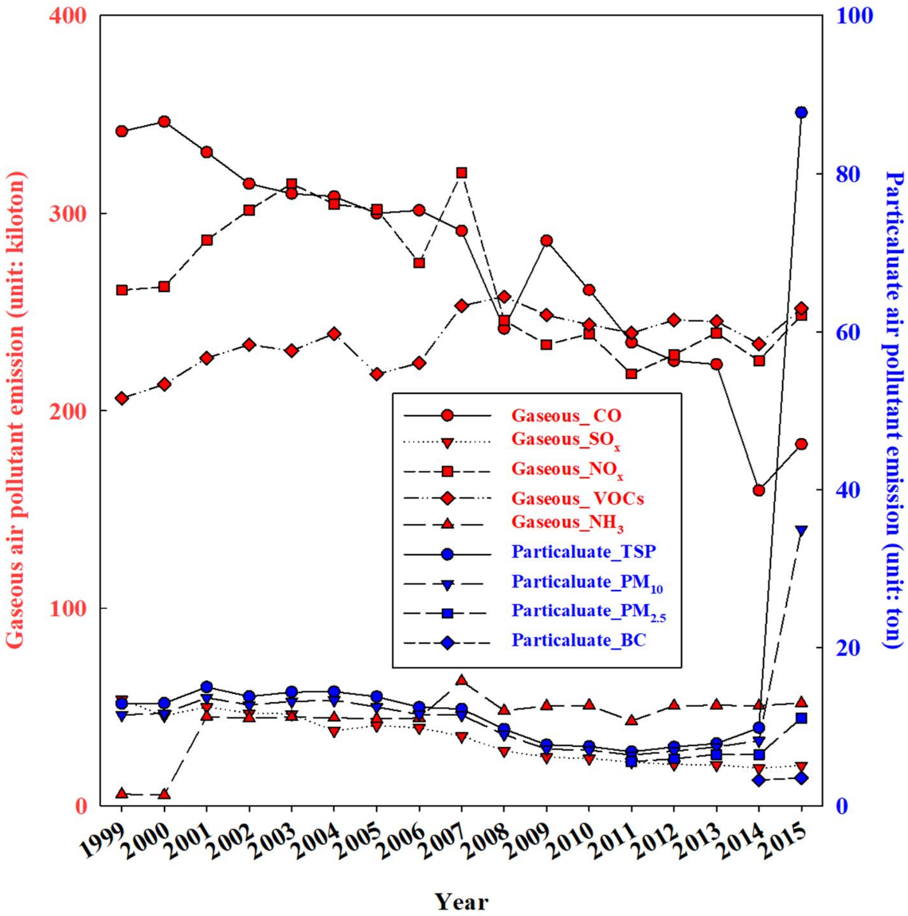

Figure 12. Annual emission trend of air pollutants in Seoul1 1999-2015.

In the case of ammonia gas emissions, it is mainly contributed by the agricultural and livestock industry, which increased sharply in 2000 and then declined slowly, and was difficult to compare it with the combustion activity suggested by the gaseous indicators of this study. The cumulative periods of $PM_{2.5}$ and Black Carbon (BC) emissions in CAPSS data are relatively short, which were limited in their use for long-term comparative analysis of this study. The emissions of TSP and PM_{10} declined steadily from 1999 to 2014, but increased sharply in 2015. This sharp increases are estimated to be due to new additions to the CAPSS data from the industry not counted during the past period. A correlation analysis of ambient concentration and annual emissions of air pollutants was performed and was shown in Figure 13.

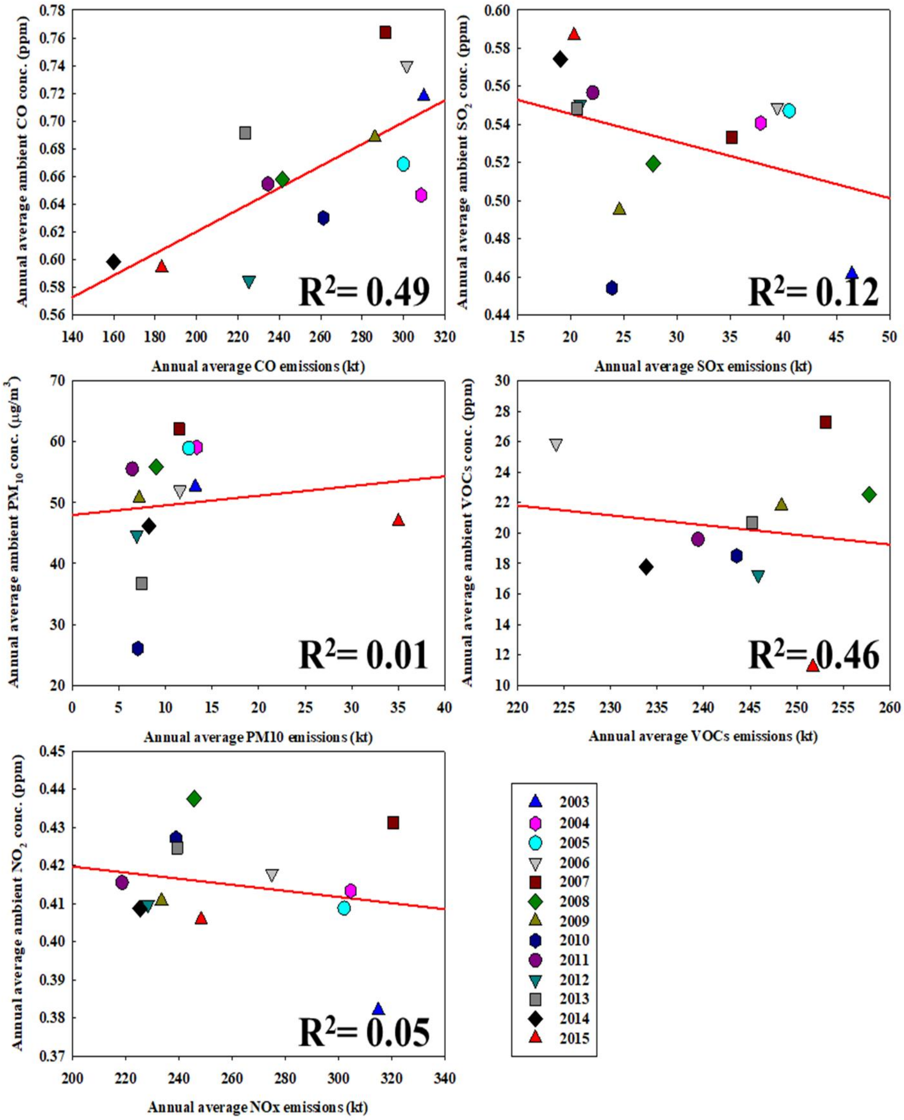

Figure 13. Correlation analysis between ambient concentration of pollutant and emission of air pollutant in Seoul.

As a result of correlation analysis, CO and VOCs showed the most similar tendency, and it was difficult to assess a clear correlation in other air pollutants.

On the other hand, in emission data set of Gyeonggi-do or whole country, which data set would be more reasonable for comparative analysis is not clear. In addition, considering the uncertainty of the effects of meteorological factors and emission data, unidentified chemical reaction, using CAPSS data as an indicator of long-term changes in emissions may lead to distorted result. Therefore, in this study, long-term trends of emissions were tracked by using ambient concentrations of pollutant, which were finally reflected in the emissions, chemical reactions, meteorological effect. Correlation analysis was performed and was compared in Figure 14 to assess the effect of determined factors as air pollutant emissions activities and meteorological factors on $PM_{2.5}$ and carbon species for each period in long-term period.

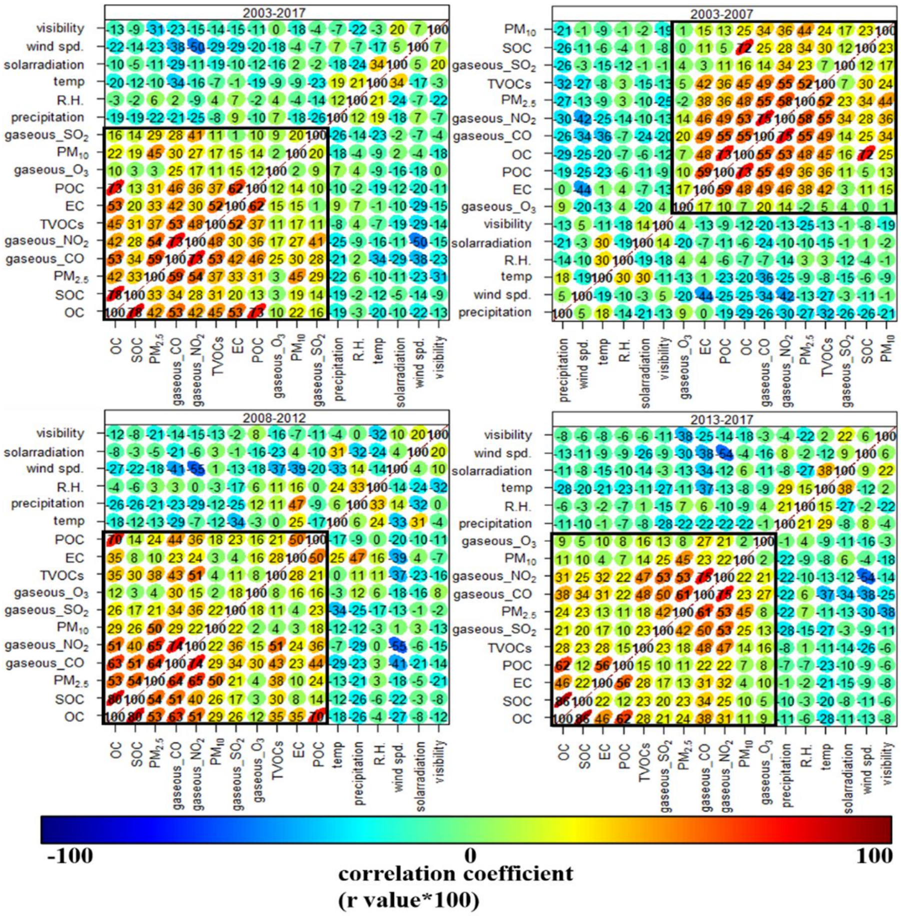

Figure 14. Correlation of meteorological factor, gaseous material, PM_{10} and Carbon species in $PM_{2.5}$ 2003-2017.

The correlations between $PM_{2.5}$, carbon species and gaseous materials were greater in all periods than in the case of meteorological factors. Given the long-term decease of gaseous materials and higher values of R^2 than meteorological factors which is non-decreasing, it is estimated that the reduction of air pollutant emissions than the meteorological factors has a greater impact on long-term decreasing trend of $PM_{2.5}$ and carbon species.

3. Local originated and long range transportation effect

3.1 Modeling result (wind rose, CPF)

The Modeling of wind rose and CPF was performed to estimate the main wind direction and the potential sources of $PM_{2.5}$ and carbon species in Seoul for a long-term period, and was shown in the figure 15. According to the analysis of wind roses, the wind direction of Seoul was mainly westerly wind, and no marked change was observed over a long-term period. The criteria concentration of the CPF model for $PM_{2.5}$ was applied at 35 μg/m^3 (55th percentile), which is corresponds to National Ambient Air Quality Standards (NAAQS). In the case of carbon species, due to the absence of carbon species NAAQS, the upper 25% value was applied as the criteria concentration for the CPF model to estimate high concentration sources. As a result of the CPF analysis, generally, the high loading of $PM_{2.5}$, OC, EC, POC and SOC were observed from strong wind speed in north-west direction, slow wind (wind speed less than 3 m/s) in north-west direction, slow wind (wind speed over 3 m/s) in south-east direction, slow wind speed in south-east direction, strong wind speed in north-west, respectively during the study period. In case of $PM_{2.5}$, the probability of High Concentration Events (HCEs) over than 35 μg/m^3 was high in southwesterly wind condition during the period of 2003-2007. While other carbon species except SOC are highly focused on slow wind, $PM_{2.5}$ has a higher probability of occurrence of HCEs in strong wind conditions. During the period after 2008, the probability of occurrence of $PM_{2.5}$ HCEs in the southwesterly winds condition markedly decreased. During the period from 2013 to 2017, the probability of occurrence of HCEs was not focused on southwesterly wind condition, but was observed at a similar level in all wind directions. In the case of OC, the probability of HCEs (mass conc. > 8.7 μg/m^3) was high in northerly and northerly-westerly wind conditions in the period of 2003-2007. During the 2008-2012 period, the probability of HCE in the northerly and northerly-westerly wind conditions was most markedly reduced. During the period of 2013-2017, the probability of HCE in the easterly winds conditions decreased and remained at the same level in the other directions. In the case of EC, probability of HCEs (mass conc. > 2.3 μg/m^3) was high in low speed conditions in all direction and high speed conditions in the south direction during the period of 2013-2017. In the period of 2008-2012, the probability of HCEs in all directions decreased markedly, and after 2013, the probability of HCEs in all wind directions was reduced to almost zero levels. In case of POC, the probability of HCEs (mass conc. > 4.6 μg/m^3) was relatively highest level in northerly wind conditions and was maintained at a similar level in other directions and during 2003-2007. During the 2008-2012 period, the overall probability of HCEs in all wind directions decreased and was largest in northerly wind conditions. During the period from 2013 to 2017, the probability of HCEs in all directions was lowered again. Also, the probability of HCEs in southeasterly wind condition was most noticeably lowered. In case of SOC, the probability of HCEs was the highest in north-westerly wind conditions in all periods. Unlike other carbon species, the probability of HCEs was high in case of strong wind conditions.

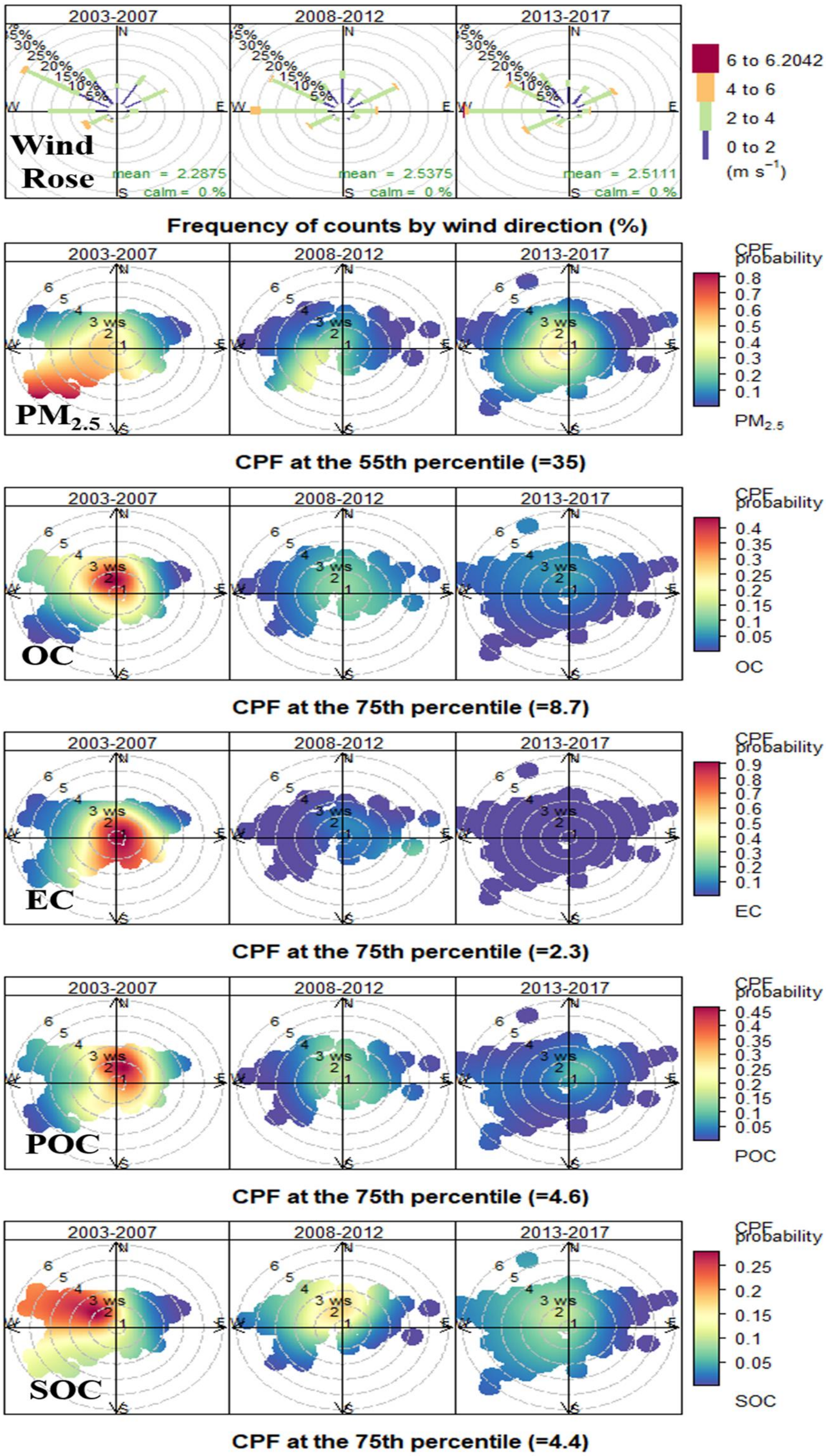

Figure 15. Wind rose and CPF result of $PM_{2.5}$ and carbon species in Seoul

2003-2017.

3.2 Modelling result (Back-trajectory analysis, PSCF, CWT)

Back-track analysis and modeling of PSCF and CWT were performed to estimate long-range transport effects of $PM_{2.5}$ and carbon species in Seoul, and were shown in Fig16-21. The direction of the 96-hour backward trajectory in Seoul included China, Mongolia, Russia, Japan, and North Korea. No marked changes were observed over a long period of time, but the number of back-trajectories was different according to the number of samples per sub-period.

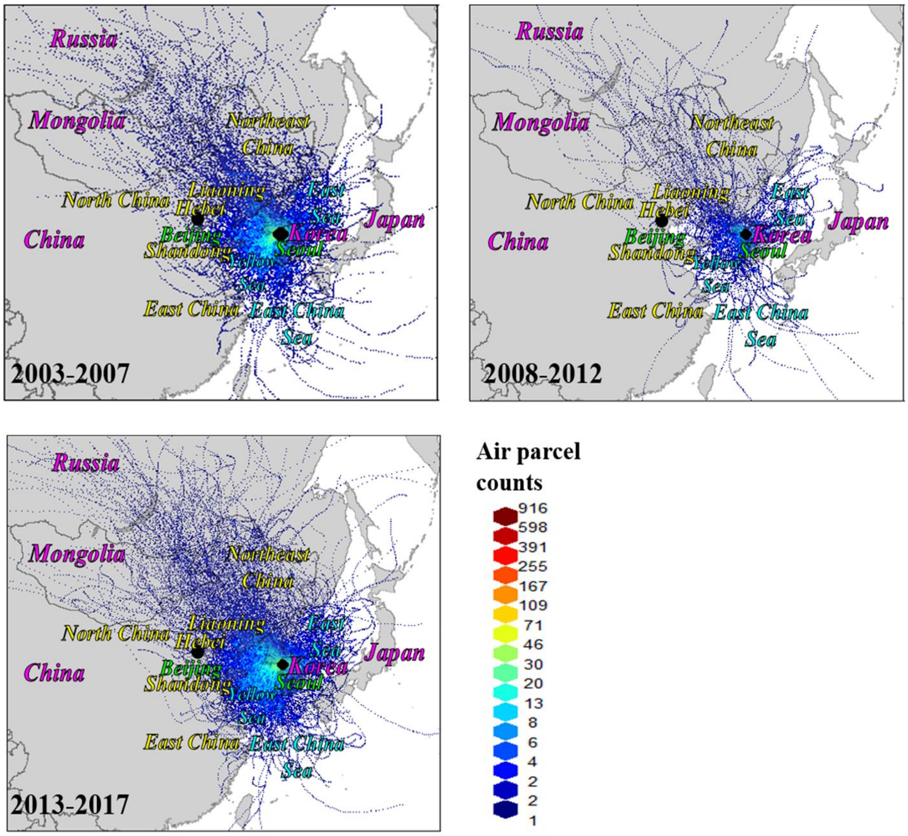

Figure 16. 96-hour back-trajectory of Seoul for collected samples in each periods.

In the 2008-2012 period, the number of back-trajectories was the smallest, and it is estimated that there was a limit to estimate the potential sources. Considering the PSCF and CWT results in terms of long-term trends, the effect of potential sources outside Korea affecting the receptor was estimated relatively high during 2003-2007, but decreasing during the period of 2008-2012, and increasing again during the 2013-2017, commonly $PM_{2.5}$ and carbon species. In Figure 17-21, High loading of $PM_{2.5}$ and carbon species from the continent including northeast China, Shandong, Hebei province, Beijing, upper area of east China and middle left of the Korea peninsula were observed. In addition, in all model results, the Yellow Sea was observed to high loading of High loading of $PM_{2.5}$ and carbon species. This could be phenomenon by that the air parcels overlapped in the Yellow Sea in front of the receptor enhances the model probability. In the case of $PM_{2.5}$, high loading of HCEs from Southeast China including Shandong was observed unlike carbon species. This result supports other potential sources such as secondary inorganic aerosols sources which contribute to high concentrations of $PM_{2.5}$.

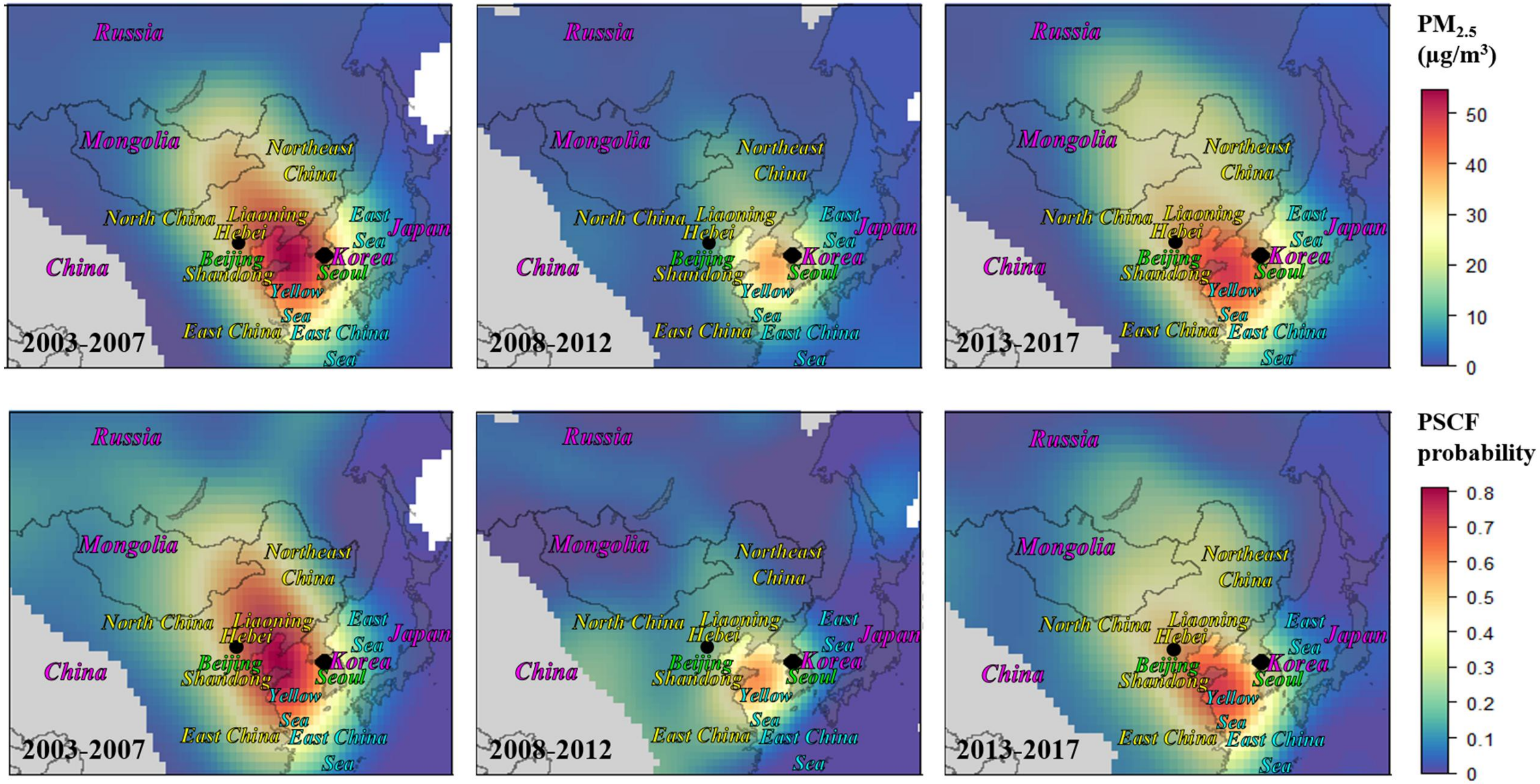
Russia
Mongolia
Northeast
China
North China
Liaoning
Hebei
Beijing
Shandong
China
East
Sea
Japan
Korea
Seoul
Yellow
Sea
East China
East China
Sea
2003-2007
2008-2012
2013-2017
$PM_{2.5}$
($\mu g/m^3$)
50
40
30
20
10
0
PSCF
probability
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

Figure 17. Results of CWT and PSCF for $PM_{2.5}$ in Seoul 2003-2017.

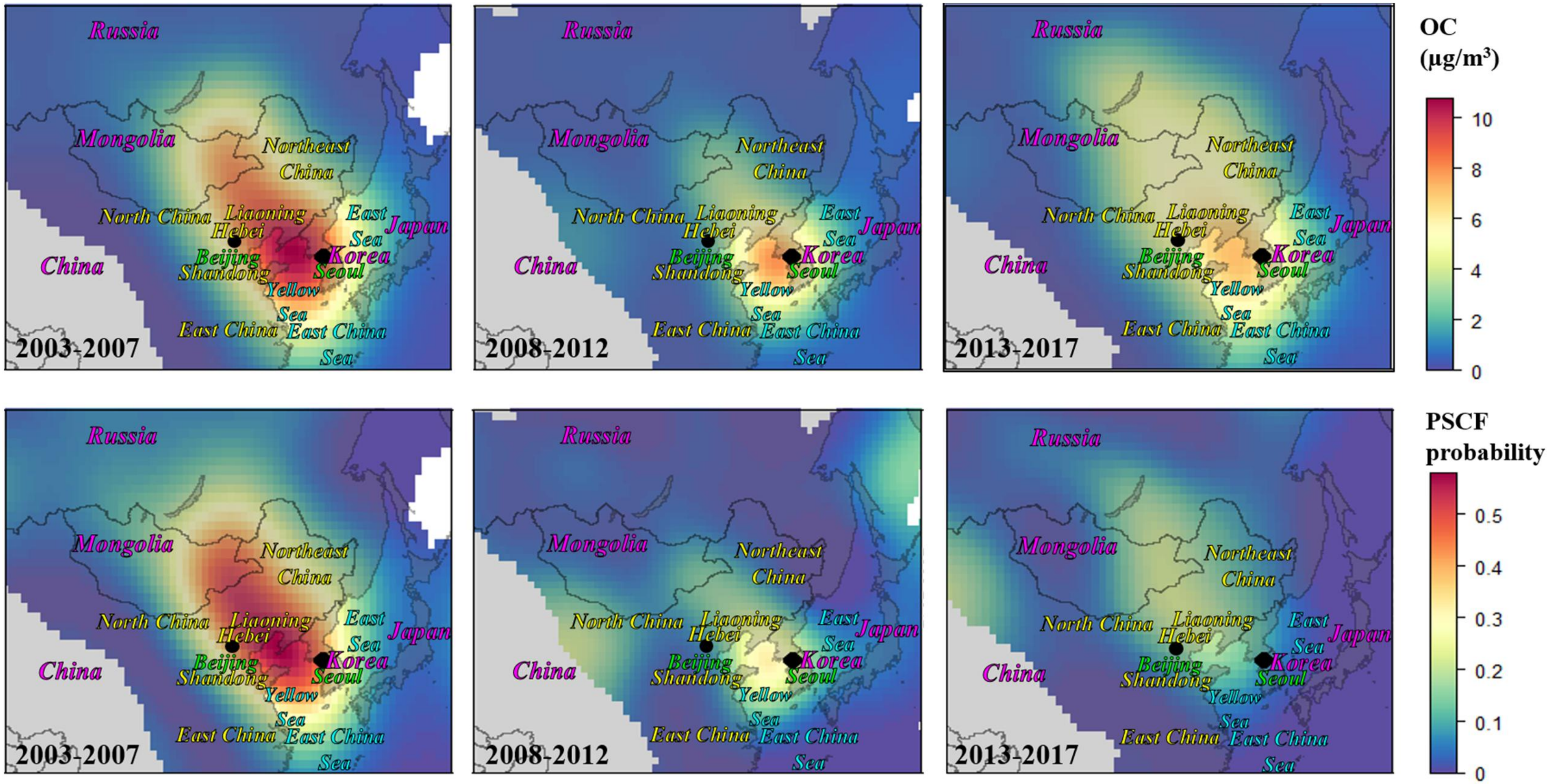

Figure 18. Results of CWT and PSCF for OC in Seoul 2003-2017.

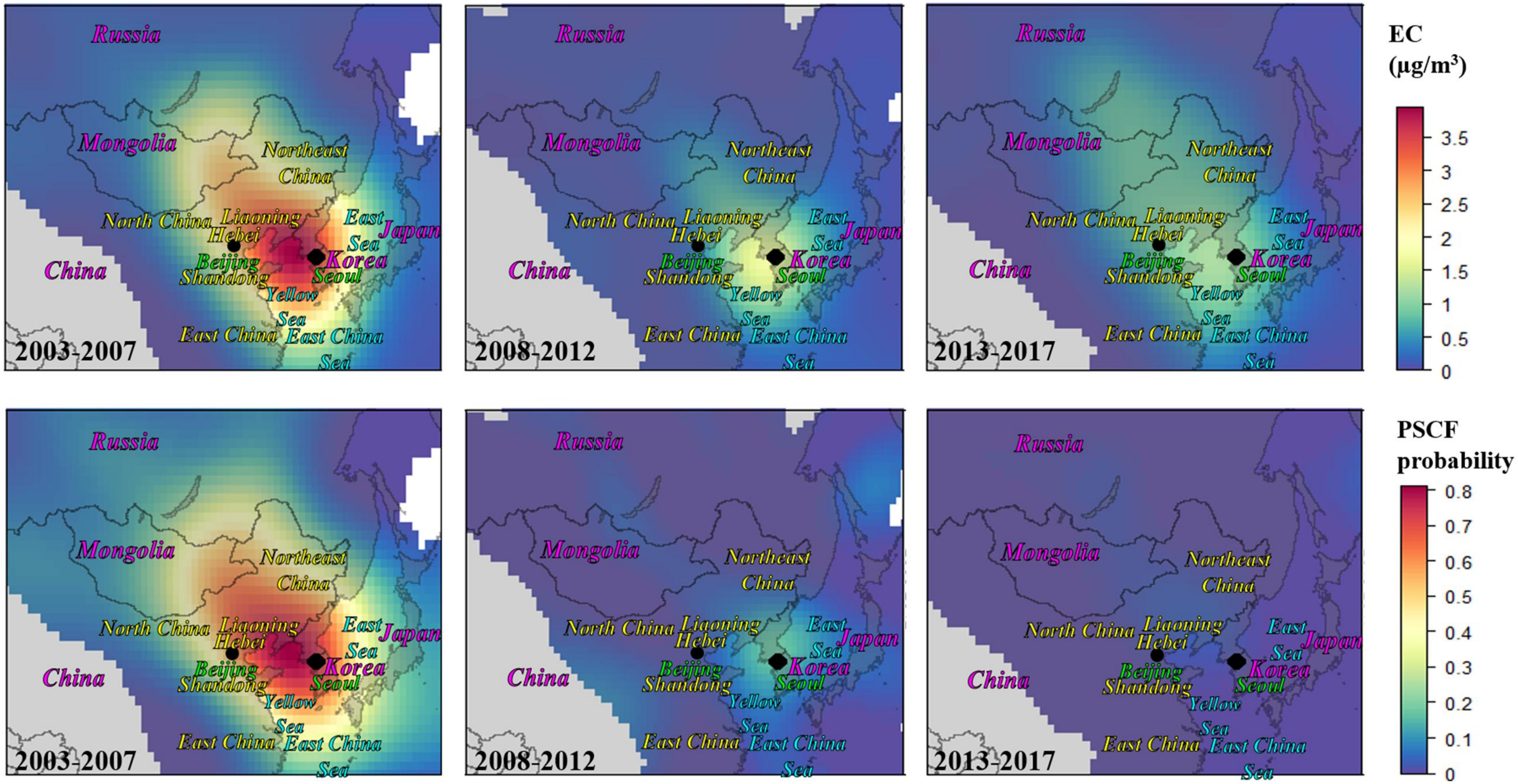

Figure 19. Results of CWT and PSCF for EC in Seoul 2003-2017.

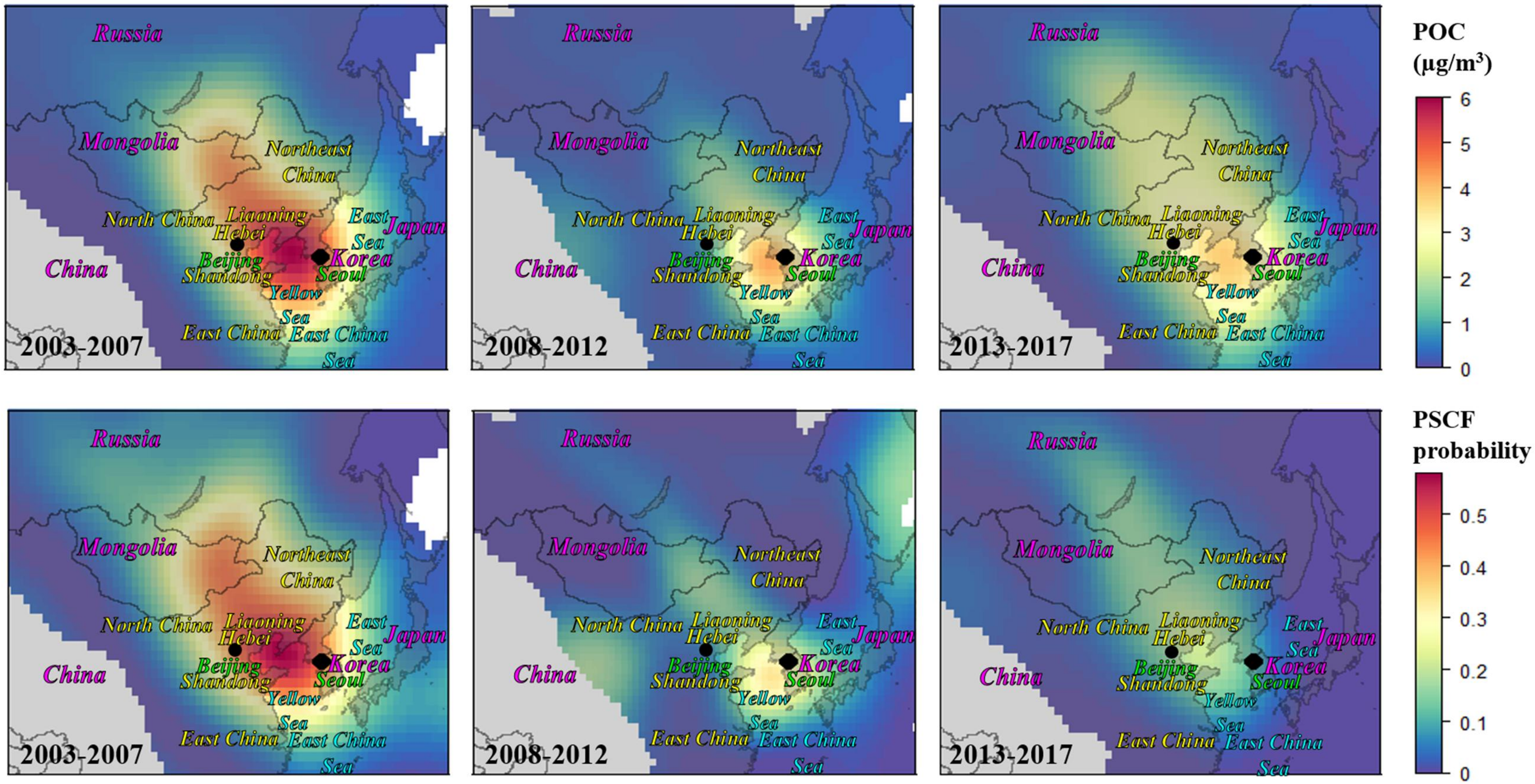

Figure 20. Results of CWT and PSCF for POC in Seoul 2003-2017.

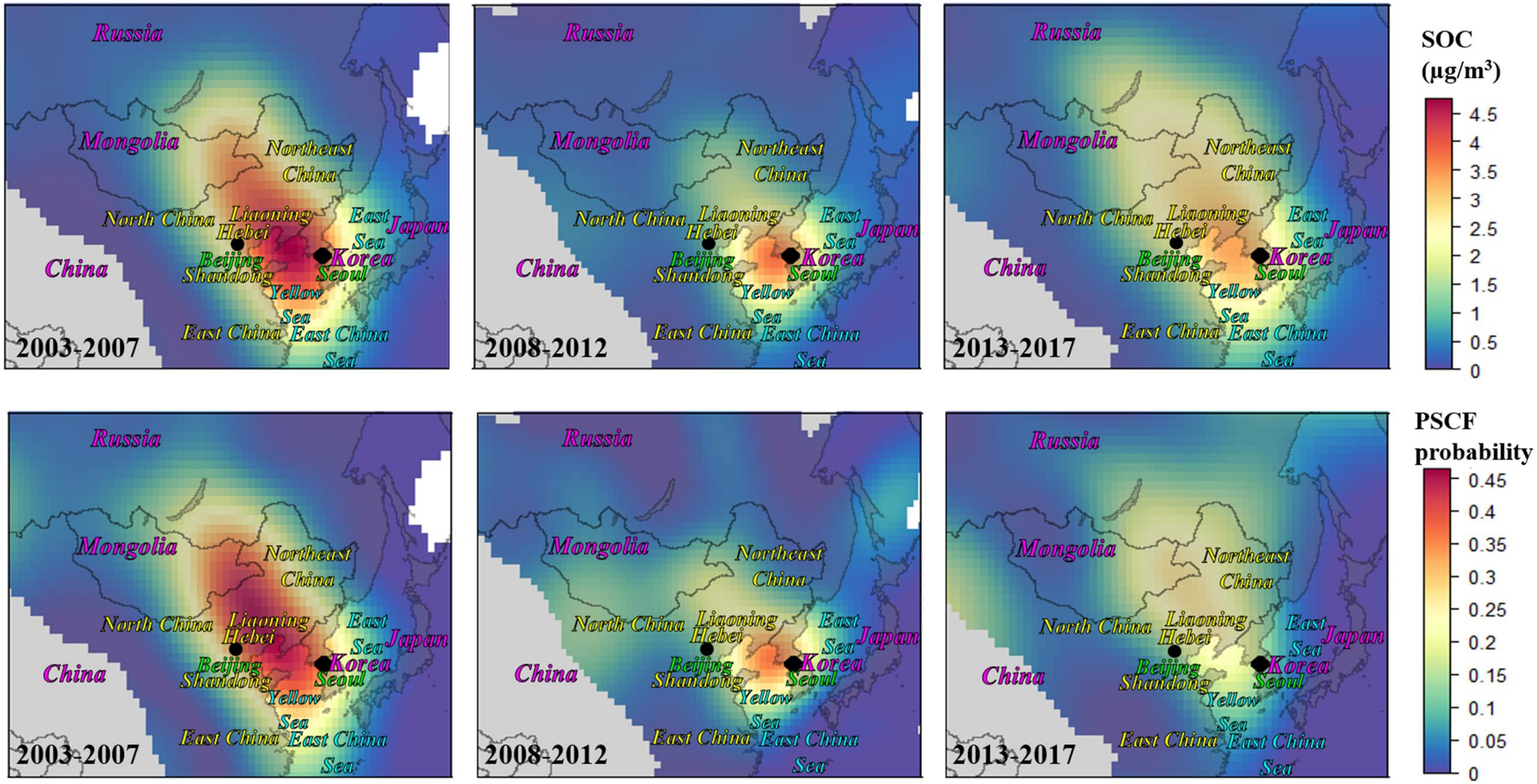

Figure 21. Results of CWT and PSCF for SOC in Seoul 2003-2017.

III. Discussion and Conclusion

Statistically significant reductions in $PM_{2.5}$, and its carbon species were observed for long-term periods in Seoul ($p < 0.001$). However, the tendency of long-term declining trend was estimated to be gradually decreasing. The improvement of air quality is consistent with trends of previous short-term studies and trends of gaseous materials including CO, NO_2, SO_2 and TVOCs, which imply reduction of anthropogenic air pollutant emission. As a result of the correlation analysis between $PM_{2.5}$, its carbon species, meteorological factors, the meteorological factors may affect the concentration change in the short term, but it is estimated that the fundamental decrease in $PM_{2.5}$ and its carbon species was more influenced by the reduction of air pollutant emissions than the short-term changes in meteorological factors.

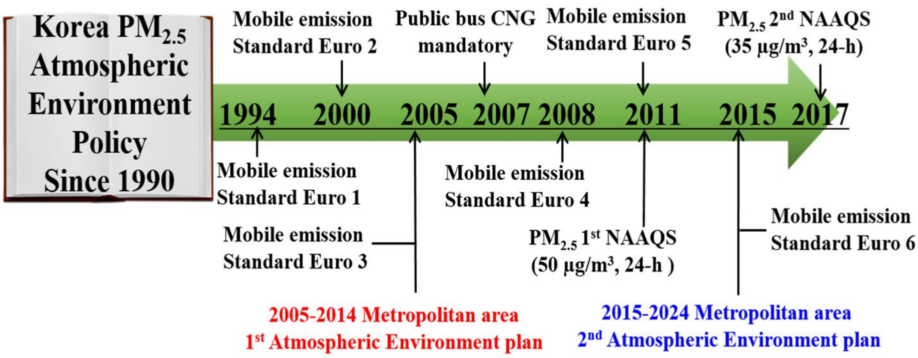

Figure 22. History of Major Atmospheric Environment Policy in the Metropolitan Area, Korea 1990-2017.

In addition, the change in the long-term meteorological factor showed a marked increase in the visibility, which support evident abatement of air pollutant in Seoul during the last 15 years. In the results of estimating local sources using CPF, potential sources of $PM_{2.5}$, SOC were estimated to be in the southwest and northwest of the receptor, respectively, while other carbon species were observed to high probabilities of high concentration events in slow wind speed (less than 3m/s) for all wind directions. In the results of estimating potential sources for long-range-transportation using PSCF and CWT, high concentration loading of $PM_{2.5}$ and carbon species were observed mainly in Middle left of the Korean peninsula, Northeast China, Shandong peninsula, Hebei province, Beijing, upper area of east China. Also, high concentration loading of $PM_{2.5}$ only was observed in Southeast China, which could be a source of secondary inorganic aerosol that contribute significantly to the high concentration of $PM_{2.5}$. Take these results into assessing the long-term trends of $PM_{2.5}$, its carbon species in Seoul, it is estimated that the declining tendency has been mainly affected by the combined effect of reducing air pollutant emissions in Korea and East Asia. In order to compare reported concentrations in other studies with this study, investigation for published literature about $PM_{2.5}$ and carbon species was compared in Figure 23. In case of $PM_{2.5}$, trend of reported concentrations shows a gradual decrease, with a marked fall from 2008 to 2012, followed by a slight increase or even nearly stable average levels since 2013.

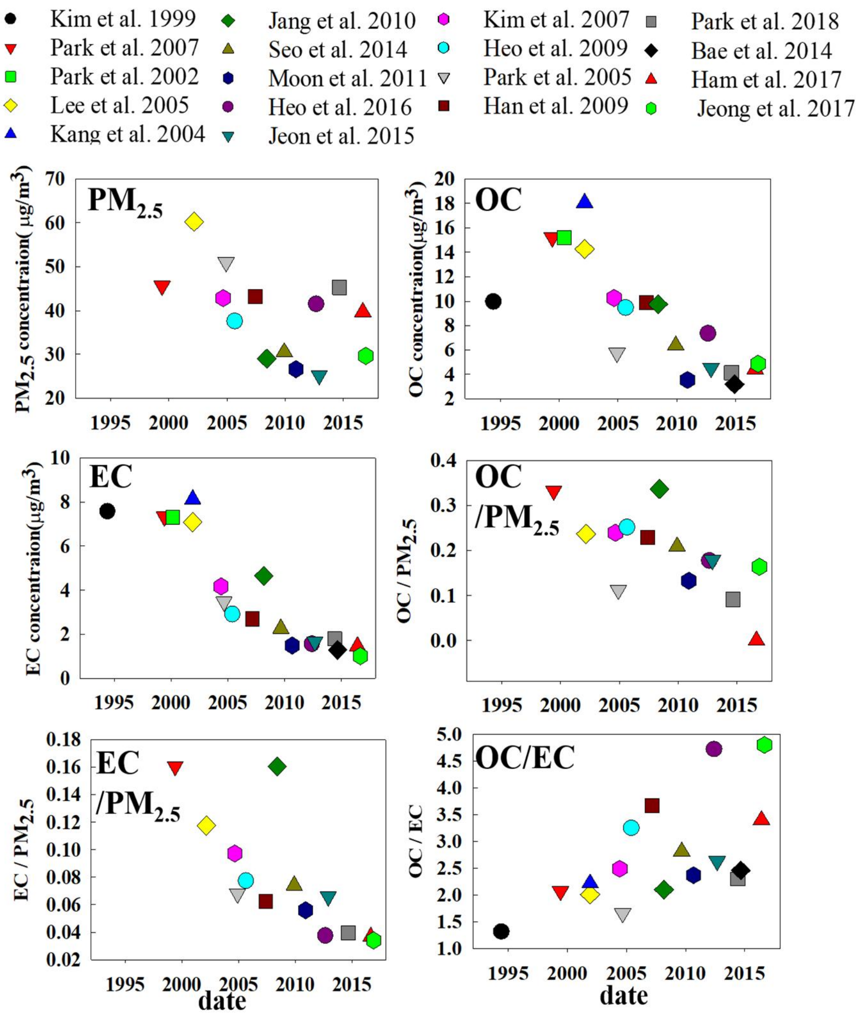

Figure 23. Previous study on carbon species in $PM_{2.5}$ in Seoul, Korea 1994-2017.

These results are consistent with the concentration levels and periods of the $PM_{2.5}$ and its carbon species of this study. Regarding Carbon species, reported concentrations of OC, EC and EC fraction to $PM_{2.5}$ are evident for a gradual decrease in early 2000s. compared with 2010s. The OC/EC ratio shows a highly increasing trend, reflecting the declining tendency of EC, which is stronger than the decreasing tendency of OC. Trends of these result on carbon species are coincide again with result of this study. This is the first study that statistically evaluated tracking the long-term (2003–2017) trends in $PM_{2.5}$, OC and EC base on ground-monitoring in Seoul. In order to effective air quality management, it is necessary to continual understand of air pollutant and verifying the achievement of the NAAQS through long-term observation as well as the review of the previous studies results.

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APPENDIX

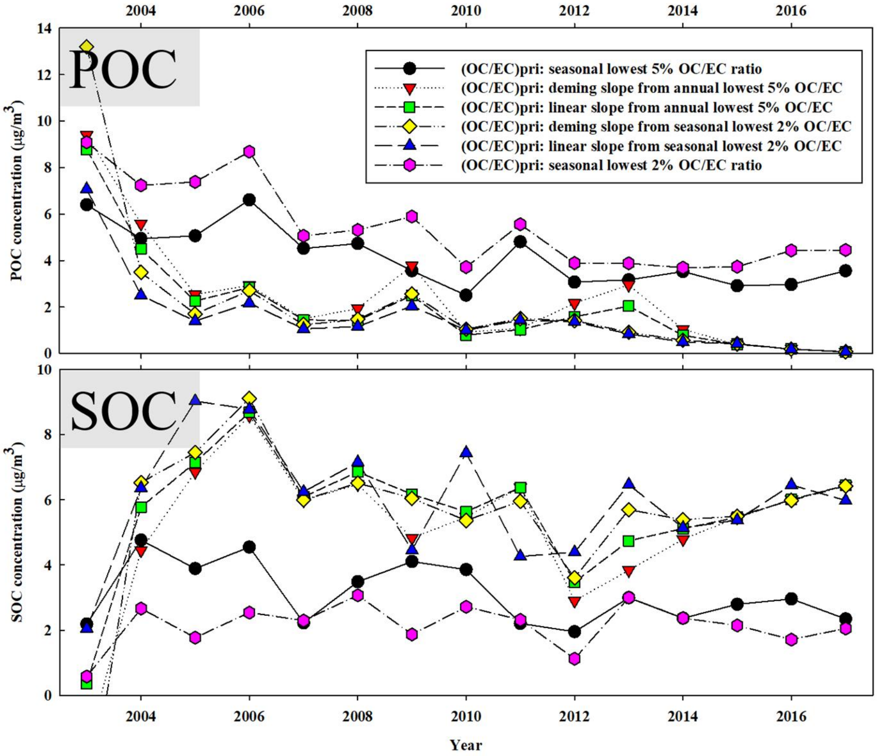

Figure 24. Comparison of SOC and POC concentrations by methods of (OC/EC) ratio calculation.

EC tracer method has been applied in previous studies and this technique is based on the following two assumptions. The most common approach is a linear regression of a subset of data in which $[OC/EC]_{prim}$ is determined as the slope and as $OC_{non\text{-}comb}$ as the y-intercept (Day et al., 2015). In fact, it is difficult to measure the $[OC/EC]_{prim}$, which has a high uncertainty due to unidentified chemical reactions and yield of precursors (Kroll & Seinfeld, 2008). In this study, the four methods to derive $[OC/EC]_{prim}$ were applied and compared. 30Through this process, the lowest 5% of each season was applied as the most reasonable $[OC/EC]_{prim}$ 5% of this study sampling design over the long-term period. Concentrations of POC calculated using the slope of the regression analysis as [OC/EC] $_{prim}$ converge to almost zero since 2014. The EC tracer method using the slope as [OC/EC] $_{prim}$ is estimated to have critical limitation for deriving POC and SOC in the study design of non- real time sampling.

국문 초록

서울의 대기 중 초미세먼지 내 탄소 성분의 15년간 (2003~2017) 농도 변화에 관한 연구

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아시아는 대기 오염이 가장 심각한 대륙 중 하나이지만 대기 환경 정책의 검증을 위한 장기적인 지상 관측과 연구는 매우 부족하다. 이에 본 연구는 초미세먼지와 주요 구성성분인 탄소 화학종(유기탄소, 원소탄소)의 장기간 추이 분석에 초점을 두고, 장기간 추이 변동의 주요 상관 인자 및 잠재적 오염원을 추정하고자 하였다.

서울의 대기 중 초미세먼지는 2003년 3월부터 2017 년 12월까지 24 시간 동안 3일에 1회 쿼츠필터와 테플런 필터에 16.7LPM의 유량으로 포집되었다. 이후 각 필터를 활용하여 질량농도와 탄소성분을 분석하였고, 원소탄소 추적자 방법을 이용하여 일차유기탄소와 이차유기탄소를 추정하였다. 15년 간의 장기간 농도 변화 추이 분석 결과, 초미세먼지, 유기탄소, 원소탄소, 일차유기탄소, 이차유기탄소는 각각 1.91%/년, 3.02%/년, 6.35%/년, 3.20%/년, 2.62%/년의 비율로 감소하는 경향을 보였다 ($p < 0.001$). 유기탄소/원소탄소 비율은 15년 동안 12.56%/년 ($p < 0.001$)의 비율로 증가하는 것으로 추정되었다. 또한, 초미세먼지와 탄소화학종은 장기간 동안 감소했지만, 감소의 경향성은 2008년 이후 상당히 약해진 것으로 추정된다. 이러한 장기간 농도 변화의 경향성은 초미세먼지, 유기탄소, 원소탄소, 유기탄소/원소탄소의 비율의 순서로 각각 최소 13년, 10년, 5년, 4년 이상의 기간부터 통계적으로 유의하게 나타났다. ($p < 0.1$). 초미세먼지 및 탄소화학종의 장기간 자료와 함께 종관기상자료 및 가스상 물질들의 상관관계 분석 결과, 가스상 물질이 기상인자보다 모든 기간에서 초미세먼지와 탄소화학종과의 상관관계가 높게 나타났다. 분석에 활용된 가스상 물질 (CO, SO_2, NO_2)은 장기간 동안 꾸준히 감소하였으며, 주로 화석연료를 기반으로 한 연소 활동에 의한 대기중으로 배출되는 것을 고려할 때, 장기간에 걸친 초미세먼지 및 탄소화학종의 근본적인 감소 경향은 5년 이하의 단기적 기상 요인의 변화 보다는 인위적인 대기오염물질 배출 활동의 변화가 더 크게 영향을 미친 것으로 사료된다. 종관기상자료를

활용한 CPF 모델링 결과, 국지적인 규모에서 초미세먼지와 이차유기탄소의 잠재적 오염원은 각각 남서풍과 북서풍 방향에 위치한 것으로 판단된다. 나머지 탄소화학종의 경우, 비교적 모든 풍향에서 느린 풍속 조건(풍속 3 m/s 이하)에서 고농도 사례(농도가 상위 25% 값 이상에 해당하는 경우) 발생 확률이 높았다. 공기 역궤적 자료를 활용한 PSCF와 CWT의 모델링 결과, 장거리 이동에 의한 초미세먼지와 탄소화학종의 잠재적 오염원 지역은 한반도 서부 중앙 지역, 중국 동북부, 산둥성, 허베이성, 북경, 중국 동부 지역이 가능 지역으로 추정되었다. 초미세먼지의 경우 탄소 화학종과 달리, 중국 남동부 지역이 주요 잠재 오염원 지역으로 추정되었다. 기상자료들을 활용한 이러한 모델링 결과들은 초미세먼지의 고농도 사례를 유발하는 이차 무기에어로졸 등의 서로 다른 오염원 지역으로부터 서울 지역으로 유입되고 있음을 시사한다. 위의 결과들을 종합적으로 해석하면, 서울의 초미세먼지와 탄소화학종의 감소 추이는 주로 국내와 동아시아의 대기 오염 물질 배출량 감소로 인한 복합적 영향이 반영된 것으로 추정된다. 또한 이러한 추이는 서울의 초미세먼지와 탄소화학종의 단기연구들의 결과 경향성과 일치한다.

본 연구는 서울에서의 실제 측정을 통한 초미세먼지와 탄소화학종 농도 변화의 장기간 추이를 통계적으로 평가한 최초의 연구이다. 향후 효과적인 대기질 관리를 위해서는 대기오염물질의 장기간 측정을 통한 대기환경기준 달성 검토와 이전 연구 결과의 꾸준한 리뷰가 이루어져야 한다.

주요 단어: 초미세먼지 ($PM_{2.5}$), 원소탄소, 유기탄소, 탄소화학종, 이차유기탄소, 일차유기탄소, 장기추이분석, PSCF, CWT, CPF

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