



Article Modeling of Organic Aerosol in Seoul Using CMAQ with AERO7

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Abstract: The Community Multiscale Air Quality (CMAQ) model with the 7th generation aerosol module (AERO7) was employed to simulate organic aerosol (OA) in Seoul, Korea, for the year 2016. The goal of the present study includes the 1-year simulation of OA using WRF-CMAQ with recently EPA-developed AERO7 with pcVOC (potential VOC from combustion) scale factor revision and analysis of the seasonal behavior of OA surrogate species in Seoul. The AERO7, the most recent version of the aerosol module of the CMAQ model, includes a new secondary organic aerosol (SOA) species, pcSOA (potential SOA from combustion), to resolve the inherent under-prediction problem of OA. The AERO7 classified OA into three groups: primary organic aerosol (POA), anthropogenic SOA (ASOA), and biogenic SOA (BSOA). Each OA group was further classified into 6~15 individual OA surrogate species according to volatility and oxygen content to model the aging of OA and the formation of SOA. The hourly emissions of POA and SOA precursors were compiled and fed into the CMAQ to successfully simulate seasonal variations of OA compositions and ambient organic-matter to organic-carbon ratios (OM/OC). The model simulation showed that the POA and ASOA were major organic groups in the cool months (from November to March) while BSOA was a major organic group in the warm months (from April to October) in Seoul. The simulated OM/OCs ranged from 1.5~2.1 in Seoul, which agreed well with AMS measurements in Seoul in May 2016.

Keywords: organic aerosol; POA and SOA; CMAQ; AERO7; OM/OC

1. Introduction

 $PM_{2.5}$ (particulate matter with an aerodynamic diameter of less than 2.5µm) harms human health [1,2] and degrades visibility [3,4]. Organic aerosol (OA) is a major chemical component of $PM_{2.5}$ in most urban areas. OA accounts for 21~69% of the submicron particulate matter mass at the 30 monitoring sites in the Northern Hemisphere [5] and accounts for 10~40% of $PM_{2.5}$ mass in Korea [6–10].

Primary organic aerosol (POA) is emitted directly from emission sources and secondary organic aerosol (SOA) is formed from volatile organic compound (VOC) precursors. Various aerosol modules simulating the aging of OA and the formation of SOA have been developed and incorporated into chemical transport models [11–17]. AERO is an aerosol module for the Community Multiscale Air Quality Model (CMAQ; [18]); AERO2 (2nd generation of AERO) is the first version of AERO including POA and SOA with simple SOA forming reactions [19]. AERO3 improves the SOA treatment by including semivolatile compounds partitioning between gas and aerosol phases [20].

As the CMAQ with AERO3 and AERO4 tended to underpredict the OA concentration [21,22], many laboratory and modeling studies were made to discover new pathways for SOA formation. AERO5 adds isoprene, sesquiterpenes, benzene, glyoxal, and methylglyoxal as new SOA precursors based on the work of Edney et al. [23] and Carlton et al. [24].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Despite the expansion of SOA precursors, the underprediction of CMAQ was not fully resolved and further expansion or update of SOA yield was recommended [14,25].

The AERO7, a newly formulated aerosol module [26], introduced a new SOA precursor named pcVOC, potential VOC from combustion, which forms potential SOA from combustion (pcSOA; [27]) through OH oxidation reactions. Similarly, Zhao et al. [28] and An et al. [29] proposed semivolatile/intermediate-volatility organic compounds (S/IVOC) from combustion sources as SOA precursors instead of pcVOC. On the other hand, organic emissions from volatile organic products (VCPs) may contribute to SOA formation [30–32]. All of these three schemes are able to produce SOA large enough to eliminate the underprediction. The emissions and oxidation mechanisms of pcSOA, S/IVOC, and VCPs are susceptible to uncertainty. Therefore, mathematical modeling of SOA using air quality models requires a careful estimation of parameters related to SOA formation using observation data.

Although the AERO7 adapted new SOA parameters, there are few studies conducting annual OA simulation using AERO7 in Korea and comparing modeled OA by AERO7 to observations. The present work was aimed at the simulation of OA using WRF-CMAQ with recently EPA-developed AERO7 with revision of the parameter of pcVOC, performance evaluation in predicting OA surrogate species, and the analysis of seasonal behaviors of OA surrogate species in Seoul. The model performance was evaluated using PM supersite monitoring data to optimize the pcSOA-related parameters. The PM supersites in KOREA monitor carbonaceous aerosol mass using the thermal/optical carbon analyzer based on the NIOSH 5040 method for routine monitoring. The mass of total organic carbon (OC) is measured without differentiating primary and secondary components. The elemental carbon (EC) tracer method [33] was applied to estimate the primary and secondary organic carbon (POC and SOC) from the total OC and EC observation data and to compare them to the model results.

2. Materials and Methods

2.1. Monitoring of Carbonaceous Aerosol and Estimation of the Secondary Organic Aerosol Concentration

The Korean Ministry of Environment established ten PM_{2.5} supersites to routinely monitor hourly PM_{2.5} chemical compositions, sulfate, nitrate, ammonium, OC, EC, and minerals. The data used for model verification were collected from two Korean PM supersites, the Bulgwang (BG) and Baengnyeong (BN) sites. The BG site is an urban site located in the North of Seoul and the BN site is a remote site located in the upwind region of Seoul as shown in Figure 1.

OA is directly emitted into the air (POA) or formed in the atmosphere through the photochemical oxidation of organic gases and subsequent gas/particle partitioning (SOA). POA and SOA have different origins and different impacts on human health [34]. Therefore, designing cost-effective mitigation strategies requires information on POA and SOA ratios.

A state-of-the-art instrument including an aerosol mass spectrometer (AMS) has been recently developed to investigate POA and SOA separately, but the cost of its installation and operation limits the number of monitoring sites and the monitoring duration. Instead, a thermal/optical carbon analyzer has been used for routine monitoring [35] by most institutes including the $PM_{2.5}$ chemical speciation network (CSN) of the US-EPA, the European Supersites for Atmospheric Aerosol Research (EUSAAR), and Korean $PM_{2.5}$ supersites [36].

The thermal/optical carbon analyzer uses the NIOSH 5040 method for separating organic carbons from inorganic carbons and the non-dispersive infrared method for the analysis of CO₂ generated from the combustion of organic and inorganic carbon. It measures the mass of OC instead of the organic matter (OM) without differentiating primary and secondary components. Turpin and Huntzicker [33] proposed the EC tracer method,

which assumes a linear relationship between the POC and EC concentrations. Then, the POC concentration can be estimated by:

$$[POC] = a + b [EC] \tag{1}$$

The intercept "a" represents the non-combustion POC concentration and the slope "b" becomes the POC to EC mass concentration ratio (POC/EC) if "a" is negligible. The POC concentration may be approximated by the OC concentration in the SOC-free conditions to yield:

$$[OC]_{SOC-free} = a + b [EC]$$
⁽²⁾

Meteorological conditions or OC to EC concentration ratios (OC/EC) were used to choose the SOC-free case [33,35,37]. In the present work, the data with OC/EC less than their fifth percentile values were chosen as a subset of the SOC-free case. The regression analysis method was applied to this subset to determine "a" and "b". Because both the SOC-free OC concentration and the EC concentration may have non-negligible uncertainties, the Deming regression method was used instead of the ordinary linear regression method. In addition, the uncertainties of OC and EC concentrations were assumed to be equal following the previous work [37].



Figure 1. The study area and the selected PM supersite locations: (**a**) outer domain, (**b**) inner domain, (**c**) BG supersite, and (**d**) BN supersite.

Once "a" and "b" are determined, one can calculate the POC concentration from the observed EC concentration using Equation (1) and subsequently the SOC concentration using:

$$[SOC] = [OC] - [POC]$$
(3)

We compared the SOC concentrations estimated by Equation (3) with those predicted by the air quality model for model validation.

2.2. Model Simulation and Performance Evaluation

WRF (Weather Research and Forecast) version 3.6 and CMAQ (Community Multiscale Air Quality) version 5.3.1 were used to model the PM_{2.5} mass and chemical compositions. The Global to Mesoscale Air Quality Forecast and Analysis (GMAF) framework [38] was employed to assign initial and boundary conditions and to carry out a grid nudging-based four-dimensional data assimilation (FDDA) for CMAQ and WRF modeling. The 0.25° Global Data Assimilation System (GDAS) dataset was used for the WRF and the 0.4° Copernicus Atmospheric Monitoring Service (CAMS) dataset for the CMAQ [39].

The 7th generation aerosol module (AERO7) was used as an aerosol module and the 3rd release of the carbon bond mechanism version 6 (CB6r3; [40]) was used as the gas-phase chemical mechanism. The WRF is configured as follows: YSU PBL scheme for the planetary boundary layer, Revised MM5 surface layer scheme for the surface layer, Unified Noah land surface model for the land surface model, WSM6 microphysics scheme for the microphysics, Kain–Fritsch cumulus convection for the cumulus parameterization, the Goddard shortwave radiation scheme for the shortwave radiation, and the RRTM longwave radiation scheme for the longwave radiation.

A nested grid domain system was adopted: 27 km grid spacing for the outer domain and 9 km grid spacing for the inner domain. The outer domain covers the Korean peninsula, eastern and southern China, part of Russia, and Japan. The study area shown in Figure 1 was taken as the inner domain, which includes South Korea and a part of North Korea. The modeling period is from 1 December 2015 to 30 November 2016, covering one whole year.

The model performance was evaluated by three statistical metrics: the correlation coefficient (R), the normalized mean error (NME), and the normalized mean bias (NMB). The formulas of the statistical metrics are:

$$\mathbf{R} = \frac{\sum_{i=1}^{i=N} (O_i - \overline{O}) (M_i - \overline{M})}{\sqrt{\sum_{i=1}^{i=N} (O_i - \overline{O})^2} \sqrt{\sum_{i=1}^{i=N} (M_i - \overline{M})^2}}$$
(4)

NME (%) =
$$\frac{1}{N} \frac{\sum_{i=1}^{i=N} |M_i - O_i|}{\overline{O}} \times 100$$
 (5)

NMB (%) =
$$\frac{\overline{M} - \overline{O}}{\overline{O}} \times 100$$
 (6)

where subscript 'O' and 'M' denote the observation and the model prediction, respectively. 'N' is the total number of paired datasets. The overbar indicates an average value. Emery et al. [41] reviewed modeling studies carried out in the United States of America (USA) and recommended a set of numerical "goals" and less restrictive "criteria" for the R, the NME, and the NMB for the evaluation of chemical transport models. We used these goals and criteria for model verification as described in Section 3.1.

2.3. Atmospheric Aerosol Chemistry

The AERO7 categorized the OA into POA, anthropogenic SOA (ASOA), and biogenic SOA (BSOA). Each OA category was further classified according to the scheme of the volatility basis set (VBS; [42,43]). The POA is composed of the directly emitted POA (EPOA) and their oxidation products (OPOA). Each of the EPOA and OPOA has five surrogate species with varying of volatility, effective saturation concentration (C*), oxygen to carbon ratio (O/C), and OM to OC ratio (OM/OC) as listed in Table 1 [27]. The C* of EPOA surrogate species, an indicator of volatility, was set to range from 0.1 to 1000 μ g/m³. The EPOA surrogate species have a high carbon content such that O/Cs and OM/OCs are low. The OPOA surrogate species are formed from the oxidation products of EPOA, which results in lower volatility and higher O/Cs and OM/OCs than the EPOA surrogate species.

	Name	C* ⁵ (µg/m ³)	O/C	OM/OC ⁶
	ALVPO1 ¹	0.1	0.185	1.39
	ASVPO1 ²	1	0.123	1.32
EPOA	ASVPO2	10	0.073	1.26
	ASVPO3	100	0.032	1.21
	AIVPO1 ³	1000	0.000	1.17
OPOA	ALVOO1 ⁴	0.01	0.886	2.27
	ALVOO2	0.1	0.711	2.06
	ASVOO1	1	0.567	1.88
	ASVOO2	10	0.447	1.73
	ASVOO3	100	0.345	1.60

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 1 A = aerosol; LV = low volatility; PO = primary organic; 2 SV = semi-volatile; 3 IV = intermediate volatility; 4 OO = oxidized organic; 5 C* = effective saturation concentration; 6 OM = organic matter, OC = organic carbon.

Anthropogenic SOA (ASOA) is formed from the oxidation products of anthropogenic VOC (AVOC) gases, which includes toluene, xylene, benzene, PAH (polycyclic aromatic hydrocarbon), and potential VOC from combustion (pcVOC). A previous version of the aerosol module tended to underestimate the SOA mass. The AERO7 postulated that the SOA-forming VOCs emitted from combustion were not fully accounted for and introduced the pcVOC as a new VOC surrogate species [27]. pcVOC reacts with the OH radical to form a low-volatility potential secondary organic gas from combustion (pcSOA). The AERO7 presumed that the pcVOC emission is proportional to the POA emissions and calculated the pcVOC emission by multiplying the POA emission by a pcVOC emission scale factor. There is no theoretical way to determine a pcVOC emission scale factor. In this work, the pcVOC emission scale factor was set to 0.0155 mole-pcVOC/g-POA based on the sensitivity runs made for Korea by Cho et al. [38].

The 6th generation aerosol module (AERO6) explicitly models the transformation of AVOCs with over twenty ASOA species. The AERO7 lumped these explicit ASOA species into four ASOA surrogate species, named AAVB1~AAVB4, according to the VBS scheme as shown in Table 2. AAVB1 has the lowest volatility with the C* of 0.01 μ g/m³, and the C* values of AAVB2, AAVB3, AAVB4 are 100, 1000, and 10,000 times the C* of AAVB1, respectively. AAVB1~AAVB4 have O/Cs in the range of 0.659~1.227 and OM/OCs in the range of 1.99~2.70, which are similar to those of the OPOA. AAVB2, AAVB3, and AAVB4 form oligomer products of ASOA compounds (AOLGA). The values of C*, O/C, and OM/OC of AOLGA are $10^{-10} \mu$ g/m³, 1.067, and 2.5, respectively. pcSOA has low volatility with the C* of $10^{-5} \mu$ g/m³, and the values of O/C and OM/OC of the pcSOA are 0.667 and 2, respectively.

The VOCs released from plants are called biogenic VOCs (BVOCs), which include monoterpenes, sesquiterpenes, isoprene, glyoxal, and methylglyoxal. BVOCs produce gas-phase oxidation products via photochemical degradation. Various heterogeneous reactions of these gaseous precursors form the biogenic SOA (BSOA) [44]. The AERO7 models these processes by 15 BSOA surrogate species as listed in Table 3. The monoterpene surrogate species in the AERO7 were divided into six volatility bins according to the VBS scheme (AMT1~AMT6). In addition, the organic nitrate from monoterpene oxidation (AMTNO3) and its hydrolysis product (AMTHYD) were added to the BSOA to account for high SOA yields from organic nitrates observed in the southeastern USA [45]. The O/Cs and the OM/OCs of AMT1~AMT6, AMTNO3, and AMTHYD are lower than those of the ASOA surrogate species. The O/C and the OM/OC of the ASQT are similar to those of the monoterpene surrogate species. On the other hand, the O/Cs and the OM/OCs of

the isoprene surrogate species (AISO1, AISO2, and AISO3) are higher than those of the monoterpene surrogate species and similar to those of the ASOA surrogate species. ASQT, AISO1, and AISO2 form oligomer products of BSOA compounds, AOLGB. AOLGB has low volatility with C* equal to $10^{-10} \ \mu g/m^3$ and with the OM/OC equal to 2.1. AGLY and AORGC are produced from aerosol uptakes and in-cloud processing of glyoxal and methylglyoxal, respectively. They also have low volatility with C* equal to $10^{-10} \ \mu g/m^3$ and with OM/OCs equal to 2.13 and 2.00, respectively.

Name	Formation Processes	C* (μg/m ³)	O/C	OM/OC
AAVB1		0.01	1.227	2.70
AAVB2		1	0.947	2.35
AAVB3	 Oxidation products of anthropogenic VOCs 	10	0.803	2.17
AAVB4		100	0.659	1.99
pcSOA	Oxidation products of pcVOCs	10^{-5}	0.667	2.00
AOLGA	Oligomer products of anthropogenic SOA compounds	10^{-10}	1.067	2.50

Table 2. Names and chemical properties of the ASOA surrogate species at 298 K.

Table 3. Names and chemical properties of the BSOA surrogate species at 298K.

Name	Formation Processes	C* (µg/m ³)	O/C	OM/OC
AMT1		0.01	0.400	1.67
AMT2		0.1	0.400	1.67
AMT3	- SOA product from monoterpane photo-ovidation	1	0.444	1.72
AMT4	- SOA product nom monoterpene photo-oxidation -	10	0.300	1.53
AMT5	-	100	0.333	1.57
AMT6	-	1000	0.200	1.40
AMTNO3	Semi-volatile organic nitrates from monoterpene oxidation	12	0.587	1.90
AMTHYD	Non-volatile organic hydrolysis product of MTNO ₃	10^{-10}	0.299	1.54
ASQT	Semi-volatile SOA product from sesquiterpene oxidation	24.984	0.283	1.52
AISO1		116.01	0.827	2.20
AISO2	- Semi-volatile SOA products from isoprene	0.617	0.851	2.23
AISO3	Acid-catalyzed isoprene SOA compounds	10^{-10}	1.307	2.80
AOLGB	Oligomer products of biogenic SOA compounds	10 ⁻¹⁰	0.747	2.10
AGLY	SOA from the aerosol uptake of glyoxal and methylglyoxal	10^{-10}	0.771	2.13
AORGC	SOA from the cloud processing of glyoxal and methylglyoxal	10^{-10}	0.667	2.00

2.4. Emissions

The Korean–United States Air Quality Study (KORUS-AQ) version 2.1 emission inventory was used for the anthropogenic emissions of the Northeastern Asian region and the Clean Air Policy Support System (CAPSS) emission inventory was used for the anthropogenic emissions of Korea. The base year of both emission inventories was 2016. The natural emissions were estimated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 [46]. Figure 2 shows the monthly emissions of POA, AVOCs, and BVOCs in the Korea model domain. The POA was mainly emitted from mobile sources, industrial combustion, and residential and commercial heating. As shown in Figure 1a, the Korea model domain includes a part of North Korea, where residential heating emitted a large amount of POA in the cool months (from November to March).



Figure 2. Monthly average VOC emissions in the Korea model domain. (**a**) POA and (**b**) AVOCs and BVOCs.

The emissions of AVOCs, defined as anthropogenic VOCs forming ASOA in this work, consisted of 66% toluene, 21% xylene, and 13% pcVOC with negligibly small benzene, PAHs, and long-chain alkanes. The monthly average emissions of pcVOC occupy the AVOCs emissions by 11% in August and 16% in January: small in the warm months (from April to September) and large in the cool months. On the contrary, the monthly average emissions of toluene and xylene in the warm months were larger than those in the cool months, offsetting the seasonal variation of pcVOC. As a result, the monthly average AVOC emissions changed by only less than 6% over the year.

Isoprene and terpenes together comprise most of the BVOC emissions in the Korea model domain. The isoprene and terpene emissions increase exponentially with temperature [47,48] and peak in the warm months. This seasonal change made the BVOCs dominate in the warm months while the AVOCs dominated in the cool months, as also shown in Figure 2b.

3. Results and Discussion

3.1. Model Evaluation on OC and EC Prediction

Detailed model performance evaluation on various meteorological parameters and inorganic chemical components including sulfate, nitrate, and ammonium have been presented elsewhere [38,49]. Therefore, we limited model validation to carbonaceous aerosol component mass and PM_{2.5} mass.

Table 4 compares the annual average concentrations of observed and modeled OC, EC, and $PM_{2.5}$ concentrations in two supersites, the BG and BN sites. In addition, the model performance metrics are also presented. The observed OC, EC, and $PM_{2.5}$ concentrations at the BG site, an urban site, are higher than those at the BN site, a remote site. As the individual component concentrations add up, the associated errors often cancel each other to improve the overall performance statistics. The correlation coefficient (R), normalized mean error (NME), and normalized mean bias (NMB) of $PM_{2.5}$ appeared better than those of OC and EC. The R of $PM_{2.5}$ was 0.81 for the BG site and 0.75 for the BN site, exceeding the goal (>0.7) set by Emery et al. [41]. The Rs of OC and EC were slightly lower than the R of $PM_{2.5}$ in most of the cases, and they were deemed reasonably good.

Table 4. Annual average concentrations of observed and modeled OC, EC, and PM_{2.5} and model performance metrics for OC, EC, and PM_{2.5} at the BG and BN sites.

		Number of Data	Average Observation (µg/m ³)	Average Model (μg/m³)	R	NME (%)	NMB (%)
06	BG	7912	3.64	3.33	0.64	30.68	-8.05
00 —	BN	6502	3.12	3.25	0.76	39.45	12.75
EC —	BG	7909	1.23	1.49	0.75	30.54	20.44
	BN	6461	0.85	0.90	0.56	44.10	11.30
PM _{2.5} —	BG	8437	27.75	25.68	0.81	22.02	-7.63
	BN	8225	21.80	20.77	0.75	29.81	-4.49

The NMEs of OC and EC satisfy the accuracy goal (<45% for OC and <50% for EC). In addition, the NMBs of OC and EC mostly meet the accuracy goal (< \pm 15% for OC and < \pm 20% for EC). Despite differences in the site characteristics between the BG and BN sites, there are no systematic differences in R, NME, and NMB between these two sites. Therefore, it may be concluded that the modeled OC and EC concentrations agree reasonably well with the observation.

Figures 3 and 4 compare daily variations of OC, EC, and PM_{2.5} concentrations between observations and modeling at the BG and BN sites. At the BG site, the modeled OC, EC, and PM_{2.5} closely follow the observed ones except for the warm months during which the model underestimates the OC and PM_{2.5} and overestimates the EC. At the BN site shown in Figure 4, the modeled OC, EC, and PM_{2.5} closely follow the observed ones except for the cost provides the provide the observed ones except for the cost provides the provide the provides the provide the observed ones except for the cost provides the provide the provides the p

3.2. Model Evaluation on SOC Prediction

The EC tracer method described in Section 2.1 assumes the POC to EC concentration ratio (POC/EC) to be spatially and temporally constant. However, the POC/EC changes with the source types; the POC/ECs of aerosol from biomass burning cover a range of 2.6~5.7; those from fossil fuel combustion are lower than 1 [35]. Therefore, an analysis period should be appropriately set; it should be short enough to have only one type of source dominate, and at the same time, it should be long enough to have a sufficient number of data available for the regression analysis. In this study, we took one month as an analysis period and applied a regression analysis to monitored the concentrations of OC and EC hourly.



Figure 3. Daily variations of OC, EC, and $PM_{2.5}$ concentrations ($\mu g/m^3$) from observation and model in BG supersite. 'obs' denotes observation and 'model' denotes modeling.



Figure 4. Daily variations in OC, EC, and $PM_{2.5}$ concentrations ($\mu g/m^3$) from observations and modeling in at BN supersite. 'obs' denotes observation and 'model' denotes modeling.

Table 5 lists the Deming linear regression analysis results, the standard errors of the regression, and the Rs at two PM supersites, the BG and BN sites, the site location and the site characteristics of which were presented in Section 2.1. The plots of the Deming linear regression analysis results for the BG and BN sites can be found in Figure S1 and Figure S2. The magnitude of intercept at both sites is one order magnitude smaller than the POC concentration, the dependent variable, and the Rs between the POC and EC concentrations are greater than 0.9 in most months. The averaged standard errors of the regression at the BG site are smaller than $0.73 \ \mu g/m^3$, and those at the BN site are smaller than $0.44 \ \mu g/m^3$. In addition, we used the slope as an estimate of POC/EC like the previous works [35,37,50].

Table 5. The intercept and slope with a 95% confidence interval calculated by the Deming linear regression, standard errors of the regression, and the correlation coefficients (R) at the BG and BN sites.

		BG		BN				
Month	Slope	Intercept (µg/m ³)	Standard Error (µg/m ³)	R	Slope	Intercept (µg/m ³)	Standard Error (µg/m ³)	R
Dec	1.43 ± 0.10	-0.21 ± 0.10	0.37	0.98	2.14 ± 0.27	-0.05 ± 0.17	0.44	0.98
Jan	1.66 ± 0.26	-0.24 ± 0.43	0.72	0.89	1.63 ± 0.20	-0.07 ± 0.11	0.20	0.94
Feb	1.20 ± 0.25	0.02 ± 0.26	0.48	0.96	1.65 ± 0.10	-0.13 ± 0.08	0.11	0.98
Mar	1.14 ± 0.20	-0.15 ± 0.38	0.51	0.90	1.36 ± 0.16	0.13 ± 0.12	0.24	0.97
Apr	1.10 ± 0.07	-0.02 ± 0.11	0.16	0.99	1.65 ± 0.17	-0.11 ± 0.13	0.24	0.96
May	0.78 ± 0.12	0.05 ± 0.13	0.35	0.93	1.73 ± 0.04	0.02 ± 0.06	0.13	0.99
Jun	1.28 ± 0.24	-0.17 ± 0.36	0.45	0.90	1.83 ± 0.37	-0.16 ± 0.20	0.12	0.82
Jul	0.82 ± 0.10	-0.14 ± 0.05	0.10	0.95	0.83 ± 0.31	0.12 ± 0.10	0.17	0.79
Aug	0.94 ± 0.09	-0.16 ± 0.05	0.11	0.97	No data	No data	No data	No data
Sep	1.05 ± 0.04	-0.12 ± 0.06	0.13	0.98	No data	No data	No data	No data
Oct	1.44 ± 0.17	-0.27 ± 0.25	0.73	0.93	2.49 ± 0.30	-0.10 ± 0.20	0.17	0.96
Nov	2.02 ± 0.25	-0.39 ± 0.50	0.29	0.93	2.07 ± 0.12	0.10 ± 0.09	0.11	0.99

The slopes, POC/ECs, range from 0.78 to 2.02 at the BG site, an urban site. The slopes are higher in the cool months (from November to March) than in the warm months (from April to October) because of the stronger effects of biomass burning in the cool months as pointed out by Pio et al. [35]. The slopes at the BN site, a remote site, are bigger than those at the BG site due to the greater contribution from biomass burning.

The EC tracer method parameters, slope and intercept, listed in Table 5 were used to calculate the monthly values of SOC to POC concentration ratios (SOC/POCs) from the OC concentrations monitored at the BG and BN sites. Figure 5 compares the SOC/POCs directly calculated by CMAQ to the EC tracer method. At the BG monitoring site, the estimated monthly SOC/POCs were 1.0~1.3 in the cool months and increased in the warm months, reaching the maximum of 4.4 in July. The modeled ratios were in good agreement with the estimated ones in the cool months. In the warm months, BVOCs emitted from plants increased to form more SOC to increase the values of SOC/POCs. The modeled and observed values of SOC/POCs at the BN site behave similarly to those at the BG site especially in the cool months, thus exhibiting the regional characteristics of SOC/POC.



Figure 5. Monthly average SOC to POC concentration ratios (SOC/POCs) from observations and modeling. (**a**) The BG supersite and (**b**) the BN supersite. 'obs' denotes SOC/POCs calculated by the EC tracer method and 'model' denotes those calculated by CMAQ.

The POC and SOC concentrations from modeling are compared to those estimated by the EC tracer method as shown in Table 6. The performance metrics including R, NME, and NMB are also presented. The model performance of individual components tends to degrade as the OC is divided into POC and SOC, resulting in the R, NME, and NMB of the POC and SOC being lower than those of the OC, as shown in Table 4. The NMEs and NMBs of POC and SOC mostly satisfy their accuracy criteria for OC (<65% for NME, <±50% for NMB). Because the threshold values of NME and NMB of the individual OC species are expected to be lower than those of the total OC, the model performance in predicting the SOC and POC is deemed reasonably good.

		Average Estimates (µg/m ³)	Average Model (μg/m ³)	R	NME (%)	NMB (%)
POC —	BG	1.39	1.03	0.68	39.77	-26.22
	BN	1.45	1.16	0.54	48.88	-20.44
SOC —	BG	2.26	2.32	0.50	41.85	2.98
	BN	1.70	2.39	0.57	72.48	40.29

Table 6. Model performance metrics for POC and SOC at the BG and BN sites.

3.3. Modeling of the Seasonal Behavior of Organic Aerosol Compositions

Figure 6a displays the monthly average concentrations of the POA, the ASOA, and the BSOA in Seoul. The POA and the ASOA occupied a larger fraction in the cool months (from November to March), while the BSOA occupied a larger fraction in the warm months (from April to October) due to the seasonal variation in precursor emissions. The monthly average POA concentrations appeared similar to the monthly average ASOA concentrations. In the warm months, the wind direction shifts from the northwest to the southeast to bring the air mass with lower PM_{2.5}, POA, and SOA concentrations. Moreover, the POA emission decreased in the warm months as shown in Figure 2a to promote a further decrease in the POA concentration.

Figure 6b shows the composition profiles of POA; ALVPO1, ASVPO1, ASVPO2, and ASVPO3 are the directly emitted POA (EPOA), and ALVOO1 and ALVOO2 are their oxidation products (OPOA) formed by reacting with the OH radical. In the cool months, the POA was mainly composed of EPOA species due to the weak solar radiation and low OH radical concentration. On the contrary, the relative contribution of OPOA species to the POA concentration increased in the warm months as the solar radiation and the OH radical concentration increased.



Figure 6. Monthly mass composition in Seoul. (a) OA, (b) POA, (c) ASOA, and (d) BSOA. The AIVPO1, ASVOO1, ASVOO2, ASVOO3, AAVB2, AAVB3, AAVB4, and AORGC are not shown in (b–d) due to their negligible mass compositions. In (d), the notation of 'AMT' means the sum of AMT1~AMT6, and the percent bars for the cool months were omitted because of negligible BSOA mass concentrations.

As shown in Figure 6c, the pcSOA was a major ASOA species in all seasons as designed, and it reduced the underestimation of ASOA. As noted in Section 2.4, the aromatic gas emissions increased in the warm months while the pcVOC emissions decreased. The AAVB1 and AOLGA are oxidation products of aromatic gases [30] and therefore increased in the warm months to occupy 17~23% of the ASOA.

Figure 6d shows the monthly average compositions of the BSOA. The AISO3, an acid-catalyzed isoprene SOA compound, had the largest percent contribution, and the AGLY, a non-volatile SOA from heterogeneous uptakes of glyoxal and methylglyoxal, and the AMTHYD, a non-volatile organic hydrolysis product of AMTNO3, had the second and third largest contributions in the warm months, respectively. The oxidation of isoprene by the OH radical at a low NO_x concentration produces IEPOX (isoprene epoxydiol) and the SOA uptakes the IEPOX to form AISO3 [51]. The production rate of IEPOX increases as the ambient temperature increases [52], which resulted in high concentrations of AISO3 in the warm months. This temperature dependency of AISO3 was also observed by Mahilang et al. [53]. The fractions of AGLY ranged from 14~35% in the warm months, which are significant percent contributions to the SOA formation consistent with previous works [13,45,54]. The oxidation of monoterpene by typical photochemical oxidants (OH radical, O₃) and NO₃ radical produces AMT1~AMT6 and AMTNO3, respectively. In addition, the hydrolysis reaction converts AMTNO3 to AMTHYD. As reported by previous works [45,55], the SOA yields from oxidation by NO₃ radical were generally higher than those by the OH radical and O₃, and therefore the sum of the AMTNO3 and AMTHYD concentrations was larger than AMT1~AMT6 as also shown in Figure 6d. The oligomer products from BSOA, AOLGB, occupied 13~23% of the BSOA during the warm months.

3.4. Organic Matter to Organic Carbon Ratio

The organic matter to organic carbon ratios (OM/OCs) were calculated using aerosol surrogate species concentrations predicted by the CMAQ with AERO7. As shown in Figure 7a, the monthly average OM/OCs of total OA ranged between 1.7~2.1, which is consistent with the AMS monitoring data [56]. In the warm months, strong solar radiation accelerated the photochemical oxidation of OAs to increase the monthly average OM/OCs of total OA to as high as 2.0. The monthly average OM/OCs dropped to as low as 1.7 in the cool months.



Figure 7. OM to OC ratios (OM/OCs) in Seoul: (**a**) seasonal variation and (**b**) diurnal variation. In (**a**), the OM/OCs of BSOA in the cool months are not shown due to negligible mass concentrations of BSOA.

Additionally displayed in the same figure are the OM/OCs of the OA subgroups, POA, ASOA, and BSOA. They exhibited monthly variations similar to the OM/OCs of the total OA: high in the warm months and low in the cool months. The ASOA has the highest OM/OC and the POA has the lowest OM/OC. The OM/OCs and O/Cs of individual species constituting each subgroup are presented in Tables 1 and 2. The seasonal variations of the OM/OCs of each subgroup were determined by seasonal changes in chemical constituents. As an oxidation of OAs proceeds, the oxygen atoms are added to the aerosol to increase the OM/OC ratios. Therefore, the concentrations of the highly oxidized form of OA, AAVB1 and AOLGA for ASOA, ALVOO1 for POA, and AISO3 for BSOA, increased in the warm months as shown in Figure 6b–d. As a result, the OM/OCs in the warm months are higher than those in the cool months by approximately 11% for the total OA, 5% for the ASOA, and 13% for the POA.

Figure 7b shows the annually average diurnal variation of the OM/OC of total OA and individual OA groups. The ASOA had the highest OM/OC and the POA had the lowest OM/OC. The diurnal variation was small compared to the annual variation: the daytime average OM/OCs of total OA, POA, ASOA, and BSOA were 1.85, 1.44, 2.05, and 2.02, respectively, approximately the same as the nighttime average OM/OCs.

4. Summary and Conclusions

It is well known that OA is one of the major components of $PM_{2.5}$ in Korea along with sulfate and nitrate [38,57]. In this work, a newly released aerosol module, the AERO7, was implemented onto CMAQ to simulate the OA for the year of 2016 in Seoul, Korea. The AERO7 introduced a new OA species to reduce the underprediction of OA suffered by the previous aerosol modules. The CMAQ model with AERO7 performs very well, satisfying the accuracy goal or criteria for EC, OC, and $PM_{2.5}$ concentrations. Moreover, the calculated OM/OCs ranged from 1.5 to 2.1, which agrees well with the AMS measurements in Seoul in May 2016.

The present model simulation shows that the POA and ASOA were major organic groups in the cool months (from November to March) while BSOA was a major organic group in the warm months (from April to October) in Seoul. The seasonal changes in the emissions of POA and VOC precursors appeared to be responsible for the seasonal variations in POA, ASOA, and BSOA. Each OA group, POA, ASOA, and BSOA, consists of 6~15 individual OA surrogate species classified according to volatility and oxygen content. The ambient temperature and solar radiation intensity affect the distribution of individual OA surrogate species within each organic group. In the present work, ALVPO1 maintains the highest fraction the whole year around. In addition, ASVPO1 and ASVPO2 were major POA surrogate species in the cool months whereas ALVOO1 was a major POA surrogate species in the cool months whereas ALVOO1 was a major BSOA surrogate species and pcSOA was a major ASOA surrogate species.

pcSOA is one of the major OA components, which is formed by the oxidation of pcVOC. The pcVOC emission is estimated by scaling the POA emissions. There is no theoretical way to estimate the pcVOC emission scale factor. Therefore, most works including the present one adjust the scale factor until the modeled OA concentration matches the observed one. It is recommended to have a better representation of pcVOC and compile the emission factors. Other VOC precursors of ASOA rather than pcVOC are aromatics and long-chain alkanes. Model performance evaluation in predicting long-chain alkanes is substantially lacking compared to aromatics, thus requiring future work on emissions and ambient concentration monitoring.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/atmos14050874/s1, Figure S1: Monthly Deming regression analysis results in BG supersite, Figure S2: Monthly Deming regression analysis results in BN supersite.

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