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Validation of SOC Estimation Using OC and EC Concentration in $PM_{2.5}$ Measured at Seoul

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ABSTRACT

The organic carbon in the ambient particulate matter (PM) is divided into primary organic carbon (POC) and secondary organic carbon (SOC) by their formation way. To regulate PM effectively, the estimation of the amount of POC and SOC separately is one of the important consideration. Since SOC cannot be measured directly, previous studies have evaluated the determination of SOC by the Elemental Carbon (EC) tracer method. The EC tracer method is a method of estimating the SOC value from calculating the POC by determining $(OC/EC)_{pri}$ which is the ratio of the measured values of OC and EC from the primary combustion source. In this study, three different approaches were applied to OC and EC concentrations in $PM_{2.5}$ measured at Seoul for determining $(OC/EC)_{pri}$: 1) the minimum value of OC/EC ratio during the measurement period; 2) regression analysis of OC vs. EC to select the lower 5-20% OC/EC ratio; 3) determining the OC/EC ratio which has lowest correlation coefficient value (R^2) between EC and SOC which is reported as minimum R squared method (MRS). Each $(OC/EC)_{pri}$ ratio of three approaches are 0.35, 1.34, and 1.77, respectively from the 1-h data. We compared the $(OC/EC)_{pri}$ ratio from 1-h data with 24-h data and revealed that $(OC/EC)_{pri}$ estimated from 24-h data had twice larger than 1-h data due to the low time resolution of sampling. We finally confirmed that the most appropriate value of $(OC/EC)_{pri}$ is that calculated by a regression analysis of 1-h data and estimated SOC values at $PM_{2.5}$ of the Seoul atmosphere.

Keywords: $PM_{2.5}$, OC/EC ratio, Primary organic carbon, Secondary organic carbon, EC tracer method

1 INTRODUCTION

Organic carbon (OC) in the ambient particulate matter (PM) can be classified into primary organic carbon (POC) and secondary organic carbon (SOC) based on their production mechanisms. The POC is directly emitted to the atmosphere from sources, such as vehicular exhaust (He *et al.*, 2008) and fossil fuel combustion (Zhang *et al.*, 2008). The SOC is formed from photochemical reactions between gaseous oxidizing agents and volatile organic compounds (VOCs) in the atmosphere (Bowman *et al.*, 1997; Odum *et al.*, 1997). The POC concentration in the atmosphere can be reduced by controlling emissions of POC to the atmosphere. However, if the concentration of SOC far exceeds that of POC, controlling the OC concentrations in the atmosphere cannot be successfully achieved by controlling the emissions of POC alone. Therefore, it is necessary to assess and quantify the secondary formation of OC to effectively reduce OC in fine PM (Larson *et al.*, 1989).

Direct measurement of SOC is difficult due to their complex formation mechanism in the atmosphere. Most studies have indirectly estimated the SOC level based on the measurements of OC and EC. Among these methods, the EC tracer method is the most widely used one. Most EC are diretly emitted from combustion sources similar to POC. This similarity of the emission characteristics of EC with POC allows it to be used as a tracer to assess the characteristics of POC (Chu and Macias, 1981; Wolff *et al.*, 1983; Gray *et al.*, 1986; Turpin and Huntzicker, 1991). The basic concept of EC trace method is based on that OC concentration changes continuously after POC is emitted to the atmosphere due to formation of SOC in the atmosphere; however, EC cannot be formed further in the atmosphere. Based on these characteristics of OC and EC, the $(OC/EC)_{pri}$ ratio has been developed in the EC tracer method, which is defined as the minimum value of the OC/EC ratio during the measurement period (Strader *et al.*, 1999). The $(OC/EC)_{pri}$ should vary substantially among different emission sources; however, each source might exhibit rather a unique value of $(OC/EC)_{pri}$ (Gray, 1986). The problem is that as the atmosphere is affected by various emission sources, the unique $(OC/EC)_{pri}$ of each emission source cannot be independently analyzed owing to spatiotemporal variations. Thus, the estimation of proper $(OC/EC)_{pri}$ evidently contains errors during the characterization of emission sources according to time or region. Despite this limitation, the EC tracer method is currently the most frequently applied method for analyzing SOC trend in the atmosphere because the $(OC/EC)_{pri}$ can be easily calculated using only the measured values of OC and EC. In practice, this method has adequately reflected SOC characteristics (Choi *et al.*, 2012; Jeon *et al.*, 2015; Kim *et al.*, 2018). Several studies have been conducted on predicting adequate $(OC/EC)_{pri}$ according to time and region (Turpin and Huntzicker, 1995; Castro *et al.*, 1999; Lim and Turpin, 2002; Lin *et al.*, 2009; Wu and Yu, 2016).

In the EC tracer method, the POC is calculated based on Eq. (1). The concentration of OC emitted from primary combustion sources is calculated by multiplying EC concentration by $(OC/EC)_{pri}$ and $OC_{non\text{-}comb}$, the OC level from non-combustion emission sources, is added. Subsequently, the SOC is finally estimated by subtracting POC from OC_{total} (Turpin and Huntzicker, 1995).

$$POC = (OC/EC)_{pri} \times EC + OC_{non\text{-}comb} \quad (1)$$

$$SOC = OC_{total} - (OC/EC)_{pri} \times EC \quad (2)$$

where $OC_{non\text{-}comb}$ refers to the OC released from non-combustion emission sources such as plant debris, spore, and pollen though its impact is assessed to be negligible as most of the OC in $PM_{2.5}$ is released during combustion (Hildemann *et al.*, 1991).

So far, three approaches have generally been applied to estimate $(OC/EC)_{pri}$. First, the minimum value of OC/EC during the measurement period is used to determine $(OC/EC)_{pri}$ (Castro *et al.*, 1999). This approach has been used when the EC tracer method was first introduced, and it allows a simple estimation of the $(OC/EC)_{pri}$. Second, regression analyses have been conducted, whereby the regression equation between OC and EC can be obtained from the lower 5–20% OC/EC data obtained during the measurement period, and the slope of the equation with the highest correlation coefficient can be used to determine the $(OC/EC)_{pri}$ (Lim and Turpin, 2002; Lin *et al.*, 2009). Third, the OC/EC ratio, with the minimum R squared (MRS) value between EC and SOC, is used to determine $(OC/EC)_{pri}$ (Wu and Yu, 2016).

In this study, the three above-mentioned SOC estimation approaches were applied to the 1-h data of OC and EC concentrations in $PM_{2.5}$ measured at Seoul, an urban area, during October 2012 to September 2013. The SOC values estimated from each method were compared to determine the most adequate $(OC/EC)_{pri}$ of Seoul area. In addition, to compare the differences of SOC estimates with respect to the time resolution of measurement of the atmospheric OC and EC, the $(OC/EC)_{pri}$ and SOC were determined from the daily mean value of the 1-h measurement data and 24-h measurement data which is general OC/EC analysis after filter collection.

2 METHODS

2.1 OC and EC Measurement Data

For the analyses of 1-h interval data for OC and EC concentrations in $PM_{2.5}$, the semi-continuous measurement data of OC and EC obtained from the Seoul Air Pollution Intensive Monitoring

Stations of the National Institute of Environmental Research (NIER) during the period of October 2012 to September 2013 were used. The 1-h measurement data were obtained by the thermal/optical transmittance and the non-dispersive infrared method based on the NIOSH and U.S. EPA STN protocols. A semi-continuous carbon monitor (SECOC Analyzer, Sunset Laboratory Inc., USA) was used for the 15 min analysis of OC and EC in $PM_{2.5}$ which were collected for 45 min in quartz filter at a flow rate of 8 LPM. The differences between the estimates of the upper 25% (Q_3) and the lower 25% (Q_1) are referred as the interquartile range (IQR). Based on the data obtained from 7,324 measurements of OC and EC concentrations during one year, the estimates above Q_3 + 1.5 IQR or below Q_1 – 1.5 IQR were excluded in this study which left 7,080 data of one year to be analyzed. That is, 1,998 data obtained during spring (March–May), 1,214 during summer (June–August), 1,828 in fall (September–November), and 2,040 in winter (December–January).

2.2 Approaches for the Determination of $(OC/EC)_{pri}$

2.2.1 Approach 1: Selection of the minimum value of OC/EC obtained during the measurement period

Determining the $(OC/EC)_{pri}$ based on the minimum value of the OC/EC ratio is based on the assumption that the OC/EC should be the lowest if POC is the dominant fraction in OC. This is because the atmospheric OC increases with the formation of SOC. Castro *et al.* (1999) reported that the adequate minimum value of OC/EC to determine $(OC/EC)_{pri}$ is the value that is consistently repeated and markedly lower than other values. Following previous studies, the OC/EC was obtained in this study for each recorded time and weather by dividing OC by EC, and the minimum OC/EC was selected to determine the $(OC/EC)_{pri}$.

2.2.2 Approach 2: Regression analysis of OC/EC in lower ranges

As mentioned for the Approach 1, the increase in OC/EC is presumed to be associated with the formation of SOC, and therefore, lower ranges of OC/EC value were selected to determine $(OC/EC)_{pri}$. While, the $(OC/EC)_{pri}$ in Approach 1 was determined based on a single estimate of OC/EC ratio, a specific low range of OC/EC was selected in this Approach 2 and adequate $(OC/EC)_{pri}$ which reflects all OC and EC data in the low range was calculated from the regression analysis. Herein, the regression line was drawn for the data within the lower 5–20% of OC/EC and the slope of the linear regression line was selected as the value of $(OC/EC)_{pri}$. Thus, this second approach reduces uncertainty of determining the $(OC/EC)_{pri}$ based on a single value obtained from the Approach 1. In this study, the data of OC/EC in the lower 5%, 10%, 15%, and 20% ranges were tested to draw the regression line. Subsequently, the $(OC/EC)_{pri}$ values in each range were obtained and compared. In addition, as the influence of the direct emission from primary source becomes dominant for both OC and EC, the correlation between OC and EC becomes stronger and, thus, the obtained $(OC/EC)_{pri}$ value becomes more reliable. The EC tracer method is most suitable in conditions where the influence of non-combustion emission sources is the lowest and the POC from combustion emission sources is the dominant form of OC. Thus, for data with strong correlations above or equal to 0.9, the OC/EC in the range where the $OC_{non\text{-}comb}$ approximates to 0, was selected for the suitable value as $(OC/EC)_{pri}$.

2.2.3 Approach 3: Applying the Minimum R Squared (MRS) method

Millet *et al.* (2005) developed an approach for determining $(OC/EC)_{pri}$ based on the assumption of the independence between the air pollutants from primary emission and secondary formation. In this approach, the POC and SOC are estimated based on the calculated $(OC/EC)_{pri}$ from Eq. (1) using a single OC/EC value that falls within the OC/EC range of the measurement data and the correlation (R^2) between the calculated SOC and the EC in the measurement data is obtained. This procedure is repeated at continuous intervals (0.01) for the entire OC/EC data within the target range. The OC/EC value corresponding to the minimum R^2 is the ratio at which the correlation between EC and SOC is the lowest and hence it is selected as the final value of $(OC/EC)_{pri}$. Wu and Yu (2016) named the method as the MRS method in the study that validated the applicability of the method for OC and EC values measured for one year in Hong Kong's atmosphere. Wu and Yu (2016) also provided a computer program, written on Igor Pro (WaveMetrics, Inc. Lake Oswego, OR, USA) for direct calculation based on the of MRS method (https://sites.google.com/site/wuchengust). This program was applied to calculate $(OC/EC)_{pri}$ of the Approach 3.

3 RESULTS AND DISCUSSION

3.1 Characteristics of OC and EC in $PM_{2.5}$ at Seoul

Table 1 summarizes the OC and EC concentrations measured at Seoul with the mean, minimum, and maximum values of OC/EC measured at 1-h intervals for a period of one year (from October 2012 to September 2013). The seasonal distributions of OC and EC concentrations and OC/EC are presented in Table 2. The mean OC concentration was the highest in winter (4.51 µg m^{-3}) and the lowest in fall (2.79 µg m^{-3}). The mean EC concentration was the highest in winter (2.08 µg m^{-3}) and the lowest in summer (1.62 µg m^{-3} µg m^{-3}) and fall (1.62 µg m^{-3}). The mean OC/EC ratio was the highest in summer (2.28) and the lowest in fall (1.89).

3.2 Determination of $(OC/EC)_{pri}$

3.2.1 Approach 1: Selection of the minimum value of OC/EC obtained during the measurement period

The minimum value of OC/EC obtained during the measurement period is shown in Table 1. The minimum OC/EC ($(OC/EC)_{min}$) in each season is presented in Table 3. Based on the 1-h interval measurement data, the $(OC/EC)_{min}$ was found to be 0.37 in spring, 0.46 in summer, 0.35 in fall, and 0.78 in winter, revealing that the ratio is lowest in fall and highest in winter (Table 3). The $(OC/EC)_{min}$ of 0.35 was observed just once in the 1-h interval data, which reflected the inconsistency in observation. Thus, it was presumed that the estimated $(OC/EC)_{min}$ did not accurately reflect the actual $(OC/EC)_{pri}$, based on which we concluded that the method based on the $(OC/EC)_{min}$ is not suitable.

3.2.2 Approch 2: Regression analysis of OC/EC in lower ranges

Fig. 1 shows the regression analysis results of the lower 5%, 10%, 15%, and 20% values of OC/EC based on the 1-h interval measurement data, respectively. The results satisfied the linearity

Table 1. OC and EC concentrations and OC/EC ratio in $PM_{2.5}$ at Seoul, Korea from October 2012 to September 2013.

	Max (µg m^{-3})	Min (µg m^{-3})	Average ± Standard Deviation (µg m^{-3})
OC	15.03	0.65	3.76 ± 2.19
EC	7.07	0.34	1.83 ± 1.02
OC/EC	7.45	0.35	2.16 ± 0.78

Table 2. Seasonal variations in OC and EC concentrations and OC/EC ratio in $PM_{2.5}$ at Seoul, Korea from October 2012 to September 2013.

	OC (µg m^{-3})	EC (µg m^{-3})	OC/EC
Spring	4.05 ± 2.22	1.88 ± 0.90	2.23 ± 0.76
Summer	3.47 ± 2.00	1.62 ± 0.85	2.28 ± 1.12
Fall	2.79 ± 1.42	1.62 ± 0.90	1.89 ± 0.75
Winter	4.51 ± 2.46	2.08 ± 1.23	2.27 ± 0.46

Table 3. Seasonal variations in $(OC/EC)_{min}$ ratio in Seoul.

$(OC/EC)_{min}$	Spring	Summer	Fall	Winter	Entire period
1 h	0.37	0.46	0.35	0.78	0.35
N*	1 (1998)	1 (1214)	1 (1828)	1 (2040)	1 (7080)

* Number of observation (Total number of measurement data).

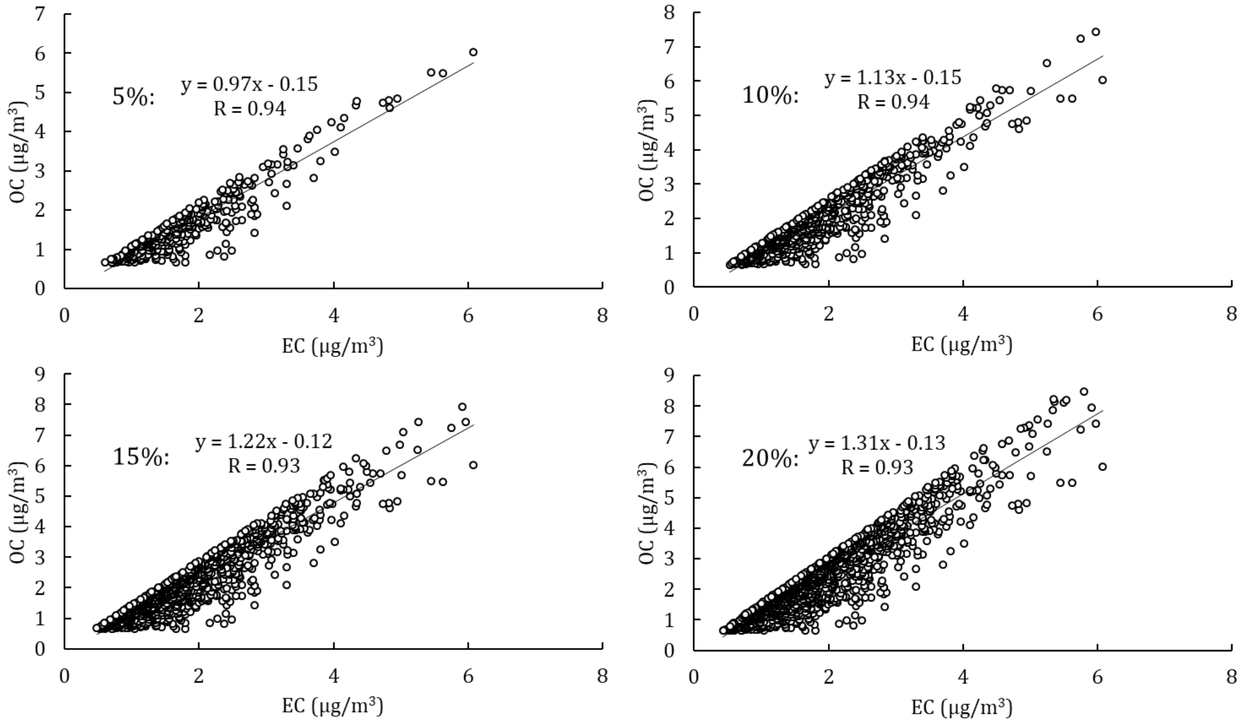

Fig. 1. Linear regression analysis of OC and EC using the range of low (OC/EC) ratios at Seoul.

Table 4. Seasonal variations in $(OC/EC)_{pri}$ ratio determined using the Approach 2 at Seoul with low 15 % data.

	Spring	Summer	Fall	Winter	Entire Period
$(OC/EC)_{pri}$ (R)	1.25 (0.87)	0.76 (0.94)	0.84 (0.95)	1.57 (0.97)	1.22 (0.93)

of regression with $R \geq 0.9$ and exhibited a trend of increasing regression slope ($(OC/EC)_{ratio}$) with the increase in the data range. However, all of the regression analysis results showed negative y-intercept values which failed to account for the influence of $OC_{non\text{-}comb}$. Lin *et al.* (2009) attributed the negative y-intercept to potential errors that arised after necessary adjustments were made to reduce the overestimating factors of OC and EC measurements in the instrument. So, Lin *et al.* (2009) suggested that, in such cases, approximating the y-intercept value being 0 should be adopted. In this study, the OC and EC correlations were all high with $R > 0.9$ regardless of the data range. Thus, $(OC/EC)_{pri}$ value was set for the lower 15% OC/EC data in each season (Table 4) and y-intercept values was approximated to 0. A seasonal variation for $(OC/EC)_{pri}$ was approximately 2-fold between minimum and maximum of the $(OC/EC)_{pri}$. By calculating the POC and SOC using the selected $(OC/EC)_{pri}$ (Table 5), the POC and SOC of the entire year were estimated to be 2.08 ± 1.24 µg m^{-3} and 1.68 ± 1.32 µg m^{-3}, respectively, and each of them accounted for 58 ± 19% and 42 ± 19% of the total OC, respectively. For the 1-h measurement interval data, the portion of SOC was the highest at 46% (1.91 µg m^{-3}) in summer, which is reflection of the enhanced photochemical reaction to form SOC in summer (Fig. 2).

3.2.3 Approch 3: Applying the Minimum R Squared (MRS) method

In this study, the MRS program provided in Wu and Yu (2016) was used to obtain the $(OC/EC)_{pri}$ across MRS points, as shown in Fig. 3. For 31.64% of all OC/EC ratios estimated based on the 1-h interval measurement data in this study, the $(OC/EC)_{pri}$ was determined to be 1.77 (Fig. 3). The MRS method was applied to each season (Table 6), and the $(OC/EC)_{pri}$ was found to plot within the range between 1.28 (fall) and 1.94 (spring).

The POC and SOC values, calculated using the $(OC/EC)_{pri}$ values estimated using the MRS method (Table 5), were 3.00 ± 1.74 µg m^{-3} and 0.76 ± 0.96 µg m^{-3} for the entire year, respectively,

Table 5. Summary of the average and standard deviation of the estimated POC and SOC determined using the three Approached described in the text.

	(µg m^{-3})	Approach 1	Approach 2	Approach 3
1 year	POC	0.64 ± 0.36	2.08 ± 1.24	3.00 ± 1.74
	SOC	3.12 ± 1.90	1.68 ± 1.32	0.76 ± 0.96
Spring	POC	0.70 ± 0.33	2.15 ± 1.13	3.36 ± 1.97
	SOC	3.36 ± 1.97	1.90 ± 1.45	0.73 ± 0.99
Summer	POC	0.75 ± 0.39	1.56 ± 0.66	2.31 ± 1.25
	SOC	2.73 ± 1.77	1.91 ± 1.63	1.17 ± 1.38
Fall	POC	0.57 ± 0.31	1.58 ± 0.76	2.00 ± 1.11
	SOC	2.23 ± 1.18	1.22 ± 0.90	0.79 ± 0.73
Winter	POC	1.62 ± 0.96	3.27 ± 1.92	3.76 ± 2.20
	SOC	2.89 ± 1.60	1.24 ± 0.91	0.75 ± 0.70

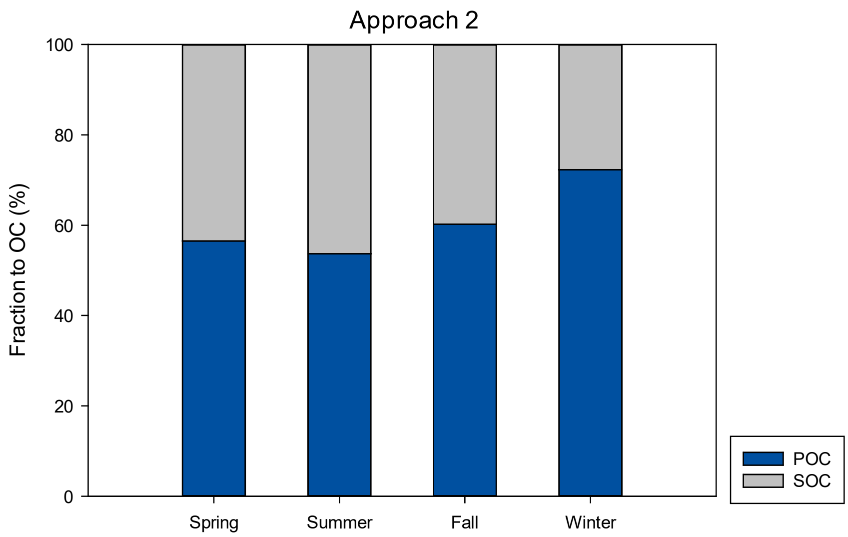

Fig. 2. Fraction of POC and SOC to OC estimated by Approach 2.

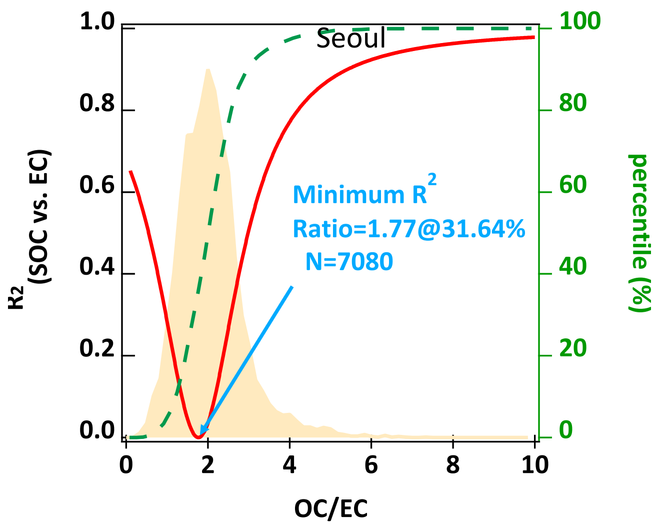

Fig. 3. (OC/EC) ratio when minimum R^2 is observed between SOC and EC for 1-h measurement data. The shaded area is the frequency distribution of the OC/EC ratio, and green percentile represents the cumulative frequency rate. N represents the number of the total measurement data set.

Table 6. Seasonal variations in (OC/EC)pri determined using Approach 3 in Seoul.

	Spring	Summer	Fall	Winter	Entire Period
(OC/EC)pri from MRS (Distribution Percentage, %)	1.94 (37%)	1.51 (26%)	1.28 (17%)	1.86 (17%)	1.77 (32%)

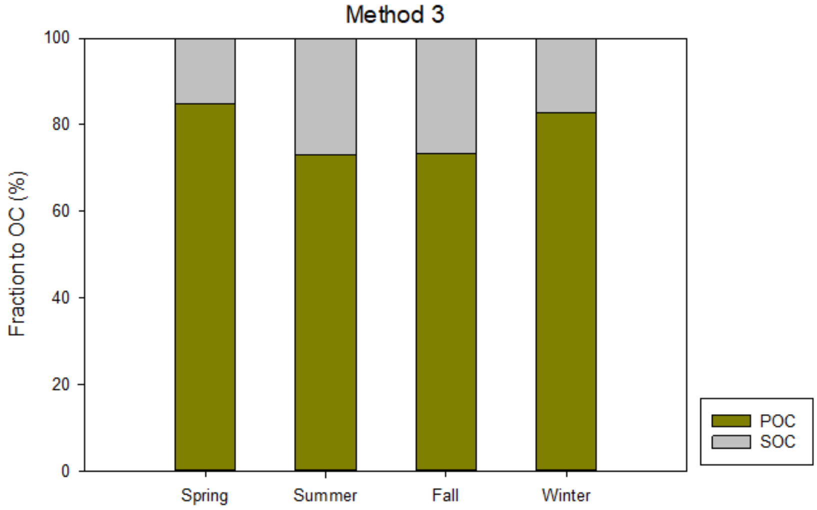

Fig. 4. Fraction of POC and SOC to OC concentration estimated by Approach 3.

and each of them accounted for 82 ± 17% and 18 ± 17% of the total OC, respectively. The POC and SOC estimates in each season demonstrated that the SOC percentage was the highest in summer (27%), which, as in the case of Method 2, was presumed to reflect the atmospheric OC/EC in summer associated with active photochemical reactions (Fig. 4).

3.3 Comparison of $(OC/EC)_{pri}$ and Estimated SOC in according with Temporal Resolution of the OC and EC Measurement Data

The value of $(OC/EC)_{pri}$ might be influenced by temporal resolution of measurement of OC and EC. Thus, to compare the variations of $(OC/EC)_{pri}$ estimations with respect to the temporal resolution of measurement at Seoul, the 24-h mean OC and EC concentrations from the 1-h interval measurement data and the OC and EC concentrations measured during 24-h (the $PM_{2.5}$ samples were collected on the filter for 24 hr and OC and EC were analyzed by lab OCEC analyzer) were used to calculate $(OC/EC)_{pri}$ and these values were compared. The results from the three individual estimation methods were compared with the $(OC/EC)_{pri}$ value estimated based on the 1-h interval data (presented in Section 3.2).

Applying the Approach 1 to the 24-h mean OC and EC concentrations determined based on the 1-h measurement data produced $(OC/EC)_{pri}$ ($(OC/EC)_{min}$) = 0.95 which was approximately three times higher than the $(OC/EC)_{min}$ = 0.35 determined based on the 1-h measurement data. Applying the Approach 1 to the 24-h measurement data of OC and EC concentrations at Seoul generated $(OC/EC)_{min}$ value of 2.22 which was approximately six times higher than the $(OC/EC)_{min}$ value of 0.35 determined based on the 1-h measurement data. It suggests that the prediction of SOC using the Approach 1 could result in approximately three- or six-fold deviation in the portion of POC contribution with respect to the time resolution of the measurement with a possibility of the underestimation of SOC concentration. The POC and SOC exhibited 49% and 50% for the 24-h mean data and 48% and 52% for the 24-h measurement data, respectively, whereby these were 18% and 81%, respectively, for the 1-h measurement data.

Applying the Approach 2 (the one using the regression analysis) to the 24-h mean data produced $(OC/EC)_{pri}$ value of 1.31. Applying the Approach 2 to the 24-h measurement data produced $(OC/EC)_{pri}$ value of 2.66 which is corresponded to the lower 5% OC/EC data. This value was two times higher than those for the 1-h measurement data case ($(OC/EC)_{pri}$ value of 1.22). The portion of POC and

SOC were 66% and 34% for the 24-h mean data and 54% and 46% for the 24-h measurement data, respectively, and it exhibited ≤ 10% deviation from the 1-h measurement data results, 58% and 42%, respectively. In terms of the 24-h mean data based on the 1-h measurement data, the smallest value was observed during fall (1.12) and the largest in winter (1.83), while in terms of the 24-h measurement data, the smallest value was observed in winter (2.14) and the largest in spring (4.42) showing over the factor of two variation. For the 1-h measurement data, the smallest value was observed in summer (0.76) and the largest in winter (1.57) showing seasonal variation of the $(OC/EC)_{pri}$ values were different by different time resolution measurement data. It was surmised that the SOC fraction be the highest in summer due to the activity of the photochemical reactions. For the 24-h mean data, the SOC fraction was 37% in summer which was lower than that in spring (63%) but higher than in fall (29%) and winter (21%). For the 24-h measurement data, the SOC fraction was 25% in summer which was lower than in spring (42%) and winter (40%) but higher than in fall (24%). For the 1-h measurement data, the SOC fraction was 46% in summer which was higher than in spring (43%), fall (40%), and winter (28%). Thus, the shortest temporal resolution data, 1-h measurement data would adequately reflecting the seasonal variation of SOC generation.

Applying the Approach 3 to the 24-h mean data, the $(OC/EC)_{pri}$ value of 1.92 was obtained. When using the 24-h measurement data, the calculated $(OC/EC)_{pri}$ value was 3.92 which was approximately two times higher than the $(OC/EC)_{pri}$ value of 1.77 estimated based on the 1-h measurement data. The portion of POC and SOC were 89% and 11% for the 24-h mean data, 77% and 23% for the 24-h measurement data, and 82% and 18% for the 1-h measurement data, respectively. Though the $(OC/EC)_{pri}$ value for the 24-h measurement data was about three times higher than that for the 1-h measurement data, the POC fraction for the 24-measurement data was lower than that for the 1-h measurement data. It was most likely due to the approximately two times higher mean concentration of OC (7.49 µg m^{-3}) and the mean OC/EC (5.31) compared to the 1-h measurement data. The $(OC/EC)_{pri}$ in each season determined using the Approach 3 revealed that the seasonal deviation in $(OC/EC)_{pri}$ ranged between 1.35 (fall) and 2.16 (spring) for the 24-h mean data and between 2.65 (fall) and 6.45 (winter) for the 24-h measurement data, reflecting large seasonal deviation. However, the deviation was relatively small for the 1-h measurement data, that is, between 1.28 (fall) and 1.94 (spring).

When using the 24-h mean data or 24-h measurement data, the tendency of the increase of $(OC/EC)_{pri}$ was observed. Thus, the POC fraction becomes higher and the SOC fraction becomes lower compared to the $(OC/EC)_{pri}$ value obtained from the 1-h measurement data. When POC and SOC are predicted by estimating the $(OC/EC)_{pri}$ from the 24-h and 1-h measurement data with identical region and period of measurement, despite the difference in specific measurement site the $(OC/EC)_{pri}$ value for the 1-h measurement data was found to be more than two times larger than that for the 24-h measurement data. This was likely due to the presence of OC in the atmosphere after being released from the emission source with prolonged time of OC and EC concentration measurements which could have led to secondary generation and consequently to the higher $(OC/EC)_{pri}$ value compared to that of the 1-h measurement data. Thus, Approaches 1 and 3 with the 24-h OC and EC data has overestimated POC concentration. Comparing the POC and SOC fractions in each season revealed that the higher level of SOC in summer was clearly observed from only the 1-hour measurement data determined based on the Approach 2.

3.4 Validation of SOC Estimates from $(OC/EC)_{pri}$ in the Atmosphere of Seoul

Fig. 5 shows the POC and SOC concentrations and their fractions in total OC, calculated based on the $(OC/EC)_{pri}$ using the three approaches described in Section 3.2.

While estimating the $(OC/EC)_{pri}$, the deviation across the three approaches could be examined and the approach with MRS (Approach 3) was found to exhibit the highest value of $(OC/EC)_{pri}$ regardless of the temporal resolution of the measurement. Therefore, as shown in Fig. 5, applying the $(OC/EC)_{pri}$ obtained through the Approach 3 provided the lowest SOC value compared to the values from the Approach 1 or 2. This implied that EC can be correlated with SOC due to the relation of emission between EC and precursors of SOC, and it made high correlation between EC and SOC. Thus, it is possible that the value of OC/EC at the point of the lowest correlation between SOC and EC might not reflect the $(OC/EC)_{pri}$ of the lowest SOC, and in the actual atmosphere, SOC might be partially reflected in POC, thereby overestimating POC (Wu *et al.*, 2019). In the case of

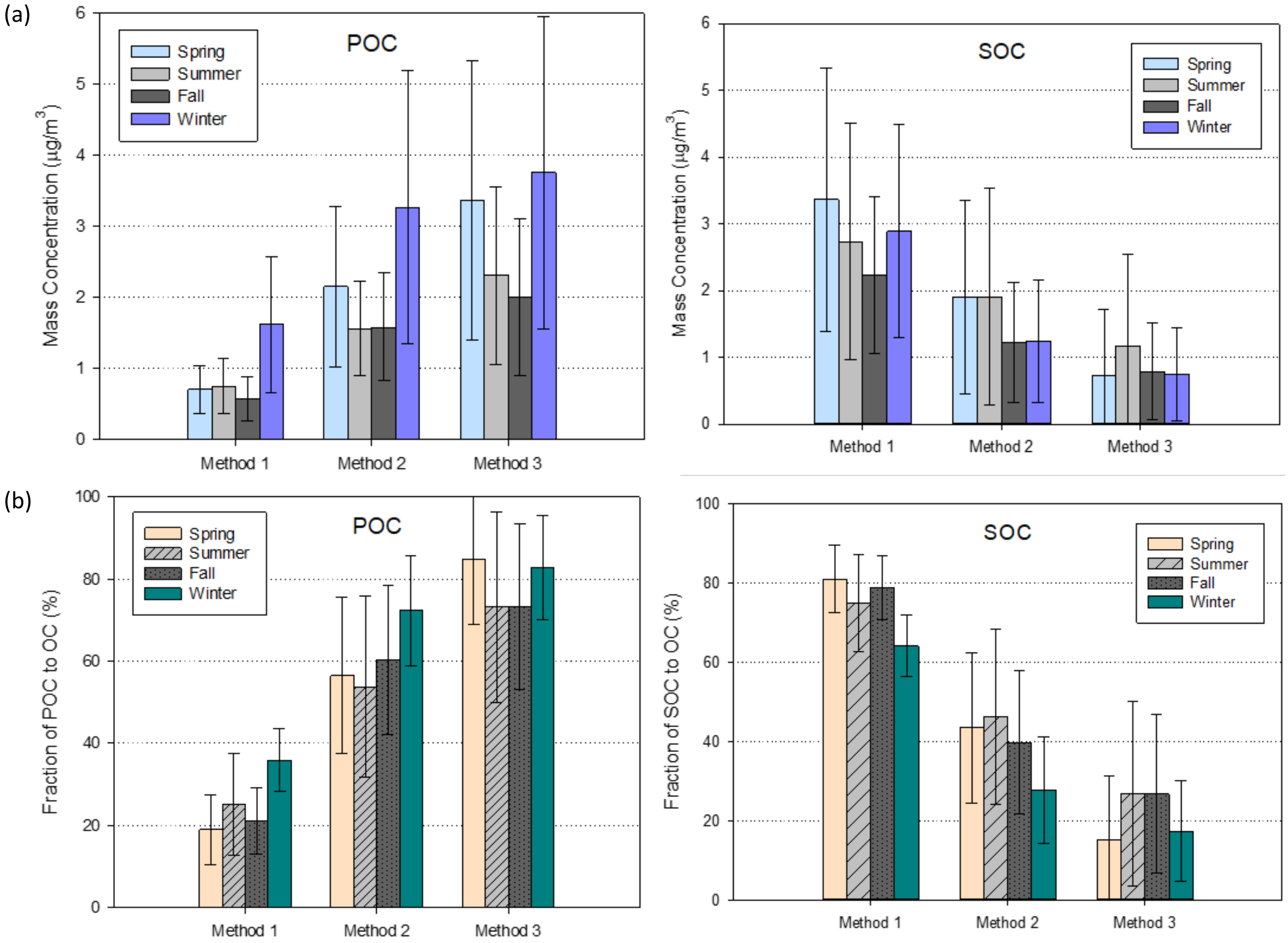

Fig. 5. (a) Average concentration and (b) fraction of POC and SOC to OC estimated from three Approaches.

Seoul, with such a significant impact of long-range transport of air pollutants, EC may not be influenced solely from the primary emission sources that existed around Seoul, implicating a possibility of underestimating SOC through the MRS method.

For Approach 1, the uncertainty in SOC estimation was found to be high if the $(OC/EC)_{pri}$ based on a single low-frequency value was used. It was due to the lack of consistency in the measurements of $(OC/EC)_{min}$ for the 1-h measurement data. As shown in Fig. 5, POC and SOC concentrations based on the Approach 1 deviated from the Approach 2 or 3 by as low as 1.09 µg m^{-3} and as high as 2.66 µg m^{-3}, whereas for the POC and SOC fractions, the SOC accounted for most of the OC in the Approach 1 in contrast to the Approach 2 or 3. This confirmed that the Approach 1 is not suitable for estimating POC and SOC at Seoul.

For the Approach 2, the resulting $(OC/EC)_{pri}$ exhibited higher correlations with OC and EC for lower range values. The observed seasonal variations in $(OC/EC)_{pri}$ corresponded with the previous studies that applied the Approach 2 (Table 7). In addition, the typical high SOC in summer was reflected (Fig. 5). Thus, for the 1-h measurement data, application of the Approach 2 using linear regression analysis of the lower range data of OC/EC was found to estimate the most adequate estimation of $(OC/EC)_{pri}$ which in turn is essential for estimating SOC in $PM_{2.5}$ in the atmosphere of Seoul.

Table 7 summarizes the $(OC/EC)_{pri}$ obtained using the EC tracer method in the previous studies. The $(OC/EC)_{pri}$ ranged between 1.0 and 2.8 from the various previous studies, and the $(OC/EC)_{pri}$ from the Approaches 2 and 3 examined in this study fell within the previous suggested range while the Approach 1 did not. Thus, the $(OC/EC)_{pri}$ determined from the Approach 2 or 3 confirmed the validity of the EC tracer method which has been widely applied in the previous studies.

Table 7. Values of (OC/EC)pri reported from previous studies.

Location	Site Type	Sampling Period	Time Resolution (h)	Approach	(OC/EC)pri	Ref.
Guangzhou	Suburban	Feb 2012–Jan 2013	1	3	2.26	Wu and Yu (2016)
Beijing	Urban	Nov 2005–Jan 2006 Mar–Oct 2006	1	2	2.6 (Win) 1.8, 1.5 (Spr) 1.5, 1.0 (Sum) 1.8, 1.4 (Fal)	Lin *et al.* (2009)
Atlanta	Supersite	Aug–Sep 1999	1	2	2.1	Lim and Turpin (2005)
Europe	Coastal, Urban, Rural	Winter/Summer	24	1	1.1 in urban to 1.5 in rural	Castro *et al.* (1999)
Seoul	Urban	Oct–Nov 2012 Jan–Feb, Apr, Aug–Sep 2013	24	1	2.8 (Spr) 2.2 (Sum) 2.5 (Fal) 2.7 (Win)	Kim *et al.* (2018)
Seoul	Urban	Jan 2011–Dec 2011	1	2	2.36 (Spr) 1.13 (Sum) 1.09 (Fal) 1.54 (Win)	Jeon *et al.* (2015)

4 CONCLUSIONS

Direct measurement of SOC contribution in $PM_{2.5}$ is impossible because SOC is formed by the oxidation in the atmosphere. Hence, the EC tracer method was developed and widely used, whereby EC is harnessed as the tracer of POC. Previous studies have hypothesized that $(OC/EC)_{pri}$ adequately reflects the emission sources of primary combustion which is based on the measured values of OC and EC. So far, various techniques adopting the EC tracer method have been applied in SOC estimation studies (Choi *et al.*, 2012; Jeon *et al.*, 2015; Kim *et al.*, 2018). In this study, three conventional approaches for $(OC/EC)_{pri}$ determination were applied to 1-h and 24-h measurement data of OC and EC concentrations in $PM_{2.5}$ for one year at Seoul, Korea to identify the most suitable approach of SOC estimation at Seoul.

Three approaches were applied to the 1-h measurement data to determine the $(OC/EC)_{pri}$ and the comparison results regarding the temporal resolution of the measurement showed that the $(OC/EC)_{pri}$ was high for the 24-h measurement data than for the 1-hour measurement data across all three approaches. This showed that the increase of $(OC/EC)_{pri}$ was due to the combination of low and high values of OC/EC with prolonged measurement of OC and EC concentrations for 24-h measurement. In addition, it is presumed that $(OC/EC)_{pri}$ from the 24-h measurement might not reflecte direct emissions of OC and EC from emission sources and seasonal variations in the ambient conditions affected the variation of OC/EC ratio.

Comparison of the three approaches based on the 1-h measurement data revealed that the $(OC/EC)_{min}$ values were inconsistent when the Approach 1 was used. Thus, it was concluded that the Approach 1 cannot reliably reflect the influence of constant emission sources. The $(OC/EC)_{pri}$ estimated using the Approach 3 was approximately 1.3 times higher than that estimated using the Approach 2 which was attributed to the inability of the correlation analysis for EC and SOC to adequately account for the independence of EC and SOC due to impact of long-range transport of air pollutants at Seoul, Korera. Lastly, the $(OC/EC)_{pri}$ estimated using the Approach 2 was more suitable for the basic application of EC tracer approach that provides $(OC/EC)_{pri}$ for the minimum ratio of OC/EC.

From this study, we concluded that the $(OC/EC)_{pri}$ estimated using linear regression analysis of OC and EC concentrations is the most suitable for the lower 5–20% OC/EC range using the 1-h measurement of OC and EC.

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