Point by Point Response to Review Comments (ACPD-14-57-2014)

Reviewer #1

By A. H. Miguel (amiguel@arb.ca.gov)

Comment

(2. Experimental 2.1 Sampling equipment and method) Review note to the authors The PM2.5 sampler and other instrument in the Mong Kok roadside air quality monitoring station are located on a platform circa 3 meters above the road level of an area with extremely high population density (130,000 person per km-2) described as the busiest district in the world (Guinness World Reports).

Response: Thanks for the note on the Mong Kok location. The unique characteristic (i.e., the busiest district) about Mong Kok is added to the revised manuscript (lines 87-88). We further add the following text to clarify the different air monitoring instruments and their respective sampling heights at this location.

> Lines: 100-105
>
> "At the Mong Kok Air Quality Monitoring Station, a few aerosol samplers are located on a platform around 3 m above the ground level and instruments for the criteria gas pollutants are housed in a room at the site with their inlets extending through the ceiling. The real-time ECOC analyzer used in this work is located on the ground with the inlet ~2 m above the ground."

Comment

Line 5 (3. Results and discussions 3.1 Organic and elemental carbon concentrations): the authors state that the annual averages OC and EC concentrations at MK AQMS during the study period were 7.82 and 4.36 $\mu gC/m^3$, respectively. The ratio OC/EC = 1.70, while the ratio EC/OC = 0.55. Could the stated values of OC and EC be reversed?

Response: The numbers of 7.82 and 4.36 $\mu gC/m^3$ were reported as annual average concentrations of OC and EC, respectively. The OC/EC ratio of 0.5 mentioned in the abstract is the $(OC/EC)_{vehicle}$, not to confuse with the average ambient OC/EC, which is 1.79 if using the annual average OC and EC concentration data. The $(OC/EC)_{vehicle}$, was estimated using both minimum OC/EC ratio approach and the dataset from select time periods when diesel-powered vehicles were dominated. In these approaches, the hourly OC and EC concentrations were examined. It is revealed that diesel-powered vehicles emitted a large amount of EC leading to an OC/EC ratio smaller than 1.

Comment

The authors state that "higher OC concentrations were recorded during winter months as a result of the contributions of regional air pollutant transport". Considering that the OC concentrations (Fig. 2) peaked in December, January and February. –while EC concentrations remained relatively constant–, could it also indicate a decrease in photochemical activity during the winter months?

Response: Since high SOA formation is usually linked with strong photochemical activities and during winter months the solar radiations decrease, our view is that the higher OC concentrations observed during winter months in this study mainly resulted from the regional transport of air pollutants, some of which could be SOA formed during transport.

Comment

Page 77, Line 7: In addition to the stated higher resolution measurements of particle-phase tracer compounds to provide a more accurate estimation of SOA contributions in the urban areas of Hong

Kong, the authors should consider the role of single-ring aromatics on SOA formation in their future studies.

Response: We agree with the reviewer's comment that single-ring aromatics (e.g. toluene, benzene, etc.) should be considered for their contributions to the SOA formation since these aromatic VOCs are also an important part of vehicular emissions. However, we note that our work focuses on estimation of primary carbonaceous $PM_{2.5}$ from vehicular sources, not SOA formation. Hence, we feel elaboration of SOA formation and precursors may not be necessary in this paper. Below text is added to acknowledge and clarify the scope of this work.

Line 448-450

"We note $OC_{vehicle}$ estimated in this way only accounts for primary OC emission from vehicles. SOC formed from volatile organic compound precursors emitted by vehicles (e.g., toluene) is not captured in this EC tracer approach."

Reviewer #2

Comment

While the manuscript does present some useful and hard won data, the analysis and interpretation is quite weak and far from convincing. As noted below, this is the case throughout the paper, but most evident in the section on the estimation of (OC/EC)vehicle. There is little or no attempt to compare and contrast the results presented with the many similar studies done by numerous researchers (including some referred to in the manuscript). Given these serious deficiencies, I cannot recommend full publication in ACP.

Response:

We would like to clarify that our analysis of the hourly OCEC data in our study site (a roadside location in a busy urban district) has led us to derive a $(OC/EC)_{vehicle}$, not $(OC/EC)_{primary}$. The latter is the ratio that has been examined and derived from ambient OCEC measurements in many other studies. As far as we are aware, this is the first study in which hourly OCEC measurements are used to derive $(OC/EC)_{vehicle}$ in a roadside environment and subsequently the contribution of vehicular emissions to carbonaceous $PM_{2.5}$ is estimated. Unlike other studies reporting OCEC measurements, we did NOT attempt to estimate POC and SOC in this work. The following text is added to clarify this point.

> Lines 316-324:
>
> "It is not a trivial task to ensure that $(OC/EC)_{pri}$ determined in these approaches is representative of the composite effect of multiple primary combustion sources, each having a time-varying contribution to the ambient OC and EC. In addition, uncertainty in estimating *b* (see discussion later in this section) introduces additional uncertainty in the estimates of POC and SOC. While we recognize the difficulty in deriving reliable POC and SOC concentrations, by comparison we see it is a much simpler task to derive an $(OC/EC)_{vehicle}$ ratio representative of vehicular emissions for our roadside environment, since it has the unique characteristic of vehicular emissions being the dominant EC source."

Comment

Major Concerns:

Section 3.2: The authors describe and use an empirically based method for estimating the contributions of primary and secondary carbon to their measurement data.

Response:

In this work we aim to estimate $(OC/EC)_{vehicle}$ using roadside ambient OC EC measurements. We did not attempt to estimate the contributions of primary and secondary carbon, although the empirical approaches in getting $(OC/EC)_{vehicle}$ in this work and $(OC/EC)_{primary}$ in many studies in the literature are similar in that EC is used as a tracer for combustion sources. In our work, we regard EC as the tracer for vehicular emissions, considering our study location being a roadside site in a busy urban district.

Comment

The authors make reference to earlier work by Harrison's group (Castro et al., 1999) and Turpin's group (Lim and Turpin, 2002). However, their analysis produces results that is not at all convincing and leads me to believe that the assumptions required to yield reasonable estimates for this method may not hold in this case. The Castro et al. work showed urban OC/BC ratios ranging from 1.1. to 1.3, while the Lim and Turpin work showed OC/EC ratios ranging from 1.75 to 2.09 for the data grouped OC/EC ratio (note that all intercepts in this work were positive, on average). In contrast, the authors present estimates for the (OC/EC)pri ratio in Tables 1, 2, and 3 that range from 0.41 to 1.49 (Table 1), from .53 to 1.41 (Table 2) and from 0.44 to 8.56 (!) (Table 3).

Response:

(1) $(OC/EC)_{primary}$ is highly location-dependent, as the mix of primary combustion sources is specific to locations. None of the measurements reported in Castro et al (1999) and Lim and Turpin (2002) were made in a roadside environment comparable to the one described in this manuscript.

(2) We mistakenly used "(OC/EC)pri" in Table 3 caption in the original ms. The correct one should be average ambient (OC/EC). The (OC/EC) ratios listed in Table 3 are not $(OC/EC)_{primary}$. Instead, they were calculated average ambient (OC/EC) by regressing OC and EC measurements in select sections of time periods in a day. Therefore the value 8.56 calculated for the 19:00-22:00 period in April 2012 should not be interpreted as an $(OC/EC)_{primary}$ estimate. In the revised ms, we have abandoned Deming regression to estimate the average (OC/EC) for the three time periods, mainly because of the poor correlation between OC and EC. We now calculate the average (OC/EC) to be the ratio of average OC to average EC in each time period in individual month. This ratio of average approach is suggested by Chu (2005) and demonstrated to be a robust estimate. Table 3 is revised accordingly.

(3) We are aware of the studies in the literature reporting semi-continuous OC and EC measurements and subsequently estimating primary and secondary OC. Besides Lim and Turpin's work, Polidori et al. (2006) conducted a one-year OC and EC measurements in Pittsburgh supersite which is located in a suburban area. They estimated the primary OC/EC ratio (1.24–3.06) from data subsets which were obtained from time periods when primary emissions were dominant. Park et al. (2005) sampled for 9 months in Baltimore supersite which is in an urban residential area. They selected several time periods expected to be dominated by primary emissions and estimated the $(OC/EC)_{primary}$ ratio as 1.70–2.98. Plaza et al. (2006) collected samples during the summer and winter of 2003 at an urban background/suburban site in Madrid, India. OC/EC ratios were then calculated for different select periods (e.g. summer, traffic period, episode, etc.) and values of 0.84 and 1.02 were obtained for summer and autumn-winter, respectively. Lin et al. (2009) conducted a year-round measurement of OC and EC on the campus of PKU, which is located in urban area of Beijing, 200 m away from a major road with heavy traffic. The sampling inlet is 15 m above ground level. They adopted the minimum (OC/EC) ratio method to derive the $(OC/EC)_{primary}$ ratio of 1.5–2.6 for daytime and 1.0–2.6 for nighttime. Yu et al. (2009) collected samples in March 2006 at two sites in Mexico City. They estimated the $(OC/EC)_{primary}$ ratio to be 0.61 for the site closer to the city and 2.26 for the site further away from the downtown Mexico City. Hu et al. (2012) conducted OC and EC measurements during the PRIDE-PRD 2006 summer campaign at a rural site that is 50 km to the northwest of Guangzhou. They gave an estimate of 1.1 as $(OC/EC)_{primary}$ during local primary emission days. They also proposed values of 1.57 and 1.42 as $(OC/EC)_{primary}$ for daytime and nighttime, respectively.

The sampling site (MK) in our study is in a roadside environment in Hong Kong, located at the junction of two major roads with heavy vehicular traffic, a significant part of which comes from the diesel-fuelled bus fleet. The dispersion of the emissions is severely hampered by the high density of tall buildings along the roads, i.e., the "street-canyon effect". As a result, the EC concentrations at MK were significantly higher than those at other general air quality monitoring stations in Hong Kong and the OC/EC ratios were quite often observed to be below 1 during morning traffic rush hours.

Comment

Another problem is the large number of negative intercepts in their regressions, some as large in magnitude as -2.16. What does this mean physically? There is no acknowledgement of this being a problem, and no explanation. After reading this section, I have no choice but to conclude that this analysis method is either inappropriate for this data set (most likely), or improperly applied. The results simply don't make sense!

Response:

We thank the reviewer for this challenging question. We've re-worked the Deming regression analysis and believe we now have a reasonable answer to this question. First, we agree that it is difficult to impart physical meaning to negative intercepts. To gain an understanding of this issue, we have re-examined the regression methods in deriving the slopes and the intercepts by applying different linear regression methods to the data sets and comparing the results. Linear regressions based on ordinary

least squares (OLS) only take into account of measurement uncertainty for y-variable while assume no measurement errors for x-variable. Deming regressions consider measurement errors in both regressed variables x and y, which is expected to provide a better best-fit line. There are different forms of Deming regression because of different ways of representing measurement errors in x and y, i.e. $\omega(X_i)$ and $\omega(Y_i)$ in the equation below for S, which is the sum of the square of the perpendicular distances between the data points and the regression line (Saylor et al., 2006).

$$S = \sum [\omega(X_i)(x_i - X_i)^2 + \omega(Y_i)(y_i - Y_i)^2]$$

The Deming regression (also referred to as default Deming regression) used in our original manuscript adopts a value of 1 for the ratio of $\omega(X_i)$ and $\omega(Y_i)$ (i.e., λ in the expression below), i.e., equal measurement uncertainties for variable X_i and Y_i.

$$\lambda = \omega(X_i)/\omega(Y_i)$$

Saylor et al (2006) compared two forms of Deming regression, default Deming regression with λ=1 and optimal Deming regression with an accurate estimate of λ (λ=Var(ε_{OC})/Var(ε_{EC}) (where Var(ε) is the variance of the measurement errors, ε). Using simulated EC and OC data, they demonstrated that the optimal Deming regression provides excellent results while the default Deming regression yields a slope of 6% larger than the true value and **a negative intercept of -1.28** due to inaccurate representation of error variance. We therefore revised our linear regression approach to optimal Deming regression in the revised paper, with λ taken to be the ratio of the measurement error variance of X and Y.

The new regression results are shown in the revised Table 1. The following text is added to describe the details on the optical Deming regression:

Lines 336-354:

> "There are different forms of Deming regression because of different ways of representing measurement errors in x and y, i.e. $\omega(X_i)$ and $\omega(Y_i)$ in eq (6) for S, which is the sum of the square of the perpendicular distances between the data points and the regression line (Saylor et al., 2006).
>
> $$S = \sum[\omega(X_i)(x_i - X_i)^2 + \omega(Y_i)(y_i - Y_i)^2] \qquad (6)$$
>
> In eq (6), X_i and Y_i are the observed data points and x_i and y_i are the adjusted points lying on the regression line. The simplest form of Deming regression, termed default Deming regression, adopts a value of 1 for λ, the ratio of $\omega(X_i)$ and $\omega(Y_i)$ (eq (7)). In another words, equal measurement uncertainties for variable X_i and Y_i are assumed.
>
> $$\lambda = \omega(X_i)/\omega(Y_i) \qquad (7)$$
>
> Saylor et al. (2006) compared two forms of Deming regression, default Deming regression with λ = 1 and optimal Deming regression with an accurate representation of λ (i.e., λ = Var(ε_{OC})/Var(ε_{EC}, where Var(ε) is the variance of the measurement errors, ε). Using simulated EC and OC data, they demonstrated that the optimal Deming regression provides excellent results while the default Deming regression yields a slope of 6% larger than the true value and a negative intercept of -1.28 due to inaccurate representation of error variance. We therefore adopt optimal Deming regression in our linear regression approach to calculate $(OC/EC)_{min}$, and λ is taken to be the ratio of the measurement error variance of X and Y. "

The revised Table 1 shows that the optimal Deming regression yields more physically reasonable intercepts. January 2012 data had the largest negative intercept (-0.58). To understand the issue of negative intercepts, let's examine regression lines obtained with ordinary least squares (OLS), default Deming, and optimal Deming regression for the January 2012 data, as shown in Figure R1 (also

included in the revised supplementary material). The OLS regression results in a positive intercept (0.86) while the two Deming regressions give negative intercepts. The different regression lines are a result of difference in assigning weights to individual observations. This result suggests that the regression line intercept is fairly sensitive to weights assigned to individual observations, or in another word, error variances for X and Y variables. For actual ambient data, it is difficult to identify a subset of data that is free of secondary OC contribution or such a subset of data does not exist. In addition, multiple primary combustion sources (having different $(OC/EC)_{primary}$) co-exist and their relative strengths vary with time at a given ambient location. Both factors would contribute to scattering of the data that are used for deriving $(OC/EC)_{primary}$, which in turn could lead to a negative intercept, as illustrated by Figure R1.

On the other hand, we note the slope is much less sensitive to different regression approaches. As we stressed earlier, the focus of this paper is $(OC/EC)_{vehicle}$ in our roadside study location, which is derived from the slope values. The negative intercept is therefore not an issue of consequence for this work. (But it will be an issue if secondary OC is the target parameter to be derived using this approach.)

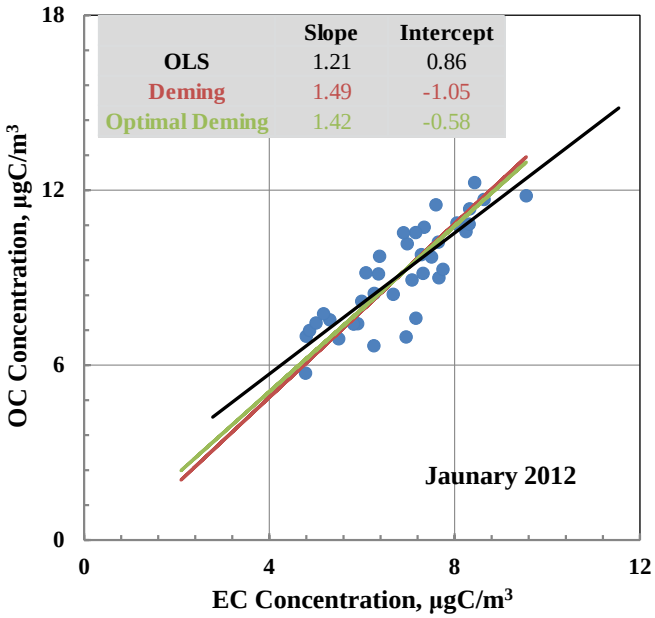

Figure R1. Regression lines of 5% lowest (OC/EC) data (n = 38) for January 2011 by ordinary least squares (OLS), default Deming, and optimal Deming regression.

The following text is added to address the negative intercept issue:

> Lines 356-377:
>
> "It is noted that some intercept values are negative, which does not seem to have a physical basis. To understand the issue of negative intercepts, we next examine regression lines obtained with OLS, default Deming, and optimal Deming regression for the January 2012 data (Fig. S4), which had the largest negative intercept (-0.58) among all the monthly $(OC/EC)_{min}$. The OLS regression results in a positive intercept (0.86) while the two Deming regressions give negative intercepts. The different regression lines are apparently a result of difference in assigning weights to individual observations. This result suggests that the regression line intercept is fairly sensitive to weights assigned to individual observations, or in another word, error variances for *X* and *Y* variables. For actual ambient data, it is difficult to identify a subset of data that

is free of SOC contribution or such a subset of data simply does not exist. In addition, multiple primary combustion sources that have different $(OC/EC)_{pri}$ co-exist and their relative strengths vary with time at a given ambient location. Both factors would contribute to scattering of the data that are used for deriving $(OC/EC)_{pri}$, which in turn could lead to a negative intercept, as illustrated by Fig. S4. This analysis about intercept shows the large uncertainty associated with the estimated *b* when using linear regression approaches. One needs to be cautious in estimating POC and SOC if a linear regression approach is relied upon for the calculation of non-combustion-derived primary OC (i.e., b in eqs. (3) and (4)). On the other hand, we note the slope is much less sensitive to different regression approaches. In the example of the January 2012 data, the slope values derived from the two Deming regressions differ less than 5% (Fig. S4). This adds to our confidence in the robustness of the derived $(OC/EC)_{min}$ using Deming regression of select ambient OC and EC data."

Tables 2 is also revised to results using optimal Deming regressions.

Comment

Page 62, line 18: I believe the average should be 0.35 ugC/m3.

Response: Thanks the reviewer for pointing out our miscalculation and the revision is made accordingly.

Comment

Page 65, lines 24-28: While the different sampling periods could increase the scatter, it is not clear how or why it could cause bias!

Response: We agree with the reviewer that the explanation of the discrepancies about TC, OC and EC between semi-continuous measurements and filter-based data was not very clear. The paragraph is revised as follows,

Lines 197-226:

"TC by the semi-continuous method agrees reasonably well with both Partisol filter measurements (R^2 = 0.98, $\%\overline{RB}$ = -29.6%, $\%\overline{RSD}$ = 23.4%) and high-volume filter measurements (R^2 = 0.99, $\%\overline{RB}$ = -16.4%, $\%\overline{RSD}$ = 15.2%). Good correlations and reasonable agreement were also observed for OC (R^2 = 0.97, $\%\overline{RB}$ = -33.8%, $\%\overline{RSD}$ = 27.7% for RT-OC vs. Partisol-OC and R^2 = 0.98, $\%\overline{RB}$ = -17.9%, $\%\overline{RSD}$ = 18.4% for RT-OC vs. HV-OC). The average Y/X ratios were 0.75±0.11 for RT-TC vs. Partisol-TC and 0.86±0.11 for RT-TC vs. HV-TC, respectively. The Y/X ratios for RT-OC vs. Partisol-OC and RT-OC vs. HV-OC were 0.72±0.14 and 0.85±0.18, respectively. These numbers suggest that in general both the TC and OC measurements from the off-line filter samples were larger than those observed by the semi-continuous method. More specifically, the discrepancies were larger between RT data and Partisol data than those between RT data and HV data. In addition to the uncertainties associated with the sampling and analysis processes, another possible reason is the positive artifacts due to organic vapor adsorption on the quartz fiber filters since no denuder was used in either the Partisol or HV samplers. The amount of OC adsorbed onto the quartz fiber filter in the Partisol samplers was expected to be higher than that in the HV samplers as the face velocity of the Partisol sampler is approximately half of that of the HV sampler (McDow et al., 1990).

The EC data comparisons show a higher degree of scatter than TC and OC (R^2 = 0.93 for RT-EC vs. Partisol-EC and R^2 = 0.86 for RT-EC vs. HV-EC) while the average Y/X ratios for EC suggested that the semi-continuous data agree better with the filter-based measurements (0.88±0.26 for RT vs. Partisol samples and 1.04±0.38 for RT vs. HV samples, respectively). Several studies reported poor agreement between thermal EC from the field analyzer and those filter-based EC measurements due to high detection limit and differences in the temperature programs (e.g. Schauer et al., 2003; Bae et al., 2004; Venkatachari et al., 2006). However, the discrepancies between RT-EC and filter-based EC measured at roadside in this study might also be attributed to the different sampling durations. The field analyzer collected $PM_{2.5}$ samples for a total of 1104 minutes on a daily basis, accounting for about 3/4 of the 24-h period. The sampled air by the RT-OCEC analyzer might not be able to fully represent the 24-h integrated sampling period by the filter-based measurements because of the high carbon concentrations with large variations at MK."

Comment

Page 67, lines 6-19: OC observed at a roadside location is pretty much always dominated by local sources, vehicles in particular. If the OC and EC were not constantly being produced by local sources, there would be a very clear decrease in the middle of the day as the boundary layer reaches its maximum depth.

Response: In MK sampling area, it is not always the case that OC is dominated by local sources. Two observations support this. First, the OC concentration levels were higher in winter (when the prevailing wind was northerlies) and in transitional seasons (when winds came from both north and south) than that in summer (when southerlies were the prevailing wind). Second, OC concentrations were lower during holidays and higher during weekdays in summer while this weekday-holiday variation became less notable in other seasons. Based on these two observations, we could conclude that local emissions are important sources for OC at our sampling site while the OC level could also be significantly influenced by regional transport of air pollutants when the wind comes from the continent.

Comment

Page 68, lines 3-11: Figures 4 and 5 show NOx levels on the order of 100-150 ppb and ozone levels on the order of 10-15 ppb. The oxidants in this environment are totally controlled by NO2, and comparing OC to ozone alone is not all that informative.

Response: We agree with the reviewer that in the roadside environment, the ozone concentration level is much lower due to titration by NO. Nevertheless, an ozone peak appearing in the early afternoon was consistently observed in different seasons (Figure 5). Such a temporal characteristic tends to serve as an indicator of photochemical activity for investigating the SOC formation through photochemical processes. The following text is added to explain this:

Lines 278-284:

"In the roadside environment, the ozone concentration level was much lower due to titration by NO. Nevertheless, an ozone peak appearing in the early afternoon was consistently observed in different seasons (Fig. 5). Such a temporal characteristic tends to indicate that ozone could be an indicator of photochemical processes even in a high NO roadside environment. In view of the consistent observation of an ozone peak in the early afternoon, it is possible that the first OC peak was related to secondary organic aerosol (SOA) formation."

Comment

Page 68, lines 12-17: The authors do not show this data. If the data is plotted with uncertainty error bars, are the “peaks” robust? The text is descriptive, but gives no physical interpretation.

Response: The diurnal profile of averaged OC/EC ratios over a year is shown in box plot in Figure R2 and this figure is now included in the supporting material document. It can be seen that three peaks of OC/EC ratio were observed during the day.

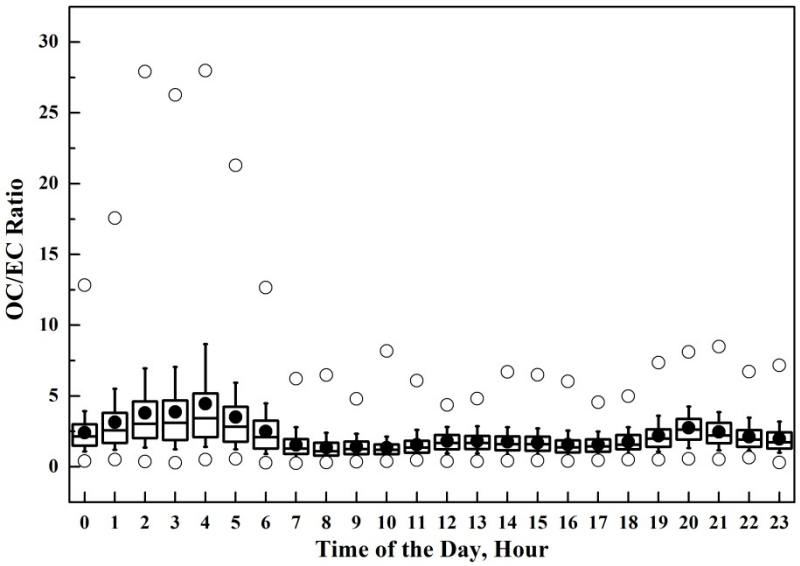

Figure R2. The diurnal variation of average OC/EC ratios. (The box length: the 25th and the 75th percentiles; the whiskers: the 10th and the 90th percentiles; the dot in the box: the average; the line in the box: the median; the circles: the minimum and maximum values).

Reference:

Saylor, R. D., E. S. Edgerton, and B. E. Hartsell: Linear regression techniques for use in the EC tracer method of secondary organic aerosol estimation, Atmos. Environ., 40, 7546-7556, 2006.

By Anonymous Referee #3

Comment

Huang et al. reported seasonal observations of carbonaceous observations using the Sunset OCEC monitor in Hong Kong. The modified NIOSH method protocol was used for particle analysis and the EC tracer method was used to decipher the contribution of vehicular carbon contributions. The authors demonstrated a thorough effort to find the suitable determination of the OC/ECpri using the EC tracer method. These discussions are of interest to the general audience with interest in air quality and atmospheric processes. A list of revision suggestions is provided for the authors to strengthen the paper before publication.

Page 85, abstract, line 27, PM was used not PM2.5. Need to be consistent in the paper. Suggest spell out particular matter or aerosol, as PM2.5 could not represent PM10 or ultrafine particles.

Response: Suggestion taken. We have replaced PM with $PM_{2.5}$ throughout the manuscript to be clear on what we refer in this work is $PM_{2.5}$.

Comment

Page 59, line 13, "Since EC undergoes little chemical transformation…", not sure I agree with this statement, as more and more observational evidence has suggested that black carbon is not as simple as what we had thought. Would suggest the authors modify this by saying "EC has been considered to undergo little chemical transformation, and thus it has been used as an indicator for primary combustion emissions."

Response: Suggestion taken and revision made accordingly.

Comment

Page 59, second paragraph, & page 60 2nd paragraph, mixed usage of PM and PM2.5.

Response: Revised and thanks the reviewer for pointing it out.

Comment

Page 59, line 26, with respect to not in respect to

Response: Revised

Comment

Page 60, line 14, please add "…processes that happen at a faster time scale". One could argue that the semi-continuous OCEC measurements could not capture fast chemical transformation as well. I would suggest the authors comment on this.

Response:

Suggestion taken and the sentence is rephrased as "…and they are inherently incapable of capturing the dynamics of pollutant emissions and atmospheric chemical conversion processes that happen on a faster time scale" (Line 78).

We agree with the reviewer's comment that the semi-continuous OCEC measurements may not be able to capture very fast chemical transformation (e.g, at a scale of minutes or shorter). However, the instrument with 1-hour time resolution does a better job in obtaining diurnal profiles of OC and EC than 24-hr integrated filter measurements. For example, as we demonstrate in the paper, the hourly ECOC data allows us to examine data obtained during rush hours to extract $(OC/EC)_{vehicle}$.

Comment

Page 60, line 23, could you describe how high the time-resolution is? Generally, Sunset OCEC measurements provide hourly measurements. It is faster than daily, but not really that high compared to other techniques. Also see my previous comment.

Response:

We specified the time resolution of the measurements in the previous sentence as “Measurements of hourly OC and EC concentrations were conducted for a year from May 2011 to April 2012”.

Comment
Page 61, line 3, instead of “one set of” just use “A”.

Response: Revised.

Comment
Page 61, line 7, the flow rate for Sunset instrument is normally 8 lpm, could you comment on why you chose 8.2 lpm? Did you do any corrections of your data considering the flow rate may affect the sample mass calculation?

Response:
The sample collection flow rate was pre-set by the instrument controlling software. It is found in the user manual that a more accurate statement of the sampling flow rate should be “around 8 LPM”. The revisions were accordingly made in the manuscript. We thank the reviewer for pointing it out.

In the data treatment, no corrections were done since the instrument monitored the flow rates during sampling so as to calculate the sampled volume for each sample. The hourly OC and EC concentrations were then calculated by the total amount of carbon measured divided by the sampled volume.

Comment
Page 64, line 10-14, could you explain more clearly the rationale to compare two different protocols? What new insights are you trying to bring? Also, for Fig. 1 on Page 86, it will be easier to see the plots by putting them into two rows, i.e., the first row for RT vs. Partisol comparisons and the second row for RT vs. HV comparisons.

Response:
The comparisons between semi-continuous measurements with two independent datasets obtained from 24-hour integrated filter measurements served as a higher level of data validation in order to identify any atypical data or systematic bias [*USEPA*, Quality Assurance Guidance Document, EPA-454/R-01-001, 2000].
Figure 1 has been revised accordingly and we thank the reviewer for this constructive suggestion.

Comment
Page 64, line 15, why do you decide to use zero-intercept linear regression analysis?

Response:
The instrument blanks for both bench-top aerosol carbon analyzer and the semi-continuous OC-EC field analyzer were estimated to be zero (by comparing the absolute blank values, the analytical uncertainties of the blank and the instrumental uncertainties of the blank). Hence, the zero-intercept linear regression analysis was applied to the comparisons of the datasets. This information is added to the revised manuscript.

Comment
Page 64, line 17 to Page 65, line 4, these equations are very simple, they should not take the main content of the paper. They belong to supplemental materials.

Response: Suggestion taken and the equations are moved to the supplemental materials.

Comment

Page 65, line 5-28, suggest the author refer to Fig. 1 when discussing the results here. Also suggest the authors bring out the key point of these comparisons. Why are you doing these measurement comparisons? What new insights are we getting from this exercises?

Response: Please see the response to the previous comment related to "Page 64, line 10-14."

Comment

Page 66, line 7, the number of significant numbers for reporting OC and EC concentrations. Considering the detection limit of Sunset OCEC is on the order of 0.1-0.2 mg/m3 (see Bauer et al., 2009 and ref therein), it is pointless to report more than 1 digit after the decimal point. I suggest the authors revise these throughout the manuscript.

Ref: Characterization of the Sunset Semi-Continuous carbon Aerosol Analyzer, J Air & Waste Management, 2009, 59(7), DOI:10.3155/1047-3289.59.7.826, Jace J. Bauer, Xiao-Ying Yu, Rober Cary, Nels Laulainen & Berkowitz.

Response: Suggestion taken and the revisions made accordingly.

Comment

Page 66, no previous description of trace gas measurements, i.e., NOx, O3, etc., please add.

Response:

The hourly data including PM2.5 mass, NO, NO2, and O3 at the sampling site are provided by the Hong Kong Environmental Protection Department (HKEPD). This information is now added to Section 2.1 Sampling equipment and method. (Lines 128-129)

Comment

Page 68-69, the EC tracer method discussions, suggest the author consider adding additional references of more recent results using the EC tracer method and how to arrive the OC/EC pri and enrich the discussions. Additional references may include the following:

Ref: Primary and secondary organic carbon downwind of Mexico City, ACP, 2009, 9, 6793-6814. doi: 10.5194/acp-9-6793-2009, X.-Y. Yu, R.A. Cary, and N. S. Laulainen

Linear regression techniques for use in the EC tracer method of secondary organic aerosol estimation, Atm. Env., 2006, 7546-7556, R.D. Saylor, ES Edgerton, BE Hartsell, doi: http://dx.doi.org/10.1016/j.atmosenv.2006.07.018

Response: The additional recent references are now added. (Line 298)

Comment

Page 70, paragraph 1, since wind seems to play a role in the OC/EC min, it is useful to show representative wind speed and wind direction data in the paper. For example, wind roses of the seasonal pattern could be useful in elucidating your points.

Response:

We totally agree with the reviewer that wind information is important in source identification. Unfortunately, the wind data at the MK AQMS is less meaningful since the monitoring station is located at the junction of two busy roads in downtown Hong Kong and surrounded by many tall buildings along the road. The street-canyon effect is significant. As a result, the wind observed at this site is either easterly or westerly (along the road) and at fairly constant speeds (see example wind data in Figure R3 below). The wind data at locations in HK with open surroundings better represent transport of regional pollutants. The seasonal wind variations in Hong Kong are well understood and have been described in details in Yu et al (2004). Therefore, we decide not to include the wind information local to Mong Kok for discussion in this manuscript. Instead we now add the Yu et al (2004) as a reference for further information on wind (Line 349).

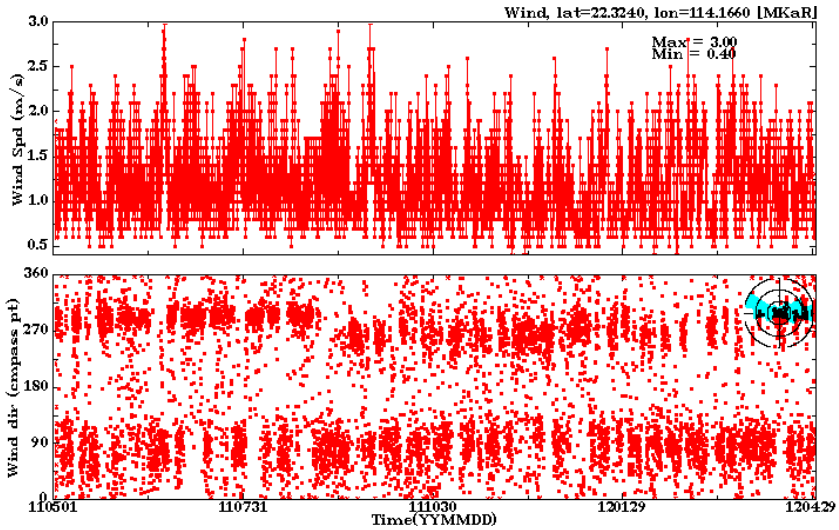

Figure R3. Example wind data at Mong Kok (Source: ENVF database)

Comment

Page 77, lines 6-11, the conclusion is somewhat unsupported by the data presented in the paper. No POC or SOC data were presented after the determination of OC/EC pri. Maybe this will go to a second paper? These should be moved to discussions or implications of your results or deleted, although the words all sound good.

I also would like to ask the authors to think about the most important take-home message after the rigorous exercise to determine OC/EC pri and compare with different methods. How would the community utilize your results in analyzing the Sunset observations in the future?

I recommend revisions in the conclusion section.

Response:

We would like to clarify that our analysis of hourly OCEC data and knowledge about this site have led us to conclude that the data is more suitable for deriving a $(OC/EC)_{vehicle}$ ratio instead of $(OC/EC)_{pri}$, unlike other ECOC measurement studies in the literature. Consequently, the focus of this work is on estimating the carbonaceous aerosol contribution from vehicular sources to $PM_{2.5}$, not the relative contributions of POC and SOC.

The diurnal variation of OC shows a nighttime OC peak around 19:00-22:00 LT. This observation combined with the knowledge of the sampling site characteristics (e.g, busy commercial district with numerous restaurants in the neighborhood and more private cars on the road in the early evening hours) suggest that there are a variety of time-varying primary emission sources in the sampling area. Hence, using a single value as the OC-to-EC ratio (derived from the minimum OC/EC ratio approach) for primary emissions to estimate POC and SOC may cause sizable biases especially when certain primary sources which emitted little EC were dominant (e.g. cooking). For these reasons, we analyzed data subsets which were obtained from a specific period of time and derived an OC-to-EC ratio that could reasonably represent the vehicular emission sources. With the derived $(OC/EC)_{vehicle}$, the OC generated by vehicle-related sources can subsequently be estimated.

In the same time, we agree with the reviewer that continuous efforts should be taken to investigate a more accurate way to differentiate POC and SOC. Specific to our sampling site, other tracers, such as C_{16} and C_{18} fatty acids for cooking-related sources, are needed. Alternative approaches, such as SOA tracers in conjunction with the bulk OC and EC measurements, may be tried to get a better handle on SOA estimation. We feel these implications for future work are important to merit mentioning in the conclusion section instead of being buried in the discussion section.