

Anonymous referee #2

The paper provides receptor-based PM_{2.5} source apportionment at 8 California sites that covers 6 year period. Although receptor-oriented techniques have been widely used for PM source apportionment, previous studies were limited particularly by a smaller data set. In this sense, the paper provides some new information that is relevant to the readers of this journal. I recommend the paper be published after the authors address the following comments.

We would like to thank the reviewer for his/her helpful and constructive comments on the manuscript. Below are detailed replies to each of the reviewer's comments. The manuscript has been also revised accordingly.

***Comment 1:** Uncertainties. Somewhere in Section 2.3.1 or 2.3.2, the authors should more clearly mention how uncertainties for different elements were estimated. In addition to analytical uncertainty, what other factors were included in calculating the uncertainties.*

Response: To address the reviewer's comment, the following statements are added to the revised manuscript:

“The uncertainties used in the PMF model were the estimated uncertainties reported in the Air Quality System (AQS) for the PM_{2.5} chemical speciation network. The uncertainties reported by STN include both the analytical uncertainties and uncertainties associated with the field sampling component (Flanagan et al., 2006). The uncertainties of elements, measured by the ED-XRF method, go through a comprehensive calculation procedure that harmonizes the uncertainties between different instruments and accounts for filter matrix effect, in addition to the field sampling and handling uncertainty (Gutknecht et al., 2010). For the other species, uncertainty is estimated as the analytical uncertainty of the instrument, augmented by 5% of the calculated concentration, assuming that this 5% is representing the total “field” variability (Flanagan et al., 2006).”

***Comment 2:** OC artifact correction. Table S2 shows corrections various quite significantly among different sites, supposedly caused by different levels of OC and the detailed chemical composition and volatility. More importantly, at a number of sites, the OC concentration might*

have decreased significantly during the six year period. Should the correction factors also be time dependent?

Response: We acknowledge the fact that OC artifact may have time variability. In our study, however, the variations of OC artifact among different years were negligible and for this reason we used an average OC artifact value for the entire study period (the approach similar to most of the past long-term PMF investigations). To further clarify this point and address the reviewer's concern, we picked the sampling site with the maximum estimated OC artifact (i.e. Los Angeles) and evaluated the year-to-year variability of the artifact values. At this sampling site, the annual average concentration of uncorrected OC (i.e. comprising the artifact) decreased from near $7\mu\text{g}/\text{m}^3$ in 2002 to about $5\mu\text{g}/\text{m}^3$ in 2007 (Figure (a)), in agreement with the reviewer's surmise. Figure (b) shows the scatter plot of OC TOT versus measured $\text{PM}_{2.5}$ mass concentration, in which the data points corresponding to each year are specified with a distinct marker/color. As described in the paper, OC artifact is estimated using the intercept of the linear regression of OC against $\text{PM}_{2.5}$ mass concentration, following the method of Kim et al. (2005). Table (a) presents the estimated OC artifacts (\pm standard errors), segregated by year, in Los Angeles. As can be seen, the OC artifact values do not show a significant year-to-year variability. This can be inferred from the levels of significance corresponding to the two-tailed t tests performed on the OC artifact values between each two consecutive years, as shown in Table (a) (p values ranging from 0.23 to 0.69), indicating that there is no statistically significant difference between OC artifacts among different years. Furthermore, the maximum difference between the individual estimated OC artifact and the average value calculated over all 6 years (i.e. $\sim 3.7\mu\text{g}/\text{m}^3$) is less than 17% of the average value. Considering these observations, for each sampling site we estimated one OC artifact, using the intercept of OC TOT vs $\text{PM}_{2.5}$, over the entire study period (i.e. 2002-2007), similarly to the approach taken in many other studies in the literature, using the $\text{PM}_{2.5}$ chemical speciation data over a long period of time (Hwang and Hopke, 2006; Kim and Hopke, 2008a, b).

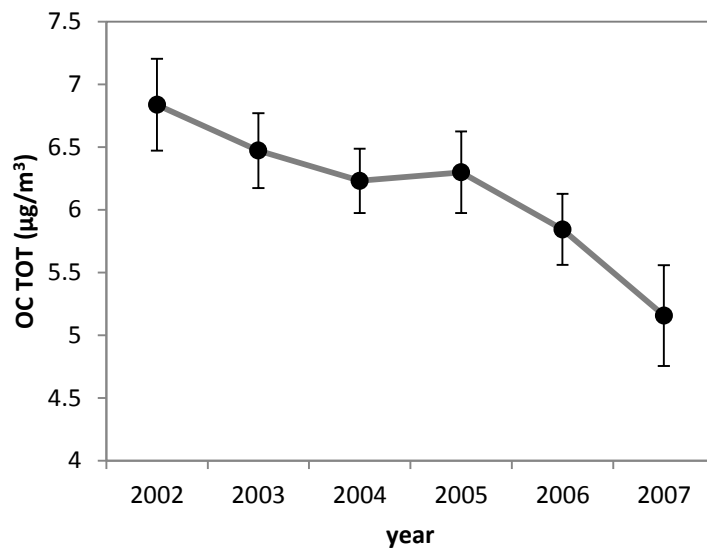


Figure (a). Annual average concentration ($\mu\text{g}/\text{m}^3$) of uncorrected organic carbon (OC) from 2002 to 2007 in Los Angeles. Error bars correspond to one standard error.

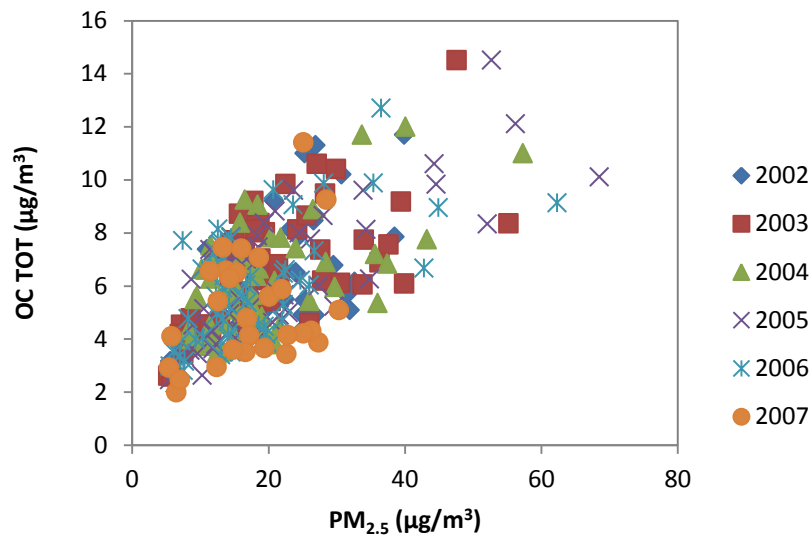


Figure (b). Scatter plot of OC mass concentration, obtained from Thermal Optical Transmittance (TOT) NIOSH 5040 method, versus $\text{PM}_{2.5}$ mass concentration in Los Angeles, segregated by year.

Table (a). Estimated OC artifacts (\pm standard errors) and the p values corresponding to the two-tailed t tests between OC artifact values in each two consecutive years. Errors correspond to one standard error.

Year	Estimated OC artifact ($\mu\text{g}/\text{m}^3$)	p value
2002	4.37 \pm 1.08	0.51
2003	3.69 \pm 0.48	0.57
2004	4.08 \pm 0.47	0.23
2005	3.32 \pm 0.41	0.53
2006	3.70 \pm 0.45	0.69
2007	3.32 \pm 1.04	

Comment 3: Is the estimated PM_{2.5} mass (as used to generate Table 3 and Figure 1) reconstructed from the resolved chemical components? If so, what is (are) the equation(s) used? Particularly, any consideration of possible seasonal variation of OM/OC when the mass was reconstructed?

Response: Since the total PM mass was included in the data matrix input to the PMF model as "total variable", the PMF model directly apportioned PM mass to each identified factor (Reff et al., 2007). Therefore, the estimated PM_{2.5} mass concentrations in Table 3 and Figure 1 are simply the sum of PM mass apportioned to each factor. Since PM mass was not reconstructed from the resolved chemical components, possible seasonal variations of OM/OC ratio would not affect the estimated PM_{2.5} mass concentrations. To clarify this, the following sentence has been updated in the revised manuscript:

“Table 3 presents the slope, intercept, and R² of the linear regressions between daily-resolved measured ambient PM_{2.5} and estimated PM_{2.5} mass concentrations, calculated by the sum of PM mass apportioned to each identified factor.”

Comment 4: "standard error". In Figures 2-8, it is stated that "error bars correspond to one standard error". It is unclear, however, the exact meaning of one standard error. Are these based on all the daily concentration data (2002-2007) that fall in a given season? If so, it represents variation of the source contributions over the years. Or, are the standard errors based on error propagation of the uncertainties in the PMF resolved species concentrations using source profile uncertainties from the boot strap runs?

Response: The standard errors shown in Figures 2-8 were calculated based on all daily-resolved source contributions (between 2002 and 2007) that fall within a given season. We did not use the output of the bootstrap analysis to calculate the standard errors accompanying the seasonal averages. To clarify this, we added the following sentence in the revised manuscript:

“The standard errors accompanying the seasonal averages were calculated based on all daily-resolved source contributions that fall within a given season”.

Comment 5: Year-to-year variation. On page 20055, the authors stated that lack of year-to-year variation in source contributions can be deduced from the small standard errors in the 6-year average. However, these are absolute concentrations. I am surprised at the small standard errors in Table S2. PM2.5 decreased quite significantly from 2002-2007 at a number of sites, for example, PM2.5 in LA decreased from ~22 to ~15ug/m3 from 2000 to 2006. Should the year-to-year variation be much more significant than ~1.0ug/m3 as shown in the Table?

Response: The reviewer’s comment is duly noted. As mentioned in the manuscript and response to the previous comment, in this study we calculated the seasonal averages and the standard errors over the 6-year period. Given the extent of the present study (i.e. 2002 to 2007) and the sampling frequency at each site (every third or sixth day), seasonal-average concentrations were calculated over a large number of data points (ranging from 90 to 180) at each site and season. These numbers are presented in the following table:

Table (c). Total number of STN sampling days at each sampling site, between 2002 and 2007, that fall within a given season.

	Spring	Summer	Fall	Winter
El Cajon	147	131	118	125
Rubidoux	174	141	141	159
Los Angeles	72	78	72	68
Simi Valley	91	95	91	95
Bakersfield	146	126	109	126
Fresno	174	176	169	160
San Jose	126	119	134	128
Sacramento	164	178	178	173

It should be noted that the standard error quantifies how precisely we know the true mean of the samples by taking into account both the values of the standard deviation and the sample size:

$$\text{Standard error} = \frac{\text{Standard deviation}}{\sqrt{\text{Sample size}}}$$

Considering the large number of data points at a given site and season (refer to Table (c)), obtaining relatively small standard error is not unreasonable. However, to address the reviewer's comment and for further clarity, we added the sample size at each site and season to Table S3. These numbers would give the readers a better perception that over how many data points the reported averages and standard errors were calculated.

References

- Flanagan, J.B., Jayanty, R.K.M., Rickman, E.E., Jr., Peterson, M.R., 2006. PM2.5 Speciation Trends Network: Evaluation of Whole-System Uncertainties Using Data from Sites with Collocated Samplers. *Journal of the Air & Waste Management Association* 56, 492-499.
- Gutknecht, W., Flanagan, J., McWilliams, A., Jayanty, R.K.M., Kellogg, R., Rice, J., Duda, P., Sarver, R.H., 2010. Harmonization of Uncertainties of X-Ray Fluorescence Data for PM2.5 Air Filter Analysis. *Journal of the Air & Waste Management Association* 60, 184-194.
- Hwang, I., Hopke, P.K., 2006. Comparison of source apportionments of fine particulate matter at two San Jose speciation trends network sites. *Journal of the Air & Waste Management Association* (1995) 56, 1287-1300.
- Kim, E., Hopke, P.K., 2008a. Characterization of Ambient Fine Particles in the Northwestern Area and Anchorage, Alaska. *Journal of the Air & Waste Management Association* 58, 1328-1340.
- Kim, E., Hopke, P.K., 2008b. Source characterization of ambient fine particles at multiple sites in the Seattle area. *Atmospheric Environment* 42, 6047-6056.
- Kim, E., Hopke, P.K., Qin, Y., 2005. Estimation of Organic Carbon Blank Values and Error Structures of the Speciation Trends Network Data for Source Apportionment. *Journal of the Air & Waste Management Association* 55, 1190-1199.
- Reff, A., Eberly, S.I., Bhave, P.V., 2007. Receptor Modeling of Ambient Particulate Matter Data Using Positive Matrix Factorization: Review of Existing Methods. *Journal of the Air & Waste Management Association* 57, 146-154.