

APPENDIX XI

MATES IV

FINAL REPORT

Estimating Diesel Particulate Matter

Authors

Philip Fine

Sang-Mi Lee

Appendix XI. Estimating Diesel Particulate Matter

XI.1. Introduction

Ambient diesel PM concentrations cannot be measured directly, but were estimated using ambient EC measurements multiplied by the ratio of diesel particulate matter (DPM) to elemental carbon (EC) based on the emissions inventory. The ratio estimated for MATES IV is 0.81, which is smaller than a ratio of 1.95 found in MATES III. This chapter describes factors contributing to this change and uncertainties associated with the estimates.

XI.2. Methodology

The ratio of diesel particulate matter (DPM) to elemental carbon (EC) can be rewritten, under well-mixed atmospheric conditions,

$$Ratio = \frac{PM_{diesel}}{EC_{total}} = \left(\frac{PM_{diesel}}{EC_{diesel}} \right) \cdot \left(\frac{EC_{diesel}}{EC_{total}} \right). \quad [1]$$

The first term, the ratio of PM from diesel to EC from diesel is determined by the combined speciation profiles of all diesel PM sources, which provides the fraction of each PM species including EC, organic matter, sulfate, nitrate and others. The speciation profiles used in MATES IV were significantly different from those used in MATES III. In the new PM speciation profile, which was developed based on recent dynamometer experiments and comprehensive source testing, heavy-duty diesel trucks have an EC fraction ranging from 23% to 68% depending on engine model year, emission control technology, driving cycle, etc. An example of the new speciation profile from heavy duty diesel truck is presented in Figure XI-1, which shows EC fraction as a function of calendar year. It increases from 50% for calendar year 2005 to 56% in 2010. Calendar year fleet is an aggregated fleet composed of various engine model years, technology groups, fuel types, operating conditions, etc.

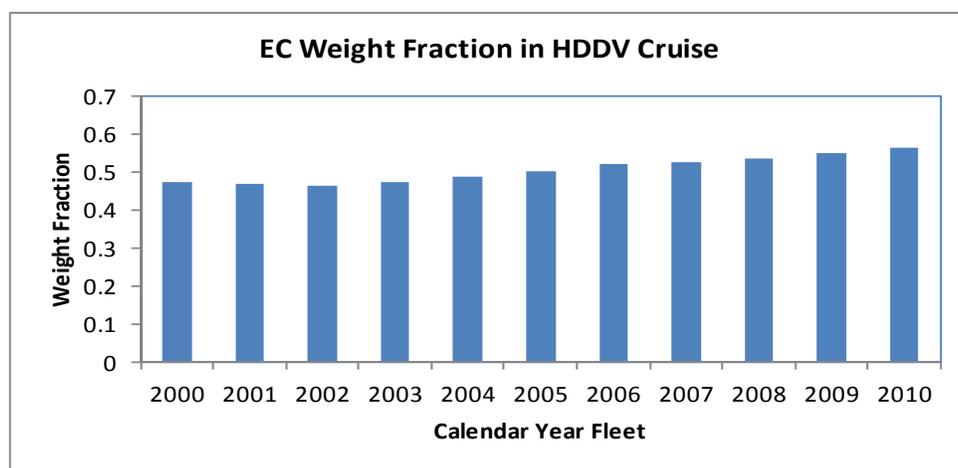


Figure XI-1. The EC fraction by weight from Heavy Duty Diesel Vehicles Exhaust in Cruise mode

On the contrary, the MATES III inventory was developed using a diesel profile based on source tests conducted on diesel tractors more than 20 years ago (Houck 1989, CARB 2008). In addition, only one speciation profile was applied to all diesel fueled mobile source categories, regardless of the fleet type, operating condition, engine technology, etc. However, at the time of MATES III, this profile was considered state-of-the-science. This PM profile assumes that 26.4% of total diesel exhaust is EC, while the MATES IV profile for heavy-duty vehicles has closer to 50% EC (Figure XI-1).

A majority of diesel emissions come from heavy-duty diesel trucks, diesel buses, ocean-going vessels, and off-road equipments categories, as shown in Table XI-1. These categories account for approximately 92% of total DPM emission in the Basin. Corresponding EC fractions and DPM/EC ratios are presented as well.

Note that the total DPM/EC ratio is an average of category specific DPM/EC ratios weighted by DPM mass from the category. So shifts among relative emissions from all diesel sources will also change the total combined speciation profile.

Some of the changes in the DPM/EC ratio could result from recent regulatory actions. Changes in PM speciation from OGV show the impact of such actions. During the period between the MATES III and MATES IV, OGV fuel regulation by California Air Resources Board became effective. The regulation requires OGVs to switch from heavy fuel oil (HFO, 1.0-2.5% sulfur content) to distillate marine diesel oil (MDO) of ~0.1% sulfur within 200 nautical miles of California coast. This requirement decreased sulfate in diesel exhaust more effectively than the other components including EC. In fact, replacement of 2.5% HFO marine fuel to 0.1% MDO marine fuel leads to a decrease in sulfate emissions of almost one-half while EC emissions remain nearly constant (CARB, 2012). The reduction in DPM emissions is well reflected in the MATES IV inventory (Table XI-1).

In all, the changes in the speciation profiles along with shifts in the relative amount of DPM emission from different diesel sources led to a lower value of the 1st term in Eq [1].

Table XI-1. Emissions for major DPM/EC source categories, total anthropogenic sources for the South Coast Air Basin and percentage change of DPM and EC from 2005 to 2012

Category	2005			2012			Changes	
	DPM (lb/day)	EC (lb/day)	DPM/EC Ratio	DPM (lb/day)	EC (lb/day)	DPM/EC Ratio	DPM (%)	EC (%)
Diesel Heavy Duty Trucks & Buses	19596	5231	3.75	9816	5298	1.85	49.91	-1.29
Other On-Road	795	3233	0.25	134	1340	0.10	83.12	58.54
Ocean Going Vessels	10365	415	25.00	990	60	16.39	90.45	85.43
Off-Road Equipment	21567	6207	3.47	5275	3865	1.36	75.54	37.72
Other Off-Road	2614	1720	1.52	2208	1670	1.32	15.55	2.88
Total Stationary and Area Sources	1045	11957	0.09	444	10928	0.04	57.55	8.60
Total Anthropogenic	55983	28761	1.95	18867	23163	0.81	66.30	19.47

The last term in Eq [1] represents the amount of diesel EC relative to the total EC emissions based on the Basin-wide inventory. The total EC, EC_{total} in Eq [1] can be split into diesel originated EC and non-diesel EC. In the Basin, the diesel EC accounts for the majority of total EC (64%). Non-diesel EC from sources such as biomass burning, cooking, residential fuel combustion, explain 36% of the total. While EC emissions from both diesel and non-diesel categories decreased between the MATES III and MATES IV, the reduction is more pronounced in the diesel category (24% reduction in diesel EC vs. 10% in non-diesel sources). A portion of changes in the non-diesel sources were driven by socio-economic growth in the Basin. Cleaning and Coating processes and Petroleum Production and Marketing categories are among those that have led to additional EC emissions between the MATES III and MATES IV period. This change in total EC decreased in the 2nd term of Eq [1]. Therefore, the overall ratio was decreased from the MATES III to MATES IV.

XI.3. Discussion and Summary

To estimate the impact of the updated speciation profile on measurements-based comparisons between the MATES III and MATES IV results, EC emissions from major diesel source categories in the MATES IV inventory were re-calculated using the older MATES III speciation profile, in which EC accounts for 26.4% of DPM. This retrospective calculation was applied to heavy-duty diesel trucks, diesel buses, off-road equipment, and farm equipment (Table XI-2).

The retrospective calculation yielded 23% less total anthropogenic EC emissions with most of the difference coming from the mobile source category. This is consistent with a ~30% reduction of EC from traffic emissions in LA and Riverside counties from the 2002-2006 to the 2008-2012 period as determined by source apportionment study (Hasheminassab, et al. 2014). The overall DPM/EC ratio from this sensitivity calculation was 1.06 and thus the overall average ambient DPM concentration was estimated to be 1.24 ug/m³ (1.17 ug/m³ basin-wide averaged measured ambient EC concentration during MATES IV, multiplied by the ratio 1.06). Using the updated profiles in MATES IV with a DPM/EC ratio of 0.81 (TableXI-1), and the measured ambient EC of 1.17 ug/m³, the overall average DPM concentration is estimated to be 0.95 ug/m³.

This sensitivity test indicates that the effect of the speciation methodology change between MATES III and MATES IV is an overall lower estimated DPM concentration from 1.24 to 0.95 ug/m³. This difference can be viewed in terms of the estimated DPM reductions based on EC measurements between MATES III (2005) and MATES IV (2012). Using the updated profiles for MATES IV and the previously published MATES III results using the older profiles, the basin-wide average reduction in DPM is 73% as cited in this report. Using the older speciation profiles for both MATES III and MATES IV yields a 2005 to 2012 DPM reduction of 64.3%. Thus, the methodology changes in the DPM speciation profile account for at most about 9% of the total stated 73% stated DPM reduction. It is also worth of note that, despite the uncertainties associated with emission inventory and measurements, the estimated DPM concentration stays within 25% of variation.

Note that the effect of this speciation methodology change only affects MATES III vs. MATES IV comparisons between estimated DPM based on EC measurements. Comparisons between 2005 and 2012 based on inventories and modeling results are not affected by the EC speciation profiles as DPM is estimated directly. Furthermore, given that the speciation profiles used in MATES IV are more recent and applied in a more detailed manner, the MATES IV results represent a refined analysis that is likely an improvement over the MATES III methods.

Table XI-2. Estimation of EC fractions from major diesel sources using the MATES III profile

Category	MATES IV			Using MATES III profile	
	DPM (lb/day)	EC (lb/day)	DPM/EC Ratio	EC (lb/day)	DPM/EC Ratio
Diesel Heavy-Duty Trucks & Buses	9816	5298	1.85	2594	3.78
Other On-Road	134	1340	0.10	1340	0.10
Ocean Going Vessels	990	60	16.39	60	16.39
Off-Road Equipment	5275	3865	1.36	1394	3.78
Other Off-Road	2208	1670	1.32	1453	1.52
Total Stationary and Area Sources	444	10928	0.04	10928	0.04
Total Anthropogenic	18867	23163	0.81	17771	1.06

The DPM/EC ratio discussed above is the basin average, yet the ratio can change from location to location depending on the dominant emission categories. The geographical variation of the ratio was evaluated using CAMx model output, which calculates atmospheric transport and mixing as well as chemistry and removal processes. The average of the predicted DPM/EC ratio is approximately 0.87 with a standard deviation of 0.06, indicating spatial variations were relatively small. Still, the ratio was higher near coastal sites and lower in inland regions, confirming the geographical dependency of diesel exhaust compositions. Non-diesel EC sources, such as biomass burning, partially contributed to the lower ratio in the inland areas, as well.

Overall, the DPM/EC ratio estimated in the current MATES IV is 0.81, significantly lower than 1.95 calculated in the MATES III. Several factors that contributed to this change include the revision of diesel exhaust profiles that provide more refined and detailed speciation data. Secondly, regulatory actions reduced some components of PM species more effectively than EC. In addition, changes in social demographics contributed to the changes of diesel originated EC to the total EC emissions, and consequently lowered the DPM/EC ratio.

XI.2 References:

- California Air Resources Board, Main Speciation Profiles. In May 19, 2008 ed.; California Air Resources Board: 2008.
- California Air Resources Board, Heavy Duty Diesel Vehicle Exhaust PM Speciation Profiles, Available at the following URL,
<http://www.arb.ca.gov/ei/speciate/profilereference/HDDV%20PM%20Profiles%20Final.pdf>
- California Air Resources Board, Ocean-Going Vessel (OGV) PM Speciation Profile Preparation, Available at the following URL,
http://www.arb.ca.gov/ei/speciate/profilereference/OGV_PM1191-93&4251.pdf
- California Air Resources Board, 2012, OGV PM Speciation Profile Development and Assignment, Available at the following URL,
http://www.arb.ca.gov/ei/speciate/profilereference/OGV_PM4252.pdf
- Hasheminassab, S.; Daher, N; Ostro, B.D.; Sioutas, C, 2014, Long-term source apportionment of ambient fine particulate matter (PM_{2.5}) in the Los Angeles Basin: A focus on emissions reduction from vehicular sources, *Environmental Pollution* **193**, 54-64.
- Houck, J. E.; Chow, J. C.; Waston, J. G.; Simons, C. A.; Pritchett, L. C.; Coulet, J. M.; Frazier, C. A. *Determination of Particle Size Distribution and Chemical Composition of Particulate Matter from Selected Sources in California*; California Air Resources Board: June 30, 1989.