

## Ocean-Going Vessel (OGV) PM Speciation Profile Preparation

### Background

PM speciation profiles 119 (*Marine Vessel-Liquid Fuel*) and 425 (*Diesel Vehicle Exhaust*)<sup>[1]</sup> were used for HFO (Heavy Fuel Oil) and MDO (Marine Diesel Oil) in the 2008 air quality modeling analysis because no OGV exhaust source testing data were available for creating speciation profiles by then. The detailed information of these two profiles used in the modeling is listed as follows:

Size Fraction (by weight)	PM <sub>2.5</sub> /TPM	PM <sub>10</sub> /TPM
PM 119	0.937	0.96
PM 425	0.92	1.0

Weigh Fraction (of PM mass)	PM <sub>2.5</sub>				PM <sub>10</sub>			
	EC	OC	SO <sub>4</sub> <sup>2-</sup>	others	EC	OC	SO <sub>4</sub> <sup>2-</sup>	others
PM 119	0.04	0	0.15	0.81	0.04	0	0.15	0.81
PM 425	0.264	0.694	0.0186	0.0235	0.261	0.689	0.0174	0.0328

In 2010, four new OGV PM speciation profiles were developed based on a series of newly conducted OGV exhaust source tests<sup>[2-5]</sup>. These profiles were prepared for OGV ME and AE operating on HFO, MDO and blend fuel, with various sulfur contents (0.1% to 2.5%), which were involved in the air quality modeling scenarios. The four profiles include:

Profile Number	Profile Name
PM 1191	Ocean-Going Vessel Exhaust--HFO (2.5% Sulfur)
PM 1192	Ocean-Going Vessel Exhaust--HFO (1.0% Sulfur)
PM 1193	Ocean-Going Vessel Exhaust-- Blend (1.0% Sulfur)
PM 4251	Ocean-Going Vessel Exhaust-- MDO (0.1% Sulfur)

### Methodology

- *PM 1191: Ocean-Going Vessel Exhaust--HFO (2.5% Sulfur)*

This profile was obtained by averaging the weight fractions of EC, OC and SO<sub>4</sub><sup>2-</sup> in total PM mass from 18 source tests<sup>[2-5]</sup> of main engine (ME) or auxiliary engine (AE) running with HFO with Sulfur contents ranging from 2.05% to 3.8%. Because the source tests were limited, it was assumed that the PM exhausts emitted from ME and AE have the same speciation composition for the same fuel. For each test, the weight fractions of EC,

OC and  $\text{SO}_4^{2-}$  were calculated by dividing the emission factors of these species by the emission factor of the total PM mass.

HFO	Emission Factor (g/kW-hr)				Weight Fraction (of PM mass)		
	PM Mass	EC	OC	$\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}$	EC	OC	$\text{SO}_4^{2-}$
2.5% S	1.501 ( $\pm 0.881$ ) <sup>*</sup>	0.015 ( $\pm 0.011$ )	0.244 ( $\pm 0.112$ )	1.080 ( $\pm 0.635$ )	0.013 ( $\pm 0.012$ )	0.212 ( $\pm 0.119$ )	0.335 ( $\pm 0.076$ )

<sup>\*</sup> Average value ( $\pm$  standard deviation)

- *PM 1192: Ocean-Going Vessel Exhaust--HFO (1.0% Sulfur)*

The emission factors of EC and OC for OGV running with 1.0%-S HFO were assumed to be the same as those for OGV running with 2.5%-S HFO, which were calculated based on the 18 source tests mentioned previously. The emission factor of  $\text{SO}_4^{2-}$  was estimated by multiplying the fuel consumption rate (195 g/kW-hr)<sup>[6]</sup>, fuel sulfur content (1.0%), conversion rate of fuel sulfur to  $\text{SO}_4^{2-}$  (3%)<sup>[6]</sup>, and molecular weight ratio of  $\text{SO}_4^{2-}$  to sulfur. The weight fractions of EC, OC and  $\text{SO}_4^{2-}$  were then calculated from the emission factors.

HFO	Emission Factor (g/kW-hr)				Weight Fraction (of PM mass)		
	PM Mass	EC	OC	$\text{SO}_4^{2-}$	EC	OC	$\text{SO}_4^{2-}$
1.0% S	1.10 <sup>[6]</sup>	0.015	0.244	0.176	0.014	0.222	0.160

- *PM 4251: Ocean-Going Vessel Exhaust-- MDO (0.1% Sulfur)*

This profile was obtained by averaging the weight fractions of EC, OC and  $\text{SO}_4^{2-}$  in total PM mass from 10 source tests<sup>[2, 3, 5]</sup> of ME or AE running with MDO with Sulfur contents ranging from 0.05% to 0.2%. For each test, the weight fractions of EC, OC and  $\text{SO}_4^{2-}$  were calculated by dividing the emission factors of these species by the emission factor of the total PM mass.

MDO	Emission Factor (g/kW-hr)				Weight Fraction (of PM mass)		
	PM Mass	EC	OC	$\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}$	EC	OC	$\text{SO}_4^{2-}$
0.1% S	0.338 ( $\pm 0.177$ )	0.020 ( $\pm 0.019$ )	0.111 ( $\pm 0.438$ )	0.042 ( $\pm 0.014$ )	0.052 ( $\pm 0.037$ )	0.522 ( $\pm 0.114$ )	0.080 ( $\pm 0.068$ )

<sup>\*</sup> Average value ( $\pm$  standard deviation)

- *PM 1193: Ocean-Going Vessel Exhaust--Blend (1.0% Sulfur)*

The emission factors of EC and OC for OGV running with 1.0%-S Blend fuel were assumed to be the average values of those for HFO (2.5% S) and MDO (0.1% S). The

emission factor of  $\text{SO}_4^{2-}$  was estimated by multiplying the fuel consumption rate ( $190 \text{ g/kW-hr}$ )<sup>[6]</sup>, fuel sulfur content (1.0%), conversion rate of fuel sulfur to  $\text{SO}_4^{2-}$  (3%)<sup>[6]</sup>, and molecular weight ratio of  $\text{SO}_4^{2-}$  to sulfur. The weight fractions of EC, OC and  $\text{SO}_4^{2-}$  were then calculated from the known emission factors.

Blend	Emission Factor (g/kW-hr)				Weight Fraction (of PM mass)		
	PM Mass	EC	OC	$\text{SO}_4^{2-}$	EC	OC	$\text{SO}_4^{2-}$
1.0% S	0.80 <sup>[6]</sup>	0.018	0.213	0.171	0.023	0.266	0.214

## Summary

It has to be noted that all the source tests cited in this work were conducted for  $\text{PM}_{2.5}$  only, and it was assumed that same speciation profiles can be used for  $\text{PM}_{10}$  and TPM for the same fuel. It was also assumed that PM 1191 and PM1192 have the same  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  size fractions as PM 119; PM 4251 and PM 1193 have the same  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  size fractions as PM 425. The size fractions, speciation profiles and factors used to convert profiles PM 119 and PM 425 to the updated profiles are summarized in the following tables.

Size Fraction (by weight)	$\text{PM}_{2.5}/\text{TPM}$	$\text{PM}_{10}/\text{TPM}$
PM 1191	0.937	0.96
PM 1192	0.937	0.96
PM 1193	0.92	1.0
PM 4251	0.92	1.0

Weigh Fraction (of PM mass)	$\text{PM}_{2.5}$ Fraction				$\text{PM}_{10}$ Fraction			
	EC	OC	$\text{SO}_4^{2-}$	others	EC	OC	$\text{SO}_4^{2-}$	others
PM 1191	0.013	0.212	0.335	0.440	0.013	0.212	0.335	0.440
PM 1192	0.014	0.222	0.160	0.604	0.014	0.222	0.160	0.604
PM 1193	0.023	0.266	0.214	0.497	0.023	0.266	0.214	0.497
PM 4251	0.052	0.522	0.080	0.346	0.052	0.522	0.080	0.346

Conversion Factor	$\text{PM}_{2.5}$ Fraction				$\text{PM}_{10}$ Fraction			
	EC	OC	$\text{SO}_4^{2-}$	others	EC	OC	$\text{SO}_4^{2-}$	others
PM 1191/ PM 119	0.33		2.23	0.54	0.33		2.23	0.54
PM 1192/ PM 119	0.35		1.07	0.75	0.35		1.07	0.75
PM 1193/ PM 119	0.58		1.43	0.61	0.58		1.43	0.61
PM 4251/PM 425	0.20	0.75	4.29	14.74	0.20	0.76	4.59	10.56

\*Note: there is no OC in PM 119, so no conversion factor can apply.

## References:

1. *California Air Resources Board Main Speciation Profiles*. California Air Resources Board: 2008; <http://www.arb.ca.gov/ei/speciate/speciate.htm>. Accessed July 7, 2010.
2. Miller, J. W.; Nigam, A.; Welch, W. A.; Cocker, D. R. *Measurement of Criteria and Greenhouse Gas Emissions from Auxiliary Engines on Ocean-Going Vessels Operating on Heavy Fuel Oil and Marine Diesel Oil*; California Air Resources Board: 2009.
3. Miller, J. W.; Agrawal, H.; Welch, W. A. *Criteria Emissions from the Main Propulsion Engine of a Post-Panamax Class Container Vessel Using Distillate and Residual Fuels*; California Air Resources Board: 2009.
4. Miller, J. W.; Agrawal, H.; Welch, W. A. *Measurement of Emissions from the Main Propulsion Engine (MAN B&W 11K90MC-C) on a Panamax Class Container Ship*; California Air Resources Board: 2009.
5. Jayaram, V.; Miller, J. W.; Nigam, A.; Welch, W. A. *Effect of Selective Catalytic Reduction Unit on Emissions from an Auxiliary Engine on an Ocean-Going Vessel*; California Air Resources Board: 2009.
6. Soriano, B. L.; Milkey, P.; Alexis, A.; Di, P.; Du, S.; Lu, J.; Hand, R.; Houghton, M.; Komlenic, M.; Suer, C.; Williams, L.; Zuo, Y.-P. *Initial Statement of Reasons for Proposed Rulemaking: Fuel Sulfur and Other Operational Requirements for Ocean-Going Vessel within California Waters and 24 Nautical Miles of the California Baseline*; California Air Resources Board: Sacramento, CA, June 2008.