PMDETAIL HYPOTHESIS H4. CAMX AND PMCAMX TREATING THE FIRE PM EMISSIONS AS SEMI-VOLATILE AND REACTIVE CAN SIMULATE ACCURATELY THE FIRE IMPACTS ON REGIONAL PM LEVELS.

Conclusion: The results for this hypothesis are mixed as there are numerous other factors affecting whether CAMx/PMCAMx can accurately simulate fire PM impacts in addition to the treatment of semi-volatile and reactive organic aerosols. However, in general the model does a good job in estimating fire PM impacts at monitoring sites/days when the observed data says fire impacts occur most of the time, as well as the model agreeing with the observations on days when the measurements indicate no fire impacts occurred. The use of the VBS organic aerosol module that has more detailed treatment of OA volatility including treating the volatility of primary organic aerosol (POA) compared to the SOAP OA module does exhibit slightly better PM and OA model performance than when the SOAP module is used.

Discussion: The evaluation of whether the improved treatment of fire organic aerosol (OA) volatility used in the Volatility Basis Set (VBS) OA module can more accurately simulate fire OA and PM impacts than the traditional SOAP OA module that assumes primary organic aerosol (POA) is non-volatile is difficult to quantitatively determine due to the inherent uncertainties in modeling fire emissions using air quality models. From a theoretical basis, the VBS module is based on more recent science than SOAP module and accounts for known processes (e.g., evaporation of POA) not treated by SOAP, so VBS should provide a more accurate simulation of fire impacts. However, the VBS approach requires OA emissions of a complete volatility range including semi-volatile and intermediate-volatility organic compounds (SVOC and IVOC), estimation of which involves a significant uncertainty. CAMx was run using the VBS and SOAP OA modules for three approximately month long episodes during 2011 (episodes A, B and C, see discussion under Hypothesis H1 for more detailed discussion of the episodic modeling). The CAMx PM2.5 and OA model performance using VBS and OA was compared to determine which OA module was better able to reproduce the observed PM concentrations. However, in order for this comparison to have meaning, we first need to establish that CAMx is capable of simulating fire PM impacts at monitoring sites when they occur (and vice versa).

Evaluation of Model's Ability to Simulate Observed Fire Impacts

As part of PMDETAIL study, PM sample filters collected at selected IMPROVE and FRM monitoring sites and days were re-analyzed by Colorado State University (CSU) to obtain levoglucosan, water soluble organic carbon (WSOC) and other measurements. Levoglucosan is a biomass burning marker and the ratio of levoglucosan to WSOC can be used to identify the filter samples that were affected by fires. For each filter sample examined, CSU made an assessment of whether the sample was affected by fires (Yes) or not (No) or was possibly affected by fires (Maybe). CAMx simulations were performed for 2008 and 2011 including two levoglucosan species: (1) LEVO was assumed to be inert; and (2) LVGC was assumed to be reactive and decay with time (see Hypothesis H3 discussions for more details on the CAMx levoglucosan modeling). The CAMx fire LEVO and LVGC model predictions were compared against the CSU filter levoglucosan measurements to determine whether CAMx can accurately simulate the occurrence of fires when they are observed and vice-versa. Figures H4-1 and H4-2 display scatter plots of predicted vs. observed 24-h average concentrations of levoglucosan from, respectively, 2008 and 2011 CAMx simulations, with the symbol colored red when there was a fire impact, colored yellow when there maybe was a fire impact and no color when there was not fire impact for that sample. Generally, the model did a good job in predicting higher levoglucosan concentrations when the filter samples indicated fire impacts occurred and lower levoglucosan concentrations when the samples were found to have no fire contributions.

A more quantitative assessment of how well the model was able to predict the observed occurrence of fire impacts was obtained by determining fire impacts using two modeled levoglucosan concentration thresholds for fire indicators: (1) the first using a fire presence concentration threshold of 0.04 $\mu g/m^3$ that is roughly based on the observed ambient filter fire presence analysis shown in Figure H4-3; and (2) assuming fire presence when modeled LEVO/LGVC is greater than 0.1 $\mu g/m^3$ and no fire impact when less than 0.01 $\mu g/m^3$ and too close to call for 0.01-0.1 $\mu g/m^3$.

Tables H4-1 and H4-2 display the CAMx fire forecast scores using the levoglucosan filter observations data for, respectively, 2008 and 2011. Using the fire presence threshold of 0.04 $\mu g/m^3$ for modeled levoglucosan concentration, the model was able to correctly simulate the observed fire occurrence (pos-pos) or non-occurrence (neg-neg) 73% to 77% of the time for the two years of modeling (2008 and 2011) and two modeled levoglucosan tracers (LEVO and LVGC). When the filters indicate fire is present, the model agrees 60% (2008) and 68% (2011) of the time using LEVO and the 0.04 $\mu g/m^3$ threshold, which is reduced to around 50% when the threshold is applied to the LVGC tracer. The model does a much better job in reproducing the non- occurrence of fires determined by filter samples with almost 80% confirmations (neg-neg) and ~20% false negatives when using LEVO. The use of a lower and wider threshold range (0.01-0.1 $\mu g/m^3$) rather than a single threshold value generally improves the forecast scores on the amount of time the model is able to predict the occurrence and non-occurrence of the observed fires.

Table H4-1a. Number and percent of samples the model and filter measurements estimate positive and negative occurrence of fire at monitoring site/days using a 0.04 µg/m^3 modeled fire levoglucosan threshold using 2008 data.

2008	0.04	Mod LEVO		Mod LVGC		2008	0.04	Mod LEVO		Mod LVGC	
# Samples		pos	neg	pos	neg	% Samples		pos	neg	pos	neg
Obs	pos	35	23	29	29	Obs	pos	17%	11%	14%	14%
	neg	32	116	18	130		neg	16%	56%	9%	63%

Table H4-1b. Number and percent of samples the model and filter measurements estimate positive and negative occurrence of fire at monitoring site/days using a 0.01 to 0.1 µg/m^3 modeled fire levoglucosan threshold using 2008 data.

2008	0.04	Mod LEVO		Mod LVGC		2008	0.04	Mod LEVO		Mod LVGC	
# Samples		pos	neg	pos	neg	% Samples		pos	neg	pos	neg
Obs	pos	31	10	23	16	Obs	pos	22%	7%	15%	10%
	neg	14	87	8	111		neg	10%	61%	5%	70%

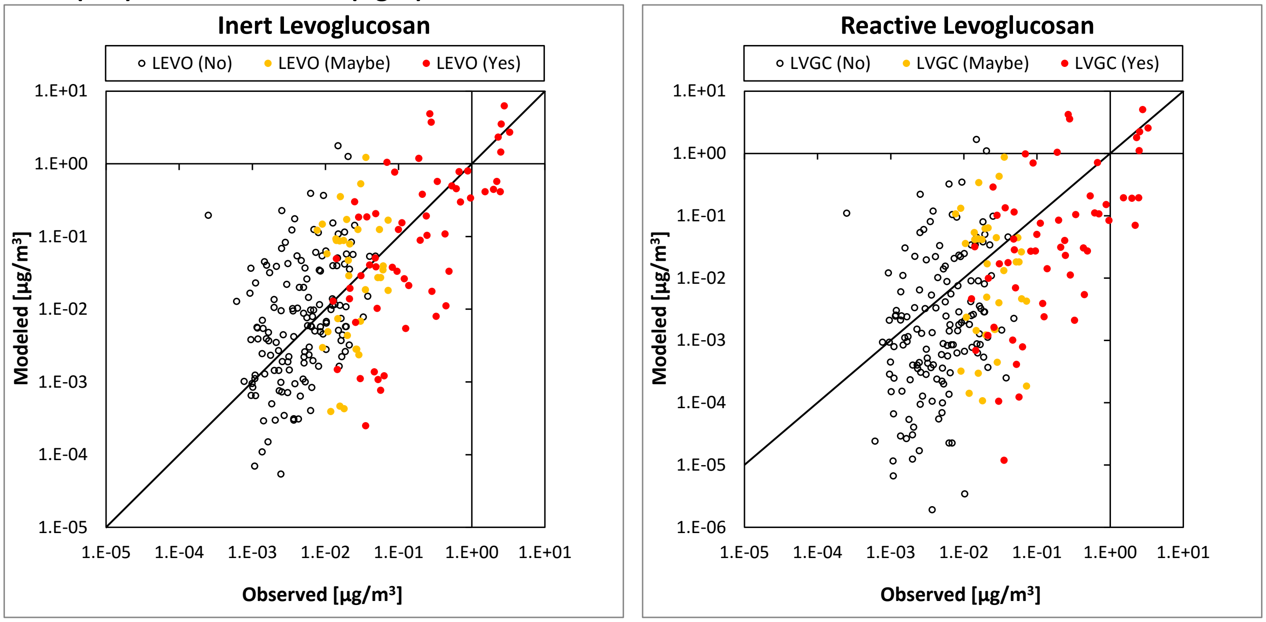
Table H4-2a. Number and percent of samples the model and filter measurements estimate positive and negative occurrence of fire at monitoring site/days using a 0.04 µg/m^3 modeled fire levoglucosan threshold using 2011 data.

2011	0.04	Mod LEVO		Mod LVGC		2011	0.04	Mod LEVO		Mod LVGC	
# Samples		pos	neg	pos	neg	% Samples		pos	neg	pos	neg
Obs	pos	136	63	101	98	Obs	pos	26%	12%	19%	19%
	neg	73	247	40	280		neg	14%	48%	8%	54%

Table H4-2b. Number and percent of samples the model and filter measurements estimate positive and negative occurrence of fire at monitoring site/days using a 0.01 to 0.1 µg/m^3 modeled fire levoglucosan threshold using 2011 data.

2011	0.04	Mod LEVO		Mod LVGC		2011	0.04	Mod LEVO		Mod LVGC	
# Samples		pos	neg	pos	neg	% Samples		pos	neg	pos	neg
Obs	pos	87	18	63	50	Obs	pos	31%	6%	18%	14%
	neg	26	148	9	234		neg	9%	53%	3%	66%

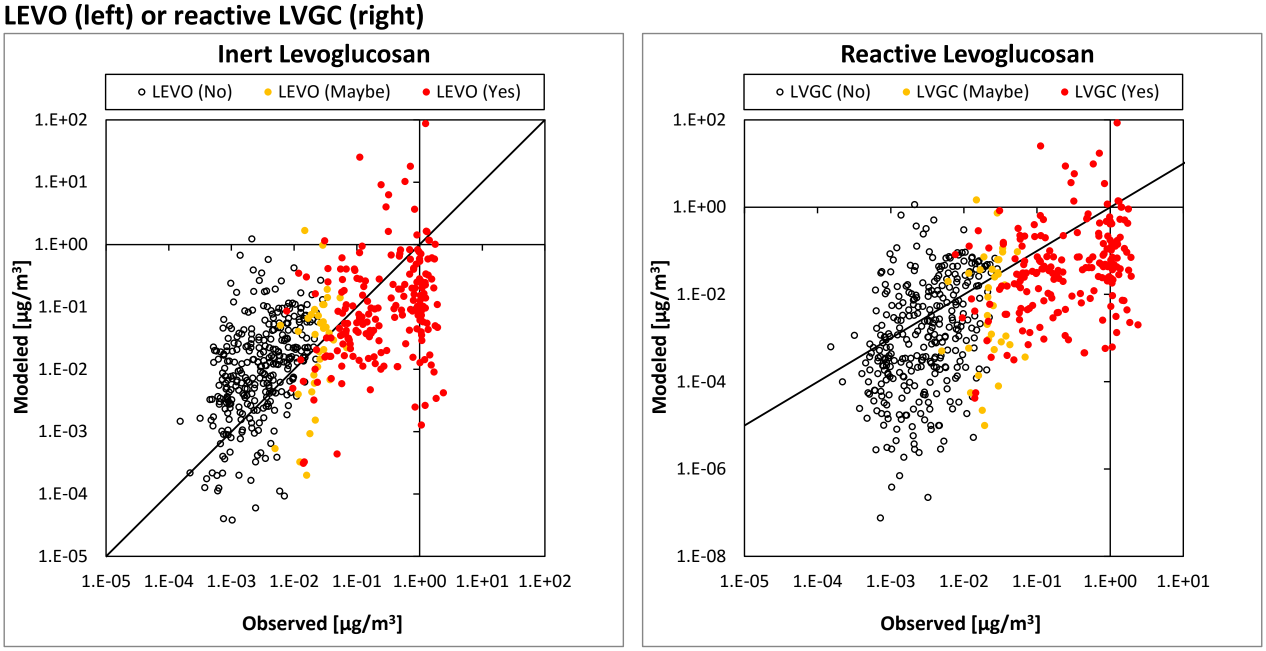
Figure H4-1. Scatter plot of predicted and observed levoglucosan concentrations during 2008 along with model performance statistics and indication of whether the observed sample were influence by fires (red), not influenced by fires (no color) or maybe influenced by fires (yellow) using modeled inert LEVO (left) or reactive LVGC (right)



NMB = 37.9%; NME = 114.1%

NMB = 0.9%; NME = 110.9%

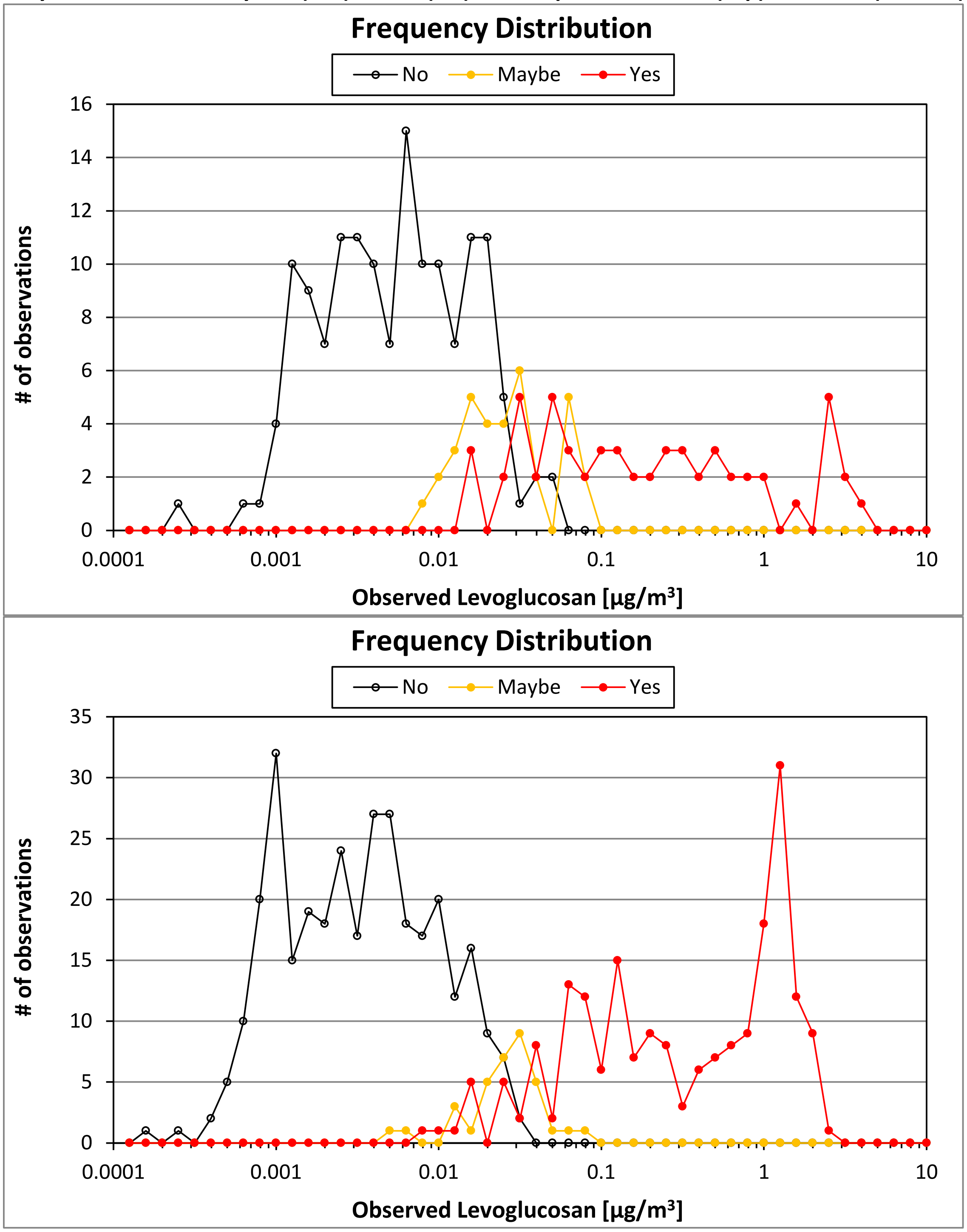
Figure H4-2. Scatter plot of predicted and observed levoglucosan concentrations during 2011 along with model performance statistics and indication of whether the observed sample were influence by fires (red), not influenced by fires (no color) or maybe influenced by fires (yellow) using modeled inert LEVO (left) or reactive LVGC (right)



NMB = 90.9%; NME = 228.5%

NMB = 69.0%; NME = 223.3%

Figure H4-3. Distribution of filter sample levoglucosan measurements and determination of whether they were influenced by fire (Yes) or not (No) for samples from 2008 (top) and 2011 (bottom).



PM and OA Model Performance Improved using VBS More Detailed OA Volatility Treatment

The CAMx $PM_{2.5}$ and OA modeling performance was assessed for the three 2011 episodic CAMx simulations using the VBS and SOAP OA modules. Figures H4-4, H4-5 and H4-6 display $PM_{2.5}$ and OA scatter plots and performance statistics for the three 2011 episodes and the CAMx simulations using the VBS and SOAP OA modules. One potential issue is that the model inputs of fire emissions on occasion have extremely high PM emissions that result in very high PM concentrations predicted by both VBS and SOAP skewing the model biases. These performance issues are related to uncertainties in the fire emissions estimates and not to the VBS or SOAP approach to modeling OA so the outliers in model predictions were removed from the model performance evaluation. The occurrence of these unreasonably high modeled PM concentrations at monitoring sites was very rare with just 6 data points out of around 5,000 pairs of observed and modeled concentrations; 5 outlier data points removed from episode A (Figure H4-4) and one from episode B (Figure H4-5). Note that corresponding high observed PM concentrations when fire plumes impact a monitor are not present because under those conditions the PM monitor becomes overloaded and the sample is invalidated.

The CAMx VBS results for episode A (Figure H4-4) exhibit comparable to slightly better $PM_{2.5}$ performance than SOAP while showing much better OA performance with lower bias (-15.6% vs. +30.0%) and error (54.2% vs. 72.7%). For episode B (Figure H4-5), the CAMx using the VBS OA module has better PM2.5 performance than using SOAP with lower bias (4.7% vs. 10.0%) and error (60.9% vs. 62.4%); OA performance is also better with VBS. And for episode C, VBS shows slightly better PM2.5 performance than SOAP and markedly better OA performance with lower bias (12.9% vs. 31.4%) and error (62.5% vs. 70.0%).

In conclusion, to show that use of more detailed treatment of OA volatility results in CAMx/PMCAMx to more accurately simulation fire PM concentrations impacts is demonstrated using a multi-prong approach:

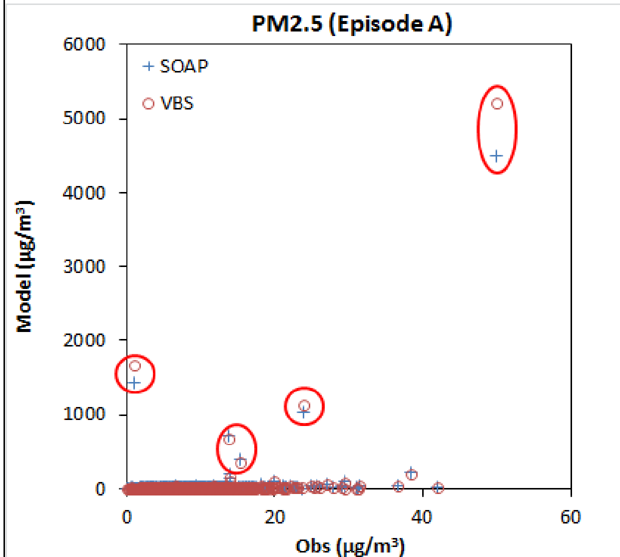
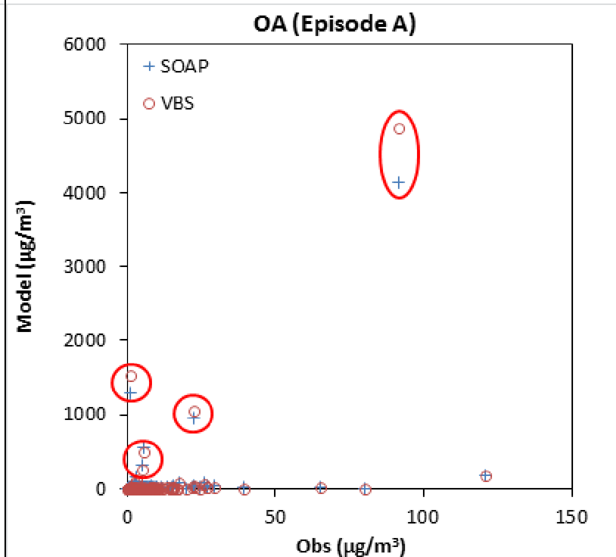
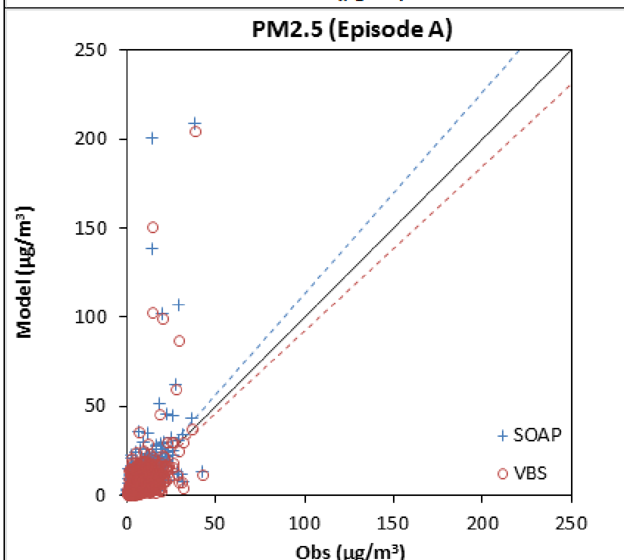
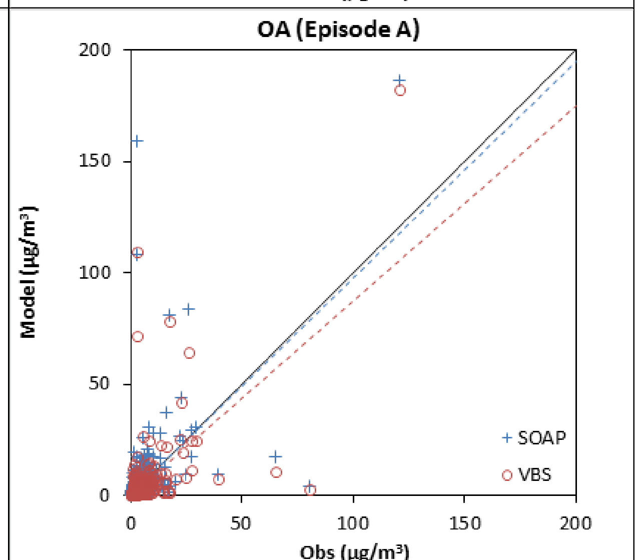
1. From a theoretical basis, the treatment of POA emission as semi-volatile and reactive and having a multi-tiered volatility treatment in the Volatility Basis Set (VBS) OA module should produce a more accurate representation of fire PM and OA impacts than treating POA emissions as non-volatile and inert as in the SOAP OA module.

2. The CAMx model was shown to agree with the observed occurrence and non-occurrence of fire impacts using the CSU special-study levoglucosan filter analysis and WSOC/levoglucosan fire marker approach most of the time.

3. The CAMx model performance statistics for PM2.5 and OA generally indicate better model performance with the VBS OA module compared to using the SOAP OA module.

These findings support the PMDETAIL Hypothesis H4.

Figure H4-4. Evaluation of modeled PM2.5 and OA at IMPROVE sites for CAMx Episode A simulation using the VBS and SOAP OA modules.

PM2.5 (all data)	OA (all data)
	
	

	NMB	NME	r^2
SOAP	**10.2%**	**47.4%**	**0.27**
VBS	**-9.2%**	**48.7%**	**0.24**

	NMB	NME	r^2
SOAP	**30.0%**	**72.7%**	**0.34**
VBS	**-15.6%**	**54.2%**	**0.40**

Figure H4-5. Evaluation of modeled PM2.5 and OA at IMPROVE sites for CAMx Episode B simulation using the VBS and SOAP OA modules.

				OA (all data)			
Episode B: PM2.5				**Episode B: OA**			
	NMB	**NME**	**r^2**		**NMB**	**NME**	**r^2**
SOAP	**10.0%**	**62.4%**	**0.18**	**SOAP**	**11.0%**	**62.9%**	**0.20**
VBS	**4.7%**	**60.9%**	**0.18**	**VBS**	**-9.3%**	**56.6%**	**0.18**

Figure H4-6. Evaluation of modeled PM2.5 and OA at IMPROVE sites for CAMx Episode C simulation using the VBS and SOAP OA modules.

	Episode C: PM2.5				Episode C: OA		
	NMB	NME	r^2		NMB	NME	r^2
SOAP	59.7%	85.7%	0.22	SOAP	31.4%	70.0%	0.20
VBS	51.8%	80.4%	0.20	VBS	12.9%	62.5%	0.15

		PM2.5				OA			
		Bias		Error		Bias		Error	
	Episode	SOAP	VBS	SOAP	VBS	SOAP	VBS	SOAP	VBS
	A: Aug-Sep	10.2%	-9.2%	47.4%	48.7%	30.0%	-15.6%	72.7%	54.2%
	B: Mar-May	10.0%	4.7%	62.4%	60.9%	11.0%	-9.3%	62.9%	56.6%
	C: Oct-Nov	59.7%	51.8%	85.7%	80.4%	31.4%	12.9%	70.0%	62.5%