PMDETAIL HYPOTHESIS H3. OXIDATION OF LEVOGLUCOSAN CREATES BIASES GREATER THAN 2X IN EXISTING MODEL ESTIMATES OF THE CONTRIBUTION OF FIRES TO AMBIENT PM LEVELS.

<u>Hypothesis H3 Conclusion</u>: Based on the PMDETAIL modeling, this hypothesis is true a majority of the time. Except near the source of the fires, accounting for the oxidation of levoglucosan reduces the levoglucosan concentration by over a factor of 2 than assuming it is inert most of the time. Without accounting for the levoglucosan decay effect, you may underestimate fire PM and ozone contributions when using levoglucosan as a fire marker. For inert levoglucosan concentrations above 0.001 µg/m^3, the inert levoglucosan concentrations is over a factor of 2 greater than the decayed levoglucosan concentrations over 80 percent of the time across the U.S.

<u>H3 Discussion</u>: When generating the 2011 fire emissions, separate emission factors were added for levoglucosan. In the past, atmospheric measurements of levoglucosan have been used as a marker for PM and ozone impacts from biomass burning (e.g., fires). However, levoglucosan decays in the atmosphere making its reliability as a fire marker less certain as it ages. PMDETAIL Hypothesis H3 notes that using levoglucosan as a fire marker and not accounting for the decay may result in underestimation biases in the fire contribution by over a factor of 2. To investigate this hypothesis, the CAMx 2011 annual simulations also modeled levoglucosan from fires. CAMx was modified to model total (gas + aerosol) levoglucosan using two levoglucosan tracers: (1) as an inert species (LEVO); and (2) with chemical decay (LVGC). Chemical decay of levoglucosan is modeled by a second-order oxidation reaction with hydroxyl (OH) radicals:

$$[LVGC] = [LVGC]_0 \exp(-k\,[OH]\,t)$$

An effective rate constant (k) of 3 x 10^{-11} cm^3 molec^{-1} s^{-1} estimated by Hennigan et al. (2011) was used that is based on the smog chamber studies during the third Fire Lab at Missoula Experiment (FLAME III) using various fuels commonly burned in North American wildfires. Both LEVO and LVGC were removed by wet and dry deposition as a component of internally-mixed fine particle (PM$_{2.5}$). Note that this decay is appropriate for gaseous levoglucosan, but was also applied to particle levoglucosan due to lack of any better data. The comparison between the modeled inert LEVO and decayed LVGC provides insight into how important it is to account for the oxidation of levoglucosan is in the atmosphere when using it as a marker for fire contributions.

It is expected that accounting for the decay in levoglucosan would have a bigger effect on aged fire emissions than near-source fire impact. However, in the CAMx modeling of fire levoglucosan we have little information on the age of the levoglucosan concentrations, although the ratio of decayed vs. inert levoglucosan from fires give an indication of the amount of photochemical processing. The concentration level of the levoglucosan is used as a surrogate for the age of the fire emissions as fresh levoglucosan fire emissions near the source will have higher concentrations than farther downwind. Although this is not perfect indicator of age as fresh levoglucosan concentrations from a small fire may be lower than aged levoglucosan emissions from a large fire.

The modeled inert (LEVO) and decayed (LVGC) levoglucosan concentrations from fires were stratified by concentration to analyze the differences in LEVO and LVGC. Modeled LEVO and LGVC concentrations were first extracted at all IMPROVE monitoring sites in the U.S. during the 2011 modeling period. Only LEVO and LVGC concentration pairs that were above 0.001 μg/m^3 were used in the analysis to eliminate trivial concentrations that approach the minimum detection limit in the levoglucosan filter sampling. We then compared LEVO and LVGC concentrations without and then with several maximum LEVO concentration to screen out high concentrations that would represent contributions from fresh fires.

Figure H3-1 displays a scatter plot of LEVO vs. LVGC concentrations at IMPROVE sites across the CONUS domain (left) and within the WESTUS domain (right) using all concentrations above 0.001 μg/m^3. The regression equation suggests on average that the inert LEVO is 2-4 percent higher than the decayed LVGC suggesting that accounting for the decay in levoglucosan would not have any effect on the average levoglucosan concentration levels. However, the regression equation average is highly influenced by the higher modeled levoglucosan concentrations with many modeled LEVO values above 10 μg/m^3 and some in excess of 100 μg/m^3 due to being very close to fire emission sources when the observed values rarely exceed 1 μg/m^3; note that a PM measurement devices will invalidate the sample when impacted by a fresh fire plume with high PM concentrations as it will overload the sampler so high fire plume concentrations are just not reported.
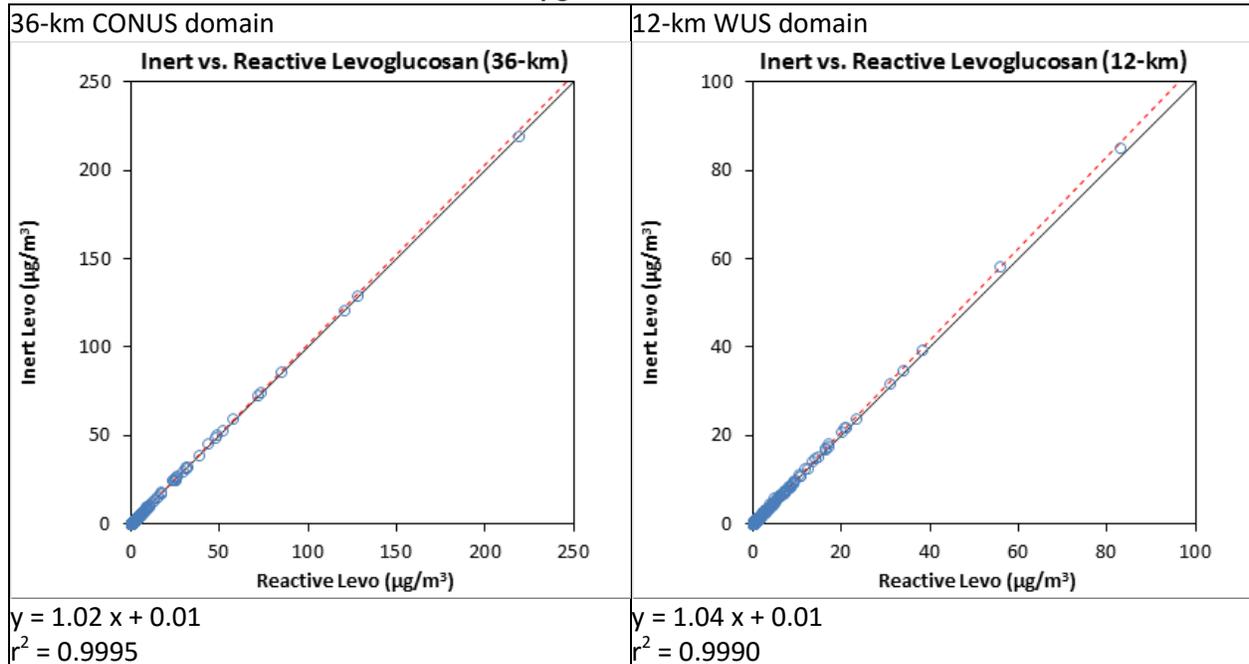
Figure H3-2 compares LEVO and LVGC concentrations when LEVO is between 0.001 and 1.0 μg/m^3. Except for LEVO concentrations between 0.001 and approximately 0.1 μg/m^3, the inert LEVO is rarely over a factor of 2 higher than the decayed LVGC. According to the regression equation, on average the inert LEVO is 18% higher than the decayed LVGC. The LEVO versus LVGC comparisons for LEVO concentrations between 0.001 and 0.1 μg/m^3 are shown in Figure H3-3. There are many more occurrences of the inert LEVO concentrations being over a factor of 2 greater than the decayed LVGC concentration. According to the regression equation the LEVO concentration is on average approximately 30 percent higher than the decayed LVGC concentrations. However, the regression equation average differences are more influenced by higher than lower concentrations.

The table below lists the frequency of occurrence that the inert LEVO concentrations is over 2x, 10x and 100x the oxidized LVGC concentrations for various LEVO concentrations ranges. Over all LEVO concentrations greater or equal to 0.001 μg/m^3, the inert LEVO is over 2 times greater than the decayed LVGC 81% of the time and is over 10x and 100x the LVGC concentration 49% and 21% of the time, respectively. When examining higher LEVO concentrations greater or equal to 0.01 μg/m^3 the LEVO concentrations is over 2x, 10x and 100x the LVGC concentration 67%, 33% and 12% of the time, respectively.
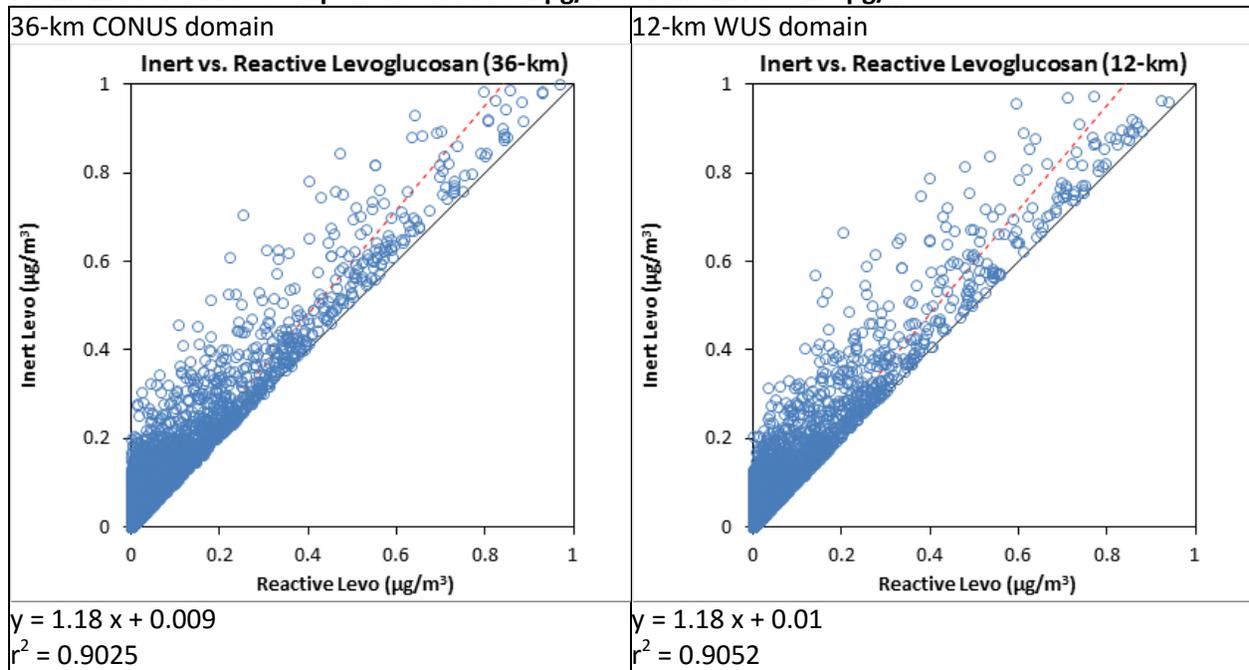
For higher LEVO concentrations greater or equal to 1.0 μg/m^3 there are no occurrences of LEVO being 2x greater than LVGC. As the LEVO concentrations get smaller there are more occurrences of the LEVO being over 2x greater than LVGC (i.e., 31%, 74% and 88%) and also higher frequency of it being 10x and 100x higher.

LEVO Range		Number	LEVO ≥ LVGC		
Min≥	<Max		>2x	>10x	>100x
0.001	250	34442	80.6%	48.8%	21.2%
0.01	250	12367	66.8%	33.0%	11.8%
1	250	240	0.0%	0.0%	0.0%
0.1	1	1571	30.6%	6.7%	1.3%
0.01	0.1	10556	73.7%	37.7%	13.6%
0.001	0.01	22075	88.3%	57.6%	26.4%

H3-1. LEVO vs. LGVC for inert LEVO > 0.001 μg/m^3

36-km CONUS domain	12-km WUS domain
y = 1.02 x + 0.01 r^2 = 0.9995	y = 1.04 x + 0.01 r^2 = 0.9990

H3-2. LEVO vs. LVGC comparisons for 0.001 µg/m³ < Inert LEVO < 1.0 µg/m³

36-km CONUS domain	12-km WUS domain
y = 1.18 x + 0.009 r² = 0.9025	y = 1.18 x + 0.01 r² = 0.9052

H3-3. LEVO vs. LVGC comparisons for 0.001 < Inert LEVO < 0.1 µg/m³

36-km CONUS domain	12-km WUS domain
y = 1.29 x + 0.007 r² = 0.5488	y = 1.32 x + 0.007 r² = 0.5356