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Modeling the formation of traditional and non-traditional secondary organic aerosols from in-use, on-road gasoline and diesel vehicles exhaust

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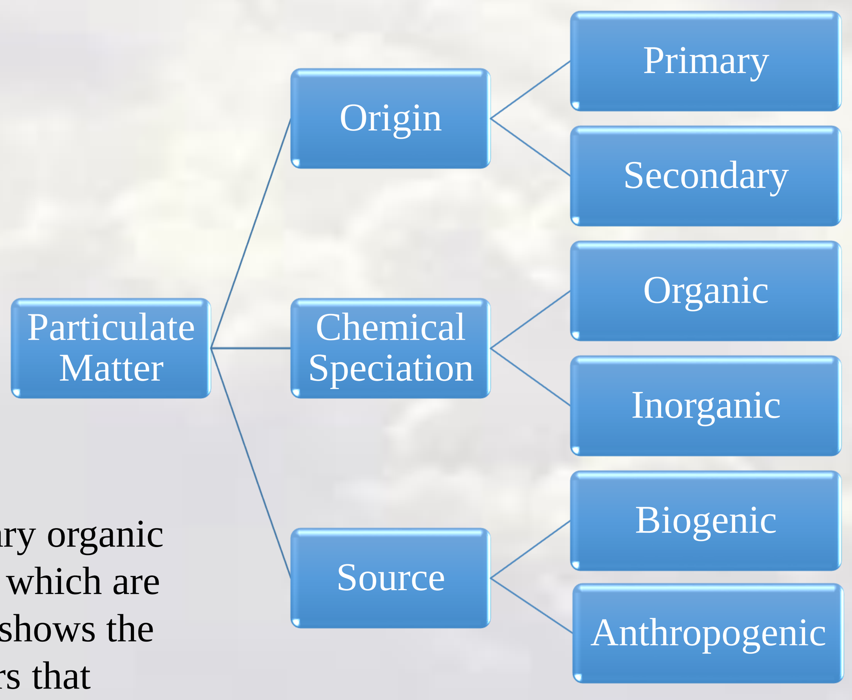
Introduction



Focus of this study is on modeling secondary organic aerosols (SOA) with anthropogenic source which are formed from vehicle exhaust. Below table shows the classification of different organic precursors that participate in SOA formation.

C^* range	Name
$1 \leq C^* \leq 10^2\ \mu g\ m^{-3}$	SVOCs
$10^3 \leq C^* \leq 10^6\ \mu g\ m^{-3}$	IVOCs
$C^* > 10^6\ \mu g\ m^{-3}$	VOCs

A considerable portion of unexplained SOA comes from the oxidation of unspeciated lower volatility organic compounds (i.e., SVOCs and IVOCs) which are usually missed from emission inventories. These are known as non-traditional SOA precursors.

Shortcomings of the existing models for NT-SOA: 1) They use the same parameterization for all types of emission sources (fossil fuel and biomass burning). 2) They assume that each oxidation step reduces the volatility of the precursors by one or two orders of magnitude, which is less than the observed reduction for the addition of common functional groups . 3) IVOC emissions are usually not measured directly, and they are estimated by scaling POA emissions.

The numerical model proposed by Jathar et al. (2012) solves the above shortcomings. We applied that model to vehicle exhaust and instead of assigning surrogate compounds, we calculated the source-specific mass yields for non-traditional SOA precursors directly from the experimental data.

Methodology

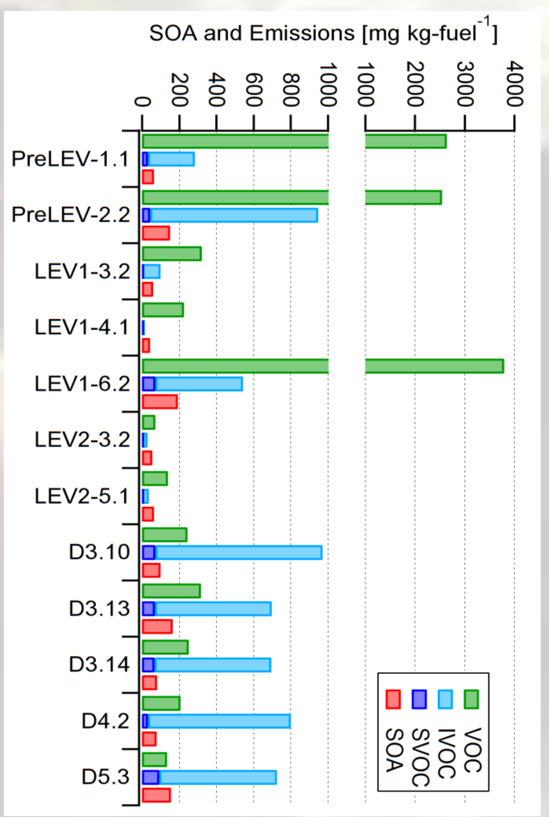
Mathematical formulation:

$$\frac{d[X_j]}{dt} = -k_{\mathrm{ox},X_j}[\mathrm{Ox}][X_j]$$

$$\frac{d[M_{i|g+p}]}{dt} = \underbrace{\sum_j \alpha_{i,j} k_{\mathrm{ox},X_j}[\mathrm{Ox}][X_j]}_{\text{first-generation products}} + \underbrace{\underbrace{\sum_k^N \beta_{i,k} k_{\mathrm{ox},M_k}[\mathrm{Ox}][M_{k|g}]}_{\text{production}} - \underbrace{k_{\mathrm{ox},M_i}[\mathrm{Ox}][\mathrm{M}_{i|g}]}_{\text{loss}}}_{\text{multi-generation oxidation}}$$

Gas/ particle partitioning ➡ $C_{OA} = \sum_{i=1}^{N} \zeta_i \times M_i|_{g+p} \qquad \zeta_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$

In order to interpret smog chamber data, above equations are used in a box model that consists of two modules: a T-SOA and NT-SOA module. The T-SOA module uses the standard VBS formulation. In the NT-SOA module, first, the amount of NT-SOA formed is calculated by subtracting predicted T-SOA from the total measured SOA in smog chamber. Then, the NT-SOA mass yield ($\alpha_{i,j}$) in the second equation is determined from fitting the NT-SOA data.



Emission factors for VOCs and S/IVOCs and measured SOA formed after 3 hours of radiation.

List of emission measurement and smog chamber experiments used.

No.	Vehicle ID	Model Year	Vehicle Class	Driving Cycle	Ref. for Emission Data	Ref. for SOA Data
1	PreLEV-1.1	1987	PC[1]	Cold UC	May et al. (2013a, 2014) Zhao et al. (2016)	Gordon et al. (2014a)
2	PreLEV-2.2	1988	PC	Cold UC		
3	LEV1-3.2	1998	PC	Cold UC		
4	LEV1-4.1	1999	PC	Cold UC		
5	LEV1-6.2	2003	PC	Cold UC		
6	LEV2-3.2	2008	PC	Cold UC		
7	LEV2-5.1	2011	PC	Cold UC		
8	D3.10	2006	HDDV[2]	2xUDDS	May et al. (2013b, 2014) Zhao et al. (2015)	Gordon et al. (2014b)
9	D3.13	2006	HDDV	2xUDDS		
10	D3.14	2006	HDDV	2xUDDS		
11	D4.2	2005	MDDV[3]	Cold UC		
12	D5.3	2001	MDDV	Cold UC		

For each vehicle, the best fit yield matrix tries to explain the arithmetic mean between lower and upper limits of wall-loss corrected OA.

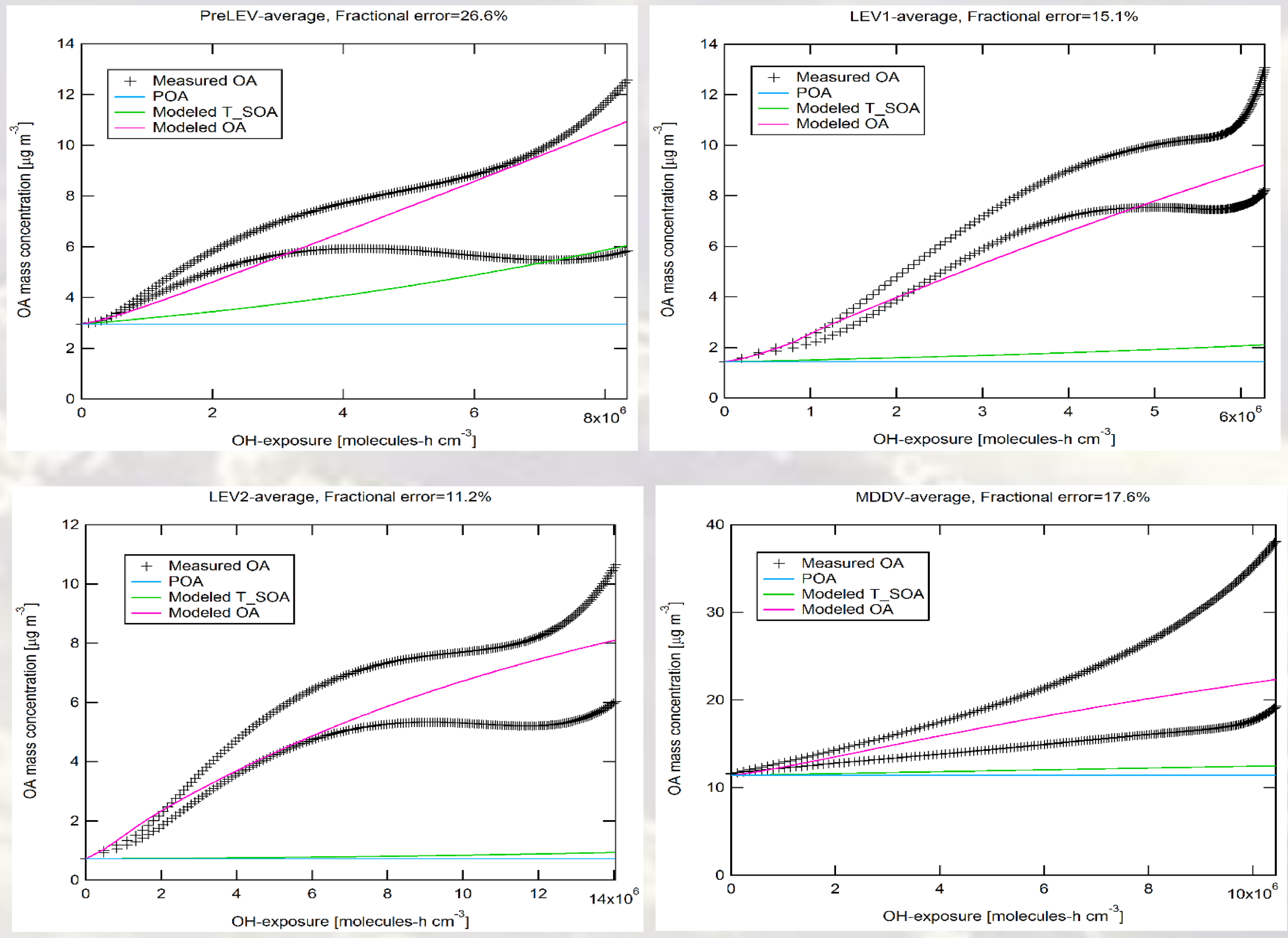
$$\begin{array}{cc}
 & \text{Precursors} \\
 & \begin{array}{cccccccc} C^*=10^0 & C^*=10^1 & C^*=10^2 & C^*=10^3 & C^*=10^4 & C^*=10^5 & C^*=10^6 & C^*=10^7 \end{array} \\
\alpha_{i,j} = & \left[\begin{array}{cccccccc}
y_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
y_2 & y_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
y_3 & y_2 & y_1 & 0 & 0 & 0 & 0 & 0 \\
y_4 & y_3 & y_2 & y_1 & 0 & 0 & 0 & 0 \\
0 & y_4 & y_3 & y_2 & y_1 & 0 & 0 & 0 \\
0 & 0 & y_4 & y_3 & y_2 & y_1 & 0 & 0 \\
0 & 0 & 0 & y_4 & y_3 & y_2 & y_1 & 0 \\
0 & 0 & 0 & 0 & y_4 & y_3 & y_2 & y_1 \\
0 & 0 & 0 & 0 & 0 & y_4 & y_3 & y_2 \\
0 & 0 & 0 & 0 & 0 & 0 & y_4 & y_3 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & y_4
\end{array}\right]
\begin{array}{c} C^*=10^{-6} \\ C^*=10^{-5} \\ C^*=10^{-4} \\ C^*=10^{-3} \\ C^*=10^{-2} \\ C^*=10^{-1} \\ C^*=10^{0} \\ C^*=10^{1} \\ C^*=10^{2} \\ C^*=10^{3} \\ C^*=10^{4} \end{array} \ \text{Products}
\end{array}$$

Results

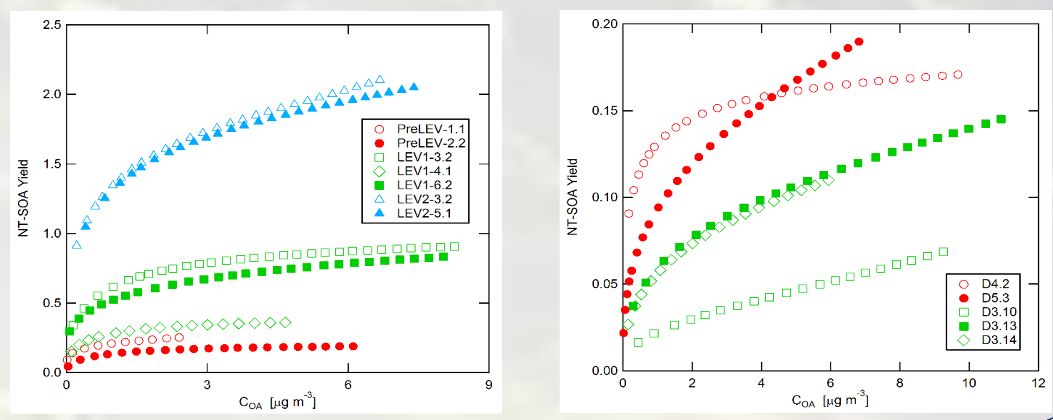
Average VBS mass yield for S/IVOCs for different types and classes of vehicles studies here

Vehicle Type	Vehicle Class	y_1	y_2	y_3	y_4
Gasoline	PreLEV	0.15	0.06	0.10	0.25
	LEV1	0.39	0.34	0.09	0.24
	LEV2	0.98	0.96	0.74	0.73
Diesel	Heavy Duty	0.00	0.00	0.00	0.36
	Medium Duty	0.07	0.01	0.01	0.32

Above table lists the average mass yields for each vehicle type and class. Application of these mass yields to hypothetical representative vehicle in each category, constructed based on average emission, oxidation, and SOA production data of the individual vehicles, is illustrated in figures below.



Effective NT-SOA Yield= $\frac{\text{NT-SOA formed}}{\text{S/IVOC reacted}}$



Conclusion

- ✓ We implemented a Hybrid model, to predict SOA formation from gasoline and diesel exhaust.
- ✓ In all cases, traditional SOA alone was not able to explain the total amount of SOA formed but adding non-traditional precursors was able to enhance the model predictions.
- ✓ Effective NT-SOA yields were calculated for each experiment, and they were comparable to published yields for individual speciated IVOCs.
- ✓ For newer, supposedly lower emitting vehicles, NT-SOA yields were higher than one, denoting that the exhaust from these vehicles are more efficient in producing SOA. This result highlights the importance of NO concentration in the exhaust. Decrease of the atmospheric NO_x level as a result of tightening emission standards, will counteract the effectiveness of these standards in reducing SOA formation in urban areas.
- ✓ For different classes of vehicles average NT-SOA parameters are provided. They are compatible with the VBS framework, and can be used in any box modeling of SOA production from on-road vehicles.
- ✓ A sensitivity assessment showed that aromatic VOCs and IVOCs have the highest impact on model predictions and need to be measured directly. However, SVOCs have lower influence, and their concentration can be approximated based on volatility distribution of POA.
- ✓ Results of the current study can be implemented in evaluating the effectiveness of emission reduction strategies in abatement of SOA formation from vehicles.

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