

Supporting Information for:

Primary and secondary sources of gas-phase organic acids from diesel exhaust

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This Supporting Information includes 9 pages, 6 figures, and 1 table.

SOA sources and contribution to measured SOA concentrations

To gain insight on the extent to which the acetate-CIMS observations represent the full suite of gas-phase organics in these experiments, we use the SIMPOL.1⁴⁹ model to predict the saturation mass concentration (C^*) of the gas-phase species identified by acetate-CIMS.⁵⁰ This model parameterizes the vapor pressure of a pure compound as a linear combination of the contributions from its functional groups, which are inferred from the number of carbon, hydrogen and oxygen atoms present.⁵⁰ Assuming quasi-ideal partitioning, we calculate the corresponding vapor pressures and estimate the mass concentration corresponding to the volatility distributions of these gas-phase species following assumptions outlined in Chhabra et al.,⁵⁰ an assumed formic acid sensitivity for all compounds other than the four organic acids described herein, and the measured organic aerosol concentrations. The calibration data from this and previous⁵¹ acetate-CIMS studies indicates that formic acid sensitivity is at or near a maximum value for this reagent ion; thus our reported mass concentrations from the total measured organic gas-phase species constitute a lower bound estimate.

Formic, butyric, propanoic, and methacrylic acids have high vapor pressures ($\log_{10}C^* = 6.8 - 8.1 \mu\text{g m}^{-3}$) are thus negligible ($< 0.5\%$) contributors to SOA (Figure S1). Unsurprisingly, less volatile organic compounds account for the bulk of the SOA mass. No change in the total contribution to organic aerosol was observed as a function of oxidation, suggesting that these four small organic acids will be poor tracers of urban OA production – but as photochemical products, they may be more accurate indicators of gas-phase photochemistry in urban environments.

To estimate the contribution of other measured gas-phase organic species to the observed SOA, we again use the SIMPOL.1 model with the full suite of organic species detected as CHO

ions by acetate-CIMS. The acetate-CIMS captured a range of gas-phase species across volatility space that exhibited a signal-to-noise ratio greater than 3 (Figure S2), with more condensable species observed in the idle experiment than in the load experiment after approximately 0.2 days of equivalent OH aging, corresponding to the greater SOA production in the idle experiments. The total identified gas-phase CHO species would at most contribute 13 (± 8)%, 28 (± 14)%, 10 (± 5)%, and 15 (± 3)% to the total measured organic aerosol for biodiesel fuel at idle conditions, biodiesel fuel at load conditions, diesel fuel at idle conditions, and diesel fuel at load conditions, respectively. The observed gas-phase species for the load conditions explains more of the observed SOA than for the idle conditions (7-22% for load, 1-11% for idle; Figure S3), likely because precursor emissions are more oxidized with the more complete combustion, and that the acetate-CIMS detects the precursor population more completely. However, the O:C ratio of the primary emissions in the gas-phase detected by acetate-CIMS is slightly higher for the load than idle conditions, which suggests that either the organic acids detected by the instrument are no more oxidized in load than idle conditions – or that the uncertainties around the O:C values in the unoxidized experiments are larger than the observed discrepancies.

However, we emphasize that the gas-phase organic concentrations for all compounds other than the four small organic acids are lower bounds, and thus our ability to constrain SOA from the measured gas-phase CHO species will also be a lower bound. For both engine conditions, the contribution to total organic aerosol decreases as oxidation increases. That the acetate-CIMS only explains a small fraction of the measured organic aerosol suggests (i) incomplete measurement of gas-phase organic species, particularly the large, low-volatility hydrocarbons and aromatics with no oxygen-containing functionality likely present in the load conditions; (ii) inaccurate mass loadings from the estimated instrument sensitivities for uncalibrated ions; (iii)

inaccurate partitioning predictions by the SIMPOL model; and/or (iv) inaccurate assumption of the gas-particle system being in equilibrium. We further acknowledge that given the high organic aerosol concentrations in the OFR, even smaller fractions of the organic species will exist in the particle phases given typical ambient atmosphere conditions.

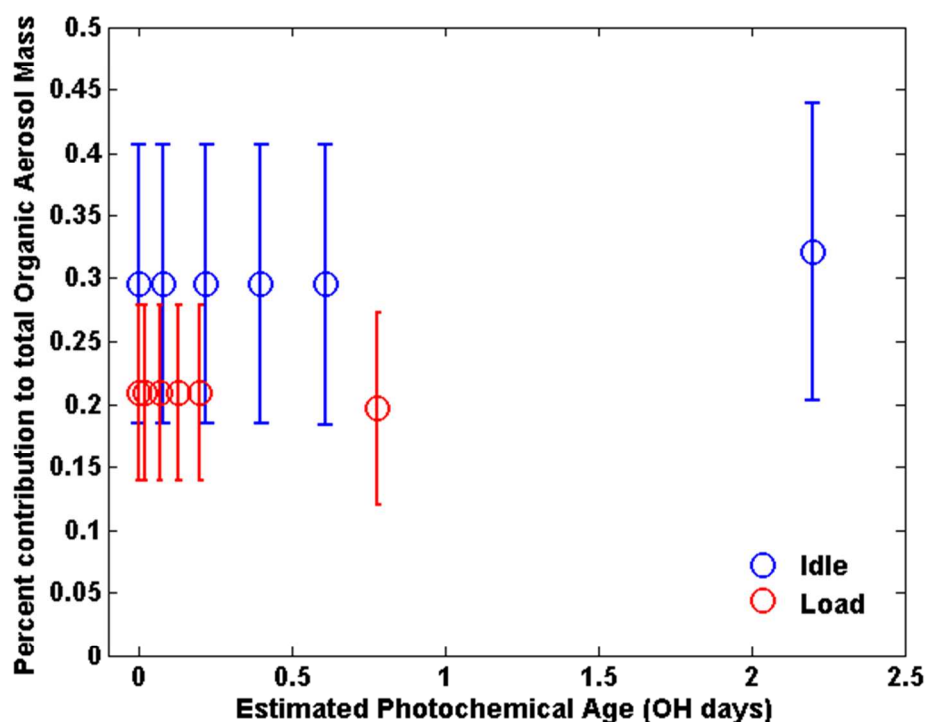
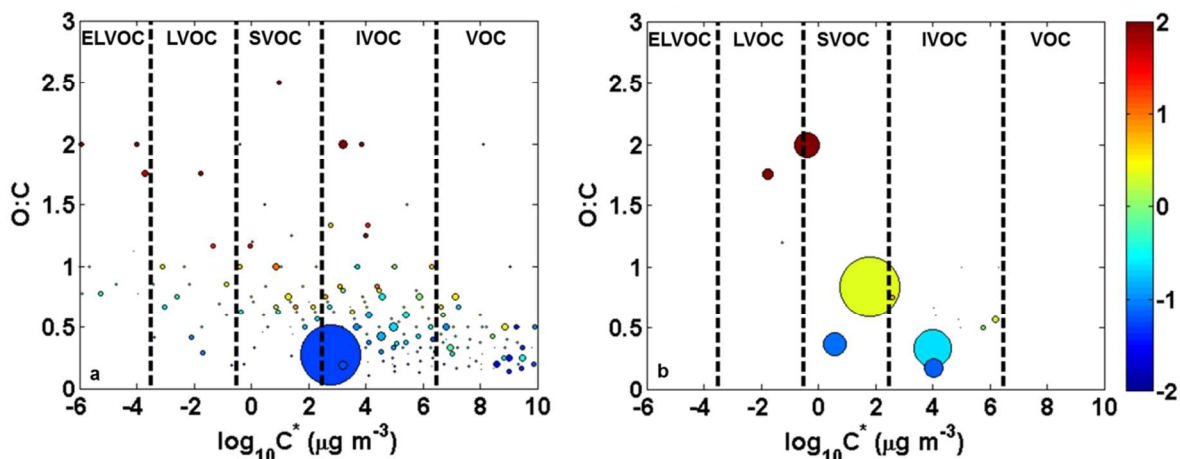


Figure S1. Percent contribution of the four organic acids to the measured organic aerosol concentrations as a function of oxidation. Differences in the total contribution between the two engine conditions are reflected in the lesser emissions of these four acids when an engine is run at load as opposed to idling.



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 58 **Figure S2.** Gas-phase O:C for each CHO-containing species detected as a separate ion signal by
 59 acetate-CIMS as a function of calculated C* values for a representative biodiesel experiment
 60 under idle (left) and 50% load (right) experiments after 0.2 days of equivalent OH aging. The
 61 size of each point corresponds to the signal enhancement (ratio of the average normalized ion
 62 signal at 0.2 days of aging to zero aging), and the color describes the calculated oxidation state of
 63 the identified molecule. All species included in this figure had a signal-to-noise ratio (mean
 64 signal relative to standard deviation) > 3. Dashed lines indicate volatility bins at a range of C*
 65 values.⁵⁵ Secondary organic aerosol mass concentrations were enhanced over primary values by
 66 3.9 (idle, left) and 3.1 (loaded, right) for these two experiments.

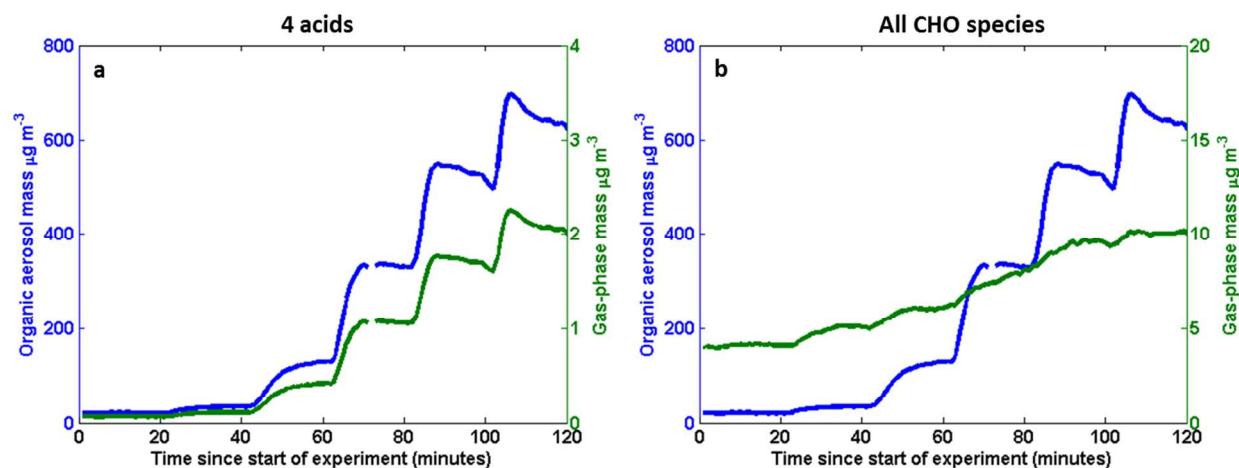


Figure S3. a) Estimated mass of the measured four small organic acids (formic, butyric, methacrylic, propanoic) in the particle phase (green) for a representative biodiesel experiment with the total organic acid concentration shown in blue. b) Estimated mass of all carbon-hydrogen-oxygen containing species in the particle phase (green) assuming formic acid sensitivity for a representative biodiesel idle experiment; total OA concentration is in blue. OH exposure was changed every 20 minutes; 0-20 minutes corresponds to zero OH exposure. 20-40, 40-60, 60-80, 80-100, and 100-120 minutes correspond to OH exposures of 0.1, 0.2, 0.4, 0.6, and 2.2 days of equivalent OH exposure, respectively.

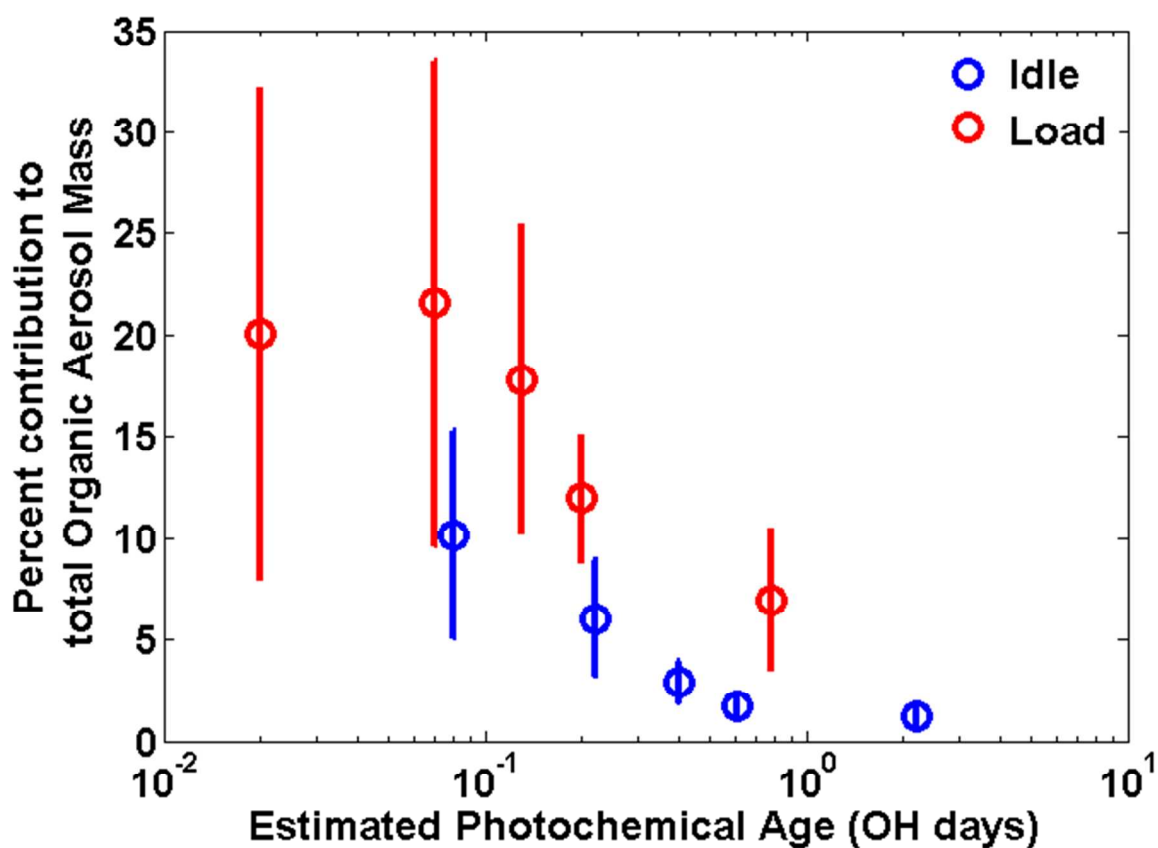
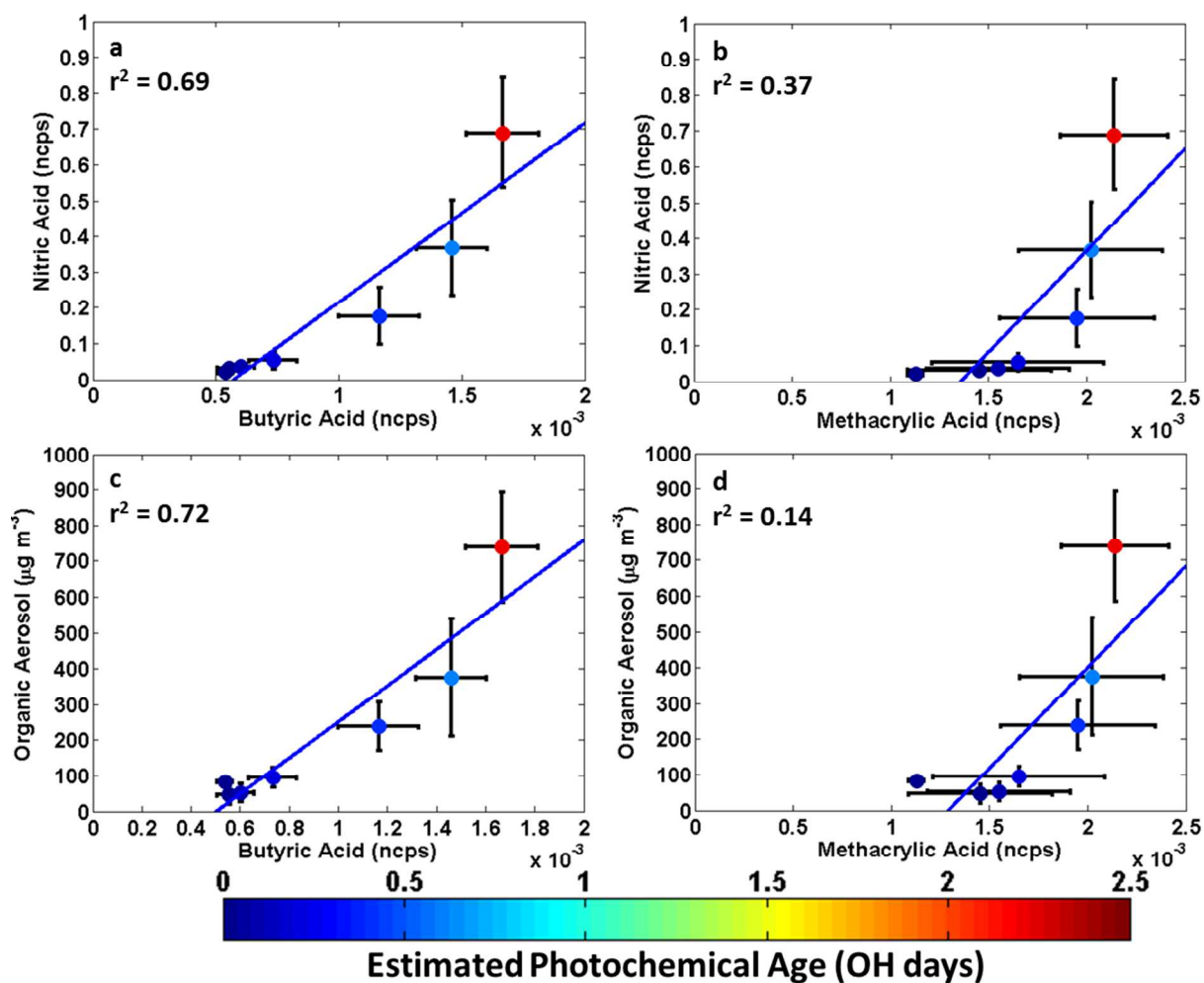


Figure S4. Average percent contribution of all gas-phase carbon-hydrogen-oxygen species measured by Acetate-CIMS and estimated by the SIMPOL.1 model to the total measured SOA as a function of oxidation from biodiesel and diesel idle experiments (blue circles) and biodiesel and diesel load experiments (red circles). Error bars represent the standard deviation from the mean.

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93 **Figure S5.** Correlations of butyric acid with nitric acid (a), methacrylic acid with nitric acid (b),
 94 butyric acid with organic aerosol (c), and methacrylic acid with organic aerosol (d). Colorbar is
 95 the estimated photochemical age. Points represent averages and standard deviations of the
 96 normalized counts per second for all experiments.

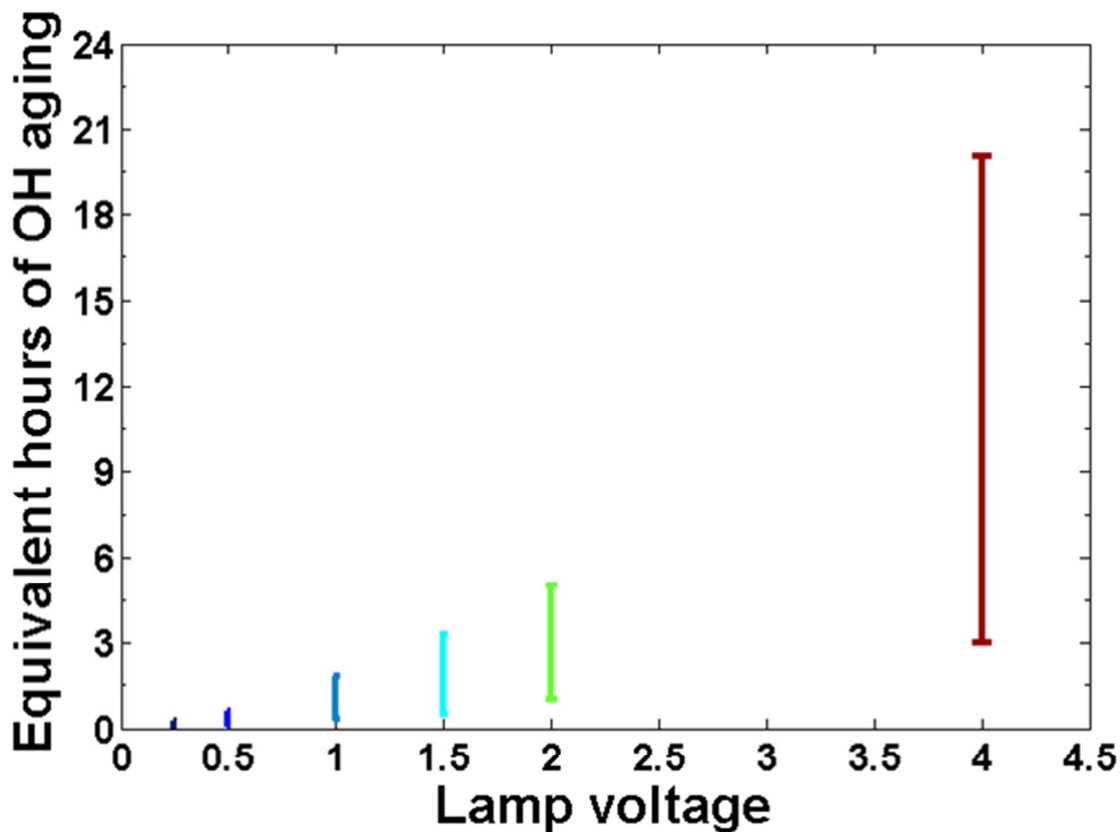


Figure S6. Calculated ranges of OH exposure (hours) as a function of UV lamp voltage.

Engine Type	Fuel Type	Concentration (ppb)			
		Formic Acid	Butyric Acid	Propanoic Acid	Methacrylic Acid
Idle	Biodiesel	3.5-20	0.2-1.7	0.3-1.8	0.6-1.1
Idle	Diesel	6.3-30	0.6-2	0.6-2.7	0.7-1.2
Load	Biodiesel	2.2-10.6	0.2-1.3	0.3-1.2	0.4-1.2
Load	Diesel	5.2-13.1	0.6-1.3	0.6-1.5	0.6-1.1

Table S1. Concentration ranges for both primary emissions and secondary production of formic, butyric, propanoic, and methacrylic acids.