Supplementary Data

n-Aldehydes Photo-oxidation with OH radical at High NO$_x$

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Species oxidized	Initial Concentration in the Smog Chamber	Initial NO$_2$:NO (ppb/ppb)	Initial VOC$_0$/NO$_x$ (ppbC/ppb)	Initial OH concentration (molecule cm^{-3})	SAR Rate Constant (cm^3 molecule^{-} s^{-})
***n*-Tridecanal 021609**	4 ppb	~300:1400	0.03	~1×10^7	n/a
***n*-Tridecanal 031009**	18 ppb	~300:1400	0.13	(average) ~7×10^7	3.9×10^{-11}
***n*-Tridecanal 041709**	250 ppb	~300:1400	2	~1×10^7	3.9×10^{-11}
***n*-Tridecanal 082109**	382 ppb	~4000:2000	0.8	~3×10^6	3.9×10^{-11}
***n*-Tridecanal 030809**	25 ppb	~4000:1000	0.07	~1×10^7	3.9×10^{-11}
***n*-Dodecane Presto et al., 2010**	19 to 58 ppb	-	0.05-0.4	-	n/a
***n*-Pentadecane Presto et al., 2010**	2 to 9 ppb	-	0.03-0.1	-	n/a
***n*-Undecanal 060909**	187 ppb	~900:500	1.3	~4×10^7	3.6×10^{-11}
***n*-Octanal 042109**	350 ppb	~500:180	4	~2×10^7	3.2×10^{-11}

***n*-Pentanal 050709**	189 ppb	~1200:300	0.8	~5×10^7	2.8×10^{-11}

Table A. Most of the information presented in this table is for initial conditions. The NO_2:NO kept relatively constant for the first 30 minutes of the oxidation. The Structure Activity (SAR) rate constants were calculated from Kwok et al., 1995 and used for "inferred *n*-aldehyde" concentrations.

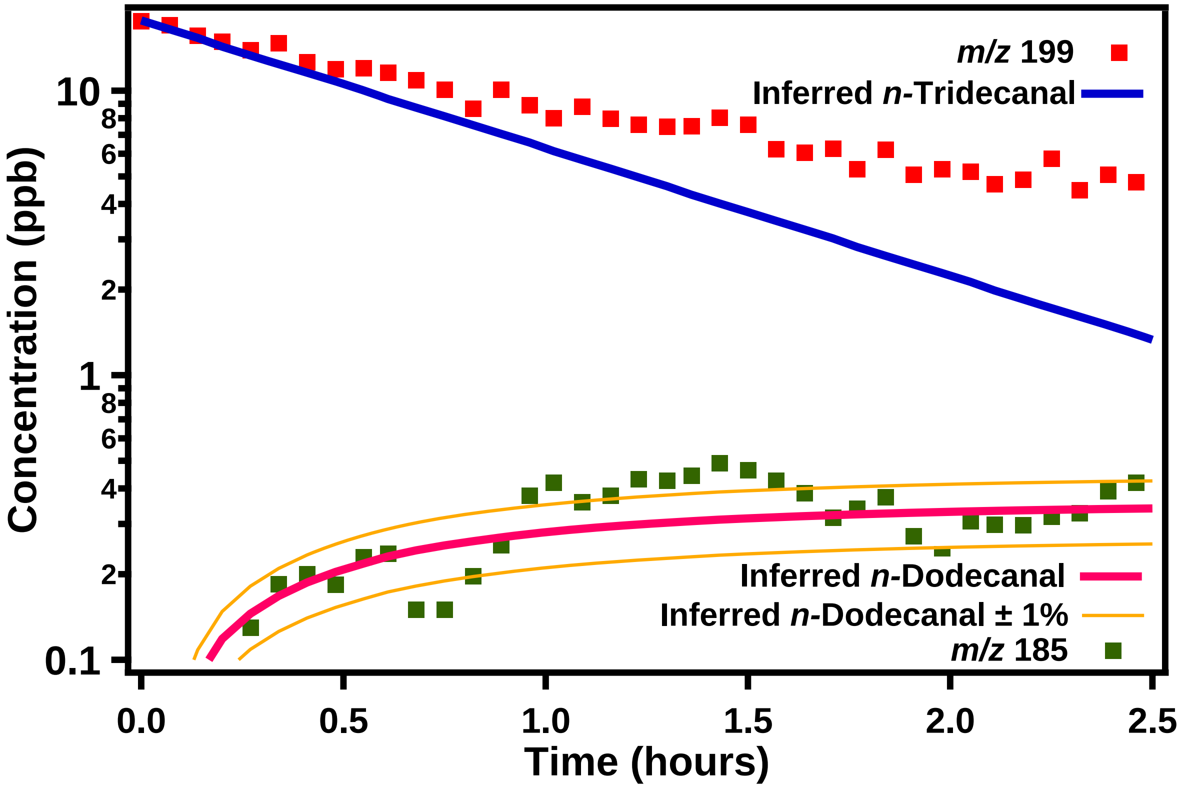

Figure A (*n*-Tridecanal 031009). After reacting *n*-tridecanal with OH radical at high NO_x conditions, it was encountered that the *n*-dodecanal molar yield formation is 4±1%; however, this yield is dependent on NO_2:NO. The Inferred *n*-tridecanal is obtained by using a SAR rate constant, and an average OH concentration obtained from methanol (tracer). The discrepancies between *m/z* 199 and inferred *n*-tridecanal have to do with the formation of other species that have the same molecular weight as *n*-tridecanal (refer to Figure 5 in the main manuscript). The inferred *n*-dodecanal was calculated as 4% of the consumed inferred *n*-tridecanal minus any consumption due to OH radical attack.

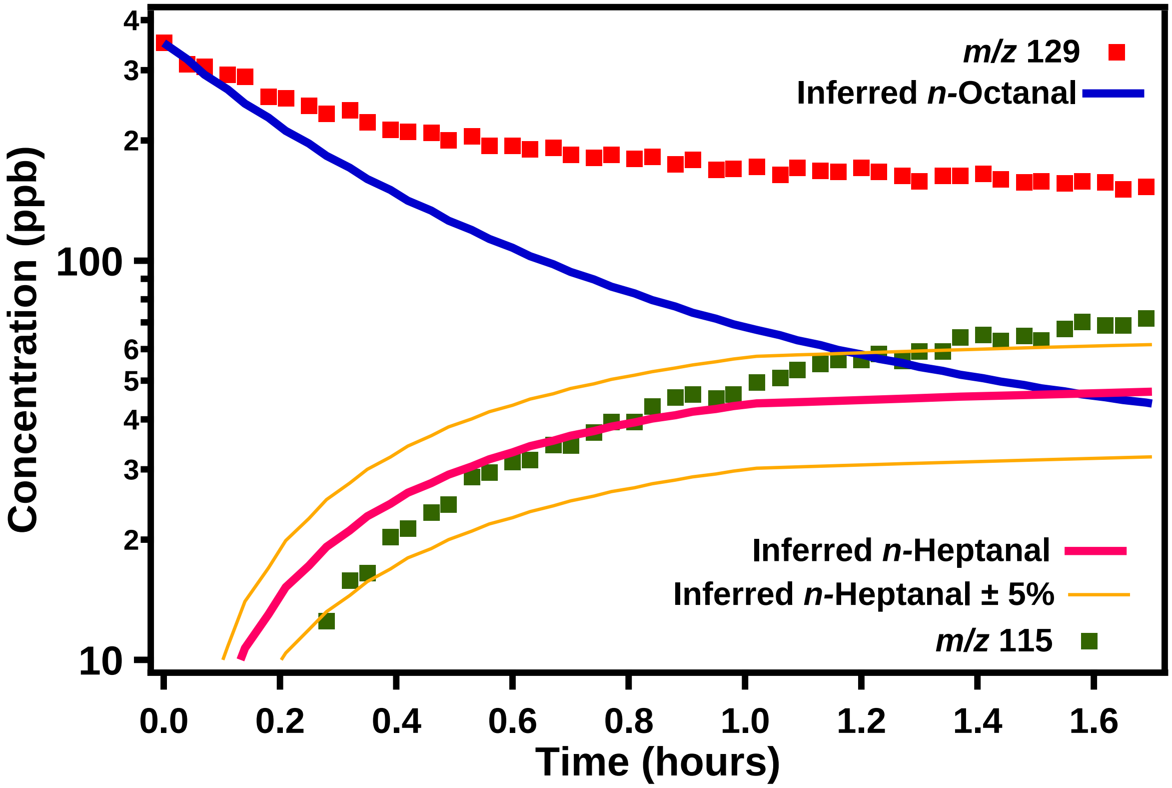

Figure B (*n*-Octanal 042109). The molar yield formation of *n*-heptanal from the OH oxidation (at high NO_x) of *n*-octanal was determined to be 16±5%. However, this yield is dependent on NO_2:NO. The inferred *n*-octanal is calculated by using a SAR rate constant (refer to Table A, Supplementary Data), and OH radical concentration obtained from the consumption of methanol. The discrepancies between *m/z* 129 and the inferred *n*-octanal are due to the formation of other species with the same molecular weight as *n*-octanal (refer to Figure 5 in the main manuscript). The inferred *n*-heptanal was calculated as 16% of the consumed inferred *n*-octanal minus any consumption due to OH radical attack.

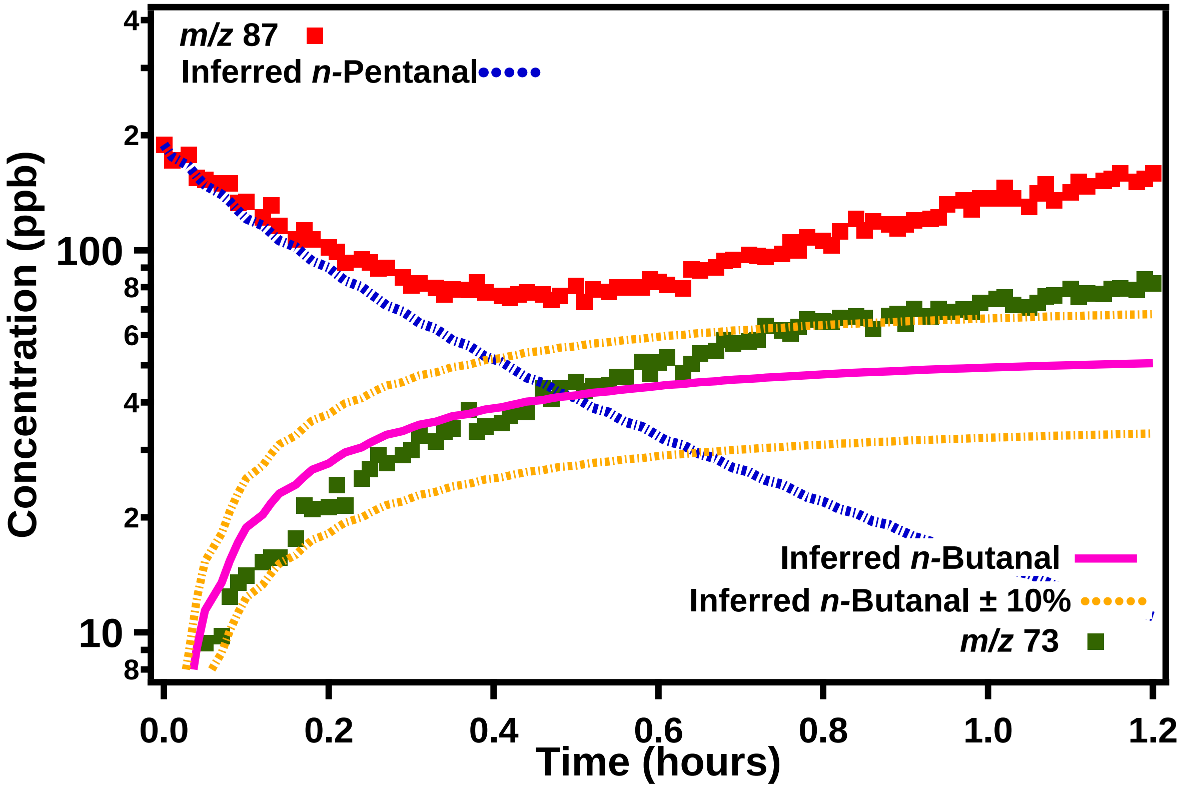

Figure C (*n*-Pentanal 050709). It was found that the *n*-butanal molar yield formation is 29±10%; however, this yield is dependent on ratio of NO_2:NO. The Inferred *n*-pentanal is obtained by using a SAR rate constant, and an OH concentration obtained from methanol (tracer). The differences between *m/z* 87 and inferred *n*-pentanal might have to do with the formation of other species that have the same molecular weight as *n*-pentanal (refer to Figure 5 in the main manuscript). However, this other(s) species may have a different sensitivity to the PTR-MS. The inferred *n*-butanal was calculated as 29% of the consumed inferred *n*-pentanal minus any consumption due to OH radical attack.

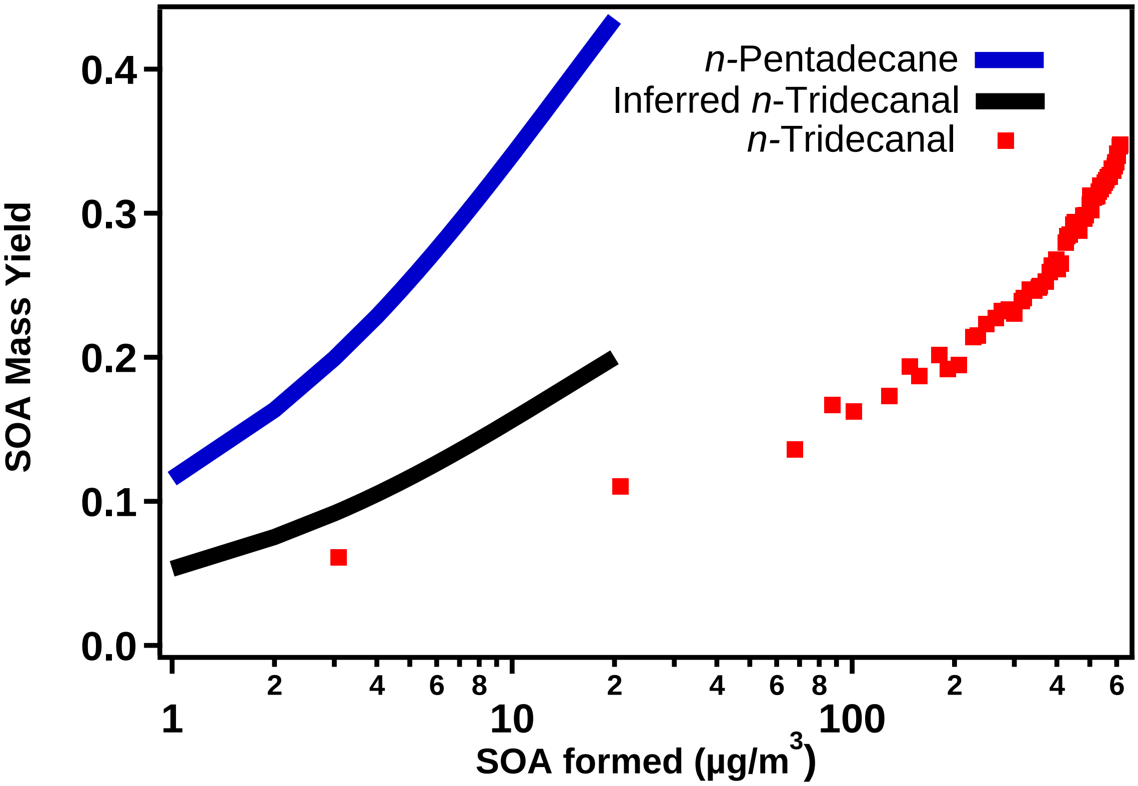

Figure D. *n*-Pentadecane yields are obtained from Presto et al., 2010, and the *n*-tridecanal yields come from this work, specifically experiment 041709 (refer to Table A). According to SAR, the OH radical attacks 54% of the time the aldehydic hydrogen of *n*-tridecanal, and 46% of the time the backbone. When the backbone is attacked, higher vapor pressures species are formed; that's not the case when the aldehydic hydrogen is attacked. *n*-Pentadecane's backbone is attacked always, as a result, *n*-tridecanal SOA yields should be about 46% of *n*-pentadecane's since both species have similar vapor pressures. The inferred *n*-tridecanal yields (black curve) is 46% of *n*-pentadecane's yields. A good match between inferred and experimental *n*-tridecanal yields is not encountered because attacking the aldehydic hydrogen (*n*-tridecanal) promotes the formation of lower vapor pressure species.

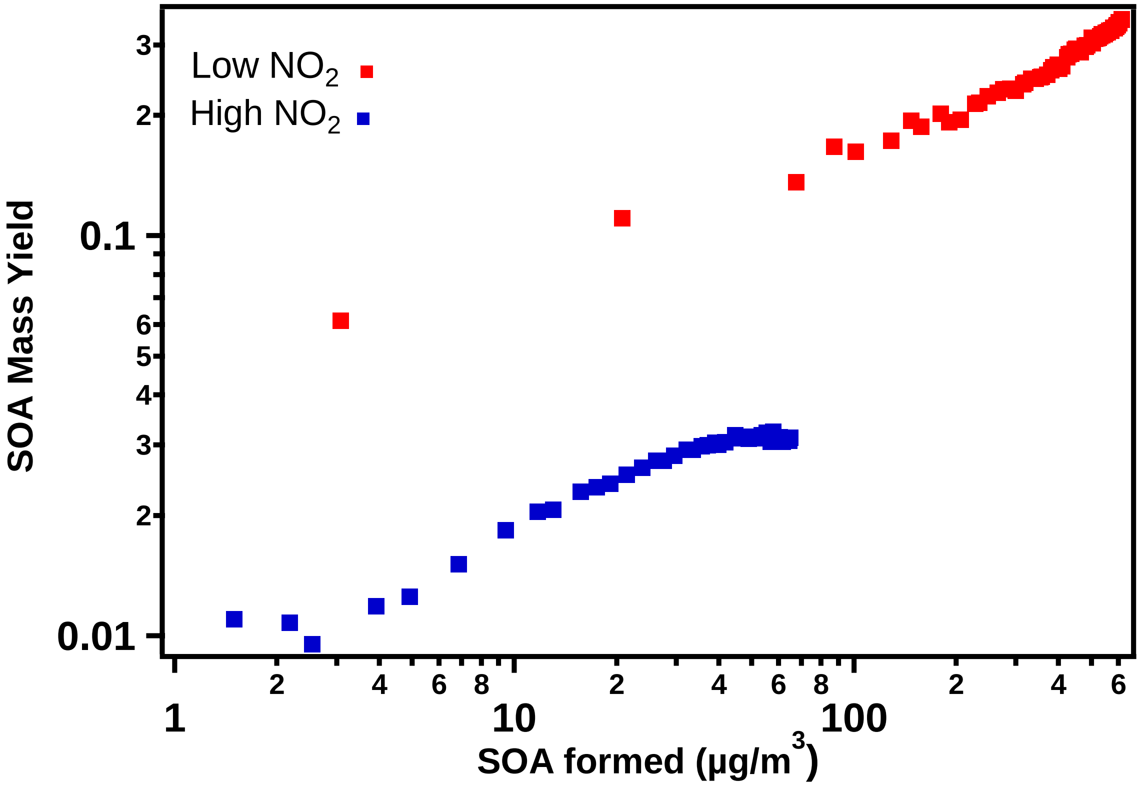

Figure E. Low (041709) versus high (082109) NO_2 *n*-tridecanal reaction with OH radical. The differences in SOA mass yields between Low and High NO_2 are considerable. The difference in VOC_0/NO_x (ppbC/ppb) between experiment 041709 and 082109 are not dramatic; however, their NO_2:NO are. When there is significantly more NO_2 than NO available (experiment 082109), the formation of PAN is dominant (refer to Figure 1, main manuscript). Forming PAN thus has an effect on SOA formation. Presumably PAN formation limits the creation of carboxylic acids by protecting Peroxyacyl Radical.

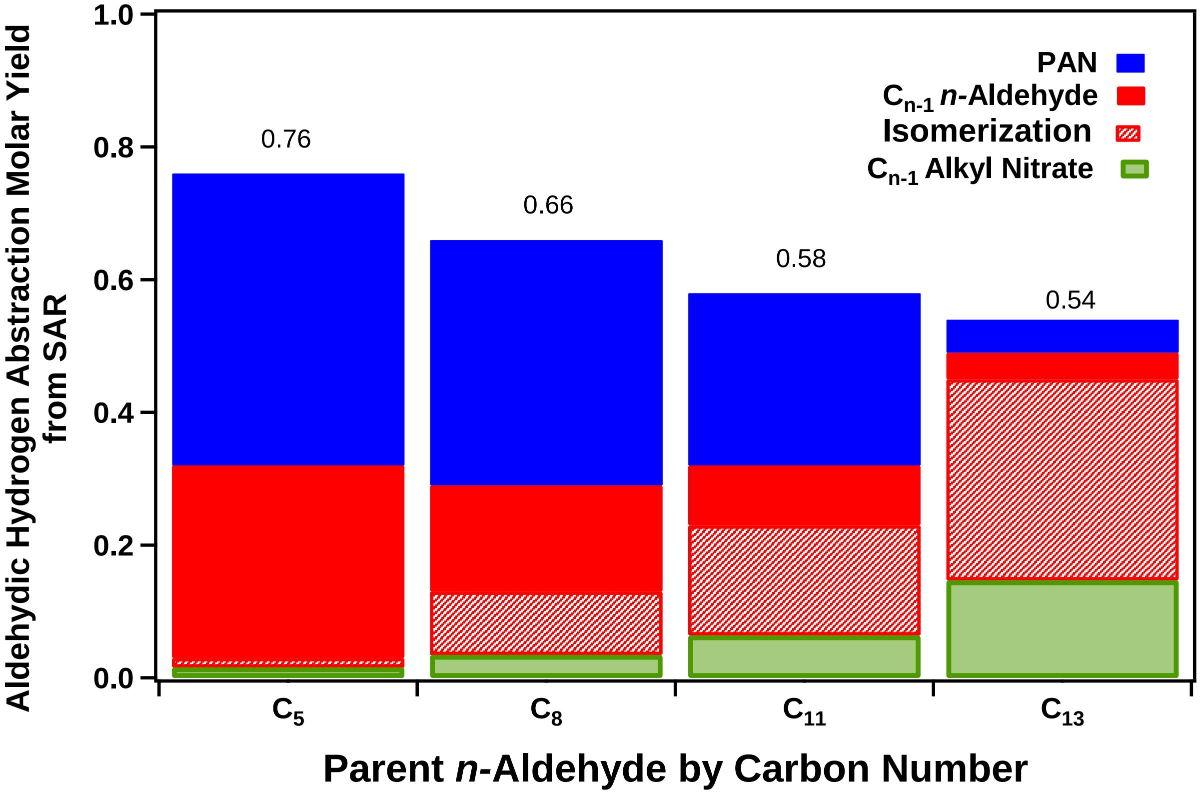

Figure F. (*n*-Pentanal 050709, *n*-Octanal 042109, *n*-Undecanal 060609, *n*-Tridecanal 031009) The height of each column is the SAR aldehydic hydrogen abstraction molar yield. After the aldehydic hydrogen abstraction, branching towards either PAN or C_{n-1} Peroxyl Radical occurs, this last one branches into a C_{n-1} Alkyl Nitrate and a C_{n-1} Alkoxy Radical. Then the Alkoxy radical branches between the C_{n-1} aldehyde and an isomerization structure. These relative yields are obtained from SAR predicted molar yields of aldehydic hydrogen abstraction induced by OH, kinetic constants for PAR branching, Alkyl Nitrate formation from Arey et al., 2001 and observed C_{n-1} aldehyde molar yields. This branching is only valid for the beginning of the experiment. Branching towards PAN is dependent on NO_2 concentration (blue arrows, Figure 1), which affects abundance of the C_{n-1} Alkyl Nitrate, *n*-aldehyde and the isomeritazion structure, but not their branching (red and green arrows, Figure1).

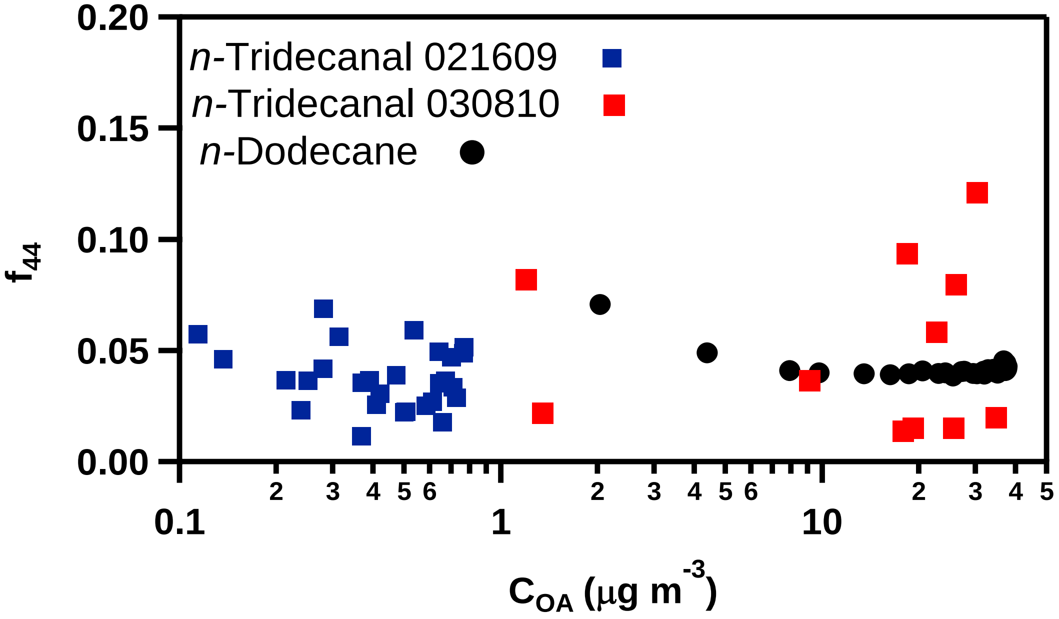

Figure G. *n*-Dodecane (Presto et al., 2010) versus *n*-tridecanal (021709 and 030810). The f_{44} is the ratio of *m/z* 44 to total organics detected by an AMS in the aerosol phase. This figure shows how oxidized both *n*-dodecane and *n*-tridecanal organic aerosols are. Since both molecules form a C_{12} alkoxy radical as a significant intermediate, it is expected to find similar level of oxidation in their organic aerosols.

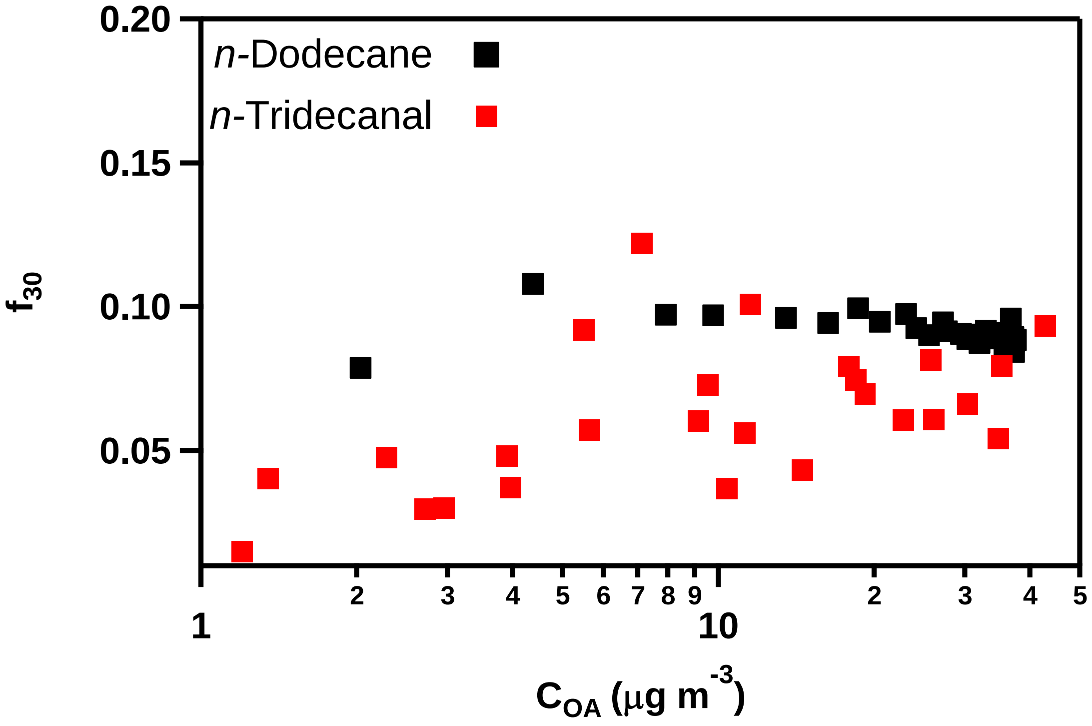

Figure H. *n*-Dodecane (Presto et al., 2010) versus *n*-tridecanal (021709). The presence of organic nitrates in the organic aerosol phase is significantly different for *n*-tridecanal versus *n*-dodecane. Most of the OH first generation reaction with *n*-tridecanal occurs at the aldehydic hydrogen, which does not form organic nitrates other than PAN. The presence of PAN is small due to a low NO_2:NO for experiment 021709.