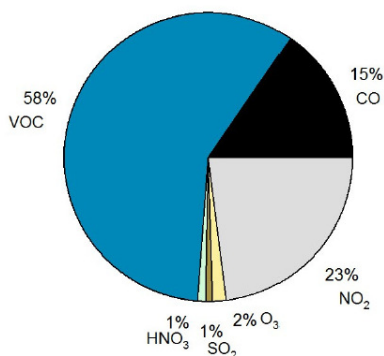
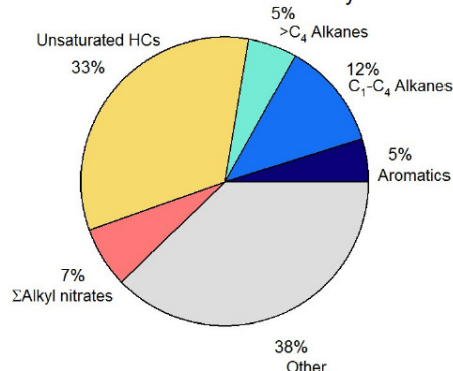


Figure S1. Relative contribution to total OH reactivity (a), of observed VOCs to calculated OH reactivity (b) and alkyl nitrate production (c,d) in the afternoon (12pm – 6pm) demonstrate that despite a small contribution to OH reactivity, high-branching ratio species contribute significantly to ANs production, which will act to remove NO_x and HO_x, suppressing O₃ formation in this system. Organic nitrate production from aromatic VOCs is highly uncertain, and the result is thus bracketed by lower and upper extremes for aromatic branching ratios (see text).

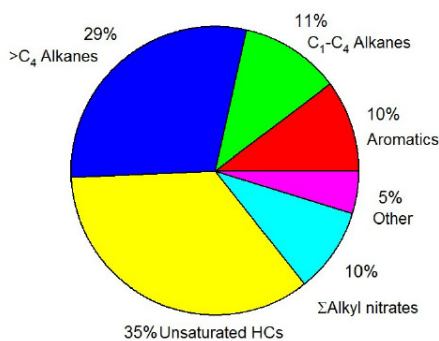
a) Contributions to total OH reactivity



b) VOC contributions to OH reactivity



c) VOC contributions to AN production (low aromatic branching ratio)



d) VOC contributions to AN production (high aromatic branching ratio)

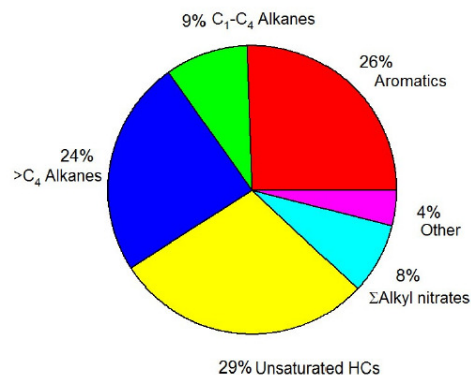


Table S1. Speciated ANs precursors observed and estimated for Tecamac, MX during MILAGRO with average afternoon concentration (ppb), branching ratio, rate constant (s^{-1}), and relative contributions to ANs and O_3 production (see text).

Species	Mixing Ratio (ppb)	α	k_{OH+VOC} ($molec^{-1} cm^3 s^{-1}$)	P_{ANs} (s^{-1})	P_{O_3} (s^{-1})
Methane	1903	0.005	$6.08E-15^{(1)}$	0.0011	0.42
Ethane	2.2	0.014	$2.34E-13^{(1)}$	0.00019	0.026
Ethene	1.4	0.0086	$8.61E-12^{(1)}$	0.0026	0.61
Ethyne	2.1	0.0086	$8.07E-13^{(2)}$	0.00037	0.084
Propane	5.7	0.036	$1.07E-12^{(1)}$	0.0055	0.29
Propene	0.42	0.015	$2.66E-11^{(3)}$	0.0050	0.65
i-butane	0.77	0.02	$2.31E-12^{(4)}$	0.00088	0.086
n-Butane	2.2	0.077	$2.51E-12^{(2)}$	0.011	0.26
n-Pentane	0.46	0.129	$3.91E-12^{(3)}$	0.0042	0.057
i-Pentane	0.78	0.058	$3.90E-12^{(3)}$	0.0036	0.12
n-Hexane	0.25	0.223	$5.61E-12^{(5)}$	0.0065	0.045
n-Heptane	0.073	0.28	$7.15E-12^{(2)}$	0.0029	0.015
Cis-2-butene	0.020	0.037	$5.70E-11^{(4)}$	0.00067	0.035
Cis-2-pentene	0.0097	0.05	$6.50E-11^{(2)}$	0.00057	0.021
Methanol	3.8	0	$9.04E-13^{(1)}$	0	0.14
1-butene	0.040	0.025	$3.17E-11^{(3)}$	0.00056	0.043

1-pentene	0.023	0.05	3.18E-11 ⁽³⁾	0.00068	0.026
2-methyl-1-butene	0.022	0.03	6.10E-11 ⁽⁶⁾	0.00083	0.054
3-methyl-1-butene	0.0055	0.025	3.22E-11 ⁽⁶⁾	8.25E-05	0.0064
Trans-2-butene	0.019	0.03	6.48E-11 ⁽²⁾	0.00080	0.052
Trans-2-pentene	0.021	0.05	6.70E-11 ⁽²⁾	0.0012	0.046
2-methyl-2-butene	0.024	0.05	8.79E-11 ⁽⁶⁾	0.0068	0.26
2-methyl-propene	0.14	0.02	5.20E-11 ^{**}	0.0027	0.27
Acetaldehyde	1.88	0	1.39E-11 ⁽¹⁾	0	1.17
Formaldehyde	4.56	0	8.39E-12 ⁽¹⁾	0	0.049
Acetone	3.18	0	1.42E-13 ⁽⁷⁾	0	0.022
CO	270	0	2.19E-13 ⁽¹⁾	0	1.95
Total Alkyl nitrates	0.66	0.05	1.60E-11 ⁽²⁾	0.016	0.60
Benzene	0.98	0.05	1.27E-12 ⁽⁴⁾	0.0015	0.057
Toluene	0.90	0.08	6.21E-12 ⁽⁴⁾	0.010	0.24
C8-benzenes	0.39	0.08	7.50E-12 ⁽⁸⁾	0.003792	0.087
C9-benzenes	0.10	0.08	7.50E-12 ⁽⁸⁾	0.00083	0.019
C10-benzenes	0.039	0.08	7.50E-12 ⁽⁸⁾	0.00031	0.0072
C11-benzenes	0.013	0.08	7.50E-12 ⁽⁸⁾	1.13e-05	0.00026
Butadiene	0.016 [*]	0.07	6.73E-11 ⁽³⁾	0.0014	0.038
1-hexene	0.0057 [*]	0.07	3.70E-11 ⁽²⁾	0.00028	0.0074
Propyne	0.058 [*]	0.01	2.97E-12 ⁽⁹⁾	0.000033	0.0065
2,2-dimethylbutane	0.20 [*]	0.2	2.32E-12 ⁽²⁾	0.0017	0.014
Cyclopentane	0.05 [*]	0.1	5.08E-12 ⁽²⁾	0.00048	0.0086

2,3-dimethyl butane	0.17 [*]	0.14	2.32E-12 ⁽¹⁰⁾	0.00048	0.0058
2-methyl pentane	0.32 [*]	0.14	5.20E-12 ⁽⁵⁾	0.0045	0.055
3-methyl pentane	0.20 [*]	0.14	5.70E-12 ⁽¹¹⁾	0.0030	0.037
Methylcyclopentane	0.044 [*]	0.15	6.00E-12 ⁽¹⁰⁾	0.00075	0.0085
Cyclohexane	0.089 [*]	0.17	7.49E-12 ⁽³⁾	0.0021	0.021
2-methylhexane	0.18 [*]	0.15	7.00E-12 ⁽¹⁰⁾	0.0035	0.040
2,3-dimethylpentane	0.026 [*]	0.15	7.00E-12 ⁽¹⁰⁾	0.00051	0.0058
3-methylhexane	0.14 [*]	0.18	7.00E-12 ⁽¹⁰⁾	0.0033	0.031
i-octane	0.15 [*]	0.25	8.70E-12 ⁽¹⁰⁾	0.0062	0.037
Methylcyclohexane	0.019 [*]	0.17	1.04E-11 ⁽²⁾	0.00065	0.0063
2,5-dimethylhexane	0.016 [*]	0.19	9.00E-12 ⁽¹⁰⁾	0.00053	0.0045
2,4-dimethylhexane	0.069 [*]	0.19	9.00E-12 ⁽¹⁰⁾	0.0022	0.019
2,3,4-trimethylpentane	0.054 [*]	0.18	9.00E-12 ⁽¹⁰⁾	0.0017	0.015
N-octane	0.040 [*]	0.226	8.68E-12 ⁽²⁾	0.0015	0.010
Nonane	0.035 [*]	0.05	1.02E-11 ⁽²⁾	0.00034	0.013
n-decane	0.050 [*]	0.3	1.6E-11 ⁽²⁾	0.0033	0.015
2-methylheptane	0.026 [*]	0.25	9.00E-12 ⁽¹⁰⁾	0.0011	0.0065
1,2,4-trimethylcyclohexane	0.013 [*]	0.2	1.00E-11 ⁽¹⁰⁾	0.0005	0.004
MTBE	2.5 [*]	0.041	3.11E-12 ⁽¹²⁾	0.0060	0.28
Styrene	0.24 [*]	0.1	5.80E-11 ⁽²⁾	0.026	0.47
Total		0.036		0.16	8.98

* Mixing ratios for several compounds were estimated based on Dunlea et al. (10).

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