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Source apportionment of VOCs, IVOCs and SVOCs by positive matrix factorization in suburban Livermore, California

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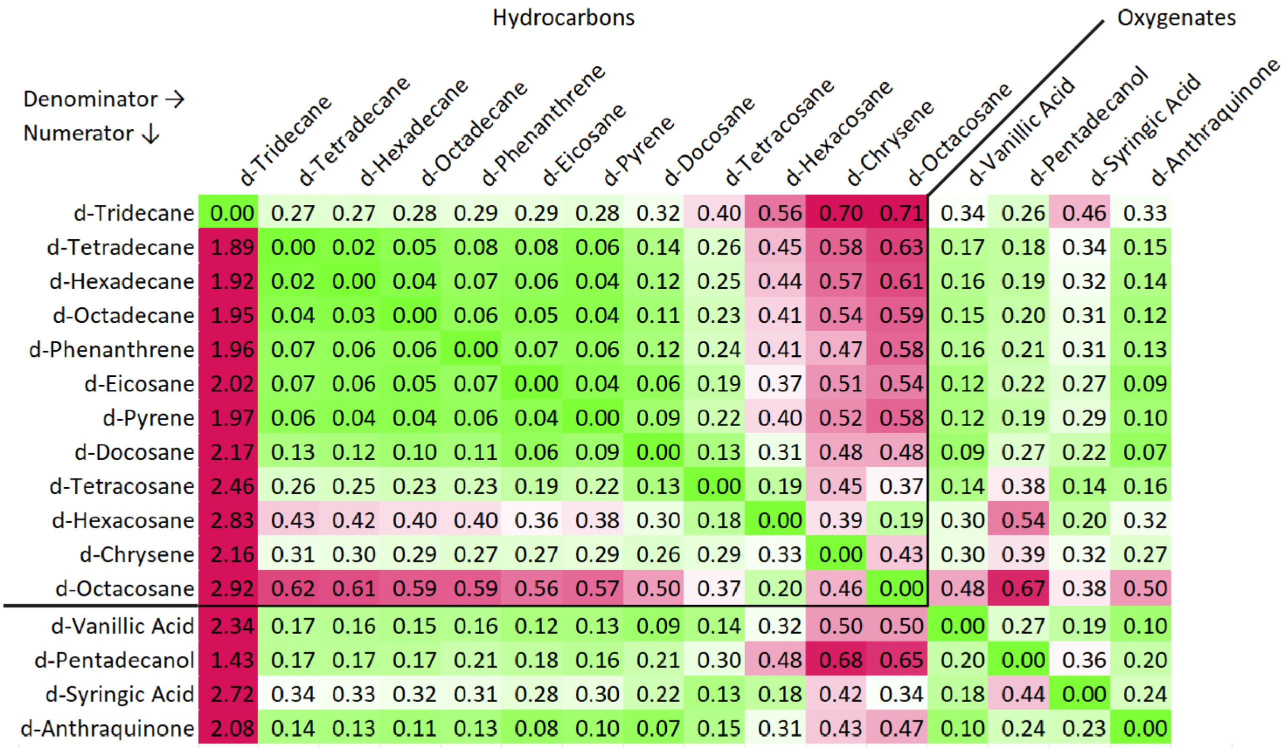
S1 Precision uncertainty histograms

Precision uncertainty is discussed in Sect. 2.2.3.2.

Figure S1 shows the relative standard deviations of the internal standard ratios for all internal standards used for normalization in this analysis. Hydrocarbons between *n*-tetradecane (C_{14}) and pyrene (elutes just before *n*-docosane (C_{22})) all correlate closely. Additionally, the distribution of internal standard ratios across samples is approximately normal (e.g., Fig. S2(a)). We thus infer that any ambient hydrocarbon observed in this volatility range could be normalized by any of the internal standards in this range with 10% or less precision uncertainty introduced. Though transfer efficiency suffers for hydrocarbons with lower volatility than *n*-docosane, leading to greater sensitivity of internal standard choice, 10% is still a satisfactory precision uncertainty for ambient compounds in this volatility range provided the analyte and internal standard retention indices differ by less than about 200. (In later deployments of cTAG, transfer efficiency remains high up to *n*-triacontane.) The best hydrocarbon pairings have a relative standard deviation of less than 5%. From this observation we conservatively estimate that compounds normalized by an isotopologue incur 5% precision uncertainty.

On the high volatility side, deuterated tridecane was lost in the refocusing step during occasional periods of high ambient temperature, causing its measured signal to drop near zero. Ambient compounds in this volatility range are therefore normalized by tetradecane with an assigned precision uncertainty of 25% based on the RSD of the tridecane-tetradecane ratio. The distribution of ratios is somewhat skewed (Fig. S2(b)); a few data points should likely be assigned a higher uncertainty and many could be assigned a lower uncertainty, but 25% represents an appropriate overall estimate for the most volatile compounds.

Oxygenated compounds exhibit greater RSD values regardless of whether they are paired with hydrocarbons or other oxygenates. Deuterated syringic acid, which elutes just before eicosane (C_{20}), produces an RSD of about 30% when paired with most other compounds, oxygenated or not, and an approximately normally distributed set of ratios (Fig. S2(c)). Ambient oxygenates are normalized by the nearest deuterated oxygenate in volatility if their retention indices are within 200 and the nearest hydrocarbon otherwise; in both cases the assigned precision uncertainty is 30%. Table S1 summarizes the categories of precision uncertainty assigned to ambient compounds for this analysis.



Denominator → Numerator ↓	Hydrocarbons d-Tridecane	d-Tetradecane	d-Hexadecane	d-Octadecane	d-Phenanthrene	d-Eicosane	d-Pyrene	d-Docosane	d-Tetracosane	d-Hexacosane	d-Chrysene	d-Octacosane	Oxygenates d-Vanillic Acid	d-Pentadecanol	d-Syringic Acid	d-Anthraquinone
d-Tridecane	0.00	0.27	0.27	0.28	0.29	0.29	0.28	0.32	0.40	0.56	0.70	0.71	0.34	0.26	0.46	0.33
d-Tetradecane	1.89	0.00	0.02	0.05	0.08	0.08	0.06	0.14	0.26	0.45	0.58	0.63	0.17	0.18	0.34	0.15
d-Hexadecane	1.92	0.02	0.00	0.04	0.07	0.06	0.04	0.12	0.25	0.44	0.57	0.61	0.16	0.19	0.32	0.14
d-Octadecane	1.95	0.04	0.03	0.00	0.06	0.05	0.04	0.11	0.23	0.41	0.54	0.59	0.15	0.20	0.31	0.12
d-Phenanthrene	1.96	0.07	0.06	0.06	0.00	0.07	0.06	0.12	0.24	0.41	0.47	0.58	0.16	0.21	0.31	0.13
d-Eicosane	2.02	0.07	0.06	0.05	0.07	0.00	0.04	0.06	0.19	0.37	0.51	0.54	0.12	0.22	0.27	0.09
d-Pyrene	1.97	0.06	0.04	0.04	0.06	0.04	0.00	0.09	0.22	0.40	0.52	0.58	0.12	0.19	0.29	0.10
d-Docosane	2.17	0.13	0.12	0.10	0.11	0.06	0.09	0.00	0.13	0.31	0.48	0.48	0.09	0.27	0.22	0.07
d-Tetracosane	2.46	0.26	0.25	0.23	0.23	0.19	0.22	0.13	0.00	0.19	0.45	0.37	0.14	0.38	0.14	0.16
d-Hexacosane	2.83	0.43	0.42	0.40	0.40	0.36	0.38	0.30	0.18	0.00	0.39	0.19	0.30	0.54	0.20	0.32
d-Chrysene	2.16	0.31	0.30	0.29	0.27	0.27	0.29	0.26	0.29	0.33	0.00	0.43	0.30	0.39	0.32	0.27
d-Octacosane	2.92	0.62	0.61	0.59	0.59	0.56	0.57	0.50	0.37	0.20	0.46	0.00	0.48	0.67	0.38	0.50
d-Vanillic Acid	2.34	0.17	0.16	0.15	0.16	0.12	0.13	0.09	0.14	0.32	0.50	0.50	0.00	0.27	0.19	0.10
d-Pentadecanol	1.43	0.17	0.17	0.17	0.21	0.18	0.16	0.21	0.30	0.48	0.68	0.65	0.20	0.00	0.36	0.20
d-Syringic Acid	2.72	0.34	0.33	0.32	0.31	0.28	0.30	0.22	0.13	0.18	0.42	0.34	0.18	0.44	0.00	0.24
d-Anthraquinone	2.08	0.14	0.13	0.11	0.13	0.08	0.10	0.07	0.15	0.31	0.43	0.47	0.10	0.24	0.23	0.00

Figure S1. Relative standard deviations of all internal standard ratios used in this study. Green = 0; Magenta = 0.7 or greater.

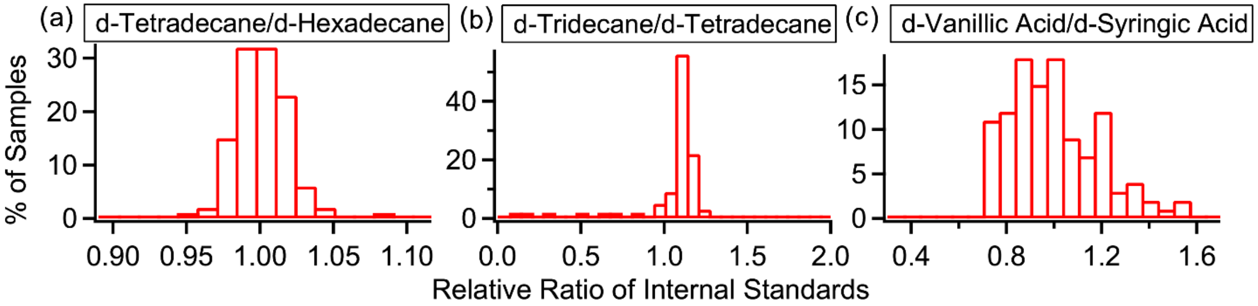


Figure S2. Example distribution of relative ratios of internal standards for (a) two hydrocarbons with a retention index difference of 200, (b) tridecane and tetradecane and (c) two oxygenated compounds.

Table S1. Summary of internal standard assignments for normalization of ambient compounds in this analysis and the precision uncertainty incurred from each assignment. Because the precision uncertainty is the only source of uncertainty that varies from sample to sample, it is the only uncertainty assigned to individual compounds as input to the PMF model.

Ambient Compound Category	**Precision Uncertainty Assigned**
Compounds with isotopologue internal standards	5%
Hydrocarbons with retention index at or above 1400 (no isotopologue)	10%
Compounds with retention index below 1400 (no isotopologue)	25%
Compounds that do not fall into any of the above categories, including most oxygenates	30%

S2 PMF evaluation of different factor solutions

S2.1 Q/Q_{exp}

A common consideration for deciding which solution best explains the data is to compare Q/Q_{exp} for solutions with different numbers of factors (Ulbrich et al., 2009). The expected value of Q, or Q_{exp}, is calculated for m compounds, n sample times and p factors as:

$$Q_{exp} = mn - p(m+n) \tag{S1}$$

Q/Q_{exp} is expected to decrease as the number of factors increases, as more of the data is able to be fit. A relatively large decrease in Q/Q_{exp} between successive solutions suggests the additional factor explains more of the data than would be expected and thus should be included. This effectively sets a minimum number of factors for the final chosen solution.

Q/Q_{exp} and the percent reduction in Q/Q_{exp} between successive solutions is shown in Fig. S3. Unusually large percent reductions are present with the addition of the 8th factor and, especially, with the addition of the 13th factor. This is one reason the 13 factor solution was chosen.

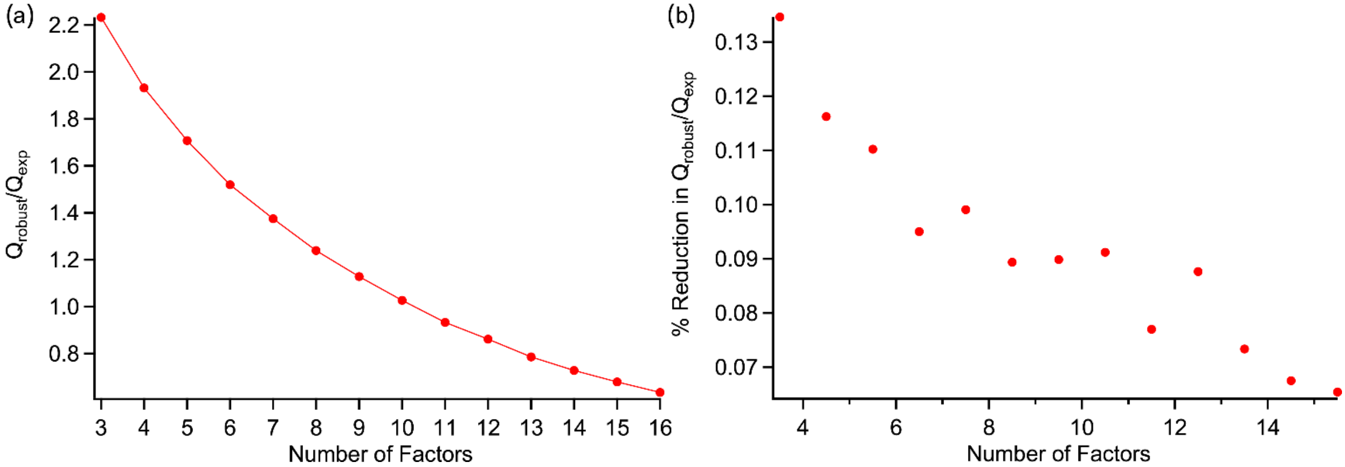


Figure S3. (a) Q/Q_{exp} for different numbers of factors. (b) % reduction in Q/Q_{exp} as the number of factors is increased.

S2.2 Beyond 13 factors: bootstrapping results

The 14 factor solution and beyond were ultimately rejected because the new factors contained low fractions of compounds from many factors, taking mass away from the other factors. Additionally, the factor timelines for 14th, 15th, and 16th factors were not very distinct from existing factors, as reflected in the decreasing average bootstrapping self-mapping fraction (89.77% for 13 factors, 88.21% for 14 factors, 86.07% for 15 factors and 87.19% for 16 factors). Finally, the additional factors had no clear physical interpretations that were distinct from factors present in the 13 factor solution.

S2.3 Factor profile uncertainty

Bootstrapping analysis performs PMF on various resampled versions of the original data set. The factors derived in each bootstrap solution are mapped to the original solution based on their correlation with each of the factors in the original solution. Repeated bootstrapping yields a distribution of values for each compound's fractional contribution to each factor, a measure of the uncertainty of the original solution. 5th and 95th percentile values from this analysis are shown in Fig. 2 and part (d) of Figs. 4-7, 10-17 and 19 as an uncertainty estimate. A more detailed description of bootstrapping analysis as a method to estimate uncertainty can be found in Paatero et al. (2014) and Brown et al. (2015).

S2.4 FPEAK rotation

FPEAK exploration is discussed in Sect. 3.1.

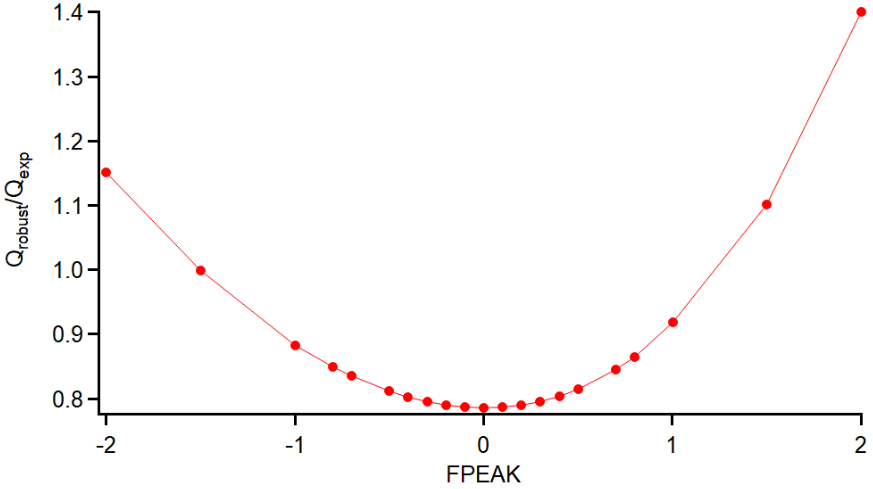


Figure S4. Q/Q_{exp} **for different values of the FPEAK parameter. The minimum value is at FPEAK = 0.**

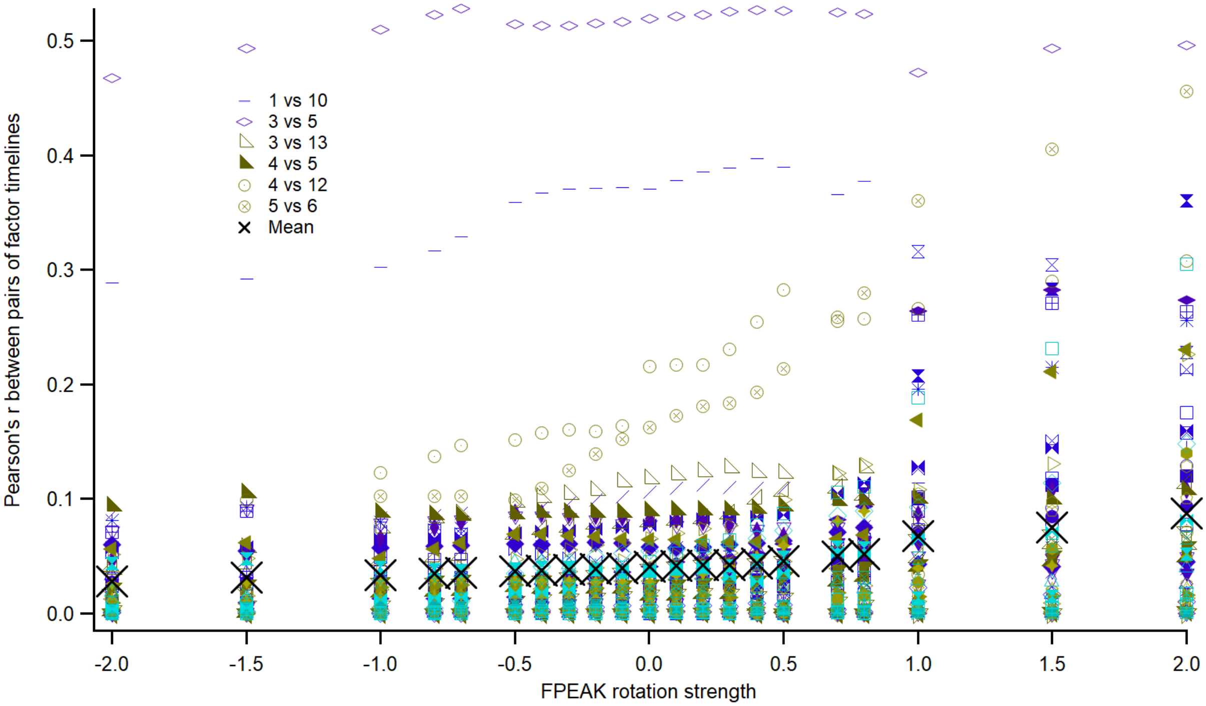
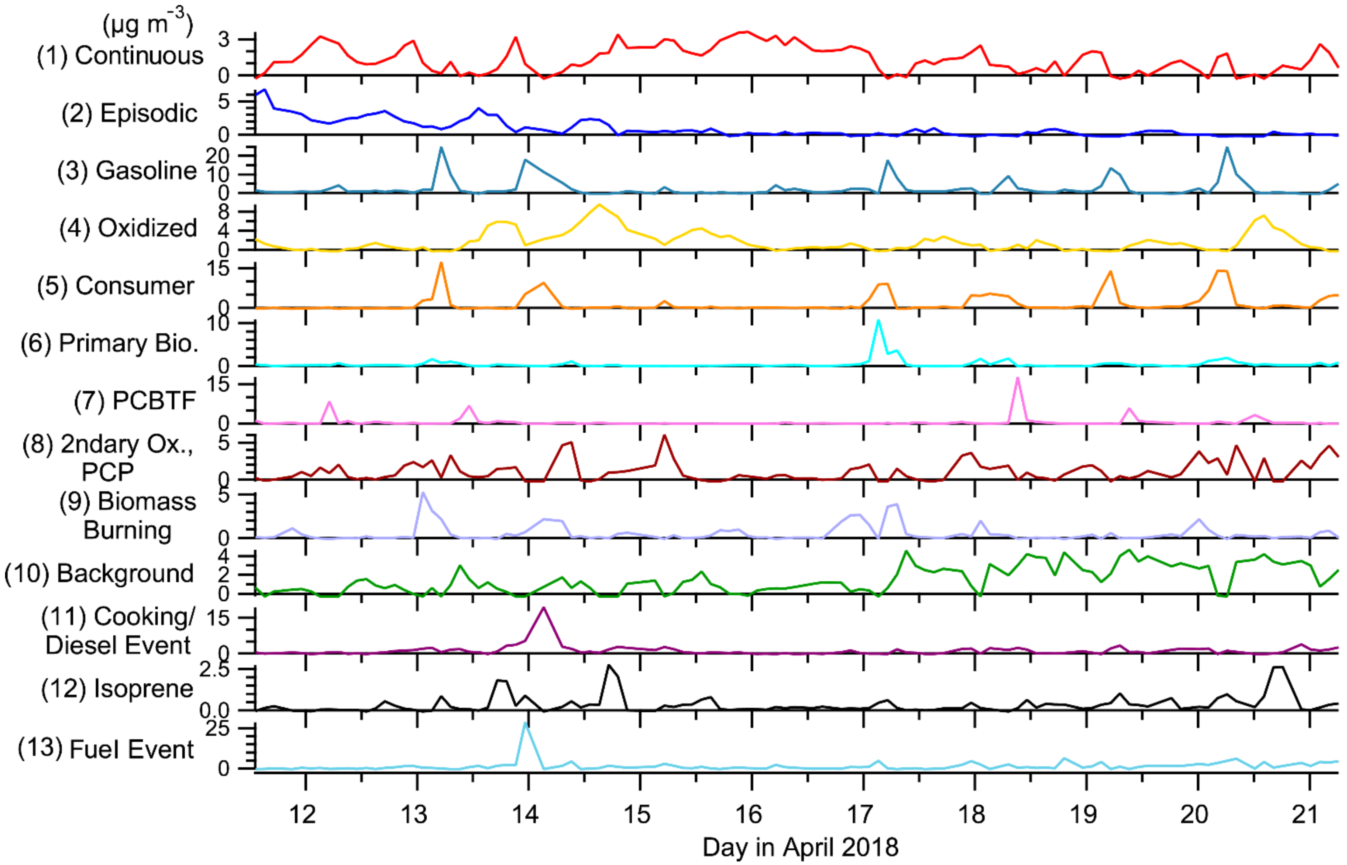


Figure S5. Pearson's r for the cross correlation between every pair of factors in the 13 factor solution, along with the mean r for each FPEAK value. Since there are a total of 78 pairings, only outliers are included in the legend. Negative values of FPEAK provide modest improvements (i.e. decreases) in r values, including the mean r, but not enough to outweigh the optimization of Q/Q_{exp} **at FPEAK = 0 (Fig. S4).**

S3 13 factor solution figures for comparison across factors



80 **Figure S6. 13 factor solution factor timelines. Bio. = Biogenic; PCBTF = Parachlorobenzotrifluoride; 2ndary Ox., PCP = Secondary Oxidation and Personal Care Products. Full factor names are in the main text (Sect. 3.1). Date labels are at midnight.**

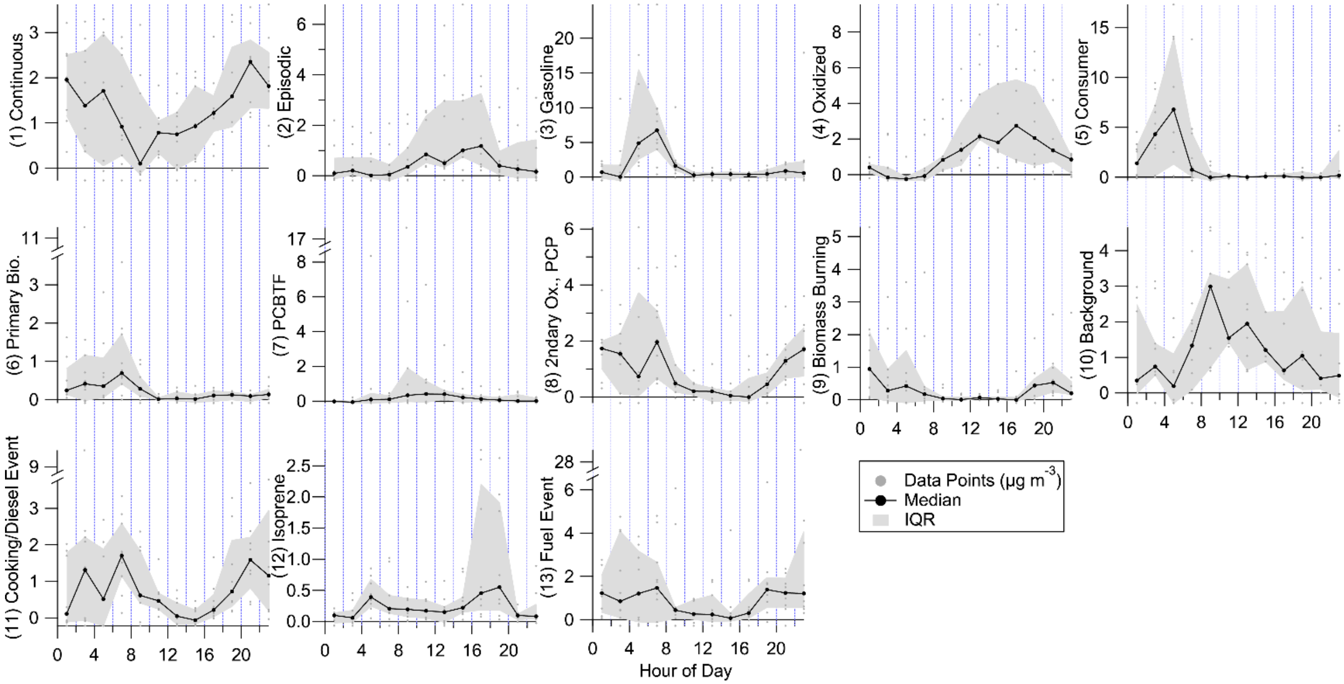


Figure S7. Diurnal profiles of the factor timelines in the 13 factor solution. IQR = Interquartile range.

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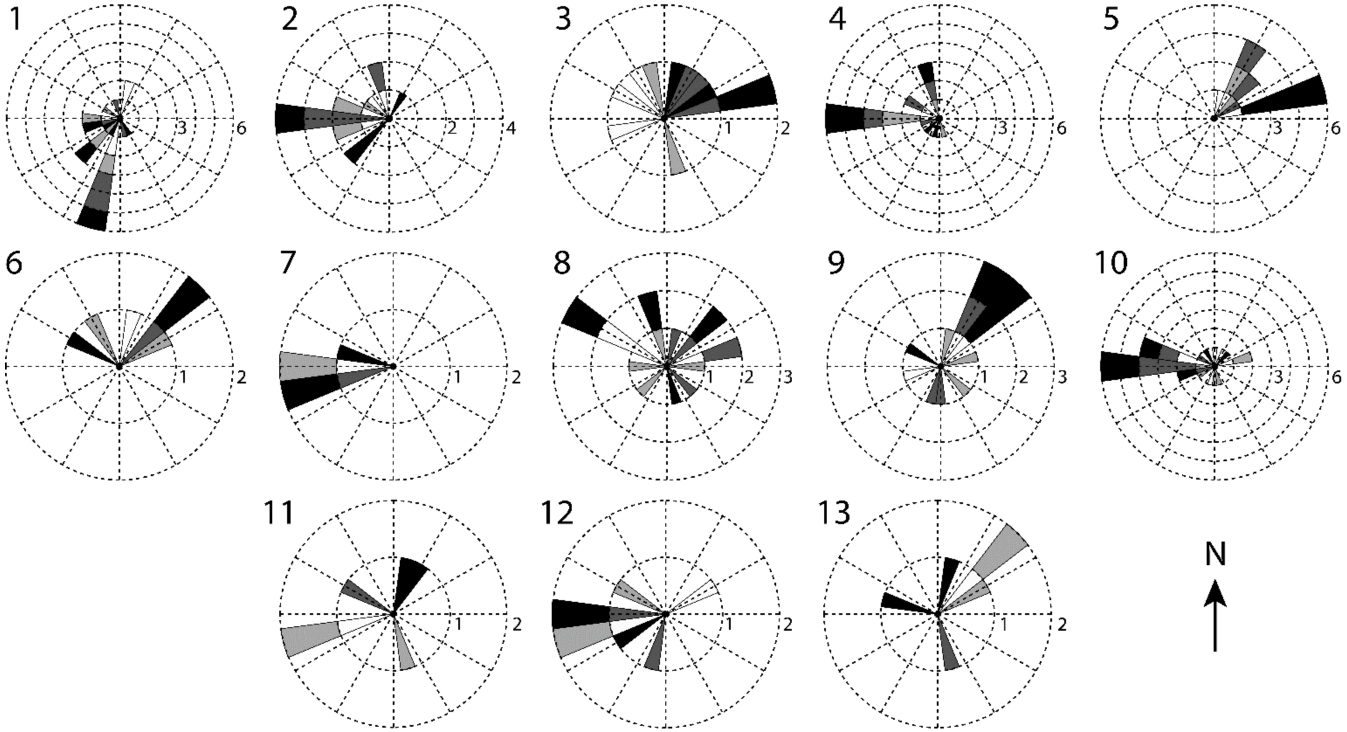

Figure S8. Rose plots, showing the correlation of emissions and wind direction, of each factor using only data points where the concentration was elevated, defined as > 1 standard deviation above the mean factor concentration. Frequency of observations are represented by the length of each wedge, where each ring corresponds to one observation. Shading corresponds to quartiles of factor concentration (darker = greater concentration).

S4 Factor apportionment of VOCs, IVOCs and SVOCs

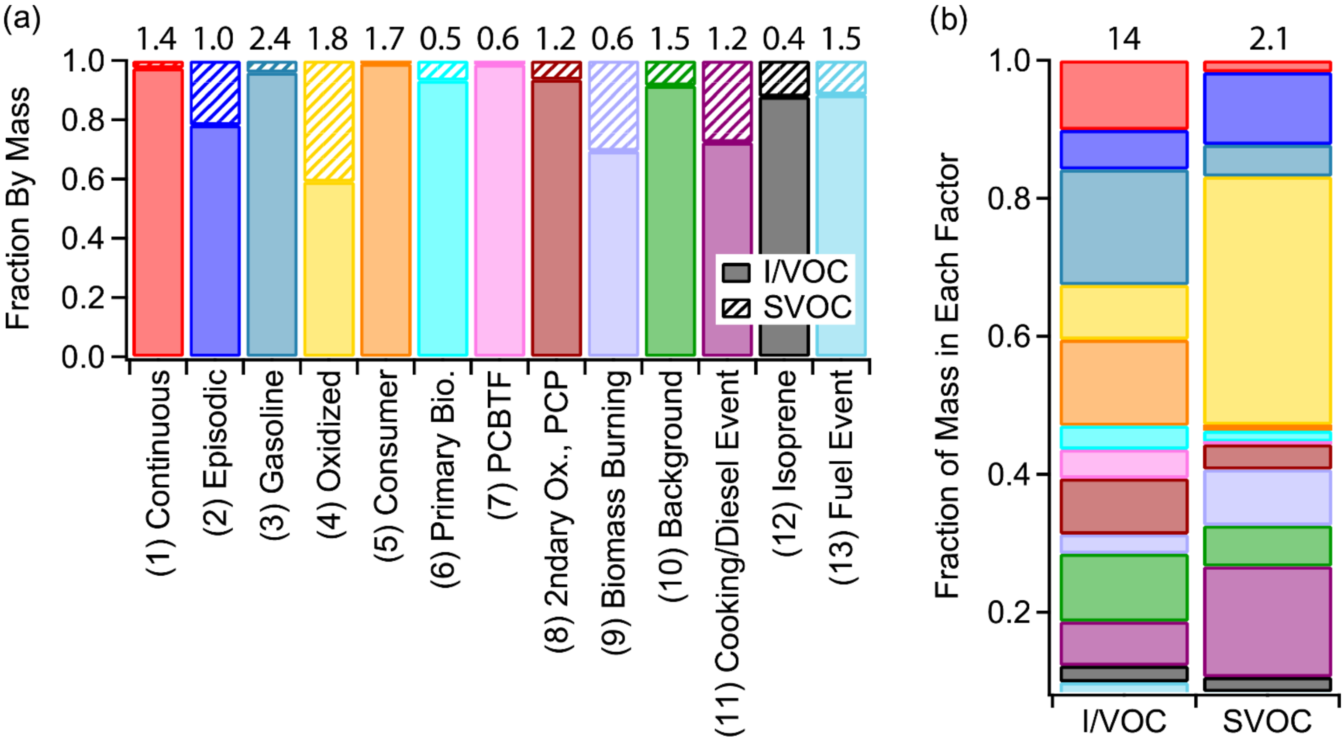

Figure S9. (a) Fraction of average mass from each cTAG measurement channel in each factor. (b) Fraction of the average total mass of compounds measured on each channel found in each factor. The numbers at the top represent the average total mass for (a) that factor or (b) that class of compounds in μg m^{-3}.

S5 Top mass contributors to each factor

Tables S2-S14 display the top 10 compounds contributing the most mass to each factor. This is distinct from the compounds that have the greatest fraction of their mass in each factor, which are presented in Fig. 2 and subfigure (d) of Figs. 4-7, 10-17 and 19 and are discussed in detail in the main text. The fraction of each compound's mass in each factor ("mass fraction") for the top 10 mass contributors is also presented in Tables S2-S14. For example, 43% of the mass of Factor 1 is chloroform, while 33% of chloroform's mass is attributed to Factor 1.

Table S2. Fractional contribution of the 10 compounds that contribute the most mass to Factor 1, along with the fraction of each compound's mass in Factor 1 ("mass fraction" as described in the main text).

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Chloroform	I/VOC	0.43	0.33
Methyl Ethyl Ketone	I/VOC	0.14	0.12
Benzene	I/VOC	0.083	0.20
3-Methylhexane	I/VOC	0.047	0.19
Acetone	I/VOC	0.042	0.14
Alpha-Pinene	I/VOC	0.033	0.098
Eucalyptol	I/VOC	0.029	0.13
Furfural	I/VOC	0.021	0.19
2-Cyclopenten-1-one	I/VOC	0.016	0.32
Toluene	I/VOC	0.015	0.023

Table S3. Fractional contribution of the 10 compounds that contribute the most mass to Factor 2, along with the fraction of each compound's mass in Factor 2.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Chloroform	I/VOC	0.33	0.180
Methyl Ethyl Ketone	I/VOC	0.16	0.098
C18 alkanoic acid (stearic)	SVOC	0.14	0.13
Benzene	I/VOC	0.065	0.11
Acetone	I/VOC	0.030	0.072
3-Methylhexane	I/VOC	0.030	0.086
PCBTF	I/VOC	0.023	0.039
Isoprene	I/VOC	0.020	0.10
DEHA	SVOC	0.019	0.038
Toluene	I/VOC	0.018	0.019

Table S4. Fractional contribution of the 10 compounds that contribute the most mass to Factor 3, along with the fraction of each compound's mass in Factor 3.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Toluene	I/VOC	0.11	0.30
m-Xylene and p-Xylene	I/VOC	0.099	0.36
Benzene	I/VOC	0.059	0.23
1,2,4-Trimethylbenzene	I/VOC	0.050	0.41
2-Methylheptane	I/VOC	0.049	0.32
2,2,4-Trimethylpentane	I/VOC	0.047	0.29
o-xylene	I/VOC	0.044	0.37
D5 Siloxane	I/VOC	0.040	0.27
Methylcyclopentane	I/VOC	0.039	0.33
C18 alkanoic acid (stearic)	SVOC	0.031	0.069

Table S5. Fractional contribution of the 10 compounds that contribute the most mass to Factor 4, along with the fraction of each compound's mass in Factor 4.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Methyl Ethyl Ketone	I/VOC	0.23	0.26
C18 alkanoic acid (stearic)	SVOC	0.18	0.31
DEHA	SVOC	0.17	0.62
Nonanal	I/VOC	0.060	0.13
Acetone	I/VOC	0.033	0.15
Benzene	I/VOC	0.032	0.098
Chloroform	I/VOC	0.030	0.030
Toluene	I/VOC	0.024	0.049
2,2,4-Trimethylpentane	I/VOC	0.018	0.082
C9 Diacid (azelaic)	SVOC	0.017	0.33

Table S6. Fractional contribution of the 10 compounds that contribute the most mass to Factor 5, along with the fraction of each compound's mass in Factor 5.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Nonanal	I/VOC	0.12	0.23
alpha-Pinene	I/VOC	0.096	0.35
Methyl Ethyl Ketone	I/VOC	0.086	0.089
Toluene	I/VOC	0.061	0.11
Limonene	I/VOC	0.059	0.66
D5 Siloxane	I/VOC	0.059	0.28
Chloroform	I/VOC	0.056	0.053
m-Xylene and p-Xylene	I/VOC	0.053	0.14
2,2,4-Trimethylpentane	I/VOC	0.031	0.14
Methylcyclopentane	I/VOC	0.028	0.17

Table S7. Fractional contribution of the 10 compounds that contribute the most mass to Factor 6, along with the fraction of each compound's mass in Factor 6.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
alpha-Pinene	I/VOC	0.30	0.32
Chloroform	I/VOC	0.097	0.027
Eucalyptol	I/VOC	0.082	0.14
Benzene	I/VOC	0.050	0.042
Limonene	I/VOC	0.047	0.15
Toluene	I/VOC	0.041	0.023
Nonanal	I/VOC	0.035	0.021
C18 alkanoic acid (stearic)	SVOC	0.030	0.014
beta-Pinene	I/VOC	0.024	0.25
m-Xylene and p-Xylene	I/VOC	0.016	0.012

Table S8. Fractional contribution of the 10 compounds that contribute the most mass to Factor 7, along with the fraction of each compound's mass in Factor 7.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
PCBTF	I/VOC	0.69	0.68
Acetone	I/VOC	0.067	0.092
Methyl Ethyl Ketone	I/VOC	0.051	0.018
Chloroform	I/VOC	0.032	0.010
Toluene	I/VOC	0.026	0.017
m-Xylene and p-Xylene	I/VOC	0.014	0.012
Eucalyptol	I/VOC	0.012	0.023
2,2,4-Trimethylpentane	I/VOC	0.012	0.017
DEHA	SVOC	0.0066	0.0078
2-Methylheptane	I/VOC	0.0064	0.010

Table S9. Fractional contribution of the 10 compounds that contribute the most mass to Factor 8, along with the fraction of each compound's mass in Factor 8.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Methyl Ethyl Ketone	I/VOC	0.18	0.12
Nonanal	I/VOC	0.10	0.14
D5 Siloxane	I/VOC	0.097	0.32
Toluene	I/VOC	0.078	0.10
Eucalyptol	I/VOC	0.073	0.28
Chloroform	I/VOC	0.054	0.035
DEHA	SVOC	0.033	0.079
Acetone	I/VOC	0.029	0.081
Methylcyclopentane	I/VOC	0.026	0.11
m-Xylene and p-Xylene	I/VOC	0.023	0.042

Table S10. Fractional contribution of the 10 compounds that contribute the most mass to Factor 9, along with the fraction of each compound's mass in Factor 9.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
C18 alkanoic acid (stearic)	SVOC	0.23	0.12
Chloroform	I/VOC	0.14	0.042
Furfural	I/VOC	0.084	0.29
Methyl Ethyl Ketone	I/VOC	0.068	0.023
Nonanal	I/VOC	0.039	0.025
Acetone	I/VOC	0.037	0.049
Benzene	I/VOC	0.033	0.030
Toluene	I/VOC	0.029	0.018
3-Methylhexane	I/VOC	0.022	0.035
Eucalyptol	I/VOC	0.022	0.040

Table S11. Fractional contribution of the 10 compounds that contribute the most mass to Factor 10, along with the fraction of each compound's mass in Factor 10.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Chloroform	I/VOC	0.29	0.23
Methyl Ethyl Ketone	I/VOC	0.22	0.19
Acetone	I/VOC	0.067	0.23
Benzene	I/VOC	0.067	0.16
DEHA	SVOC	0.047	0.14
3-Methylhexane	I/VOC	0.044	0.18
Toluene	I/VOC	0.040	0.064
PCBTF	I/VOC	0.032	0.080
Methylcyclopentane	I/VOC	0.013	0.065
2-Methylheptane	I/VOC	0.010	0.041

Table S12. Fractional contribution of the 10 compounds that contribute the most mass to Factor 11, along with the fraction of each compound's mass in Factor 11.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
C18 alkanoic acid (stearic)	SVOC	0.22	0.25
Nonanal	I/VOC	0.18	0.25
m-Xylene and p-Xylene	I/VOC	0.073	0.13
Toluene	I/VOC	0.052	0.069
1,2,4-Trimethylbenzene	I/VOC	0.046	0.19
Chloroform	I/VOC	0.036	0.024
o-xylene	I/VOC	0.028	0.12
C9 Diacid (azelaic)	SVOC	0.022	0.28
PCBTF	I/VOC	0.021	0.043
2-Methylheptane	I/VOC	0.020	0.069

Table S13. Fractional contribution of the 10 compounds that contribute the most mass to Factor 12, along with the fraction of each compound's mass in Factor 12.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Isoprene	I/VOC	0.37	0.73
Toluene	I/VOC	0.088	0.036
DEHA	SVOC	0.075	0.057
alpha-Pinene	I/VOC	0.057	0.044
m-Xylene and p-Xylene	I/VOC	0.048	0.027
Acetone	I/VOC	0.030	0.026
C18 alkanoic acid (stearic)	SVOC	0.029	0.010
Furfural	I/VOC	0.022	0.050
Eucalyptol	I/VOC	0.021	0.026
Benzene	I/VOC	0.021	0.013

Table S14. Fractional contribution of the 10 compounds that contribute the most mass to Factor 13, along with the fraction of each compound's mass in Factor 13.

Compound Name	Meas. Channel	Fractional Contribution to Total Mass	Mass Fraction
Toluene	I/VOC	0.10	0.17
m-Xylene and p-Xylene	I/VOC	0.083	0.19
C18 alkanoic acid (stearic)	SVOC	0.073	0.11
Methyl Ethyl Ketone	I/VOC	0.071	0.065
2,2,4-Trimethylpentane	I/VOC	0.070	0.27
Nonanal	I/VOC	0.061	0.11
2-Methylheptane	I/VOC	0.061	0.26
Methylcyclopentane	I/VOC	0.037	0.20
o-xylene	I/VOC	0.036	0.19
1,2,4-Trimethylbenzene	I/VOC	0.028	0.15

S6 Ratio of isoprene to benzene in gasoline exhaust

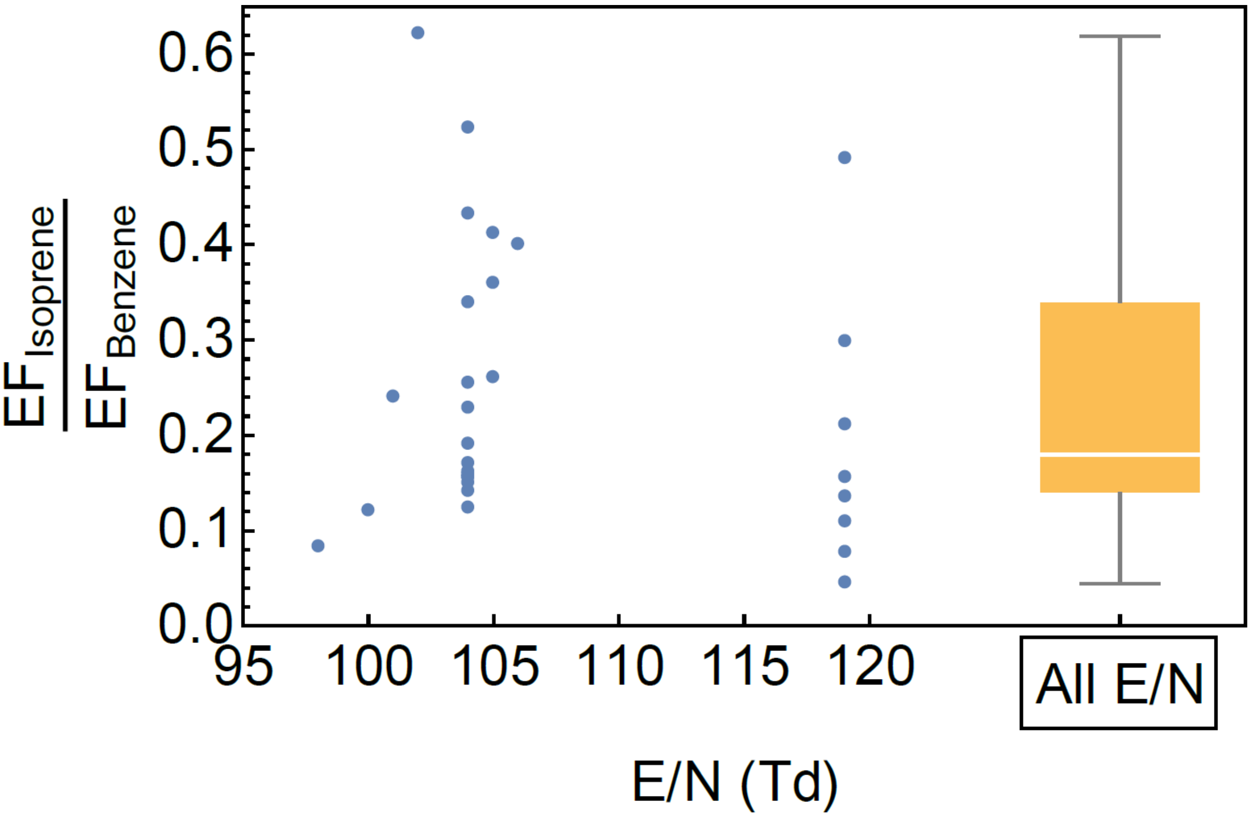

Figure S10. The ratio of isoprene to benzene emission factors (EF) (mg (kg Fuel)$^{-1}$) for cold-start emissions for a wide range of vehicle classes, showing a mean value of 0.18. Observed ratios are sorted by the E/N (electric field density ratio) used in measurements made by a quadrupole proton transfer reaction mass spectrometer. Vehicles span model year 1990 - 2014 and Pre-LEV to SULEV emissions categories. There is no trend with E/N, suggesting a minimal effect of substituted cyclohexanes on isoprene measurements (Gueneron et al., 2015).

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