

bulk carbon measurements. Compounds are grouped by compound class and sorted by increasing molecular weight within each class.

720 **Figure 6.** Resolved organic molecular markers broken down by compound class and season. The sum of all species averaged annually and by season is displayed above the corresponding bars.

Figure 7. Ratio-ratio plots for a) two hopanes normalized by EC and b) two polycyclic aromatic hydrocarbons (PAHs) normalized by EC covering 1.5 years of daily measurements. The ambient measurements are stratified by weekdays, weekends and holidays (New Years, Thanksgiving and Christmas). The numbered triangles represent the location of published gasoline and diesel vehicle emission profiles on the ratio-ratio plots. Profiles 1 and 2 are from Robinson et al. (2006a,b) and represent an average of many published mobile source profiles for 1) gasoline vehicles and 2) diesel vehicles. Profiles 3 – 8 are from the NFRAQS study (Zielenska et al., 1998) and represent average Denver mobile source profiles for 3) low emitter gasoline vehicles, 4) non-smoking gasoline vehicles, 5) high emitter gasoline vehicles, 6) smoking gasoline vehicles, 7) light duty diesel vehicles and 8) heavy duty diesel vehicles. Profile 9 is from a separate published report on the NFRAQS study (Watson et al., 1998) for 9) heavy duty diesel vehicles.

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Figure S1. Flow rate and temperature profiles for the PTV inlet and GC oven used during all GC-MS analyses. In the beginning of the analysis, the PTV is heated quickly at a rate of 300 °C/min and obtains a maximum temperature of 345 °C. During the data collection phase, the GC

740 oven is heated at 30 °C/min to a maximum temperature of 325 °C where it is held for ten
minutes.

Figure S2. Example calibration curves for a) heptacosane, b) benz[a]anthracene, c) dodecanoic acid and d) a combination of decanoic acid and dodecanoic acid. The latter is an example of a
745 combined calibration curve used to quantify undecanoic acid which was not present in the quantification standards. In each example, the open circles are the observed calibration points measured at five dilutions of the calibration standards: 50:1, 100:1, 200:1, 400:1 and 800:1. The solid line is the quadratic fit to the calibration points and the dashed lines are the empirically derived uncertainty bounds.

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Figure 1, Supplemental

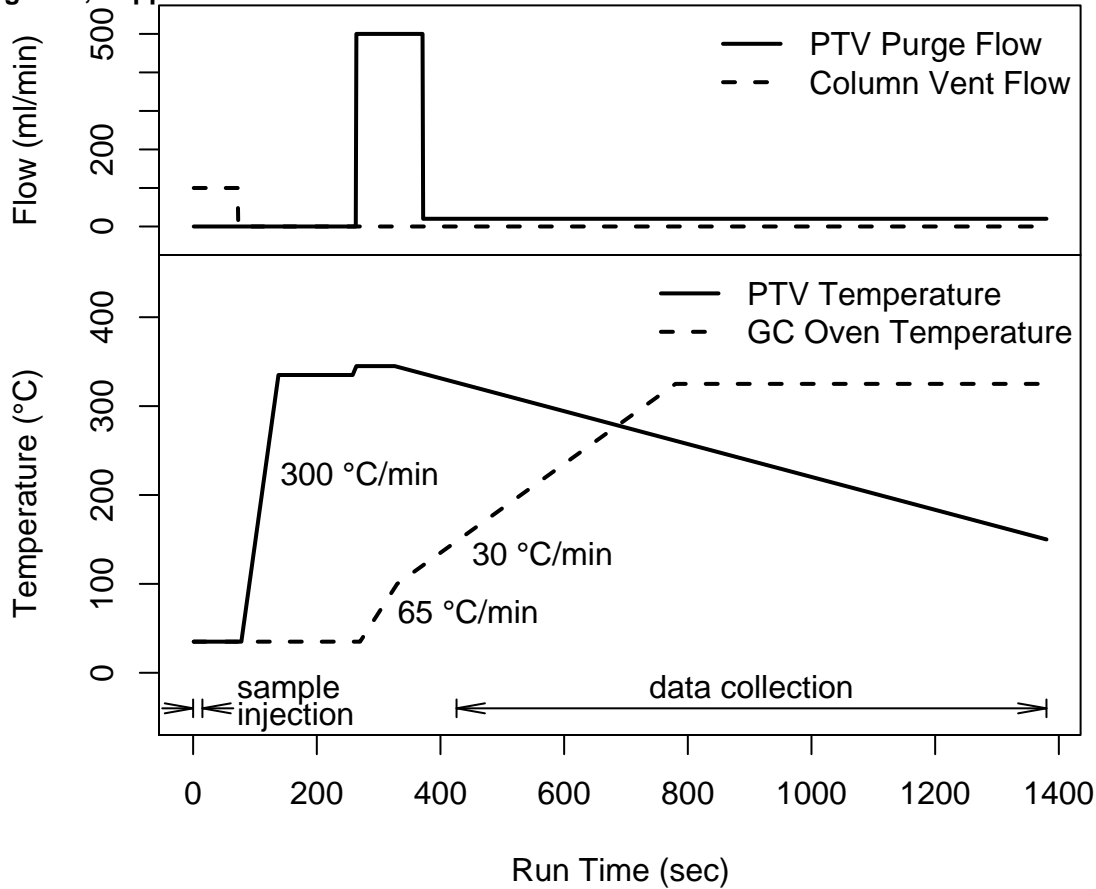


Table S1: Organic molecular marker compounds and their referenced internal standards.

| Compound Name (Empirical Formula) | M/Z ^a | Internal Standard (Empirical Formula) ^b |
|--|------------------|---|
| alkanes and cycloalkanes | | |
| docosane (C ₂₂ H ₄₆) | 310 | eicosane (C ₂₀ D ₄₂) |
| tricosane (C ₂₃ H ₄₈) | 324 | eicosane (C ₂₀ D ₄₂) |
| tetracosane (C ₂₄ H ₅₀) | 338 | octacosane (C ₂₈ D ₅₈) |
| pentacosane (C ₂₅ H ₅₂) | 352 | octacosane (C ₂₈ D ₅₈) |
| hexacosane (C ₂₆ H ₅₄) | 366 | octacosane (C ₂₈ D ₅₈) |
| heptacosane (C ₂₇ H ₅₆) | 380 | octacosane (C ₂₈ D ₅₈) |
| octacosane (C ₂₈ H ₅₈) | 394 | octacosane (C ₂₈ D ₅₈) |
| nonacosane (C ₂₉ H ₆₀) | 408 | octacosane (C ₂₈ D ₅₈) |
| triacontane (C ₃₀ H ₆₂) | 422 | octacosane (C ₂₈ D ₅₈) |
| hentriacontane (C ₃₁ H ₆₄) | 436 | octacosane (C ₂₈ D ₅₈) |
| dotriacontane (C ₃₂ H ₆₆) | 450 | hexatriacontane (C ₃₆ D ₇₄) |
| tritriacontane (C ₃₃ H ₆₈) | 464 | hexatriacontane (C ₃₆ D ₇₄) |
| tetratriacontane (C ₃₄ H ₇₀) | 478 | hexatriacontane (C ₃₆ D ₇₄) |
| pentatriacontane (C ₃₅ H ₇₂) | 492 | hexatriacontane (C ₃₆ D ₇₄) |
| hexatriacontane (C ₃₆ H ₇₄) | 506 | hexatriacontane (C ₃₆ D ₇₄) |
| heptatriacontane (C ₃₇ H ₇₆) | 520 | hexatriacontane (C ₃₆ D ₇₄) |
| octatriacontane (C ₃₈ H ₇₈) | 534 | hexatriacontane (C ₃₆ D ₇₄) |
| nonatriacontane (C ₃₉ H ₈₀) | 548 | hexatriacontane (C ₃₆ D ₇₄) |
| tetracontane (C ₄₀ H ₈₂) | 562 | hexatriacontane (C ₃₆ D ₇₄) |
| pentadecylcyclohexane (C ₂₁ H ₄₂) | 294 | eicosane (C ₂₀ D ₄₂) |
| nonadecylcyclohexane (C ₂₅ H ₅₀) | 350 | octacosane (C ₂₈ D ₅₈) |
| PAHs | | |
| fluoranthene (C ₁₆ H ₁₀) | 202 | chrysene (C ₁₈ D ₁₂) |
| pyrene (C ₁₆ H ₁₀) | 202 | chrysene (C ₁₈ D ₁₂) |
| benzo[ghi]fluoranthene (C ₁₈ H ₁₀) | 226 | chrysene (C ₁₈ D ₁₂) |
| cyclopenta[cd]pyrene (C ₁₈ H ₁₀) | 226 | chrysene (C ₁₈ D ₁₂) |
| benz[a]anthracene (C ₁₈ H ₁₂) | 228 | chrysene (C ₁₈ D ₁₂) |
| chrysene/triphenylene (C ₁₈ H ₁₂) | 228 | chrysene (C ₁₈ D ₁₂) |
| benzo[b&k]fluoranthene (C ₂₀ H ₁₂) | 252 | chrysene (C ₁₈ D ₁₂) |
| benzo[j]fluoranthene (C ₂₀ H ₁₂) ^c | 252 | chrysene (C ₁₈ D ₁₂) |
| benz[a&e]pyrene (C ₂₀ H ₁₂) | 252 | chrysene (C ₁₈ D ₁₂) |
| perylene (C ₂₀ H ₁₂) | 252 | chrysene (C ₁₈ D ₁₂) |
| indeno[1,2,3-cd]pyrene (C ₂₂ H ₁₂) | 276 | dibenz[ah]anthracene (C ₂₂ D ₁₄) |
| benzo[ghi]perylene (C ₂₂ H ₁₂) | 276 | dibenz[ah]anthracene (C ₂₂ D ₁₄) |
| dibenz[ah]anthracene (C ₂₂ H ₁₄) | 278 | dibenz[ah]anthracene (C ₂₂ D ₁₄) |
| picene (C ₂₂ H ₁₄) | 278 | dibenz[ah]anthracene (C ₂₂ D ₁₄) |
| coronene (C ₂₄ H ₁₂) | 300 | dibenz[ah]anthracene (C ₂₂ D ₁₄) |
| methyl-202-PAH sum (C ₁₇ H ₁₂) ^c | 216 | chrysene (C ₁₈ D ₁₂) |
| retene (C ₁₈ H ₁₈) | 234 | chrysene (C ₁₈ D ₁₂) |
| methyl-228-PAH sum (C ₁₉ H ₁₄) ^c | 242 | chrysene (C ₁₈ D ₁₂) |
| oxy-PAHs | | |
| acenaphthenone (C ₁₂ H ₈ O) ^c | 168 | acenaphthene (C ₁₂ D ₁₀) |
| fluorenone (C ₁₃ H ₈ O) ^c | 180 | acenaphthene (C ₁₂ D ₁₀) |

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| 1H-phenalen-1-one (C ₁₃ H ₈ O) ^c | 180 | acenaphthene (C ₁₂ D ₁₀) |
| xanthone (C ₁₃ H ₈ O ₂) ^c | 196 | chrysene (C ₁₈ D ₁₂) |
| 1,8-naphthalic anhydride (C ₁₂ H ₆ O ₃) ^c | 198 | chrysene (C ₁₈ D ₁₂) |
| anthracene-9,10-dione (C ₁₄ H ₈ O ₂) ^c | 208 | chrysene (C ₁₈ D ₁₂) |
| benz[de]anthracene-7-one (C ₁₇ H ₁₀ O) ^c | 230 | chrysene (C ₁₈ D ₁₂) |
| steranes | | |
| 20R-abb & 20S-aaa-cholestane (C ₂₇ H ₄₈) | 372 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| 20R & S-abb-methylcholestane (C ₂₈ H ₅₀) | 386 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| 20R & S-abb-ethylcholestane (C ₂₉ H ₅₂) | 400 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| a-22,29,30-trisnorhopane (C ₂₇ H ₄₆) | 370 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| ba-30-norhopane (C ₂₉ H ₅₀) | 398 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| ab-hopane (C ₃₀ H ₅₂) | 412 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| 22S-ab-30-homohopane (C ₃₁ H ₅₄) ^c | 426 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| 22R-ab-30-homohopane (C ₃₁ H ₅₄) ^c | 426 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| 22S-ab-30-bishomohopane (C ₃₂ H ₅₆) ^c | 440 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| 22R-ab-30-bishomohopane (C ₃₂ H ₅₆) ^c | 440 | 20R-aaa-cholestane (C ₂₇ D ₄ H ₄₄) |
| fatty acids | | |
| dodecanoic acid (C ₁₂ H ₂₄ O ₂) | 200 | decanoic acid (C ₁₀ D ₁₉ HO ₂) |
| tridecanoic acid (C ₁₃ H ₂₆ O ₂) ^{c,d} | 214 | decanoic acid (C ₁₀ D ₁₉ HO ₂) |
| tetradecanoic acid (C ₁₄ H ₂₈ O ₂) | 228 | heptadecanoic acid (C ₁₇ D ₃₃ HO ₂) |
| pentadecanoic acid (C ₁₅ H ₃₀ O ₂) ^{c,d} | 242 | heptadecanoic acid (C ₁₇ D ₃₃ HO ₂) |
| hexadecanoic acid (C ₁₆ H ₃₂ O ₂) | 256 | heptadecanoic acid (C ₁₇ D ₃₃ HO ₂) |
| heptadecanoic acid (C ₁₇ H ₃₄ O ₂) ^{c,d} | 270 | heptadecanoic acid (C ₁₇ D ₃₃ HO ₂) |
| octadecanoic acid (C ₁₈ H ₃₆ O ₂) | 284 | heptadecanoic acid (C ₁₇ D ₃₃ HO ₂) |
| oleic acid (C ₁₈ H ₃₄ O ₂) | 282 | heptadecanoic acid (C ₁₇ D ₃₃ HO ₂) |
| sterols and methoxyphenols | | |
| cholesterol (C ₂₇ H ₄₆ O) | 386 | cholesterol-2,2,3,4,4,6 (C ₂₇ D ₆ H ₄₀ O) |
| stigmasterol (C ₂₉ H ₄₈ O) | 412 | cholesterol-2,2,3,4,4,6 (C ₂₇ D ₆ H ₄₀ O) |
| vanillin (C ₈ H ₈ O ₃) | 152 | 4,4-dimethoxybenzophenone (C ₁₅ D ₈ H ₆ O ₃) |
| acetovanillone (C ₉ H ₁₀ O ₃) | 166 | 4,4-dimethoxybenzophenone (C ₁₅ D ₈ H ₆ O ₃) |
| coniferaldehyde (C ₁₀ H ₁₀ O ₃) | 178 | 4,4-dimethoxybenzophenone (C ₁₅ D ₈ H ₆ O ₃) |
| syringaldehyde (C ₉ H ₁₀ O ₄) | 182 | 4,4-dimethoxybenzophenone (C ₁₅ D ₈ H ₆ O ₃) |
| acetosyringone (C ₁₀ H ₁₂ O ₄) | 196 | 4,4-dimethoxybenzophenone (C ₁₅ D ₈ H ₆ O ₃) |

a) Mass to charge ratio (m/z).

b) Referenced internal standard (IS) compounds isotopically labeled by deuterium (D) substitution.

c) Additional compounds not included in the quantification standards. Calibration curves for the next closest compound based on molecular structure and weight were used for quantification of these compounds.

d) A combined calibration curve based on calibration points from the two neighboring compounds was used to quantify these odd alkanolic acids not present in the quantification standards.

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