Quality Assurance

Figure S1 shows the agreement between collocated MOUDI and RAAS measurements for 28 organic compounds of interest in the present study. Panels (a-k) illustrate agreement for hopanes and steranes that are useful tracers for motor oil. Panels (l-bb) illustrate agreement for polycyclic aromatic hydrocarbons (PAHs) that contribute to the toxicity of diesel particulate matter. The RAAS filter masses shown in Figure S1 have been multiplied by a factor of 3 to adjust for the flow rate difference between RAAS (10 L min⁻¹) and MOUDI (30 L min⁻¹) samplers. The error bars in Figure S1 reflect the analytical uncertainty of the GC-MS analysis.

The solid line shown in each panel of Figure S1 is a linear regression analysis between the MOUDI and adjusted RAAS measurements for each organic compound. The dashed line shown in each panel of Figure S1 is a linear regression analysis between MOUDI and adjusted RAAS measurements for the average value of organic carbon measured using thermal optical carbon analysis(1). The MOUDIs collect less organic carbon than the RAAS filter samplers because of greater volatilization losses associated with the higher flow rates in the MOUDI. RAAS measurements included multiple quartz filters downstream of the front filter to quantify positive adsorption artifacts. The amount of organic carbon collected by the MOUDIs during the 6 HDV tests was approximately 65% of the organic carbon collected by RAAS filter samplers. The individual organic compounds shown in Figure S1 generally have MOUDI losses that are equal or greater than the volatilization of organic carbon. Table S1 lists the regression slope and correlation coefficients for each organic compound and for the maximum and average values of organic carbon measured by MOUDI vs. RAAS filter sampler.

Consistency between MOUDI and filter measurements is a necessary check to build confidence in the accuracy of the size distribution measurements. Hopanes $17\alpha(H)$ - $21\beta(H)$ -29-norhopane (Figure S1 a) and $17\alpha(H)$ - $21\beta(H)$ -hopane (Figure S1 c) appear to exhibit the most consistent behavior between MOUDI and filter measurements as demonstrated by correlation slopes = 0.5515-0.4596 and correlation coefficients R² = 0.8828- 0.6728. Likewise, steranes $\alpha\beta\beta$ -20R-stigmastane (Figure S1 i) and $\alpha\beta\beta$ -20S-stigmastane (Figure S1 j) exhibit the most consistent behavior between MOUDI and filter measurements with correlation slopes = 0.4809 - 0.3830 and correlation coefficients R² = 0.9487- 0.7113. These four species appear to have the greatest promise as size-resolved tracers for diesel particulate matter. The majority of the PAH species appear to behave consistently when collected with MOUDI and filter samplers although some species are present at concentrations that are below the analytical uncertainty. Regressions statistics for all compounds are summarized in Table S1.

Comparison to Previous Measurements

The current study is the first to examine the size distribution of particulate trace organic species emitted from on-road heavy duty diesel vehicles operated under realistic driving cycles with a dilution sampling system. Comparisons to previous measurements made using simpler test conditions and to those of roadside studies can help to illustrate common trends in the data as well as emphasize new trends identified in the current tests due to the more realistic test conditions.

Zielinska et al. (2) measured the size distribution of PAHs emitted from military diesel vehicles operated under several steady-state load conditions. Most of the four to six ring nonvolatile PAHs detected in the current study were also observed in that previous work. Zielinska et al. found that the PAH size distribution emitted from diesel vehicles was different under low vs. high steady state loads. The results of the current study suggest that the peak in the PAH size distribution shifted to larger sizes for the idle-creep load condition vs. the full 5-mode HHDDT test.

Figure S2 shows a comparison of the emission factors (μ g analyte /kg of fuel burned) for the fine particle size range measured in the current study with those of Phuleria et al.(3), Zielinska et al.(2), Schauer et al.(4), Rogge et al. (5). Values for the three lubricating oil tracers measured in current study fall in the range of the values reported in the previous studies. Lighter PAHs such as pyrene and fluoranthene also show strong agreements with the previous studies. Larger non-volatile PAHs reported in this study closely match those values reported by Zielinksa et al., but are much lower than those reported by Phuleria et al. (with the exception of coronene).

Figure S3 shows a comparison of emissions factors for particles with aerodynamic diameter less than 180 nm measured in the current study with the results of Phuleria et al.(3). Emission factors on a mass per fuel basis (μ g analyte / kg of fuel burned) agree quite well for the 3 lubricating oil tracers. Values for the 1998 Kenworth with an inertial load of 66,000 lbs are slightly higher for both of the measured hopanes which is not surprising considering the peak in the observed size distribution pattern shifted to smaller particles with the increased inertial load. Values for the PAHs measured by Phuleria et al. are higher than those observed in the current study for all PAHs except indeno[1,2,3-cd]pyrene and coronene which agree quite strongly. These trends are consistent with the fine particle results discussed above.

| Compound | slope | \mathbf{R}^2 | | | | |
|----------------------------------------------------------|-------------------|-----------------|--|--|--|--|
| Hopanes | • | | | | | |
| $17\alpha(H)-21\beta(H)-29$ -norhpane | 0.5515 | 0.8828 | | | | |
| $18\alpha(H)-29$ -norneohopane ¹ | -0.1328 | 0.2757 | | | | |
| $17\alpha(H)-21\beta(H)$ -hopane | 0.4596 | 0.6728 | | | | |
| $22S-17\alpha(H)-21\beta(H)-30$ homohopane ¹ | 0.2788 | 0.3482 | | | | |
| $22R-17\alpha(H)-21\beta(H)-30$ homohopane ¹ | 0.3541 | 0.2500 | | | | |
| Steranes | | | | | | |
| $20R,13\beta(H)-17\alpha(H)$ -diacholestane ¹ | 0.1188 | 0.1218 | | | | |
| $20S,13\beta(H)-17\alpha(H)$ -diacholestane ¹ | 0.1905 | 0.2807 | | | | |
| $\alpha\alpha\alpha$ -20S-stigmastane ¹ | 0.3151 | 0.4800 | | | | |
| αββ-20R-stigmastane | 0.4809 | 0.9487 | | | | |
| $\alpha\beta\beta$ -20S-stigmastane ¹ | 0.3830 | 0.7113 | | | | |
| $\alpha\alpha\alpha$ -20R-stigmastane ¹ | 0.2034 | 0.4294 | | | | |
| PAHs | | | | | | |
| Phenanthrene | 0.5528 | 0.9657 | | | | |
| Anthracene | 0.8578 | 1.0000 | | | | |
| A-methylphenanthrene | 0.4424 | 0.9396 | | | | |
| B-methylphenanthrene | 0.4685 | 0.9173 | | | | |
| C-methylphenanthrene | 0.4471 | 0.9602 | | | | |
| D-methylphenanthrene | 0.4512 | 0.9169 | | | | |
| Fluoranthene | 0.4325 | 0.9060 | | | | |
| Pyrene | 0.4094 | 0.8844 | | | | |
| benzo[ghi]fluoranthene | 0.7132 | 0.9435 | | | | |
| Chrysene | 0.4732 | 0.8796 | | | | |
| benzo[b]fluoranthene | 0.3729 | 0.8403 | | | | |
| benzo[k]fluoranthene | 0.4466 | 0.7125 | | | | |
| benzo[e]pyrene | 0.2600 | 0.4450 | | | | |
| benzo[a]pyrene | 0.5261 | 0.9033 | | | | |
| indeno[1,2,3-cd]pyrene | 0.5082 | 1.000 | | | | |
| benzo[ghi]perylene | 0.8596 | 0.8831 | | | | |
| Coronene | 0.2577 | 1.000 | | | | |
| Organic Carbon | | | | | | |
| organic carbon (average) | 0.6609 | 0.9715 | | | | |
| organic carbon (maximum) | 0.7804 0.9740 | | | | | |
| ¹ Analyte identification based on compar | isons to relative | retention times | | | | |
| to those in the literature. | | | | | | |

Table S1. Comparison of MOUDI mass to co-located filter mass for trace organiccompounds. Filter mass was pre-multiplied by a factor of 3 to normalize flow rates.

| | 1999 | | 1999 | | 1998 | | 1998 | | 1992 | | 1985 | |
|----------------------------------------------------------------------------------------------------------------------------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|-------|-------|--------|-------|
| | Frt | Inr | Frtlnr | | Knwrth | | Knwrth | | Volvo | | Frtlnr | |
| Compound | Idle/C | Creep | 56K | | 56K | | 66K | | 56K | | 56K | |
| Hopanes | ratio | error | ratio | error | ratio | error | ratio | error | ratio | error | ratio | error |
| 17α(Η)-21β(Η)-29- | | | | | | | | | | | | |
| norhpane | 724.1 | 72.2 | 104.2 | 8.5 | 218.6 | 19.6 | 114.9 | 10.9 | 28.4 | 2.1 | 45.8 | 3.2 |
| $17\alpha(H)-21\beta(H)$ -hopane | 386.9 | 38.6 | 74.3 | 6.1 | 213.6 | 19.2 | 138.4 | 14.0 | 45.9 | 3.4 | 51.2 | 3.7 |
| Steranes | | | | | | | | | | | | |
| αββ-20R-stigmastane | 211.3 | 21.1 | 47.7 | 3.9 | 102.3 | 9.2 | 57.5 | 6.7 | 12.8 | 1.0 | 44.5 | 3.2 |
| $\alpha\beta\beta$ -20S-stigmastane ¹ | 173.0 | 17.3 | 37.4 | 3.1 | 86.6 | 7.8 | 17.8 | 4.5 | 19.8 | 1.4 | 30.7 | 2.3 |
| PAHs | | | | | | | | | | | | |
| phenanthrene | 19.2 | 6.1 | 58.7 | 6.9 | 95.9 | 12.0 | 22.1 | 6.3 | 14.5 | 1.9 | 109.5 | 10.7 |
| anthracene | ND | | ND | | ND | | ND | | ND | | 6.3 | 1.5 |
| A-methylphenanthrene | ND | | 36.5 | 15.5 | 54.1 | 22.0 | 116.8 | 43.1 | 8.0 | 6.7 | 97.3 | 12.0 |
| B-methylphenanthrene | ND | | 85.7 | 17.4 | 109.5 | 24.5 | 144.7 | 44.1 | 20.2 | 7.0 | 127.9 | 14.3 |
| C-methylphenanthrene | ND | | 31.4 | 15.4 | 52.3 | 21.9 | 80.6 | 42.2 | 13.1 | 6.8 | 71.3 | 10.2 |
| D-methylphenanthrene | ND | | 25.4 | 15.3 | 44.1 | 21.7 | 58.3 | 41.9 | 11.0 | 6.8 | 52.3 | 9.2 |
| fluoranthene | 46.3 | 7.7 | 70.2 | 7.9 | 70.2 | 9.0 | 50.4 | 8.4 | 59.9 | 6.1 | 118.8 | 11.6 |
| pyrene | 99.9 | 14.9 | 152.4 | 16.6 | 216.3 | 26.0 | 110.5 | 15.0 | 134.2 | 13.4 | 202.4 | 19.7 |
| benzo[ghi]fluoranthene | 27.1 | 5.7 | 9.4 | 2.4 | 43.1 | 6.0 | 29.4 | 4.7 | 15.6 | 1.9 | 27.5 | 2.8 |
| chrysene | 10.4 | 6.0 | ND | | 18.6 | 4.6 | 21.8 | 8.3 | 4.0 | 1.3 | 9.7 | 1.8 |
| benzo[b]fluoranthene | 24.7 | 16.6 | ND | | 19.2 | 11.5 | 36.6 | 39.4 | 4.6 | 3.6 | 16.1 | 7.6 |
| benzo[k]fluoranthene | 9.0 | 3.6 | ND | | 3.3 | 2.4 | 3.0 | 19.7 | ND | | 1.6 | 3.8 |
| benzo[e]pyrene | 21.5 | 7.2 | ND | | 14.1 | 4.9 | 10.9 | 6.0 | 6.2 | 1.6 | 10.8 | 1.6 |
| benzo[a]pyrene | 17.5 | 8.2 | ND | | 14.3 | 5.7 | 1.5 | 6.7 | ND | | 3.5 | 1.3 |
| indeno[1,2,3- | | | | | | | | | | | | |
| cd]pyrene | 17.7 | 15.3 | ND | | ND | | ND | | ND | | ND | |
| benzo[ghi]perylene | 76.2 | 12.1 | ND | | 15.9 | 6.3 | 8.9 | 16.6 | ND | | ND | |
| coronene | 33.7 | 6.2 | ND | | ND | | ND | | ND | | ND | |
| ¹ Analyte identification based on comparisons to relative retention times to those in the literature. ² ND = not detected | | | | | | | | | | | | |

Table S2. Ratio of analyte mass (µg) to elemental carbon mass (g) for the RAAS filter measurements from HDDVs in the PM1.8 size fraction. Uncertainty values represent analytical uncertainty.

| | 1999 | | 1999 | | 1998 | | 1998 | | 1992 | | 1985 | | |
|------------------------------------------------------------------------------------------------------------------|--------|------------|--------|-------|--------|-------|--------|-------|-------|-------|--------|-------|--|
| | Frt | lnr | Frtlnr | | Knwrth | | Knwrth | | Volvo | | Frtlnr | | |
| Compound | Idle/(| Idle/Creep | | 56K | | 56K | | 66K | | 56K | | 56K | |
| Hopanes | ratio | error | ratio | error | ratio | error | ratio | error | ratio | error | ratio | error | |
| 17α(H)-21β(H)-29- | | | | | | | | | | | | | |
| norhpane | 513.4 | 46.5 | 98.3 | 6.7 | 84.7 | 6.1 | 290.7 | 21.0 | 35.5 | 2.1 | 24.6 | 1.6 | |
| $17\alpha(H)-21\beta(H)$ -hopane | 435.8 | 39.5 | 88.6 | 6.1 | 90.0 | 6.5 | 337.0 | 24.8 | 34.5 | 2.1 | 33.0 | 2.4 | |
| Steranes | | | | | | | | | | | | | |
| αββ-20R-stigmastane | 144.0 | 13.1 | 47.1 | 3.2 | 33.6 | 2.4 | 101.1 | 8.3 | ND | | ND | | |
| $\alpha\beta\beta$ -20S-stigmastane ¹ | 130.2 | 11.9 | 33.8 | 2.3 | 23.9 | 1.8 | 80.6 | 7.1 | ND | | ND | | |
| PAHs | | | | | | | | | | | | | |
| phenanthrene | 68.3 | 10.7 | 74.5 | 7.8 | 22.5 | 4.1 | 31.9 | 6.4 | 23.5 | 2.4 | 62.3 | 5.8 | |
| anthracene | ND | | ND | | ND | | ND | | ND | | 20.9 | 2.5 | |
| A-methylphenanthrene | ND | | 77.9 | 17.4 | 16.6 | 18.8 | ND | | 16.9 | 5.8 | 76.3 | 11.1 | |
| B-methylphenanthrene | ND | | 109.8 | 18.8 | 23.9 | 18.8 | ND | | 35.7 | 6.4 | 96.4 | 12.2 | |
| C-methylphenanthrene | ND | | 46.7 | 16.4 | 9.5 | 18.7 | ND | | 21.5 | 5.9 | 54.3 | 10.2 | |
| D-methylphenanthrene | ND | | 42.6 | 16.3 | 7.5 | 18.7 | ND | | 16.9 | 5.8 | 39.2 | 9.7 | |
| fluoranthene | 21.4 | 6.7 | 115.7 | 11.4 | 23.8 | 3.8 | 32.4 | 6.5 | 70.9 | 6.5 | 93.9 | 8.5 | |
| pyrene | 34.6 | 10.7 | 255.5 | 24.8 | 60.4 | 7.7 | 104.1 | 12.6 | 177.9 | 16.0 | 147.7 | 13.3 | |
| benzo[ghi]fluoranthene | 9.5 | 5.7 | 11.4 | 2.6 | 27.9 | 3.9 | 25.6 | 3.9 | 15.1 | 1.6 | 25.1 | 2.4 | |
| chrysene | 7.9 | 7.5 | ND | | 14.8 | 3.9 | 14.2 | 7.6 | 3.6 | 1.1 | 8.7 | 2.0 | |
| benzo[b]fluoranthene | 19.0 | 20.9 | ND | | 14.4 | 10.0 | 19.1 | 37.4 | ND | | 13.7 | 8.8 | |
| benzo[k]fluoranthene | 5.9 | 4.4 | ND | | ND | | ND | | ND | | ND | | |
| benzo[e]pyrene | 19.2 | 8.7 | ND | | 5.2 | 4.0 | 13.8 | 5.8 | ND | | ND | | |
| benzo[a]pyrene | 14.9 | 10.2 | ND | | 4.7 | 4.8 | ND | | ND | | ND | | |
| indeno[1,2,3- | | | | | | | | | | | | | |
| cd]pyrene | 8.3 | 19.4 | ND | | ND | | ND | | ND | | ND | | |
| benzo[ghi]perylene | 42.7 | 12.0 | ND | | ND | | ND | | ND | | ND | | |
| coronene | ND | | ND | | ND | | ND | | ND | | ND | | |
| ¹ Analyte identification based on comparisons to relative retention times to those in the literature. | | | | | | | | | | | | | |
| 2 ND = not detected | | | | | | | | | | | | | |

Table S3. Ratio of analyte mass (µg) to elemental carbon mass (g) for the MOUDI measurements from HDDVs in the PM0.1 size fraction. Uncertainty values represent analytical uncertainty.



Figure S1. Comparison between collocated MOUDI and RAAS filter measurements for organic compounds emitted from HDVs in the PM1.8 size fraction. Uncertainty bars represent analytical uncertainty. The dashed line represents agreement between MOUDI and filter measurements of total organic compounds.



Figure S2: Comparison of PM1.8 emission factors (μ g analyte / kg fuel burned) measured in the current study with those of Phuleria et al. (2006), Zielinska et al. (2004), Schauer et al. (1999), and Rogge et al. (1993).



Figure S3: PM0.18 emissions factors measured in the current study with and without the MOUDI after filter (AF). Note that PM0.18 is not the definition of ultrafine particles used in the current study (PM0.1). Results measured by Phuleria et al. 2006 are shown for comparison. PAH trends are similar to those shown in Figure S2.

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