Source Profiles for Diesel Trucks and Gasoline Vehicles Determined for the Squirrel Hill Tunnel in Pittsburgh, PA

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ABSTRACT

The Squirrel Hill Tunnel is located on the eastern side of the city of Pittsburgh. This tunnel is a major east-west access road on Interstate-376 carrying both commercial and non-commercial traffic. It is a 4,225 ft long twin-bore tunnel with two lanes in each bore. The twin-bore follows a constant 2.5 percent grade rising from east to west. PM2.5 sampling was conducted in the tunnel's west-bound tube during November of 2002. Furthermore, ambient background samples were collected as well to correct for intrusion of ambient air into the tunnel.

All together more than twenty PM2.5 Filter/PUF sample pairs were collected from the tunnel and nearby ambient sites. These samples were analyzed for: n-alkanes, iso- and anteiso-alkanes, n-alkanoic acids, n-alkenoic acids, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, alkylcyclohexanes, resin acids, levoglucosan, phenolic type compounds, sterols, thiazoles, hopanes, steranes, PAHs, oxy-PAHs, N-hetero-PAHs, S-hetero-PAHs, and others.

Here, the tunnel measurements are corrected for ambient organic compound concentrations. Using information about the type of vehicles entering the tunnel, we determined emission factors for three categories: High-Truck, Low-Speed and High-Speed. This source profiles will be helpful for source/receptor apportionment studies for the Eastern US.

PROBLEM AND APPROACH

Purpose of the Study:

The ability of air quality models to reliably predict contribution from different sources to ambient air pollution levels strongly depends on the quality of the emissions inventory and the source profiles. One approach to determine the source profiles for motor vehicles is to conduct tunnel emission studies. Tunnel studies provide the opportunity to determine the average emission factors considering a large number of vehicles under actual on-road driving conditions in the specific region of interest. In this case, the objective is to characterize the profile of the primary particle-phase organic compounds emitted from motor vehicle traffic for the Pittsburgh area, as part of the Pittsburgh Air Quality Supersite (PAQS).

Approach:
Tunnel and Ambient PM2.5 Sampling

Sampling took place in 2002 during November 12-15 (Tuesday-Friday), and November 18-21 (Monday-Thursday). The average traffic density and fleet composition in the tunnel were determined to be as follows*:

Date	Time Period	Traffic Density (vehicles/hour)	Average Speed (mph)	Average Truck Fraction (Fuel Basis) % fuel	Concentration to Emission Factor Conversion Multiplier	Period Identification Name
Nov. 15	00:00 - 6:00	867	58	29%	10.3	High-Truck (Early Morning)
Nov. 18	00:00 - 6:00	944	56	28%	10.4	High-Truck (Early Morning)
Nov. 19	00:00 - 6:00	923	58	33%	9.3	High-Truck (Early Morning)
Nov. 12	07:00 - 09:00	3,766	30	13%	2.7	Low-Speed (Rush Hour)
Nov. 13	07:00 - 09:00	3,877	29	13%	2.6	Low-Speed (Rush Hour)
Nov. 20	07:00 - 09:00	4,058	29	9%	2.8	Low-Speed (Rush Hour)
Nov. 15	10:00 - 16:30	3,312	48	17%	3.6	High-Speed (Midday)
Nov. 21	10:00 - 16:30	3,152	41	21%	4.8	High-Speed (Midday)

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For tunnel sampling, the PM2.5 sampler was set up above the ceiling of the tunnel at approximately 12 feet above the road and approximately 100 feet from the exit-end of the tunnel. Sampling was performed using a Tisch Environmental, Inc. Model TE-1000 PUF sampler operated at a flow rate of 145 lpm. A PM2.5 cut was obtained with a URG cyclone installed upstream of the Tisch sampler.
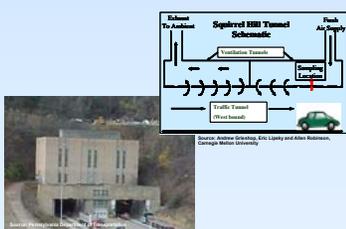
In parallel to the tunnel study, five ambient PM2.5 samples were collected, three at the PAQS central site and two on the roof of the Bussiness Building at Carnegie Mellon University. Ambient samples were 24-hours samples. PM2.5 samples were collected on 4" quartz filters with 3" PUF plugs (Tisch Environmental, Inc.) as backup.

Field blanks at both the tunnel and the ambient locations were also collected and analyzed.

Sample Extraction and Analysis

Filter/PUF pairs were stored in pre-cleaned glass jars and kept frozen at <-23°C until the time of extraction. Just before extraction, each filter was spiked with a known amount of an internal standard mix consisting of a suite of seven perdeuterated n-alkanes (C12, C16, C20, C24, C28, C32 and C36) to correct for losses incurred throughout the analytical procedure. Extraction was performed with dichloromethane using mild ultrasonication for the filters, and a Repeated Compression Extraction Apparatus (RCEA) for the PUFs. Both extracts were combined and rotavaporated to reduce the solvent volume to about 2 ml. The volume was further reduced to ~200µl using a gentle stream of ultrapure N2. The extracts were methylated using freshly prepared diazomethane in order to convert fatty acids to their methyl esters analogs prior to GC/MS analysis.
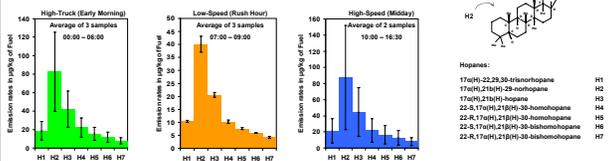
GC/MS analysis of derivatized extracts was carried out on a GC model HP-6890 coupled to a MSD model HP-5973 (Agilent Technologies). The GC was operated in the splitless mode and was equipped with a capillary column DB-5MS. Temperature programming of the GC consisted of the following steps: isothermal at 60°C for 2 min, temperature ramp of 6 °C/min up to 300°C, and isothermal hold for 18 min. The injector temperature was set at 300 °C and the GC/MS interface temperature at 285 °C. Helium was used as carrier gas with a flow rate of 1.2 ml/min. The injected sample volume was 1µl. The MSD was operated in the electron impact mode at 70 eV electron energy, scan range 50-550 amu. The GC/MS data was acquired and processed using a Agilent ChemStation.

Emission Factors for Organic Compounds associated with PM2.5

The concentrations of the 96 organic compounds identified in the PM2.5 of the tunnel samples were corrected by subtracting their ambient concentration levels corresponding to the days when the tunnel samples were collected. These corrected concentrations were then converted to fuel-based emission factors by multiplying the compounds concentrations by the conversion factor reported in the table above. The multipliers to convert concentrations to their equivalent emission factors were calculated for each sample by Grieshop et. al., based on the background-corrected CO_2 and CO concentrations measured in the tunnel, and the carbon fraction in the diesel fuel and gasoline, weighted by the fleet composition.

RESULTS

Emission Profiles for Hopanes at three different Time-periods

Hopanes:
17α(H)-22,29,30-trisnorhopane — H1
17α(H),21β(H)-29-norhopane — H2
17α(H),21β(H)-hopane — H3
22-S,17α(H),21β(H)-30-homohopane — H4
22-R,17α(H),21β(H)-30-homohopane — H5
22-S,17α(H),21β(H)-30-bishomohopane — H6
22-R,17α(H),21β(H)-30-bishomohopane — H7

Of the more than 160 individual organic compounds in our target list, 96 were identified and quantified in the tunnel samples. The Figures here show the emission factors for seven individual hopanes, calculated as an average of the samples collected at each of the time periods considered. Comparing the emission factors profiles for the "High-Truck", "Low-Speed" and "High-Speed" periods, they are very similar. The emission profiles for the steranes for the same three periods show the same trend, and the ratio of total hopanes to total steranes was found to be 1.67 ± 0.07 µg/Kg. Likewise, our findings show that the emission factors profiles for n-alkanes (C19-C32), and n-alkylcyclohexanes (C17-C28), are as well very similar for all three time-periods, as illustrated in the Figures below, indicating that the composition of these organic compounds in the fleet emissions from gasoline and diesel powered vehicles is preserved throughout all driving conditions.

Emission Factors in µg/kg of Fuel
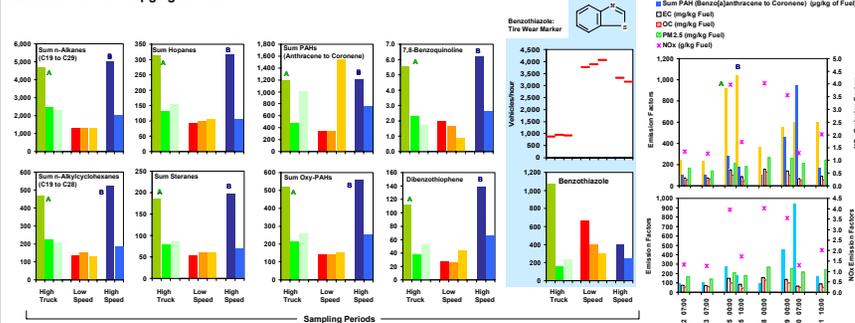
- The profiles for total PAHs and hetero-PAHs differ from the uniform trends followed by n-alkanes, n-alkylcyclohexanes and the vehicular exhaust markers, hopanes and steranes.
- The emission factors for Benzothiazole, a marker recognized in the literature as a tracer for tire-wear, follows the same trend as the number of vehicles per hour, with increasing emissions, as expected, during the "Low-Speed" period. The sample from November 15 00:00-06:00 shows a significantly higher emission factor.
- Emission factors for all organic compounds, for all samples except A and B follow closely the trends of OC, EC, PM2.5 and NOx. Figures on the right show that the sharp increases in emission factors for PAHs and hopanes in the first sample from the "High-Truck" period and the first sample from the "High-Speed" period are attributed to an increase of the emission factors of the lower molecular weight PAHs (anthracene, fluoranthene, pyrene and cyclopentaphenanthrene), rather that the higher molecular weight PAHs (from benzo[a]anthracene, to coronene, sequence is given in the graph in panel below). These sharp increases were observed only on the sampling day November 15. Literature data show that emission factors for hopanes, steranes and PAHs can vary widely depending on specific fleet and operating conditions.

Tunnel Average Emission Factors (µg/kg of Fuel) vs. Ambient Concentrations (ng/m³)
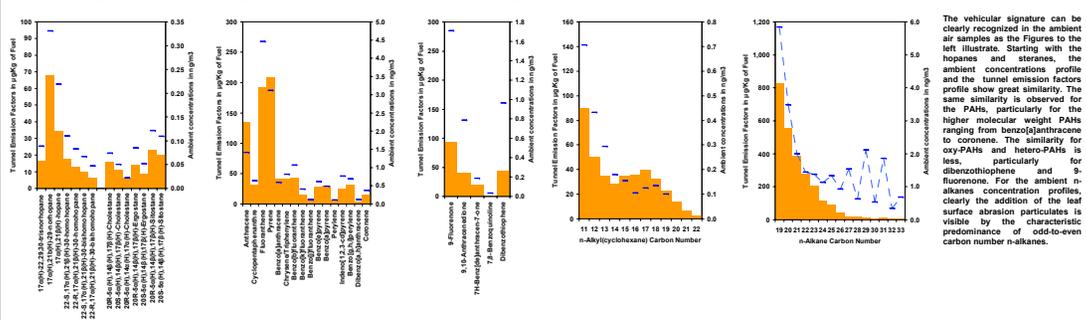
The vehicular signature can be clearly recognized in the ambient air samples as the Figures to the left illustrate. Starting with the hopanes and steranes, the ambient concentrations profile and the tunnel emission factors profile show great similarity. The same similarity is observed for the PAHs, particularly for the higher molecular weight PAHs ranging from benzo[a]anthracene to coronene. The similarity for oxy-PAHs and hetero-PAHs is less, particularly for dibenzothiophene and 9-fluorenone. For the ambient n-alkanes concentration profiles, clearly the addition of the leaf surface abrasion particulates is visible by the characteristic predominance of odd-to-even carbon number n-alkanes.

Emission Rates for PAHs and Oxy-PAHs (µg/kg of Fuel) vs. EC/OC Ratios
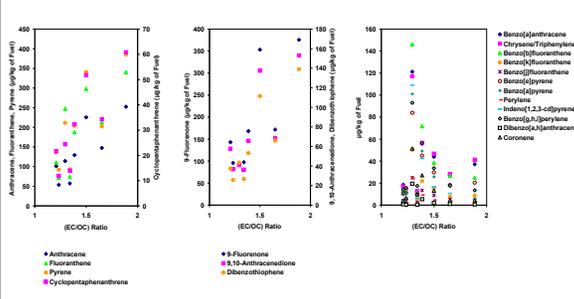
Different correlations among chemical species and PM2.5, OC, and EC were analyzed in order to help identify potential organic compounds which could be used to differentiate gasoline from diesel powered vehicles. The trends identified are illustrated in the Figures above. The lower molecular weight PAHs (anthracene, fluoranthene, pyrene and cyclopentaphenanthrene) show a trend of increasing emission factors with increasing EC/OC ratio. Similarly, oxy-PAHs and hetero-PAHs, particularly dibenzothiophene, also show the same trend. In contrast, the higher molecular weight PAHs (from benzo[a]anthracene to coronene) do not display a clear correlation with the EC/OC ratio. The quality of both trends remains the same irrespectively of whether all the samples are considered together, or samples A, B or both are left out from the statistical evaluation.

CONCLUSIONS

- For the first time, emission factors for vehicular traffic has been determined for the Pittsburgh area. This will help in quantifying the contributions of vehicular PM2.5 emissions to the ambient fine particulate matter burden.

- Irrespectively of traffic density and fleet composition, the emission profiles for n-alkanes, n-alkylcyclohexanes, hopanes and steranes were found to be very similar.

- A trend was found of increasing emission factors for anthracene, fluoranthene, pyrene and cyclopentaphenanthrene with increasing EC/OC ratio. A similar trend was observed for the oxy-PAHs and hetero-PAHs, particularly dibenzothiophene and 9-fluorenone. On the other hand, no apparent correlation was observed between EC/OC ratio and the emission factors for higher molecular weight PAHs: benzo[a]anthracene, chrysene/triphenylene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, dibenzo[a,h]anthracene, and coronene.