GC/MS Biomarker Signatures in Particle Emissions From Stationary and Mobile Sources

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ABSTRACT

One of the goals of the Canadian Atmospheric Fine Particle Research Program is to determine the sources of particles and their relative contributions to atmospheric carbonaceous fine particles. The data from this program will contribute to a database of particle emission rates that will be used in computational atmospheric models to help in determining the contribution of various transportation sources to ambient fine particle levels in Canada. Recent work on quantifying the impact of vehicle emissions to ambient air quality has been focused on using the unique chemical and molecular composition of particle emissions to take advantage of conserved tracers to link particles from source to ambient atmosphere. The potential for using these tracers also known as "biomarkers" to identify the various sources of carbonaceous particles has been recognized. It is in this context that particulate matter (PM) samples (< 2.5µm) were collected from the exhausts of in-use passenger cars and trucks at the BC AirCare Research Facility in Burnaby, British Columbia. Lube oil samples were also collected. In parallel, PM samples were also collected from a residential water heater running with no. 2 fuel oil and a research furnace set up to represent a large utility boiler tested with no. 6 fuel oil. The analysis of these samples is the focus of this work. The PM, lube and fuel oil samples were extracted and fractionated using column chromatography to examine paraffins, biomarkers (hopanes and steranes), PAH's and polars in PM. All non-polar fractions were analyzed by GC/MS for 70 biomarkers, i.e., 38 hopanes and 32 steranes. Chromatographic response factors were obtained for 8 pure hopanes and 6 pure steranes. The response factors of pure R- and S-αβ-homohopane were applied to other R,S-αβ-homohopanes (αβ-homohopane, bis-, tris-, tetra- and pentakis- αβ-homohopanes). The extrapolated response factor used for the other hopanes was obtained by averaging the response factors of 3 selected αβ-hopanes. For steranes, a regression correlating the response factors of the pure steranes as a function of carbon number was calculated. This linear equation was used to extrapolate response factors for the steranes unavailable as pure compounds. Extracted ion chromatograms typical of biomarkers from PM and lube oil fractions demonstrate that the biomarkers analyzed in this work come mainly from the lube oils. In addition, the results show clearly that, for most vehicles used in this study, the biomarker chromatograms from the PM and lube oil samples are nearly identical. Comparison of GC/MS biomarker signatures of lube oil, diesel fuel, no. 2 and no. 6 fuel oils, and their PM are also presented to show that emission profiles of mobile and stationary sources are related.

Vehicle Emission - PM Collection – Lubricating Oils

PM Sample Collection. In-use light duty vehicle emissions testing conducted in September and October of 1999 at the B.C AirCare Research Facility (Burnaby, B.C.). Vehicles selected to represent the model year distribution of the fleet of vehicles subject to the AirCare inspection and maintenance program.

- 75 in-use light duty gasoline vehicles tested on a chassis dynamometer in as-received condition using on-board fuel over 2 repeats of phase 3 of the FTP-75 driving cycle (16.83 min in duration).
- Vehicle emissions collected and diluted using a constant volume sampling (CVS) system commonly used in vehicle emissions studies (CVS: total dilute exhaust volume flow rate of 325 scfm and average dilution ratios were between 5:1 and 20:1).
- $PM_{2.5}$ samples of the dilute exhaust were collected on 90 mm diameter EMFAB filters for semivolatile organic compounds at a flow rate of 91 $Lmin^{-1}$. $PM_{2.5}$ samples were pooled to increase the amount of material in a given sample. Vehicles were grouped according to their $PM_{2.5}$ and organic carbon emission rates (O_{rganic} C_{arbon}/$E_{lemental}$ C_{arbon} data not shown here).
- In some instances a sample corresponds to a single vehicle, other samples correspond to up to 21 vehicles with similar $PM_{2.5}$ and OC emission rates. This strategy was employed to prevent a single high-emitting vehicle from dominating the emission profile of a group of vehicles.

Lubricating Oils. For each of the 75 in-use vehicles tested a 2 mL sample of lubricating oil was extracted from the engine crankcase through the dipstick opening using a Teflon tube connected to a syringe. For PM samples that were composite, a composite oil sample was created by mixing equal weights of the lube oil samples from each of the vehicles in the group.

Furnace PM Sample Collection – Petroleum Products

- Emissions from two stationary combustion sources were collected:
  - An oil fired residential scale hot water heater was operated on a no. 2 light fuel oil.
  - a research flame tunnel furnace was operated on a no. 6 heavy fuel oil (residual fuel oil).
- PM samples collected during continuous operation of the burners. They were diluted using a dilution method being currently developed at CETC-O in Ottawa and applied to stationary sources.
- Configuration of the tunnel furnace used in this work, most closely represents large utility-scale boilers. The research furnace has a high temperature combustion zone with a flue gas temperature of ~400 °C at the sampling point and achieves a nearly complete "char burnout" due to the excess air (20%) and long residence time in the combustion zone. As a result, particle phase carbon emissions are very low in this configuration. Other common installations may have smaller, lower residence time combustion zones with relatively colder walls, resulting in higher PM emission rates.
- The emissions were sampled isokinetically, at one point in the stack. The stack gas was diluted with purified air maintained at 40% relative humidity and at ~20°C. The dilution ratio was constant during sampling, in the range of 20:1 to 60:1. PM_{10} (using an impactor) and $PM_{2.5}$ (using a cyclone) samples were collected from the diluted stack gas. The temperature of the diluted emissions at the sampling point was ~20°C. Teflon coated borosilicate glass fibre filters (Pallflex EMFAB) were used to collect samples for OC speciation. The filters were weighed before and after sample collection to determine the mass of material collected.

Filter Sample Processing

- Sodium sulphate and distilled chromatographic grade acetone, hexane, dichloromethane and methanol used without further purification. Diesel fuel, no. 2 and no. 6 fuel oils from Petro-Canada.
- Silica gel (Aldrich;100-200 mesh, pore size 150 Å, pore 1.2 cm^3/g, and active surface 320 m^2/g), was washed, dried overnight at 110°C, then activated at 250°C for 24 hours prior to use. The silica gel is kept in an oven at that temperature until used.
- Sterane and hopane standards from Chiron Laboratories (Trondheim, Norway).
- PM2.5 filters extracted using a pressurized solvent extractor (ASE 200, DIONEX) after being spiked with appropriate recovery standards.
- Filters extracted sequentially with DCM twice followed by methanol using the following conditions:

  - Cell pressure and temperature: 2000 psi at 100°C
  - Extraction time: 5-min heat up and 5-min static
  - Nitrogen purge at 100 psi for 240 seconds

- DCM extract subjected to solvent exchange to hexane (automated solvent evaporator (Zymark)

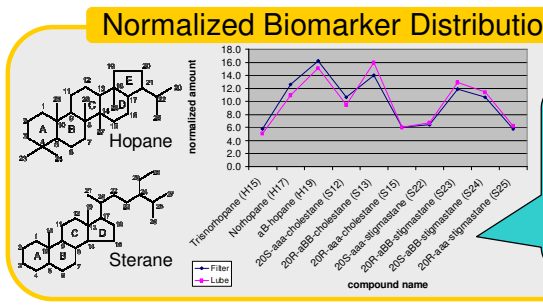
- Chromatographic column separation scheme used: ~5 g of 5% deactivated silica (water added to activated silica).
- Chromatographic column is packed with glass wool, deactivated silica; topped with ~1 g of sodium sulphate.
- Column is pre-cleaned with 15 mL of hexane. Hexane is added to collect paraffins and biomarkers in first fraction.
- Next, column eluted with 15 mL hexane/acetone (50/50) to collect mostly PAH's and some polars.
- Finally, column eluted with two 15 mL aliquots of methanol to collect polars.

Each fraction was concentrated to 1 mL using an automated solvent evaporator. Next, these fractions were concentrated to a preinjection volume of 0.1 mL using nitrogen blowdown in a precalibrated vial or Kuderna-Danish concentrator.

Analysis of Hopanes and Steranes

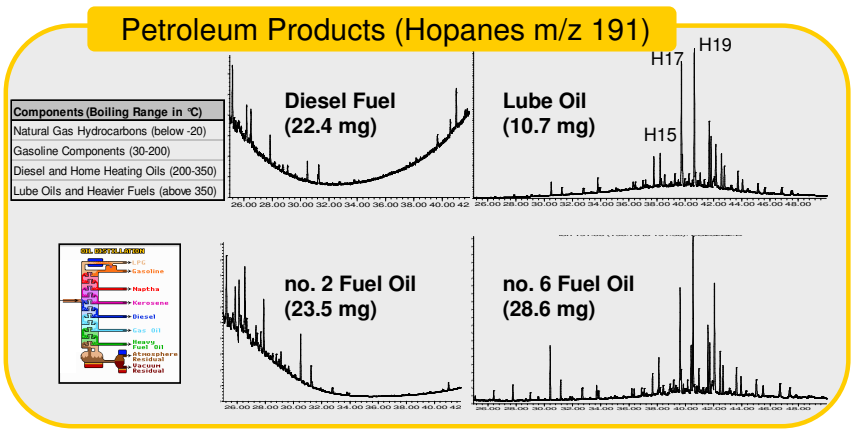
- Analysis performed on a HP6890 GC equipped with a 5972A mass selective detector (MSD).
- System control and data acquisition achieved with Chemstation software
- SP-B5 (5% phenyl methyl siloxane) fused silica capillary column, 30 m x 0.25 mm id (0.25 µm film)
- Chromatographic conditions: carrier gas, helium (1.5 mL min^{-1}); splitless injection; injector & detector @ 275°C & 280°C
- Temperature program used: initial temperature, 50°C, no hold; ramp to 300°C at 6°C min^{-1}; 10 min hold at 300°C
- MSD operated in scan mode to evaluate chromatography and in selected ion mode (SIM) for quantitative analysis of following target ions:
  m/z 191 ion (hopanes) m/z 217/218 ions (steranes)
- Quantitative measurements of 38 hopanes and 32 steranes, achieved using the external standard method. Concentrations determined using peak integration listings from HP Chemstation software as input data for BIOMQUANT, an EXCEL spreadsheet supplemented with Visual Basic code that handles also calibration curves and biomarker assignment.

Normalized Biomarker Distribution in Lube Oil & PM

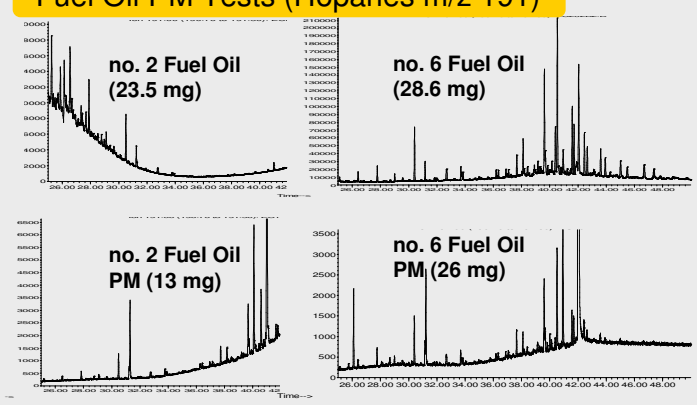


- Mass concentrations of biomarkers of interest vary greatly from one lube oil to the next (not shown).
- However, normalized to the total of the named compounds in each class, the lube oil profile shows remarkable similarities to that of the PM.
- Biomarkers are mostly found in lube oil and not likely to be found in gasoline due to the different boiling ranges.

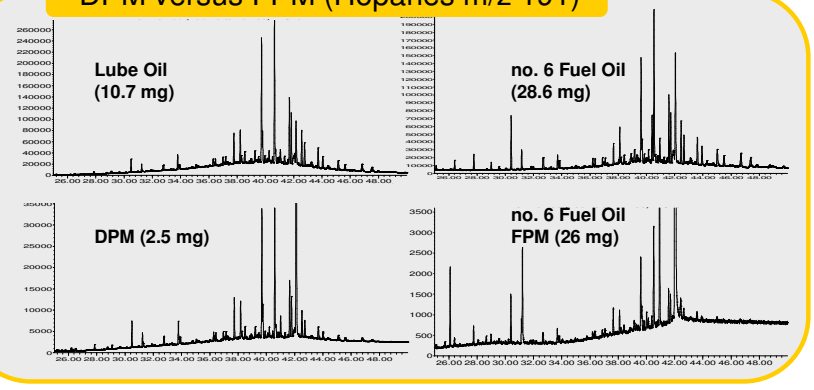
Petroleum Products (Hopanes m/z 191)



Fuel Oil PM Tests (Hopanes m/z 191)



DPM versus FPM (Hopanes m/z 191)



DPM versus FPM (Hopanes m/z 191)

	Sample	
	DPM (01-57)	FPM (no. 6)
PM mass (mg)	2.5	26
αβ- Norhopane [H17] (ug)	0.36	0.006
αβ- Hopane [H19] (ug)	0.36	0.007
Concentration H17 (ug/mg)	0.14	0.0002
Concentration H19 (ug/mg)	0.14	0.0003
ratio FPM/DPM H17		0.0016
ratio FPM/DPM H19		0.0019

- Biomarkers account for only a tiny fraction of the total FPM mass (low OC)
- Characteristics of stationary combustion systems – high temperature, long residence time, excess oxygen for combustion

CONCLUSIONS

- GC/MS analysis expanded to 70 biomarkers (extrapolated GC response factors)
- Similar distribution of biomarkers in GC profiles of PM and lube collected from light duty vehicles in the BCAirCare study; the way biomarkers might be used to separate diesel from gasoline emissions is through the diesel fuel contribution to PM since diesel and gasoline PM emissions will share the same lube oil signatures.
- Lower OC/EC ratio in stationary versus mobile sources because of longer residence time, higher temperature and air-to-fuel ratio resulting in a cleaner burn
- This contrasts with combustion conditions in internal combustion engines: very short residence time, lower temperature and rapid quenching of exhaust gases as they exit the combustion chamber.
- No. 6 fuel oil and lube oil have similar biomarker GC signature; similar observation for no. 2 fuel oil and diesel fuel

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