Semi-Volatile Organic Compounds in Snowmobile Exhaust and in the Snowpack

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ABSTRACT

Two-stroke snowmobiles emit high levels of PM, over 90% of which is classified as organic carbon. Analysis for semi-volatile organic compounds (SVOC) identified 86 species of polynuclear aromatic hydrocarbons (PAH) and 36 species of hopanes and steranes in snowmobile exhaust and in snow taken from the snowmobile trail. Evolution of SVOC deposited to the snowpack is documented for four days following snowmobile activity. Environmental parameters such as ultraviolet radiation, snowpack and ambient air temperature, and the accumulation of new snow over the snowmobile trail were monitored. Species of SVOC found to be the most stable include the hopanes, steranes, and some species of PAH with 5 or 6 aromatic rings. Those found to be the least stabile are typically species with 2 or 3 aromatic rings, and are suspected of loss by volatilization. Additionally, photo-reactive compounds such as anthracene, phenanthrene, or fluorene may be readily photolyzed when exposure to UV radiation remains high. Accumulation of fresh snow over the snowmobile trail isolates contaminants from UV radiation incident on the snow surface and from gas exchange with boundary layer air, effectively reducing the degradation by photolysis and losses by volatilization.

OBJECTIVES

- Speciate SVOC in snowmobile exhaust and snow collected from snowmobile trails. Determine most stabile species and most labile species.
- 2. Monitor environmental parameters likely to influence stability of SVOC in polluted snowpack and correlate with SVOC stability

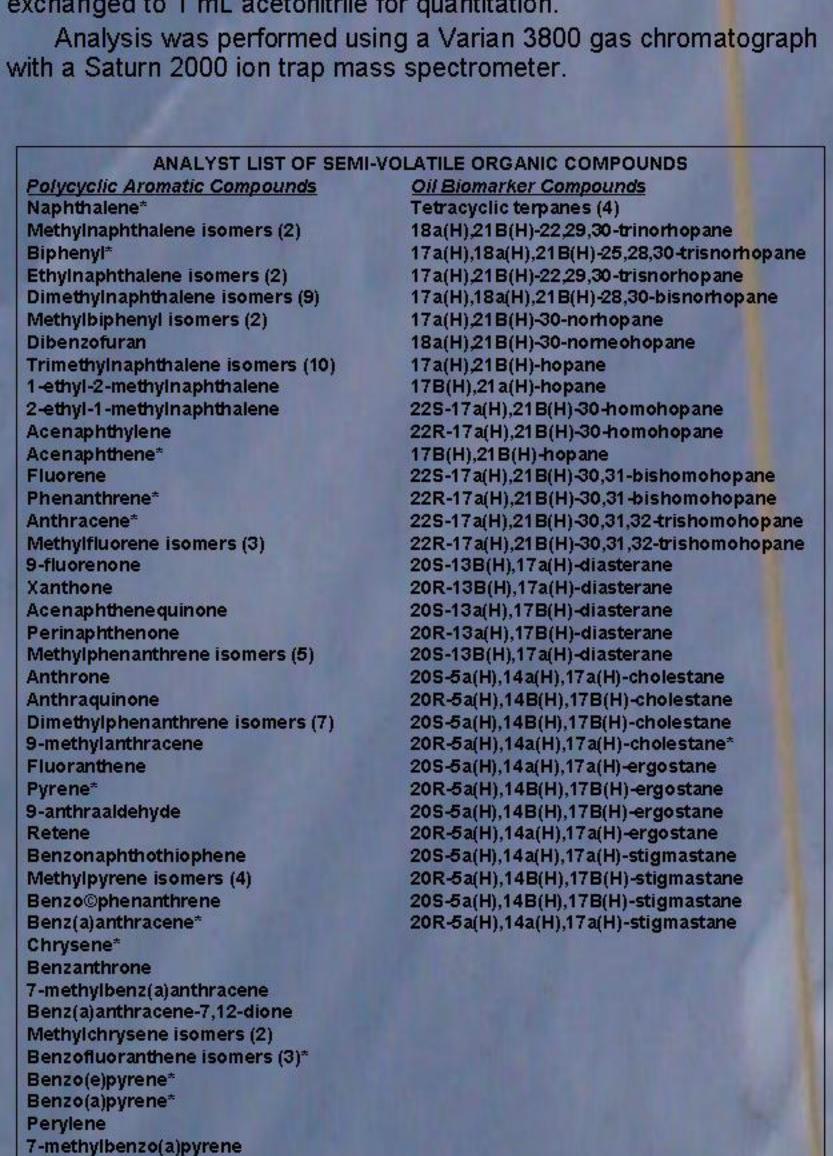
FUTURE RESEARCH

Develop chemical profile for 2-stroke and 4-stroke snowmobile engines to be used with Chemical Mass Balance model in fate and transport study of snowmobile contaminants in watershed.

METHODS

SVOC were collected from snowmobile exhaust on Teflon impregnated glass fiber filters followed by solid phase adsorbent cartridges (polyurethane foam + XAD resin) with a battery powered personal sampler. During sampling, snowmobiles were operated at various speeds and load conditions ranging from idle to 100% throttle. Samples were spiked with a surrogate mixture of deuterated PAH and extracted by Microwave Assisted Extraction (filter and XAD with dichloromethane, PUF with hexane). Extracts were exchanged to 1 mL acetonitrile for quantitation.

Samples of snow from snowmobile trails were collected using a solvent washed metal snow shovel and transported in stainless steel containers. Once melted, SVOC in snow water were extracted with C₁₈ solid phase extraction disks (CPI NuPhase, 100 mm). Disks were eluted sequentially with acetone, dichloromethane, and hexane. Eluted fractions were dried with anhydrous sodium sulfate and exchanged to 1 mL acetonitrile for quantitation.



perdeuterated form added as surrogate for quantitation

9,10-dihydrobenzo(a)pyrene-7(8H)-one

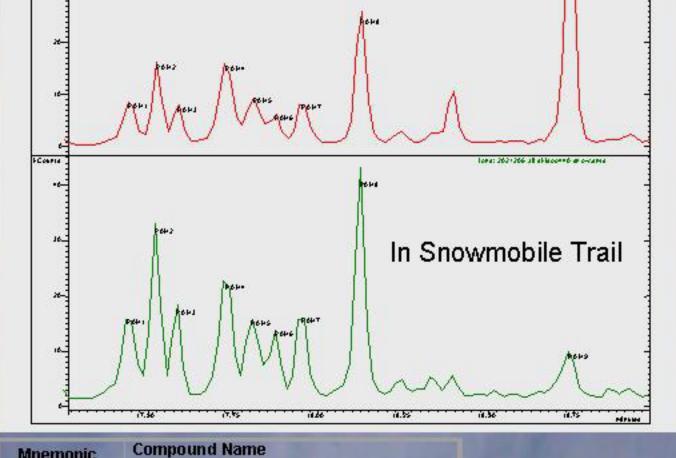
Indeno[123-cd]pyrene

Benzo(ghi)perylene*

Coronene*

Dibenzoanthracene isomers

A) Dimethylphenanthrenes and 202a.m.u. PAH B) 252a.m.u. PAH In Exhaust In Exhaust



3,6-dimethylphenanthrene

C- dimethylphenanthrene isomer

1,7- dimethylphenanthrene isome

D- dimethylphenanthrene isomer

E- dimethylphenanthrene isomer

PAH1

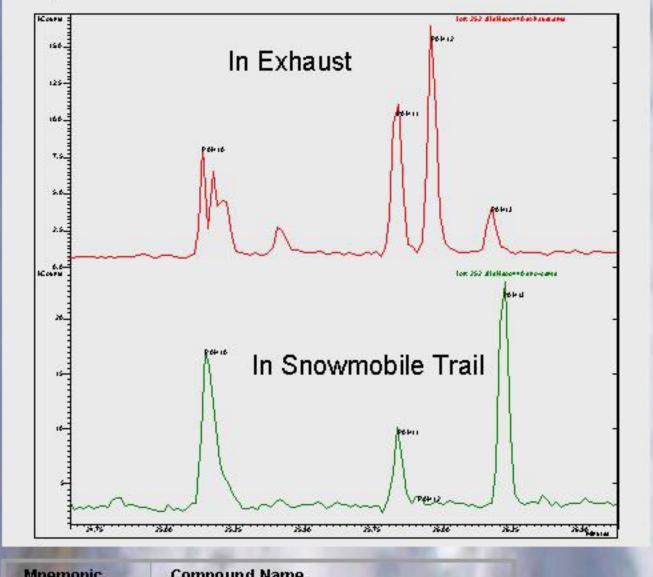
PAH2

РАН3

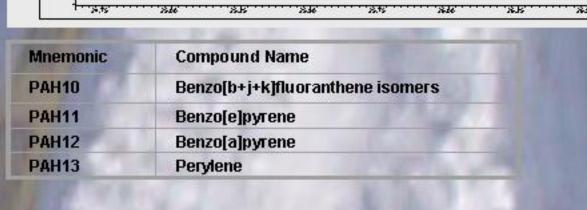
PAH4

PAH5

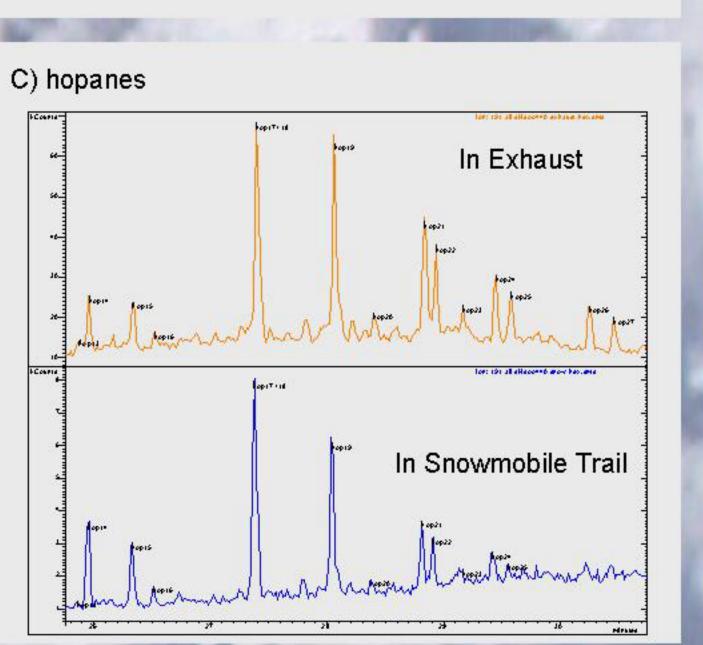
PAH6



SVOC in Exhaust & Snowpack Samples

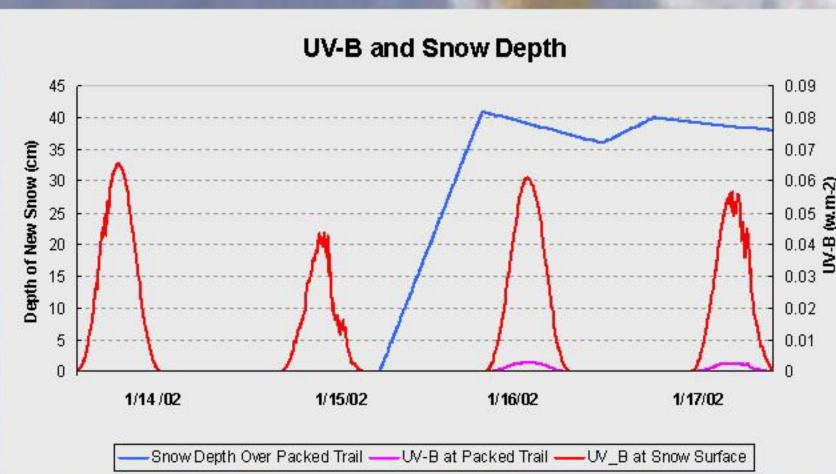


- Chromatograms shown above illustrate the presence of select SVOC both in samples of snowmobile exhaust and in snow taken from the snowmobile's trail.
- Persistent species of SVOC are detected both in exhaust and snow samples at approximately equal relative abundances
- Labile species of SVOC are less abundant or even missing in snow samples.

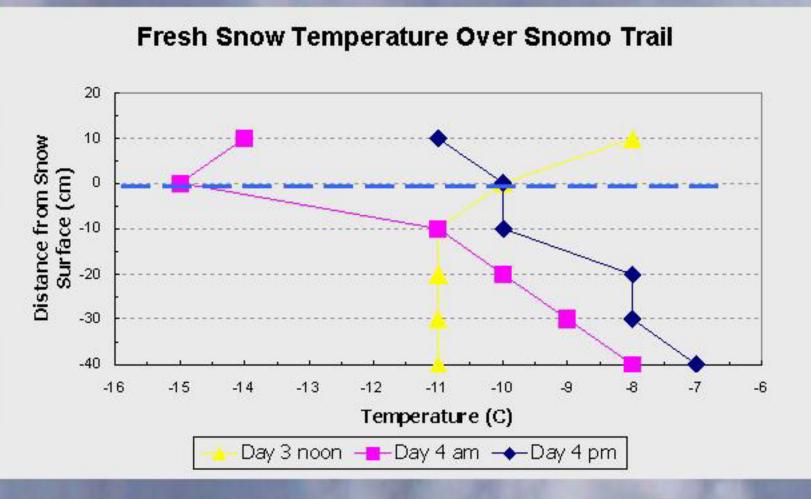


Mnemonic	Compound Name
Hop13	18a(H),21B(H)-22,29,30-Trisnorhopane
Нор14	17a(H),18a(H),218(H)-25,28,30-Trisnorhopane
Hop15	17a(H),21B(H)-22,29,30-Trisnorhopane
Hop16	17a(H),18a(H),218(H)-28,30-Bisnorhopane
Hop17+18	17a(H),21B(H)-30-Norhopane + 18a(H),21B(H)-30-Norneohopane
Нор19	17a(H),21B(H)-Hopane
Hop20	17B(H),21a(H)-hopane
Hop21	22S-17a(H),218(H)-30-Homohopane
Hop22	22R-17a(H),21ß(H)-30-Homohopane
Нор23	17B(H),21B(H)-Hopane
Нор24	22S-17a(H),218(H)-30,31-Bishomohopane
Нор25	22R-17a(H),21B(H)-30,31-Bishomohopane
Нор26	22S-17a(H),21B(H)-30,31,32-Trisomohopane
Hop27	22R-17a(H),218(H)-30,31,32-Trishomohopane

Environmental Conditions and SVOC Stability in Snowpack

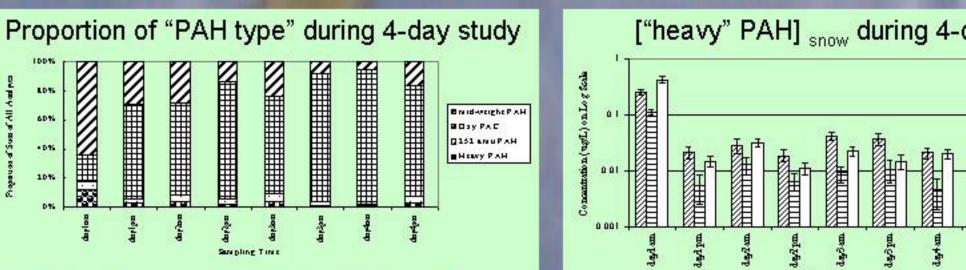


Study Plot

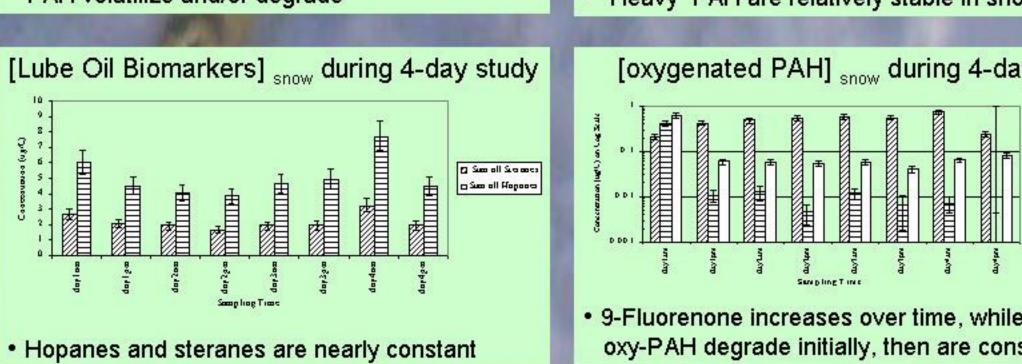


UV-B Irradiance at the surface of the snow and at the depth of the snowmobile trail plotted with snow depth over the packed snowmobile trail.

· 40 cm snowfall event between Jan. 15th and 16th reduced UV-B reduced at polluted layer by 95%

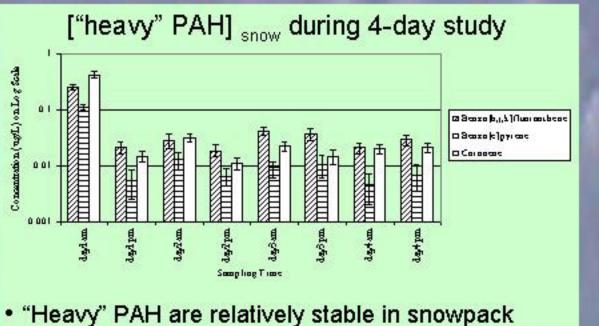


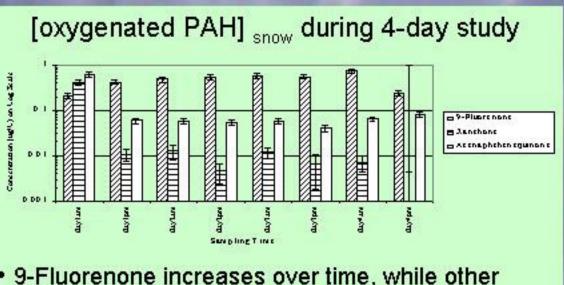
 Oxy-PAH increases in proportion as other PAH volatilize and/or degrade



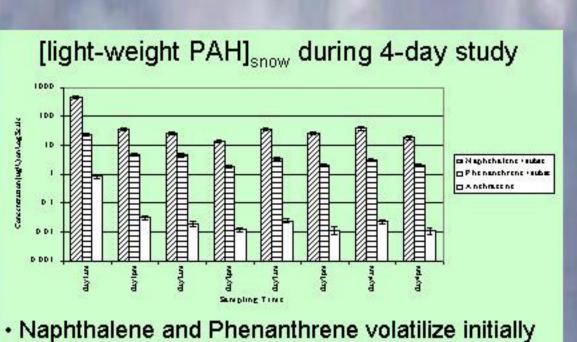
[mid-weight PAH] snow during 4-day study m Plubranchene Pyrene raubae m Chrysene raubae

· mid-weight PAH degrade initially, then remain stable throughout remainder of study





 9-Fluorenone increases over time, while other oxy-PAH degrade initially, then are constant



Anthracene likely degrades

- Immediately following snowfall event, the temperature of the overlaying snow maintained the ambient air temperature from the previous night.
- · By the following day, a temperature gradient in the snowpack developed, with warmer snow near the snow-soil interface and cooler temperatures near the snow-atmosphere interface.

CONCLUSIONS

- Semi-volatile organic compounds present in exhaust of snowmobiles can be deposited to the snow surface in the snowmobile trail
 - Some species of SVOC are more likely to persist in the snow pack, depending on volatility and reactivity of each species
- Environmental conditions can affect the persistence of SVOC in a polluted snow layer
 - Burial of polluted snow layer by fresh snow reduces UV-B irradiance driving photochemical reactions and thereby reduces degradation rates of photo-active compounds
 - Temperature gradients in the snowpack effect air movement in the pack, thereby influencing the distribution of gas-phase molecules, potentially redistributing vapor-phase SVOC by advection with net air movement
- Transformation of PAH to oxygenated-PAH can occur in-situ following deposition to the snow pack
 - irradiated species of PAH may have altered biological activity
- oxygenated-PAH have greater water solubility and therefore higher mobility in spring run-off