



Snowmobile exhaust emissions in the snowpack of Yellowstone National Park
by Jason Douglas Young

A thesis submitted in partial fulfillment Of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

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Analysis of snow samples was performed with a modified version of EPA method 525.2 originally developed for the determination of organic compounds in drinking water by liquid-solid extraction and GC/MS. N-Alkanes C15-22 were detected at concentrations of 0.2-3.7ppm in the snow. Organic Acids C-12,14,16, and 18 were also detected in the snow samples. Three PAH compounds were detected in the snow samples. fluorene and phenanthrene were identified at concentrations of 10-200ppt, and naphthalene was detected at concentrations of 5-25ppb.

Data indicates that contamination is localized to the road with snowmobiles being the primary contributor to hydrocarbon contamination of the snowpack. The concentration of all analytes was observed to decrease rapidly with distance from the road. The concentration of N-Alkanes C15-22 decreased an average of 89% and Organic Acids C-12,14,16, and 18 decreased an average of 90% within 50 feet of the road. PAH concentrations were also noted to decrease with distance from the road.

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Jason Douglas Young

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

The use of snowmobiles within national park boundaries is a source of intense controversy. Exhaust emission levels of two-stroke engines used in snowmobiles are high in comparison to four-stroke engines, with as much as 30% of the fresh air-fuel mixture exiting the cylinder with the exhaust stream. In May of 1997, The Fund for Animals, Biodiversity Legal Foundation, Predator Project, Ecology Center, and five individuals filed suit against the National Park Service for failure to comply with the National Environmental Policy Act (NEPA), the Endangered Species Act (ESA), and other federal laws and regulations in connection with winter use in the three national parks. As a result, many investigations were initiated addressing issues such as air quality, exhaust emission levels in the snowpack due to snowmobiles, and emission reduction methods for snowmobiles. The purpose of this Masters thesis is to determine the levels of snowmobile exhaust products in the West Yellowstone snowpack. This research in combination with other completed and on-going investigations will determine the environmental impact of snowmobiles upon the West Yellowstone ecosystem.

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CHAPTER 1

INTRODUCTION

The use of snowmobiles within national park boundaries is a source of intense controversy. Environmental groups cite the high pollution levels of snowmobiles and a depreciated aesthetic value of the park due to noisy machines as grounds for the banning their use within national park system. Advocates of snowmobile use state that snowmobiles provide a recreational benefit and allow those less physically capable to enjoy the park in winter.

In 1972, President Nixon issued an executive order concerning the use of off-road vehicles on public lands. This order was amended in 1978, and prohibited snowmobiles and other vehicles from off-road activities within National Parks if they “adversely affect the natural, aesthetic, or scenic value”. The National Park Service was also required to monitor the effects of off-road vehicle use. In 1979, it was determined that snowmobiles should be banned from National Parks except in designated areas where their use was considered appropriate [1].

In May of 1997, The Fund for Animals, Biodiversity Legal Foundation, Predator Project, Ecology Center, and five individuals filed suit in the U.S. District Court for the District of Columbia. They accused the National Park Service (NPS) of failure to comply with the National Environmental Policy Act (NEPA), the Endangered Species Act (ESA),

and other federal laws and regulations in connection with winter use in the three national parks [2]. In compliance with the settlement, many investigations were initiated addressing issues such as air quality, contamination levels of the snowpack due to snowmobiles (water quality), and emission reduction methods for snowmobiles. The focus of this Masters thesis is to determine the levels of snowmobile exhaust products in the West Yellowstone snowpack. This research in combination with other completed and on-going investigations will determine the environmental impact of snowmobiles upon the West Yellowstone ecosystem.

In addition, the NPS agreed to prepare a comprehensive environmental impact statement addressing a full range of alternatives for all types of winter use in the parks. The resulting publication "Winter Use Plan Draft Environmental Impact Statement for the Yellowstone and Grand Teton National Parks and John D. Rockefeller, Jr., Memorial Parkway" offers seven possible winter use alternatives. These seven alternatives offer a wide range of options for regulating winter visitation to the parks. While each alternative has its own area of emphasis alternative B is the most comprehensive and is referred to by the National Park System as the preferred alternative. It combines stringent resource protection measures with recreational opportunities for visitors [2]. For a summary of the seven winter use plans see Appendix A.

Environmental Concerns

Snowmobiles use small displacement (400-800cc) two-stroke engines as a power source. Exhaust emission levels of two-stroke engines are high in comparison to the emission levels of modern four-stroke engines. As much as 30% of the fresh air-fuel mixture exits the cylinder with the exhaust stream resulting in very poor fuel economy and high levels of pollution [3]. For every 10 gallons of fuel used by snowmobiles 2-3 gallons are sent directly into the air and snow without combustion. Optimal design solutions for two-stroke engines invariably favor operation with a 'rich' fuel charge resulting in high emission levels.

The EPA is currently establishing emission standards for snowmobiles and all other ATV's using engines rated above 25 horsepower. The basis for this action is that these engines significantly contribute to ozone or carbon monoxide emissions into the environment, and the particulate matter emissions of these engines could cause or contribute to air pollution levels which could endanger public health and welfare. The EPA estimates that snowmobiles and ATV's produce 1.1 million tons of hydrocarbons each year, or about 15% of all hydrocarbons emitted by mobile sources such as automobiles. It is estimated that this impact could increase to 19% by 2010 [1].

Political Aspects

The political side of this issue involves both economic and public interest concerns. To focus on the economics of the issue one must look closely at the small town of West Yellowstone, MT. West Yellowstone is a gateway community to YNP and enjoys a thriving winter economy largely due to snowmobile rentals and services provided to tourists snowmobiling in the park. Between the last week of January and the first week of March 1999 winter visitors to YNP and GTNP were surveyed by the national park service regarding the activities they participated in during their visit to the Greater Yellowstone Area (GYA)[2]. Overall, 61% of respondents reported snowmobiling, 9.8% reported riding a snowcoach, and 24.6% reported cross-country skiing as one of the activities they participated during their visit. Many people participated in a combination of these three activities during their visit. Of those surveyed at the West Entrance to YNP 90.1% of those surveyed reported snowmobiling as a primary activity during their visit to the area. This survey clearly shows the importance of snowmobile-related activities and services to the winter economy of West Yellowstone.

Both economic and public interest issues are an underlying factor in any political decision. Protection of the environment is a strong public interest issue that can often have significant economic implications. A survey by the National Park Service revealed very divided opinions among winter visitors who reside in the GYA. Response to the

1999 winter visitor survey, indicated that 41% favor the existing winter access policy, while 39% would prefer either ski and snowshoe only or ski, snowshoe, and snowcoach access [2]. Regardless of public opinion on this issue there are some very serious environmental concerns associated with snowmobile operation in YNP. The high volume of snowmobile traffic, combined with the high pollution levels of two-stroke engines, sets the stage for significant pollution of Yellowstone National Park.

On April 27, 2000, the National Park Service announced a nationwide ban on snowmobile use within national parks. However, this ban did not include Yellowstone National Park (YNP) or Grand Teton National Park (GTNP) where environmental impact studies are currently underway. The issue of banning snowmobiles in YNP is a highly controversial subject involving environmental, economic, and public interest issues. The result is a highly charged political and emotional environment. The intent of this thesis is to evaluate the situation using scientific methods and present the results in a professional and unbiased manner, providing administrators with solid science upon which to base their decisions about the fate of snowmobiles in West Yellowstone National Park.

CHAPTER 2

BACKGROUND

Snowmobile exhaust emissions are a growing environmental concern in environmentally sensitive areas such as the national park system. Due to the design of conventional two stroke engines the exhaust stream carries much higher levels of pollution than the exhaust stream of a four-stroke motor. This class of internal combustion engine is presently the subject of exhaust emission regulations, which are being developed by the California Air Resources Board and the U.S. Environmental Protection Agency, in accordance with the Clean Air Act Amendments of 1990. Prior to this era, design and development of these engines was motivated predominantly by output power, cost, and durability. As part of an environmental preservation plan for the national park system, snowmobiles will only be allowed to enter the national park system if they meet strict emission and sound standards.

Basic Operation of Internal Combustion Engines

Internal combustion engines produce mechanical power from the chemical energy contained in hydrocarbon fuels. The power producing part of an engines cycle begins with the compression of an air-fuel mixture contained within the cylinder. The air-fuel

mixture is then ignited and expands performing mechanical work on the piston. Almost all internal combustion engines utilize the reciprocating piston in cylinder design. As the piston is forced down the oscillating motion of the piston is converted to rotary motion of the crankshaft, which transmits the engines power as needed. Each upward or downward motion of the piston is called a stroke. There are two commonly used spark-ignited internal combustion engine cycles: the two-stroke cycle and the four-stroke cycle. Both cycles derive their power from the following sequence of events: compression of air-fuel mixture, combustion of compressed air-fuel mixture, and expansion of the burning gases. The fundamental difference between these two cycles is the number of strokes required to complete this sequence.

The four-stroke cycle begins with a downward movement of the piston called the intake stroke, where a fresh charge of air-fuel mixture is drawn through the intake valve and into the cylinder. The compression stroke follows as the upward movement of the piston compresses the air-fuel mixture into the combustion chamber. The air fuel mixture is then ignited and begins the power stroke where expanding gases force the piston downward and create power for the engine. Finally the exhaust stroke clears the cylinder of hot gases by moving upward and forcing the gases out through the exhaust valve.

The two-stroke cycle is a much simpler design. As the piston nears the bottom of the power stroke, the burned gases are forced out of the cylinder by the incoming fresh air-fuel mixture. The air-fuel mixture is compressed by the upward movement of the piston and ignited at the top of the pistons' stroke.

This begins the power stroke and the cycle repeats itself. In a two-stroke engine, the sparkplug fires every time the piston reaches the top of its oscillatory path, in a four-stroke engine the sparkplug fires every other time.

Weaknesses of the Two-stroke Design

Snowmobiles use small displacement (400-800cc) two-stroke engines as a power source. Exhaust emission levels of two-stroke engines are high in comparison to the emission levels of modern four-stroke engines. However, their high power to weight ratio and reliable cold weather performance make them a natural choice for snowmobile applications. The primary reason that two-stroke engines emit higher levels of pollution is the design. The design of the two-stroke engine is very different from that of the four-stroke engine. The two most significant differences are the lack of timed valves and the lack of a dedicated lubrication system.

A two-stroke engine does not have timed intake and exhaust valves to allow the delivery of the fresh air-fuel mixture and evacuation of the exhaust gases. Instead, the exhaust gases are forced out by fresh air-fuel mixture entering the cylinder. This simplicity of design allows the engine to be lighter and cheaper to manufacture however it has severe repercussions in the areas of fuel efficiency and exhaust emission levels. The lack of timed intake and exhaust valves results in an overlap, which allows raw fuel to pass directly from the intake stream into the exhaust stream without combustion. As a result, raw fuel passes out the exhaust manifold directly into the environment. As much as 30% of the fresh air-fuel mixture exits the cylinder with the exhaust stream resulting in

very poor fuel economy and high levels of pollution. For every 10 gallons of fuel used by snowmobiles, 2-3 gallons are sent directly into the air and snow without combustion.

Another key difference is that a two-stroke engine has no contained lubrication system for the cylinder walls. The lack of a lubrication system requires the addition of oil directly into the fuel. Snowmobiles typically operate in a fuel:oil ratio range of 30:1 to 50:1. The lower the fuel number the 'richer' the fuel mixture. This is a huge concern as a large portion of the snowmobiles in the Yellowstone area are rentals. By keeping the fuel mixture 'rich' snowmobile renters protect the cylinder walls with excess oil, which makes the exhaust emissions even worse. As a result the exhaust emissions from a two-stroke motor are a combination of unburned fuel and oil, fuel combustion products, and oil combustion products.

Current Research to Improve Snowmobile Emissions

There are many approaches being tried by the snowmobile industry to make machines that will retain current performance characteristics while producing a more environmentally friendly exhaust stream. The most significant approaches are the use of synthetic or bio-based lubricating oils for existing two-stroke engines, direct injection of fuel into the combustion chamber, and the development of four-stroke engine for snowmobile applications.

Use of Synthetic Fuels and Lubricants

In the winter of 1997-1998 the National Park Service began to use bio-based lubricants in their fleet snowmobiles. The hope was that these biologically based

lubricants would biodegrade more readily in the snowpack. Bio-based fuels and lubricants are a promising alternative that could potentially reduce the damage caused by raw fuel and lubricants entering the snowpack.

The Southwest Research Institute, San Antonio, TX; published a report for the Montana Department of Environmental Quality (DEQ) [4]. This report titled "Emissions from Snowmobile Engines using Bio-Based Fuels and Lubricants", compared the emissions from snowmobile engines using a variety of fuels and lubricants. The focus of this study was to determine the potential emissions benefits of using bio-based fuels and lubricants in snowmobile engines. Candidate fuels and lubricants were evaluated using a fan-cooled 488cc Polaris engine, and liquid-cooled 440cc Artco engine. According to a usage survey conducted by the Montana DEQ, Polaris and Artco snowmobile engines accounted for approximately 81% of the 1400 sled rental fleet in West Yellowstone, MT during the 1995-96 winter season. Fuels tested include a reference gasoline, gasohol (10% Ethanol Blend), and an aliphatic gasoline. Lubricants evaluated include a bio-based lubricant (CONOCO Bio-Synthetic), a fully synthetic lubricant (CASTROL XPS), a high polyisobutylene (PIB) lubricant (TORCO Smokeless), as well as a conventional mineral based lubricant (ARTIC Extreme). Emissions and fuel consumption were measured using a five-mode test cycle that was developed from analysis of snowmobile field operating data. Emissions measured include total hydrocarbons (THC), carbon monoxide (CO), nitrogen oxides (NO_x), carbon dioxide (CO₂), particulate matter (PM), polycyclic aromatic hydrocarbons (PAH both particulate bound and vapor phase), individual hydrocarbon species (C₁-C₁₂ and C₁₃-C₂₂), ammonia (NH₃), and sulfur dioxide (SO₂).

From the experiments it was determined that proper engine setup for temperature and elevation is important. HC, CO, and PM emissions were all significantly increased by richer operation resulting from incorrect setup. It was found that the use of gasohol produced 16% less HC, 9% less CO, and 24% less PM emissions compared to gasoline with a fan-cooled engine. NOx emissions were slightly increased, and engine power was about the same. Lubricant formulation was seen to affect PM emission rates. The high PIB TORCO Smokeless lubricant created significantly less PM than the other three lubricants tested. Particulate emission levels were influenced by lubrication rate, and may also be influenced by the engine cooling system design. It was noted that the fan-cooled engine had significantly higher sparkplug seat temperatures (and by inference, higher cylinder temperatures) and substantially lower PM emissions than the liquid-cooled engine. Other air toxins for the baseline gasoline fuel were present in proportions similar to those observed from other sources such as passenger cars.

The results of this testing protocol show that moderate reductions in emissions can be achieved in the near term through the use of gasohol and low PM lubricants. The most promising candidates from this study were recommended to the National Park Service for further evaluation and a field demonstration in Yellowstone National Park.

Direct Injection Technology

Perhaps the most promising technological advance in two-stroke design is the development of direct fuel injection technology. In February of 1998, Outboard Marine Corporation (OMC) agreed to license proprietary low-emission FICHT fuel injection technology to Polaris industries of Minneapolis, MN. This technology is designed for use

on two-stroke motors. OMC claims that the FFI system provides improved fuel economy, reduced particulate emissions, and reduced hydrocarbon exhaust emissions as much as 80%. The most important feature of the system is that it injects a fuel charge above the cylinder after the exhaust port is closed, preventing raw fuel from exiting through the exhaust system before it has had a chance to combust. The French Institute of Petroleum investigated a similar system known as IAPAC [5]. The Compressed Air Assisted Fuel Injection process introduces the fuel charge separately from the scavenging air in order to minimize fuel 'short-circuiting'. This process provides the advantages of direct injection, but uses conventional low-pressure injection technology with commercially available gasoline injectors. The focus of this research was the reduction of pollutants created by two-stroke outboard engines. When tested on a two-stroke marine engine this system improved fuel consumption 25%, and reduced hydrocarbon emissions by 70 to 90%, while maintaining or improving performance characteristics. While direct injection style technology is not currently in use on snowmobiles it holds great promise for the future of two-stroke motor applications.

Four-stroke Snowmobile Engines

Arctic Cat is the only snowmobile manufacturer currently acknowledging development of a four-stroke motor for snowmobile application. If successful this would greatly reduce the environmental impact of snowmobile exhaust emissions. Arctic Cat provided the rangers of YNP with a prototype four-stroke snowmobile to test under field conditions experienced in YNP. According to park rangers the snowmobile had adequate performance for use as a touring sled within the park. For the winter season of 2000-01

Arctic Cat will provide 50 four-stroke snowmobiles to serve as rentals within the park. Specific emissions information is still considered proprietary information, however Arctic Cat maintains that the improvements over two-stroke emissions will be significant.

PAH and Petroleum Review

The four-stroke internal combustion motors used for automobiles have long been the focus of environmental studies to reduce pollution. Improvements in engine efficiency and the implementation of catalytic converters have greatly reduced the environmental impact of these engines. The demand for improved fuel economy and reduced emissions levels has resulted in improvements in combustion technology through the implementation of multi-port fuel injection and 4-valve per cylinder head designs. Modern internal combustion engines release very little unburned fuel and the primary pollution concerns are PAH and combustion products such as NO_x and CO. By comparison the two-stroke engines used in recreational vehicles such as snowmobiles and personal watercraft are horribly inefficient with as much as 30%^[3] of the fuel supplied to the motor released as raw fuel into the environment. The exhaust stream of a two-stroke motor consists of raw fuel and lubricating oil, fuel and oil combustion products, CO, and PAH.

Petroleum products and PAH are the primary emissions of concern for this literature review. Petroleum products and PAH have an enormous impact on the aquatic environment. When released into the environment many of the compounds contained in these pollutants can have carcinogenic and mutagenic effects.

One of the largest classes of environmental carcinogens known today is the Polycyclic Aromatic Hydrocarbons (PAH). This class of compounds is found throughout the environment in the air, soil, snow, and water. Because they do not dissolve easily in water and generally do not degrade, they can persist in the environment for months to years [6]. In the environment, PAH are found as gaseous phase compounds and adsorbed to particulate matter in the atmosphere. Due to their hydrophobic nature a mixture of PAH released in the water would be expected to adsorb to particulate matter and dissolved organic matter. The degree of sorption depends on the mechanism, which is determined by the identity of the sorbate. The fraction not sorbed would be subject to photolysis and subsequent breakdown. They also tend to bio-accumulate in aquatic organisms, due to their relative non-polarity. Volatilization, biodegradation, and adsorption to particulate matter and sediment are all processes which affect the fate of PAH in water [7],[8].

It is difficult to isolate and analyze PAH in the laboratory, due to the fact that they exist naturally as mixtures of many compounds. It is fairly recently that chemical characterization of sources to PAH emissions was initiated. Reliable analysis of PAH emissions requires instrumentation which has only been available for the last 40-50 years, and even today the quantitative information about PAH emissions from man-made as well as natural sources is limited. A number of analytical methods have been developed and applied to PAH identification and quantification. Foremost among these techniques are gas chromatography / mass spectroscopy (GC/MS), and high performance liquid chromatography (HPLC) with fluorescence detection. The advantage of HPLC lies in the

strong and characteristic absorption by the conjugated systems found in the PAH. Both of these methods have adequate sensitivity and resolution to be used for quantification of trace amounts of PAH in complex environmental matrices, however it is advantageous to employ both methods whenever possible [9].

Sources of PAH Contamination

It is generally agreed that the primary source for PAH is fossil or synthetic fuels and the combustion or high temperature reaction of organic materials. PAH are found naturally in crude oil, creosote, coal tar, and coal. They are also man-made during incomplete combustion of hydrocarbons like coal, oil, gas, tobacco, and during forest fires. To evaluate the sources of PAH contamination in the Chicago metropolitan area, the possibility of fingerprints for specific sources of PAH was investigated [10].

“Although numerous researchers have measured PAH concentrations in ambient air, very few studies link their presence to a specific source. Motor vehicles are thought to be the major source of atmospheric PAH in the United States, accounting for 35% of the yearly total.” The purpose of this research was to determine the chemical composition of major sources of PAH in the Chicago, IL area. Emissions from coke ovens, diesel engines, gasoline engines, and wood combustion were analyzed. On average, the predominant PAH in gasoline exhaust were naphthalene, fluorene, benzo(e)pyrene, acenaphthylene, pyrene, and acenaphthene. Another PAH noted in traffic samples was phenanthrene. Naphthalene accounted for the majority of the mass in coke oven, highway tunnel, and gasoline engine emission samples. Diesel engine and wood combustion samples did not have a significant concentration of naphthalene in their emissions.

A number of studies have focused on the type and quantity of PAH present in the exhaust stream of four-stroke gasoline engines. One such study [11] investigated the PAH emissions from a gasoline-powered engine under a variety of load conditions. This study used two fuels; a 95 octane unleaded gasoline (95-LFG) and a premium leaded gasoline (PLG). The engines were operated under conditions imitating travel at idle, 40, 80, and 110 km/hr, and the concentrations of 21 individual PAH were determined by GC/MS. Prior to testing, background PAH levels were determined in the ambient air. Combustion of the fuel was found to be a generation process for 11 of the PAH and a depletion process for the other 10 PAH quantified. Gasoline was found to be the primary source of PAH in the system. Naphthalene was the most concentrated PAH present accounting for 98.3% of the total liquid phase PAH present in the 95-LFG and 76.6% in the PLG gasoline. Benzo(a) Pyrene, another very important PAH due to its' carcinogenicity, was present at levels of 2.92 and 2.47 $\mu\text{g}/\text{km}$ for the 95-LFG and PLG respectively.

A follow-up study [12], focused on the effects of gasoline additives on PAH emissions. Gasoline additives are generally used to increase the Octane number of the fuel and improve the efficiency of combustion. While these additives help to reduce the emission levels of traditional air pollutants they often contain more aromatics and increase the amount of PAH released. It was found that the additives blended into gasoline contain more of the carcinogenic PAH than the gasoline itself. Two common fuel additives in Taiwan are SA and SB. In both of these additives the mean concentration of benzo(a)pyrene is 785 times greater than in 95-LFG, 92-LFG, and PLG.

These additives also increase the amounts of PAH present in the exhaust stream. PAH analysis was performed using GC/MS in single-ion monitoring mode (SIM). Naphthalene was the greatest contributor to the total PAH measurements. H-H Mi et al recommend that in the future individual additives be evaluated for PAH content and environmental impact before commercialization.

In London, a study was undertaken [13] to determine PAH levels in the air. A roadside site in South Kensington, London was selected and the levels of 18 PAH were monitored. Traffic on this road is considered moderate (1500-1700 motor vehicles per hour), with the majority of traffic consisting of light-duty motor vehicles. Collection of particulate PAH was performed by filtration with a low-volume sampler using 47mm PTFE filters. Extraction of the analytes was performed using a Soxhlet apparatus with dichloromethane as the solvent. Five of the measured PAH: Phenanthrene, Fluoranthene, Pyrene, Benzo(c)phenanthrene, and Benzo(b)naphtho(1,2-d)-thiophene accounted for 70% of the average total PAH. Brown et al, discussed an increase in PAH emissions which has been noted from 1987 to 1991 in the UK. This increase is believed to be a result of replacing leaded fuels with unleaded fuels containing higher quantities of PAH. Subsequently a decrease in total PAH levels in the US since 1986 has been correlated with the use of catalytic converters. PAH usually exist in the exhaust stream adsorbed to particulate matter (PM) or in the gas phase.

A similar study by the Denmark Department of Environmental Science and Technology [14], addressed the presence of particulate PAH in the air of a busy street in central Copenhagen and in a nearby park. The PAH concentration was also determined

for the air of a street containing only diesel busses. Benzo(e)pyrene was used as an indicator for traffic contribution to total PAH. Samples were taken with a conventional Hi-Vol air sampler using glass fiber filters. Extraction of the filters was accomplished by sonication in dichloromethane and samples were analyzed by HPLC. In the street traffic was found to provide the majority of PAH pollution, 90% on working days and 60% on weekends. A profile for PAH originating from traffic sources was determined. In the park traffic sources provided a serious contribution to the total PAH, but the majority of the PAH were contributed by other sources. The street experiencing only bus traffic had considerably lower PAH levels, however no comparison of traffic volume was made.

Engine type is obviously a key factor in the emission levels of PAH. The fuel required and the operating systems of two-cycle and four-cycle engines are different so naturally different emissions would be expected. While automotive engines have long been the target of environmental scrutiny, very few studies have focused on PAH levels in two-stroke engine emissions. This is probably due to the fact that most research concerning the polluting effects of internal combustion motors has focused on four-stroke and diesel designs used in automobiles. Until recently the environmental impacts of two-stroke motors used in snowmobiles and other recreational vehicles has not been a topic of concern. The Southwest Research Institute, San Antonio, TX, published a report on snowmobile exhaust emissions for the Montana Department of Environmental Quality (DEQ)[4]. This report focused on emissions improvements through the use of bio-based fuels and lubricants. PAH emissions were present in significant levels in both the vapor phase and solid phase. Solid phase samples accounted for 61% of the total PAH and

vapor phase accounted for 39%. Total PAH emissions were reported as "high, as would be expected from engines with high total hydrocarbon emissions". PAH reported were: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, 1-Nitropyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(e)pyrene, Indeno(1,2,3-cd)pyrene, Dibenzo(ah)anthracene, and Benzo(ghi)perylene. It was noted that total PAH emissions were significantly reduced with the use of gasohol.

One PAH found in exhaust emissions is Naphthalene. Naphthalene is an important hydrocarbon raw material used in the manufacture of celluloid and hydro-naphthalene (used in lubricants), and of motor fuels. A review of the available literature indicated that naphthalene, when measured, is often the highest percentage of total PAH in gasoline engine emissions and raw gasoline [11]. However, the report by White and Carroll indicated naphthalene as only a minor contributor to the total PAH in snowmobile emissions. These results are contradictory to the expected outcome. Because snowmobiles emit large quantities of unburned fuel, containing high levels of naphthalene, it was expected that naphthalene emissions would be high. When contacted Mr. White agreed that his data seemed inconsistent with other reports on naphthalene levels in gasoline and suggested several possibilities. He noted that automotive research performed at the Southwest Research Institute verified that naphthalene is a substantial component of the total PAH concentration in automotive exhaust. However, the list of species analyzed for automotive exhaust was not as extensive as in the snowmobile analysis. Mr. White agreed that the naphthalene numbers seemed low in the snowmobile

analysis and explained that there tends to be a lot of variability in reported values of naphthalene. Unfortunately, Mr. White was unable to find any other two-stroke data to compare with the snowmobile data. Mr. White mentioned that the Southwest research institute is currently working on a project for CARB, which will evaluate PAH levels in the emissions of two-stroke outboard motors (Personal Communication July 12, 2000, Appendix B). Results of this research could be of interest for future literary reviews.

PAH and Hydrocarbons present in precipitation

Various studies have shown that precipitation (i.e. rain, snow, and fog) has the ability to scavenge hydrophobic organic compounds and PAH from the atmosphere. In southern California, a study of PAH and n-alkanes in rural and urban areas [15], evaluated rain and snow samples. Samples were studied for solvent extractable compounds including n-alkanes, PAH, and hydrocarbon mixtures. Urban samples taken in the Los Angeles area exhibited a large Unresolved Hydrocarbon Mixture (UCM) weakly present or absent in the rural snow samples. The UCM hump is attributed to incompletely combusted hydrocarbons from automotive traffic. PAH were present in all samples however, concentrations were much higher in urban samples. Phenanthrene, Fluoranthene, and Pyrene were identified as the major contributors to total PAH. These PAH are commonly seen in analysis of auto-exhausts, urban runoff, and coastal sediments. Straight chain alkanes C-17 to C-35 were identified in both urban and rural samples. Urban samples expressed a low Carbon Preference Index (CPI) ranging from 1.4 to 3.0 which is characteristic of petroleum hydrocarbons. In contrast, rural samples expressed a CPI ranging from 3.5 to 13.0. Kawamura and Kaplan explain that similar

results have been reported in studies of rural aerosols and rainwater, and the n-alkanes in rural samples are likely due to plants. Similar findings were reported [16] in a study of mid-west rain and snow samples. Samples were collected in a semi-rural region of Indiana. Straight chain fatty acids C12-28 and n-alkanes C23-31 from biological sources were reported as the dominant compounds.

In Switzerland the presence of PAH and aliphatic hydrocarbon species in rain, snow, and fog samples was investigated [17]. During the summer months it was found that samples contained a series of odd numbered n-alkanes resulting in a high CPI (7.1 in summer compared with 2.1 in winter) indicating dominance by biogenic sources. In winter months n-alkane contamination was primarily due to residential combustion of oil, which is the primary source of heat for this area. Snow samples were collected on a glass sheet and melted immediately for processing in a rain sampling device. Sixteen PAH were identified by mass spectra and GC retention time. PAH concentration was found to vary slightly with collection source: fog > snow ~ winter rain > spring rain > summer rain. The level of PAH pollution varied between seasonal rain with a ratio of 5:2:1 (winter:spring:summer). However, the types of PAH collected were consistent between seasons indicating similar sources and scavenging mechanisms. The high PAH levels during winter months emphasize the importance of heating oil contribution to PAH pollution.

In Finland, snow samples and moss bags were used to determine the level of airborne pollutants at varying distances from a highway [18]. PAH were determined from snow samples taken during the winter at distances of 10, 30, 60, and 100m from the

east and west sides of the road. In the summer, moss bags containing 20g of fresh red-stemmed feathered moss were placed at the same sites. The deposition of organic pollutants from road traffic was observed up to 60m from the road. Viskari et al noted that snow is a good collector of inorganic pollutants from traffic and can be used as a 'passive' collector of organic pollutant loads from traffic. For monitoring PAH the moss bags were more effective indicating that vegetation may be an important sink for PAH produced by traffic. Snow samples were melted at room temperature and analytes were extracted by liquid-liquid extraction using hexane in a separatory funnel. Analysis was performed by HPLC equipped with a Fluorescence detector. Thirteen PAH were identified by retention time and quantification was achieved by comparison of fluorescence response with standards of known concentration. Moss samples were extracted for 16h with dichloromethane by Soxhlet extraction, and sample volume reduction was achieved with rotary evaporation. The majority of the pollutants in the snow were present within 30m of the road. The most prominent PAH in the snow samples were Fluorene, Phenanthrene, Anthracene, Chrysene, and Pyrene. Viskari et al suggest that future research should combine snow sampling with other technique such as moss bags. Also addressed is the fact that as traffic loads increase more attention must be paid to the roadside ecosystems, which are acutely effected.

Contamination of the Aquatic Environment

The accumulation of PAH in the snowpack of highly polluted urban areas and busy highways is a source of concern for the local aquatic ecosystem. A discussion on fates of PAH in the environment [19] states that atmospheric-formed hydrophobic PAH

are mainly adsorbed on aerosol particles smaller than 10 μ m. These aerosol particles then act as condensation nuclei during the formation of snow crystals in clouds, and are scavenged to the ground by snowfall. Lacking knowledge of particle distribution within the snow crystal, it is assumed that PAH are concentrated at the center of the crystal. In shallow snowpacks, PAH are released with the first melt. However, in deep snowpacks, PAH are retained and condensed allowing for a large release during the major spring melt. The issue of PAH accumulation in the snowpack of an urban area of Canada was investigated [8], and focused on a large steel mill as the point source for PAH contamination in the area. While narrow band contamination as seen from traffic sources was not addressed, some important properties and behaviors of PAH in the snowpack were discussed. Boom and Marsalek assert that the accumulations of PAH in urban snowpacks provide a good preliminary indication of PAH deposition from diffuse sources and could possibly be used to estimate annual depositions of PAH for a given sampling site. They reported that no information was available on PAH losses in the snowpack. Boom and Marsalek referenced a study by Versar et al (Versar,1979), stating that processes important for degradation of PAH in the aquatic ecosystem, such as photolysis, do not occur or are severely impeded in the snowpack. This would indicate that as the snowpack melts, accumulated PAH would be suddenly released into the local aquatic environment. This may or may not be a problem depending on local geography and associated contamination levels.

A small lake near Oslo, Norway was studied to determine the effects of highway runoff on the local aquatic environment [20]. As 95% of the drinking water in Norway is

provided by surface water, it is important to evaluate all potential sources of pollution to the aquatic environment. Prior to the construction of a 4-lane highway nearby, Lake Padderudvann was a drinking water source. As part of this study, water samples for inlets and outlets, winter snow samples, and lake sediment samples were analyzed. Snow samples were collected with plexi-glass snow core devices 8 cm in diameter. PAH were removed by liquid-liquid extraction and analyzed using gas chromatography with a glass capillary column. The majority of pollutants were found to be concentrated in the snow immediately beside the road, degrading to less than 1/5 within 13m of the road. PAH levels were quite high (12.23ppb total PAH) within 50m of the road, but degraded to levels indistinguishable from background at 150m. Some of the heavier and more carcinogenic PAH (i.e. benzo(a),(e)pyrene) were not detected at distances greater than 50m from the road. In summary, a considerable amount of PAH accumulate in the snowpack within 5 m of the road and some are transported by air as much as 300m from the roadway. The level of PAH and other organic pollutants are high during the spring melt. A study of lake sediment samples revealed that most of the PAH entering the lake are retained by the soil. In an adsorption study, PAH were passed through 8cm samples of soil to determine an adsorption profile for different soil types. The soil with the lowest organic content (least effective for retaining PAH) retained all but 8% of the PAH, and rich forest soil retained 99% of the PAH. It was concluded that runoff from the highway is highly polluted however the lake acts as an effective biological sink for the PAH and prevents their escape in the lakes' out-flowing streams.

Accumulation of Contaminants in Aquatic Species

As discussed by Gjessing et al., [20] PAH are readily adsorbed into aquatic sediments and Viskari et al. [18] addressed the affinity of PAH for moss and possibly other types of vegetation. Strong presence of PAH in the aquatic ecosystem suggest that they would naturally find their way up the food chain. In Maine, USA, the brook trout of a small pond were examined to determine the impact of snowmobile emissions on the local aquatic species [21]. In the week following the spring melt and clearing of ice from the pond surface, fingerling brook trout that had been held in fish cages were examined. Prior to snowmobiling, hydrocarbon levels were undetectable in fish tissues. During ice-out hydrocarbon levels in the water reached as much as 10ppm and hydrocarbon levels in tissues of the exposed fish were 1 ppm. Snowmobile exposure of the pond was determined to be equivalent to one snowmobile burning approximately 250 liters of fuel and operating on a .405 hectare pond with an average depth of 1m. In France, the PAH levels in whole gall bladders and liver of several fish species in the Natural Reserve of Camargue were investigated [22]. It was noted that fish are known to rapidly metabolize PAH to intermediates, which either bind to liver DNA or form conjugates, which then pass into the bile. The composition and concentration of PAH metabolites in fish whole gall bladder would thus be expected to indicate the extent of exposure. Whole gall bladders and livers were collected from eels, goldfish, and catfish. These species were chosen as they are the most abundant and have different feeding habits, which would indicate different sources of PAH deposition. In whole gall bladder the most abundant PAH found were phenanthrene, naphthalene, and fluorene. In liver phenanthrene is

dominant, however in eel livers, naphthalene, anthracene, fluoranthene, and benzo(a)anthracene is also abundant. No significant differences were observed in PAH levels in fish captured at different sites, but variation between species was significant. Because catfish, eels, and goldfish are divergent evolutionarily it is not surprising that their biliary PAH compositions are different. The size of a fishes liver was compared to its age and body weight in order to estimate the life long exposure of a particular fish to PAH. A larger liver to body weight ratio would indicate an elevated level of PAH and pollutant exposure. The subject of PAH toxicity was not addressed in this article.

A study on the British coast investigated the presence of PAH residues in the eggs of coastal-nesting birds [23]. Seabirds and coastal species are vulnerable to exposure to crude oil released into the marine environment. The oiling of adult birds and eggs can have adverse effects on egg structure and quality. For example, a study referenced by Shore et al. showed that 2% southern Louisiana crude incorporated into the diet of an adult mallard hen caused significant reductions in the size and weight of the eggs, lighter shells, and less yolk. Direct contact of micro-liter amounts of crude with the eggshell can also prove toxic to the developing embryo or cause developmental abnormalities. Shore et al attribute the toxicity of the crude to PAH present. The eggs of four species of coastal birds were analyzed for PAH to determine whether there was contamination from a nearby oil spill. Although no evidence was found of elevated hydrocarbon or PAH levels in eggs near the incident, the study provided good background on PAH levels in eggs. Naphthalene and fluorene were the two most abundant PAH present. There was little

evidence of species-specific patterns of PAH contamination, however the overall PAH levels varied widely between the different species of bird.

Toxicity

PAH have been in the spotlight with respect to cancer and other human and animal health concerns for some time. In a supplementary article of Pathophysiology, Rita Schoeny, Health and Environmental Criteria Division, EPA, explains human risk assessment procedures for PAH. She states " Human health risk assessment at the US EPA follows published guidelines. Those used in assessment of PAH are Complex Environmental Mixtures and Carcinogens, which are being revised to reflect the current state of science. Revised hazard characterizations for individual PAH and for mixture containing PAH indicate that these materials should be treated as though they are known human carcinogens". Studies of the carcinogenic potential of PAH on humans often focus on Benzo(a)pyrene (BaP). Potency factors of many PAH species are calculated by comparison to BaP for oral cancer.

A comparison of the use of toxic equivalency factors and the "classical BaP approach" was performed [24], to address the risk associated with airborne PAH mixtures in the work environment. Due to it's high carcinogenic potential, BaP levels are traditionally used to estimate the level of human exposure and risk due to airborne PAH. It was noted that a significantly higher incidence of lung cancer is present in employees of steel mills, coke plants, and gasworks facilities. Air samples were taken in these three work environments in an attempt to identify individual PAH with carcinogenic potential, and determine the relative risk factor due to BaP. It was determined that while other

carcinogenic PAH were present, the carcinogenic potency of BaP alone was in the range of 27-67% of total carcinogenic potential, confirming the importance of BaP as a surrogate compound in airborne PAH measurements used to determine the risk associated with human exposure.

A study by Li et al investigated the relationship between PAH present in diesel exhaust and the binding of dioxin receptor ligands. Polycyclic Aromatic Compounds (PAC) are noted to have the ability to increase their own metabolism. The binding of ligands by the dioxin receptors results in an activation process where it dimerizes with a protein. The dimer then interacts with specific DNA sequences and alters the transcription rates of target genes. This results in an increased rate of PAC metabolism. "Metabolic activation of these compounds (PAC) in mammalian tissues leads to more chemically reactive species and constitutes a key step in the events leading to carcinogenicity and genotoxicity." Dioxin receptor binding has also been associated with the initiation of a variety of toxic effects including teratogenesis, tumor promotion, and cellular hyperplasia. The interaction of PAH with DNA is a serious concern for humans and animals alike. Mathieu et al. reported the detection of PAH-DNA adducts in the brain and liver tissues of arctic Beluga Whales. The relative abundance of PAH contaminants in the environment is a source of concern and more studies are needed to evaluate the potential danger of these contaminants to humans and the environment.

While many PAH in their natural state are suspected carcinogens, there is other research which targets the mutagenic and carcinogenic properties of PAH metabolites and oxidation products. PAH are subject to several degradation pathways in the aquatic

environment. The most important of these degradation processes are photo-oxidation, chemical oxidation, and biological transformation by bacteria, fungi, and animals [7]. One study [25], focused on the photo-induced toxicity of PAH to macro-invertebrates in the aquatic environment. It was determined that the toxicity of anthracene and fluoranthene in water and sediment samples increased with exposure to UV light. The photo-induced toxicity of these PAH were directly influenced by the concentration of PAH and the level of UV exposure. A similar study [26] addressed the effects of UV-B light and PAH exposure on sea urchin development and bacterial bioluminescence. Arrested development of proliferating sea urchin cells was observed and bacterial bioluminescence was decreased. PAH and UV light have been demonstrated to have additive or greater than additive toxicological effects in aquatic organisms in freshwater systems. It is suggested that UV light enhances the toxicity of PAH through the production of free-radical oxygen molecules, which deplete cell protection membranes.

A similar toxicity pathway is seen in a study on Naphthalene induced oxidative stress. It was concluded that "naphthalene may induce toxic manifestations by enhanced production of oxygen free radicals, resulting in lipid peroxidation and DNA damage" [27]. Concerns also exist with the bio-activation of naphthalene by the human liver [28]. The toxicity of naphthalene is suggested to be dependent upon the bio-activation of 1-naphthol. Data indicates that the genotoxicity of naphthalene is associated with the formation of quinones from 1-naphthol rather than naphthalene-1,2-epoxide, the primary metabolite of naphthalene.

Summary

As evident from this literature review, PAH and hydrocarbons are abundant environmental contaminants present in plant life, sediments and the aquatic environment. The ability of precipitation (i.e. rain, snow, etc.) to scavenge additional hydrocarbons and PAH from the atmosphere results in global contamination via long range transport [29].

The majority of literature addresses PAH contamination in the environment. While some studies address the presence of n-alkanes, and fatty acids in snow, most attribute the primary reason for their presence to biogenic sources [16]. Literature concerning hydrocarbon contamination in the marine environment focuses on anthropogenic sources, however studies primarily concentrate on the effects of large-scale contamination (i.e. oil spills) and literature on trace level contamination was difficult to find.

A wide variety of publications are available concerning PAH as an environmental contaminant. Several publications concerning PAH contamination in the air of urban areas were reviewed [13] [14]. Of great interest to this review were publications concerning PAH deposition in the snowpack near highways [18] [17] [20], and the fate of PAH after entering the snowpack [8]. The affinity of PAH for vegetation in both the terrestrial and aquatic environment [18] is a great source of concern as these are direct pathways to human and animal ingestion.

Another key area of concern is the retention of PAH by aquatic sediments [20] and vegetation. The effects on aquatic life are immediate and there is an ever-increasing potential for bioaccumulation. There is a consensus in the literature that PAH are potential carcinogens and require further investigation and possibly regulation.

CHAPTER 3

FIELD SAMPLING METHOD

Sample Collection

Finding an appropriate sampling protocol turned out to be one of the most challenging tasks. The initial focus was to measure deposition and degradation of snowmobile emissions in the snow pack. This approach consisted of aerosol studies, snow samples, and snow columns doped with lubricating oils and snowmobile exhaust.

As with all environmental sampling, contamination was a key concern and great measures were taken in an attempt to reduce and eliminate sources of potential contamination. Initially we were concerned about three general areas of sample contamination, namely equipment, containers, and handling. All equipment and containers were cleaned thoroughly, as specified in the following sections, in order to reduce sample contamination. To avoid human contamination, polyethylene gloves were worn at all times during sample collection and handling. Care was taken during sample collection not to lean over or otherwise potentially contaminate the sample area.

Field Sampling Method (Spring 1999)

For the first season (Spring 1999), samples were taken from the various layers of snow at the West Yellowstone Entrance Gate approximately 25ft from the road. As a reference, snow samples were taken in an undisturbed location near the Tower Ranger Station where no snowmobile activity is permitted. These samples were taken in order to establish background values of any possible contaminants present in Yellowstone National Park. Air samples were collected by filtration at both the Tower Ranger Station and the West Yellowstone Entrance. Snow columns were doped with exhaust products and lubricants, then placed in an undisturbed location near the Tower Ranger Station.

Snow Sampling

Snowpits were dug in the shape of a trench and samples were taken from the snow at each existing layer. When layers were greater than 3" in depth a sample was taken every 3-4". Samples were placed in pre-rinsed (3 times with DI water and then ethanol) and dried 1 gallon polyethylene bags with zip-sealable tops. When melted, each bag yielded approximately 1 liter of water. Prior to using the bags to contain samples, a test was performed to determine whether the bags would contaminate the samples.

Initially the concern was that as the snow melted it would run down the sides of the bag, absorbing the extrusion lubricants and phthalate ester plasticizers present on the surface of the bags, before dripping into the amber glass bottle used to contain the melt. In order to determine the maximum amount of contamination that would result from water contacting the sides of the bag, a polyethylene bag containing nano-pure water was

placed at room temperature for 72 hours. The amount of contact between the liquid water and the surface of the bag was greatly exaggerated in this test. The water was then extracted per EPA method 525.2, a method developed for the analysis of organic compounds in drinking water, and analyzed using GC/MS. Upon analysis no contaminants were detected.

Upon analysis of the snow samples from the west gate and Tower ranger station we found that the samples were heavily contaminated with stearamids, used as extrusion lubricants for the plastic bags (Figures #1-4).

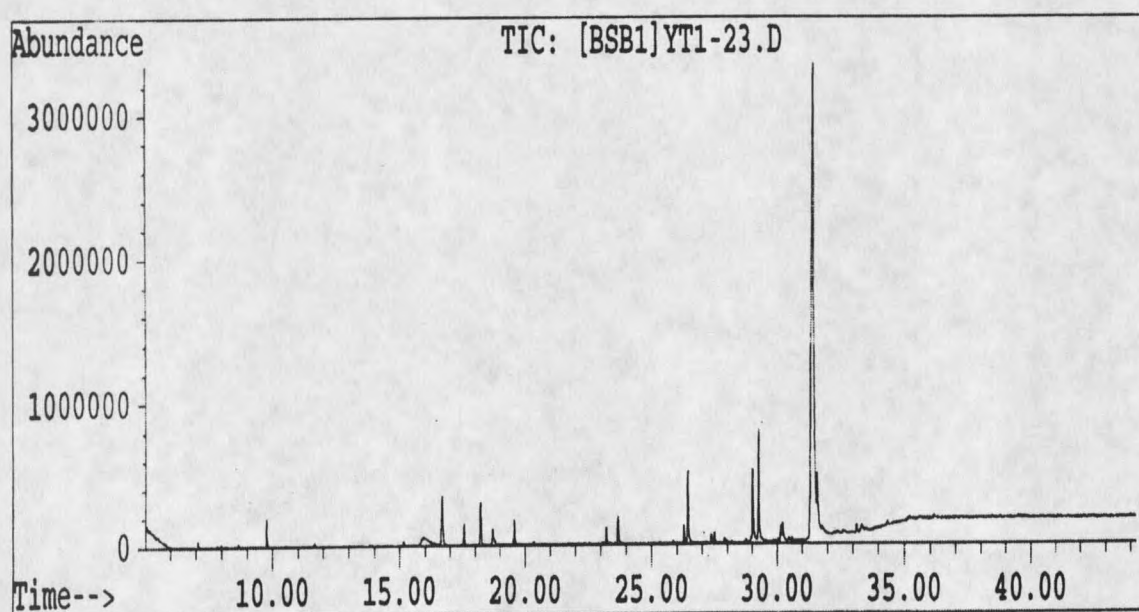


Figure 1. Snow sample taken at the Tower Ranger Station 1-23-99, Chromatograph shows heavy contamination by stearamids.

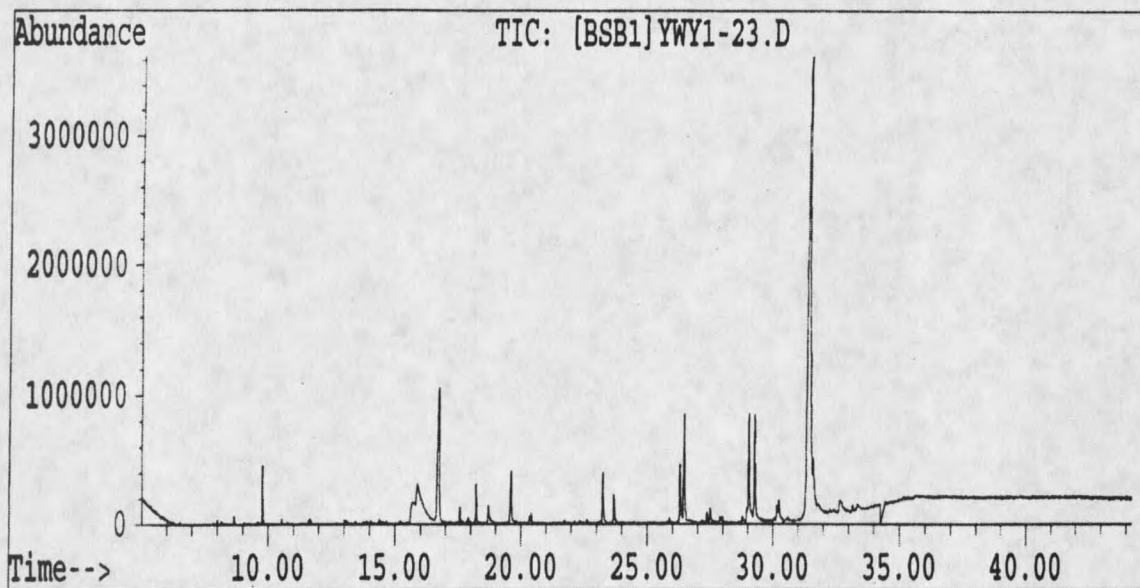


Figure 2. Snow sample taken at West Gate 1-23-99, Chromatograph shows heavy contamination by stearamids.

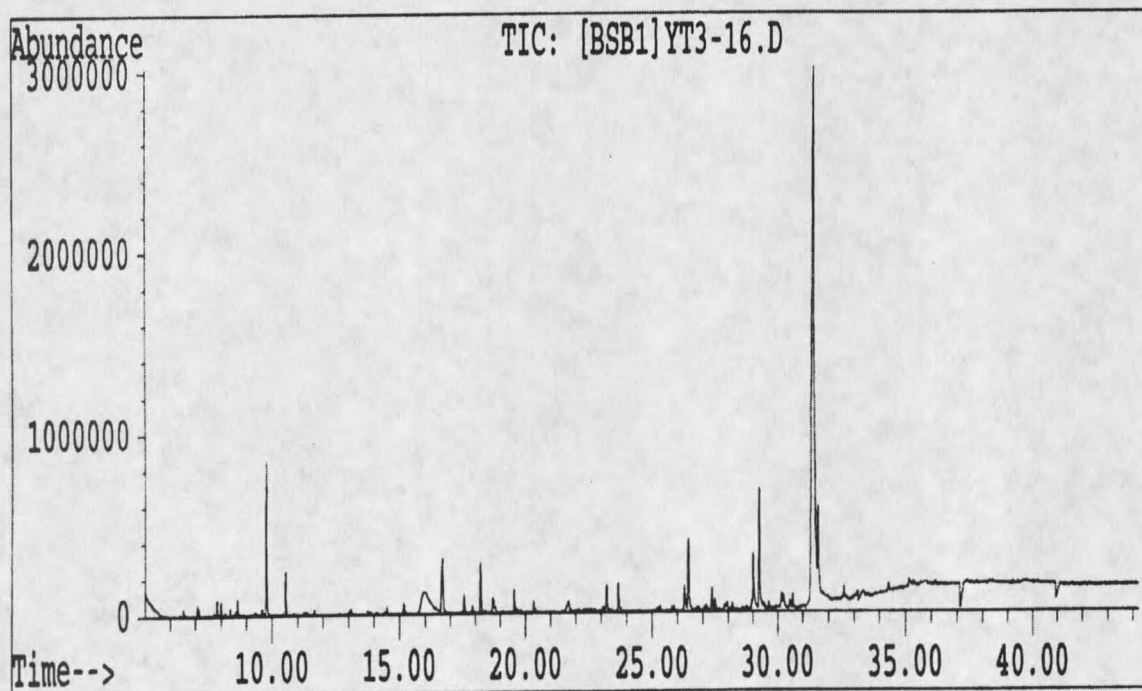


Figure 3. Snow sample taken at Tower Ranger Station 3-16-99, Chromatograph shows heavy contamination by stearamids.

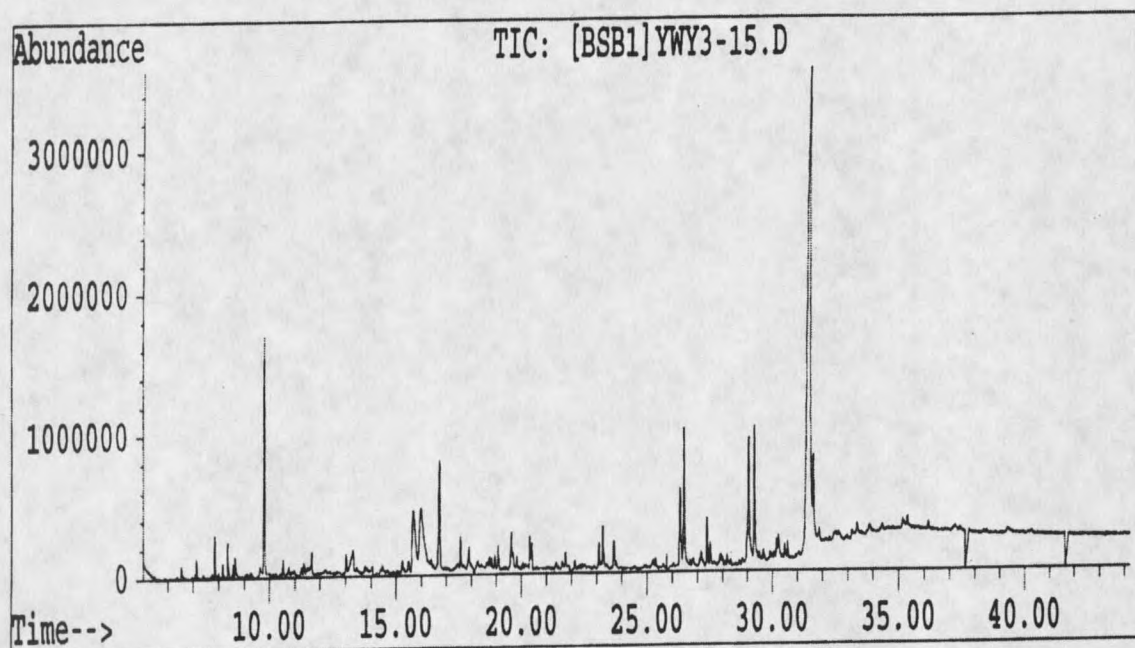


Figure 4. Snow sample taken at West Gate 3-15-99, Chromatograph shows heavy contamination by stearamids.

It is believed that the source of contamination in the snow samples is due to the snow scraping extrusion lubricants (stearamids) from the surface of the bags during the collection, storage, and analysis periods. Due to contamination problems the use of polyethylene bags for sample collection was abandoned.

Air Samples

Air samples were collected at both the Tower Ranger Station and the West Yellowstone Entrance. Samples were collected on 47mm Millipore Fluoropore FALP filters with a 1 micron pore size by total filtration. The filters used were capable of collecting particles in the sub micron range. A carbon vane vacuum pump operating at about 3 standard cubic feet per minute (SCFM) was used for sample collection and the total air volume sampled was measured using a dry gas meter provided by Montana

Power. The pump and dry gas flowmeter were placed inside a barn at Tower safe from the weather.

At the West Yellowstone entrance the pump and flowmeter were placed inside a research kiosk with other environmental sampling equipment. A PVC hose was run through an opening in the wall and out to the filtration apparatus. The filtering apparatus was prepared by drilling a hole in the bottom of a 3 gallon bucket and running the hose through the hole to attach it to the polycarbonate nucleopore filtration cassette. The bucket was then suspended in a inverted position from the roof of the research kiosk. The sides of the bucket shielded the filtration cassette from snow and blowing debris.

The initial plan was to allow the pump to run throughout the week and replace the filter each weekend when snow samples were collected. However, the filters were becoming plugged within a few days causing the pump to over heat. YNP rangers assisted us by regularly checking a vacuum meter used to determine the pressure drop across the filter, and shutting the pump off when the pressure drop exceeded a pre-determined limit. The filters were then replaced each weekend after collecting snow samples.

When changing the filtration cassette, care was taken not to contaminate the samples. Polyethylene gloves were worn at all times, the filtration cassette was removed and placed in a polyethylene bag. The polyethylene bag was then placed in a Tupperware container, which was then placed in another polyethylene bag for transportation.

Air sampling conditions at the Tower Ranger Station were similar to those at the west gate. The vacuum pump and dry gas flowmeter were placed inside a barn and a

PVC hose was fed out to the filtering apparatus. The filtering apparatus was the same type as used at the west gate. Filters did not plug quickly as seen at the west gate and filters were changed weekly when snow samples were taken. The procedure for changing the filtration cassette was followed with the same care taken at the west gate.

Doped Snow Columns

Snow columns were doped with lubricating oils and exhaust product diluted in hexane, and then placed in an undisturbed location near the Tower Ranger Station. Snow columns were made of 8" PVC irrigation piping, and were approximately 3 feet in height. The columns were lined with teflon sheeting. Prior to lining the columns the teflon sheeting was thoroughly cleaned with ethanol. Snow was carefully weighed and added to the columns approximately 1 kg at a time. Dopant was applied to the column after each snow addition in order to evenly distribute the hydrophobic dopant materials throughout the snow matrix. The total quantity of snow per column ranged from 5.5 to 7.5 kg. Columns 1 and 2 were filled with 'clean' snow to act as a background sample for the local snow. Columns 3 and 4 were doped with fresh bio-based oil diluted in hexanes. Columns 5 and 6 were doped with exhaust products from a two-stroke lawnmower engine operating on 30:1 ratio of SCAT oil. Columns 7 and 8 were doped with exhaust products taken from a snowmobile used in the YNP fleet and operating with Bio-based lubricating oil.

Exhaust products from the two-stroke engines were collected in a two part cold trap apparatus. A glass cold trap cooled by liquid nitrogen was connected to a section of half-inch diameter teflon tubing, which was placed in the exhaust stream of the two-

stroke engines. After the exhaust gases passed through the first cold trap, they entered a second cold trap constructed of a stainless steel coil immersed in liquid nitrogen. The two cold traps were connected by 2 ft of half-inch diameter teflon tubing. All remaining exhaust products exited the stainless steel coil into the atmosphere. Exhaust products were recovered from the cold traps via solvent rinse with methylene chloride. It was difficult to recover exhaust products from the stainless steel coil and impossible to determine any kind of recovery percentage. It is recommended that future attempts to sample exhaust streams use two or more glass cold traps as they are easily handled and can be thoroughly cleaned to prevent cross contamination between sampling events. Columns 9 and 10 were doped with the same exhaust products taken from a snowmobile used in the YNP fleet and operating with Bio-based lubricating oil and sealed to try to compare aerobic and anaerobic effects on biodegradation. Columns 11 and 12 were doped with fresh SCAT oil. Table #1 specifies the measured quantities of snow and dopant materials added to the columns.

Table 1. Contents of snow columns set up at Tower Ranger Station (Winter 1998-99).

Column #	Dopant Material	Quantity of Dopant	Quantity of Snow	Other Information
1	Blank	None	5.667 kg	
2	Blank	None	6.418 kg	
3	Bio-based oil	9.5g	6.807 kg	
4	Bio-based oil	11.31g	7.044 kg	
5	SCAT exhaust	26.71g	7.480 kg	
6	SCAT exhaust	20.77g	6.612 kg	
7	Snow. Exh.	23.84g	7.170 kg	
8	Snow.Exh.	14.26g	6.515 kg	
9	Snow. Exh.	13.32g	6.564 kg	Sealed Column
10	Snow. Exh.	10.06g	6.291 kg	Sealed Column
11	SCAT oil	20.32g	6.851 kg	
12	SCAT oil	13.69g	7.696 kg	

Upon analysis of the snow columns by modified EPA method 525.2 extraction and GC/MS, it was found that high levels of phthalate contamination dominated the spectra and prevented data analysis (figures # 5-6). Polyethylene spray bottles were used to apply the dopant and are the primary suspect of the phthalate contamination.

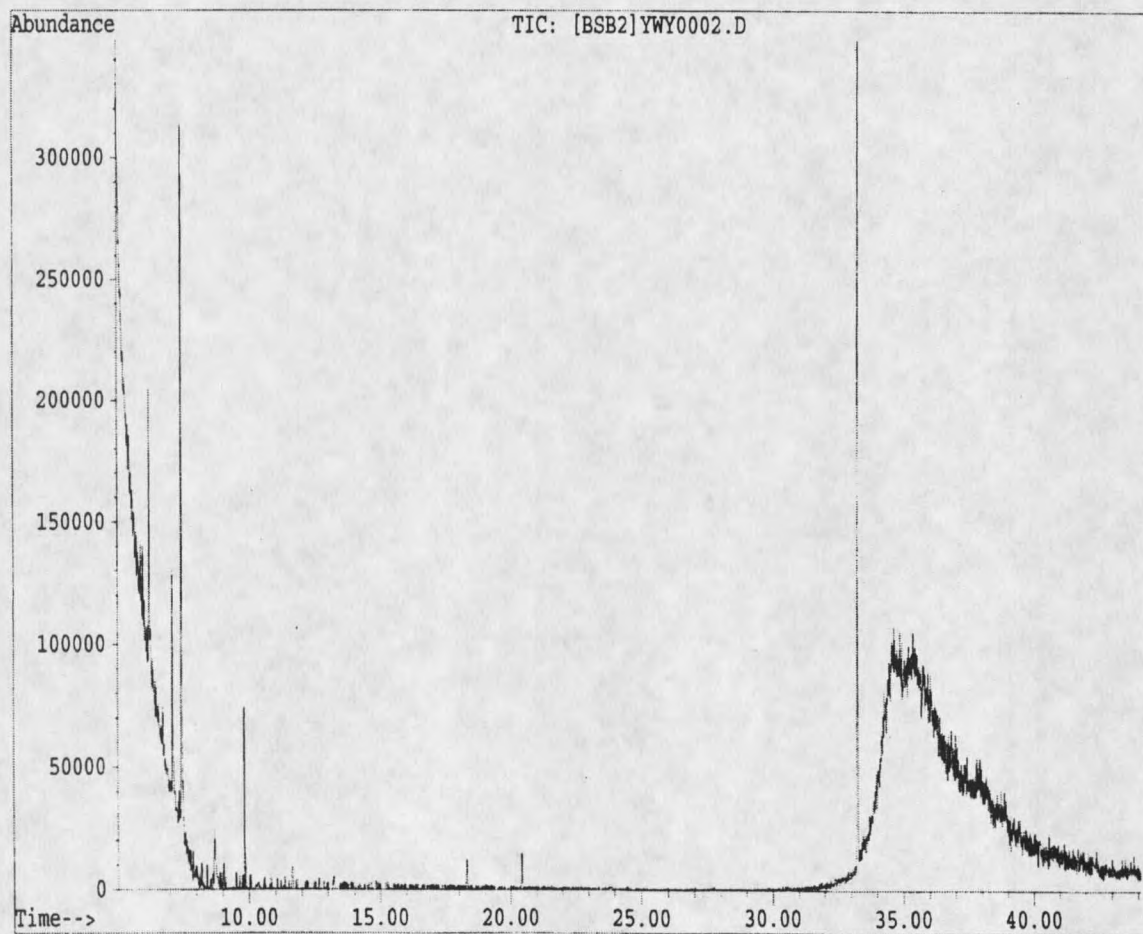


Figure 5. Snow column doped with Bio-Based oil, and heavily contaminated by phthalates.

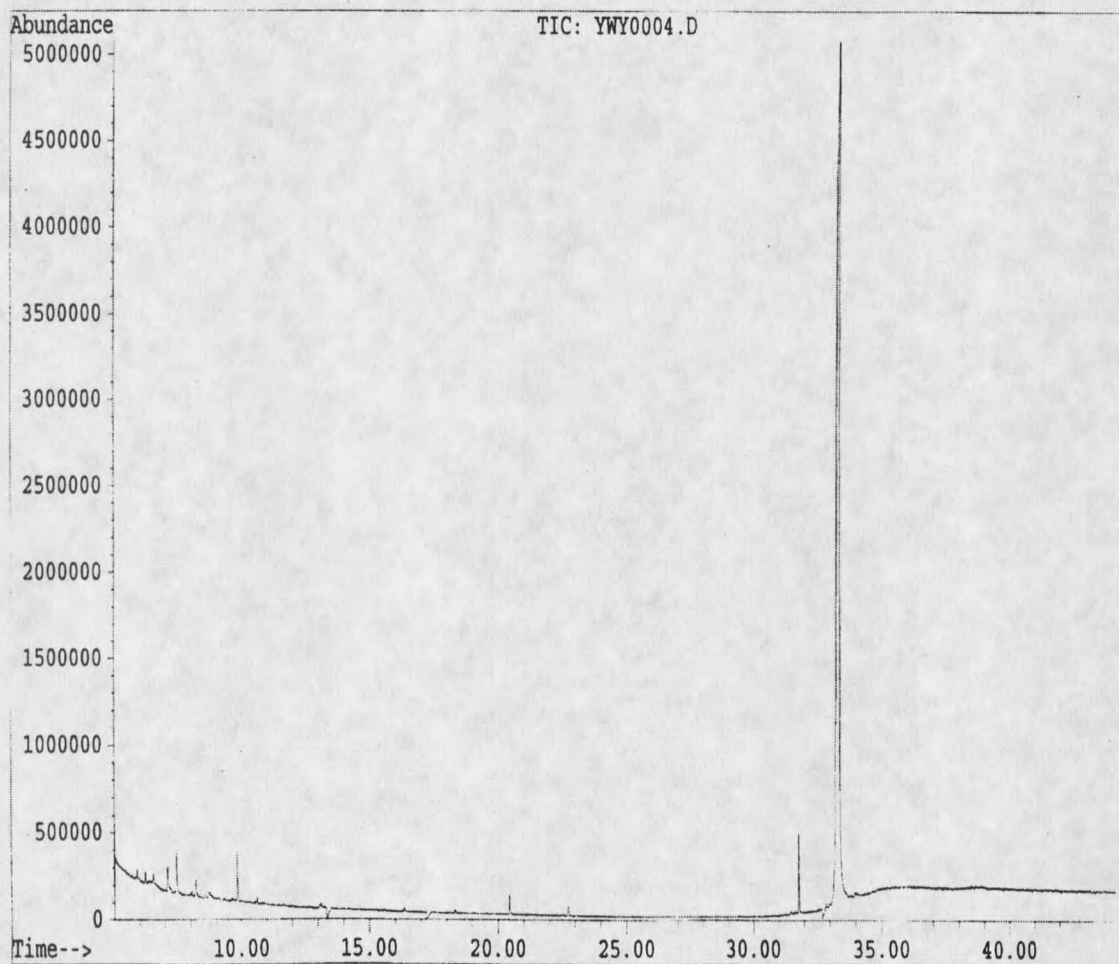


Figure 6. Snow column doped with snowmobile exhaust, and heavily contaminated with phthalates

The teflon sheeting worked well at keeping the snow away from the walls of the PVC piping. However when the snow melted during the spring, liquid water came into contact with the walls of the piping. It was also noted that large quantities of SCAT and Bio-based oil had adsorbed to the teflon sheeting. The teflon sheeting was rinsed with methylene chloride, however the percent recovery from the sheeting is uncertain. A piece of the teflon sheeting was soaked in 10ml of methylene chloride for 2 hours. The solvent was then concentrated and analyzed by GC/MS (Figure # 7).

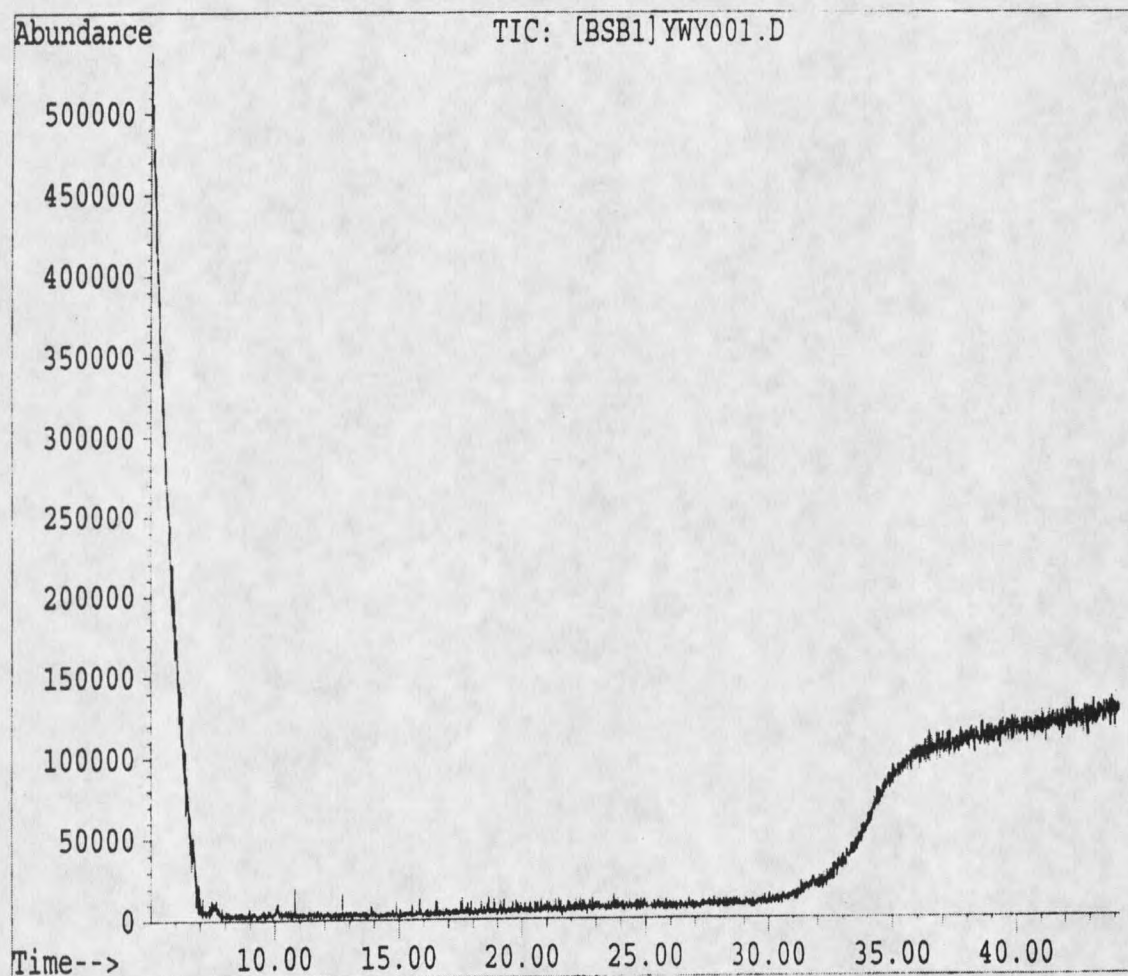


Figure 7. Chromatogram of Teflon liner soaked in methylene chloride

The results of this test show that the telfon liner was not the source of the phthalate contamination. A similar test of the PVC piping produced a minor, unidentified, peak (figure # 8), however this was also not the source of phthalate contamination.

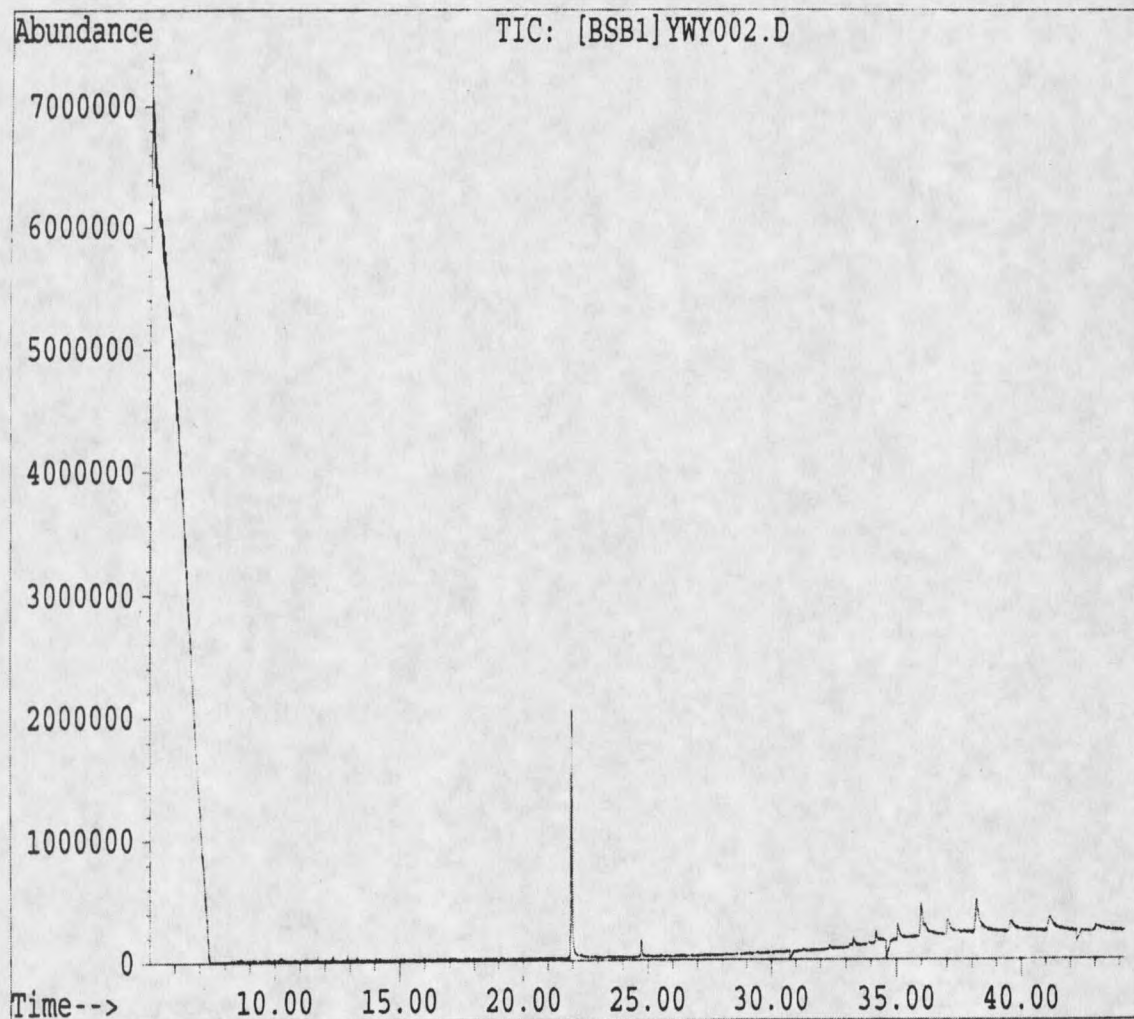


Figure 8. Chromatogram of PVC soaked in methylene chloride. The peak in the chromatogram was not identified, but it was not the contaminant of concern.

Brief melting events throughout the winter allowed liquid water to come into contact with the walls of the piping. While the piping was eliminated as a source of phthalate contamination, it is not 'clean' enough to allow a solvent rinse to ensure a good recovery percentage. A new type of snow column and a method for distributing the dopant was required for this experiment to be successful. A suitable method for modeling the behavior of oils in a controlled snow sample was not established.

Field Sampling Method (Spring 2000)

The sampling protocol was changed for the second season (Spring 2000). The focus of the snow sampling was to determine the level of contamination due to snowmobile exhaust emissions at the West Yellowstone entrance and determine the rate at which they diminished with distance from the road.

Snow samples were obtained from the roadside and at distances of 20ft and 50ft from the road. Samples obtained to represent snow conditions on the road were taken from the large piles of snow adjacent to the park entrance. Sampling sites away from the road were chosen in undisturbed (by humans, snowmobiles, or animals) areas adjacent to the West Yellowstone entrance.

Due to extensive contamination in the previous season a new method of containing and transporting the samples was necessary and this proved to be a difficult task. Glass would have been the first choice, however it is difficult to transport and containers of suitable size are expensive. Teflon lined 20 quart pots were used to collect snow samples. It was believed that the organic compounds in the sample would not be strongly attracted to the teflon surface of the pot, however that idea was quickly disproved with collection of the first samples. Organic compounds readily adhered to the inner surface of the pot and a solvent rinse was the only viable method of removal. The inner surface of the pot was initially tested with methylene chloride however this proved to be too strong of a solvent and the teflon binding agent was dissolved. The inner surface was then tested with both ethyl acetate and hexanes. Approximately 10ml of each solvent was applied via glass pipet to the inside walls of the container. The solvents

collected in the bottom of the containers and were allowed to sit for approximately 2 minutes.

The solvent volume was then reduced to 1ml and each sample was evaluated by GC/MS. Upon analysis it was determined that phthalates contained in the binding agent were extracted into the solvent (figure # 9-10). These solvents left the inner surface of the containers intact. However, the extraction of phthalates prevented a solvent rinse, making the container useless.

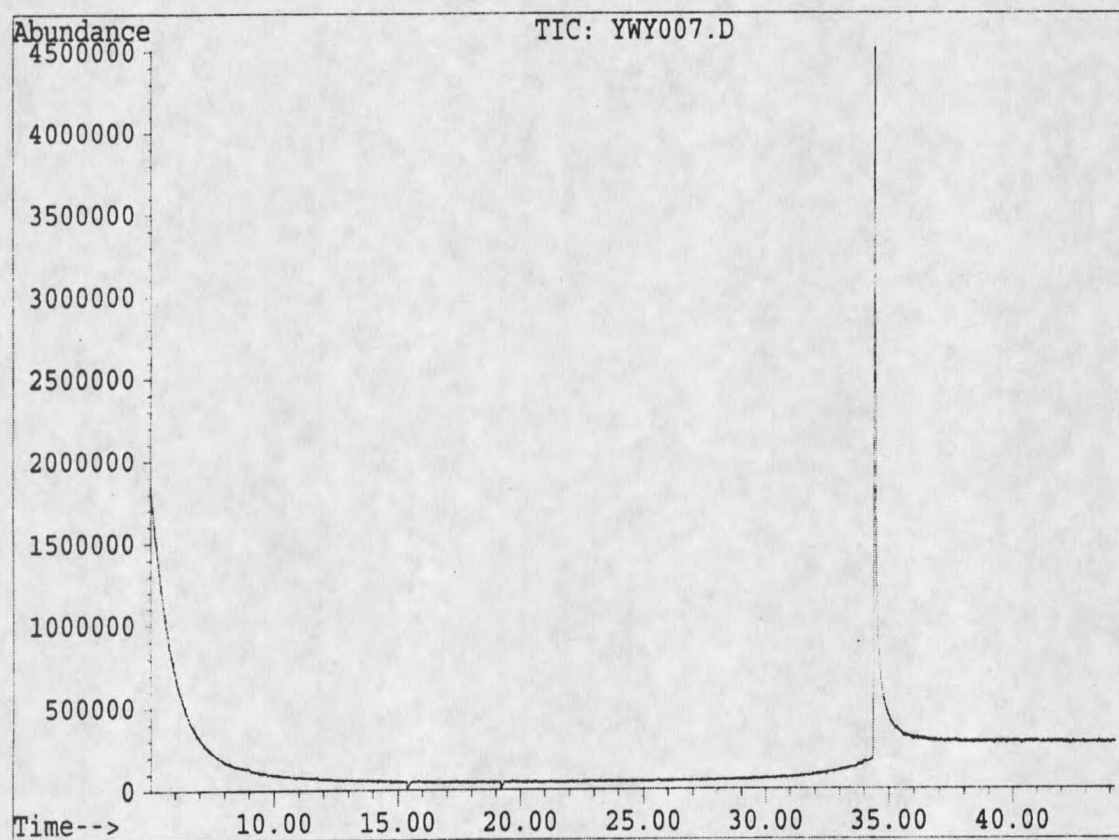


Figure 9. Results of rinsing a Teflon lined sampling container with ethyl acetate.

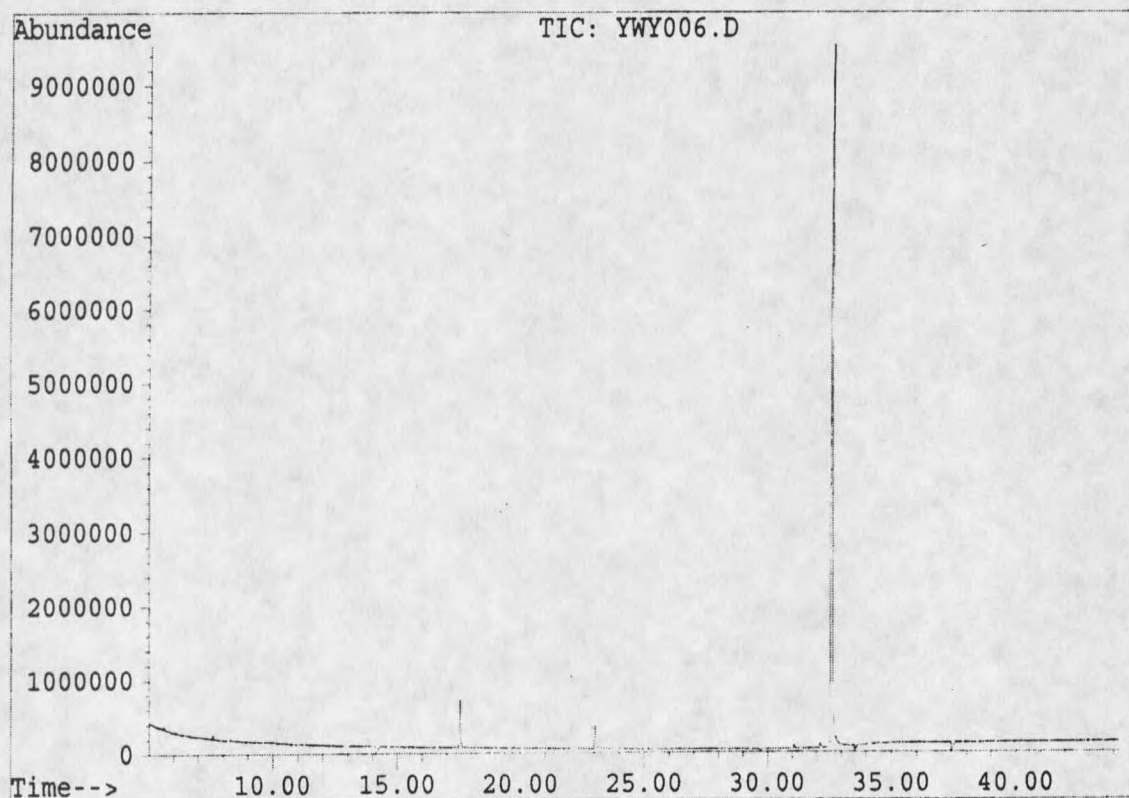


Figure 10. Results of rinsing a Teflon lined sampling container with Hexanes.

Samples were then collected in 20 quart stainless steel pots. Prior to sample collection the containers were washed thoroughly with detergent followed by an acetone rinse to remove any oils that may have adhered to the inner surface of the container. The containers were then rinsed twice with distilled water and covered. Upon melting each pot yielded approximately 5-7 liters of liquid sample, and hydrocarbons could be rinsed from the surface safely. This entirely eliminated the sample contamination problems experienced in the previous season.

CHAPTER 4

SAMPLE ANALYSIS METHOD

Snow Sample Preparation

Snow samples were prepared for analysis in a variety of ways because of the different sample collection methods and containers used. Initially, the 1 gallon polyethylene bags used for sample collection and storage were suspended over glass funnels with one corner of the bag cut for water to escape. As the snow melted it would drip into the funnels and then into the 1 liter amber glass bottles used for temporary storage and procurement of the liquid sample. The polyethylene bags were suspended in a way that would minimize the amount of contact between liquid water and the inner surface of the bags. When the melting was complete the bags were rinsed slightly with nano-pure water. The glass funnels were also rinsed with water but in retrospect the surface of the glass funnels is another potential source of analyte loss and could have been rinsed with solvents.

Snow samples in Stainless steel pots were allowed to melt at room temperature and immediately after melting the samples were acidified. Acidification of the samples was performed in the stainless steel containers in order to avoid storage of the sample liquid in multiple bottles with a large quantity of glass surface area. The liquid sample

was acidified to a pH < 2 by adding 12ml of 6M Hydrochloric Acid (HCL). It was noted that corrosion of the container surface occurred. While no contamination was detected it is recommended that acidification only take place in the amber glass bottles. The sample liquid was transferred from the stainless steel containers to the sample reservoir of the extraction apparatus as needed using a 1 liter amber glass bottle and extracted per modified EPA method 525.2.

Prior to extraction of samples collected in stainless steel containers the sample liquid was pre-filtered using glass fiber filters. The pre-filtration was performed using vacuum filtration with the disk extraction apparatus. Prior to sample filtration the filters were washed twice with 5ml portions of methylene chloride.

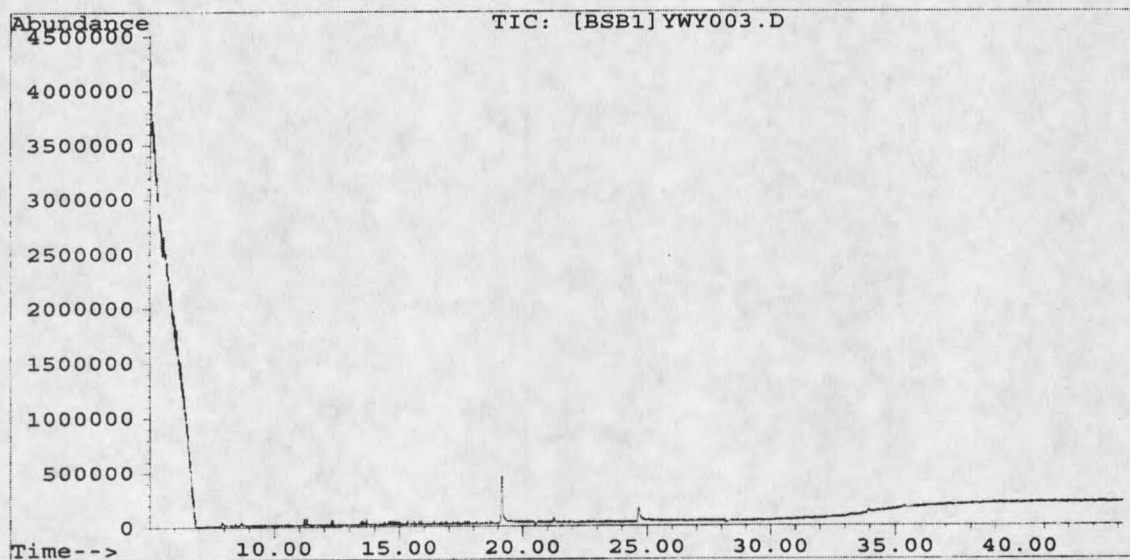


Figure 11. Chromatograph of the solvent used to rinse the glass fiber filters. The peaks present are the internal standard.

Experiments were performed to verify that the glass filters would not contaminate the sample liquid. A glass fiber filter was washed twice with methylene chloride and the solvent was collected, concentrated, and analyzed by GC/MS (figure #11).

After washing the glass fiber filter, 5 liters of nano-pure water was acidified, pre-filtered, and then extracted per modified EPA method 525.2. No contaminants were detected as a result of pre-filtration (figure #12).

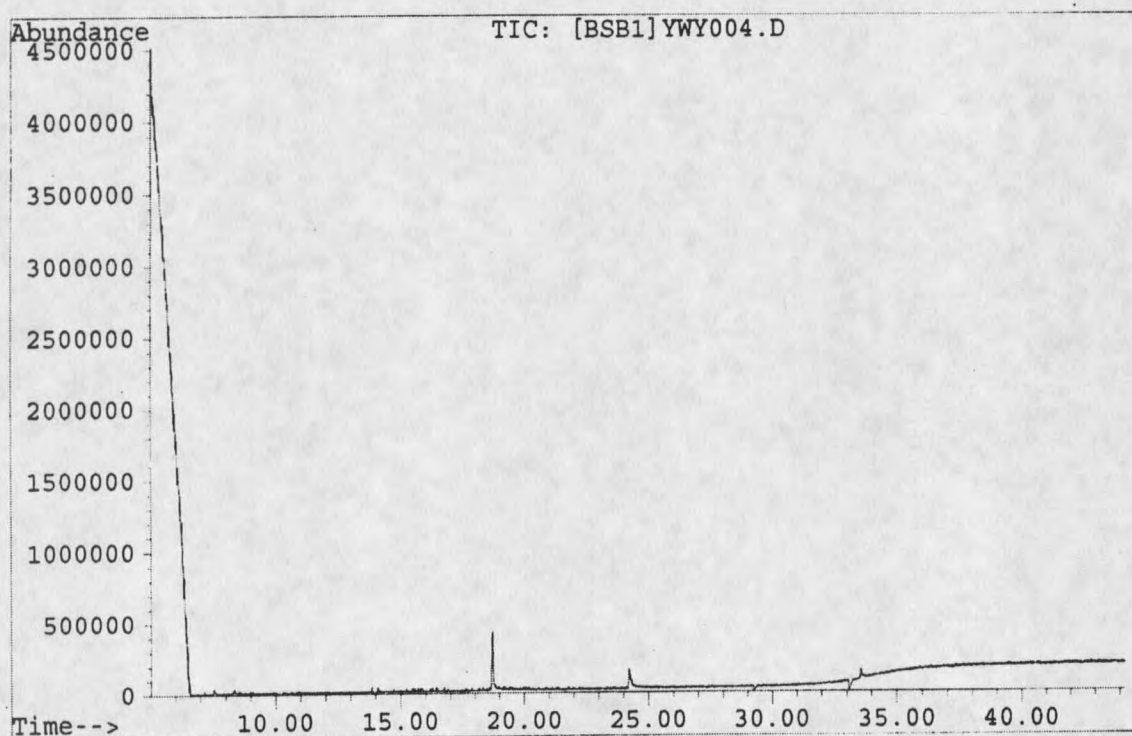


Figure 12. Chromatogram of nano-pure water, pre-filtered and extracted per modified EPA method 525.2. Peaks present are internal standards.

Snow Sample Analysis Method

The analysis of trace organic contaminants in water is commonly performed by either liquid-liquid solvent extraction or solid phase disk extraction. Due to unknown

levels of pollution in the YNP snow samples, large sample volumes were concentrated for analysis, and a method was required that could handle large volumes of water efficiently and reproducibly. Liquid-liquid extraction requires a large solvent to solute ratio (v:v) to achieve good recovery percentages. Solid phase disk extraction does not require sophisticated instrumentation for sample preparation and targets sample volumes of 0.1 - 10 liters. An analysis of PAH and organochlorine compounds by Grimalt et al. reports recovery percentages of 80-100%. For the analysis of trace organic compounds in the snow pack of YNP it was decided that EPA method 525.2 would be most appropriate starting point.

EPA Method 525.2 (Summary)

Environmental Protection Agency analysis method 525.2 was created for the determination of organic compounds in drinking water by liquid-solid extraction and capillary column Gas Chromatography / Mass Spectrometry. This method is applicable to a wide range of organic compounds, which are separated from the water and bond with the C18 coating of the SPE disk. The organic compounds are then eluted from the disk using methylene chloride and ethyl acetate. The solute is then concentrated to 1ml and analyzed using GC/MS. There are several potential sources of contamination, which must be addressed to ensure the analytical integrity of the method. Solvent blanks should be analyzed by GC / MS to confirm adequate purity. Each batch of SPE disks should be evaluated to determine the potential level of contamination from this source, and ensure that it will not hinder data recovery and analysis. All glassware should be meticulously cleaned with detergent and then thoroughly rinsed with distilled water or solvents. There

are three major procedures required for proper recovery and analysis of the samples, namely sample preparation and storage, sample extraction, and sample concentration.

Sample Preparation

Proper sample preparation and storage is vital to the success of this method. The analysis of trace level contaminants requires that strict measures be taken to prevent sample contamination. Sampling equipment must be free of plastic tubing, gaskets, or other parts that may leach interfering analytes into the water. Samples should be acidified using HCl to a pH < 2, immediately after collection to prevent microbiological degradation of analytes during storage. This is the same pH required during the extraction phase and is required to recover acidic compounds such as pentachlorophenol. It is very important when analyzing PAH to limit sample contact with sources of UV light as photo-oxidation is the primary pathway for PAH degradation. All samples should be iced or refrigerated at 4 °C and kept in the dark from the time of collection until extraction. Results of the time/storage study, by the EPA method 525.2 developers, showed that all method analytes of interest in this study are stable for 14 days in water when properly prepared and refrigerated. Samples must be extracted within 14 days of entering the liquid phase and sample extracts can be stored for up to 30 days at 4 °C.

Sample Extraction

Proper preparation and elution of the SPE disks is vital to ensure good recovery of the analytes. The extraction procedure was developed using 47mm diameter disks.

If larger disks are used solvent, volume will need to be increased. The SPE disk is placed

in the vacuum filtration apparatus. The disk is then rinsed with 5ml of a 1:1 mixture of ethyl acetate and methylene chloride by adding the solvent to the disk, drawing about half the solvent through the disk, allowing it to soak for about a minute and then drawing the remaining solvent through the disk. The disk is then pre-wet with 5ml of methanol by adding the methanol to the disk and allowing it to soak for about a minute, then drawing most of the remaining methanol through the disk but leaving a thin layer of methanol on top of the disk to prevent drying. This is a critical step for a uniform flow of the sample through the disk and good recovery, the disk must not go dry from this point throughout the extraction process. The disk is then rinsed with 5ml reagent water by adding water to the disk and drawing most of it through again leaving a thin layer of water on top of the disk. Approximately 5ml of methanol is added to each 1 liter bottle of sample and mixed well. The sample water is then added to the reservoir of the apparatus and full vacuum is applied. Particulate free water may pass through the disk in as little as 5 min. without reducing analyte recoveries. The entire sample should be extracted, draining as much water from the sample containers as possible. The waste flask holds slightly more than 1 liter of water. After each liter of water passes through the disk the vacuum is shut off temporarily and the flask is emptied (Note: it is important to leave a thin film of water on the disk while emptying the flask in order to ensure the disk stays wet). When the entire sample has passed through the disk, vacuum is maintained and the disk is allowed to dry for approximately 10 minutes. The filtration top is then removed from the apparatus and the flask containing the extracted water should be emptied. A collection tube is added under the filtration apparatus to collect the extraction solvents.

The walls of the sample container are rinsed with 5ml of ethyl acetate using a disposable glass pipet and the solvent is allowed to collect in the bottom of the container. The solvent is then transferred to the disk, rinsing the walls of the sample reservoir in the process. About half the solvent is drawn through the disk and allowed to soak for a minute. The remaining solvent is then drawn through the disk into the collection tube. This procedure is repeated with 5ml of methylene chloride. The walls of the filtration reservoir are rinsed using a disposable glass pipet and two 3 ml portions of a 1:1 mixture ethyl acetate: methylene chloride. The solvent is drawn through the disk and into the collection tube.

Sample Concentration

After the extraction process is complete the eluted samples must be concentrated for analysis. The eluants are concentrated to between 0.5 and 1ml under a gentle stream of nitrogen. A heating block or water bath is used to heat the sample gently at 37 °C. In order to avoid analyte loss, the eluant is not concentrated to less than 0.5ml.

Method Performance

Before analyzing irreplaceable samples it was important to determine the performance of EPA method 525.2 for the specified application. Reproducibility of results is critical, but requires familiarity and experience with the method. It was also important to determine the percent recovery being achieved in order to evaluate the method for this application and make adjustments where necessary.

Since the PAH calibration stock (Supelco EPA 525 Semi-volatile calibration mix) contained many of the compounds that were expected to be present in the snow, experiments were performed with known quantities of calibration stock in order to determine the reproducibility and percent recovery of the sample extraction method. Three replicate samples were made and the samples were processed using the extraction method specified by EPA method 525.2.

Each sample consisted of 200 μ l Supelco EPA 525 Semi-volatile Calibration Stock (100ng/ μ l) in nano-pure water contained in pre-washed and rinsed 1 liter amber glass bottles. Samples were then acidified to a pH < 2 and stored in a dark refrigerated room for 48 hours. According to EPA method 525, acidified samples can be stored for up to 14 days. Samples were then extracted per EPA method 525.2. A reference sample of 200 μ l Semi-volatile calibration stock (100ng/ μ l) in 1 ml of methylene chloride (pesticide grade) was prepared. An internal reference standard, EPA 525 Internal Standard Mix (50 μ g/ml each: Acenaphthene d-10, Phenanthrene d-10, and Chrysene d-10), was purchased from Supelco and 100 μ l was added to all samples before injection into the GC/MS. The percent recovery of each analyte was determined by measuring the response of each analyte in the samples to the internal standards and comparing sample data with reference data. Samples were analyzed using a HP5980 Gas Chromatograph / Mass Spectrometer (GC/MS) equipped with a quadrupole mass analyzer. Gas phase separation was achieved using a J+W, DB-5 column. Reproducibility was acceptable with the average variability in data equal to 5.27%, however recovery percentages

averaged less than 20%. Only 15 of the 24 targeted pollutants were recovered. Results of this experiment for each individual species can be found in Table # 2.

Table 2. Percent recovery and identifying mass peak for each species in EPA 525 Semi-volatile Calibration Mix.

Order	Compound Name	MS Peak	Percent Recovery
1	Isophorone	82	11 %
2	Hexachlorocyclopentadiene	237	NR
3	Dimethyl Phthalate	163	9.8%
4	Acenaphthylene	152	22 %
5	2,6-Dinitrotoluene	165	3 %
6	Acaenaphthene-d10	162	REF
7	2,4-Dinitrotoluene	165	2 %
8	Fluorene	166	30 %
9	Diethyl Phthalate	149	54 %
10	Hexachlorobenzene	284	20 %
11	Pentachlorophenol	266	NR
12	Phenanthrene-d10	188	REF
13	Phenanthrene	178	15 %
14	Anthracene	178	34 %
15	Dibutyl Phthalate	149	32 %
16	Pyrene	202	14 %
17	Butyl Benzyl Phthalate	149	8 %
18	Bis(2-ethylhexyl)adipate	129	6 %
19	Benzo[a]anthracene	228	NR
20	Chrysene-d12	240	Unresolved
21	Chrysene	228	Unresolved
22	Bis(2-ethylhexyl)phthalate	149	4 %
23	Benzo[k]fluoranthene	252	NR
24	Indeno(1,2,3-cd)pyrene	276	NR
25	Dibenzo[ah]anthracene	278	NR
26	Benzo[ghi]perylene	276	NR

There was serious concern at this point about instrument quality and method integrity. The GC/MS instrument used for analysis was a general use instrument used by

graduate students working on a variety of projects. The performance of the column was suspect so a Zebron "Phenomenex" DB-5 column, 30 meters in length, .25mm ID, .25um phase thickness, was purchased. The EPA was contacted to determine possible sources of analyte loss and gain some insight on method weaknesses. A scientist working for the EPA at Manchester Labs reported an average recovery of ~ 40%, and mentioned that this method would not generally give high recovery percentages. Liquid-liquid extraction was recommended, however due to the large volume of solvent required this was not a reasonable approach for this project. In spite of initial failures solid phase extraction was considered the most reasonable approach for large samples, and efforts were directed at improving technique and method performance.

There was concern that some of the analytes were not being retained by the extraction disk. To test this concern 200µl of the Semi-volatile calibration stock was added to 100ml of nano-pure water. The extraction disk was prepared according to EPA method 525.2 and the sample was passed through the disk. The water was then extracted in 25 ml portions by liquid-liquid extraction with methylene chloride. The solvent was then concentrated and analyzed by GC/MS. None of the analytes were detected in the water, indicating retention of the analytes by the SPE disk.

A series of experiments were performed to determine the areas and quantities of analyte loss in the method. There were four areas of suspicion; losses to the GC column, losses to glassware, insufficient extraction of analytes from SPE disk, and losses during the concentration step. The purpose of the first experiment was to identify any improvements obtained with the new GC column and provide an updated percent

recovery for the method. Three replicate samples were prepared by adding 200 μ l Semi-volatile Calibration Mix #525 (diluted with ethyl acetate) to 1 liter of nano-pure water. Each sample was refrigerated for 48 hours and then processed per EPA method 525.2. The average percent recovery for this procedure was 42.81 %, which was a tremendous improvement over previous results. However only 15 of the 23 compounds were recovered.

The purpose of the second experiment was to eliminate glassware from the process as much as possible to determine the extent of analyte loss in that area. Three replicate samples were prepared by directly applying 200 μ l Semi-volatile Calibration Mix #525 (diluted with ethyl acetate) to the surface of the SPE disk. Each sample was then extracted per EPA method 525.2. The average percent recovery for this procedure was 80.72 %. This experiment emphasized the importance of reducing losses to glassware. Once again only 15 of the 23 compounds were recovered.

The intent of the third experiment was to determine the extent of analyte loss during the concentration step. Three replicate samples were prepared by adding 200 μ l Semi-volatile Calibration Mix #525 (diluted with ethyl acetate) to 20 ml of methylene chloride and concentrated per EPA method 525.2. The average percent recovery for this procedure was 95.22%. The results of this experiment indicated that losses during the concentration step were minimal, and heating of the extracted solution during concentration was not an area of concern.

While the overall percent recovery was greatly improved many species had yet to be recovered. The data indicated that Fluorene and Bis(2-ethylhexyl)adipate were not

being recovered from the extraction disk. The instrument was not able to detect Benzo[a]anthracene, Chrysene-d12, Chrysene, Benzo[k]fluoranthene, Indeno(1,2,3-cd)pyrene, Dibenzo[ah]anthracene, Benzo[ghi]perylene. The fact that a compound in the internal standard could not be detected was a source of concern. Detailed results of each experiment are listed for each individual species in Table # 3 below.

Table 3. Percent recovery of each individual species in EPA 525 Semi-volatile calibration mix.

Order	Compound Name	MS Peak	Exp. #1 Full Extraction Method	Exp. #2 Direct Application	Exp. #3 Blowdown Step
1	Isophorone	82	37.5 %	98.7 %	90.3 %
2	Hexachlorocyclopentadiene	237	75.8 %	51.2 %	78.0 %
3	Dimethyl Phthalate	163	46.3 %	99.0 %	98.1%
4	Acenaphthylene	152	65.1 %	108.1 %	90.4 %
5	2,6-Dinitrotoluene	165	22.4 %	108.3 %	88.1 %
6	Acaenapthene-d10	162	REF	REF	REF
7	2,4-Dinitrotoluene	165	12.5 %	95.9 %	95.5 %
8	Fluorene	166	ND	ND	94.8 %
9	Diethyl Phthalate	149	64.4 %	99.4 %	93.1 %
10	Hexachlorobenzene	284	50.9 %	100.2 %	103 %
11	Pentachlorophenol	266	42.6 %	58.0 %	109 %
12	Phenanthrene-d10	188	REF	REF	REF
13	Phenanthrene	178	59.7 %	102.7 %	98.3 %
14	Anthracene	178	57.8 %	108.9 %	102 %
15	Dibutyl Phthalate	149	70.3 %	107.6 %	98.3 %
16	Pyrene	202	18.3 %	30.2 %	86.2%
17	Butyl Benzyl Phthalate	149	50.2 %	101.6 %	101 %
18	Bis(2-ethylhexyl)adipate	129	ND	ND	101 %
19	Benzo[a]anthracene	228	ND	ND	ND
20	Chrysene-d12	240	REF, ND	REF, ND	REF, ND
21	Chrysene	228	ND	ND	ND
22	Bis(2-ethylhexyl)phthalate	149	53.9 %	102.5 %	91.7 %
23	Benzo[k]fluoranthene	252	ND	ND	ND
24	Indeno(1,2,3-cd)pyrene	276	ND	ND	ND
25	Dibenzo[ah]anthracene	278	ND	ND	ND
26	Benzo[ghi]perylene	276	ND	ND	ND

ND is used to represent compounds that have yet to be recovered with consistency

Method Modification

Aside from instrument difficulties, the experiments indicated that the glassware was a major source of analyte loss. This was not surprising as the aromatic compounds in the calibration standard are hydrophobic and were expected to adhere readily to glassware.

Treatment of the glassware was attempted in order to reduce losses. Silanation of the glassware before contact with the sample liquid was attempted. The bottles were washed thoroughly, rinsed with nano-pure water, and dried. The bottles were then filled with a 5% solution of dichlorodimethylsilane in toluene and allowed to soak for 30 minutes each. They were then rinsed with toluene, followed by an acetone rinse. The bottles were then filled individually with methanol and allowed to soak for 10 minutes each. Unfortunately this process was expensive and the results were inconclusive.

The most successful improvement of analyte recovery from the glassware was achieved by thoroughly rinsing the inside of the glass bottles with methylene chloride to a far greater extent than called for in EPA method 525.2. Approximately 25 ml of methylene chloride was used to rinse the inside of the bottles. This solvent was then used to rinse the inside surface of the sample reservoir. This process doubled the amount of solvent used in the disk extraction step.

Solvent volume was then reduced using the nitrogen concentration technique specified by EPA method 525.2, and the samples were heated slightly in a water bath to (37°C). Initially, ultra-pure nitrogen provided by a local supplier was used, and this was expensive. The boil off of the University liquid nitrogen tank (house nitrogen) was used

to concentrate 20 ml of methylene chloride, which was then analyzed by GC/MS. No contaminants were detected. The use of house nitrogen greatly reduced the cost of this step. During the concentration step the solvent volume is reduced to less than 1 ml and 100ul of EPA 525 internal standard mix is added. Volume is then adjusted to 1 ml with methylene chloride.

Current Method Performance

A recent experiment was performed to determine the percent recovery of PAH and petroleum compounds from a snow sample. Two replicate snow samples were prepared by filling each 20 quart stainless steel pot with snow and adding 1 ml Semi-volatile calibration standard #1 (10 µg/ml), and 1 ml of Hydrocarbon calibration standard #3 (20 µg/ml). These quantities are comparable to the contamination levels found in the snowpack of YNP. Each sample was allowed to melt at room temperature, acidified, and extracted by the modified version of EPA 525.2. The liquid sample was transferred from the stainless steel container to the sample reservoir with 1 liter amber glass bottles. The bottles were rinsed as described in the method modification section. A reference sample was prepared by adding 1 ml of each reference standard to approximately 10ml of methylene chloride. This volume was then reduced by the nitrogen concentration technique described earlier. During the concentration step the volume of all samples was reduced to less than 1 ml and 100µl of EPA 525 internal standard mix is added. Volume was then adjusted to 1 ml with methylene chloride.

The inability to recover all compounds with the general use GC/MS necessitated the use of a more sensitive instrument. Samples analysis was performed using a HP 5890

GC with a VG-70E-HF MS, operated by Dr. Joe Sears, MSU, Department of Chemistry. An average percent recovery of 68.1% for the Semi-volatile calibration mix, and 48.5% for the n-alkanes C-16 through C-20, was achieved with an average variability of 6.27%. Compound loss was minimal with 27 of 29 analytes detected in the samples. Data for each individual species is listed in Tables # 4-5.

Table 4. Current percent recovery, characteristic MS peak, and retention time, of each species in EPA 525 Semi-volatile calibration mix.

Order	Compound Name	MS Peak	Retention Time	Percent Recovery
1	Isophorone	82	15:29	8.78%
2	Hexachlorocyclopentadiene	237	21:34	13.47%
3	Dimethyl Phthalate	163	24:35	13.61%
4	Acenaphthylene	152	24:28	86.20%
5	2,6-Dinitrotoluene	165	24:48	NR
6	Acaenaphthene-d10	164	25:12	REF
7	2,4-Dinitrotoluene	165	26:32	NR
8	Fluorene	166	27:40	95.87%
9	Diethyl Phthalate	149	27:55	112% *
10	Hexachlorobenzene	284	30:35	73.47%
11	Pentachlorophenol	266	31:34	73.66%
12	Phenanthrene-d10	188	31:56	REF
13	Phenanthrene	178	32:02	101.71%
14	Anthracene	178	32:14	82.74%
15	Dibutyl Phthalate	149	35:37	117% *
16	Pyrene	202	38:30	67.96%
17	Butyl Benzyl Phthalate	149	42:29	97.89%
18	Bis(2-ethylhexyl)adipate	129	43:14	104.41%
19	Benzo[a]anthracene	228	44:10	43.10%
20	Chrysene-d12	240	44:15	REF
21	Chrysene	228	44:21	68.28%
22	Bis(2-ethylhexyl)phthalate	149	45:33	171% *
23	Benzo[k]fluoranthene	252	50:09	57.94%
24	Indeno(1,2,3-cd)pyrene	276	54:18	94.87%
25	Dibenzo[ah]anthracene	278	54:30	69.04%
26	Benzo[ghi]perylene	276	55:09	72.91%

NR Species not recovered

Species present in excess due to contamination of sample

Table 5. Current percent recovery, characteristic MS peak, and retention time, of each species petroleum calibration mix.

Order	Compound Name	MS Peak	Retention Time	Percent Recovery
1	Naphthalene	128	17:19	19.39%
2	Hexadecane (C-16)	NS	28:01	26.66%
3	Heptadecane (C-17)	NS	30:15	37.13%
4	Octadecane (C-18)	NS	32:22	51.40%
5	Nonadecane (C-19)	NS	34:23	61.60%
6	Eicosane (C-20)	NS	36:19	65.79%

Determination of Detection Limits

For EPA method 525, Supelco supplies a Semi-volatile Calibration Mix #525, recommended for instrument calibration. The 1ml semi-volatile calibration mix is diluted with ethyl acetate in a 10ml volumetric flask to a stock concentration of 100 µg/ml from which the other calibration standards are made. A total of six standards are prepared by series dilution, and range from 0.1 to 10 µg/ml. These standards are used to calibrate the instrument and establish the detection level of each individual species (Appendix C).

A series of calibration standards was also prepared for C-16 through C-20 and naphthalene. The individual species were purchased from ChemService Inc. Approximately 100 mg of each individual species was weighed on a four-place analytical balance, dissolved in methylene chloride, and added to a 100ml volumetric flask. A serial dilution was then performed using the combined stock solution of 100 µg/ml to create six calibration standards ranging from 1 to 100 µg/ml (Appendix D).

These standards were then used to create calibration curves for PAH and petroleum species. Table #6 lists the priority pollutants and petroleum products targeted and the current detection limits for each. Current detection limits for all compounds quantified.

Table 6. Current detection limits for all compounds quantified.

Order	Compound Name	MS Peak	Retention Time (Minutes)	Detection Limit in Cal. Std. (ng/ μ l)	Corresponding Concentration in Sample * (ppb)
1	Isophorone	82	15:41	≤ 0.1	0.016
2	Hexachlorocyclopentadiene	237	21:47	0.5	0.083
3	Acenaphthylene	152	24:42	0.5	0.083
4	Dimethyl Phthalate	163	24:49	≤ 0.1	0.016
5	2,6-Dinitrotoluene	165	25:01	0.5	0.083
7	2,4-Dinitrotoluene	165	26:46	1.0	0.167
8	Fluorene	166	27:56	≤ 0.1	0.016
9	Diethyl Phthalate	149	28:10	≤ 0.1	0.016
10	Hexachlorobenzene	284	30:51	≤ 0.1	0.016
11	Pentachlorophenol	266	31:48	1.0	0.167
12	Phenanthrene	178	32:17	0.5	0.083
13	Anthracene	178	32:30	≤ 0.1	0.016
14	Dibutyl Phthalate	149	35:51	≤ 0.1	0.016
15	Pyrene	202	38:46	≤ 0.1	0.016
16	Butyl Benzyl Phthalate	149	42:44	≤ 0.1	0.016
17	Bis(2-ethylhexyl)adipate	129	43:29	≤ 0.1	0.016
18	Benzo[a]anthracene	228	44:27	1	0.167
19	Chrysene	228	44:37	0.5	0.083
20	Bis(2-ethylhexyl)phthalate	149	45:49	≤ 0.1	0.016
21	Benzo[k]fluoranthene	252	49:11	1.0	0.167
22	Indeno(1,2,3-cd)pyrene	276	54:33	5.0	0.833
23	Dibenzo[ah]anthracene	278	54:41	5.0	0.833
24	Benzo[ghi]perylene	276	55:22	2.0	0.333
25	Hexadecane	NS	28:15	≤ 1.0	.0167
26	Heptadecane	NS	30:28	≤ 1.0	.0167
27	Octadecane	NS	32:36	≤ 1.0	.0167
28	Nonadecane	NS	34:37	≤ 1.0	.0167
29	Eicosane	NS	36:33	≤ 1.0	.0167
30	Naphthalene	128	17:35	≤ 1.0	.0167

NS – No unique mass number available for this compound.

NA – Detection limit not yet determined.

Detection limits of each individual species were determined by examining the data from the standard calibration curves and identifying the lowest concentration at which a species was detected. Detection limits of ≤ 0.1 ng/ μ l or ≤ 1.0 ng/ μ l indicate that this species was detected in the calibration standard with the lowest concentration and no attempt was made to identify the absolute detection limit of this species. For each detection limit the corresponding concentration of the species in a hypothetical 6 liter (melted) sample is listed.

Air Sample Analysis

Air samples were collected on teflon based Millipore Fluoropore FALP filters with a 1 micron pore size. These filters are adequate to trap particles down to the sub-micron range. For analyte extraction from the filters, sonication and refluxing were considered as the two most promising methods. An experiment was performed in which SCAT two-stroke oil was diluted with methylene chloride and applied to the surface of three different filters. Upon application the SCAT oil stained the surface of the filters red indicating its presence. The first filter was rinsed with 30ml of methylene chloride. The second filter was sonicated for 1 hour, in an amber glass vial containing 30ml of methylene chloride, in a water bath at ambient temperature. The third filter was sonicated for 2 hours, in an amber glass vial containing 30ml of methylene chloride, in a water bath at ambient temperature. In all experiments the SCAT oil was readily removed from the filters. Initially there was some uncertainty as to the amount of time required to remove the trapped analytes from the filters. Sonication and refluxing were

both under consideration for sample analysis so an experiment was performed to compare the two methods. A filter collected at the west gate was cut into four sections. One section was treated by sonication for 2 hours, in an amber glass vial containing 30ml of methylene chloride, in a water bath at ambient temperature. Another section was sonicated for 2 hours, in an amber glass vial containing 30ml of methylene chloride, in a water bath at 37 °C. The remaining two sections were refluxed for 2 and 4 hours respectively in 30ml of methylene chloride. It was noted that when sonication occurs in a heated water bath the methylene chloride vaporizes and escapes the amber glass vial. This method is not recommended for sample analysis. After refluxing and sonication the solvent volume was reduced with the sample concentration process used for EPA method 525. Sample analysis was performed by GC/MS on the general use instrument. Upon analysis no analytes were detected in any of the samples. Suspecting a sensitivity problem the samples were analyzed using a GC/FID equipped with a DB-1 column, however no analytes were detected. The reason for using this particular instrument was to inexpensively determine if any analytes were being extracted or if a longer reflux period was necessary. Refluxing was considered the method of choice due to sample exposure to heated solvent as well as agitation provided by the boiling solvent. Similar samples were successfully extracted by Baek et al [30] using a Soxhlet extraction apparatus and refluxing for 16 hours in methylene chloride. Due to the nature of the air samples a Soxhlet apparatus was not deemed necessary however reflux time was increased to 16 hours. A filter from the west gate was refluxed for 16 hours and then analyzed using the general use GC/MS, still no analytes were detected. This same

sample was then given to Dr. Joe Sears for analysis on the VG-70E-HF instrument. No analytes were detected initially however when concentrated 10x the sample revealed trace amounts of hydrocarbons. There was some concern that analytes were not being adequately removed from the filter media. A section of a filter from the west gate was removed and analyzed using ESCA to determine the amount of carbon present on the surface prior to refluxing.

CHAPTER 5

RESULTS AND CONCLUSIONS

Data Analysis (Winter 1998-99)Snow Samples

Upon analysis, snow samples from the West Gate and Tower ranger station were found to be heavily contaminated with stearamids. These compounds are commonly used as extrusion lubricants during the production of the polyethylene bags, which were used for sample collection and storage. While care was taken to clean the polyethylene bags thoroughly, and experiments were performed to determine the contamination potential of the polyethylene bags (as discussed in Chapter 3), the abrasive qualities of snow were overlooked. It is believed that the source of contamination in the snow samples is due to the snow scraping extrusion lubricants (stearamids) from the surface of the bags during the collection, storage, and analysis periods. Samples were prepared per modified EPA method 525.2 and analyzed by GC/MS. The level of contamination was significant enough that peaks for the stearamids dominated the mass spectra and raised the background level to the extent that trace contaminants could not be identified (Chapter 3, pg. 34-36, Figures 1-4). Due to contamination problems, the use of

polyethylene bags for sample collection was abandoned and no data was obtained from the first sampling season.

Snow Columns

Snow columns were suspended over stainless steel containers and allowed to melt at ambient temperature. The liquid samples were then acidified and extracted by modified EPA method 525.2 and analyzed using the 'general use' GC/MS. It was found that high levels of phthalate contamination dominated the spectra and raised the background level (Chapter 3, pg. 40, figures 5-6). Polyethylene spray bottles used to apply the dopant to the snow were identified as the primary source of sample contamination.

Air Samples

A filter from the West Yellowstone entrance was refluxed for 16 hours and then analyzed using the general use GC/MS, however no analytes were detected (Figure 13). This same sample was then given to Dr. Joe Sears for analysis on the VG-70E-HS instrument. No analytes were detected initially however when concentrated 10x the sample revealed a small hydrocarbon hump from trace amounts of hydrocarbons (Figure 14).

File Text: JASON 16H

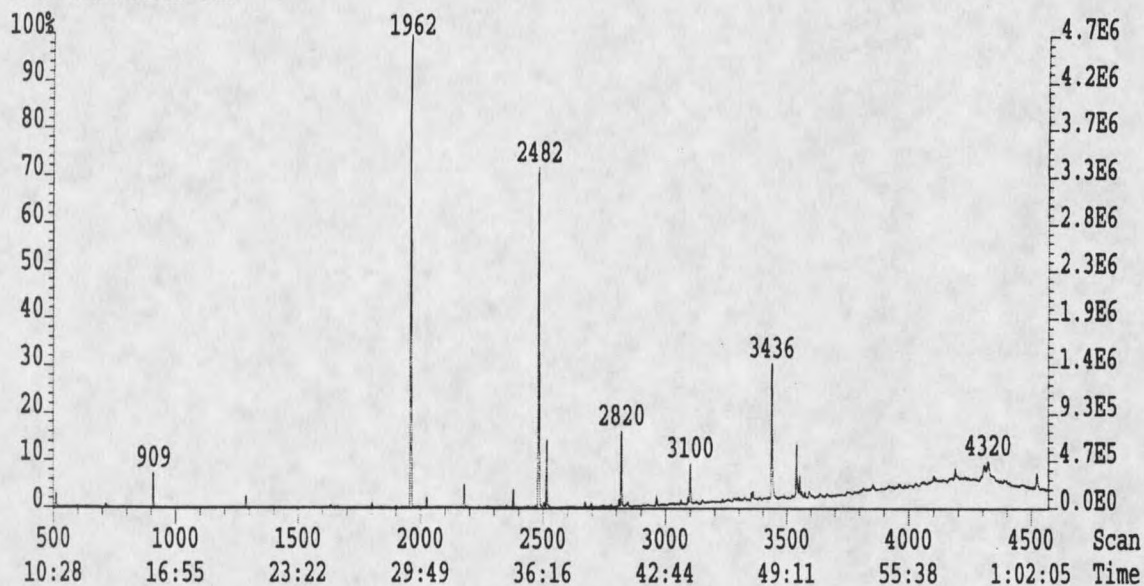


Figure 13. Chromatogram of air sample extracted by a 16 hour reflux in methylene chloride. Dominant peaks are internal standard mix 525, phthalate peaks, and column bleed.

File Text: JASON 16H CONCENTRATED

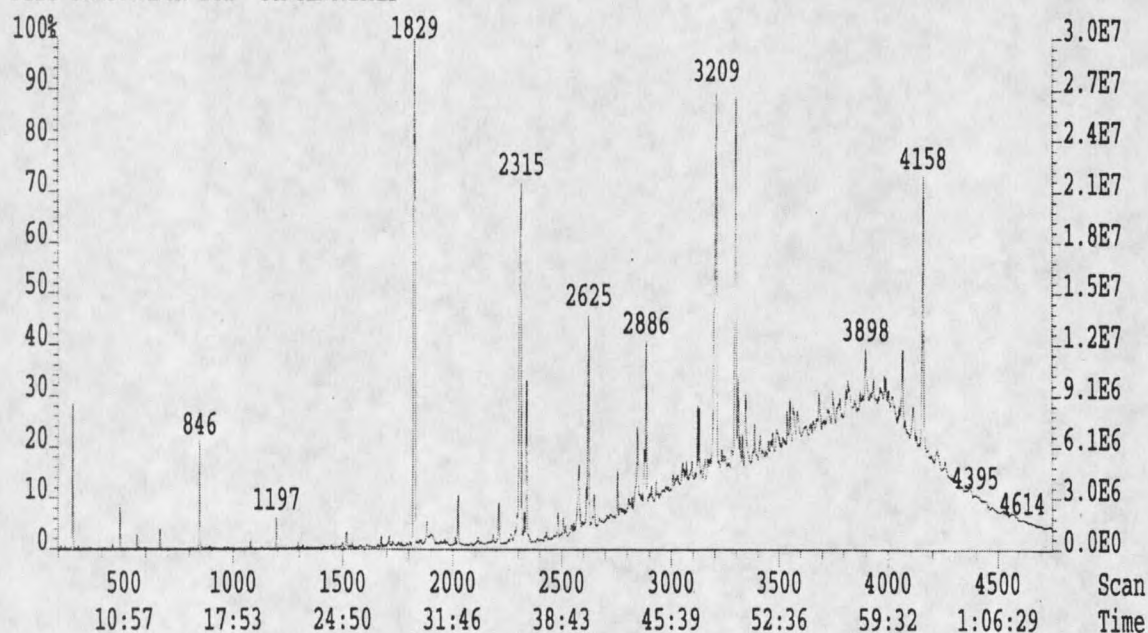


Figure 14. Chromatogram of the air sample in figure 13 after further concentration by nitrogen blowdown.

Trace amounts of even numbered hydrocarbons C18-24 were detected in the concentrated air sample. Peaks 2340, 2625, 2886, and 3127 were identified as even numbered hydrocarbons C18-24. Peaks 1829 and 2315 are the internal standards acenaphthene d-10 and phenanthrene d-10 respectively. The two peaks near 3209 are due to phthalates. Concentrations of n-alkanes in the ppb range are easily detectable. The requirement of an additional concentration step to detect these compounds indicates concentrations well below ppb.

There was some concern that analytes were not being adequately removed from the filter media. A section of a filter from the west gate was removed and analyzed using Electron Spectroscopy for Chemical Analysis (ESCA) to determine the amount of carbon present on the surface prior to refluxing. The remaining portion was refluxed for 16 hours and the surface was analyzed using ESCA. Additional reflux periods of 16 hour increments were performed on this section to determine the benefits of increased reflux time. Figure 15 shows the results of the XPS analysis. The peak at 293 eV arises from the teflon filter and the peak at 285 eV arises from hydrocarbon. The relative intensity of the hydrocarbon peak decreases markedly after the first 16 hr reflux period indicating that hydrocarbon have been removed from the surface of the filter. The additional reflux periods result in small but measurable decreases in the hydrocarbon on the filter surface. From the ESCA results it was concluded that the largest portion of carbon was being removed from the surface during the first 16 hour reflux period.

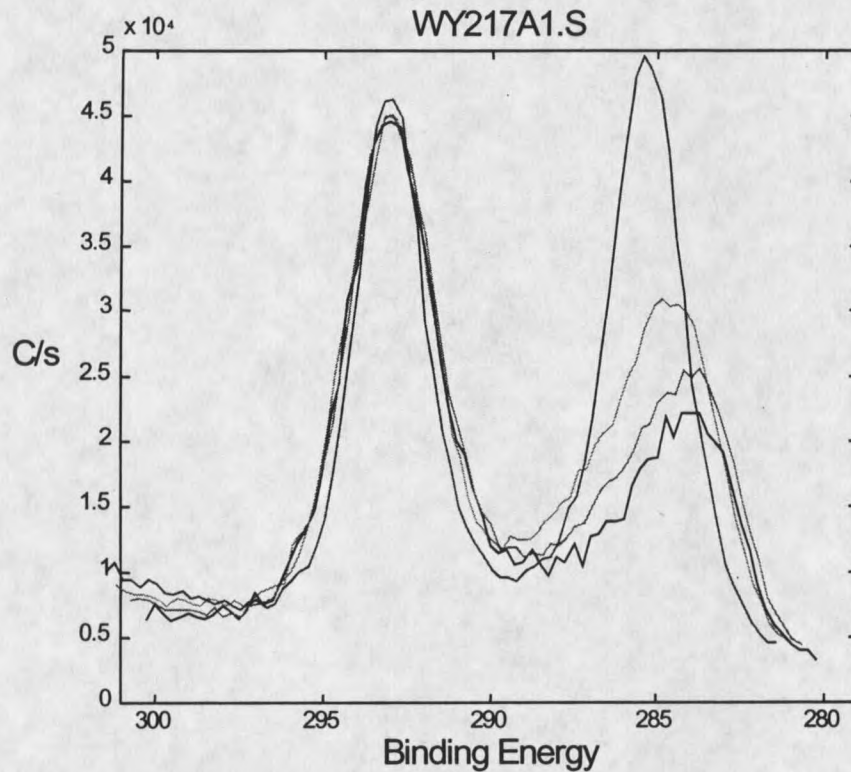


Figure 15. ESCA figure

The extremely low concentration of organic species detected on the filter extracts by GC/MS analysis is inconsistent with TOF-SIMS analysis of the atmospheric aerosol collected in the same location[31]. It is suspected that the low concentrations are the result of prolonged storage of the samples prior to analysis. Additional samples should be collected and analyzed rapidly to confirm this hypothesis.

Data Analysis (Winter 1999-2000)

A suitable method for sample collection and transportation was developed and samples were collected for the final analysis at the West Gate shortly after the park was closed to snowmobiles. Three samples were collected in 20 Quart stainless steel containers, one from the roadside, 20 feet, and 50 feet from the road. Samples were then transported to MSU where they were immediately allowed to melt at room temperature. The samples were acidified and extracted per the modified version of EPA method 525.

A preliminary data analysis was performed using the 'general use' HP 5890 GC/MS. Past experience has proven this instrument to have limited sensitivity, therefore it was used only as an inexpensive method to identify the key components in the samples so standards could be prepared for an accurate quantitative analysis. The preliminary analysis identified C-17, C-18, and C-19 present in all samples. Though no naphthalene or priority pollutants were identified in the preliminary analysis, their presence was anticipated.

Final analysis of the samples was performed by Dr. Joe Sears using a HP 5890 gas chromatograph with a VG-70E-HF mass spectrometer. The table below lists the species found and the concentrations of all species for which calibration standards were prepared.

Table 7. Snow Sample Analysis

Species Found	Concentration on Road (ppm)	Concentration at 20 feet from road (ppm)	Concentration at 50 feet from road (ppm)	Concentration in remote location (ppm)
Pentadecane	D	D	D	ND
Hexadecane	1.78	0.58	0.21	ND
Heptadecane	3.43	1.70	0.19	ND
Octadecane	3.42	2.11	0.36	ND
Nonadecane	3.67	2.36	0.45	ND
Eicosane	3.35	2.76	0.46	ND
C-12 Acid	100 %	90.1%	19.1%	ND
C-14 Acid	100%	79.2%	11.6%	ND
C-16 Acid	100%	42.4%	5.4%	ND
C-18 Acid	100%	24.8%	3.2%	ND

* Species were identified upon examination of background noise and accurate quantification is difficult.

ND – indicates that this species was not detected in this sample.

Final analysis of the samples identified three key categories of contaminants; petroleum products (N-alkanes), lubricant combustion products (Organic Acids), and trace amounts of priority pollutants. All contaminants were observed to decrease in concentration rapidly with distance from the heavily traveled road.

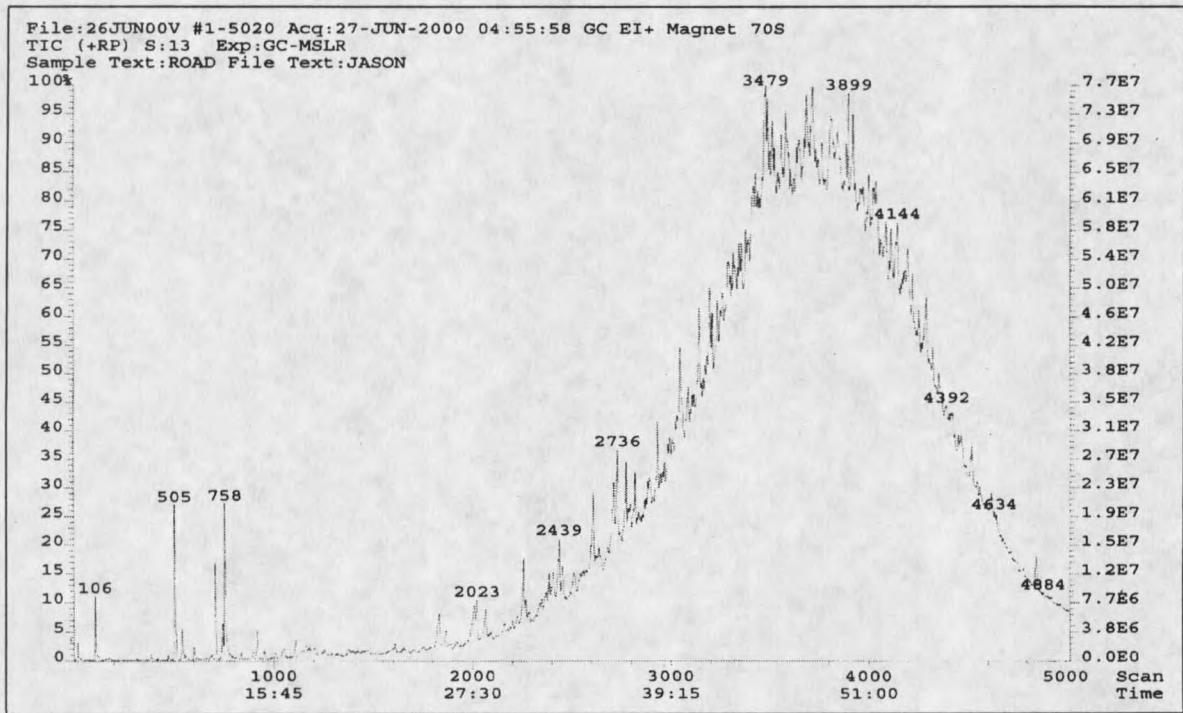


Figure 16. Chromatogram of snow sample taken from snow piles adjacent to the road at the West Gate

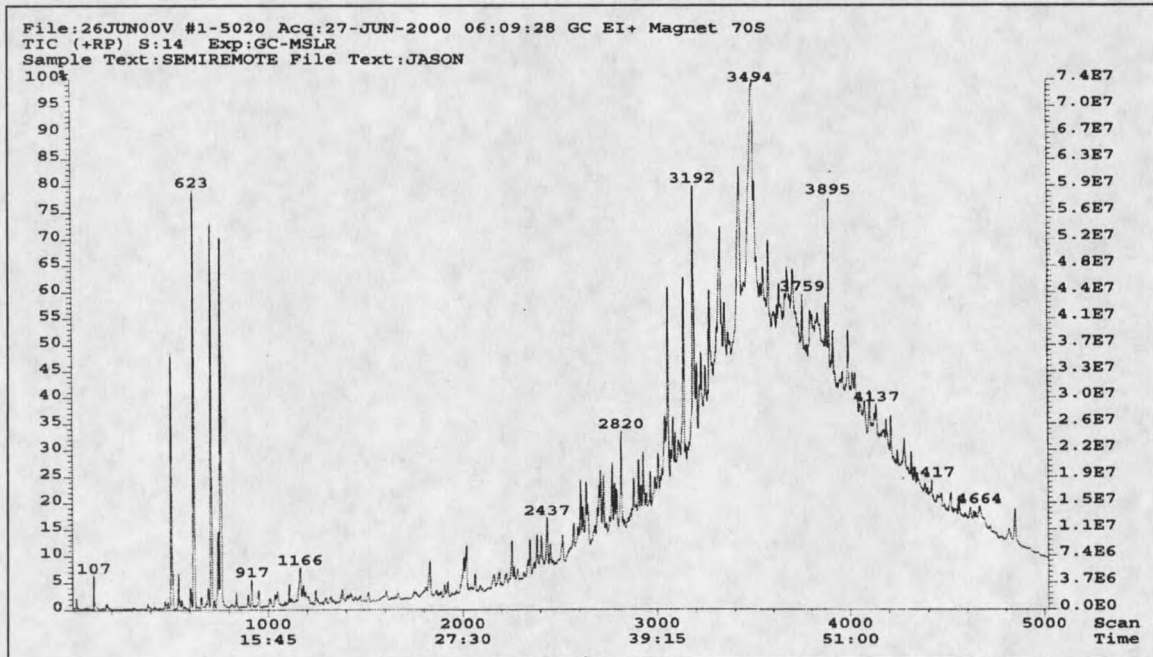


Figure 17. Chromatogram of sample taken 20ft. from road adjacent to West Yellowstone entrance.

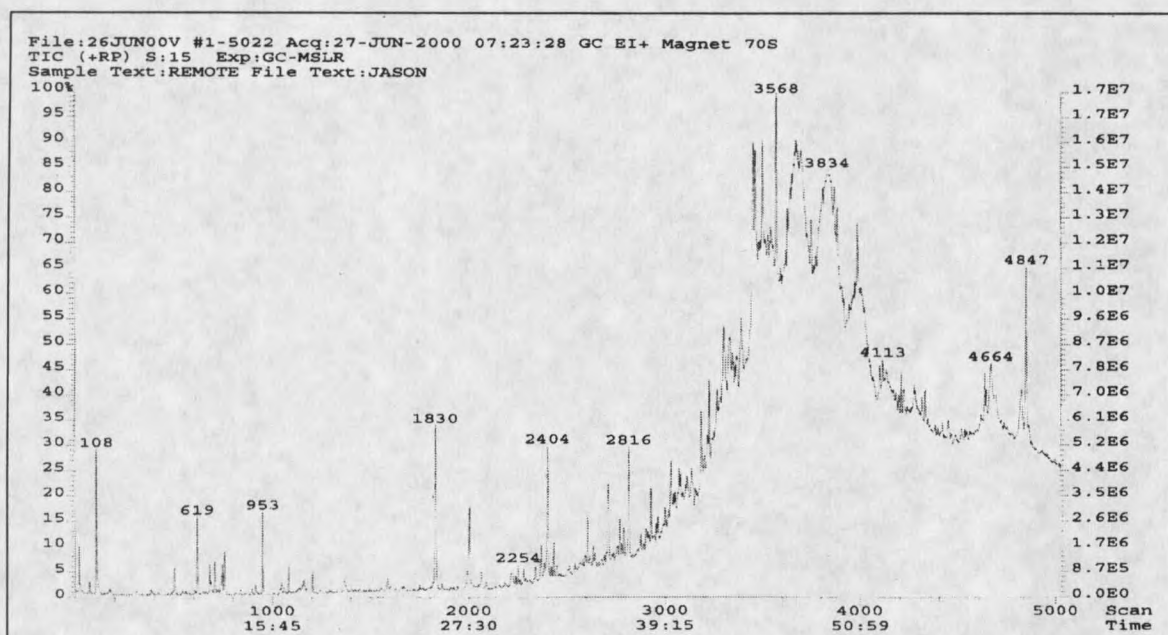


Figure 18. Chromatogram of snow sample taken 50 ft. from the road adjacent West Yellowstone entrance.

Figures 16-18 show the total ion chromatograms for samples at the road, 20 ft from the road, and 50 ft from the road. The primary feature observed in all of these chromatograms was a large unresolved hydrocarbon hump. Because of the high background, individual compounds could not be identified in the total ion chromatogram, however several compounds could be identified using single ion chromatograms. The presence of N-Alkanes C15-22 was detected observed in the mass 57 chromatogram for all samples (Figure 19). These contaminants are due to unburned lubricant exiting in the exhaust stream. The level of contamination decreased an average of 89% within 50 feet of the road. Standards were previously prepared for n-alkanes C16-20, allowing identification by retention time and mass identification, as well as accurate quantification.

Sample Text:ROAD File Text:JASON

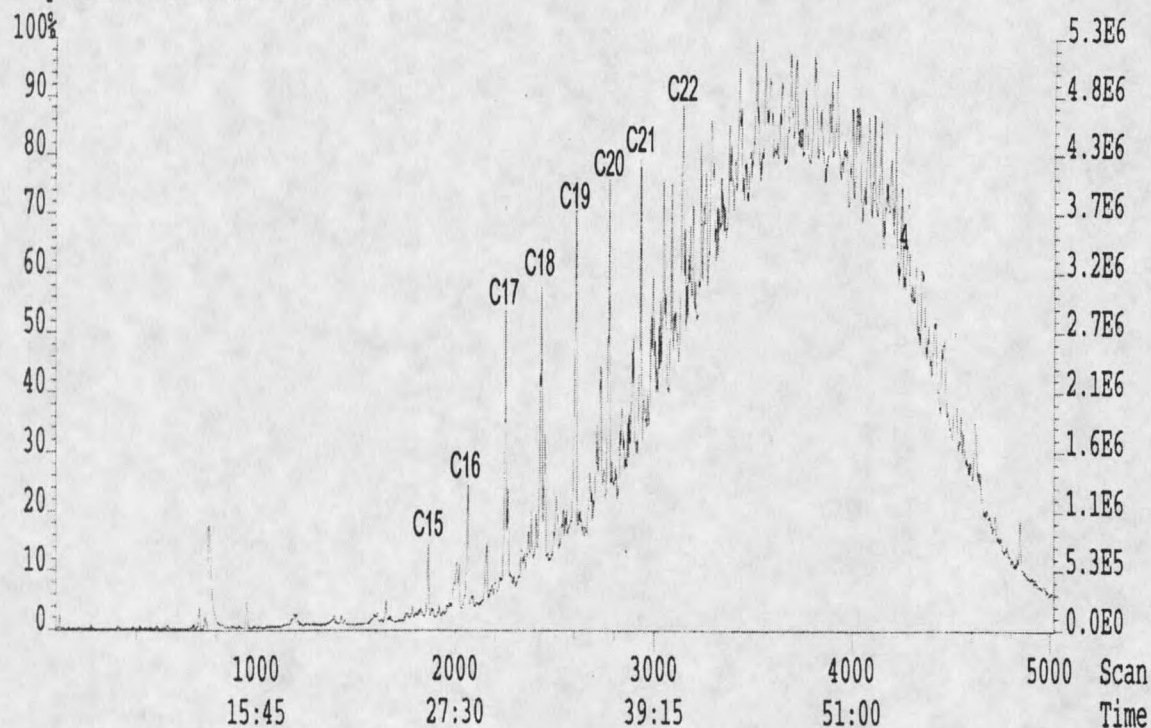


Figure 19. Single ion chromatogram of mass 57, N-Alkanes C15-C22 were identified.

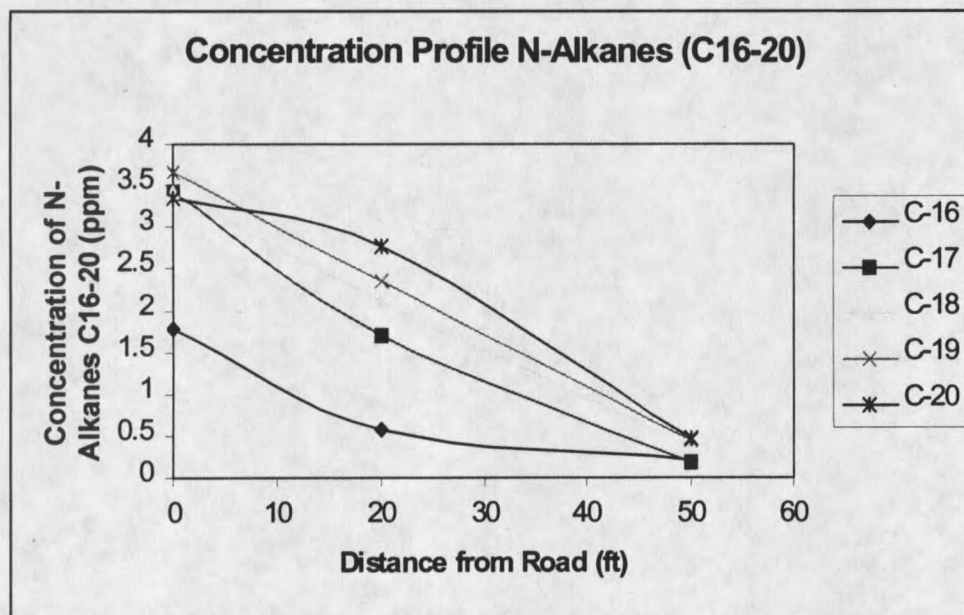


Figure 20. Data demonstrating decreasing n-alkane concentrations with distance from the road.

A series of organic Acids C-12,14,16, and 18 were detected in all three samples from the mass 60 chromatogram shown in Figure 21. These organic acids are suspected to be combustion products from lubricating oil. No standards were prepared for these species so accurate quantification was not possible.

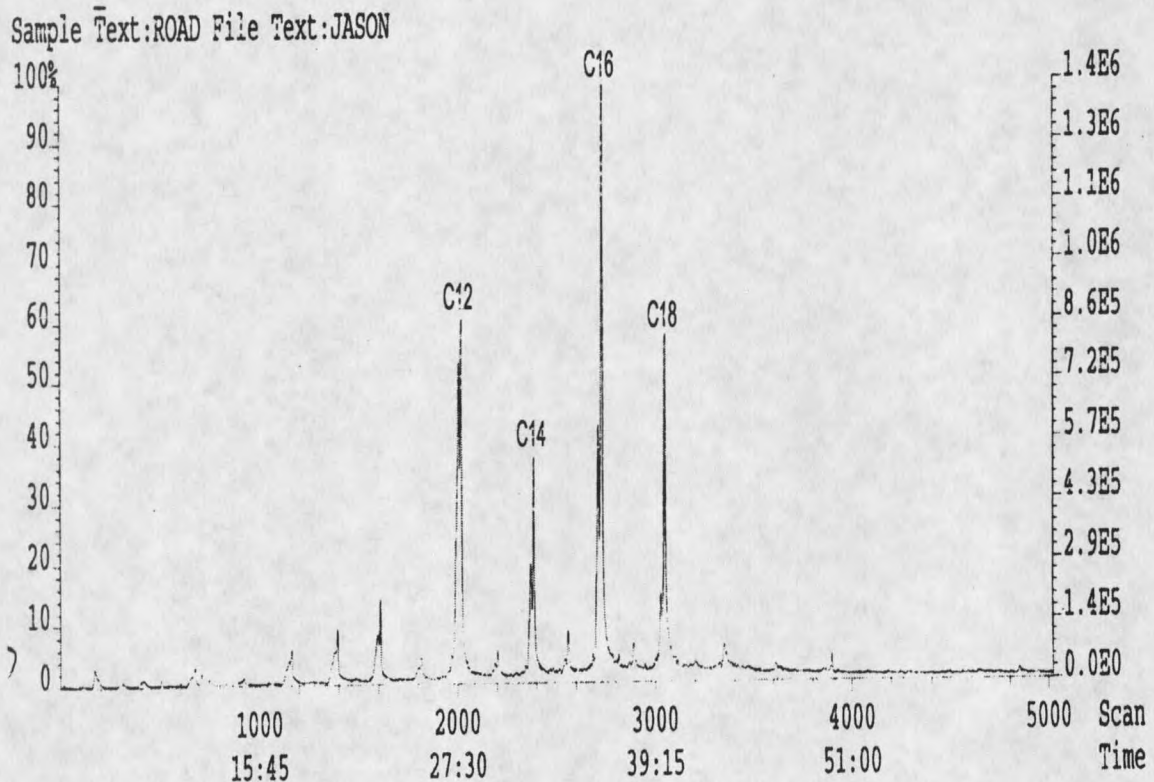


Figure 21. Single ion chromatogram of mass 60, organic acids C12,14,16,and 18 were identified.

In the figure below, they are shown to decrease rapidly with distance from the road. The sample taken from the road is considered to be the maximum contamination level (100%) and the samples at 20 feet and 50 feet are shown as a percentage of the amount present on the road. These contaminants decreased by an average of 90% within 50 feet of the road.

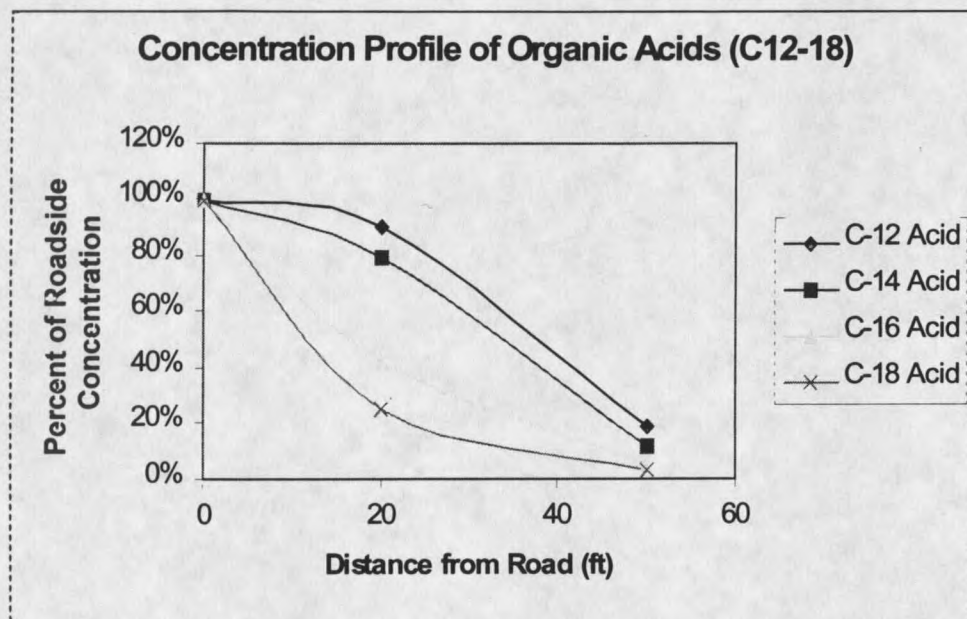


Figure 22. Data demonstrating decreasing Organic Acid concentration with distance from the road.

Naphthalene was detected at the ppb level in all samples. The sample taken from the road and the sample taken 20 ft from the road were approximately the same concentration, however the concentration of naphthalene decreased by 80% in the sample taken 50 feet from the road.

Upon close examination of the background using single ion chromatograms Fluorene, Phenanthrene, Dibutyl Phthalate, and Bis(2-ethylhexyl) Phthalate were identified at very low concentrations.

Table 8. PAH and other contaminants detected in snow samples.

Species Found	Concentration on Road (ppm)	Concentration at 20 feet from road (ppm)	Concentration at 50 feet from road (ppm)	Concentration in remote location (ppm)
Other Contaminants (ppb)				
Naphthalene	25.83 ppb	24.54 ppb	5.175 ppb	ND
* Fluorene	0.062 ppb	0.011 ppb	ND	ND
* Phenanthrene	0.183 ppb	ND	ND	ND
* Dibutyl Phthalate	0.332 ppb	0.313 ppb	0.122 ppb	ND
* Bis(2-ethylhexyl) phthalate	1.93 ppb	2.00 ppb	1.60 ppb	D

* Species were identified upon examination of background noise and accurate quantification is difficult.

ND – indicates that this species was not detected in this sample.

D – indicates species was detected but not quantified.

The concentration of these pollutants was near the detection limit which made quantification difficult, however these contaminants were quantified as accurately as possible using the semi-volatile calibration standard for EPA method 525. Bis(2-ethylhexyl) phthalate was detected in background sample taken at a site where snowmobiles are not allowed. Bis(2-ethylhexyl) Phthalate was also pretty consistent in concentration throughout the samples which indicates that it is probably a contaminant introduced during the sample preparation and analysis process.

Conclusions

Data indicates that contamination is localized to the road with snowmobiles being the primary contributor to hydrocarbon contamination of the snowpack. The concentration of all analytes was observed to decrease rapidly with distance from the

road. The concentration of N-Alkanes C15-22 decreased an average of 89% and Organic Acids C-12,14,16, and 18 decreased an average of 90% within 50 feet of the road. PAH concentrations were also noted to decrease with distance from the road, however since PAH levels were near the detection limits a constant rate of decrease was not observed.

The conclusion of pollutant localization is consistent with the results of a study by Ingersoll [32], which observed elevated levels of ammonium and sulfate in the vicinity of roads experiencing snowmobile traffic. The highest pollutant levels were present in samples taken directly from the road. Ingersoll noted that roads experiencing higher volumes of snowmobile traffic expressed higher levels of ammonium and sulfate contamination, indicating these contaminants as viable tracers for snowmobile exhaust products.

No other studies on snowmobile or two-stroke engine emissions in snow were found for data comparison, however the localization conclusion was supported in literature on automotive emissions. Studies by Viskari et al [18], and Gjessing et al [20], both noted a significant reduction in PAH due to automobile exhaust emissions within 100m of the highways studied. Gjessing et al concluded that the majority of pollutants in the snowpack are present in the banks of snow along the side of the road and pollution levels are reduced approximately 80% within 13m of the road. Oddly no quantification data was presented for roadside samples, however concentrations of phenanthrene and fluorene were reported as 1.4ppb and 96ppt respectively in samples collected 50m from the highway. Results of the study by Viskari et al [18], reported high variability between sampling sites for individual PAH species in snow. A general trend of decreasing PAH

concentration within 100 meters of the road was noted. Levels of Fluorene and Phenanthrene in the snow samples ranged from (15-1ppb) and (2-0ppb) above background respectively in samples taken 10-100m from the road. Naphthalene was not detected in snow samples. Snow sampling was not suggested as an effective method of PAH determination for future studies. Moss bag samples expressed a consistent trend of decreasing PAH concentration with distance from the road. Naphthalene, fluorene, and phenanthrene were observed at respective concentrations of 5-0.2ppb, 4-1ppb, and 25-1ppb above background in samples taken 5-100m from the road.

The PAH levels observed in the snow samples for this study range from 10-200 ppt for fluorene and phenanthrene, and from 4-25ppb for naphthalene. Observed pollution levels in literature are slightly higher with the exception of naphthalene. Further comparison of the results is complicated due to significantly different engine designs and a lack of information on traffic levels. However, it seems reasonable to conclude that the majority of pollution entering the snowpack due to mobile sources is localized within 50m of the travel lanes. Further more, the study by Viskari et al [18], implies that more precise and consistent measurements of PAH can be made by monitoring vegetation rather than snow.

Suggestions for Future Research

The PAH analysis of the Moss bags identified and consistently quantified 15 PAH, while only 6 PAH were identified in snow samples with highly variable results between collection sites. This suggests that roadside vegetation may be an important

biological sink for PAH present in snowmobile exhaust emissions [18]. In Germany a study by Jacob et al [33], addressed the topic of decreasing PAH pollution levels over the past decade. Vegetation such as Spruce sprouts or Poplar and Beech leaves, were used as passive samplers to determine PAH levels in the environment. This study supports the assertion that vegetation can play an important role in PAH removal from the environment and can be used effectively as a passive monitor. Future studies concentrating on PAH levels resulting from snowmobile exhaust emissions should consider using some type of vegetation as a co-monitor of PAH emissions.

Adsorption of PAH to particulate matter in engine exhaust streams [13] and aerosols in the environment [7] are the two primary pathways suggested for hydrophobic PAH to enter the snow pack. During the spring melt the majority of PAH trapped in snow crystals adsorb to organic particulate and are deposited in the soil or soil sediments of a nearby aquatic body [20]. This is also a reasonable fate for hydrophobic petroleum products expelled in the exhaust stream of a snowmobile engine. It seems likely that PAH and petroleum products accumulated in the snowpack of YNP would adsorb to soil particulate near the road as water from the melting snow diffuses down through the soil and into the watertable. Soil sampling prior to the snowmobile season and immediately after the spring melt could potentially give an indication of the amount of PAH and petroleum products accumulated in the snowpack throughout the winter. In conjunction with this study, the portion of the water that remains on the surface until joining a permanent water source should be analyzed for PAH and hydrocarbon content in a comprehensive attempt to determine the fate of snowmobile exhaust products in YNP.

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APPENDICES

APPENDIX A: SUMMARY OF WINTER USE ALTERNATIVES

The following is a brief outline describing each winter use alternative proposed by the National Park Service in the Draft Environmental Impact Statement for the Yellowstone and Grand Teton National Parks and John D. Rockefeller, Jr. Memorial Parkway, July 1999.

Actions Common to All Alternatives

- Determine winter use capacities with studies focusing on visitor experience and resource conditions. If necessary, implement techniques such as reservations, permits, and differential fees.
- Unless otherwise noted, implement all actions the winter following the "Record of Decision" for the winter use plans and environmental impact statement.
- If the Environmental Protection Agency (EPA) at anytime adopts more stringent standards or measurement methods for snowmachine emissions and sound levels than those identified in this document, the more stringent standards or methods would be required. A grace period of two years would be allowed for implementation unless EPA allows a phased-in schedule. If the EPA schedule allows more than two years to meet the standards, NPS reserves the ability to require the more stringent standards sooner.

Actions Common to all Yellowstone Alternatives

- Highway 191 and the road from Mammoth to Tower and Tower to the Northeast Gate (Cooke City) would continue to be plowed throughout the winter.
- Grand Canyon of the Yellowstone would continue to be closed to winter use.
- Sand would continue to be used for traction on all plowed winter roads, no salts or other chemical abrasives would be used.
- Before spring opening, sand removal operations would continue on all plowed park roads.

- Where snow depth warrants, and at periodic intervals, routine plowing operations would include the plowing or laying back of roadside snow-banks that may prohibit wildlife from exiting the road corridor.

Alternative A

This is referred to as the “No Action” alternative and would maintain the current policy regulating winter use in YNP. Some important features are listed below.

- The oversnow speed limit is 45 mph.
- Bio-based fuels and lubricants are used by the NPS and are available for purchase in gateway communities.
- Snowmobiles are required to operate at or below 78 decibels as measured on the A-weighted scale at 50 feet and full throttle.
- Roads for snowmobile travel will be groomed as before allowing approximately 180 miles of groomed road.
- Non-motorized travel will continue to be allowed in all areas of the park except in the Grand Canyon of the Yellowstone.
- The winter season of operation for oversnow routes is from about mid-December to mid-March.

Alternative B

This is referred to as the preferred alternative and provides a moderate range of affordable and appropriate winter visitor experiences. Air quality and oversnow vehicle sound would be addressed by an advisory committee that would make recommendations on the phasing and implementation of sound and emission standards over the next 10 years. By winter 2008-2009, strict emission and sound requirements would be required

by all oversnow vehicles entering the parks. This alternative will incorporate the results of any ongoing research into the park management policy as appropriate. Results indicating a significant disturbance to wildlife or the ecosystem would result in trail closures or other actions as deemed appropriate. Some key points of this alternative include the following.

- By winter 2008-2009 snowmobiles would be required to reduce hydrocarbon emissions by 70%, carbon monoxide by 40%, and particulates by 75%.
- A committee would be formed to recommend and implement phasing of the new standards. The committee would be disbanded after implementation of the standards is complete.
- By winter 2008-2009 sound levels would be reduced to less than 70 decibels as measured on the A-weighted scale at 50 feet and full throttle.
- If technology is not sufficient to allow snowmobiles to meet these standards by winter 2008-2009 then oversnow transportation in the park would be limited to snowcoaches until the required standards are met.
- Improve groomed trail conditions and safety, prohibit late night oversnow travel.
- Provide visitors with a higher quality experience by increasing educational opportunities about the ecosystem, implementing an aggressive information and enforcement program concerning snowmobile speed and proper recreational etiquette within the park, and making visitors aware of all recreational opportunities available within the park.
- Improve affordable access to key interior points of the park through the addition of wheeled vehicle access on certain roads.
- Continue scientific studies and monitoring regarding winter visitor use and park resources. Implement closures or restrictions as deemed necessary by the impact studies.

Alternative C

This alternative offers maximum winter visitor opportunities for a range of park experiences, while preserving natural resources and addressing safety concerns. Some key highlights of this alternative are mentioned below.

- Beginning in winter 2002-2003 sell only 10% ethanol blend gasoline and synthetic low emission lubricant oil for snowmobiles.
- Strictly enforce the current sound standards.
- Implement an information program on snow and trail conditions, points of interest, and available winter recreational activities.
- Increase the number of groomed trails for both motorized and non-motorized use.
- Improve affordable access to the parks' interior by adding wheeled vehicle access.
- Provide a greater range of winter recreation opportunities by adding winter camping in certain areas, special access to quiet areas for snowshoeing and skiing, and increasing overall access to the parks interior.

Alternative D

This alternative emphasizes opportunities for visitor access to the unique winter aspects of the park (i.e. geysers, wildlife, and scenic vistas), and protection of those resources by phasing in clean and quiet modes of transportation. Winter access to the parks would be focused around gateway communities and key destination areas. Support facilities would have minimal amenities. Some key points of this alternative are mentioned below.

- By winter 2002-2003 sell only 10% ethanol blend fuel and synthetic lubricating oil for snowmobiles, and require all oversnow vehicles to meet the strict emission standards mentioned earlier by winter 2007-2008.
- Prohibit late night oversnow travel.
- The east entrance to YNP would be closed to travel during the winter months.
- The motorized route from West Yellowstone to Old Faithful would be groomed more regularly and to a higher standard of quality.
- When possible use separate areas of the park for different uses, for example create for trails and non-motorized access in areas of the park off-limits to motorized travel.
- Emphasize motorized travel opportunities in the southwest and western regions of the park while emphasizing non-motorized travel in the north and northwest regions of the park.

Alternative E

This alternative emphasizes the protection of wildlife and other natural resources while allowing park visitors access to a range of winter recreational experiences. An adaptive plan is recommended in response to ongoing research, and a committee is recommended to oversee the implementation of emission and sound restrictions. This is very similar to the protective approach mentioned in alternative B. Some highlights unique to this alternative are mentioned below.

- Allow nighttime oversnow travel however at a reduced speed of 35 mph.
- Continue scientific studies
- Limit oversnow travel in range areas.

Alternative F

This alternative emphasizes protection of wildlife resources by focusing winter visitor activities near scenic areas in the eastern and southern portion of YNP. These areas are generally outside important winter range for large ungulate wildlife species.

Some key points of this alternative are listed below.

- As technology becomes available for emissions and sound reduction (i.e. mass produced and available for public purchase), require these technologies allowing a 2 year implementation period.
- Prohibit nighttime oversnow travel.
- Reduce the number of roads available for motorized travel.
- Increase the size and number of warming huts and other day-use facilities.

Alternative G

This alternative emphasizes clean quiet oversnow access to the parks using the technologies available today. Allowing motorized access to the parks only in the form of mass transit vehicles. Some key elements of this alternative are mentioned below.

- Mass transit vehicles must meet strict emission and sound standards as specified by this alternative.
- Prohibit nighttime oversnow travel.
- When snowmobiles can meet the strict emission and sound requirements the NPS may consider allowing them into the parks.
- Emphasize an increase in groomed trails for non-motorized use.

APPENDIX B: PERSONAL COMMUNICATION WITH DR. WHITE

Personal Communication with Dr. White of the Southwest Research Institute via e-mail, July 12, 2000.

Jason

As I look back at the snowmobile data, I agree that the naphthalene numbers seem low compared to other species. Our experience with measurement of this compound is that due to its low MW, there tends to be a lot of variability in reported values. I looked at some automotive data, which showed naphthalene as a substantial component of total PAHs, but the list of species analyzed was not as extensive as in the snowmobile work. I also found that some PAH work doesn't even look for naphthalene – likely because it's not a toxic species, and thus gets less attention. In any event, I haven't found any other 2-stroke data to compare it against. We are doing a project for CARB, which will look at PAH emissions from 2-stroke outboard motors. The experimental portion of that work will not begin till later this year. I'll keep you posted if I find anything else of use.

Jeff J. White
SwRI Automotive Products and Emissions Research Division
Phone: 210 – 522 – 2649
E-mail: jjwhite@swri.org

APPENDIX C: PAH STANDARD CALIBRATION CURVES

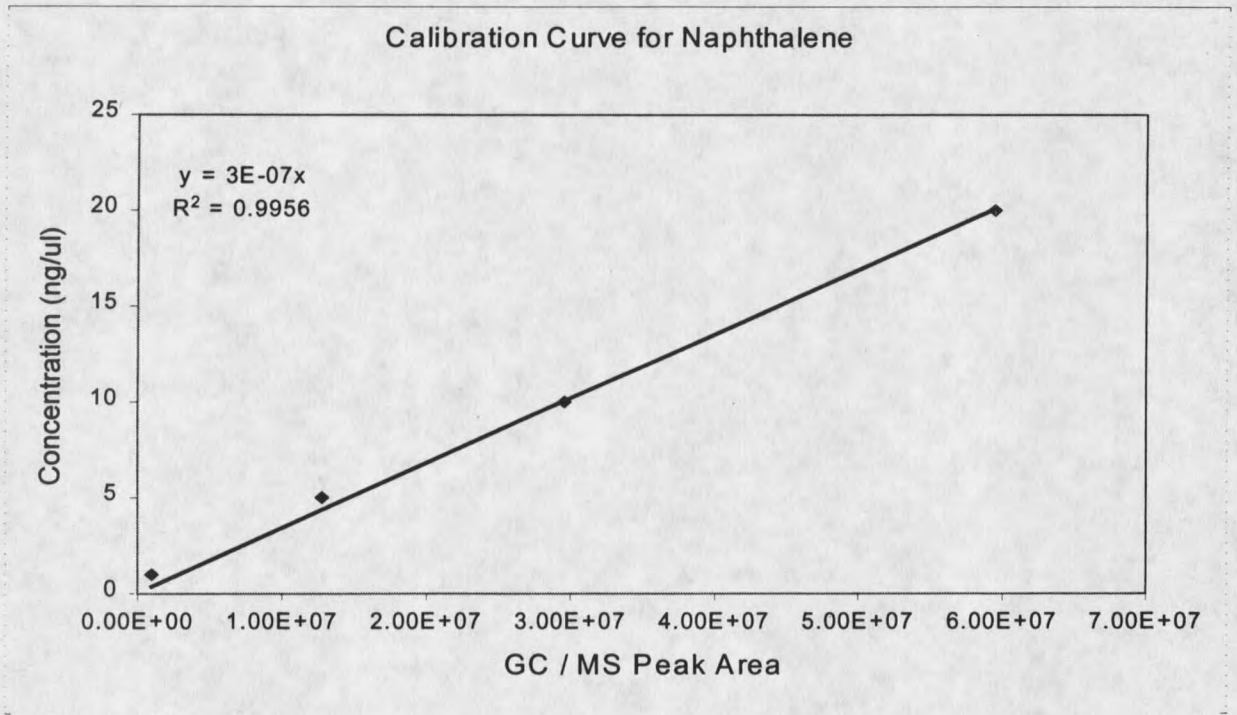


Figure 23. Calibration curve for naphthalene diluted in methylene chloride.

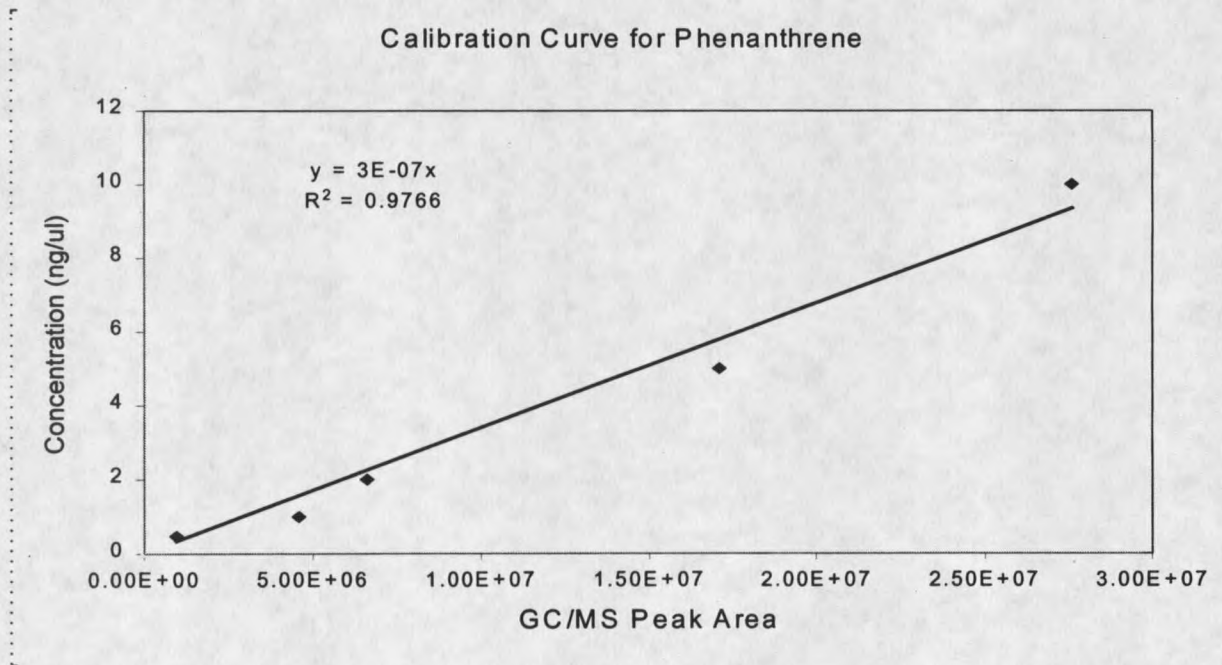


Figure 24. Calibration curve for phenanthrene diluted in ethyl acetate.

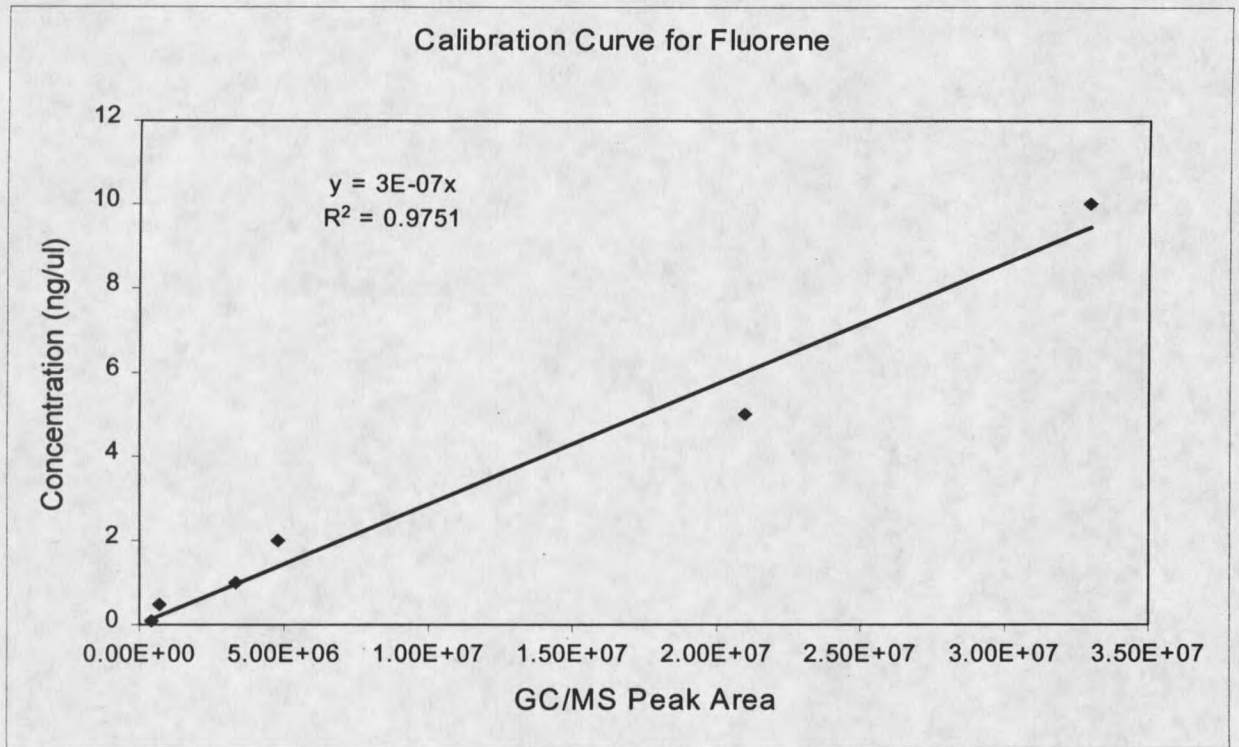


Figure 25. Calibration curve for fluorene diluted in ethyl acetate

APPENDIX D: HYDROCARBON STANDARD CALIBRATION CURVES

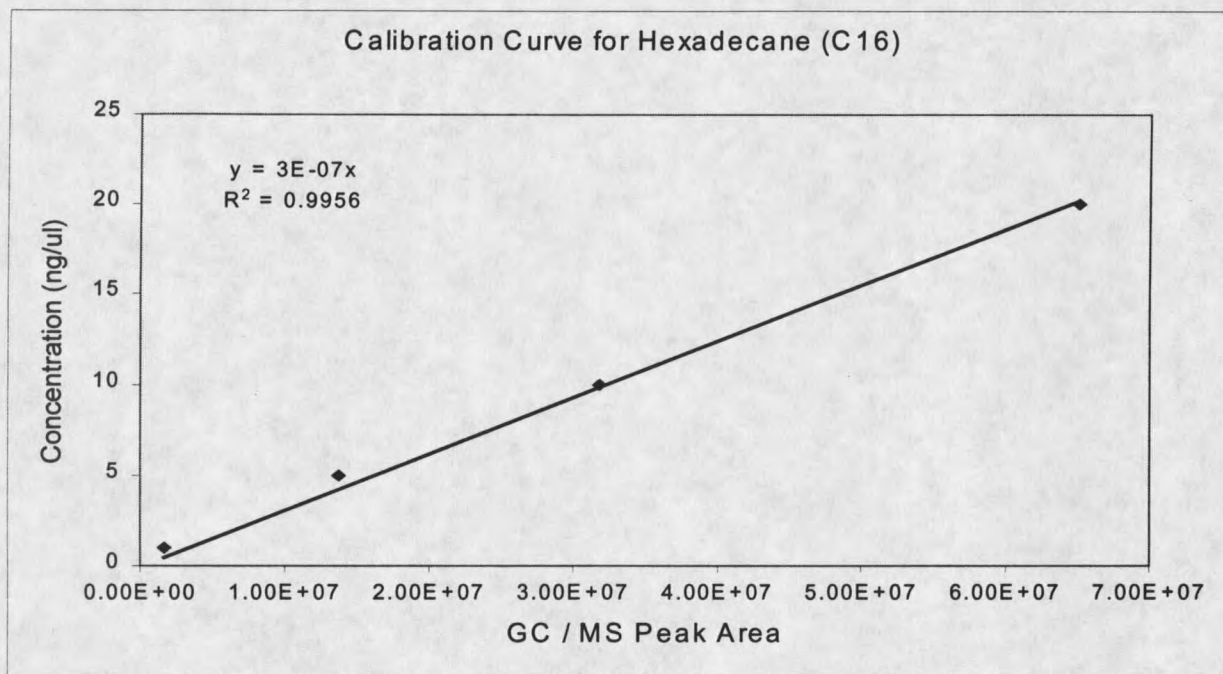


Figure 26. Calibration curve for N-Hexadecane (C16) diluted in methylene chloride.

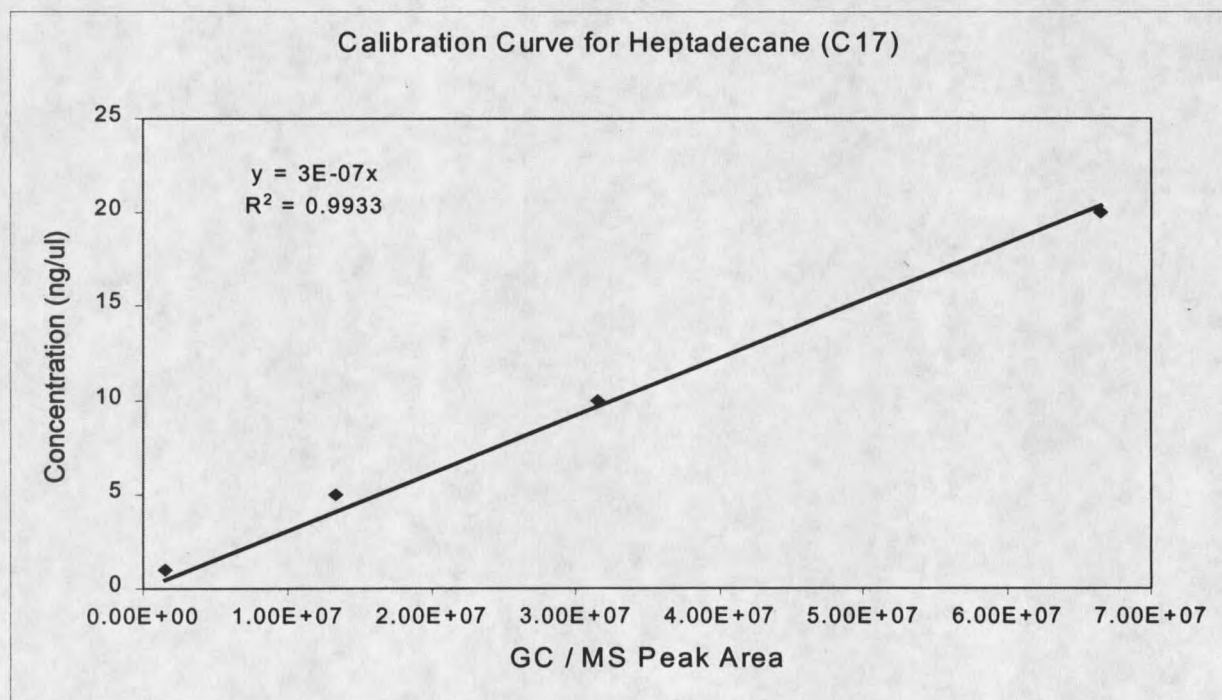


Figure 27. Calibration curve for N-Heptadecane (C17) diluted in methylene chloride.

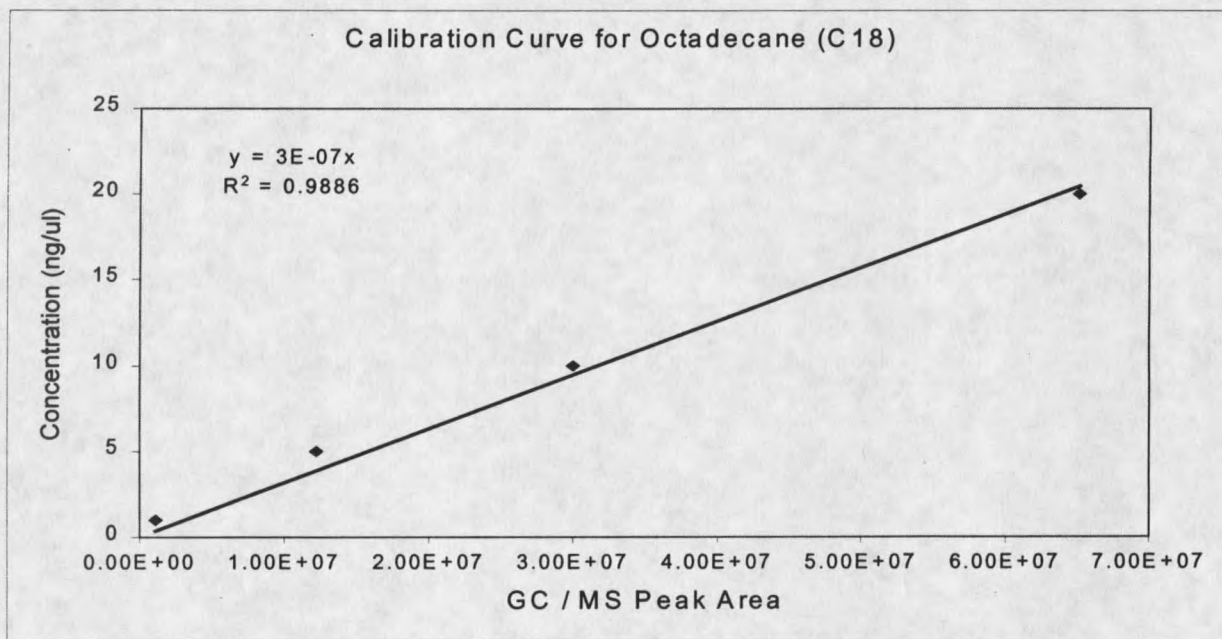


Figure 28. Calibration curve for N-Octadecane (C18) diluted in methylene chloride.

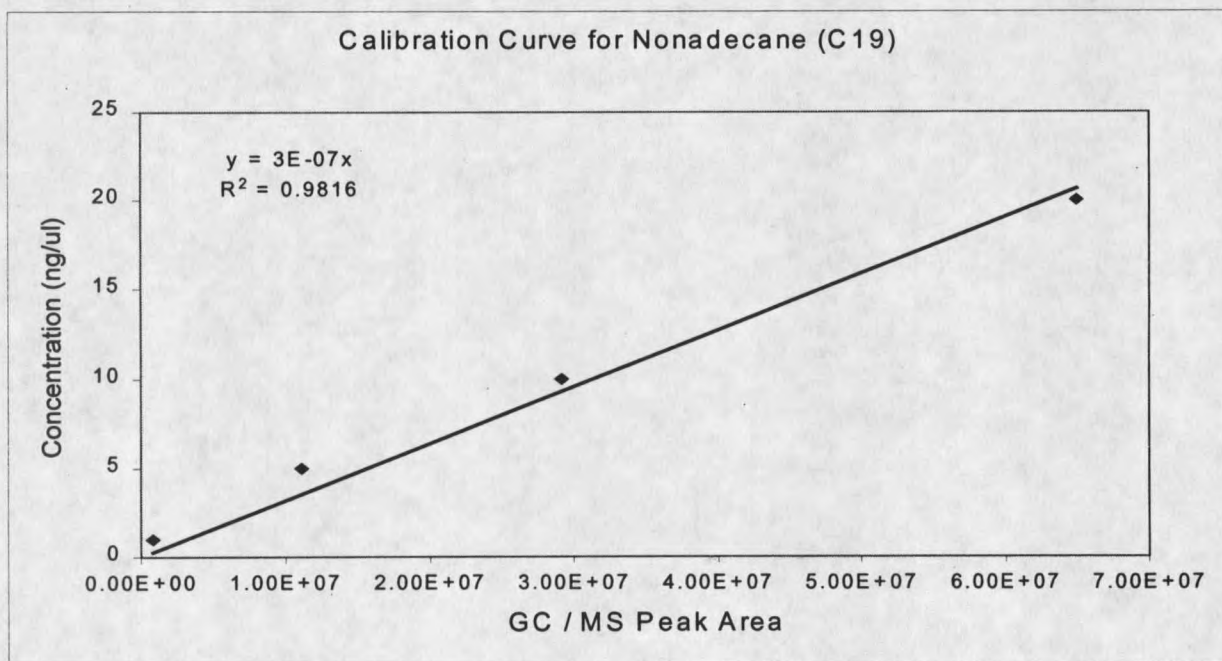


Figure 29. Calibration curve for N-Nonadecane (C19) diluted in methylene chloride.

