Environmental and Occupational Exposure to Toxic Air Pollutants from Winter Snowmobile Use in Yellowstone National Park

FINAL REPORT

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GLOSSARY OF TERMS AND ABBREVIATIONS

AIRS	Air Information and Retrieval System
ATSDR	Agency of Toxic Substances and Disease Registry
BTEX	Benzene, Toluene, Ethylbenzene, and o-, p-, m-xylenes
CO	Carbon Monoxide
DCM	Dichloromethane
DNPH	2,4-dinitrophenylhydrazine
EPA	Environmental Protection Agency
GC/MS	Gas Chromatography/mass Spectrometry
HPLC	High Performance Liquid Chromatograph
IARC	International Agency for Research on Cancer
LPM	Liters Per Minute
MDEQ	Montana Department of Environmental Quality
MRL	Minimal Risk Level
MQL	Method Quantifiable Limit
NAAQS	National Ambient Air Quality Standard
NPS	National Park Service
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standard and Technology
PM	Particulate Matter
PM2.5	Particulate Matter 2.5 Microns Aerodynamic Diameter and Smaller
PM4	Particulate Matter 4 Microns Aerodynamic Diameter and Smaller
PM10	Particulate Matter 10 Microns Aerodynamic Diameter and Smaller
PPM	Parts Per Million
PEL	Permissible Exposure Limit
PerPM	Personal Exposure to Particulate Matter
REL	Reference Exposure Limit

GLOSSARY OF TERMS AND ABBREVIATIONS (cont'd)

STEL	Short-term Exposure Limit
SwRI	Southwest Research Institute
TSP	Total Suspended Particulate
TWA	Time-weighted Average
UCD	University of California at Davis
VOC	Volatile Organic Compounds

I. Executive Summary

A. Background

During the winter, Yellowstone National Park and the city of West Yellowstone become a major center for recreational snowmobile use with over 50,000 snowmobiles entering the Park by the end of the season. On peak days, over 1,000 snowmobiles enter the Park through the West Entrance. Snowmobiles are powered by 2-stroke engines and have been reported to emit higher levels of regulated and toxic air pollutants than 4-stroke engines (White and Carroll, 1998; Kado et. al., 2000). Approximately 20 to 30 percent of the fuel is emitted unburned and up to 5 percent of the fuel is lubrication oil. National Park personnel and other individuals exposed to snowmobile exhaust have reported increased clinical symptoms such as headaches, nausea, and dizziness. These reports led to the initial development of this project. Also important was the concern that individuals and the environment may be exposed to toxic air pollutants, including compounds that are known to cause cancer. This study was an initial investigation to evaluate Park employee and environmental exposure to air pollutants, including toxic air pollutants, and the relationship of these pollutants with snowmobile use.

The study described herein was part of a multi-disciplinary and multi-organizational investigation of winter air pollution and its sources in Yellowstone National Park. Specifically, we studied human occupational and environmental exposure to particulate matter and toxic air pollutants during heavy and typical snowmobile use in the Park. This study incorporated multiple integrated fixed-site and personal sampling for the analyses of airborne particulate matter (PM) and volatile organic compounds (VOCs). Both types of air pollutants are known to be toxic and their specific components can be found on both

national (U.S. EPA) and California (Cal EPA) toxic substances lists. The fixed-site samples were collected using sampling devices that were placed in stationary locations typically near areas of worker activity. Personal PM and VOC samples were collected from workers wearing portable sampling devices that were attached to their shirt or jacket collars and positioned several inches away from the breathing area (nose and mouth). Sampling took place primarily during the Presidents' Day holiday weekend and throughout the following week (February 13 -22, 1999) and samples were collected during typical visiting and working hours (8 a.m. to 5 p.m).

B. Methods and Approaches

Particulate matter samples of 2.5 and 10 µm (micron or micrometer) aerodynamic diameters were collected using fixed-site samplers at the West Entrance, Madison Junction, and Old Faithful Visitor Center and at two locations in the town of West Yellowstone. Morning (typically 8 a.m. to 12 noon) and afternoon (typically from 12 noon to 5 p.m.) samples were acquired for fixed-site samplers. Personal exposure to respirable particulate matter (PerPM) was also investigated for Park employees in various jobs at these locations. To study exposure to VOCs, fixed-site and personal samples were obtained and analyzed. Peak exposures were also determined. Personal exposure to aldehydes was also determined.

The source of PM and VOCs were evaluated using two approaches. First, the relationship of the number of snowmobiles and airborne concentrations of CO and PM were conducted. Second, gas chromatographic/mass spectral analyses of selected VOCs in gasoline acquired from West Yellowstone gasoline stations were compared to grab samples of VOCs collected at the West Entrance.

The assessment of cancer risk was estimated from the measured concentrations of benzene and US EPA risk numbers for benzene exposure.

C. Results and Discussion

Approximately 90 percent of the snowmobiles and coaches that enter the West Entrance of the Park do so by 12 noon. Over 80 percent of the snowmobiles that enter the Park travel to Old Faithful (OF), where the observed number of snowmobiles in the parking lots peak between 10 a.m. and 2 p.m.

A maximum concentration of 160 µg/m^3 particulate matter of 2.5 µm diameter (PM2.5) was collected during the morning (8:30-12:30) at the West Entrance fixed-sites. Personal respiratory PM samples (PerPM) that were collected to evaluate the workday exposure of National Park Service (NPS) employees at the West Entrance also had a maximum concentration near 160 µg/m^3, but were highest for a Park Service mechanic working indoors (4-hour sampling time) with a concentration of approximately 500 µg/m^3. NPS West Entrance employees with the highest PerPM exposures typically worked outside the kiosk and in the Express Lane near snowmobiles entering the Park. Mobile patrol rangers were exposed to PerPM ranging from approximately 40 to 100 µg/m^3, which was less than that for West Entrance employees. PerPM for workers working typically outdoors at the remote sites was approximately 20 µg/m^3 for employees at Madison and 60 µg/m^3 for employees at Old Faithful. Measurement of PerPM within the NPS office environment ranged from approximately 10 to 30 µg/m^3.

A number of occupational studies have focused on worker exposure to particulate matter from combustion sources such as from diesel engines and have reported PM

concentrations in the range of exposure observed for Park Service employees. Some Park employees exceeded measurements reported for workers exposed to diesel exhaust, however.

Different mass size-selective sampling devices were used in parallel for evaluating fixed-site PM measurements at the West Entrance. The concentrations (ug/m^3) of PM10 and Total Suspended Particulate matter (TSP) were virtually identical to PM2.5 concentrations collected at the same location, especially for the morning sampling period when the highest concentrations were observed, indicating that particles were all less than PM2.5 in size. Particles of this size or less are known to enter the deepest parts of the lung where they could reside and cause damage.

A spatial analysis of airborne PM10 concentrations was conducted simultaneously at four locations during a sampling day. The locations incorporated a residential neighborhood in West Yellowstone, the West Yellowstone downtown location (a US EPA site), the West Entrance, and the Old Faithful location. There was a gradient of PM10 concentrations observed for the sample collected during the day, with the lowest levels measured at the residential location, higher levels at the downtown location, peak levels at the West Entrance location near worker-assigned areas, and slightly lower levels at the Old Faithful location.

Personal exposure to VOCs was studied for employees in various job categories. For example, benzene concentrations measured for employees at the West Entrance were approximately 100 to 300 µg/m^3, and approximately 100 to 200 µg/m^3 for the mobile patrol employees. A mechanic working indoors had the highest benzene exposure at approximately 500 µg/m^3 for a 4-hour working period. If this level was maintained over a 6 to 8 hour period, it would exceed the National Institute for

Occupational Safety and Health (NIOSH) Recommended Exposure Level (REL) for benzene (320 µg/m^3). National Park workers were exposed to benzene concentrations that are many times higher than benzene concentrations reported for urban workers who worked in traffic (Crebelli et al, 2001). The National Park workers were also exposed to benzene many times higher than short term 2-hour commutes in Los Angeles (Rodes et al., 1998) and for benzene concentrations reported for 12-hour exposures measured indoors in Los Angeles homes (Sheldon et al. 1992).

The level of concern as determined by the U.S. EPA for excess risk of cancer is usually 1 per 1,000,000 persons or greater. The risk for cancer for benzene at 1 µg/m^3 for a lifetime of 70 years exposure (referred to as "unit risk") is 2 to 8 per million based on U.S. EPA estimates (U.S. EPA, 2001) and 3 per 100,000 based on California Office of Environmental Health Hazard and Assessment (OEHHA) estimates (OEHHA, 2001). Based on worker exposures to benzene at the West Entrance and calculated for a median exposure concentration of 190 µg/m^3 (for the winter season of 65 working days) the risk would be approximately 1 to 4 per 100,000 or 1 per 10,000 based on U.S. EPA or OEHHA unit risks, respectively. This is considered a relatively high level of risk for exposure to a single compound. This estimate is conservative and based on a 20 year working lifetime for Park employee, and is in addition to any other benzene exposure occurring during a lifetime, including daily ambient exposures, and work exposures that may occur during other seasons at the Park. Many Park employees are exposed to relatively high levels of benzene. For example, a mechanic was exposed to over 500 µg/m^3 over a 4-hour work period, while West Entrance employees were exposed to average maximum concentrations of approximately 300 µg/m^3. The risk was calculated for benzene, but workers were also exposed to other carcinogenic

compounds such as formaldehyde and to acetaldehyde that would add risk to that from benzene exposure alone.

Another risk determinant for a number of toxic substances is called the Minimal Risk Levels (MRL) as established by the Agency of Toxic Substances and Disease Registry (ATSDR; Centers for Disease Control, Atlanta, GA.). An MRL is a substance-specific estimate of the daily exposure to a hazardous chemical likely to be without appreciable risk of adverse non-cancer health effects. The MRL for acute exposure to benzene (1-14 days; 162 $\mu g/m^3$) was exceeded by some employees at the West Entrance, mobile patrol, and the mechanic. The MRL for intermediate exposure to benzene (15-365 days; 12.96 $\mu g/m^3$) was exceeded by all employees monitored.

Peak personal exposure to aldehydes typically occurred before 10 a.m. each day. For example, the highest short-term personal exposure to formaldehyde was 88 $\mu g/m^3$ at the West Entrance. Two of the West Entrance employees exceeded the acute exposure (1-14 days) MRL of 62 $\mu g/m^3$ for formaldehyde.

Employee exposure to high concentrations of carcinogens and toxic air pollutants for a relatively short period of time over a number of winter seasons presents challenges for estimating cancer risk. Some recent animal bioassays for carcinogenicity seem to indicate that short-term exposures at higher doses may increase cancer risk beyond that of an equivalent total dose administered at lower levels over a longer period of time (Halmes et al., 2000). This implies that short-term relatively high occupational exposures may increase risks of cancer above that estimated for lower doses with an equivalent lifetime of exposure. This may be consistent with toxic biological mechanisms where toxic compounds are known to damage sensitive biological targets

such as DNA and chromosomes, for example, and where damaged genetic material could remain in the body for a long period of time.

Another important factor to consider when assessing potential health risk is the possibility of gender differences in sensitivity to toxic compounds. For example, one study has reported that women may metabolize 23-26% more benzene than men when subject to the same exposure scenario (Brown et al., 1998). The most serious benzene-related adverse health effects are caused by benzene metabolites. Therefore, if men and women are exposed to equivalent amounts of benzene, but women metabolize more benzene than men, then women may be at relatively higher risk for certain health effects related to benzene exposure. Since the current standards are based on occupational data predominantly from male workers, this raises questions regarding certain occupational standards and how protective they are for the female worker.

Snowmobiles as an emission source were statistically evaluated. The number of snowmobiles entering the Park and average carbon monoxide (CO) concentrations were recorded for the morning and afternoon hours. There was moderate correlation between the average morning CO concentrations and the number of snowmobiles entering the Park ($R^2 = 0.68$) and weak correlation for the corresponding average afternoon CO concentrations ($R^2 = 0.212$). However, a strong correlation was observed between the number of snowmobiles entering the Park at the West Entrance and the average daily (morning and afternoon) PM2.5 ($R^2 = 0.88$). This correlation improved slightly when only the morning PM2.5 value was used in the calculation ($R^2 = 0.93$).

To further evaluate the source of the VOC toxic air pollutants, gas chromatograms were evaluated for similarities to gasoline samples obtained from local West

Yellowstone gasoline stations. The VOC samples from the West Entrance and the gasoline samples contained similar chemical components. This indicates that the source of VOCs were gasoline-derived.

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As part of evaluating the toxic air pollutants emitted from snowmobiles, PM was collected from a snowmobile engine operated under controlled conditions using a mineral based lubricant or a synthetic lubricant (bio-lubricant) with the engine connected to an engine dynamometer (SwRI, 1999). The PM was collected during 5 separate operating modes (industry-developed steady state tests for each mode) and tested in a bioassay for mutagenic activity. The highest activity was detected in Mode 1 (full throttle) and in Mode 5 (idle). Total mutagenic emissions were higher using the mineral based lubricant than for the biolubricant.

D. Conclusions and Recommendations

In this study, we examined occupational and environmental exposure to particulate matter and toxic air pollutants at Yellowstone National Park. This study is the first investigation of personal exposure to particulate matter and toxic volatile compounds from 2-stroke snowmobile engines. Many of these toxic compounds are reported to cause chronic health effects such as cancer and other non-cancer diseases. The particulate matter collected under controlled conditions from a snowmobile engine was mutagenic (caused DNA damage) for all test modes (full throttle to idle).

The time, job, and geographic dependence of particle matter and VOC concentrations support the hypothesis that Park employees and the surrounding environment are exposed to relatively high levels of many toxic pollutants as a result of snowmobile use within the

Park. These exposures are measurable for defined areas monitored during typical working and visiting hours, and are measurable with personal sampling. Exposures for many employees exceed some published risk levels. These exposures also exceed occupational exposures reported in other studies for VOCs as well as for PM.

Efforts to dramatically decrease Park employee exposure to toxic air pollutants should be a high priority and implemented immediately. Mitigating approaches could include incorporating 4-stroke engine technology into the snowmobile fleet, outdoor ventilation, and as a last defense, use of charcoal and filter mask units.

An integrated study of worker, visitor and environmental exposure to airborne PM and toxic compounds during heavy tourist seasons (winter and summer) is recommended. Ideally, these studies should include some baseline exposure measurements and baseline worker health surveillance data established prior to the implementation of changes in emission control strategies. Studies should be initiated during the transition period when controls for emissions change (for example, if portions of the fleet change technology) so that exposures projected to be intermediate from the baseline could be obtained. From the perspective of protecting Park employees, visitors, and the environment for the future, the fate and transport of toxic compound emissions from snowmobiles as well as other vehicular sources should be investigated within the Park. These types of research efforts will benefit from interdisciplinary interaction between state and federal agencies, as well as from industry and academic institutions.

II. Introduction

During the winter, Yellowstone National Park and the city of West Yellowstone transform into a major center for recreational snowmobile use and travel. Hundreds of snowmobiles and riders enter Yellowstone National Park daily, with over 1,000 snowmobiles reported entering the West Entrance alone on a peak day. Snowmobiles are powered by 2-stroke engines and have been reported to emit higher levels of regulated and toxic air pollutants than 4-stroke engines (White and Carroll, 1998; Kado et. al., 2000). Approximately 20 to 30 percent of the fuel is emitted unburned and up to 5 percent of the fuel is lubrication oil. National Park personnel and other individuals exposed to snowmobile exhaust have reported serious clinical symptoms such as headaches, nausea, and dizziness.

Airborne particulate matter, especially particles that are less than 10 microns (PM10) or less than 2.5 microns (PM2.5), are associated with increases in respiratory disease, lung damage, cancer, and premature death (Schwartz and Dockery, 1992; Dockery, et al., 1993; Abbey et al., 1995). The National Research Council of the National Academy of Sciences has indicated that a research priority is to "investigate quantitative relationships between particulate matter concentrations measured at stationary outdoor monitoring sites and the actual breathing-zone exposures of individuals to particulate matter and gaseous co-pollutants…" (NRC, 1998). Although the stationary sites indicated by NRC are referring to air pollution monitoring sites in regions, cities, or neighborhoods, the concept of evaluating fixed-site and individual exposure to particulate matter and gaseous co-pollutants is important to study.

A number of occupational studies have focused on worker exposure to particulate matter from combustion sources. For example, respirable PM collected

by personal samplers for non-smoking diesel railroad workers ranged from 104 $\mu g/m^3$ (inside workers) to 143 $\mu g/m^3$ (carmen). Non-smoking shop workers (a large indoor repair shop) were exposed to a median concentration of 113 $\mu g/m^3$ (Schenker et al., 1990). Diesel particulate exposures were determined for workers in a major southeastern US electric utility company during normal working hours (Whittaker, et. al., 1999). Based on total organic carbon measurements, the range of mean PM was from 16 $\mu g/m^3$ for background measurements (n= 18) to 198 $\mu g/m^3$ (n=5) for samplers positioned near idling trucks. For personal samples, non-smokers typically had lower exposures (57 $\mu g/m^3$, n=60) compared to smokers (71 $\mu g/m^3$, n=42). Overall, the investigators reported winter exposure for the workers was 80 $\mu g/m^3$ (n=103). All personal samples were taken near the worker's breathing zone for 6 to 7.5 hrs. Again, these levels lower that PM concentrations than measured for many of the measured Park employees.

Toxic air pollutants (for example, benzene and formaldehyde) are associated with chronic diseases such as cancer. Benzene is considered a known human carcinogen by the US EPA, and by the International Agency for Research on Cancer (IARC). Benzene is known to be responsible for leukemia in occupational environments.

Occupational exposure to benzene from mobile sources has been reported in a number of studies. For example, urban workers who worked in traffic (traffic police) were studied for benzene exposure (Crebelli et al, 2001). Personal samplers were used. The time-weighted average exposure to benzene was higher among traffic police (6.8 $\mu g/m^3$) than among indoor workers (3.5 $\mu g/m^3$). Mean ambient benzene levels were 12.6 $\mu g/m^3$, and generally did not correlate with personal concentrations of benzene measured.

A number of studies have reported short-term to volatile toxic air pollutants. For example, Rodes et al. (1998) studied 120 minute exposure levels inside of commuting vehicles traveling on major highways in Sacramento, CA. and Los Angeles, CA. Similar measurements were taken outside of the vehicle and along the traveled roadways. Benzene concentrations were elevated inside of the vehicle relative to roadside station concentrations. Very high concentration short-term (2 minute) exposures of benzene and gasoline associated VOCs have also been reported when refueling (Backer, et al, 1997).

The emissions of hydrocarbons (including toluene) and carbon monoxide from snowmobiles at Yellowstone has been reported (Bishop, et al, 2001) for the same sampling period reported in the current study. Snowmobiles were reported to account for annual emissions of 27% of CO and 77% of the hydrocarbons. Snowpack samples have also been collected at about the time of maximum annual snow accumulation at numerous locations throughout the park. Concentrations of ammonium, nitrate, sulfate, benzene, and toluene in snow were positively correlated with snowmobile use (Ingersol, 2000).

This study is part of a multi-disciplinary winter science investigation in collaboration with the National Park Service (NPS), Yellowstone Park Foundation, The Pew Charitable Trusts, Montana Department of Environmental Quality, and the University of California. The primary goal of the present study is to examine human occupational and environmental exposure to the particulate matter and toxic air pollutants emitted by snowmobiles in Yellowstone. Exposure of Park employees, visitors, and the environment to relatively high levels of pollutants from snowmobile emissions is a major environmental health concern.

III. Materials and Methods

Measurement of airborne particulate matter and toxic compounds at Yellowstone presents challenges due to the cold weather, the different types of samples to be collected, and logistical coordination of multiple sampling locations within and outside of the Park. The cold weather presents a challenge to mechanical components used for air sampling. A complex matrix of samples were collected at fixed-sites and for personal exposure.

A. Logistics, site selection, and preparation

Studies were conducted on selected days during two periods of high snowmobile use: Jan 15 - 19, 1999 and Feb 13 - 22, 1999. The January sampling trip was conducted to evaluate logistics and to provide initial samples for the evaluation of sampling and analytical methods. With cooperation from NPS, the West Entrance office was set up as a mini-laboratory. Two additional sampling sites remote from the West Entrance (West) were investigated. The first was at Madison Junction, approximately 14 miles east of West Entrance, and the second was at Old Faithful, approximately 15 miles south of Madison and about 30 road miles from the West Entrance. The February sampling trip focused on using specific methods to sample at the West Entrance, the remote locations within the Park, and within the town of West Yellowstone. The NPS staff provided critical logistical support throughout these studies.

B. Sampling Sites

The West Entrance to Yellowstone National Park is located on the eastern edge of West Yellowstone, Montana and has three major lanes for snowmobile entry into the Park. Two of the lanes generally require visitors to stop and purchase an entry pass. The third lane is an express lane for individuals with pre-purchased entry passes who typically slow down, but do not generally stop. In general, more snowmobiles enter the Park through the express lane than either of the other two lanes. A map of the West Entrance and location of air sampling equipment is illustrated in Figure 1. Many riders of snowmobiles (snowmobilers) travel from the West Entrance (West) to Old Faithful (OF) and stop at Madison Junction (Madison), the halfway point between West and Old Faithful. At Madison, there is a portable trailer warming hut that has mini-food service. Air samplers were placed approximately 10 feet from the north side of the warming hut and approximately 30 feet southwest from the snowmobile parking area as illustrated in Figure 2. The area is open with trees surrounding the open area. During sampling, the woodstove in the warming hut was not in use. The Old Faithful site has two major parking lots for snowmobiles, a visitor center, and separate permanent buildings that serve as warming huts. Air samplers were placed approximately 30 to 40 feet upwind from the warming hut building closest to the two parking lots and approximately 30 to 50 feet downwind from the edge of the parking area as illustrated in Figure 3. One of two woodstoves was operational and the stack on the roof was located approximately 70 feet downwind of the samplers. When possible, sampling was coordinated so that air samples were acquired from all locations at approximately the same time.

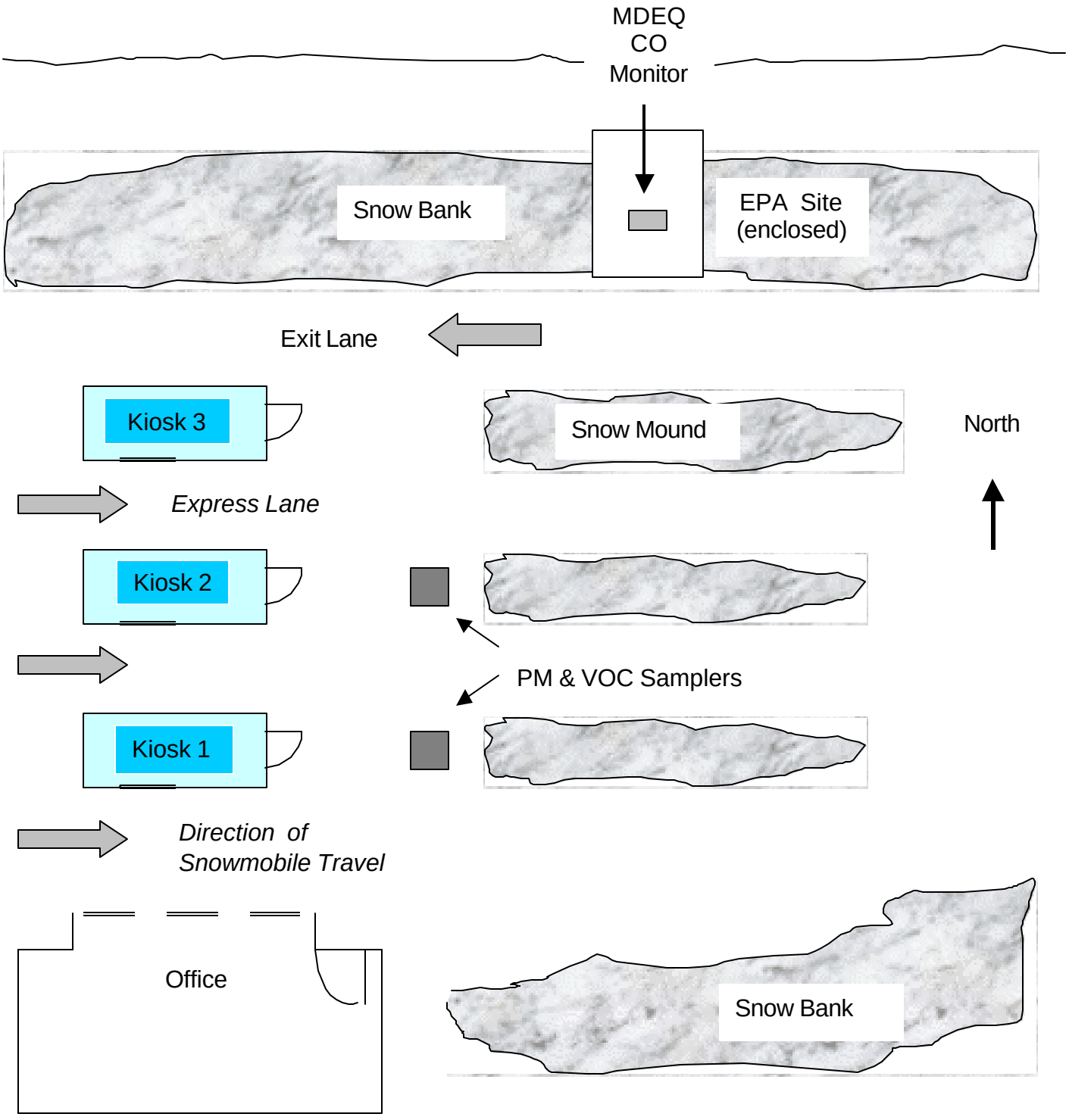

Figure 1. West Entrance and Location of Air Monitoring Samplers.

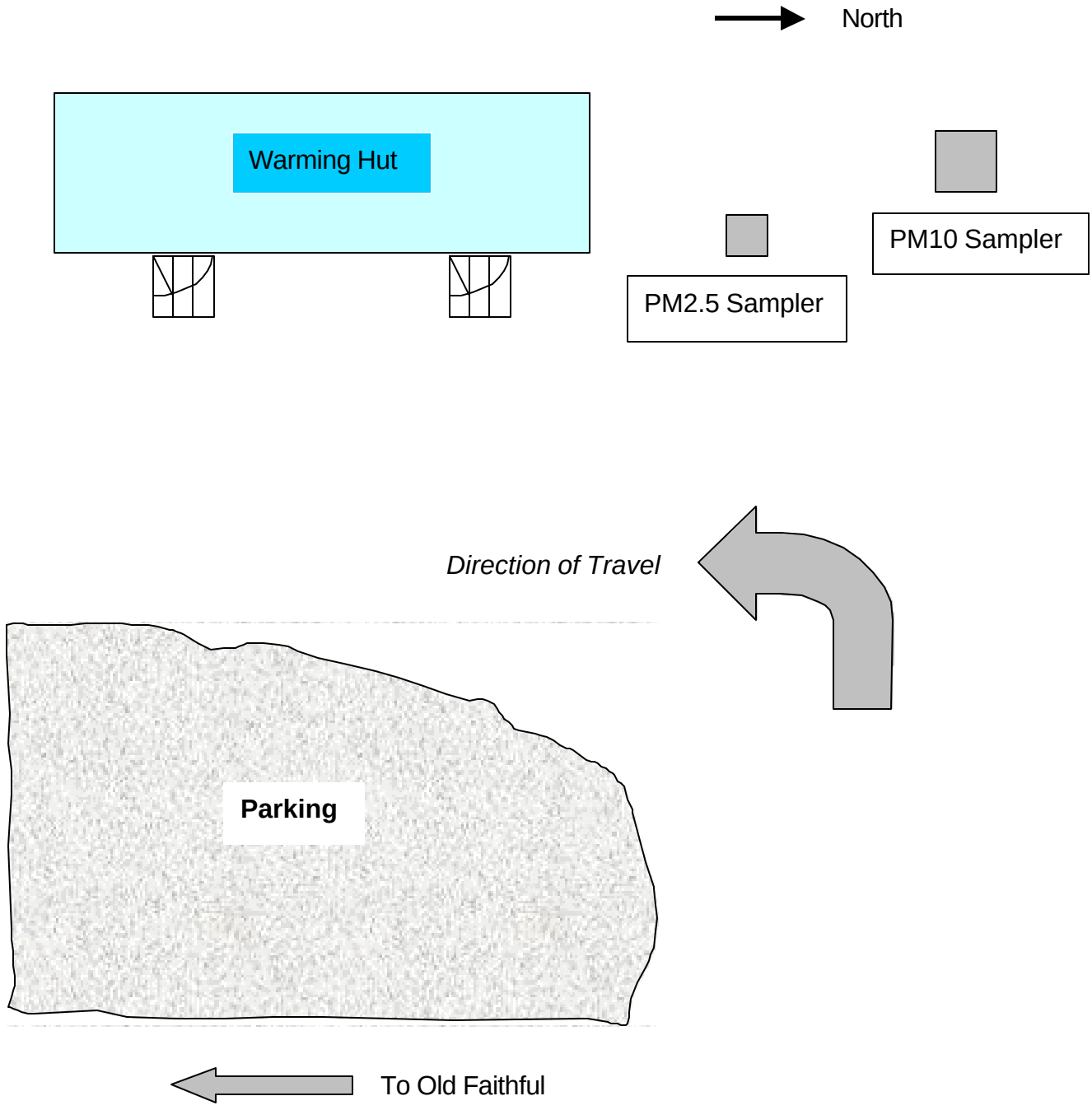

Figure 2. Madison Junction Site and Location of Air Samplers.

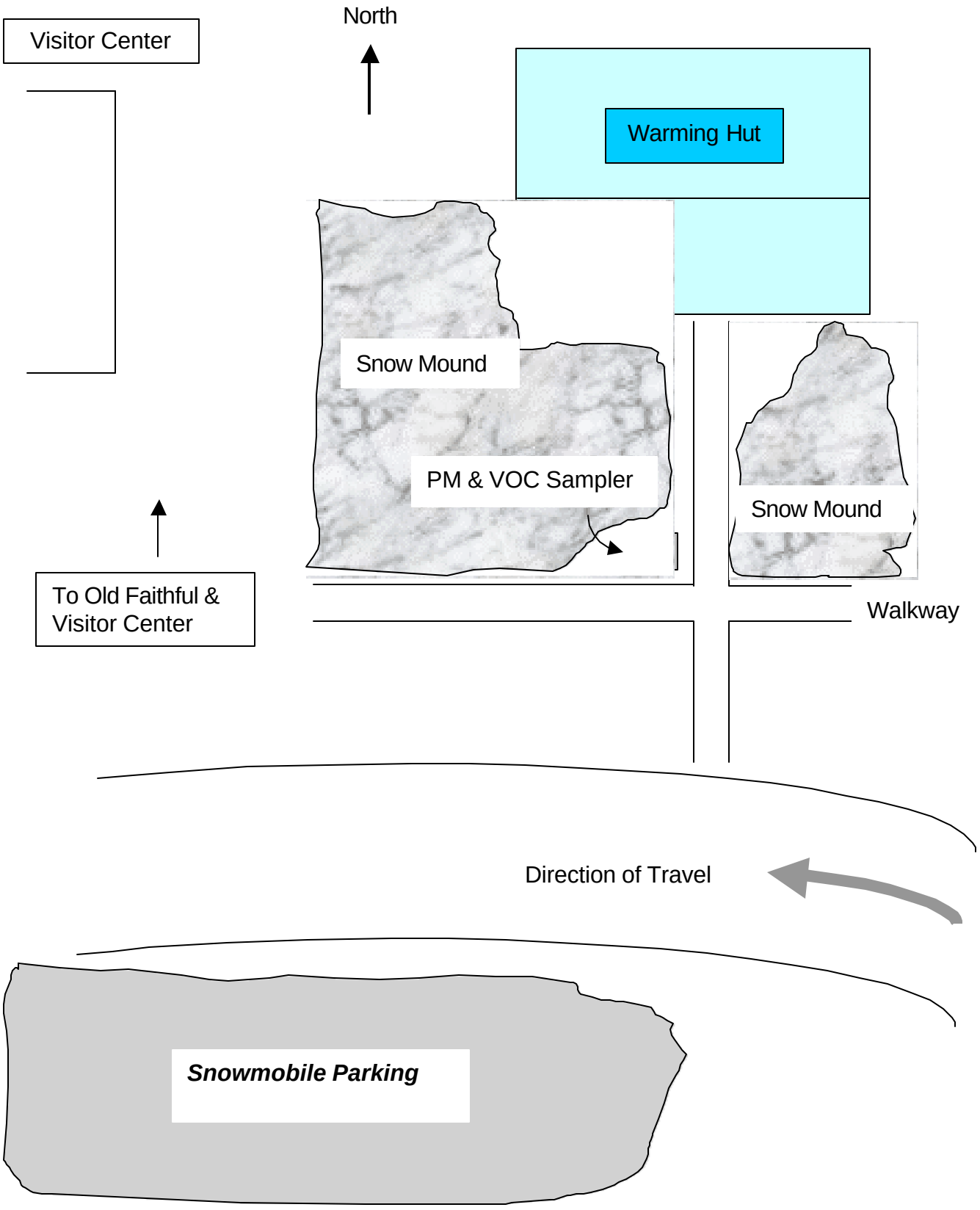

Figure 3. Old Faithful Monitoring Location.

C. Carbon Monoxide

Carbon monoxide (CO) is routinely monitored at the West Entrance Station by the Montana Department of Environmental Quality (MDEQ). The location of the monitoring equipment at the site is illustrated in Figure 1. Average hourly concentrations are reported as part of the US EPA Air Information and Retrieval System (AIRS) network. Hourly average CO concentrations were provided by MDEQ for the study days of the current investigation.

D. Particulate Matter

Particulate matter (PM) was collected for both fixed-site and personal measurements. Fixed-site samples were derived from sampling devices placed in a fixed location typically near worker activity areas, while personal respirable PM samples were obtained from individuals wearing portable sampling devices attached to their shirt or jacket collars several inches away from the breathing area (nose and mouth). For the fixed-site samples and on selected days, PM2.5 or PM10 (PM with aerodynamic diameters of 2.5 or 10 µm or less) was collected. For the personal samples, respirable PM (PM with aerodynamic diameters of 4.0 µm or less) was collected.

Fixed-site samples were collected using medium-volume (med-vol) samplers at a flowrate of 16.7 liters per minute (LPM) and fixed-site high-volume (hi-vol) samples were collected at a nominal flowrate of 1,000 LPM. The med-vol samplers used either PM2.5 or PM10 size-selective inlet devices and filter holding cases (Partisol Model 2000, Rupprecht & Patashnick Co., Albany, NY) attached to a vacuum pump. Hi-vol PM10 samplers (volumetric flow controlled; Anderson Instruments, Smyrna, GA.) were kindly

provided by the Montana Department of Environmental Quality and met EPA specifications for PM10 sampling. Personal samplers consisted of PM 4.0 size-selective devices (aluminum cyclone: SKC, Inc., Eighty Four, PA) attached to a personal sampling pump (SKC, Inc., Eighty Four, PA). The nominal flow rate was 2.5 LPM, which is the published optimal flow rate to capture respirable PM of 4.0 μm aerodynamic diameter. Personal sampling pumps were either worn on the belt (protected from the cold by a jacket if needed), or placed in a backpack with the sampling line leading to the cyclone. The cyclone was attached to the shirt or jacket collar several inches away from the breathing area (nose and mouth).

Filters for the med-vol samplers were 47 mm Teflon and for the personal samplers were 37 mm Teflon (Gelman Sciences, Ann Arbor, MI). The filters were pre-cleaned using methanol and dichloromethane (DCM), and allowed to dry in a HEPA-filtered hood (Baker Hoods, Sanford, ME) with 100% exhaust. Hi-vol samples were also collected using 8 x 10 inch high purity quartz microfibre filters (Whatman, Maidsone, England). After sample collection, all filters were packaged in glassine paper, foil wrapped, labeled, inventoried, and shipped to the UC Davis laboratory in an insulated shipping chest containing blue ice. Filters were inventoried and stored at -20° C to minimize loss of semi-volatile compounds.

Unless noted, flow rates were determined for the med-vol and personal sampling pumps prior to and after each sampling period using a primary flow calibration device. Flow rates for the hi-vol samplers were determined by the Montana Department of Environmental Quality either prior to sampling, or for the EPA sanctioned site, during scheduled calibration checks.

Prior to and after sampling, filters were conditioned and weighed in a temperature and humidity controlled filter weighing room. The 37 and 47 mm filters were weighed on a microbalance (MC5, Sartorius, Gottingen, Germany) that is accurate to 1 microgram (µg). The 8 x 10 inch hi-vol filters were weighed on an analytical balance (Sartorius, Gottingen, Germay) that is readable and reliable to 0.1 mg.

Fixed-site med-vol samplers were placed at West, Madison, and OF. Hi-vol samplers were located at West and Madison. One hi-vol sampler was located at a joint DEQ/EPA monitoring site in downtown West Yellowstone (approximately 1/3 mile or 2 blocks west of West Entrance). This site is close to small houses, lodging establishments, businesses (including a major snowmobile rental company), restaurants, a gasoline station, and a major highway. On two days, a hi-vol sampler and a med-vol sampler were located in a predominantly residential area of West Yellowstone approximately 1 mile north of the downtown district (or 1.2 miles from the West Entrance site).

E. Volatile Organic Compounds

Volatile organic compounds (VOCs) were measured using both fixed-site and personal monitors. For fixed-site evaluation, a number of different sampling approaches were used. First, to develop a qualitative survey of the airborne VOCs present, Carbotrap adsorbent tubes were connected to personal sampling pumps to collect VOCs at a nominal flow rate of 1 liter per minute (LPM). The Carbotrap samplers were placed near the location of the fixed-site PM2.5 samplers and samples were collected over a period of approximately 3 hours. Following collection, the samples were stored

at -20 °C and shipped to Dennis Endicott (Caterpillar Technical Center, Mossville, Ill) for thermal desorption and gas chromatography-mass spectral (GC/MS) analyses.

Peak short-term VOC exposure samples were acquired using an evacuated chamber to inflate a Tedlar bag with sample air. Before collecting sample air, the Tedlar bags were pre-cleaned with ultrapure (99.999%) nitrogen. After collection, the Tedlar bag samples were analyzed on-site using a portable gas chromatograph equipped with a photoionization detector (Photovac, Norwalk, CT). A lecture bottle containing a standard mix of VOCs (benzene, toluene, xylenes, for example) and traceable to the National Institute of Standard and Technology (NIST) was used to quantitate the samples. Some Tedlar bags were also returned to UC Davis for GC/MS chemical analyses following EPA method TO-15.

Personal VOC exposure samples were obtained using a passive diffusion monitor (3M, St. Paul, MN.). These monitors are badges that are clipped onto a shirt or jacket lapel several inches away from the breathing zone (nose and mouth) and have passed performance review following ASTM standard D 6246 (ASTM, 1998). The sampling time was initiated by opening the factory-sealed container with the badge inside, removing the badge, placing it on the individual worker or fixed-site location, and recording the time. At the end of the sampling period (typically from 4 to 8 hours), a protective cover was snapped over the badge to seal it, and then the badge was placed back into the original container with lid and the ending time of the sampling period was recorded. The badge samples were returned to the UC Davis laboratory in an insulated shipping chest containing blue ice and stored at -20° C prior to extraction and analysis.

The VOC badge samples were extracted and analyzed following the methods of ISO/DIS 16200-2 (1998) and Rodriguez, et al. (1982), except samples were extracted using sonication. The gas chromatographic system is a Hewlett Packard Model 5890 Series II Plus Gas Chromatograph interfaced to a Model 5972 quadrupole mass selective detector. The following compounds were quantitated: benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, 1,3,5-trimethylbenzene, and 1,2,4 trimethylbenzene. The physicochemical properties of these compounds are listed in Table 1. Benzene-d_6, toluene-d_8, and ethyl benzene-d_{10} served as internal standards during extraction. A five-point calibration curve that brackets the concentrations of all compounds was developed. Each concentration for the calibration curve was determined in triplicate. Regression analyses of all standard curves resulted in r^2 values of 0.99 or higher (Appendix B). The method quantifiable limit (MQL) was estimated by the lowest concentration of the calibration curve. The MQL is the minimum concentration of a compound that can be accurately and precisely measured. The estimated MQL's for all the VOCs quantitated was approximately 5 to 7 µg/m3 for an 8-hour exposure.

Carbotrap (thermal desorption) tubes were used at the West Entrance and OF locations to qualitatively investigate the spectrum of VOCs present in the samples. Tedlar bag samples were collected at the West Entrance to provide a short-term peak concentration and a near real-time ambient sample for VOCs, especially those compounds that contain aromatic rings such as benzene. Samples in Tedlar bags were analyzed on-site within 6 hours of collection using a portable gas chromatograph (Photovac Model 10S) equipped with a photoionization detector and encapsulated capillary column. The samples

were run isothermally at 30°C. A gas calibration standard stored within a Scotty IV cylinder contained 500 ppb of each of the following compounds: benzene, 1,3-butadiene, chlorobenzene, styrene, toluene, and m-, p-, and o-xylene. Before analyzing the samples, the gas calibration standard was used to construct a four-point calibration curve. A 500 µl sample of air was withdrawn from the Tedlar bag and injected into the gas chromatograph. A selected number of bags were returned to the UC Davis laboratory for analyses following US EPA method TO-15. To assess personal exposure to VOCs, passive diffusion badges were worn by Park employees, usually for an entire daily work period. The badges were distributed to employees in different occupations, including employees working in an office setting. In addition, VOC badges were used as fixed site samplers at specific sites.

Table 1. Physicochemical Properties of Selected VOCs.

Compound	CAS #	Molecular weight	Vapor pressure (mm Hg)	Boiling point (°C)
Acetaldehyde	75-07-0	44.05	740 (20°C)	21°
Benzene	71-43-2	78.11	100 (26.1°C)	80.1°
Ethylbenzene	100-41-4	106.16	9.53 (25°C)	136.25°
Formaldehyde	50-00-0	30.03	3883 (25°C)	-19.5°
Toluene	108-88-3	92.13	28.1 (25°C)	110.6°
1,2,4-Trimethyl-benzene	95-63-6	120.19	2.03 (25°C)	169-171°
1,3,5-Trimethyl-benzene	108-67-8	120.19	2.0	165°
Xylenes (o-, m-, p-)	1330-20-7	106.2	6.6-8.7 (25°C)	137°-144°

F. Aldehyde Analyses

1. Sample collection

Personal exposure to aldehydes was determined using Sep-pak XPoSure^{TM} Aldehyde Sampling cartridges (Waters Corp., Milford, MA) connected to a personal air sampling pump (SKC, Inc., Eighty Four, PA). Briefly, these sampling cartridges contain silica coated with acidified 2,4 dinitrophenylhydrazine (DNPH), which traps formaldehyde and other aldehydes and reacts with them to form the more stable DNPH derivative. The XPoSure^{TM} cartridges have been previously validated for 15-minute short-term exposure limit (STEL) measurements and for 8-hour permissible exposure limit (PEL) measurements of formaldehyde. The current OSHA 15-minute STEL for formaldehyde is 5 ppm, or 6.15 $\mu g/m^3$.

Prior to sample collection, each personal sampling pump was calibrated at a flowrate of 1 LPM. The pumps were clipped onto the employee's belt and the sampling cartridge was attached to their shirt or jacket collars several inches away from the breathing area (nose and mouth). Personal aldehyde exposure samples were collected between February 13-20, 1999 from National Park Service employees for varying lengths of time ranging from approximately 15 to 463 minutes. Most of the personal exposure samples were collected during the morning hours from employees at the West Entrance and a few were collected from employees at Madison Junction. For each sample, the starting and stopping times were recorded on data sheets. After each sample was collected, the calibration of each pump was rechecked and the flowrate was recorded. The flowrate and total sampling time were used to calculate the total volumes of air sampled, which ranged from 15 to 466 L.

After each sample was collected, the cartridge was capped with plastic end plugs, and placed in its packaging pouch. The pouch containing each sample cartridge was marked with the appropriate sample ID, sealed shut with staples, and shipped to the UC Davis laboratory in an insulated container with blue ice. Samples were stored at -20 ° C until extraction and analyses. Field blanks were collected and represented 10% of the total number of samples collected and were handled and stored in the same manner as the samples.

2. Sample Extraction and Analyses

Samples were extracted and analyzed for aldehydes using a modification of California Air Resources Board Method SOP-MLD-022. Briefly, carbonyl-free acetonitrile is used as the extracting solvent and the extract is stored at 4° C until analysis by high performance liquid chromatography (HPLC). Calibration standard solutions were from AccuStandard, Inc. (New Haven, CT). Each standard solution contained 13 carbonyl compounds as DNPH derivatives. For sample analysis, a Waters gradient HPLC system was used, consisting of a U6K injector, two Model 510 pumps, a Waters Nova-Pak C18 column (3.8 x 150 mm), a Waters Model 481 variable wavelength UV detector operating at 360 nm, and a Hewlett-Packard Model 3390A integrator. Initial running conditions were used as follows: A = Water/Acetonitrile/Tetrahydrofuran 60/30/10 (v/v/v) and B= Acetonitrile/Water 60/40 (v/v). A 23-minute gradient program was used to analyze the carbonyl derivatives as follows: 100% A for 1 minute, a linear gradient from 100% A to 100% B in 10 minutes, 100% B for 11 minutes, and then a linear gradient from 100% B to 100% A in 1 minute.

Calibration of the HPLC was checked each day by first analyzing a calibration standard. The calibration was checked again after each day's runs using the same standard. Following HPLC analysis, the data from each chromatogram were entered into a spreadsheet program. The concentration (µg/mL) of each carbonyl present in a sample was calculated based on extrapolation to data from the standard calibration curve. All calibration curves had linear regression coefficients and r^2 values of 0.99 or higher. Each concentration for the calibration curve was determined in triplicate.

G. Bioassay Analyses of Engine Emissions

Bioassays for genotoxic effects (damage to genetic material DNA) have been used to evaluate toxicity of complex environmental mixtures such as diesel exhaust, ambient air particulate matter, and other environmental samples. The most widely used and validated short-term test for genotoxicity is the Salmonella/microsome test (Ames et al., 1975). The assay has been used for the screening of potentially carcinogenic compounds. The bioassay routinely used at UC Davis is the microsuspension procedure developed previously by Kado et al. (1983, 1986). The microsuspension procedure is a simple modification of the standard Salmonella/microsome assay and is approximately 10 times more sensitive.

Bioassay analyses were conducted on particulate matter obtained from recent snowmobile engine dynamometer studies conducted by Southwest Research Institute (SwRI, 1999). Briefly, particulate matter was collected from each mode of a 5-mode industry developed and approved steady-state test. Two lubricants were tested, a standard mineral based lubricant and a biosynthetic lubricant. The tests were

conducted to examine any differences in the emissions of regulated and unregulated pollutants. The bioassay serves to investigate the biological effects of the complex mixture of compounds present on the particulate matter.

IV. RESULTS AND DISCUSSION

A. Meteorological Conditions and Number of Snowmobiles

Meteorological data at the West Entrance were recorded by National Park Service (NPS) personnel and are summarized for the periods of study in Table 2. For the January pre-test, there were no sub-zero minimum temperatures. The minimum and maximum temperatures were 3° and 36° F. For the February study, the minimum and maximum temperatures recorded during the study period were –18° and 38° F. The overall conditions for both sampling trips, including wind conditions, were conducive for sample collection. The morning and afternoon average windspeed and direction data are summarized in Table 3 for three sampling days in February. Windspeed and direction data for other sampling days were not available.

B. Snowmobile Counts

The number of snowmobiles entering the Park at the West Entrance (snowmobile counts) is electronically registered to provide a total count for the day. For selected days, hourly traffic summaries were also obtained and kindly provided by NPS personnel from the ticket receipts acquired at each kiosk. The number of snowmobiles entering the West Entrance for the January 1999 sampling trip is illustrated in Figure 4. For the January pre-test, the daily count ranged from 434 to 848 snowmobiles. The maximum number occurred on the Saturday of the Martin Luther King holiday. The snowmobile counts for the February Presidents' Day holiday sampling trip are illustrated in Figure 5. The peak days were on Saturday (2/13/99), Sunday (2/14/99), and Friday

(2/19/99). As in previous years, the snowmobile counts decrease during midweek and increase during the weekend. The maximum number of snowmobiles entering the Park through the West Entrance has been higher in previous years.

The number of snowmobiles that entered the West is illustrated in Figures 6 and 7, for the 1999 President's Day holiday weekend. Approximately 90 percent of the snowmobiles enter the Park before noon. The vast majority travel to Old Faithful. Snowmobile counts were also obtained by NPS personnel at the OF parking lots between February 13 - 16 and on February 20th (Figure 8). Counts were obtained when possible three times per day as follows: at approximately 10 a.m., between 12 noon and 1 p.m., and in the late afternoon (about 3:30 p.m.). There is a consistent pattern, with peak numbers of snowmobiles present by the 12 noon to 1 p.m. period and a considerable decrease observed by 3 p.m. Many rental companies in West Yellowstone require their snowmobiles to be returned by 5 p.m., so leaving the OF parking lots by 3 or 4 p.m. typically provides enough time to return to West Yellowstone or other Park entrances.

Table 2. West Entrance Weather Data during UC Davis Sample Collection.

Date	Min (°F)	Max (°F)	New Snow (inches)	Snow Accumulation (inches)	Weather Observations
1/15/99	20	30	3	31	Lightly snowing, overcast, gusty southwest wind
1/16/99	15	33	4	34	Steady snow, overcast, gusty
1/17/99	3	32	3	35	Mostly clear, dry, calm
1/18/99	7	25	1	36	Cloudy, calm
1/19/99	18	36	1	35	Mostly cloudy, calm
2/13/99	-17	22	0	48	Clear, calm
2/14/99	-12	38	0	47	Clear, calm
2/15/99	1	34	4	51	Mostly cloudy, calm
2/16/99	5	29	2	52	Light snow, cloudy, calm
2/17/99	14	31	4	54	Moderately snow, overcast, calm
2/18/99	-6	31	2	52	Mostly clear, calm
2/19/99	14	27	4	55	Moderately snow, overcast, breezy west wind
2/20/99	-17	29	1	55	Clear, calm
2/21/99	-18	26	0	54	Overcast, calm

Table 3. Windspeed and Direction for Selected February Sampling Dates at the West Entrance.*

Date	Time**	Average Windspeed (meters/ second)	Average Windspeed (miles/hour)	Wind Direction
2/13/99	A.M.	0.10	0.22	S, SW
	P.M.	0.18	0.40	NW, NE, E
2/14/99	A.M.	0.26	0.58	SE, S, SW
	P.M.	0.68	1.52	SW, NW
2/15/99	A.M.	0.58	1.30	W, SW, S
	P.M.	1.32	2.95	S, SW

* Data provided by Montana Department of Environmental Quality. Windspeed and direction data for other sampling dates not available.

** A.M. = 8 a.m. to 12 noon, P.M. = 12 noon to 5 p.m.

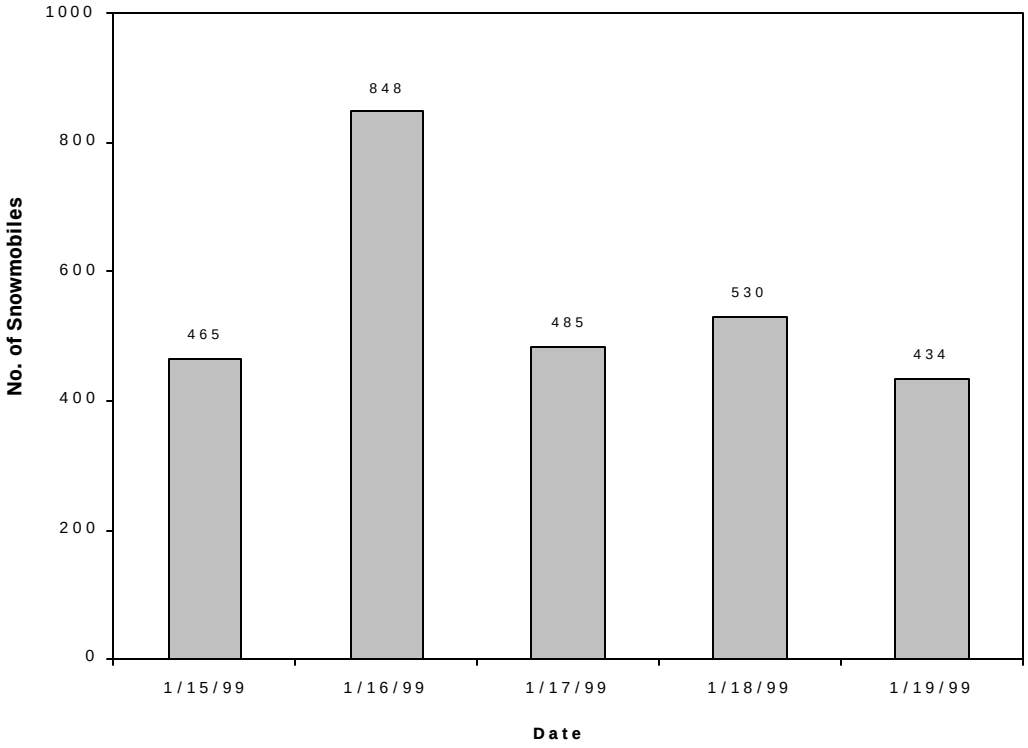

Figure 4. Yellowstone West Entrance snowmobile counts for the January 1999 pre-test.

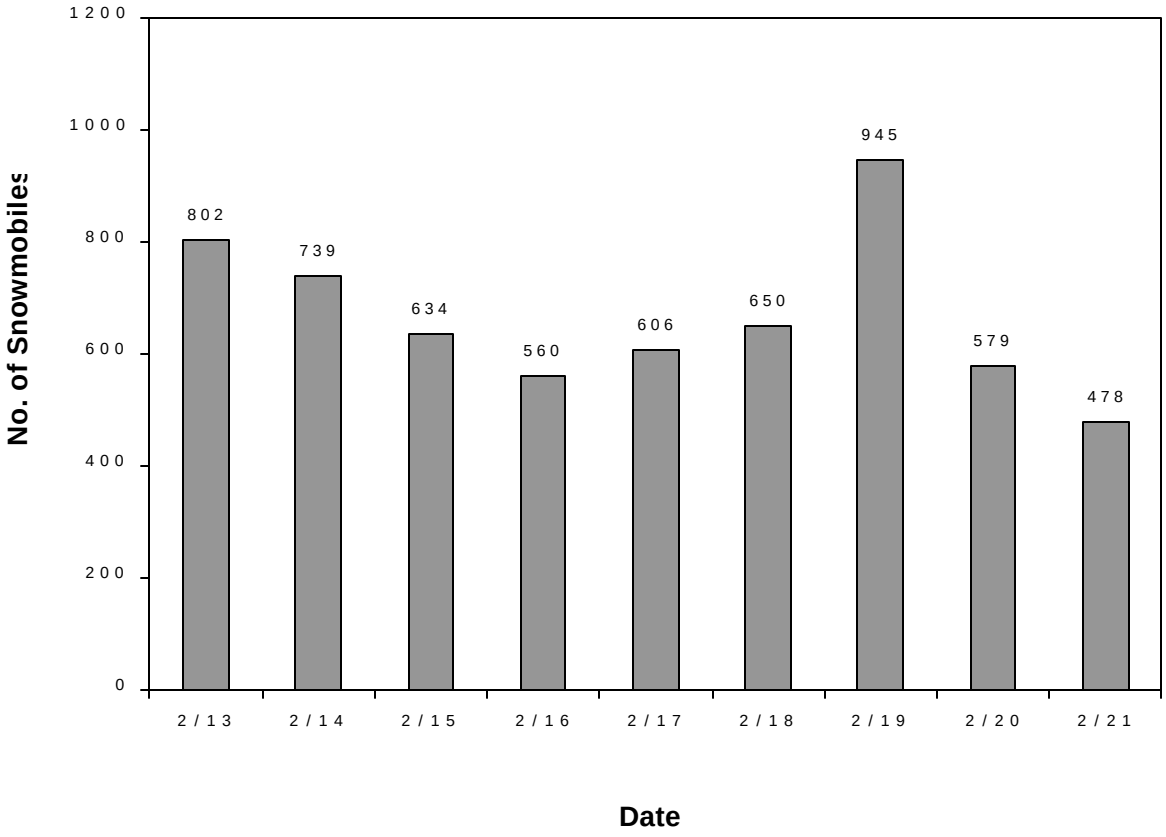

Figure 5. Yellowstone West Entrance snowmobile counts for the February 1999 study. Saturday and Sunday February 13 and 14 are the Presidents' Day Holiday weekend.

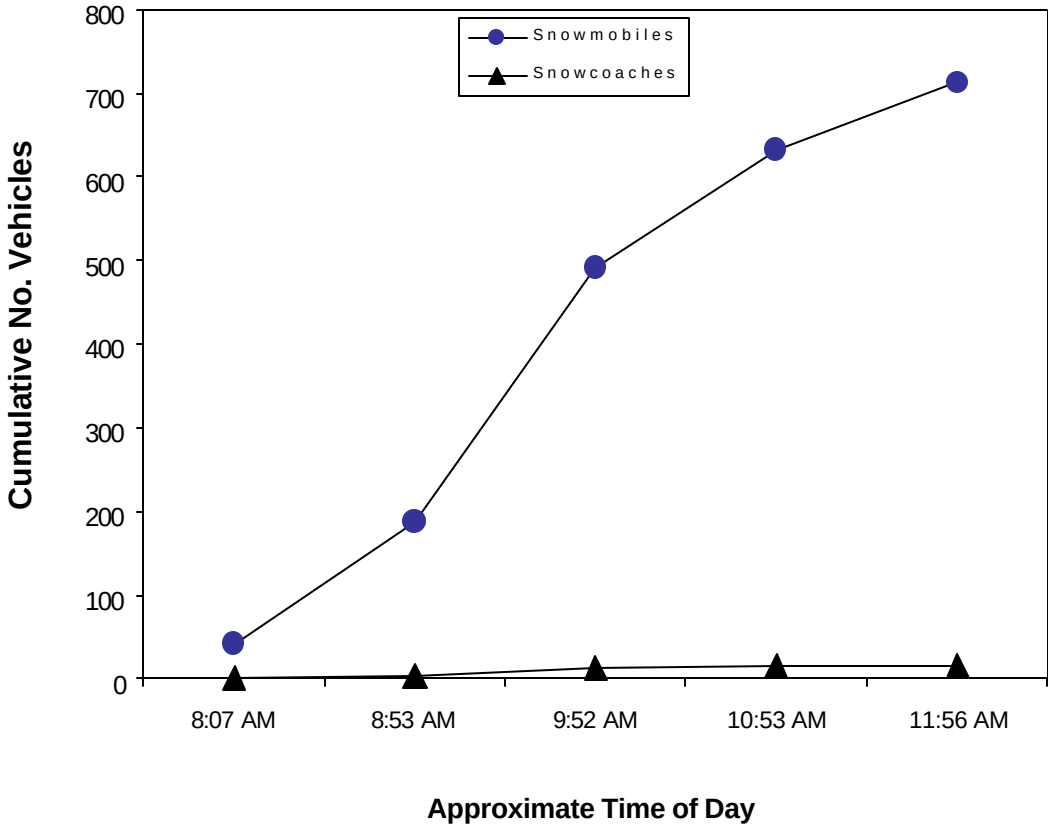

Figure 6. Cumulative number of snowmobiles and snow coaches entering Yellowstone through West Entrance kiosks on Saturday morning, February 13, 1999.

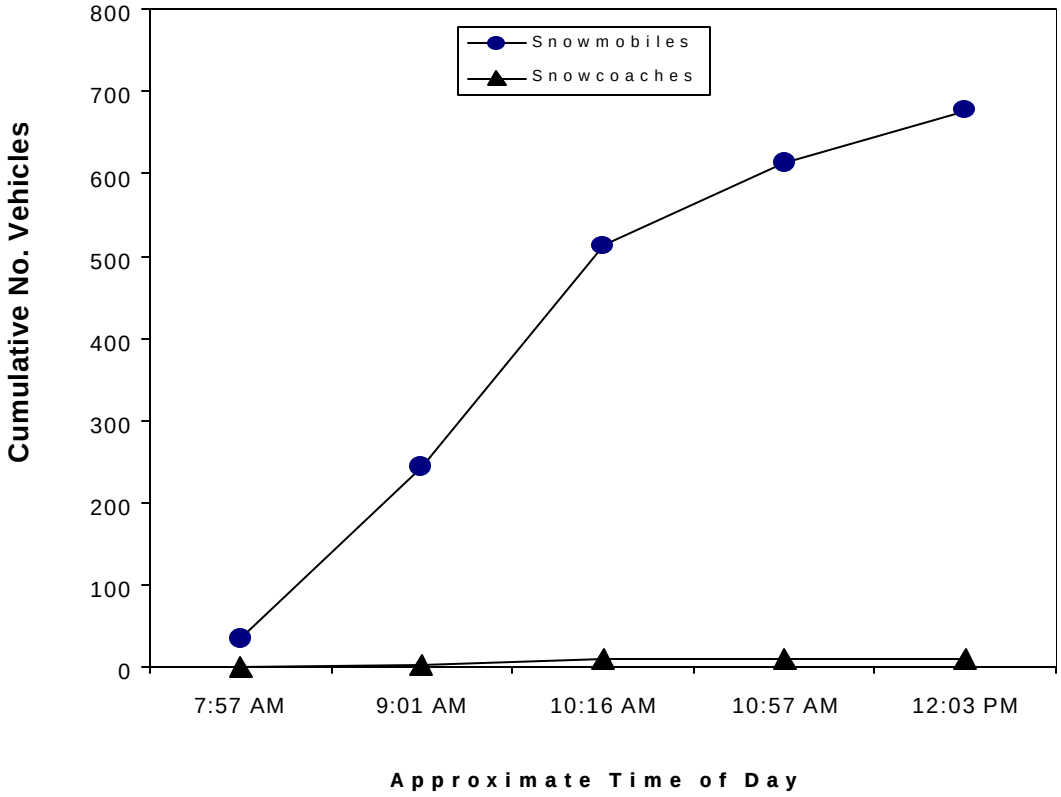

Figure 7. Cumulative number of snowmobiles and snow coaches entering Yellowstone through West Entrance kiosks on Sunday morning, February 14, 1999.

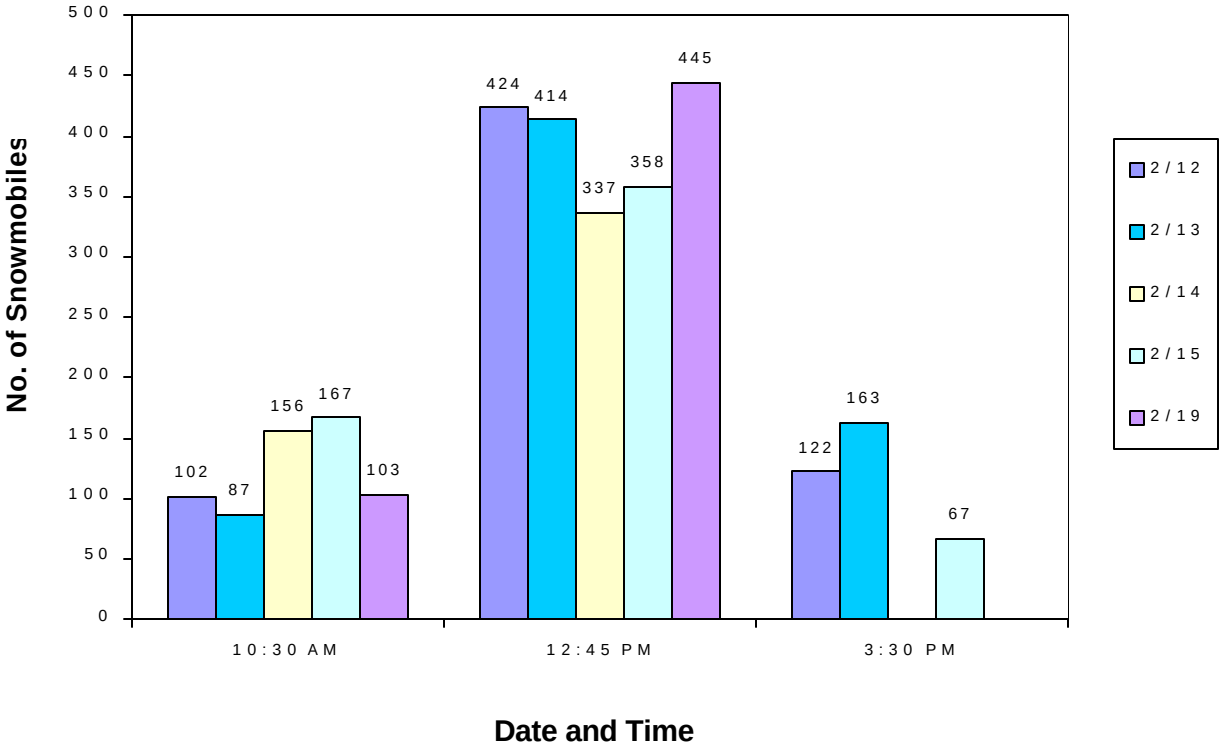

Figure 8. Snowmobile counts at Old Faithful parking lots for February 13-16 and the 20th. Counts were taken three times per day. No bars (*) indicate that no counts were taken during the time period.

C. Particulate Matter

1. Fixed-Site - PM2.5 Samples

Particle samples of 2.5 microns (PM2.5) were obtained from fixed-sites at the West and OF sampling locations on February 13-16, and from Madison on February 13 -14, 1999. Sampling occurred nominally from 8:30 am to 4:30 p.m. The average concentrations of PM2.5 for the Presidents' day holiday weekend are summarized in Table 4. The average concentration from West is approximately 2 times higher than the concentrations from either the Madison or OF sampling locations. One explanation of this result is that although all samplers were placed near work and public areas for all sampling sites, the West Entrance was possibly more "enclosed" due to the kiosks, high roof structure over the kiosks, and snow banks. The average concentrations of PM2.5 measured at Madison and OF were very similar to each other and may indicate a general exposure to PM2.5 at these locations for the entire day. However, to provide some insight into the time-dependent nature of PM exposure to the employees and visitors, the sampling was split into two sampling periods.

PM2.5 samples were collected in the morning (a.m., nominally from 8:30 to 12:30) and in the afternoon (p.m., nominally from 12:30 to 4:30). To calculate a daytime average concentration for the workday, the PM2.5 concentration was "time-weighted" based on the minutes of actual sampling time. The time-resolved nature of exposure to PM2.5 at West is illustrated in Figure 9. The a.m. concentration of PM2.5 on February 13th and 14th was 116 and 112 $\mu g/m^3$. This represents approximately 80 percent of the total measured morning and afternoon PM2.5 collected for these two days and coincides with the period when approximately 90 percent of the total daily count of

snowmobiles have entered the Park at the West Entrance. The a.m. concentrations were approximately 3 to 5 times higher than those observed for the p.m. samples.

Table 4. Average 8-hr concentration of PM2.5 measured during working and typical visiting hours at fixed-site locations during the Presidents' Day holiday weekend.

	PM2.5 Concentration ($\mu g/m^3$)		
Location	West Entrance [a]	Madison [b]	Old Faithful [a]
Average	62.1	26.5	24.7
Std. Dev.	17.7	3.73	10.8
Median	66	27	21.3
Range	38.6 - 78.0	24 - 29.3	16.7 - 39.5
n	6	4	6

[a] West and Old Faithful samples collected 2/13-2/16/99.

[b] Madison samples collected 2/13-2/14/99.

Morning and afternoon concentrations of PM2.5 for the West, Madison and OF locations were measured during the Presidents' Day weekend and are illustrated in Figure 10 for Feb 13th and in Figure 11 for Feb 14th. For Feb 13th, the highest concentrations of PM2.5 observed at West were more than 3 times higher than the concentrations measured at the Madison or OF locations. The p.m. concentrations of

PM2.5 at Madison and OF were approximately one-half the p.m. concentrations at West. For Feb. 14th, the Madison a.m. concentration of PM2.5 is slightly increased from the day before, both in absolute concentration, and relative to the a.m. sample from the West location. The concentration of PM2.5 at OF for this day was slightly higher than the previous day.

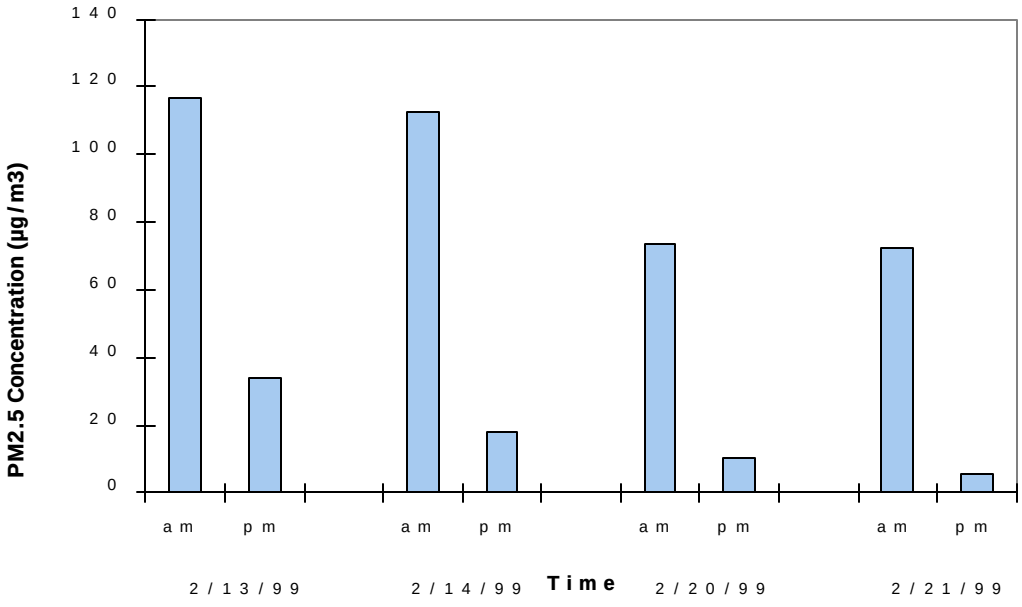

Figure 9. PM2.5 concentrations measured at the West Entrance for the morning nominally from 8:30 a.m. to 12:30 (a.m.) and in the afternoon from 12:30 to 16:30 (p.m.).

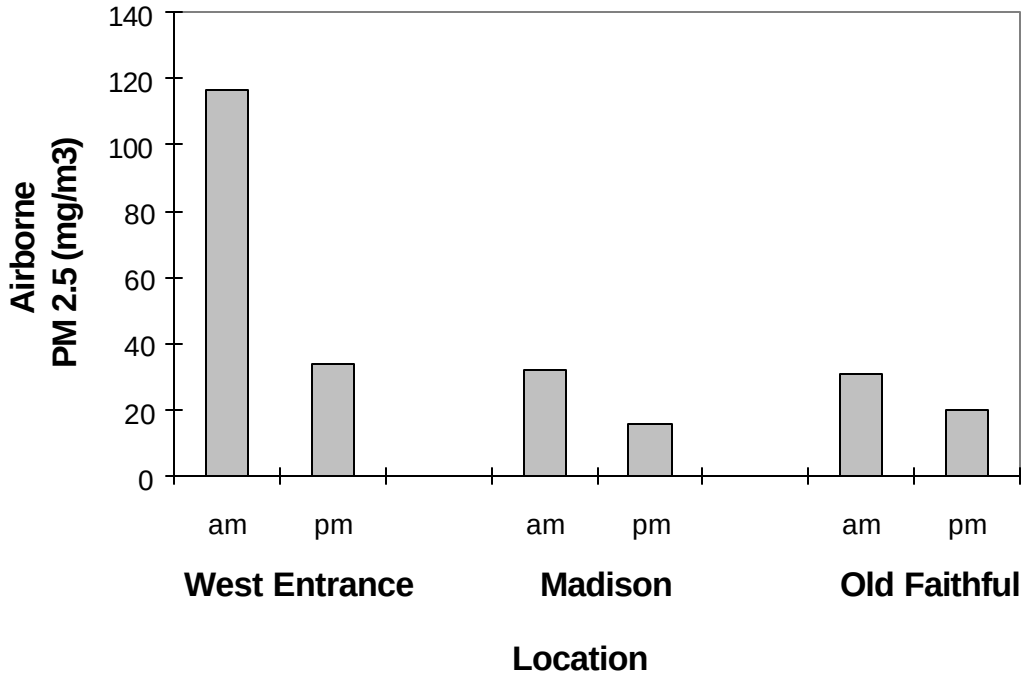

Figure 10. PM2.5 concentrations measured at the West Entrance, Madison, and Old Faithful on the same day, February 13, 1999, nominally from 8:30 to 12:30 (a.m.) and from 12:30 to 16:30 (p.m.).

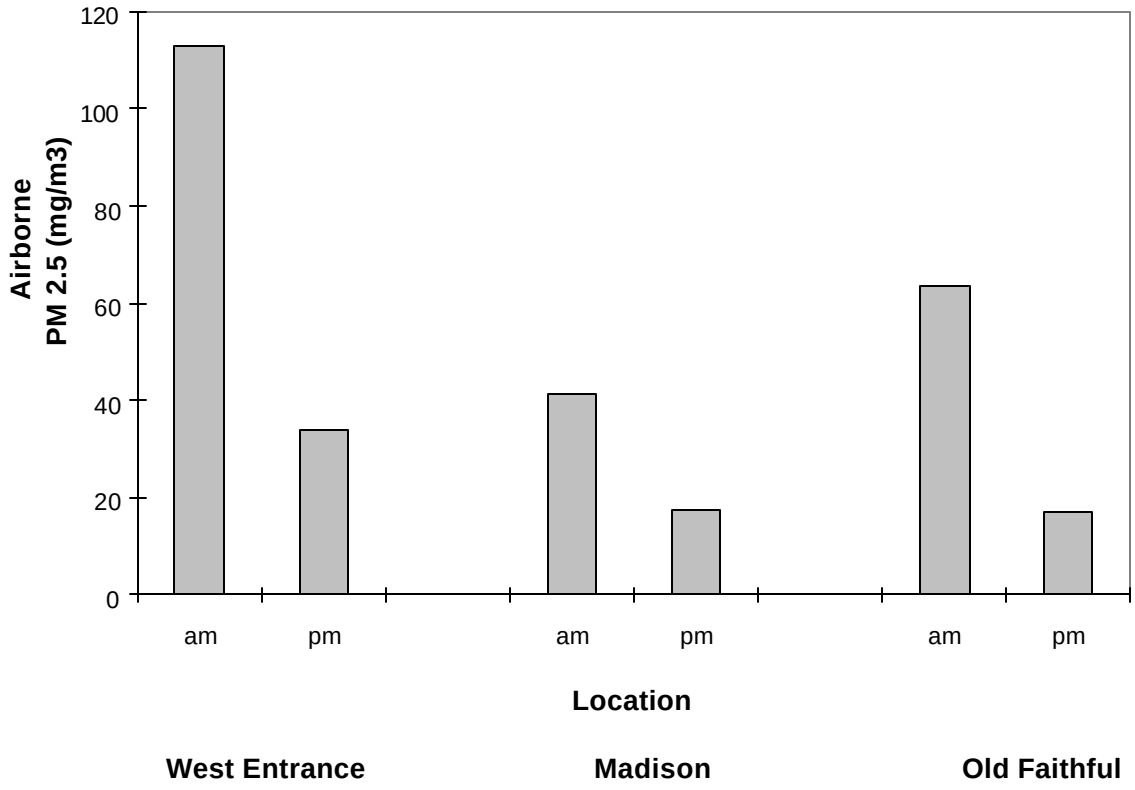

Figure 11. PM2.5 concentrations measured at the West Entrance, Madison, and Old Faithful on the same day, February 14, 1999, nominally from 8:30 to 12:30 (a.m.) and from 12:30 to 16:30 (p.m.).

Weekday samples were collected throughout the day (8:30 -16:30) at the West and OF locations, as shown in Figure 12. The sample from Monday February 15, 1999 is technically part of the Presidents' Day weekend. For the weekday samples, the concentrations of PM2.5 were lower than the average concentrations measured (time-weighted) from the a.m. and p.m. data from each site for the Presidents' Day weekend. The concentration of PM2.5 at West on Tuesday February 16, 1999 was lower than during the holiday weekend, including Monday, February 15. The PM2.5 concentrations measured at OF for both February 15th and 16th were very similar at approximately 17 $\mu g/m^3$ and for each day there were approximately 340 snowmobiles in the parking lot at around 12:30 p.m.

The lower concentrations of PM2.5 at the Madison and OF locations could be due to these locations greater openness, which may contribute to better dispersion of snowmobile emissions compared to the more confined area at West. Also, most snowmobile drivers turn off their snowmobile engines upon arrival at Madison and OF, while at West drivers typically keep their snowmobile engines running.

Regarding exposure to ambient levels of PM, a number of studies have reported concentrations for periods less than 24-hours. For example, investigators have studied the concentration of PM and VOCs inside and outside of vehicles traveling in Sacramento and in Los Angeles (Rodes, et al., 1998). Samples were collected inside vehicles during 120-minute a.m. and p.m. commutes through major roadways. Ambient fixed-site samples placed near commute routes also were collected in parallel for 120 minutes. The concentration of PM2.5 inside the vehicle was reported to range from 6 to 22 $\mu g/m^3$ for the 120-minute commutes in Sacramento while ambient concentrations ranged from 6 to 11 $\mu g/m^3$. For commutes in Los Angeles, the concentration of PM2.5 inside the vehicle ranged from 29 to 107 $\mu g/m^3$, with ambient concentration of 32 to 64

µg/m3. Many Park employees are exposed to concentrations of PM2.5 that exceed these ranges and generally for longer periods of time.

For reference to 24 hour levels, airborne fine particle PM 2.5 concentrations were obtained from two Southern California cities. The average fine particle concentrations for Azusa, CA were 18, 16, and 20 µg/m^3 for 1997, 1998, and 1999. Concentrations for North Long Beach, CA were 17, 16, and 17 µg/m^3 for 1997, 1998 and 1999. Fine particle samples were collected every 6^{th} day on average, but the samples for 1999 were available only from January through April.

2. Fixed-Site PM10 Samples

PM10 was typically collected using high-volume sampling as described in the Methods section. We also used PM10 size-selective devices with the medium-volume sampler. An additional PM10 sampling site was located in a residential neighborhood approximately 1 mile north of the downtown district, after it was noted that the downtown West Yellowstone EPA-sanctioned PM10 high-volume site was located approximately 50 feet downwind from an operational woodstove in a residential area and across the street from a busy snowmobile rental company and gas station. The current experiment focused on PM10 to incorporate data from the EPA downtown West Yellowstone site. The experimental design was to collect PM10 samples spanning a series of sites varying from a residential site outside of the Park all the way to Old Faithful on the same day to investigate any geographical distribution of PM10 at a time when snowmobiles were in use.

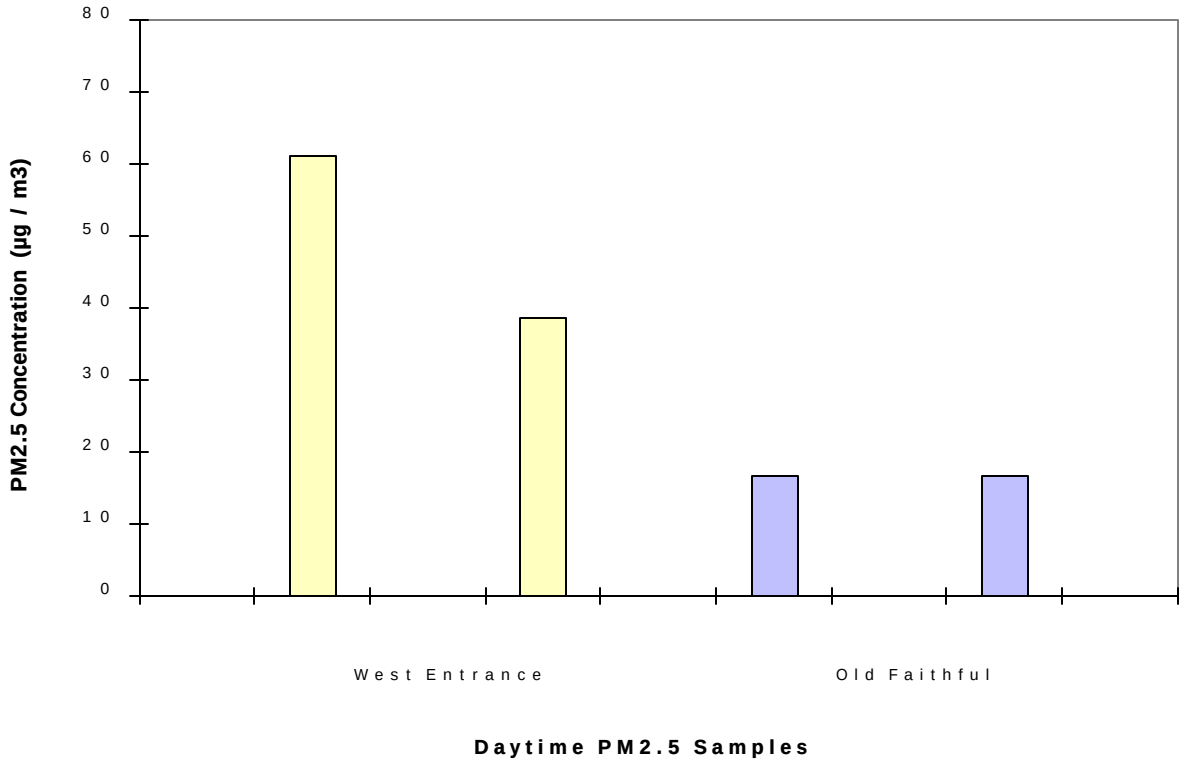

Figure 12. Weekday concentrations of PM2.5 measured from 8:30 to16:30 at the West Entrance and Old Faithful on Monday 2/15/99 (Presidents' Day holiday) and Tuesday 2/16/99 (regular workday).

The results are presented in Figure 13. The concentration of PM10 (collected from 8:30 to 17:30) appears to increase from the residential site to the downtown site, peaking at the West Entrance, and decreasing at Old Faithful. The PM10 concentration at Old Faithful is higher than in downtown West Yellowstone. However, sampling at the Old Faithful site was only from 8:30 to 14:00. Weather conditions were clear and calm as reported at the West Entrance. The residential site concentration is considerably lower than the downtown site concentration. This observed gradient of PM10 concentration is consistent with snowmobile traffic originating from the downtown area and traveling through the West Entrance to Old Faithful and returning at the end of the day. The West Entrance serves as a focal zone for snowmobile travel.

The morning and afternoon PM10 concentrations on Feb. 20th at the West Entrance and Old Faithful are illustrated in Figure 14. The morning PM10 concentrations at the West Entrance are many-fold higher than the afternoon concentration, which is consistent with PM2.5 concentrations measured at this location. The afternoon PM10 concentration measured at Old Faithful is higher relative to the OF a.m. sample, and coincides directly with peak snowmobile counts (around 12 noon to 2 p.m.).

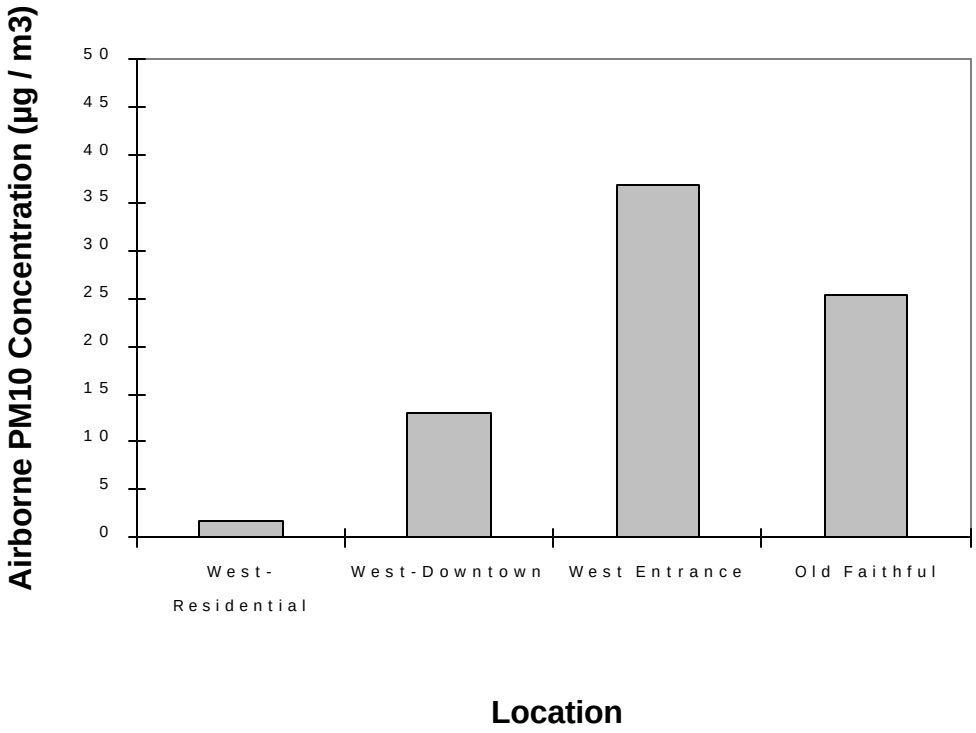

Figure 13. PM10 concentrations incorporating data from West Yellowstone residential and downtown sites sampled on the same day. PM10 samples were collected on February 20, 1999 between 8:30 and 17:30 (between 8:30 and 14:00 for Old Faithful).

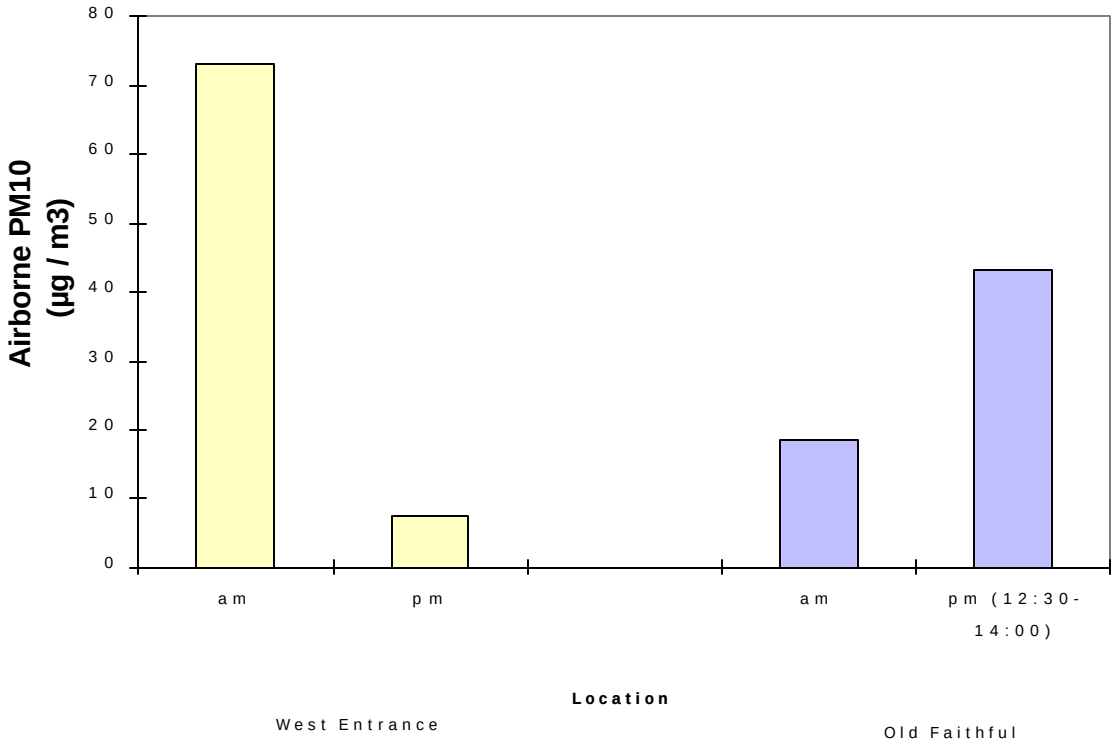

Figure 14. Concentrations of PM10 measured at the West Entrance and Old Faithful sites on Saturday February 20, 1999, one week after the Presidents' Day weekend. The afternoon PM10 sample at Old Faithful was collected from 12:30-14:00.

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3. Personal Exposure to Particulate Matter

Personal exposure to respirable particulate matter (PM4.0; PerPM) was investigated over several days with a number of Park employees whose job duties could expose them to snowmobile exhaust. These results are summarized in Figure 15 and each sample ID reflects an entire workday at a specific job and location between February 13 – 21, 1999. Concentrations of PerPM for individuals working at West were measured at levels up to 160 µg/m^3, which is higher than concentrations measured indoors and outdoors in southern California (Kado et al., 1994). The lowest concentrations were measured at Madison, while PerPM at the OF location approached concentrations for some of the Park employees assigned to the West Entrance. The employees who patrol on snowmobiles were exposed to concentrations of PM that were also very close to the concentrations measured for employees at West. The concentrations of PerPM measured in the offices at the West Entrance or West District were the lowest, with levels typically near or below 20 µg/m3. The highest exposure was detected one day for a mechanic (non-smoker) working mostly indoors on snowmobiles. His PerPM was approximately 500 µg/m3. The overall range of personal exposure, from the highest to the lowest, was the Mechanic (one day) > West Entrance > Mobile Patrol > Old Faithful/Madison > Office.

The bimodal (high, less high) PerPM concentrations at West were further investigated. The job activity and location for each employee was recorded and examined with respect to personal sampling data. When job location is considered, the bimodal distribution of personal exposure on peak snowmobile days February 13 – 15,

1999 can be explained as illustrated in Figure 16. When employees are working in the general area of the regular entrance lanes where snowmobilers stop and pay their entrance fee, or when individuals are stationed in a kiosk and occasionally walk outside, their PerPM appears to be near 60 µg/m3. However, when the job assignment requires working in the express lane or requires the individual to stay outside all the time, employee PerPM more than doubles to approximately 130 µg/m3. The express lane is known to be used by a considerably higher percentage of the total snowmobiles entering the Park, which is consistent with the increased levels of exposure observed for employees working in this lane.

a. Particle Size

Particle sizes measured during this study were PM10, PM4.0, and PM2.5. Particulate matter collected from a snowmobile engine under controlled studies was reported to be sub-micrometer (less than 1 µm, or approximately 50 nanometers) in size which is orders of magnitude smaller than PM2.5 (White and Carroll, 1999). To evaluate if particulate matter collected during the current study was PM2.5 or smaller, we collected samples using our standard PM2.5 size-selective device which was co-located (sampling in parallel at the same location) with a PM10 sampler at the West Entrance. The sampling units were identical with identical flow rates. The size-selective device placed at the sampler inlet. Two samples were collected by each unit, one in the morning (a.m.) and one in the afternoon (p.m.). The a.m. and p.m. results are illustrated in Figure 17. There was virtually no difference between mass concentrations measured for either PM2.5 or PM10, indicating that the PM10 collected

was no larger in particle size than PM2.5. To confirm this observation, morning and afternoon PM2.5 samples were collected on a separate day (2/21/99) in parallel with total suspended particle (TSP) samples collected at the West Entrance. TSP samplers collect airborne particulate matter, regardless of particle size. The results are presented in Figure 18. The TSP mass concentrations were virtually identical to the PM2.5 mass concentrations for the morning and afternoon samples. This result supports the hypothesis that airborne particles emitted from snowmobile engines are at least smaller than PM2.5 and possibly sub-micrometer in size. In summary, all particles collected in the Park were probably smaller than PM2.5. These small particles are of concern since they can reach the deepest portions of the human respiratory system.

b. Occupational PM exposure studies

A number of investigators have reported on worker exposure (during typical working hours) to fine respirable PM. For example, respirable PM collected by personal samplers for non-smoking diesel railroad workers ranged from 104 $\mu g/m^3$ (inside workers) to 143 $\mu g/m^3$ (carmen). Non-smoking shop workers (a large indoor repair shop) were exposed to a median concentration of 113 $\mu g/m^3$ (Schenker et al., 1990).

Diesel particulate exposures were determined for workers in a major southeastern US electric utility company during normal working hours (Whittaker, et. al., 1999). Based on total organic carbon measurements, the range of mean PM was from 16 $\mu g/m^3$ for background measurements (n= 18) to 198 $\mu g/m^3$ (n=5) for samplers positioned near idling trucks. For personal samples, non-smokers typically had lower exposures (57 $\mu g/m^3$, n=60) compared to smokers (71 $\mu g/m^3$, n=42). Overall, the investigators

reported winter exposure for the workers was 80 $\mu g/m^3$ (n=103). All personal samples were taken near the worker's breathing zone for 6 to 7.5 hrs. Again, these levels were generally lower that PM concentrations than measured for many of the measured Park employees. Some Park employees exceeded measurements reported for workers exposed to diesel exhaust.

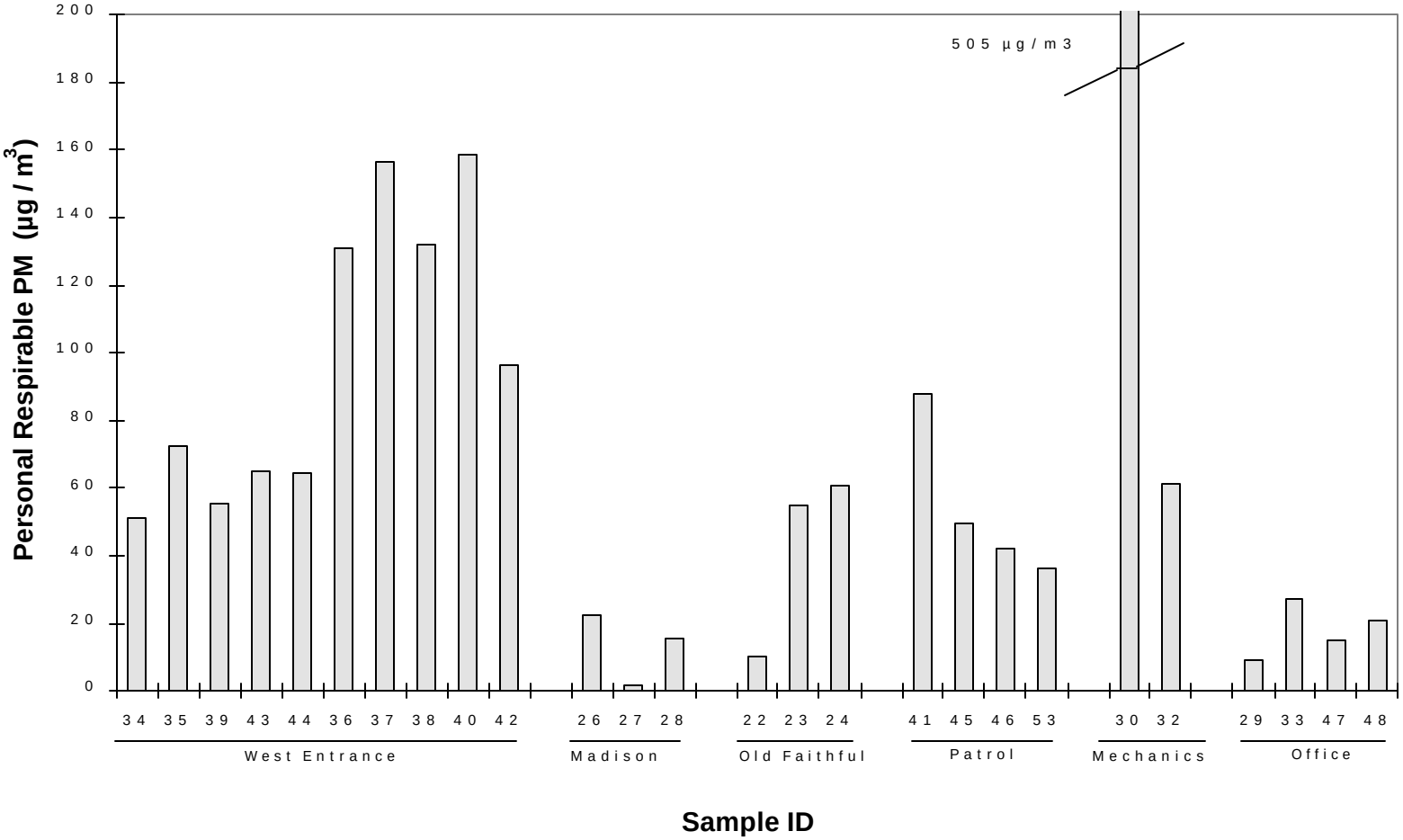


Figure 15. Personal exposure to respirable particulate matter (PerPM) by job category or location within the Park. Samples were collected February 13 – 21, 1999.

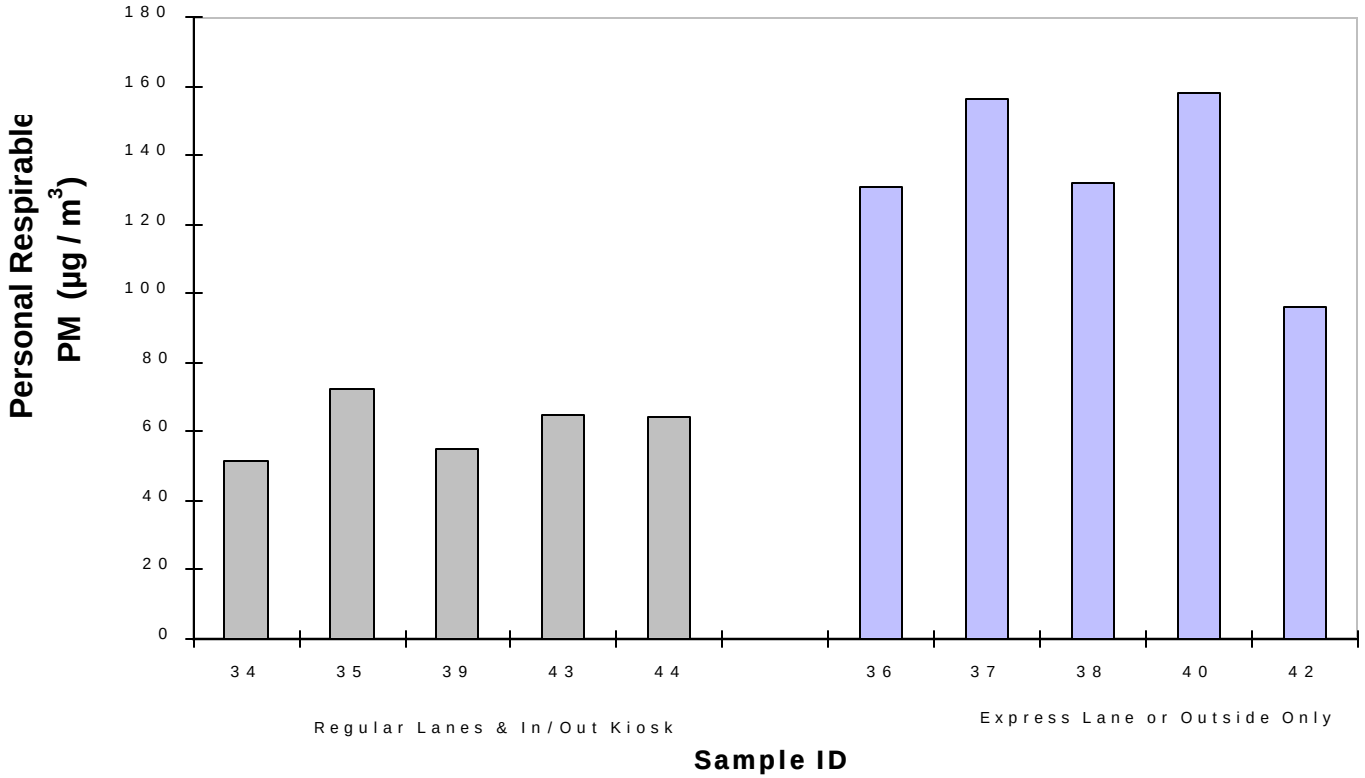


Figure 16. Personal exposure to repirable particulate matter (PerPM) at West Entrance according to job location. Samples were collected February 13 – 15, 1999.

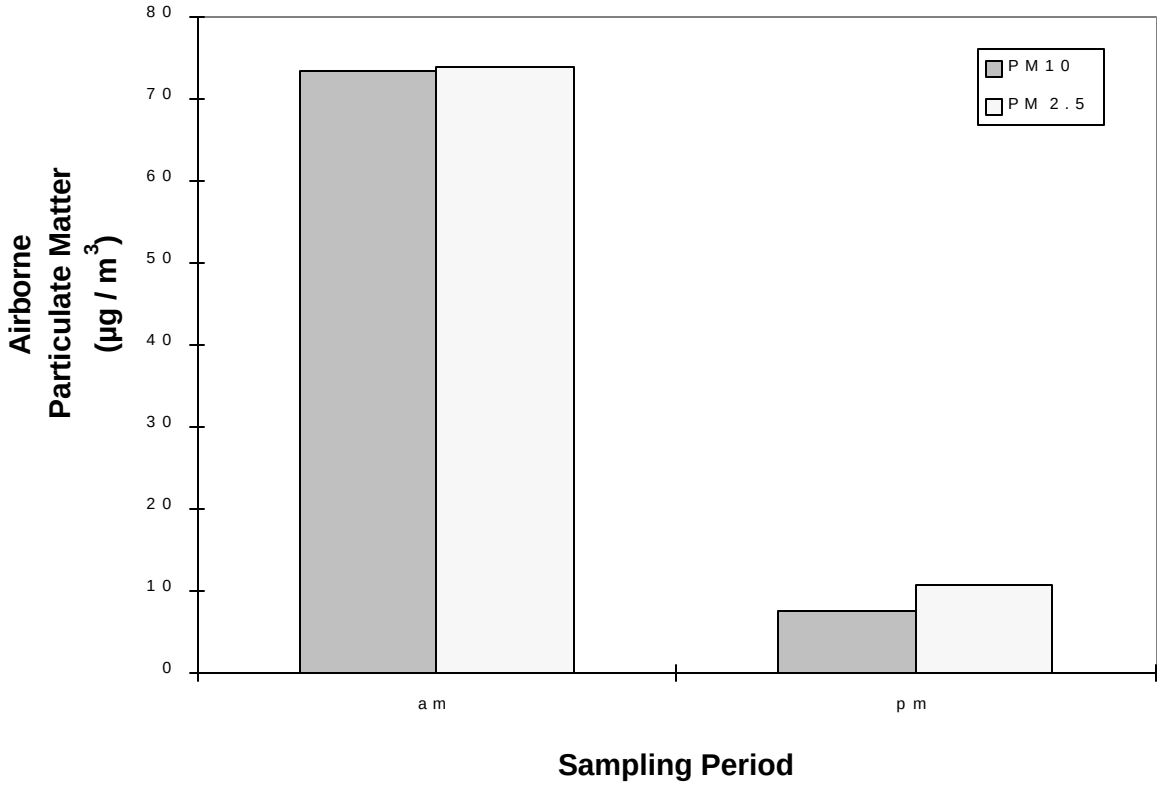


Figure 17. Comparison of PM10 and PM2.5 collected on February 20, 1999. Samplers were co-located at the West Entrance. Results show that virtually all PM10 collected, especially in the a.m. is less than PM2.5 in size.

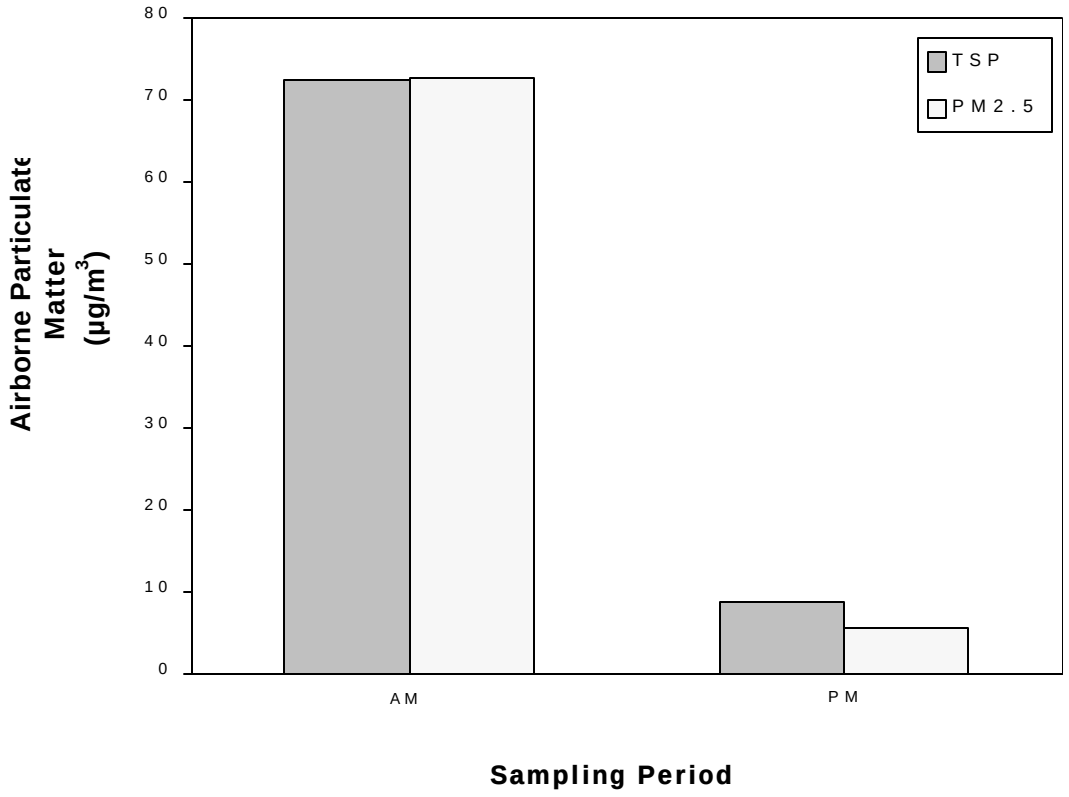


Figure 18. Comparison of total suspended particulate matter (TSP) and PM2.5 measured at the West Entrance on Sunday February 21, 1999. Results show that virtually all TSP collected, especially for the a.m. is less than PM2.5 in size.

D. Volatile Organic Compounds

Volatile organic compounds (VOCs) were measured for both fixed-site and personal samples. The fixed-site samples were primarily used to provide a general survey of ambient exposure in the work area over a relatively short period of time (typically between 15 and 180 minutes), while personal samples provided an integrated measurement of actual worker exposure during a daily work shift. The fixed-site samples were collected using two different sampling methods. For the first method, VOCs were collected using a solid adsorbent cartridge, or Carbotrap tube. After sample collection, the Carbotrap is sent back to the laboratory for analyses by GC/MS to qualitatively identify the compounds that were present. Using the second method, an air sample is captured in a Tedlar bag. Tedlar is similar to Teflon and these bags are routinely used to collect and hold air samples for qualitative and/or quantitative chemical analysis. The VOC samples provided a general survey of airborne hydrocarbon levels and were collected using Carbotrap adsorbent tubes (for 1 to 3-hour samples), Tedlar bags (for 15-minute samples). The chromatogram for a vapor phase sample collected at West on February 16, 1999 using a Carbotrap tube is illustrated in Figure 19. There are many types of hydrocarbons, including short chain (4 to 6 carbons) hydrocarbons such as butane and pentane and their branched derivatives. There are also many aromatic hydrocarbons such as benzene and its derivatives. The chromatogram shows many airborne compounds that are present. A similar spectrum of compounds is seen at the OF location on the same day as illustrated in Figure 20, suggesting that there were similar sources at both locations. The highest peaks were hydrocarbons such as butane, pentane, and hexane and their derivatives. These compounds are present in

gasoline. The results for a trip blank, or blank sample that was processed in a manner identical to the other samples, is presented in Figure 21. The VOC samples were analyzed for known toxic organic compounds present in gasoline, including benzene, toluene, ethyl benzene, and xylenes, for example.

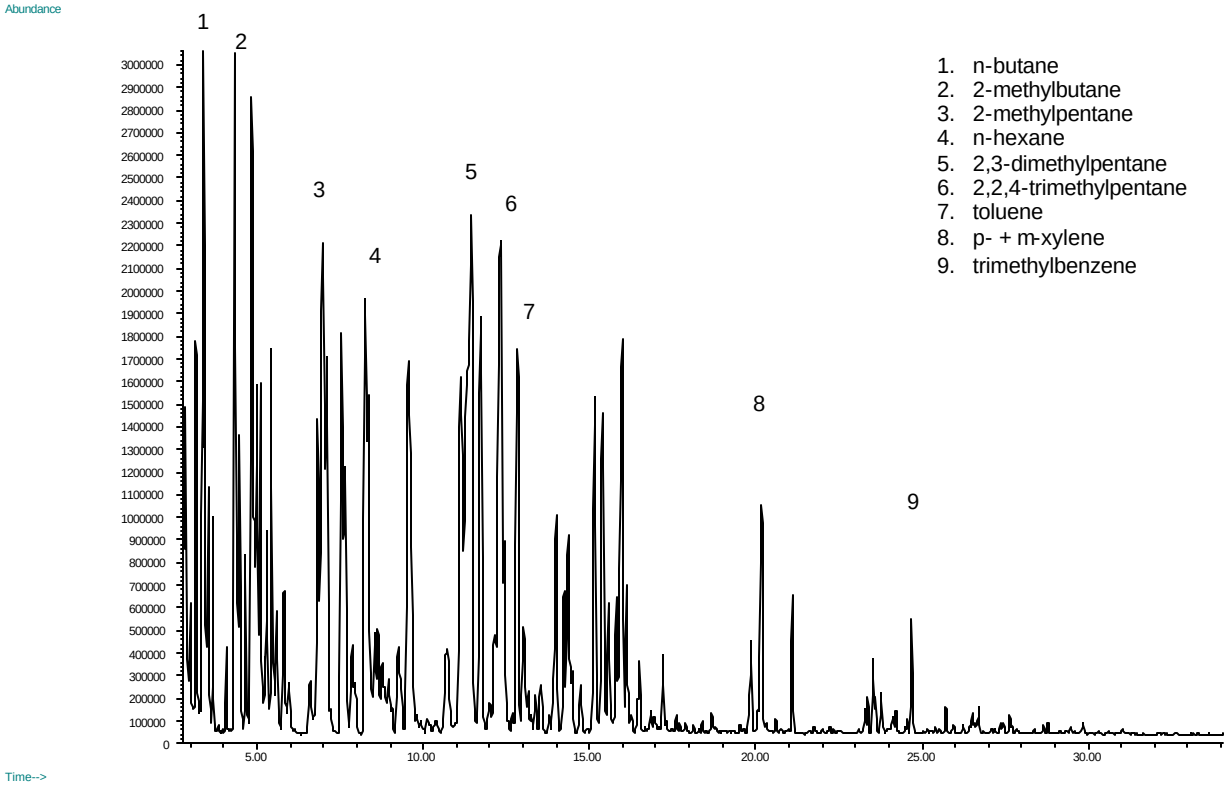
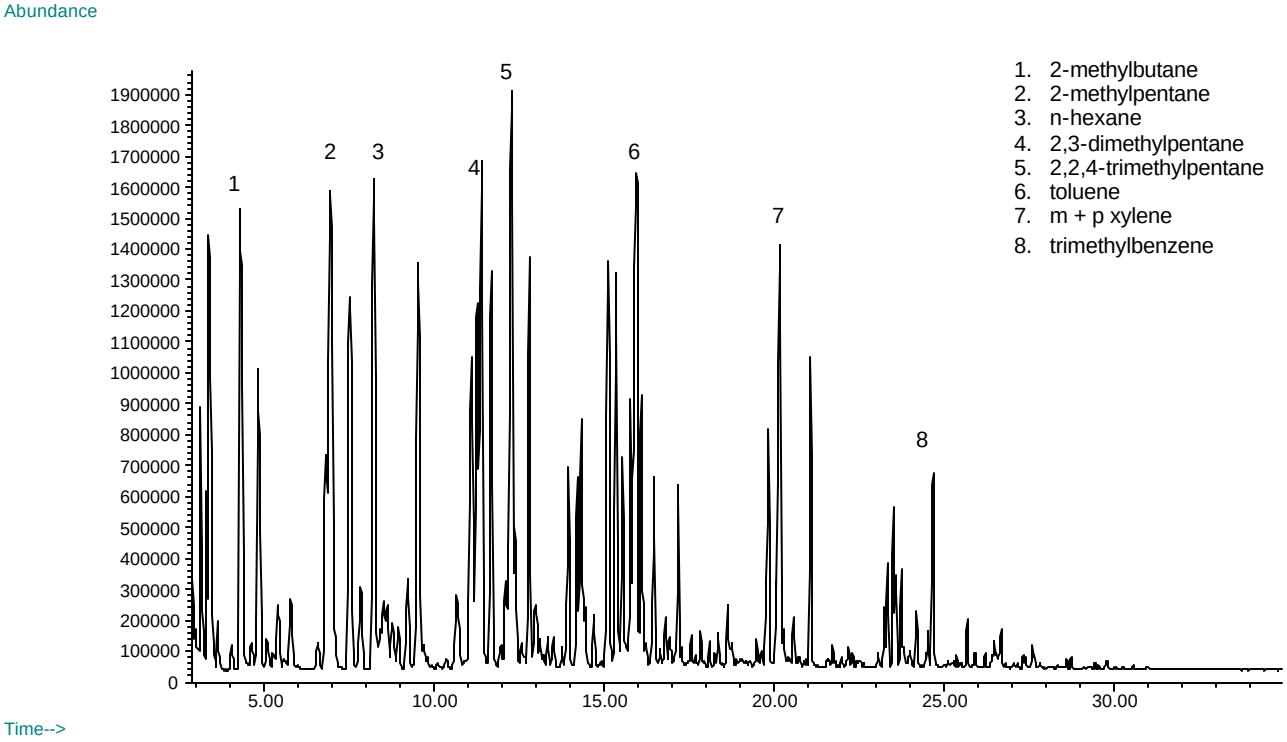
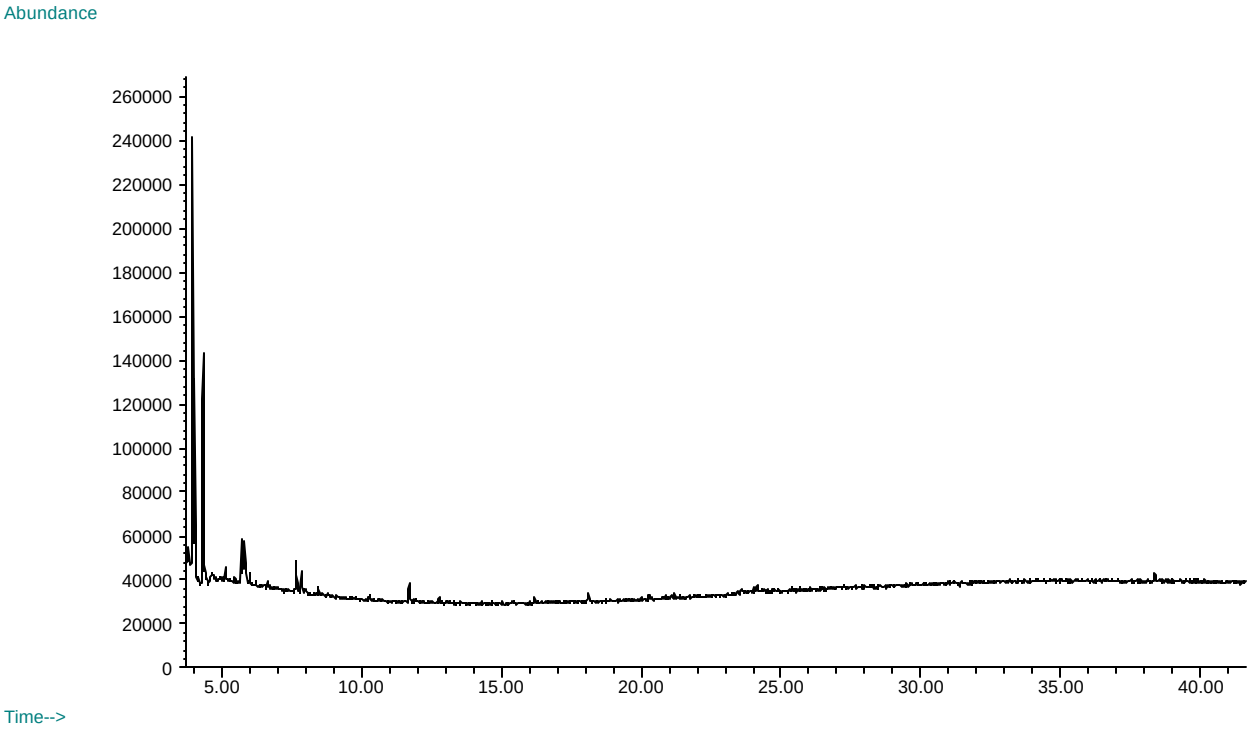


Figure 19. Gas chromatographic/mass spectral scan of VOCs at West Entrance (2/16/99). Screening sample obtained by Carbotrap tube.



Old Faithful 2/16/99 10:00-15:00

Figure 20. Gas chromatographic/mass spectral scan of VOCs at Old Faithful (2/16/99). Screening sample obtained by Carbotrap adsorbent tube.



Trip Blank

Figure 21. Gas chromatographic/mass spectral scan of adsorbent tube used as a trip blank. Trip blank was handled, shipped, stored, and analyzed in a manner identical to that of the sample.

E. Personal Exposure to VOCs - Passive Monitors

The personal monitoring devices (organic vapor badges) for VOCs were positioned on each employee's shirt or jacket lapel several inches from the breathing area (nose and mouth). The badge works on the principle of diffusion of the VOC onto a charcoal adsorbent pad located inside the badge. The compounds adsorb onto the pad during the work shift and therefore represent an integrated sample for the entire work period. A protective membrane allows for diffusion of VOCs, but minimizes the effects of wind on absorption. Badges were analyzed for the seven gasoline-associated VOCs listed in Table 5. A typical GC/MS chromatogram for a VOC standard is illustrated in Figure 22. The chromatogram illustrates the standard compounds at 1.25 nanogram/microliter concentration and the internal standards. A nanogram is 10^{-9} or one billionth of a gram, so the standard is 1.25 billionth of a gram per microliter.

Table 5. Gasoline-associated volatile organic compounds (VOCs) measured in personal sampling badges.

benzene	o-xylene
toluene	1,3,5-trimethylbenzene
ethylbenzene	1,2,4-trimethylbenzene
m,p-xylene	

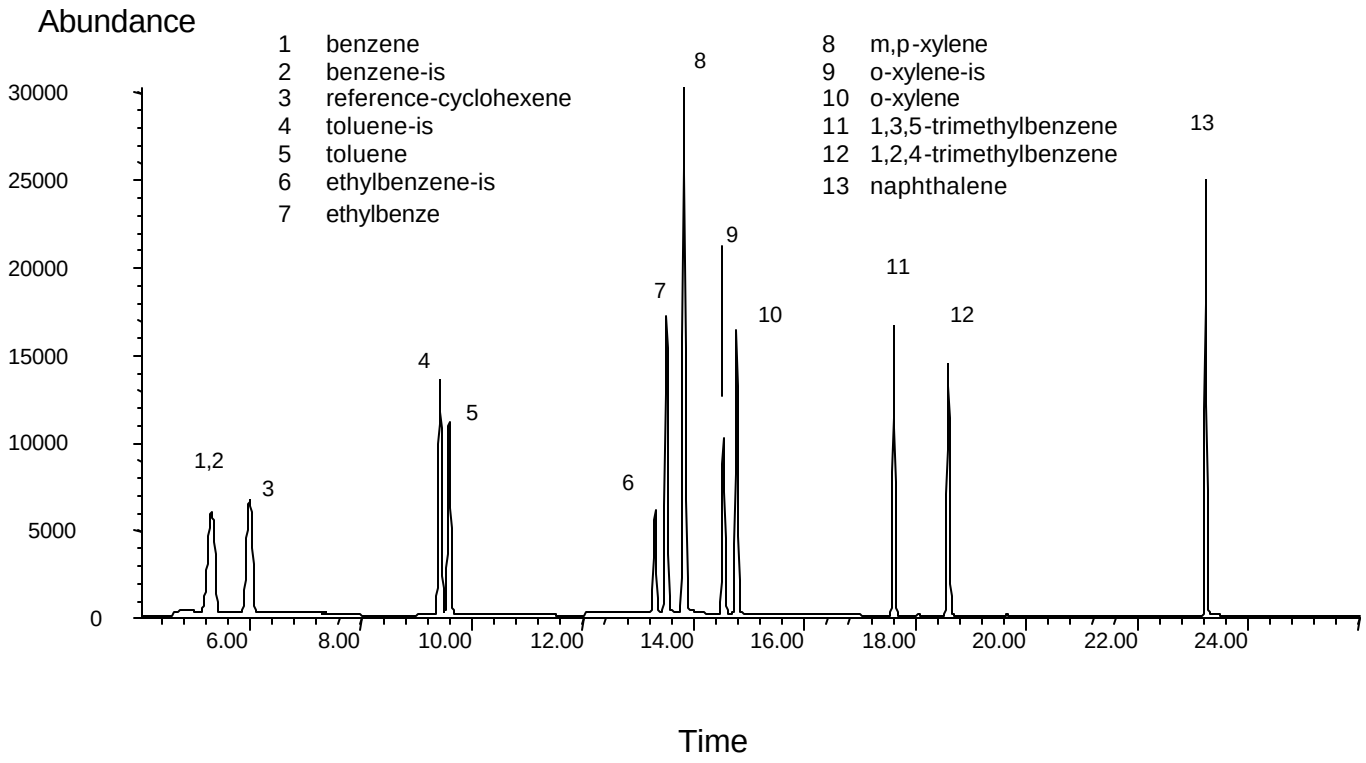


Figure 22. Gas chromatographic/mass spectral scan of a 1.25 ng/µl VOC and internal (is) standard for quantitating personal exposure using passive monitor badges.

Specific rates of diffusion for each of the compounds measured are known for the badges and were used to calculate the concentrations. For the employees at West, data for personal exposure to VOCs between February 13 and 14, 1999 are summarized in Table 6. On February 13 and 14, there were 802 and 739 snowmobiles that entered the Park at West, respectively (Figure 5). Employees monitored at West were exposed to benzene at an average work shift concentration of 212 µg/m^3, with a maximum concentration of 303 µg/m^3 observed. The VOC with the highest measured

concentration was toluene at 1,036 µg/m^3. Employees on mobile patrol duty and who also used snowmobiles during their shift were also exposed to VOCs as summarized in Table 7. Mobile patrol personnel were exposed to lower VOC concentrations than employees at the West Entrance. Mobile patrol employees were exposed to benzene at an average concentration of 137 µg/m^3. The lowest VOC exposures measured were for individuals working in offices or indoors where the average benzene concentration was 25 µg/m^3 (Table 8).

Table 6. West Employee Personal Exposure to VOCs 2/13 – 2/14/99. Samples (9) Collected from 7 Employees during an Average Work shift both Inside and Outside of the Kiosks.

VOC	Average	Std. Dev.[a]	Median	Minimum	Maximum
			Concentration (µg/m^3)		
benzene	176.69	77.32	188.95	92.12	302.63
ethylbenzene	149.93	70.15	163.72	67.70	257.40
m,p-xylene	249.14	122.09	275.01	107.63	425.70
o-xylene	125.91	75.39	136.22	48.61	185.63
1,3,5-TMB [b]	71.71	32.11	75.24	34.24	120.75
1,2,4-TMB [b]	150.23	68.68	160.01	66.04	243.69
toluene	850.51	400.26	922.56	406.01	1482.61

[a] Standard deviation reflects the wide range of VOC concentrations for West employee exposure. The standard deviation as a percentage of the mean is consistent for all VOCs measured.
[b] Trimethylbenzene

Table 7. Mobile Patrol Employee Personal Exposure to VOCs 2/13 – 2/14/99. Samples Collected from 3 Employees during an Average Workshift.

VOC	Average	Std. Dev.	Median	Minimum	Maximum
			Concentration (µg/m^3)		
benzene	137.20	33.73	118.76	108.65	184.18
ethylbenzene	118.80	27.59	105.46	92.45	158.50
m,p-xylene	181.50	40.33	161.96	143.03	239.50
o-xylene	87.20	19.52	79.10	66.28	116.23
1,3,5-TMB a	58.89	14.53	52.78	43.45	80.43
1,2,4-TMB a	122.98	30.62	111.68	87.82	169.45
toluene	654.69	143.18	589.46	511.07	863.55

[a] Trimethylbenzene

Table 8. Indoor Concentration of VOCs at the West District Office and Old Faithful Visitor Center during an Average Workshift. Personal samples Collected from 2 Employees at West District Office 2/17/99 – 2/18/99 and from 1 Employee at Old Faithful Visitor Center on 2/15/99.

VOC	Average	Std. Dev.	Median	Minimum	Maximum
			Concentration ($\mu g/m^3$)		
benzene	25.35	9.20	25.35	18.17	37.90
ethylbenzene	21.86	7.49	21.86	14.18	32.85
m,p-xylene	28.50	11.39	28.50	18.91	44.35
o-xylene	14.60	4.44	14.60	9.45	21.35
1,3,5-TMB a	13.45	2.07	13.45	9.81	17.05
1,2,4-TMB a	25.12	6.42	25.12	17.63	34.92
toluene	159.84	40.31	159.84	160.26	199.94

[a] Trimethylbenzene

The VOC concentrations measured at the Madison and OF locations were very similar and are summarized in Table 9. The mechanic was exposed to the highest concentrations of VOCs of all the employees that were monitored. For example, the concentration of benzene measured for the mechanic on February 17, 1999 was 514 $\mu g/m^3$ for a 4-hour work exposure. On that same day, the same mechanic was also exposed to the highest concentration of PerPM (505 $\mu g/m^3$).

Table 9. Remote Site VOC Concentrations during an Average Workshift.

Location:	Madison 1	Madison 2	Old Faithful 1	Old Faithful 2[b]	Mechanic	Mechanic
Date:	2/13/99	2/14/99	2/13/99	2/13/99	2/17/99	2/18/99
VOC	Concentration ($\mu g/m^3$)					
benzene	48.83	41.31	41.82	48.29	**514.1**	120.2
ethylbenzene	56.98	40.70	46.83	31.40	**869.9**	109.9
m,p-xylene	92.80	61.86	63.44	47.10	**1282**	168.5
o-xylene	43.96	30.93	28.70	22.68	**644.1**	79.37
1,3,5-TMB [a]	30.42	23.66	20.38	18.11	**449.9**	50.70
1,2,4-TMB [a]	63.75	49.18	37.18	33.18	**1,004**	114.7
toluene	307.15	278.84	291.55	192.60	**2,526**	609.3

[a] Trimethylbenzene

[b] Old Faithful 2 was a fixed site sample located next to the PM 2.5 sampler.

Personal exposure to benzene, ethylbenzene, toluene, xylenes, and trimethylbenzenes are illustrated in Figures 23 through 27 for all occupations. In general, concentrations of all VOCs were consistent in proportion for each worker. The highest exposure to benzene was for the mechanic on one of the two sampling trips, as illustrated in Figure 23. The benzene concentration was 514 $\mu g/m^3$ averaged over the working period of 4 hrs. The NIOSH recommended exposure limit (REL) for a 8-hr exposure is 0.1 ppm, which is approximately 300 $\mu g/m^3$. The mechanic surpassed this level in only 4 hrs. The next highest exposed were the employees at the West Entrance, followed by the mobile patrol employees.

For the PM measurements at the West Entrance, personal samples were highest for those workers who were stationed in the express lane and who worked

predominantly outside. The VOC exposures at the West Entrance were also highest for those individuals who were stationed at the express lane and predominantly outdoors. For example, in Figure 23 for benzene exposures, workers No. 160, 162, 170, and 179 were in these outdoor locations.

The stability of VOCs on the passive diffusion monitor badge was investigated by first adding the internal standards of benzene, toluene, and ethylbenzene to the badge using procedures identical to those used for the samples. The badges were stored at -20 ° C and after 28 weeks were extracted and analyzed. Chlorobenzene-d5 was used as a recovery standard and was added to the extraction solution just prior to injection into the GC/MS. The percent of VOC on the badge after this storage period was 80 percent for benzene, 106 percent for toluene, and 104 percent for ethylbenzene. These values indicate that after 28 weeks of storage at -20 C, there is some loss of benzene and little or no loss of toluene and ethyl benzene.

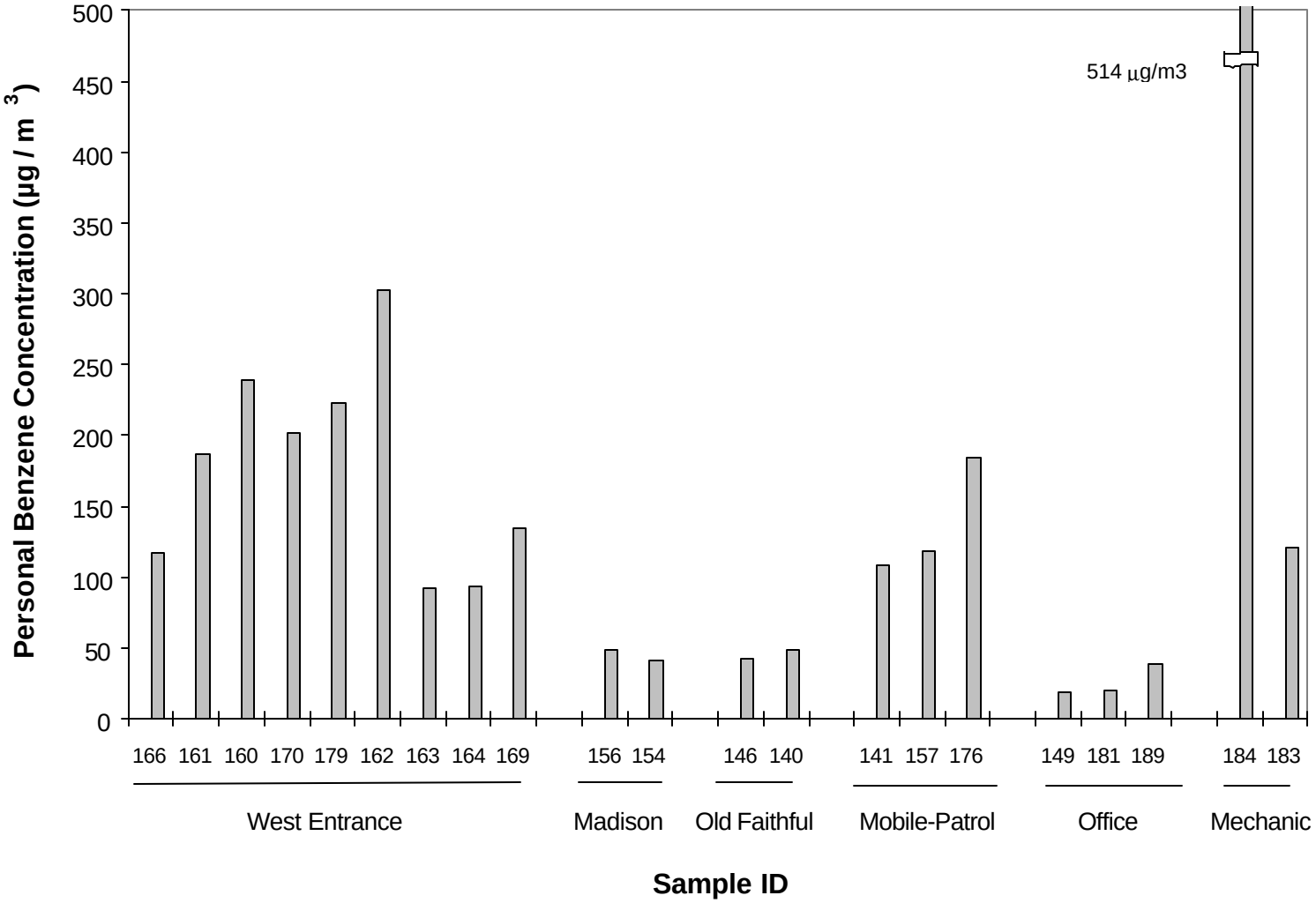


Figure 23. Personal exposure to benzene by job category or location - passive sampling badge.

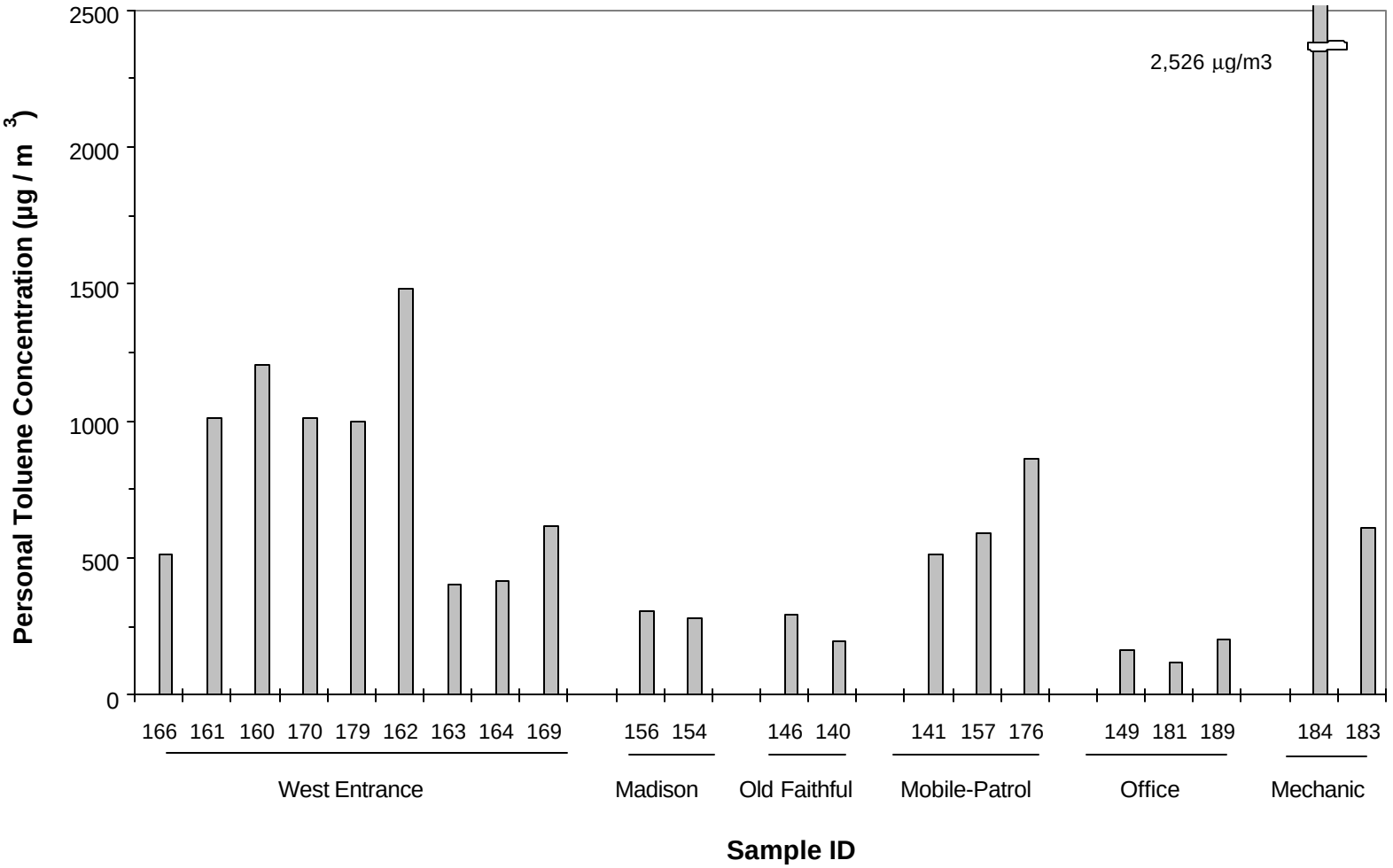


Figure 24. Personal exposure to toluene by job category or location – passive sampling badge.

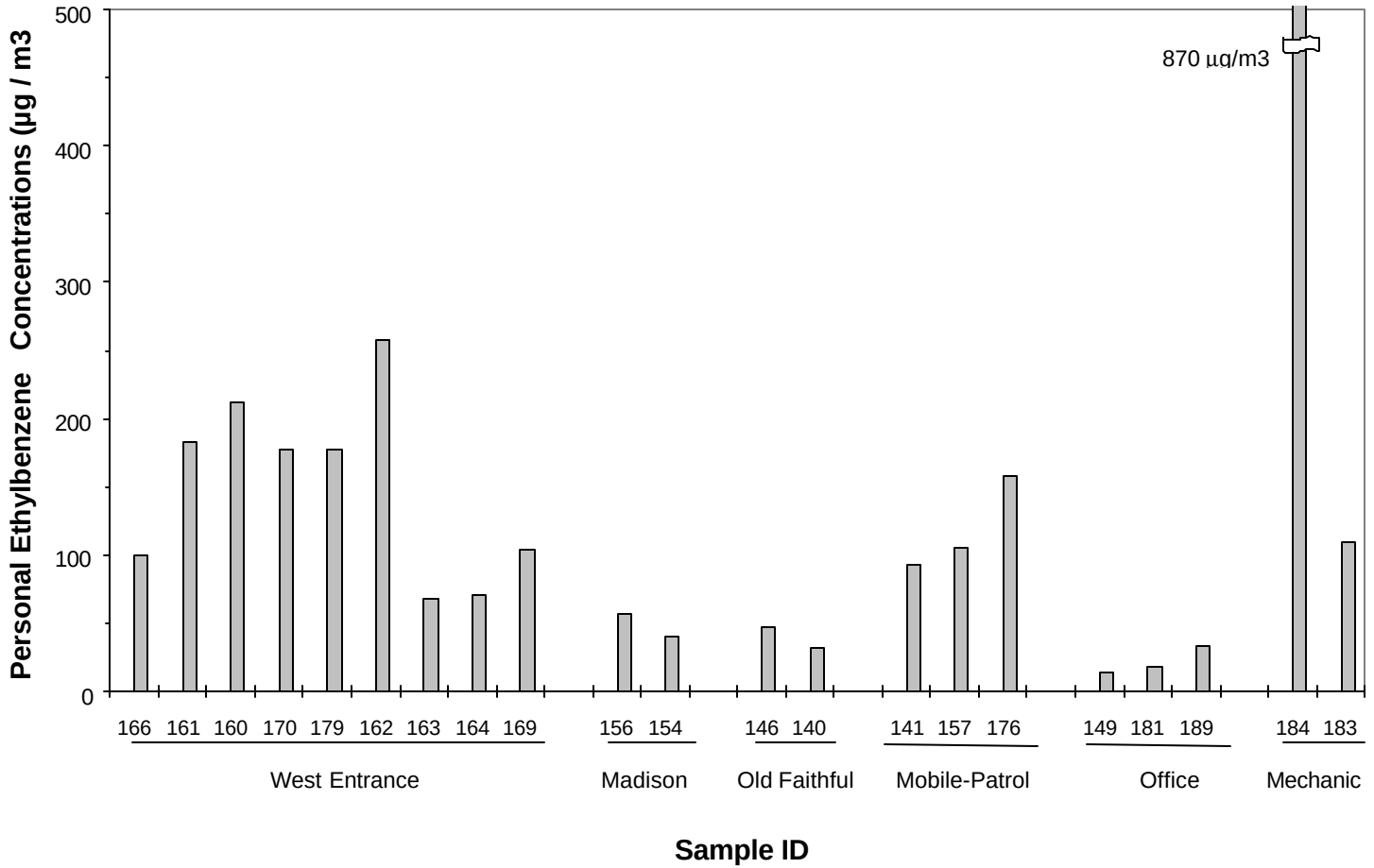


Figure 25. Personal exposure to ethylbenzene by job category or location – passive sampling badge.

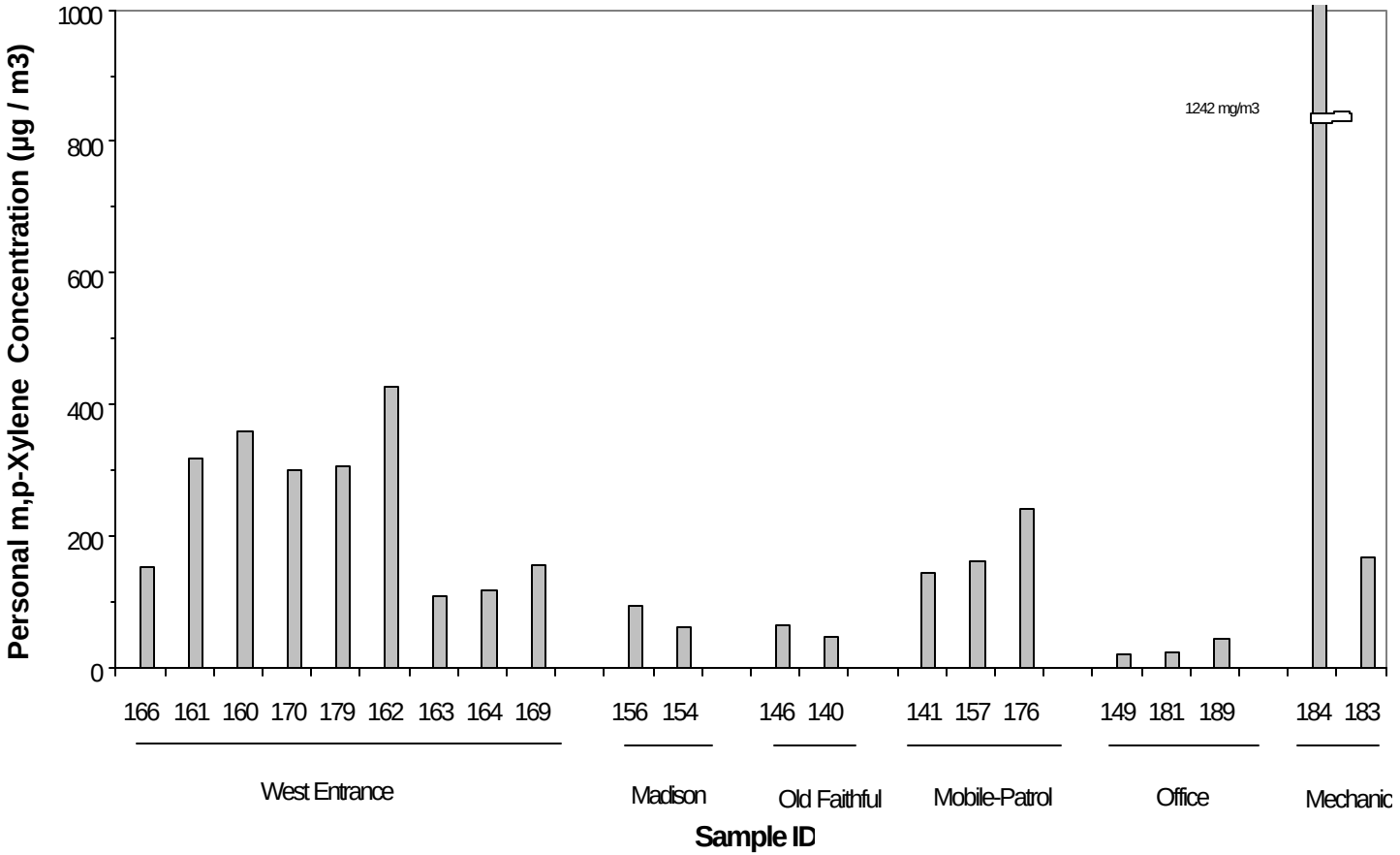


Figure 26. Personal exposure to m,p-xylenes by job category or location – passive sampling badge.

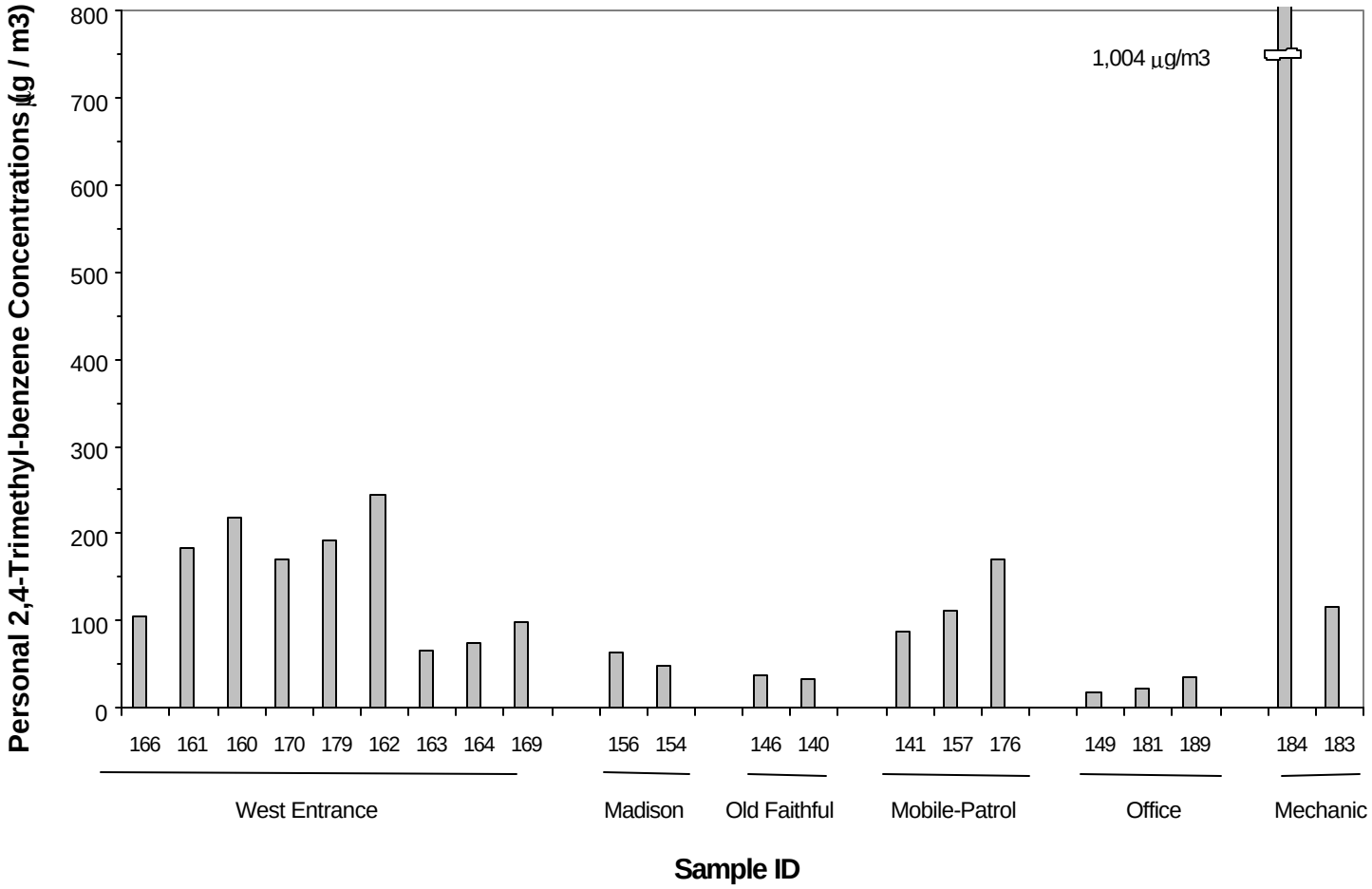


Figure 27. Personal exposure to 2,4-trimethylbenzene by job category or location – passive sampling badge.

1. Peak Short-Term VOC Exposure

Short-term (15-minute) samples were acquired at the West Entrance to determine worker and environmental exposure to peak VOC concentrations during snowmobile entry into the Park. To measure peak short-term exposure. Tedlar bag samples were collected at West Entrance close to Park employees stationed outside of the kiosk areas. These samples were collected near the employees breathing zone, which is located within several inches of the nose and mouth. Samples were also collected near the exit lane in the late afternoon (usually no Park employees are near this area in the late afternoon) and inside the West Entrance office located adjacent to the kiosks. Samples were analyzed within 6 hours of collection, using a portable GC equipped with a photoionization detector as previously described. Certified gas standards were used to quantitate levels. Selected samples were also returned to UC Davis for analyses by GC/MS following EPA Method TO-15. Peak concentrations of benzene, toluene, m,p-xylene, and o-xylene are presented in Table 10.

Peak work area exposures to benzene and toluene near the kiosks were considerably higher than the integrated concentrations detected by the badges for the entire work shift. For example, a peak work area benzene concentration of 842 $\mu g/m^3$ was measured, which is approximately 1.5 times higher than the highest personal benzene concentration detected in the integrated VOC badge samples. The West Entrance office that is located next to the kiosks also had detectable indoor concentrations of benzene and toluene, though lower than measured outdoors. The office sample was taken during the late afternoon.

Benzene is considered a Class 1 carcinogen by the International Agency for Research on Cancer (IARC) and a group A carcinogen by EPA. These are the highest categories for classification of a compound for its potential to cause cancer in humans. Both classifications mean that there is sufficient evidence that benzene causes cancer in humans. In general, exposure to higher concentrations of benzene over a lifetime, could result in a higher risk of cancer or other health effect. This will be described in a later section.

2. Occupational exposure

Occupational exposure to benzene from mobile sources has been reported in a number of studies. For example, urban workers who worked in traffic in Rome (traffic police) were studied for benzene exposure (Crebelli et al, 2001). Personal samplers were used and the time-weighted average exposure to benzene was higher among traffic police (6.8 $\mu g/m^3$) than among indoor workers (3.5 $\mu g/m^3$). Mean ambient benzene levels were 12.6 $\mu g/m^3$, and generally did not correlate with personal concentrations of benzene measured. Workers were exposed to benzene in traffic areas in Rome that were relatively higher than indoor office measurements.

These benzene concentrations are considerably lower than concentrations measured for many Park employees. For example, the median benzene concentrations at the West Entrance were 190 $\mu g/m^3$.

The occupational results are consistent with domestic studies of benzene in vehicles and on roadways. When the air inside vehicles was sampled during 2-hour commutes in California, benzene was detected at concentrations of 3 -15 $\mu g/m^3$ in Sacramento and 10 - 22 $\mu g/m^3$ in Los Angeles (Rodes, et al. 1998). During similar 2-hour sampling periods,

ambient concentrations of benzene measured during the same period as the in-car measurements averaged benzene concentrations of 1 - 3 µg/m^3 in Sacramento and 3 - 7 µg/m^3 in Los Angeles. Benzene concentrations for Park employees ranged from approximately 3 to 44 times the concentrations of occupational exposure for traffic workers in Rome. The median exposure for West Entrance employees was approximately 28 times the concentration of traffic workers. The benzene concentrations measured for the Yellowstone mechanic for a longer exposure period were approximately 30 to 160 times higher than concentrations measured inside commuter vehicles in Sacramento and 20 to 50 times higher than inside vehicles in Los Angeles. Benzene concentrations measured at the West location were approximately 10 to 30 times higher than concentrations measured inside commuter vehicles during a 2-hour commute in Sacramento and 5 to 10 times higher than inside vehicles commuting in Los Angeles. Employees at the West location are exposed to concentrations of benzene up to 100 times higher than ambient 2-hour levels measured at the same roadway taken by the commuter vehicle in either Sacramento or Los Angeles. The West and mobile patrol employees are exposed to concentrations of ethyl benzene, m,p-xylene, o-xylene, and that are approximately 10 times higher than concentrations measured inside of commute vehicles in Sacramento and Los Angeles and more than 10 times higher than ambient 2-hour roadside concentrations in these cities.

Table 10. Peak Short-Term VOC concentrations measured at the West Entrance near worker breathing zone (nose, mouth and upper chest area) using Tedlar bag samples.

Date	Concentration ($\mu g/m^3$)			
	benzene	toluene	m,p-xylene	o-xylene
2/16/99	842.8	2,851	918.1	575.2
2/19/99	324.1	579.0	136.5	313.6
2/21/99 [a]	621.1	2,101	357.2	458.0
2/23/99 [a]	277.4	939.0	169.0	216.0
2/17/99 [a] (Exit Lane 4 p.m.)	62.5	221	9.5	23
2/13/99 (West Entrance Office air)	46.8	373	ND [b]	ND
2/14/99	481.4	1,189	NQ [c]	NQ

[a] Analyzed by GC/MS as per EPA Method TO-15.
[b] Not detected.
[c] Not quantifiable.

F. Personal Exposure to Aldehydes

Personal exposure to aldehydes was determined by monitoring six employees at West and Madison during the Presidents' Day weekend. A total of 30 personal aldehyde exposure samples were collected, extracted, and chemically analyzed by HPLC. No samples were collected from employees working at OF or on mobile patrol. A series of 13

different aldehydes were examined for each sample including formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, 2-butanone, methacrolein, n-butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde, and hexaldehyde. Many of these compounds are carcinogenic and mutagenic and are oxidation products of automotive engine combustion. A sample HPLC chromatogram for these aldehydes is presented in Figure 28.

Acetaldehyde and formaldehyde have been measured in snowmobile emissions (Hare et al., 1975) and acetaldehyde levels have been shown to increase and formaldehyde levels decrease with the use of gasoline containing ethanol (White and Carroll, 1998). Ethanol-blend gasoline may be used during the winter months to fuel snowmobiles in West Yellowstone. The results for morning and noontime samples acquired for employees at West and Madison are illustrated in Tables 11 and 12. Up to 8 aldehydes were detected and quantitated for selected employees during the Presidents' Day weekend (Feb. 13 and 14, 1999). Employee exposure to formaldehyde and acetaldehyde was higher in the morning than in the later noon to early afternoon, a trend that was observed for most of the aldehydes detected. The exposure at West was higher than Madison for most of the aldehydes in both morning and noon time samples. This is consistent with the results for exposure to PM and VOCs, where a.m. concentrations were higher than the p.m., especially at West.

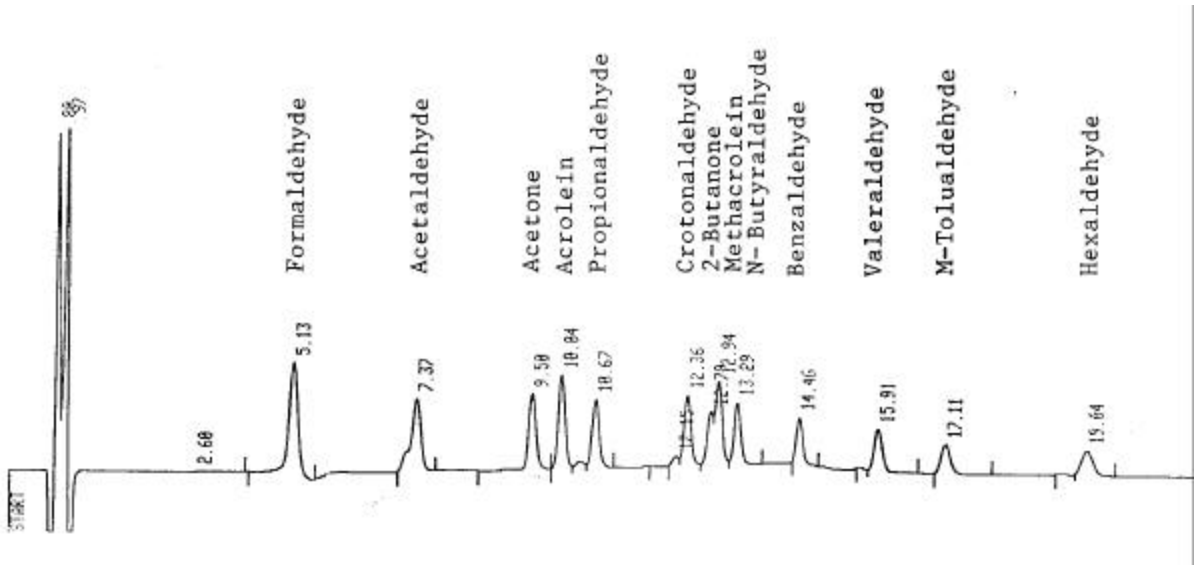


Figure 28. Sample HPLC chromatogram for a 0.1875 µg/ml aldehyde-DNPH standard mixture. The numbers indicated near peaks are retention times, or times when the compounds are eluted.

Table 11. West Entrance Park Service Employee Exposure to Aldehydes (120-130 minute sampling periods).

Employee #1 West Entrance (Lanes B and C)	Exposure during specified time period on 2/13/99 ($\mu g/m^3$)	
Aldehyde	9:10 - 11:20 am	11:32 am - 1:34 pm
Formaldehyde	80	28
Acetaldehyde	52	25
Acetone	25	31
Propionaldehyde	14	9
n-Butyraldehyde	8	5
Benzaldehyde	14	7
m-tolualdehyde	12	7
hexaldehyde	4	2

Employee #2 West Entrance (Lane B)	Exposure during specified time period on 2/14/99 ($\mu g/m^3$)	
Aldehyde	9:10 - 11:10 am	11:19 am - 1:25 pm
Formaldehyde	51	16
Acetaldehyde	33	13
Acetone	19	15
Propionaldehyde	28	7
n-Butyraldehyde	4	2
Benzaldehyde	10	3
m-tolualdehyde	7	not detected
hexaldehyde	not detected	not detected

Table 12. Madison Junction Park Service Employee Exposure to Aldehydes (120-133 minute sampling periods).

Employee #3 Madison Junction	Exposure during specified time period on 2/13/99 ($\mu g/m^3$)	
Aldehyde	9:50 am - 12:03 pm	12:06 - 2:15 pm
Formaldehyde	20	10
Acetaldehyde	16	10
Acetone	18	20
Propionaldehyde	10	5
n-Butyraldehyde	3	2
Benzaldehyde	5	not detected
m-tolualdehyde	4	not detected
hexaldehyde	not detected	3
Employee #4 Madison Junction	Exposure during specified time period on 2/14/99 ($\mu g/m^3$)	
Aldehyde	9:26 - 11:30 am	1:33 - 3:33 pm
Formaldehyde	16	12
Acetaldehyde	16	13
Acetone	21	24
Propionaldehyde	18	8
n-Butyraldehyde	3	2
Benzaldehyde	4	not detected
m-tolualdehyde	3	not detected
hexaldehyde	2	4

Employee #1, whose work area included the Express Lane, was exposed to higher levels of formaldehyde and acetaldehyde during both sample collection periods than Employee #2 at West or Employees #3 and #4 at Madison. For comparison to the holiday weekend, employees were also monitored during the morning on a separate weekend day, as summarized in Table 13. Specific work areas for these employees were not noted. West Employee #2 was exposed to 88 µg/m^3 of formaldehyde, the highest concentration of the samples collected and tested. The concentrations were very similar to the West Entrance a.m. samples summarized in Table 11.

Table 13. West Entrance Park Service Employee Exposure to Aldehydes on 2/19/99 (170-176 minute sampling period).

	Exposure during specified time period (µg/m^3)		
	Employee #1	**Employee #2**	**Employee #5**
Aldehyde	8:30 - 11:20 am	8:38 - 11:28 am	8:27 - 11:22 am
Formaldehyde	59	88	30
Acetaldehyde	35	43	18
Acetone	15	19	12
Propionaldehyde	10	20	6
n-Butyraldehyde	4	3	3
Benzaldehyde	11	14	5
m-tolualdehyde	9	10	4
hexaldehyde	2	not detected	1

To examine time-dependent exposure to aldehydes, a series of short- term (30-min) samples were obtained for three West employees starting at approximately 8:30 a.m. on February 20, 1999. HPLC chromatograms for these 30-min samples are illustrated in Figure 29.

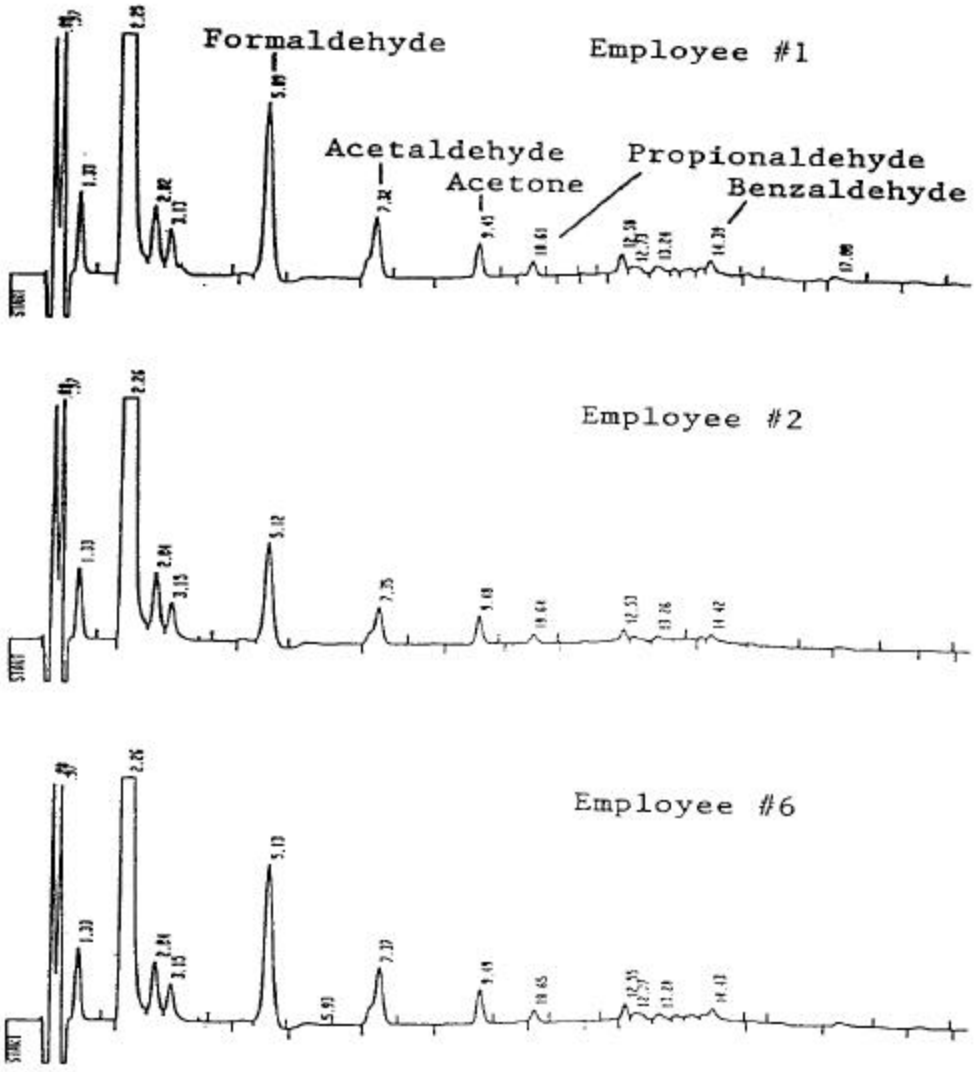


Figure 29. Sample HPLC chromatograms for personal exposure to aldehydes. Each employee sample was collected for 30 minutes on 2/20/99. Data from these chromatograms were used to calculate the exposure concentrations reported in Table 14.

Data from the chromatograms in Figure 29 were used to calculate the personal exposure concentrations shown in Table 14. Employees #1 and #6, who worked in the Express Lane, were exposed to higher levels of formaldehyde and acetaldehyde than was Employee #2, who worked in the entrance lane farthest away from the Express Lane.

Table 14. West Entrance Park Service Employee Exposure to Aldehydes on 2/20/99 (30-minute sampling period).

	Exposure during specified time period ($\mu g/m^3$)		
	Employee #1 (Lane C – Express)	**Employee #2** (Lane A)	**Employee #6** (Lane C, Express)
Aldehyde	8:23 - 8:53 am	8:21 - 8:51 am	8:25 - 8:55 am
Formaldehyde	79	46	73
Acetaldehyde	40	25	38
Acetone	21	18	21
Propionaldehyde	11	7	7
n-Butyraldehyde	10	not detected	6
Benzaldehyde	20	7	not detected
m-tolualdehyde	9	not detected	not detected

Immediately following collection of the 30-minute samples, a series of 15-minute samples was collected for the same employees, as shown in Table 15.

Table 15. West Entrance Park Service Employee Exposure to Aldehydes on 2/20/99 (14-18 minute sampling periods).

Employee #1 West Entrance (Lane C, Express)	Exposure during specified time period ($\mu g/m^3$)		
Aldehyde	9:08 - 9:23 am	9:56 - 10:12 am	10:33 - 10:47 am
Formaldehyde	73	38	34
Acetaldehyde	42	13	17
Acetone	25	10	13
Propionaldehyde	10	7	not detected
n-Butyraldehyde	not detected	not detected	not detected
Benzaldehyde	not detected	not detected	not detected
Employee #2 West Entrance (Lane A)			
Aldehyde	9:06 - 9:21 am	9:54 - 10:10 am	10:31 - 10:49 am
Formaldehyde	35	23	34
Acetaldehyde	29	15	15
Acetone	24	13	14
Propionaldehyde	15	5	7
n-Butyraldehyde	not detected	not detected	not detected
Benzaldehyde	not detected	not detected	not detected
Employee #6 West Entrance (Lane C, Express)			
Aldehyde	9:10 - 9:26 am	9:59 - 10:16 am	10:34 - 10:50 am
Formaldehyde	76	26	29
Acetaldehyde	46	17	18
Acetone	27	24	29
Propionaldehyde	9	9	8
n-Butyraldehyde	3	not detected	not detected
Benzaldehyde	16	not detected	not detected

Once again, Employees #1 and #6 were exposed to higher levels of formaldehyde and acetaldehyde compared to Employee #2, indicating that working in the Express Lane

results in higher employee exposure to these two aldehydes. Due to the shorter sampling periods, only 6 to 7 of the 13 aldehydes measured were detectable, as shown in Tables 14 and 15. None of the measurements for formaldehyde exceeded the NIOSH 15-minute STEL (short-term exposure limit) of 4.5 mg/m^3 (2 ppm). In addition to the personal aldehyde exposure samples, a trip blank sample was also collected and analyzed as shown in Figure 30. The trip blank was handled, shipped, stored, and analyzed in a manner identical to that used with the sample. There were no detectable aldehydes in the trip blank.

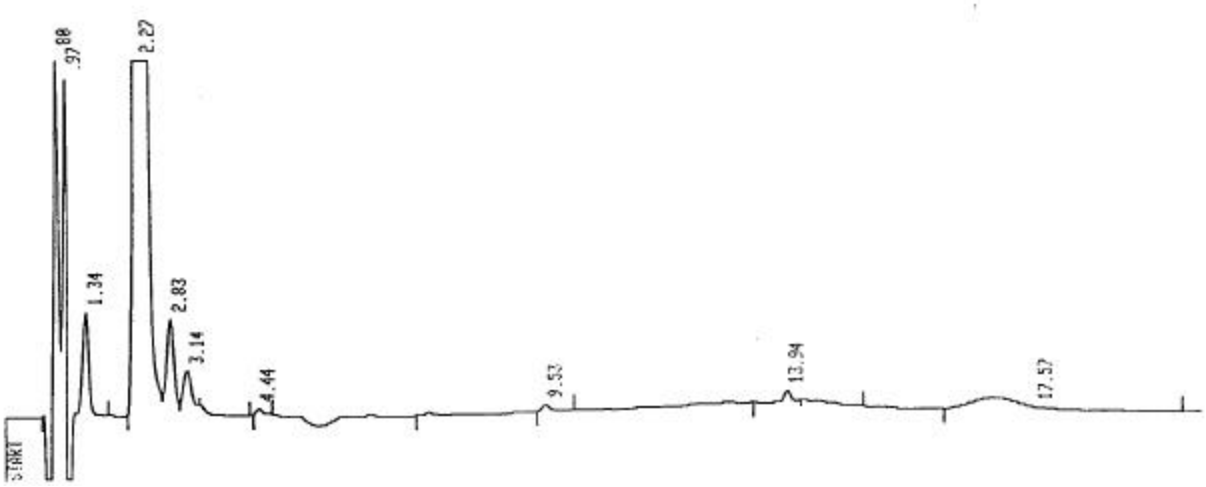


Figure 30. HPLC chromatogram of a trip blank sample.

Although each personal exposure sample was analyzed for the presence of 13 different aldehydes, not all were detected. Those aldehydes not detected in any sample included

acrolein, crotonaldehyde, 2-butanone, methacrolein, and valeraldehyde. Formaldehyde and acetaldehyde are two compounds that are of greatest toxicological interest. These two aldehydes were detected in every personal exposure sample that was collected. They were also present in the emissions from a snowmobile engine run under controlled conditions with an engine dynamometer (White and Carroll, 1998).

G. Carbon Monoxide

Carbon monoxide is directly emitted from snowmobiles and coaches. Average daily a.m. and p.m. concentrations were calculated from the hourly concentrations and are shown in Figures 31 and 32. The a.m. concentrations are calculated from 4 consecutive hourly averages during the 8 a.m. to 12 p.m time period. The p.m. concentrations are calculated from 4 consecutive hourly averages from 12 p.m. to 4 p.m. Both a.m. and p.m. CO concentrations are therefore considered to be nominally 4-hour average concentrations representative of the exposure during the working day. The range of average a.m. (4-hour average) CO concentrations were from approximately 0.5 ppm to 4 ppm and from approximately 0.5 ppm to 2 ppm for the p.m. (4-hour average) samples.

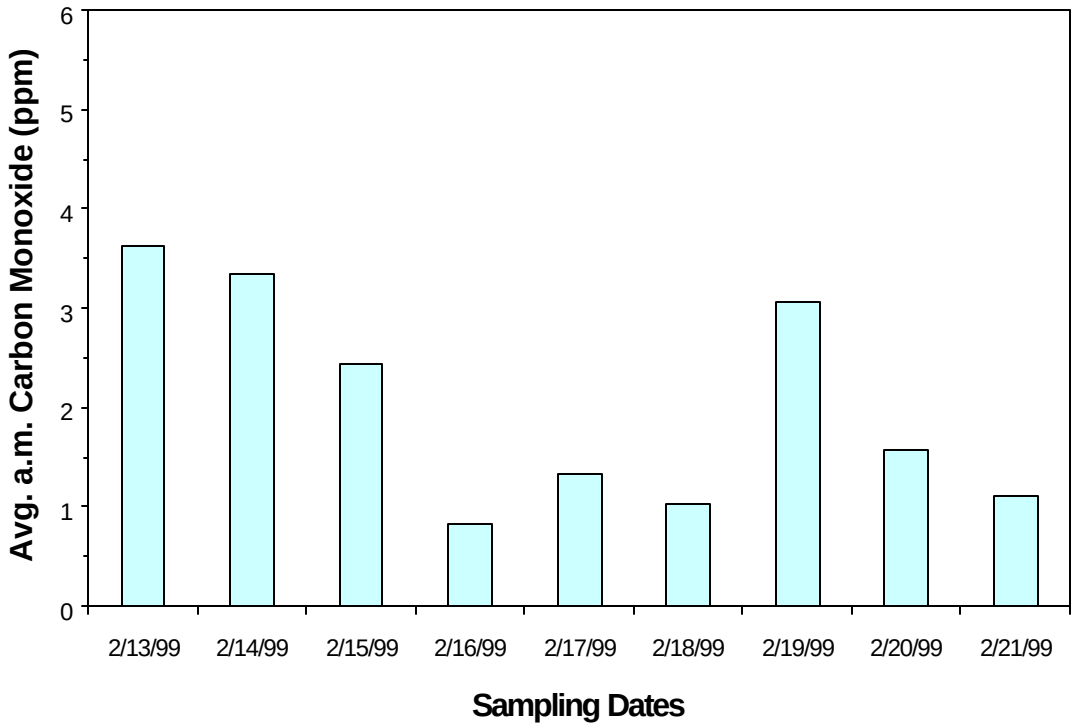


Figure 31. Average morning (8:00 to 12:00) carbon monoxide concentrations at the West Entrance monitoring station collected during the study dates. The station is located on the north side of the Entrance and just east of the kiosks. Presidents' Day weekend was 2/13/99 and 2/14/99 (Saturday and Sunday).

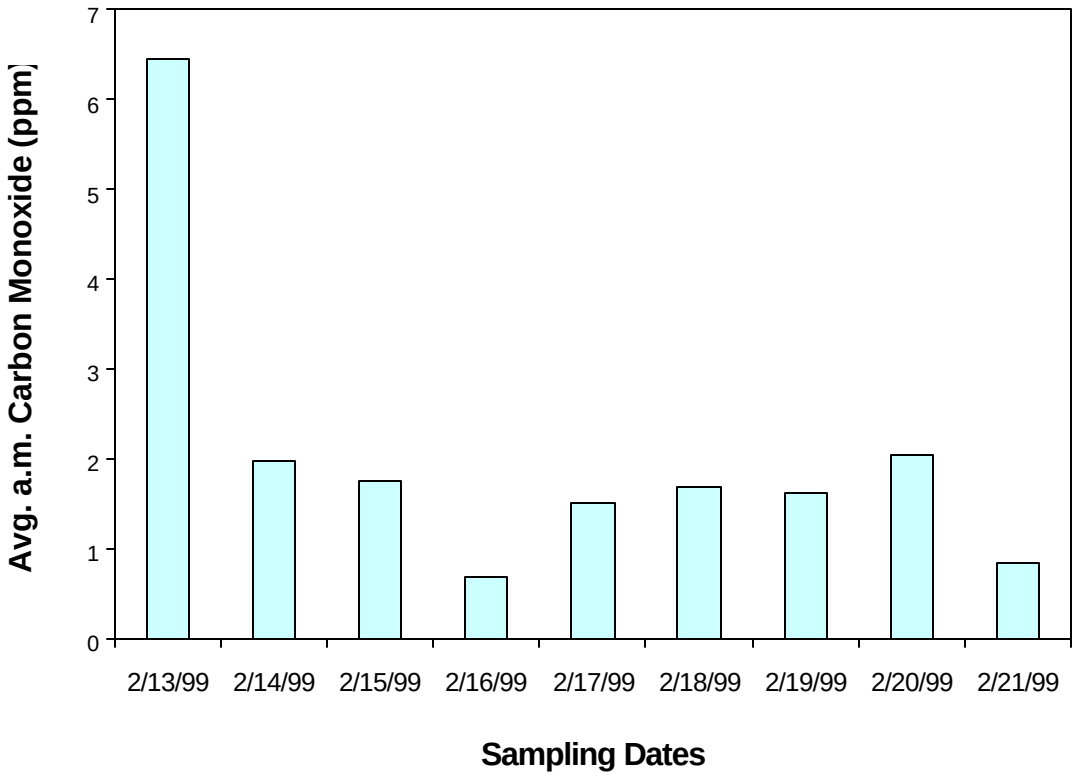


Figure 32. Average afternoon (12:00 to 16:00) carbon monoxide concentrations at the West Entrance monitoring station collected during the study dates. The station is located on the north side of the Entrance and just east of the kiosks.

H. Bioassay Analyses of Engine Emissions

Bioassay analyses were completed for the particulate matter obtained from SwRI for a snowmobile engine that was run under controlled conditions on a dynamometer. The results for the different modes and emissions are presented in the SwRI report as part of the winter science studies (White and Carroll, 1999). The snowmobile engine tested was a 500 cc, two-cylinder, two stroke air-cooled model that was considered representative of engines used in Yellowstone National Park. Specific information on the engine, fuel, and oil used is detailed in a Final Report by Carroll and White (1999). Briefly, particulate matter from each of 5 modes was extracted and tested as described in the Methods section. Each mode represents a different percentage of engine speed or torque run at steady state. Modes 1 through 5 represent 100%, 85%, 75%, 65%, and idle speed, respectively.

Particulate matter collected from the snowmobile engine was mutagenic for both the mineral-based (Base) and biosynthetic (Bio) lubricants. Dose-response curves were developed for each particulate sample and used to determine the specific mutagenic activity of the particulate matter as summarized in Table 16**.** The specific mutagenic activity is expressed as the number of revertants per microgram (µg) of particulate matter. The higher the number of revertants, the more damage to DNA. Mutagenic activity is typically reported with (+S9) and without (-S9) metabolic enzymes added to the test. These enzymes are added so that certain compounds that require metabolism can be detected. Other compounds may not be detected without the addition of enzymes. The highest mutagenic activity per particle mass was observed in Mode 5 (idle speed) for both lubricants. Mutagenicity for Modes 1 through 4 was considerably higher with the mineral-based lubricant than with the biosynthetic lubricant.

Table 16. Specific Mutagenic Activity of Particles Collected from a Snowmobile Engine.

Test Mode	Specific Mutagenic Activity (revertants/µg particles)	
	With Metabolic Enzymes (+S9)	Without Metabolic Enzymes (-S9)
Base Mode 1	44	24
Base Mode 2	17	5
Base Mode 3	10	2
Base Mode 4	4	1
Base Mode 5	52	4
Bio Mode 1	13	6
Bio Mode 2	7	1
Bio Mode 3	5	1
Bio Mode 4	1	0
Bio Mode 5	50	3

Blank filters = 0 mutagenic activity.

The specific mutagenic activity (+S9) for mode 1 and for the mineral-based lubricant is approximately 3.5 times the specific activity of mode 1 biosynthetic lubricant. Mode 1 is 100 percent speed and the combustion conditions or the lubricant itself may be more favorable for the formation of mutagenic compounds during this mode. Specific mutagenic activity when no metabolic enzymes were added was many times lower for each mode.

However, the specific mutagenic activity (-S9) for the mineral-based lubricant during mode 1 is the highest of all modes for both lubricants tested without metabolic enzymes added.

Mutagen emission rates were calculated using specific mutagenic activity (revertants/µg particles) and the particle emission rate (g particles/ br-hphr). The calculated values are "weighted," or adjusted based on the contribution of each mode during a typical driving trip on a snowmobile. For example, mode 4 (65 percent speed, 19 percent torque) represents 31 percent of the total driving trip. The mutagen emissions from the tailpipe during all five modes represent compounds on the particulate matter that can damage DNA.

The total mutagen emission rates are summarized in Table 17 for all five modes of the test. The mutagen emission rate when the mineral-based lubricant used was 9.3×10^{6} revertants/br-hphr, while the mutagen emission rate for the biosynthetic lubricant was 6.2×10^{6} revertants/br-hphr. These mutagen emission rates are based on the mutagenic activity when metabolic enzymes are added. The use of the biosynthetic lubricant appears to decrease the total emissions of mutagenic activity. The mutagen emission rate with no metabolic enzymes added was 3.0×10^{6} revertants/br-hphr and 1.2×10^{6} revertants/br-hphr for the mineral-based and biosynthetic lubricants, respectively. These mutagen emission rates are lower than when metabolic enzymes are added. The mutagen emission rates indicate that compounds such as polycyclic aromatic hydrocarbons that can only be detected with the addition of metabolic enzymes, are probably present on the particulate matter. The mutagen emission rates with metabolic enzymes are similar to those observed for a 10-liter heavy-duty diesel engine using pre-1993 No. 2 diesel fuel (data not shown).

Table 17. Total Mutagenic Activity Emissions based on Particles Collected from a Snowmobile Engine. Tested with a mineral-based or biosynthetic lubricant.

Lubricant	Total Mutagenic Activity Emissions [a] (revertants/br-hphr)	
	With Metabolic Enzymes (+S9)	Without Metabolic Enzymes (-S9)
Base Mineral	**9.3×10^6**	**3.0×10^6**
Bio Lubricant	**6.2×10^6**	**1.2×10^6**

[a] Emissions were weighted based on snowmobile driving patterns.

I. Emission Source Evaluation

One approach in evaluating the sources of environmental and personal exposure to air pollutants is to investigate relationships of the pollutants with potential sources. In the current study and in previous studies, snowmobile emissions have been implicated as a source of specific toxic air pollutants. As a first step in source evaluation, we examined the relationship between airborne CO levels and numbers of snowmobiles entering the Park. This relationship was further examined to include airborne particulate matter. An additional approach for evaluating the potential sources of air pollutants is to investigate specific types of compounds derived from those sources that are present in the ambient air. We identified specific compounds in the airborne VOC samples, many of which are present in the fuel and in the exhaust of gasoline-powered vehicles. The VOC content in gasoline samples obtained in West Yellowstone and available to fuel snowmobiles was compared to some ambient air samples collected during the study.

1. Relationship between Snowmobiles and CO

A correlation of the concentrations of CO with the number of snowmobiles entering the West Entrance of the Park over the entire test period (February 13 - 21, 1999) is illustrated in Figures 33 and 34. Based on the correlation between the morning CO levels and the number of snowmobiles entering the Park through the West Entrance, approximately 64 percent of the CO levels measured can be accounted for by the daily snowmobile counts.

However, when afternoon CO levels are taken into consideration, only about 21 percent of the afternoon CO levels are explained by the daily snowmobile count (Figure 34).

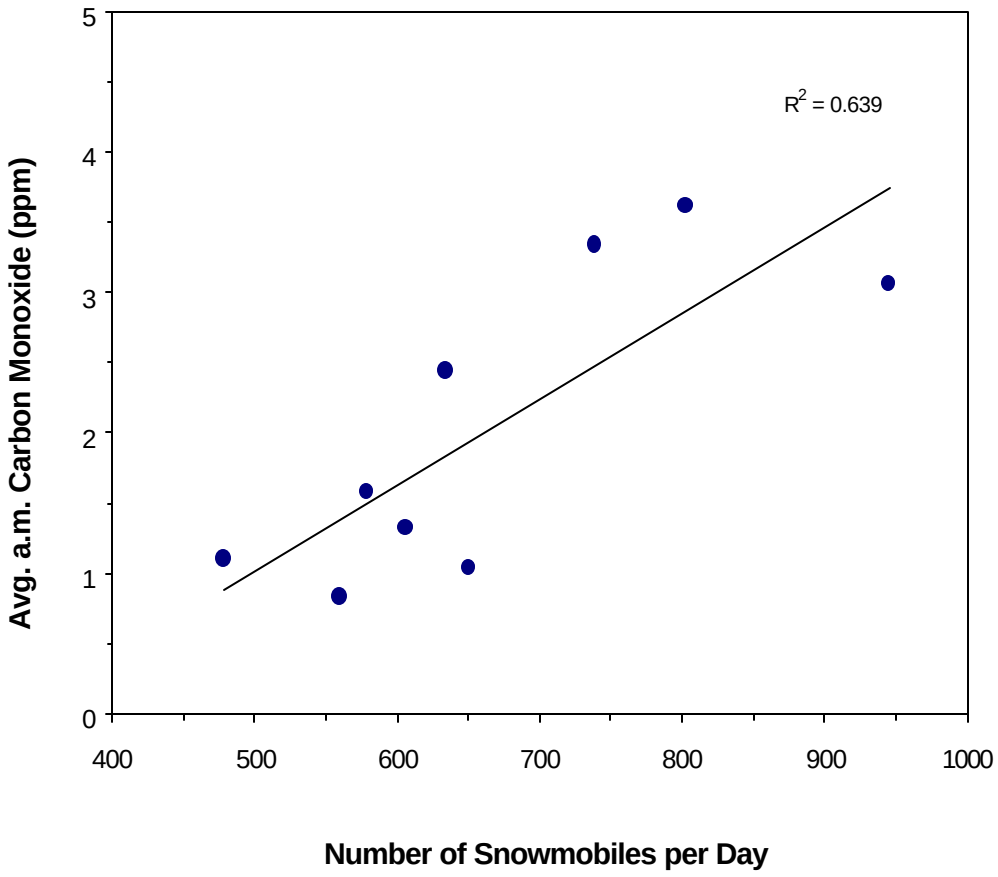


Figure 33. Relationship between the number of snowmobiles entering the Park each day through the West Entrance and the average a.m. CO levels measured at the West Entrance EPA-recognized fixed-site sampling location near the exit lane. Each data point represents the number of snowmobiles counted between 8:00 and 12:00 during the 9 days of sample collection 2/13/99 - 2/20/99 and the corresponding average morning CO level for that day.

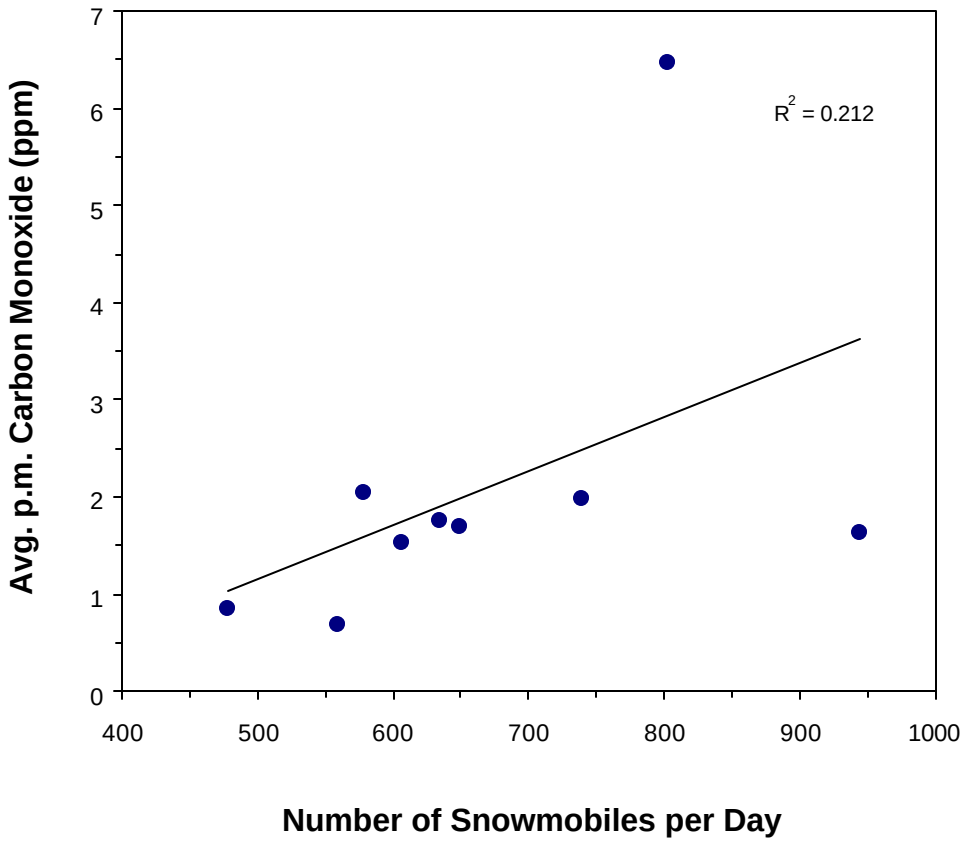


Figure 34. Relationship between the number of snowmobiles entering the Park each day through the West Entrance and the average p.m. CO levels measured at the West Entrance EPA-recognized fixed-site sampling location near the exit lane. Each data point represents the number of snowmobiles counted between 12:00 and 16:00 during the 9 days of sample collection 2/13/99 - 2/20/99 and the corresponding average afternoon CO level for that day.

The snowmobile count is somewhat more predictive of the morning CO concentrations than the p.m. CO concentrations. This is most probably due to the following factors: 1) approximately 90 percent of the daily number of snowmobiles that enter the Park through the West Entrance do so by 12 noon, and 2) the number of snowmobiles that are counted each day only include those that enter the Park and not those that exit the Park. Although the rate of snowmobiles exiting the Park through the West Entrance is not known, most snowmobile rentals start to return in the late afternoon between 3 and 4:30 p.m., 3) the CO concentrations are measured at a fixed-site location next to the exit lane and may be affected by the prevailing winds which may shift in the afternoon to the South. Further, snowmobiles exiting the Park typically do not stop or idle at the West Entrance like they do when entering the Park.

2. Number of Snowmobiles and Particulate Matter Concentrations

The correlation between the number of snowmobiles entering the Park at West and the concentration of airborne PM2.5 (fixed-site samples) was evaluated. PM2.5 samples for the entire workday (8 a.m. to 5:00 p.m.) were collected on February 13, 14, 15, 16, 20 and 21, 1999. The fixed-site PM2.5 samples were collected near the outdoor employee work area and the results are summarized in Figure 35. There is good correlation between the number of snowmobiles entering the Park and levels of PM2.5 that were measured for the sampling days, with a statistical correlation value of R^2 = 0.878, indicating that approximately 88 percent of the PM2.5 concentrations can be accounted for by the daily snowmobile counts. Both a.m. and p.m. samples were collected on February 13, 14, 19, 20, and 21, 1999.

There was excellent correlation between PM2.5 levels measured in the a.m. and the number of snowmobiles entering the Park as illustrated in Figure 36 with a correlation value of $R^2 = 0.934$. This indicates that approximately 93 percent of the PM2.5 concentrations determined for the sampling day can be accounted for by the daily snowmobile counts. The sample collected on 2/19/99 was PM10 (approximately 165 $\mu g/m^3$). However, all PM was virtually PM2.5 or less in size, independent of the size-selective collection device used.

There is very good correlation between the number of snowmobiles entering the Park and measured levels of PM2.5 (entire day or a.m. only samples), which supports the hypothesis that airborne PM2.5 at the West Entrance is directly attributable to snowmobile use. Chemical analyses of area VOC samples and gasoline samples were conducted to determine if the PM and VOCs were from the snowmobile exhaust.

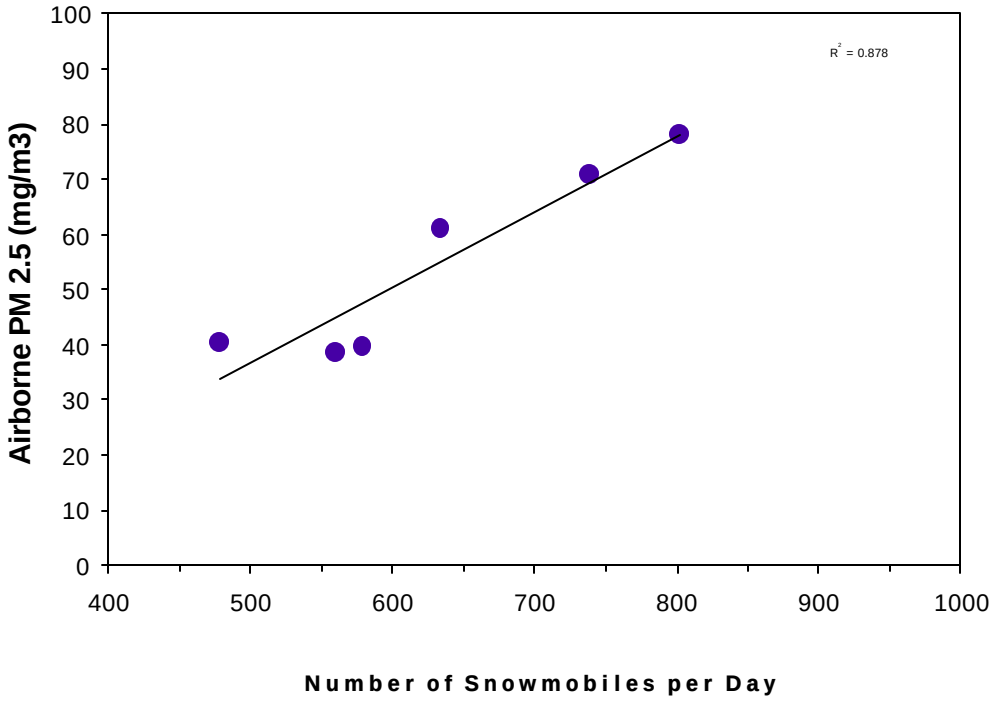


Figure 35. Relationship between the number of snowmobiles entering the Park at the West Entrance and corresponding airborne PM2.5 measured during worker hours. Samples were collected on February 13, 14, 15, 16, 20, and 21, 1999. Concentrations of PM2.5 are reported as micrograms of particulate matter present in one cubic meter of air ($\mu g/m^3$).

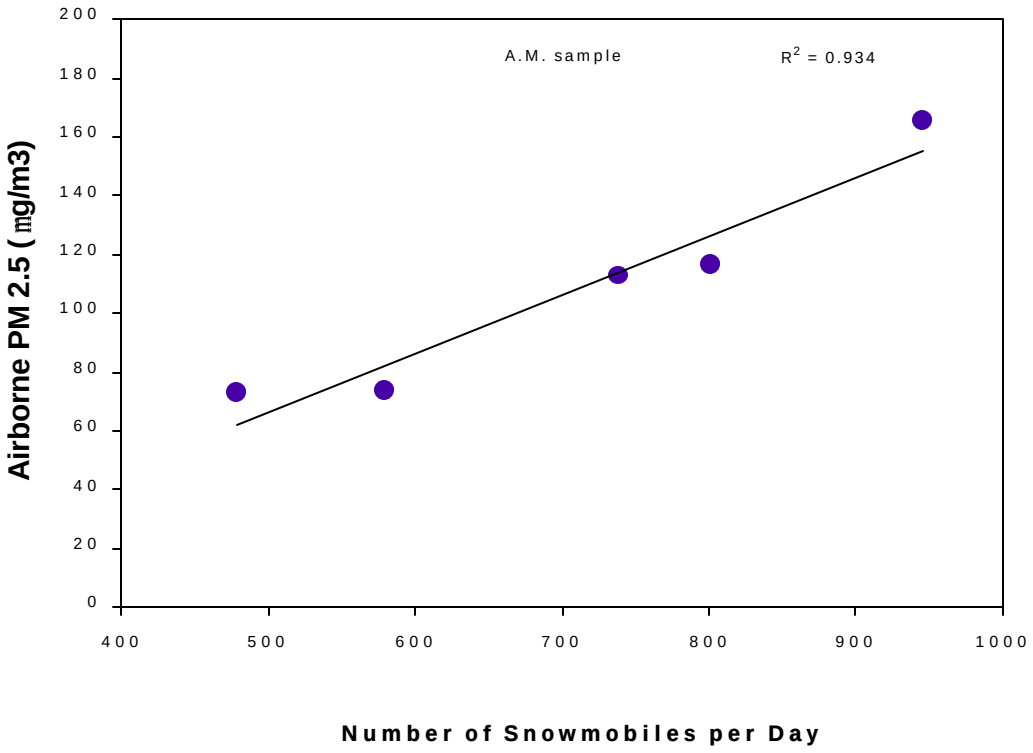


Figure 36. Relationship between the number of snowmobiles entering the Park at the West Entrance and the corresponding airborne PM measured for that morning (8 a.m. to 12 noon). Samples were collected on February 13, 14, 19, 20, and 21, 1999. The sample collected on 2/19/99 was PM10 (approximately 165 µg/m^3). Concentrations of PM are reported as micrograms of particulate matter present in one cubic meter of air (µg/m^3).

3. Chemical Analyses of Airborne VOC Samples and Gasoline

The ambient air VOC bag samples collected from the employee work areas at the West Entrance kiosks were analyzed for specific gasoline-associated VOCs, such as benzene, toluene, ethylbenzene, and o-, p-, m-xylenes (referred to as BTEX compounds). Additional compounds that were quantified included 1,3,5-trimethylbenzene and 1,4,6-trimethylbenzene. Snowmobiles were the only vehicles present during sample collection. The results from analyses of these ambient samples were qualitatively compared to those from the analysis of locally obtained gasoline samples. The results of 10-minute bag samples collected on February 19 and 23, 1999 are illustrated in Figures 37 and 38. The compounds that were identified in each sample included benzene, toluene, ethylbenzene, xylenes, and trimethylbenzenes. Other compounds that were detected included butane, pentane, hexane (alkanes), and unsaturated compounds (alkenes). These compounds typically contained alkyl (methyl or ethyl) groups.

Many of these VOCs, especially the BTEX and alkane compounds, are associated with gasoline and gasoline combustion. The presence of BTEX compounds in the ambient sample collected at West was very similar for the two different days these samples were collected. The relative amounts of the BTEX compounds followed the order (from highest to lowest) of toluene > m,p-xylene > benzene > o-xylene = 1,4,6-trimethylbenzene > ethylbenzene > 1,3,5-trimethylbenzene. Vapors from unleaded 85.5 octane gasoline samples that were obtained on February 18, 1999 from two different major brand gas stations in West Yellowstone were analyzed and the results are shown

in Figures 39 and 40**.** The gasoline vapor samples contained BTEX compounds that were very similar to the ambient sample and the concentrations followed the order of highest to lowest: toluene > m,p-xylene > benzene, except for 1,4.6-trimethylbenzene, which appeared to have a slightly higher concentration than o-xylene. The 1,3,5-trimethylbenzene had the lowest concentration, similar to the ambient air sample. For both ambient and gasoline VOC samples, chromatographic peaks were analyzed using the HP ChemStation mass spectral library of candidate VOC compounds (Appendix C). Based on a comparison of the ambient bag samples taken at the West Entrance and the analyses of gasoline samples acquired from West Yellowstone gas stations, the BTEX compounds found in each of these indicates that the airborne compounds were from gasoline-powered vehicles. The relative ratios of area peaks for the BTEX compounds were similar for the ambient and gasoline samples. Since only snowmobiles were present during the collection of the ambient samples, they seem to be the most likely source of airborne BTEX at the West Entrance.

The compounds detected in these samples are also identical to the compounds found in the Carbotrap tubes as seen in Figures 19 and 20. Very similar chromatographic patterns are seen in the Carbotrap, Tedlar bag, and gasoline vapor samples, indicating that the emission source used gasoline and emitted unburned fuel. This is also highly consistent with snowmobile use.

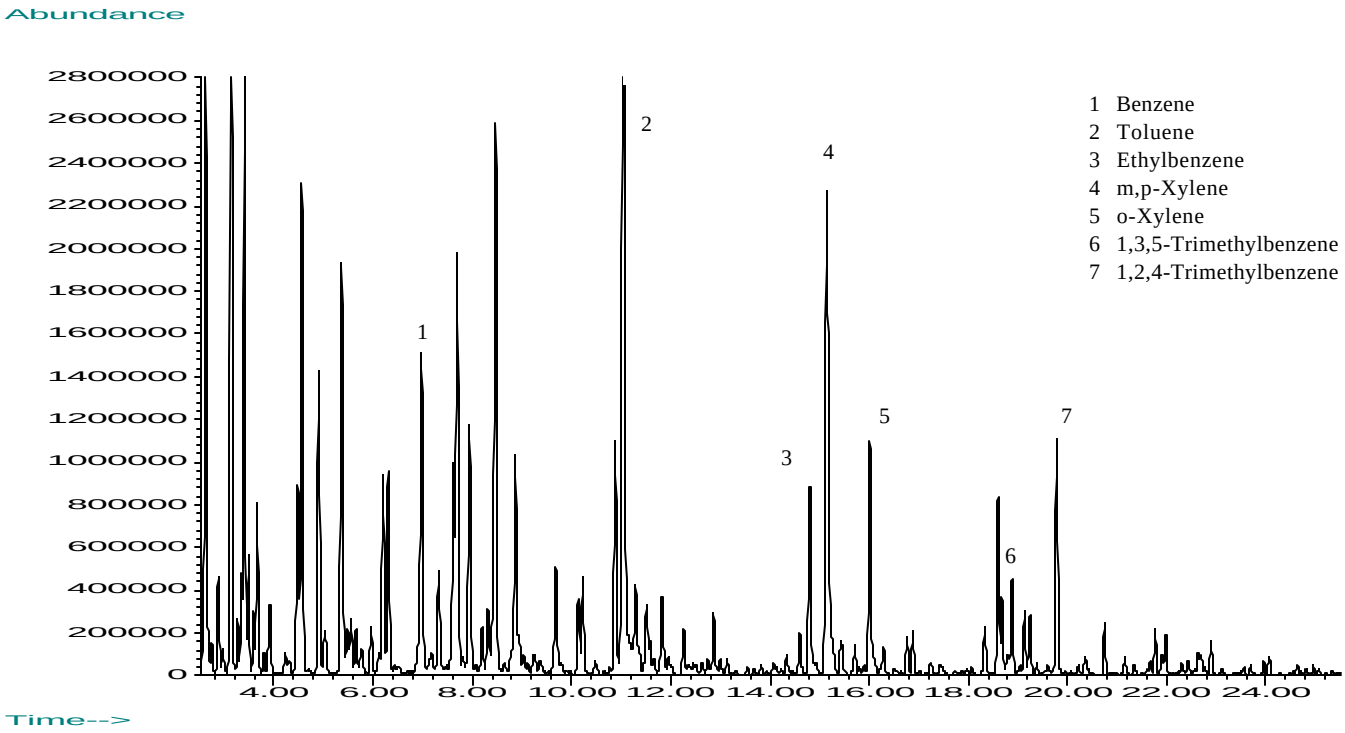


Figure 37. Sample chromatogram from the GC/MS analysis of an ambient air Tedlar bag sample (10-minute) taken near the employee work area at the West Entrance on February 19, 1999.

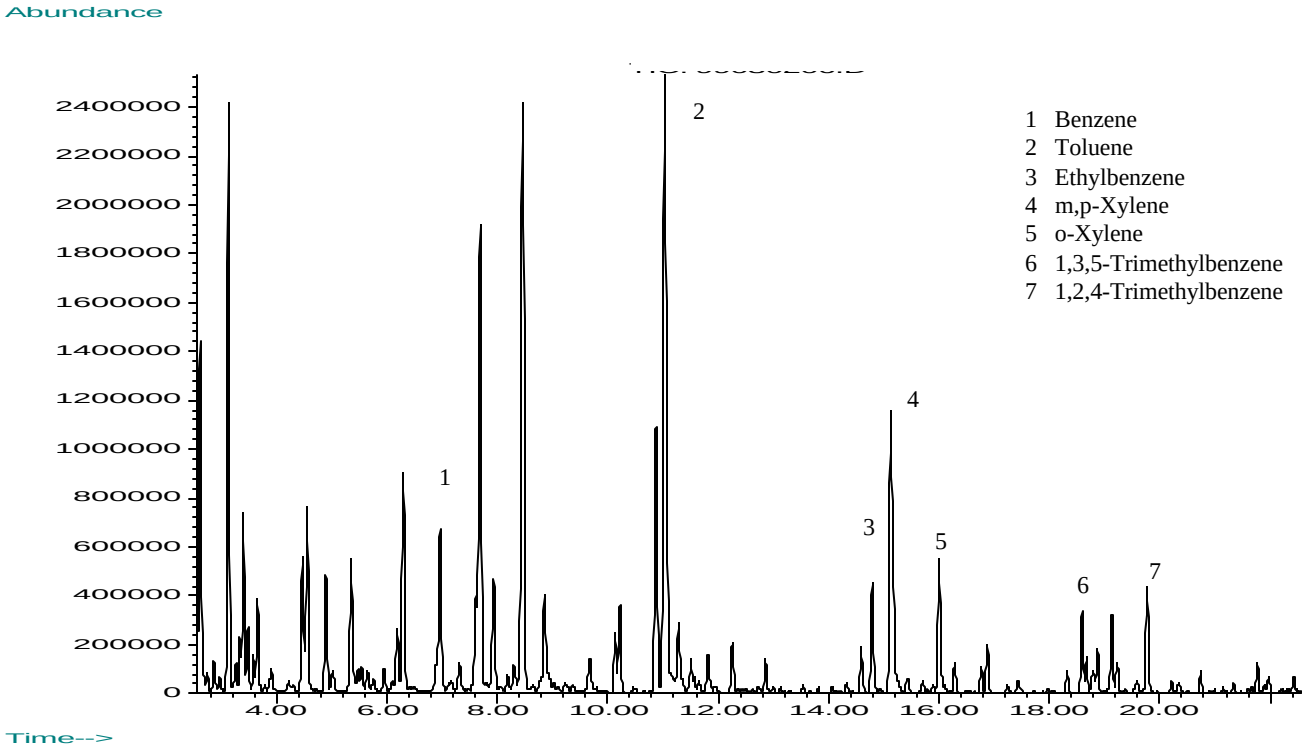


Figure 38. Sample chromatogram from the GC/MS analysis of an ambient air Tedlar bag sample taken near the employee work area (10 minute sample) at the West Entrance on February 23, 1999.

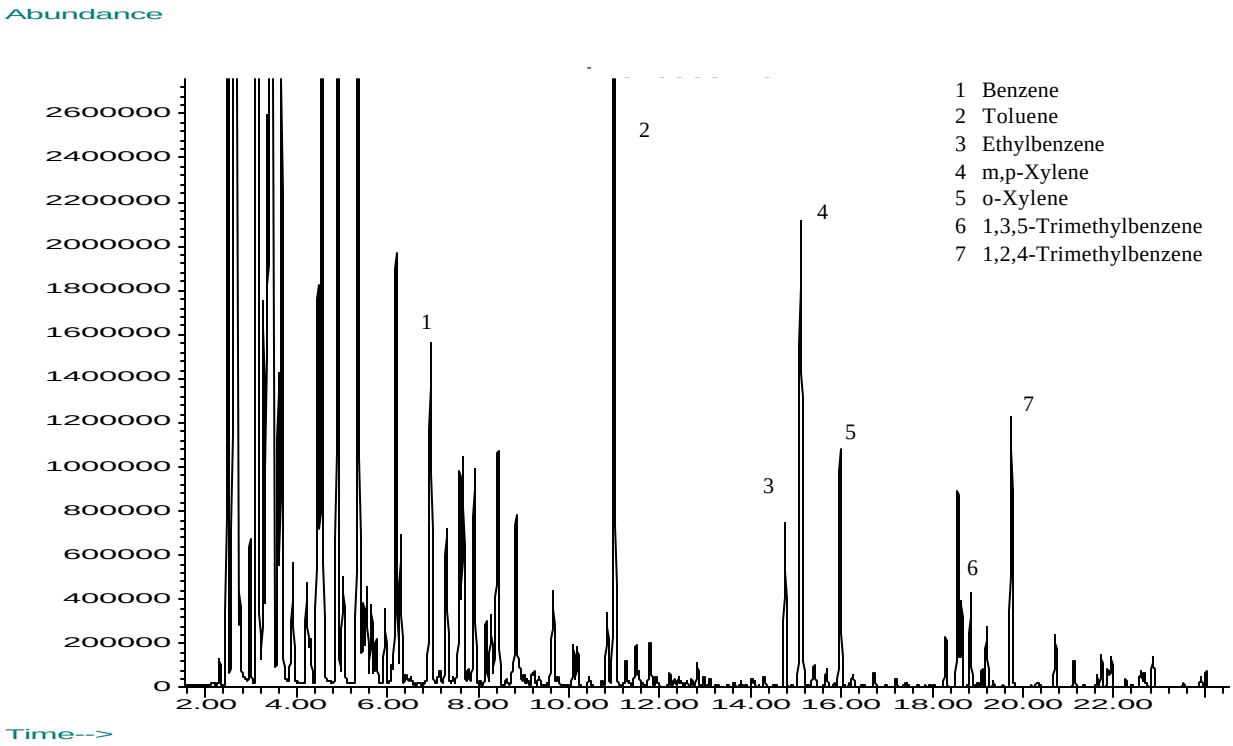


Figure 39. Sample chromatogram from GC/MS analysis of vapors from a gasoline sample that was obtained on February 18, 1999 from one major brand gas station in West Yellowstone. Peaks eluting before 6 minutes are hydrocarbons typically present in gasoline.

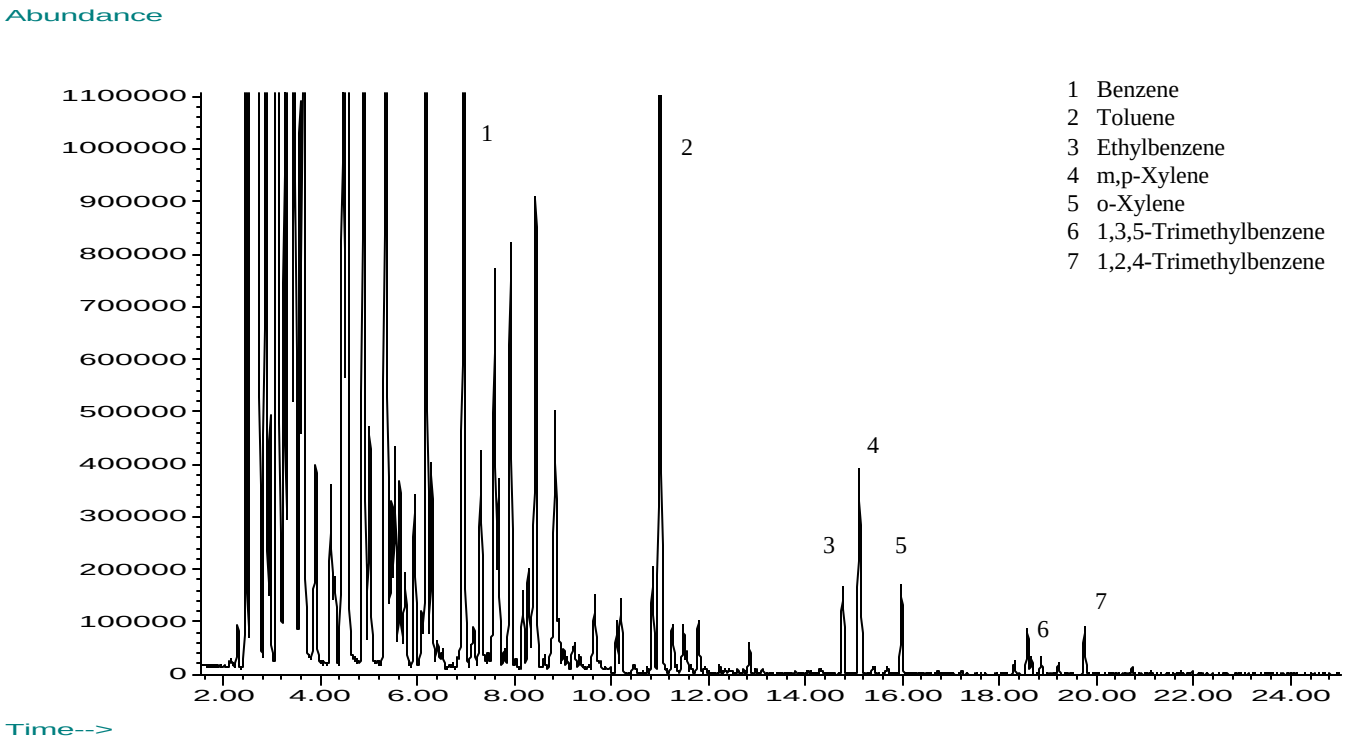


Figure 40. Sample chromatogram from GC/MS analysis of vapors from a gasoline sample that was obtained on February 18, 1999 from a second major brand gas station in West Yellowstone. Peaks eluting before 6 minutes are hydrocarbons typically present in gasoline.

J. Evaluation of Risk

The focus of the present study was to examine both human occupational and environmental exposure to particulate matter and toxic air pollutants emitted by snowmobiles operating in Yellowstone National Park. As mentioned, up to 30 percent of the fuel and oil used by snowmobiles is emitted unburned in the exhaust. These emissions of unburned fuel and oil plus combustion products of the fuel and oil contain high levels of regulated and toxic air pollutants, especially on peak snowmobile days and in congested areas. Since Park employees and visitors to the Park can be exposed to these pollutants during the winter months and some have reported symptoms such as headache, nausea, and dizziness, it is important to examine these and other reported health risks associated with exposure to some of the specific compounds that are present in the snowmobile emissions.

The U.S. EPA is required by the Clean Air Act to set National Ambient Air Quality Standards (NAAQS) for those pollutants that are harmful to public health and the environment. Primary standards are set to protect public health, especially for sensitive individuals such as asthmatics, children, and the elderly. Secondary standards are intended to protect the public welfare by preventing reduced visibility and by reducing damage to plants, animals, and buildings. These standards are for ambient air concentrations that are averaged over 1, 8, or 24 hours depending on the air pollutant that is being measured. The ambient air quality standards for pollutants relevant to the present study are listed in Table 18. National standards must not be exceeded more than once per year. California standards, which are not to be exceeded, are generally more stringent than National standards and are provided here for purposes of comparison. The

Montana CO 1-hour maximum standard is more stringent (at 23 ppm) than the National Standard (35 ppm).

Table 18. Ambient Air Quality Standards for Selected Criteria Pollutants.

Pollutant	Averaging Time	National Standard	Type	California Standard
Carbon Monoxide	8-hour	9 ppm (10 mg/m^3)	Primary	9 ppm (10 mg/m^3) [a]
Carbon Monoxide	1-hour	35 ppm (40 mg/m^3)	Primary	20 ppm (40 mg/m^3)
PM10 (Respirable)	24-hour	150 µg/m^3	Primary and Secondary	50 µg/m^3
PM2.5 (Fine)	24-hour	65 µg/m^3	Primary and Secondary	No state standard

[a] The 8-hour standard for Lake Tahoe, California (elevation 6,225 feet above sea level) is 6 ppm (7 mg/ m^3).

Based on the CO data recorded during the current study period, neither the NAAQS (1-hour or 8-hour avg) nor the California Standard (1-hour or 8-hour avg) for carbon monoxide was exceeded. The highest recorded 1-hour and 8-hour CO concentrations for the current study period were 18.2 ppm and 8.86 ppm, respectively, on 2/13/99 at the West Entrance (data not shown). The 8-hour concentration for CO was almost identical to the Federal 8-hour standard.

The PM10 averaging time for the NAAQS and the California Standard is 24 hours. Since a typical workday for Park employees is 8 hours, any comparisons of PM10 exposure to these standards would be difficult since the averaging time for PM10 or PM 2.5 is 24

hours. However, personal exposure to respirable PM (PerPM) was measured during working hours.

The concentrations of PerPM for individuals working at the West entrance were measured at levels up to 160 µg/m^3 (Figure 14). The measurement of human exposure to airborne PM is important because particles that are 10 µm aerodynamic diameter or smaller can enter the respiratory system and deposit on the trachea, bronchi and into the deep air-exchange portions of the lung (alveoli) (Schlesinger, 1985). Exposure to PM has been associated with increased respiratory infections, decreased lung function and even premature death (Further, 1986; Pope et al., 1992; Dockery et al., 1992). In addition, PM contains numerous carcinogenic and mutagenic compounds (Daisey, 1987; Sheldon et al., 1992; Atkinson et. al., 1988). The PM from outboard marine engines, especially 2-stroke carbureted or direct-fuel injected engines, contains relatively high levels of carcinogenic PAHs and mutagenic activity (Kado, et al., 2000). Since snowmobiles are the most widely used form of transportation within the Park during the winter and are predominantly powered by 2-stroke engines, exposure to their PM and VOC emissions would seem to be likely causes of respiratory problems that have been reported by Park employees.

In addition to PM, snowmobiles also emit a number of volatile toxic air contaminants such as VOCs. The National Institute for Occupational Safety and Health (NIOSH) has established Recommended Exposure Limits (RELs) and Short-Term Exposure Limits (STEL) for occupational exposure to a number of compounds including VOCs and other air contaminants. The Occupational Safety and Health Administration (OSHA) has established Permissible Exposure Limits (PELs) and Short-Term Exposure Limits (STEL) for occupational exposure to volatile air contaminants. The limits for the volatile air

contaminants of interest and measured in this study are listed in Tables 19 and 20. The NIOSH REL and OSHA PEL are exposure limits based on an 8-hour time-weighted average (TWA). The TWA is calculated by weighting the various concentrations throughout an 8-hour workday to give an average full-shift exposure level. The STEL is a 15-minute exposure limit that should not be exceeded during any portion of the workday.

Table 19. NIOSH Recommended Exposure Limit (REL) and Short-Term Exposure Limits (STEL) for Occupational Exposure to Selected Volatile Air Contaminants.

Compound	NIOSH REL (8-hour TWA)		NIOSH STEL (15-minute)	
	(mg/m^3)	(ppm)	(mg/m^3)	(ppm)
Benzene	0.326	0.1	3.26	1
Formaldehyde	0.02	0.016	0.123	0.1
Acetaldehyde	a	a	a	a
Carbon monoxide	40	35	229 (Ceiling)	200
Ethylbenzene	435	100	545	125
Toluene	375	100	560	150
1,2,4-Trimethylbenzene	125	25	a	a
1,3,5-Trimethylbenµg zene	125	25	a	a
Xylenes	435	100	655	150

[a] No exposure limit..

Table 20. OSHA Permissible Exposure Limit (PEL) and Short-Term Exposure Limit (STEL) for Occupational Exposure to Selected Volatile Air Contaminants.

Compound	OSHA PEL (8-hour TWA)		OSHA STEL (15-minute)	
	(mg/m^3)	(ppm)	(mg/m^3)	(ppm)
Benzene	3.26	1	16.3	5
Formaldehyde	0.92	0.75	4.5	2
Acetaldehyde	180	100	a	a
Carbon monoxide	55	50	a	a
Ethylbenzene	435	100	545	125
Toluene	375	100	560	150
1,2,4-Trimethylbenzene	a	a	a	a
1,3,5-Trimethylbenzene	a	a	a	a
Xylenes	435	100	655	150

[a] No exposure limit..

The OSHA PEL for occupational exposure to benzene and toluene were not exceeded for personnel working at West and on Mobile Patrol (see Tables 6 and 7). The OSHA PEL for occupational exposure was not exceeded for carbon monoxide, ethylbenzene, or xylenes in any of the samples collected. The OSHA STEL was not exceeded for either acetaldehyde or formaldehyde. There currently are no OSHA PELs or STELs for either 1,2,4-trimethylbenzene or 1,3,5-trimethylbenzene. NIOSH does have RELs for these compounds.

Some of the VOCs that Park employees are exposed to have been evaluated by the US EPA and the International Agency for Research on Cancer (IARC). As summarized in Table 21, both EPA and IARC have classified these compounds with respect to their ability to cause cancer in humans and laboratory animals. Benzene has been classified as a known human carcinogen by both EPA and IARC, while formaldehyde has been classified as a probable human carcinogen. EPA has classified acetaldehyde as a probable human carcinogen and IARC has classified it as a possible human carcinogen. Acetaldehyde is also carcinogenic to laboratory animals. Compounds that are not classifiable as to human carcinogenicity include ethylbenzene, toluene, and xylenes.

For estimating cancer risk, the US EPA reports this risk at a daily exposure of 1 $\mu g/m^3$ concentration over a lifetime of 70 years. This is referred to as the "unit risk" and is calculated to compare risk estimates for different airborne toxic pollutants. Since occupational exposures are typically for 6 to 8 hours/day, an average daily exposure can be estimated by determining the number of cubic meters of air breathed in a 6 to 8 hour workday, and multiplying by the number of days worked. For example, if a person is exposed to a chemical at an average concentration of 100 $\mu g/m^3$, and assuming the person breathes 10 m^3 of air during the workday, then that person will breath or inhale 1000 µg of the compound during the workday (100 x 10). In the Park during the winter, a worker at the West Entrance is exposed to a median concentration of about 190 $\mu g/m^3$ benzene (range of 100 to 300 $\mu g/m^3$) as measured during the study period. The worker could be exposed to chemicals for up to approximately 90 days based on the winter season, but more typically for 65 days. Peak exposures would occur less than

14 days per year. Based on this information, the total exposure to a chemical can be estimated for the winter working season. For example, for benzene at median daily airborne concentration of 190 µg/m^3, the total exposure would be 190 µg/m^3 x 10 m^3 / day x 65 days which equals 123,500 µg (or approximately 123 mg) benzene exposure for a winter season (assuming breathing 10 m^3 per work period day). A worker at the West Entrance would be exposed in a 20 year employment period to approximately 2.5 million µg (123,500 µg /year x 20 years). The average daily mass of benzene attributable to working during the winter for 20 out of 70 years would be 2.5 million µg / (365 days/year x 70 years) = 96.7 ug/day.

In comparison, for a non-work environmental exposure to benzene at an average concentration of 1 µg/m^3 and assuming breathing 20 m^3 of air per day, the total amount of compound per day would be 1 µg/m^3 x 20 m^3/day = 20 µg. For a 70 year lifetime of exposure to benzene at 1 µg/m^3, the unit risk range as estimated by the US EPA (2001) is approximately 2 to 8 per million, and as estimated by the California OEHHA (2001) as 3 per 100,000 (OEHHA, 2001). In the sample calculation above, and assuming working 65 winter days per year, and a working lifetime of 20 years, a winter season exposure to a median benzene concentration of 190 µg/m^3 would result in a risk approximately 5 times the unit risk. This would be equal to approximately 1 to 4 per 100,000 based on EPA risk estimates, or approximately 1 per 10,000 based on OEHHA estimates. This risk would be in addition to the risk from non-work exposure to benzene, or work exposure from non-winter seasons at Yellowstone.

If the worker is exposed to benzene concentrations above the 190 µg/m^3 median concentrations – for example, some West Entrance workers were exposed to 300

ug/m3 per winter day and the mechanic was exposed to above 500 ug/m^3 benzene, the risk for cancer increases proportionately above the risk calculated for the median 190 µg/m^3. These risks are relatively high for cancer considering this would be incremental over the current daily exposure to benzene. Also, if the worker were to be exposed to higher than ambient levels of benzene during the other months of working, this would add to the risk. The risk indicated is only for exposure to benzene taking place during the winter season. Workers are also exposed to other carcinogenic compounds such as formaldehyde and acetabldehyde measured in this study and these exposures would also add to the cancer risk.

Table 21. EPA and IARC Carcinogen Classification of Selected Volatile Air Contaminants.

Compound	EPA Classification		IARC Classification	
Acetaldehyde	Group B2	Probable human carcinogen of low carcinogenic hazard	Group 2B	Possibly carcinogenic to humans
Benzene	Group A	Known human carcinogen of medium carcinogenic hazard	Group 1	Carcinogenic to humans
Ethylbenzene	Group D	Not classifiable as to human carcinogenicity	Not reviewed	
Formaldehyde	Group B1	Probable human carcinogen of medium carcinogenic hazard	Group 2A	Probably carcinogenic to humans
Toluene	Group D	Not classifiable as to human carcinogenicity	Group 3	Not classifiable
Xylenes (total)	Group D	Not classifiable as to human carcinogenicity	Group 3	Not classifiable

The Agency for Toxic Substances and Disease Registry (ATSDR) has developed Minimal Risk Levels (MRLs) for certain hazardous substances, according to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) as amended by the Superfund Amendments and Reauthorization Act (SARA). Briefly, an MRL is a substance-specific estimate of the daily exposure to a hazardous chemical that is likely to be without appreciable risk of adverse non-cancer health effects over a specified period of exposure. An MRL is derived for a chemical after ATSDR has determined that adequate and reliable data are available to characterize a chemical's route of exposure, identifying the health effects for target organs of concern, and the specific period of exposure needed to cause the effects. The MRL is considered a screening level that is typically used by ATSDR to identify contaminants and potential health effects that may be of concern at hazardous waste sites. MRLs for some of the VOCs and aldehydes that were detected in either VOC badges or aldehyde cartridges are presented in Table 22. MRLs are based on inhalation as the route of exposure for either acute (1 to 14 days), intermediate (15 to 364 days), or chronic (365 days or more) exposure durations.

Employees in Yellowstone can be classified as being in the acute or intermediate exposure durations. Employees in certain job categories and locations were exposed to concentrations of some compounds that exceeded the MRLs established by ASTDR. For example, based on the data illustrated in Figure 26, there were five employees at the West Entrance, one mobile patrol employee, and one mechanic who were exposed to levels of benzene that exceeded both acute and intermediate MRLs.

Table 22. ATSDR Minimal Risk Level (MRL) for Exposure to VOCs by Inhalation.

Compound	MRL (ppm)	MRL (µg/m^3)	Duration	Most Sensitive Health Effect
Benzene	0.05	162	Acute	Immunological
	0.004	12.96	Intermediate	Neurological
Ethylbenzene	0.2	868	Intermediate	Developmental
Formaldehyde	0.05	62	Acute	Respiratory
	0.01	12.4	Intermediate	Respiratory
	0.003	3.72	Chronic	Respiratory
Toluene	4	15000	Acute	Neurological
	0.4	1500	Chronic	Neurological
Xylenes, total	1	4340	Acute	Neurological
	0.7	3038	Intermediate	Developmental
	0.1	434	Chronic	Neurological

A mechanic was exposed to approximately 870 µg/m^3 ethylbenzene on 2/17/99, which exceeded the intermediate MRL (see Table 9). The same mechanic on the same day exceeded the chronic MRLs for both toluene and total xylenes, with exposure to approximately 2,526 µg/m^3 toluene and 1,900 µg/m^3 total xylenes. The acute MRL for toluene is 15,000 µg/m^3 and 4,340 µg/m^3 for xylenes. One employee at West was exposed to a toluene concentration of 1482 µg/m^3 that was near the chronic MRL for toluene (1500 µg/m^3), as shown in Table 6.

On various days, employees working outside at West were exposed to levels of formaldehyde that exceeded the acute, intermediate, and chronic MRLs. For

example, the acute, intermediate, and chronic MRLs were exceeded by Employee #1 during a 2-hour sampling period in the morning at West on 2/13/99. The same employee also exceeded the intermediate and chronic MRLs during a 2-hour sampling period in the afternoon at West on the same day. The acute MRL for formaldehyde is 62 µg/m^3 and Employee #1 was exposed to approximately 80 µg/m^3 during this period of sample collection, as previously shown in Table 11. This employee worked outside of the kiosk in the Express Lane, an area where employee exposure to PM and VOCs from snowmobile exhaust is much higher than in other work areas. Employee #2 also worked outside of the kiosk and exceeded the intermediate and chronic MRLs on 2/14/99 for both the morning and afternoon sample collection periods.

Personal exposure to aldehydes was also measured for employees working at Madison between 2/13 to 2/14/99. On both days during the morning sample collection period, employee exposure to formaldehyde exceeded the intermediate MRL of 12.4 µg/m^3 and the chronic MRL of 3.72 µg/m^3. Additional personal aldeyhde exposure samples were collected for employees working at West during the morning on 2/19/99. As shown in Table 13, all three employees were exposed to levels of formaldehyde that exceeded the intermediate and chronic MRLs. One of those employees who worked in or near the Express Lane was exposed to 88 µg/m^3 of formaldehyde, which exceeded the acute MRL of 62 µg/m^3.

Employees working in the Express Lane at West in the morning were exposed to levels of formaldehyde that exceed the acute MRL established by ASTDR. Typically, the MRL was exceeded until approximately 9:30 a.m., a time when most

snowmobiles have passed through the West Entrance. For example, as shown in Tables 14 and 15, Employee #1 and Employee #6 were both exposed to levels of formaldehyde exceeding the MRL. Both of these employees worked in the Express Lane.

Although the MRLs are based on either acute (1 to 14 days), intermediate (15 to 364 days), or chronic (365 days or more) exposure duration, the period of employee exposure measured in this study was for a limited number of peak days. However, occupational exposure to compounds for even a short number of peak days at concentrations exceeding the MRLs established by ASTDR are of concern with respect to the various deleterious health effects previously reported by Park employees and visitors to the Park. It is important to note, however, that exposure to compounds at concentrations above the MRL potentially may cause adverse non-cancer health effects.

The risk of developing cancer is important considering that benzene is a known human carcinogen, formaldehyde has been classified as a probable human carcinogen, and that acetaldehyde may be a human carcinogen. The US EPA has estimated the increased risk of developing cancer as a direct result of breathing air containing various chemicals over a lifetime. The increased risk estimates for acetaldehyde, benzene, and formaldehyde at varying concentrations are shown in Table 23 for a lifetime exposure of 70 years.

While employee exposure to acetaldehyde, benzene, and formaldehyde may seem to indicate an increased risk of developing cancer based on EPA and OEHHA estimates and should be of great concern, many other factors should also be

considered when evaluating this risk. First, the data reported for PerPM and VOCs is for a limited period of study, though sufficient for purposes of a pilot study of occupational exposure to these compounds. The sample size, or number of employees available to collect samples from, should be expanded. Further multi-winter studies of longer duration than two weeks, covering both peak and normal exposure days, would be necessary to provide a better evaluation of occupational exposure and cancer risk.

Table 23. EPA Estimates of the Increased Risk of Developing Cancer as a Direct Result of Breathing Air Containing Listed Compounds over a Lifetime.

Compound	Concentration ($\mu g/m^3$)	Increased risk of developing cancer not greater than:
Acetaldehyde	0.5	1 per 1,000,000
	5.0	1 per 100,000
	50	1 per 10,000
Benzene	0.1	1 per 1,000,000
	1.0	1 per 100,000
	10.0	1 per 10,000
Ethylbenzene[a]	---	---
Formaldehyde	0.08	1 per 1,000,000
	0.8	1 per 100,000
	8.0	1 per 10,000
Toluene[b]	---	---
Xylenes (total)[a]	---	---

[a] Insufficient data to determine cancer risk.

[b] Limited studies with no statistically significant increased cancer risk.

Second, the EPA cancer risk estimates are based on exposure to a single compound over a lifetime exposure of 70 years. Since Park employees are exposed to a complex mixture of toxic substances during the winter season, the cumulative health effects of exposure to such mixtures are unknown and require further investigation. Cancer risk estimates for specific compounds such as benzene could be derived by extrapolating employee winter exposure to 365 days (one year) and considering the number of years an employee has worked. Additional exposures during the summer months could also be evaluated.

EPA estimates that the risk of developing cancer is based on a lifetime or prolonged exposure. A number of factors are important to consider when assessing this risk. Park employees work in various job categories and locations and for varying lengths of time. The winter snowmobile season at Yellowstone National Park lasts from approximately mid-December to mid-March, a period of three months. Employee exposure to carcinogens and toxic air pollutants during the winter could at first be considered as acute and/or intermediate in nature. However, exposure to high concentrations for a relatively short period of time over a number of seasons presents challenges for estimating cancer risk. Indeed, some recent animal bioassays for carcinogenicity have incorporated high dose-shorter term exposures. The results seem to indicate that these short-term exposures at higher doses may increase cancer risk beyond that of an equivalent dose administered over a longer period of time (Halmes et al., 2000). This implies that short-term relatively high occupational exposures may present increased risks of cancer over estimates for equivalent lifetime exposures.

Toxic compounds are known to damage sensitive biological targets such as DNA and some damaged genetic material could remain in the body for a long period of time.

With respect to time of exposure, Finkelstein (2000) reported that the risk of leukemia following benzene exposure varied with time in a manner similar to time of exposure to ionizing radiation. This is important because more recent exposures (less than 20 years) were more strongly associated with risk than were more distant exposures (greater than 20 years previously). The author concludes that these results suggest that standards for certain compounds should be selected to control exposures over a narrower time frame than the usual lifetime one that is used. For benzene, the author indicates that risk was attributable to exposures occurring during the last 10 to 20 years, with the most potent exposures that occurred during the last 10 years having the greatest potency. If calculations for lifetime of 70 year of exposure are reduced to 10 to 20 years, the risk may be higher than the unit risk values.

Another important factor to consider when assessing potential risk is the possibility of gender differences in sensitivity to toxic compounds. For example, Brown et al. (1998) reported that women may metabolize 23 to 26 percent more benzene than men when subject to the same exposure. The most serious benzene-related adverse health effects are caused by benzene metabolites. Therefore, if men and women are exposed to equivalent amounts of benzene, but women metabolize more benzene than men, then women may be at relatively higher risk for certain health effects related to benzene exposure. Since the current standards are based on occupational data from male workers, existing standards may not be protective for the female population.

Finally, worker exposure to these compounds during other seasons of the year, particularly in the summer, could be substantial but is unknown and requires further study. These factors may influence any increased risk of developing cancer and other health problems as a result of exposure to these compounds via snowmobile emissions.

V. SUMMARY AND CONCLUSIONS

The objective of this project was to evaluate the environmental and occupational exposure to particulate matter and toxic air pollutants during the winter in Yellowstone National Park. Specifically, exposure to air pollutants from snowmobiles and other over-snow vehicles used within the Park were investigated. To meet this objective, the following specific aims were proposed:

1. Collect statistical information on the number and rate of snowmobiles entering the Park at the West Entrance and on the number of snowmobiles parked at Old Faithful.
2. Measure work area concentrations of size-segregated particulate matter of 2.5, and 10 μm aerodynamic diameter.
3. Investigate employee exposure to fine respirable particulate matter.
4. Determine the size of airborne particulate matter emitted in close proximity (within a few feet) to snowmobiles.
5. Investigate the concentrations of particulate matter in locations spanning from a residential neighborhood in West Yellowstone to Old Faithful.
6. Investigate work area concentrations of toxic volatile organic compounds (VOCs).
7. Investigate employee exposure to toxic VOCs and aldehydes.
8. Investigate the relationship between the measured levels of carbon monoxide and the number of snowmobiles entering the Park.

9. Investigate the relationship between measured levels of airborne particulate matter and the number of snowmobiles entering the Park.
10. Chemically analyze VOCs contained in gasoline samples from West Yellowstone and VOCs present in both personal and environmental exposure samples.
11. Test particulate matter collected from a snowmobile engine for mutagenic activity.
12. Evaluate the risk from exposure to toxic compounds measured in this study.
13. Provide recommendations to reduce exposure to PM and toxic air pollutants for worker and environmental health.
14. Provide recommendations for future research efforts.

With the cooperation of many dedicated individuals from the National Park Service, the Montana State Department of Environmental Quality, the Yellowstone Park Foundation, the California Air Resources Board, and the University of California at Davis, the specific aims were addressed in the current study.

Specific conclusions follow, based on the results from each component of this winter study:

Snowmobile Use Statistics and Patterns

- Approximately 90 percent of the snowmobiles that enter the park at the West Entrance have entered by 12 noon. At Old Faithful, the number of parked snowmobiles generally peaked between 10 a.m. and 2 p.m.

- Peak concentrations of snowmobile PM and VOC emissions at the West Entrance occur in the mornings between 8 a.m. and 12 noon.

Carbon Monoxide

- Carbon monoxide (CO) concentrations obtained at the West Entrance did not exceed Federal (1-hour or 8-hour average) or California state (1-hour or 8-hour average) standards. One 8-hour concentration was within 90% of the Federal 8-hour standard. The CO sampling site is located within a few feet of the exit lane, but located away from snowmobile entrance lanes and at rooftop levels such that these measurements may not represent worker concentrations at the West Entrance kiosks.

Particulate Matter

- There was a consistent pattern of higher PM2.5 concentrations measured in the morning than in the afternoon at the West Entrance.

- Highest personal exposure to respirable PM was measured for a snowmobile mechanic who worked indoors, and for West Entrance employees who were stationed primarily outside the kiosks.

- The PM collected near snowmobiles was 2.5 micrometer diameter (PM2.5) or smaller and are consistent with PM size measurements collected under controlled conditions reported for a snowmobile engine.

- A concentration gradient of PM10 (same day sample collected during work hours) was observed for locations within approximately a mile of the West Entrance. The lowest concentration of PM10 was from a residential area (1.2 miles away) and the highest concentration was detected at the West Entrance. Downtown West Yellowstone 1/3 mile away had concentrations intermediate between the residential and West Entrance locations.

- The airborne concentrations of PM at the West Entrance (a.m. or p.m.) and personal respirable PM (PerPM) for all workers, except those in offices, were higher than the concentrations measured in other studies (For example, occupational studies regarding diesel PM exposure; studies inside vehicles traveling during 2 hour commutes in Los Angeles). Any comparisons however, should consider the variety of different PM and possible differences in PM chemical composition and size characteristics.

Toxic Volatile Organic Compounds

- Volatile organic compounds (VOCs) typically found in gasoline were detected in both fixed-site and personal exposure samples. VOC profiles of air taken at the West Entrance were similar to VOCs present in gasoline samples obtained during the study period from West Yellowstone gasoline stations. Snowmobiles emit approximately 20-

30 percent of gasoline unburned so that compounds present in gasoline could be expected in the air near snowmobiles.

- Employee exposure to benzene, ethylbenzene, m,p-xylene, o-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene were generally highest for the snowmobile mechanic, followed by the West Entrance workers and mobile patrol rangers.

- The Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and Short-term Exposure Limit (STEL) for occupational exposure were not exceeded for either benzene (PEL = 3.26 mg/m^3; STEL = 16.3 mg/m^3) or toluene (PEL=375 mg/m^3; STEL=560 mg/m^3) for personnel working at West and on mobile patrol.

- The National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) for benzene (REL = 0.326 mg/m^3 or 326 $\mu g/m^3$-8 hour working day) was very close to being exceeded by the snowmobile mechanic who was exposed to concentrations of benzene near 500 $\mu g/m^3$ during a 4-hour working period and by the West Entrance personnel exposed to a maximum of approximately 303 $\mu g/m^3$ benzene – 8 hr working day.

- Minimal Risk Level (MRL) for benzene established by the Agency for Toxic Substances and Disease Registry (ATSDR), Centers for Disease Control and Prevention (CDC), Atlanta Georgia for non-cancer health effects were exceeded by five employees at the West Entrance, one mobile patrol employee, and the mechanic for both the acute and intermediate exposure levels.

- Of the VOCs measured, benzene is known to have the highest level of evidence as a cancer-causing (causing leukemia) agent for humans. Formaldehyde was next. A winter season exposure to a median benzene concentration of 190 µg/m^3 as measured during this study at the West Entrance was evaluated for cancer risk. Assuming a seasonal working period of 65 winter days per year, and a working lifetime of 20 years, the cancer risk is approximately 1 to 4 per 100,000 based on US EPA risk estimates, or approximately 1 per 10,000 based on the California Office of Environmental Health Hazard Assessment estimates.

- VOCs measured in the current study are consistent with measurements conducted by NIOSH and OSHA during the winter of 2000 for workers at Yellowstone.

Aldehydes

- Based on short-term measurements, West Entrance employees working in the Express Lane were exposed to higher levels of formaldehyde and acetaldehyde than employees working in the entrance lane located farthest away from the Express Lane.

- None of the measurements for personal exposure to formaldehyde exceeded the NIOSH 15-minute STEL (short-term exposure limit = 123 µg/m^3). The highest short term (30 min) exposure for formaldehyde was approximately 80 µg/m^3.

- One employee at the West Entrance was exposed to concentrations of formaldehyde during the morning sample collection period on 2/13/99 that exceeded the acute MRL value established by ASTDR (MRL=62 $\mu g/m^3$).

Correlation of CO levels with Number of Snowmobiles Entering the Park

- There was some correlation of CO concentrations with the total number of snowmobiles entering the Park. However, the relationship improves when only the morning CO data were used in the analyses ($R^2 = 0.69$) than when the afternoon CO data were used ($R^2 = 0.15$). The CO concentrations appear to increase during the morning as the number of snowmobiles entering the Park increases.

Correlation of PM levels with Number of Snowmobiles Entering the Park

- There is a relationship between the concentration of PM2.5 measured at fixed-sites at the West Entrance and the number of snowmobiles entering the Park at the West Entrance each day ($R^2 = 0.88$). This correlation appears to increase ($R^2 = 0.93$) when only a.m. PM2.5 concentrations are used in the analyses. In general, PM2.5 concentrations increase as the number of snowmobiles entering the Park increases.

- This correlation and the finding that higher exposure of PerPM occurs outside of the kiosks and especially in the express lanes supports the hypothesis that snowmobiles are the primary source of the measured PM2.5.

Bioassay of PM Emissions from a Snowmobile Engine

- The PM collected from a snowmobile engine during tests conducted under controlled conditions was mutagenic (damages DNA) and the mutagenic activity per mass of particles was similar to that of particles collected from a diesel engine (based on previous studies).

- The total emissions of PM mutagenic activity emissions were highest during modes 1 and 5 of a 5 mode test, and decreased by approximately 30 percent when using biosynthetic lubricant compared to using the mineral-based lubricant.

Risk Evaluation

- Risk evaluation to toxic compounds such as benzene incorporates a number of factors including concentrations, time on the job, gender, and timing of exposure. Risks based on calculations of lifetime exposures of 70 years may underestimate risk.

VI. RECOMMENDATIONS FOR FUTURE RESEARCH

1) Many Park workers are exposed to concentrations of particulate matter and VOCs many times higher than levels recently measured in a number of studies (for example, inside vehicles traveling on Los Angeles roadways for 2 hours). Strategies to dramatically decrease exposure of Park employees to toxic air pollutants should be investigated immediately.

2) More information on exposure of Park mechanics to particulate matter and VOCs should be collected over the winter season, since the level of exposure for mechanics appears to span a very wide range that includes the highest among employees for whom exposures were measured. Strategies to dramatically decrease exposure to toxic air pollutants for this occupational group should be investigated immediately.

3) Personal monitoring of Park employees both for particulate matter and for VOCs should be increased beyond two weeks to provide a winter season-based data set that covers both peak and normal exposures. Employee time-activity pattern data should also be collected to help determine what activity results in the greatest exposure to toxic compounds. It is highly recommended that this personal monitoring should be in place before, during, and after implementation of any mitigating controls for snowmobile exhaust.

4) Toxic compounds such as polycyclic aromatic hydrocarbons (PAHs) should be quantitated both in the particle and vapor-phases to assess personal and environmental exposure to these potent carcinogens . Emissions from 2-stroke engines are known to contain high levels of these toxic compounds.

5) Bioassay analyses of the airborne particulate matter should be incorporated into the study design to help evaluate ambient and personal exposure to the complex mixture of toxic compounds that may cause DNA damage. These bioassays also monitor the progress of any emission control strategies.

6) Personal exposure to emissions from non-snowmobile vehicles such as snow coaches should be investigated to evaluate their contribution to the total amount of toxic air pollutants.

7) Visitor exposure to toxic air pollutants should also be investigated, especially for individuals such as children and the elderly, who may be more susceptible to the effects of these air pollutants.

8) A study of exposure to particulate matter and VOCs during the summer should be conducted and compared with exposure during the winter. During the summer, the numbers of employees, vehicles, and visitors increase substantially. Many of the vehicles are automobiles with pollution controls, but the increasing number of vehicles, particularly sport utility vehicles and diesel-powered vehicles, plus the generation of resuspended PM due to traffic may expose Park employees and visitors to undesirable levels of particulate matter and toxic air pollutants.

9) A medical surveillance program for Park Employees should be implemented to establish baseline health status and to monitor the health status of Park employees during their continued employment.

10) A biomonitoring program for toxic compounds for employees should be explored to determine absorbed concentrations to toxic compounds.

11) PM monitoring should be initiated at the West Entrance EPA site and should incorporate real-time measurements.

12) Relocating the downtown West Yellowstone PM10 monitoring site should be considered to avoid confounding local PM sources such as woodsmoke (current site is approximately 50 feet downwind from an actively used woodburning stove), snowmobile rental companies and highway traffic, or an additional new "residential" site should be established.

13) The concentrations of toxic compounds associated with the particle and vapor-phase emissions should be monitored in the snow and snow melt to track fate of these compounds.

14) Workers in the snowmobile rental business should be monitored for exposure to snowmobile PM and toxic VOCs.

15) Snowmobile mechanic's exposure to exhaust could be reduced if exhaust is directly connected to piping that is routed outdoors. The vent should be located away from personnel. Local ventilation is also recommended to reduce exposure to any fugitive PM and vapor-phase emissions.

16) As a last line of defense, workers could temporarily decrease exposure to PM and VOCs by being fitted with non-obtrusive respirators that contain filter and charcoal elements. One approach would be to mount, incorporate, and integrate these on or under existing snowmobile helmets, for example.

VII. REFERENCES

Abbey, D.E., B.L. Hwang and R.J. Burchette (1995a) Long-term ambient concentrations of PM10 and airway obstructive disease, Arch. Environ. Health, 20(2): 139-152.

Abbey, D.E., B.E. Ostro, F. Peterson and R.J. Burchette (1995b) Chronic respiratory symptoms associated with estimated long-term ambient concentrations of fine particulates less than 2.5 microns in aerodynamic diameter (PM2.5)_ and other air pollutants, J. Expos. Anal. Environ. Epidem., 5(2): 137-160.

American Society of Testing Materials (ASTM, 1998) Standard Practice for Evaluating the Performance of Diffusive Samplers. ASTM D6246-98.

Ames, B.N., J. McCann and E. Yamasaki (1975) Methods for detecting carcinogens and mutagens with the *Salmonella*/mammalian microsome mutagenicity test, Mutation Res., 31, 347-364.

ATSDR (Agency for Toxic Substances and Disease Registry), http://www.atsdr.cdc.gov/mrls.html.

Bishop, G.A., Morris, J.A., and Stedman, D.H. (2001). Snowmobile contributions to mobile source emissions in Yellowstone National Park. Environ. Sci. Tech.

Brown, E.A., Shelley, M.L., Fisher, J.W. (1998). A pharmacokinetic study of occupational and environmental benzene exposure with regard to gender, Risk Anal., 18:205-213.

Backer, L.C., Egeland, G.M., Ashley, D.L., Lawryk, N.J., Weisel, C.P., White, M.C., Bundy, T., Shortt, E., and Middaugh, J.P. (1997). Environ. Health Persp. 105:850-885.

VII. REFERENCES (cont'd)

Dockery, D.W., C.A. Pope, X. Xu, J.D. Spengler, J.H. Ware, M.A. Fay, B.G. Ferris Jr. and F.E. Speizer (1993) An association between air pollution and mortality in six U.S. cities, N. Engl. J. Med., 329(24): 1753-1759.

Hare, C.T., K.J. Springer, and T.A. Huls. (1975) Snowmobile Engine Emissions and Their Impact, Paper 740735, SAE – Society of American Engineers Technical Paper, SAE, Inc.

Halmes, N.C., Roberts, S.M., Tolson, J.K., and Portier, C.J. (2000) Reevaluating cancer risk estimates for short-term exposure scenarios. Tox. Sci. 58:32-42.

Ingersoll, G.P. (1999). Effects of Snowmobile Use on Snowpack Chemistry in Yellowstone National Park, 1998. U.S. Geological Survey. Water-Resources Investigations Report 99-4148.

International Agency for Research on Cancer (1978) Monographs.

International Organization for Standardization (ISO, 1998) Workplace Air Quality – sampling and Analysis of Volatile Compounds by Solvent Desorption/Gas Chromatography.

Kado, N.Y., S.D. Colome, M.T. Kleinman, D.P. Hsieh and P. Jaques (1994) Indoor-outdoor concentrations and correlations of PM10-Associated mutagenic activity in nonsmokers' and asthmatics' homes, Environ. Sci. Technol., 28 (6): 1074-1078.

Kado, N.Y., D. Langley and E. Eisenstadt (1983) A simple modification of the *Salmonella* liquid incubation assay. Increased sensitivity for detecting mutagens in human urine, Mutation Res., 121, 25-32.

Kado, N.Y., Okamoto, R.A., Karim, J., and Kuzmicky, P.A. 2000. Airborne particle emissions from 2- and 4- stroke outboard marine engines: polycyclic aromatic hydrocarbon and bioassay analyses, *Environ. Sci. Technol*. 34:2714-2720.

VII. REFERENCES (cont'd)

National Research Council (NRC, 1998) Research Priorities for Airborne Particulate Matter: I. Immediate Priorities and Long-Range research Portfolio. National Academy Press.

National Institute for Occupational Safety and Health (1997) NIOSH Pocket Guide, NIOSH Publication No. 97-140.

Norbeck, J.M., T.J. Truex, M.R. Smith, J. Arey, N. Kado, B. Okamoto, K. Kiefer, P. Kuzmicky, and I. Holcomb (1998) Evaluation of factors that affect diesel toxicity. Final Report to California Air Resources Board. Contract No. 94-312.

Rodes, C., L. Sheldon, D. Whitaker, A. Clayton, K. Fitzgerald, J. Flanagen, F. DiGenova, S. Hering and C. Frazier (1998) Measuring Concentrations of Selected Air Pollutants Inside California Vehicles. Final Report under Contract No. 95-339. California Air resources Board.

Rodriguez, S.T., D.W. Gosselink and H.E. Mullins (1982) Determination of desorption efficiencies in the 3M 3500 organic vapor monitor. Am. Ind. Hyg. Assoc. J., 43(8): 569-574.

Schenker, M.B., Samuels, S.J., Kado, N.Y., Hammond, S.K., Smith, T.J., and Woskie, S.R. (1990). Markers of Exposure to Diesel Exhaust in Railroad Workers. Health Effects Institute. Research Report 33.

Schwartz, J. and D. Dockery (1992) Increased mortality in Philadelphia associated with daily air pollution concentrations. Am. Rev. Respir. Dis., 145: 600-604.

U.S. Department of Labor, OSHA, Billings Area (2000). Industrial Hygiene Survey of Park Employee Exposures During Winter Use at Yellowstone National Park.

White, J.J and J.N. Carroll (1999) Characterization of Snowmobile Particulate Emissions. Final Letter Report to Yellowstone Park Foundation, Inc. Southwest Research Institute Project 08-2478.

VII. REFERENCES (cont'd)

White, J.J and J.N. Carroll (1998) Emissions from Snowmobile Engines using Bio-Based Fuels and Lubricants. Final Report by Southwest Research Institute for State of Montana department of Environmental Quality.

Whittaker, L.A., MacIntosh, D.L., and Williams, P.L. (1999) Employee exposure to diesel exhaust in the electric utility industry. Am. Indus. Hyg. Assoc. J. 60:635-40.

APPENDIX A

Table A-1. Conversion Factors for Occupational Exposure to Selected Volatile Organic Compounds.

Compound	Conversion Factor		
Acetaldehyde	1 ppm	=	1.8 mg/m^3
Benzene	1 ppm	=	3.26 mg/m^3
Ethylbenzene	1 ppm	=	4.34 mg/m^3
Formaldehyde	1 ppm	=	1.23 mg/m^3
Toluene	1 ppm	=	3.77 mg/m^3
1,2,4-Trimethylbenzene	1 ppm	=	4.92 mg/m^3
Xylenes (total)	1 ppm	=	4.34 mg/m^3