# SPATIAL VARIATION OF VOLATILE ORGANIC COMPOUNDS ASSOCIATED WITH SNOWMOBILE EMISSIONS IN YELLOWSTONE NATIONAL PARK

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## TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# EXECUTIVE BRIEF

## Overview

This report presents the findings of an investigation of the composition and spatial distribution of air pollutants in Yellowstone National Park (YNP) during the period February 12-16, 2003, conducted by an independent group of research scientists.

## Approach

### *Field Sampling*

A total of 218 whole air samples were collected and analyzed for 85 volatile organic compounds (VOCs), carbon monoxide (CO) and methane ($CH_4$). The whole air samples were obtained at a variety of locations that included 21 sites selected to provide "parkwide snapshots" of air quality. Samples were acquired at these 21 sites in the early morning and early afternoon of both February 12 and 15 in order to both observe any trends in local enhancements and for days that were characterized by differing levels of traffic. Additional samples were also collected in the community of West Yellowstone, Montana, in order to assess ambient air quality conditions on February 15 and 16. Exhaust samples were also acquired from representative snowmobiles, a snowcoach, and a snowplow in order to obtain "fingerprints" from each of these sources. Additionally, a full set of diurnal (i.e., 24 hour) samples were acquired at Lake Ranger Station. Analytical instruments were placed at the National Park Service (NPS) air quality monitoring site adjacent to the Station for measurements of particles, ozone, nitric oxide (NO), and total reactive nitrogen (NOy).

## Findings

### *Exhaust Samples*

Ten separate exhaust samples were collected from oversnow vehicles that are representative of the population used in YNP. The exhaust samples were used to compare the relative emission levels of VOCs from the 2-stroke snowmobiles and from various 4-stroke and diesel vehicles. The results indicate consistently higher emission levels for the 2-stroke snowmobiles. In general, the relative contributions from 2-stroke snowmobiles are 2-20 times greater than for 4-stroke snowmobiles and snowcoaches, and significantly larger than those of the diesel snowcat. Additionally, the 2-stroke engine types emitted much larger quantities of air toxics (i.e., benzene, and toluene) than the other engine types.

### *VOCs*

The whole air samples were analyzed for 85 VOCs and the results indicate that the majority of these compounds were derived from local sources with air masses ages on the order of 1-2 days. Furthermore, the results suggest that oversnow vehicle emissions represented the primary local source for the VOCs and CO observed in the Park. The data indicate significant enhancements in YNP above background levels commonly observed in northern hemispheric air masses, and even larger enhancements in the community of West Yellowstone.

The height of the atmospheric boundary layer increased on both February 12 and 15 during the daylight hours. Thus, dilution occurred during the daylight hours, decreasing the mixing ratios of most gases measured. However, certain aromatic VOCs that are major components of 2-stroke engine exhaust (i.e., benzene, toluene, ethylbenzene, xylenes) had median mixing ratios that were enhanced 2-55% during the afternoon hours which can only be attributed to large amounts of local emissions.

The data also show that the increased levels of snowmobile traffic observed on February 15 as compared with February 12 generated higher VOC and CO median mixing ratios in most locations.

The abundance of gases in the Park were also seen to vary spatially. For all gases that are indicative of 2-stroke emissions, the highest levels were observed in those areas of the Park that experienced higher levels of traffic.

Near-road and off-road sample analysis indicated that the mixing ratios of all gases measured did decrease significantly as distance from the road increased. This suggests that the relatively still surface wind conditions present during sample periods did not serve to rapidly dilute emissions in a given area. Thus mixing ratios under such conditions are likely to be negatively correlated with distance from road. These findings have important implications for human and wildlife exposure to pollutants and air toxics.

Levels of a number of VOCs that are air toxics subject to study and regulation by federal research institutes and regulatory agencies (i.e., the Agency for Toxic Substances and Disease Registry, the National Institute for Occupational Health and Safety, and the Occupational Safety and Health Administration) were not found to exceed recommended or permitted exposure levels at any of the regular sample sites located in the Park. However samples acquired on February 16 beneath the West Entrance Station's roof enclosure did show enhanced levels that are likely have implications for human exposure to air toxics. Further investigation of the Entrance Station should be conducted because it is likely that the area under the roof enclosure at the West Gate Entrance Station could sustain elevated levels that could exceed regulatory standards because of the constant traffic flow. Additionally, it should be noted that Park employees working in this vicinity were likely exposed to significantly higher levels of toxic compounds, increasing their risk of possible health effects due to increased exposure.

*Visibility*

Total particle counts were enhanced several orders of magnitude above background levels during the sampling period at Lake Ranger Station, in addition to NO, NOy and various other gases representative of 2-stroke emissions. These findings suggest a potential exists for visibility impacts from direct emissions of particles from snowmobiles. Further work should be conducted on assessing the impact of primary emissions of particles from snowmobiles on visibility in the Park.

**Recommendations**

Based on the findings discussed above, a number of recommendations are offered:

- The discontinuation of 2-stroke snowmobile technology in the Park will improve the quality of air by reducing VOC and CO emissions.
- Reducing or holding overall levels of snowmobile usage steady along with a reduction in the amount of 2-stroke snowmobile traffic will likely reduce VOC and CO emissions.
- Snowmobiles should not be idled for extended periods of time (exceeding manufacturer recommendations) while in use in the Park, which regularly occurs at sites of interest to visitors.
- Engage in improved monitoring of oversnow traffic levels in all areas of the Park
- Establish a continuously operated diurnal sampling station with full instrumentation at the West Entrance to supplement the data coming from the Lake R.S. sampling site.
- Continue to monitor air quality in the Park during periods of oversnow use, and expand monitoring to periods that the Park is not open for oversnow recreation in order to obtain improved background data on air quality in the Park.

# EXECUTIVE SUMMARY

## Overview

This report presents the findings of an investigation of the composition and spatial distribution of air pollutants in Yellowstone National Park (YNP) during the period February 12-16, 2003. The investigation, conducted by an independent research group composed of scientists from the University of New Hampshire and Central Michigan University, complements a previous investigation conducted in February, 2002, entitled *Spatial Variation and Characteristics of Volatile Organic Compounds Associated with Snowmobile Emissions in Yellowstone National Park*. This report is available from the Office of Planning at YNP or from the investigators.

Owing to the resource management challenges presented by high levels of motorized recreation in YNP during the winter season, a broad spectrum of research focusing on air and water quality impacts, exposure to air toxics, and oversnow vehicle (i.e., snowmobile) interactions with wildlife has been conducted over the last decade by a variety of investigators. While this body of research had improved knowledge in each of these topical areas, the issue of the broader spatial distribution and levels of air pollutants experienced by the Park remained uncertain. The investigation summarized here and described in more detail in the body of this report was undertaken in order to fill this gap in our knowledge. As such, it directly complements existing research and provides considerable additional information concerning the origin, distribution, and fate of ground level volatile organic compounds and other pollutants in the Park during the winter season.

## Approach

### *Field Sampling*

A total of 218 whole air samples were collected during the study period and were analyzed for 85 different volatile organic compounds (VOCs), carbon monoxide (CO) and methane ($CH_4$). The whole air samples were obtained at 21 sites whose locations were selected to provide "parkwide snapshots" of air quality during each 3-5 hour sample period. The linear distance separating these sites ranged from 5 to 20 km, with less distant sites being located where levels of oversnow traffic are higher. Samples were acquired at two separate times on each of two separate days in order to both observe any trends in local enhancements on an hourly basis and for days which are characterized by differing levels of traffic. Wednesday, February 12, 2003 was expected to exhibit moderate levels of traffic whereas the following Saturday (2/15/2003) was expected to show the highest level of traffic for the season. Exhaust samples were also acquired from representative snowmobiles, a snowcoach, and a snowplow in order to obtain a "fingerprint" from each of these different sources. Whole air samples were also collected in the community of West Yellowstone, Montana, in order to assess ambient air quality conditions in this area. Additionally, a full set of diurnal (i.e., 24 hour) samples were acquired at the Lake Ranger Station which was selected on the basis of its relatively remote location in the Park and the lower levels of oversnow traffic experienced there. Additional analytical instruments were placed at the National Park Service (NPS) air monitoring site adjacent to the Station for measurements of particles, ozone, nitric oxide (NO), and total reactive nitrogen (NOy). These instruments acquired data which were aggregated to one minute averages.

Air samples were collected in specially prepared canisters which were cleaned and evacuated at the University of New Hampshire. In the field, the researchers located the sampling site, moved to a position approximately 500 m upwind of any immediately adjacent VOCs sources (i.e., roads), and slowly filled the canister in such a way as to ensure that the contents would be representative of the larger volume of ambient air surrounding the site. This required that the researcher slowly walk in an upwind direction with the canister held above eye-level to ensure that a fresh stream of ambient air be encountered by the valve port. At each site the location at which the valve was first opened was determined with the use of a Global Positioning System (GPS) receiver/data logger, and these data as well as other site and collection data were logged. A second sample was acquired at each site at a position within 100 m of the nearest road in order to assess the influence of distance from nearest road on pollutant levels.

## Findings

Owing to the variety of analyses that were conducted, these are described and their results summarized separately in the sections below.

### *Exhaust Samples*

Ten separate exhaust samples were collected in canisters placed directly in the exhaust streams of oversnow vehicles that are representative of the population used in YNP. This type of source "fingerprinting" enables the influence of each engine type on the air mass composition to be assessed. The vehicles sampled included both 2-stroke and 4-stroke snowmobiles whose engines were hot and which were either idling or accelerated to a 3,500–4,000 rpm to simulate operation under differing conditions. Additionally, exhaust samples were collected from a 1978 Bombadier snowcoach and a NPS Ford Power Stroke V-8 Sno-Van while idle and a NPS Snowcat was sampled under load conditions. The exhaust samples were used to compare the relative emission levels of VOCs from the 2-stroke snowmobiles and from various 4-stroke and diesel vehicles. Emission ratios of 16 NMHCs relative to CO were used to evaluate the different vehicle types. The values corresponding to similar engine types were averaged due to similar emission ratios under different conditions. The results indicate consistently higher emission levels for the 2-stroke snowmobiles. In general, the relative contributions from 2-stroke snowmobiles are 2-20 times greater than for 4-stroke snowmobiles (and snowcoaches), and significantly larger than those of the diesel snowcat. Additionally, the 2-stroke engine types emitted much larger quantities of air toxics (i.e., benzene, and toluene) than the other engine types. These results are consistent with those obtained in 2002, and with those documented by other investigators.

### *VOCs*

The speciation and abundance of alkyl nitrates provides important information regarding the photochemical history of air masses present over a given region, with particular attention to the role of local and more distant sources of air pollution. Alkyl nitrates are photochemically produced (i.e., in the presence of solar energy) from parent alkanes (compounds such as propane and n-butane) in the presence of oxides of nitrogen (NO and $NO_2$). As such, their abundance relative to the parent alkanes indicates the extent of air mass processing and allows for the relative dating of an air mass and its pollutants.

The mixing ratios measured for several alkyl nitrates from the whole air samples collected during the study period were compared with those coming from samples acquired at remote sites along the western coast of the United States during March of 2002. The results demonstrated that the air masses sampled in the Park during the study period had not been photochemically processed to the same extent as that sampled on the coast, indicating a local source. These results were corroborated by the analysis of the alkyl-nitrate/parent alkane ratios that were plotted along predicted photochemical production lines derived from photochemical modeling experiments. This analysis revealed that these emissions that were derived from local sources were relatively fresh with ages on the order of 1-2 days. Furthermore, the results suggest that oversnow vehicle emissions represented the primary local source for these compounds and the NMHCs observed in the Park.

Similar trends were also observed for the alkanes ($C_4$-$C_{10}$), aromatics, alkenes, and ethyne. For each of these NMHC grouping, the data indicate significant enhancements in YNP above levels measured at remote sites, and even larger enhancements in the community of West Yellowstone owing to very high levels and densities of snowmobile traffic there. The observed mixing ratios of various halocarbons, which have a large range of atmospheric lifetimes (from days to hundreds of years), were similar to those measured at remote sites and validate the conclusion that 2-stroke snowmobile emissions in the Park and West Yellowstone served to significantly enhance the levels of the VOCs.

Although atmospheric sounding data indicated that the height of the boundary layer (lower portion of the atmosphere that serves to restrict the mixing of air both above and below it because of a temperature inversion) had increased during both sample days during the daylight hours in response to surface warming, the mixing ratios for the different classes of gases measured were variable and source dependent. In general, gases that are expected to be better mixed and that have longer atmospheric lifetimes (i.e., $C_2$-$C_3$ alkanes, various halocarbons) were diluted during the daylight hours, whereas certain aromatics that are major components of 2-stroke engine exhaust (i.e., benzene, toluene, ethylbenzene, xylenes) had median mixing ratios that were enhanced some 2-55% during the afternoon hours owing to their high levels of abundance and continual replenishment via emissions.

The data also show that the increased levels of snowmobile traffic observed on Saturday (February 15, 2003) as compared with Wednesday (February 12, 2003) generated higher NMHC median mixing ratios in most locations within YNP. These results are similar to those obtained from the 2002 field campaign. It was not possible make this comparison for the West Yellowstone samples given that none were acquired there on a more moderate traffic day.

The abundance of gases in the Park was also seen to vary spatially. For all gases that are indicative of 2-stroke emissions and fuel evaporation, the highest levels were observed in those areas of the Park that experienced higher levels of traffic (i.e., West Entrance to Madison Junction, the Loop Road, and West Thumb to South Entrance). While the mixing ratios were not seen to be well correlated with average daily snowmobile use indicators derived from 1992-1999 Entrance Station data, the correlations do suggest some degree of association between levels of snowmobile traffic and abundance of gases. Enhanced levels of traffic on the West Thumb – South Entrance road segment owing to improved road conditions were observed in the field and contributed to higher mixing ratios of many gases in this area.

Analysis of the near-road and off-road observations indicate that even though there were no statistically significant differences between these, the mixing ratios of all gases subjected to this test did decrease as distance from nearest road increased. This suggests that while both sets of samples were acquired from well-mixed ambient air, the relatively still surface wind conditions that were present during all sample periods did not serve to rapidly dilute emissions in a given area and thus mixing ratios under such conditions are likely to be negatively correlated with distance from road. This has important implications for human and wildlife exposure to pollutants and air toxics.

While levels of a number of NMHCs and halocarbons that are air toxics subject to study and regulation by the Agency for Toxic Substances and Disease Registry (ATSDR), National Institute for Occupational Health and Safety (NIOSH), and the Occupational Safety and Health Administration (OSHA) were not found to exceed either regulatory or suggested exposure levels at any of the regular sample sites located in the Park, samples acquired beneath the West Entrance Station's roof enclosure and in both immediately upwind and downwind locations (these samples were acquired on Sunday, February 16, 2003) did show that levels were enhanced downwind and beneath the enclosure. Additionally, it should be noted that Park employees working in this vicinity were likely exposed to significantly higher levels of toxic compounds, increasing their risk of possible health effects due to increased exposure.

### *Visibility*

Given that potential air pollution impacts on visibility in the Park is an important issue with regard to managing wintertime oversnow vehicle use, aerosol measurements (particles/cm$^3$) were made and secondary organic aerosol levels determined through modeling to determine their potential for formation from the gas phase VOC data. Total particle counts were enhanced several orders of magnitude above background levels during the sampling period and suggest that even at this more remote site within the Park, a potential exists for visibility impacts from direct emissions of particles from snowmobiles. Overall, further research involving particle size and composition measurements is critical to better understand oversnow vehicle emissions on Park visibility.

## Recommendations

Based on the findings discussed above, a number of recommendations are offered that are conditioned by air quality considerations coming from the Clean Air Act and other federal laws that bear on wintertime recreational planning in YNP:

- ➢ The discontinuation of 2-stroke snowmobile technology in the Park (as under the implementation of SEIS Alternative 4) will improve the quality of air by reducing VOC and CO emissions.
- ➢ By reducing or holding overall levels of snowmobile usage steady, a reduction in the amount of 2-stroke snowmobile traffic will likely reduce both CO and VOC emissions, including the air toxics benzene and toluene.
- ➢ Snowmobiles should not be idled for extended periods of time exceeding manufacturer recommendations while in use in the Park, which regularly occurs at sites of interest to visitors. Requiring snowmobile operators to shut-off their machines will likely contribute to a reduction in overall emissions.
- ➢ Engage in improved monitoring of oversnow traffic levels in all areas of the Park whether using automated devices, logs maintained by vehicle operators, or a combination of these.
- ➢ Establish a continuously operated diurnal sampling station with full instrumentation at the West Entrance to supplement the data coming from the Lake R.S. sampling site as well as to provide an important contrast with this more remote location.
- ➢ Continue to monitor air quality in the Park during periods of oversnow vehicle use, and expand monitoring to acquire baseline data during periods that the Park is not open for oversnow recreation.

## Abstract

The results of a spatial investigation of emissions associated with oversnow travel in Yellowstone National Park during the period February 12-16, 2003, are presented. The National Park Service is currently engaged in the monitoring of winter air quality in Yellowstone National Park, including toxic air pollutants and those pollutants that have a role in negatively affecting visibility. This investigation supplements a similar investigation conducted in February of 2002 which found that volatile organic compounds (VOCs) emitted from snowmobiles are widespread within the Park, especially between the community of West Yellowstone, MT, and Old Faithful, and along the loop road. A total of 218 whole air samples whose locations were georeferenced using global positioning system receivers/data loggers and 10 exhaust samples were analyzed by gas chromatography with flame ionization and electron capture detection in order to determine the mixing ratios (i.e., relative proportion of molecules of a gas to given quantity of air) of some 85 VOCs, carbon monoxide (CO), and methane ($CH_4$). Atmospheric soundings were acquired with the use of radiosonde equipped weather balloons to assess boundary layer heights, which can restrict the vertical transport of these gases. Additional monitoring of ozone ($O_3$), nitric oxide (NO), total reactive nitrogen (NOy), and particulate matter (CN) was conducted at the Lake Ranger Station (Lake R.S.) to assess the extent of atmospheric processing of ozone precursors and the formation of secondary organic aerosols. Utilizing these instruments, whole air samples, and a geographic information system to show the extent of oversnow vehicle emissions in Yellowstone National Park, the findings indicate that 2-stroke snowmobile engine emissions in the Park and West Yellowstone appear to contribute large quantities of VOCs, including air toxics, and CO to the Yellowstone Park airshed.

## 1. Introduction

This report presents the findings of an intensive study of the spatial distribution of volatile organic compounds (VOCs) associated with oversnow vehicular travel in Yellowstone National Park (YNP) during February, 2003[1]. This report constitutes a set of final results and is being submitted to the National Park Service (NPS) in satisfaction of the requirements set forth in a cooperative agreement reached between the NPS and the University of New Hampshire (UNH) in February, 2003[2], and for consideration by the NPS in its capacity as lead agency in the development of winter use plans for the Yellowstone and Grand Teton National Parks, and the John D. Rockefeller, Jr., Memorial Parkway, as required by settlement agreements[3] established with litigants in 1997, and 2001.

### 1.1 Statement of Problem

This investigation was undertaken to investigate the spatial distribution of VOCs, carbon monoxide (CO) and methane ($CH_4$) associated with oversnow vehicular travel in YNP. Like many other U. S. National Parks, YNP has been designated a mandatory Class I Airshed under the federal Clean Air Act (CAA), and is thus subject to the requirement that the quality of air within its boundaries remain in a high-quality state such that it does not suffer from impairment

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[1] YNP investigation: “Spatial variation of volatile organic compounds associated with snowmobile emissions in Yellowstone National Park” (YNP Research Permit No. 05268).

[2] Agreement Number CA1571-03-2022.

[3] These settlement agreements led to the development of a Final Environmental Impact Statement (10/10/2000) and associated Record of Decision (11/22/2000) and Final Rule (1/22/2001), and Final Supplemental Environmental Impact Statement (February 2003) and associated Final Record of Decision (3/25/2003).

of visibility [*Clean Air Act - Section 169A.a.1,* 1970, 1990]. Owing to a steady increase in wintertime oversnow recreational vehicle use in the Park since the late 1960s, which has significantly increased mobile-source (i.e., snowcoach and especially snowmobile) emissions, air quality and visibility within the Park have been acknowledged to have decreased to levels that have prompted Park Managers to consider alternative regulatory strategies [*National Park Service,* 1999, 2000a, 2000b]. In response to the need to remedy impairment of visibility in the Park resulting from manmade air pollution (as required by the CAA - Section 169A.a.1; and as required by the Federal Regional Haze Rule[4] which mandates the identification and remediation of visibility resulting from anthropogenic impacts) and to address the issue of human exposure to toxic air pollutants, also mandated by the CAA, the Occupational Safety and Health Administration (OSHA) and the Agency for Toxic Substances and Disease Registry (ATSDR), extensive research has been conducted within the Park to characterize and quantify snowmobile emissions with respect to carbon monoxide, VOCs, and particulate matter emissions as well as their impacts on human health [*National Park Service,* 1995, 1996; *Ingersoll et al.,* 1997; *Snook and Davis,* 1997; *Radke,* 1997; *Carrol and White,* 1999; *Ingersoll,* 1999; *Morris et al.,* 1999; *Institute for Environment and Natural Resources,* 2000; *Kado et al.,* 2001; *Bishop et al.,* 2001, *Sive et al*., 2002; *Southwest Research Institute*, 2002].

Based on the results of this body of research and additional studies concerning snowmobile-wildlife interactions, the NPS published a Record of Decision (ROD) based on a "Winter Plans Final Environmental Impact Statement…" [2000a] which would have steadily reduced snowmobile use in the Park over the period 2001-2003 and encouraged winter visitation thereafter only via NPS-managed snowcoaches. However, the NPS has since been forced to set aside its ROD and develop additional or modified alternative courses of action for regulating oversnow travel in the Park in a Supplemental Environmental Impact Statement (SEIS) [*U.S. Dept. of Interior*, 2002]. Published in February, 2003 [*U.S Dept. of Interior,* 2003a], this Winter Plans Final Supplemental Environmental Impact Statement (FSEIS) included five separate management alternatives that ranged from no limitation on the entry of snowmobiles and snowplanes into the YNP-Grand Teton National Park-John D. Rockefeller, Jr., Memorial Parkway planning units to the preferred alternative (1A) from the 2000 FEIS noted above. The Final Record of Decision (FROD) for the FSEIS published on March 25, 2003, has now established Alternative 4, which provides for the development and implementation of daily snowmobile entry limits in addition to best available technologies (BATs) for these vehicles and snowcoaches together with monitoring and adaptive management, as the preferred alternative to be implemented beginning in the winter season of 2003-2004 [U.S. Dept. of the Interior, 2003b].

The preferred management alternative (Alternative 4), as noted above, requires that oversnow vehicles entering the YNP beginning in December, 2003, employ BATs which include the following initial requirements:

- "…any snowmobile commercially available that can achieve a 90% reduction in hydrocarbons and a 70% reduction in carbon monoxide from EPA's [*Environmental Protection Agency*] baseline assumptions for uncontrolled snowmobiles as published in the Federal Register on November 8, 2002. Thus, any recreational snowmobile entering YNP must achieve emissions below 15 g/kW-hr for hydrocarbons and 120 g/kW-hr for carbon monoxide. Snowmobiles must be tested on a 5-mode engine dynamometer with all test data provided to the NPS for review.

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[4] 64 FR 35714, July 1, 1999.

- Snowmobiles would also be required to operate at or below 73 dB(A), as measured at full throttle according to Society of Automotive Engineers (SAE) J192 (1985) test procedures.
- For non-historic snowcoaches, BAT air emissions would be the same as those for snowmobiles: 15 g/kW-hr for hydrocarbons and 120 g/kW-hr for carbon monoxide by the winter of 2005-2006.
- For sound emissions, snowcoaches would be required to operate at or below 75 dB by the winter of 2008-2009 as measured at 25 mph on the A-weighted scale at 50 feet.
- Historic snowcoaches (defined as a Bombardier snowcoach manufactured in 1983 or earlier) would initially be exempt from air and sound requirements; however, NPS would work with snowcoach owners to retrofit historic snowcoaches to meet BAT requirements. Because of the relatively few Bombardier snowcoaches currently operating (about 29), the NPS believes it is reasonable and prudent to work with outfitters and concessioners to determine how best to upgrade their equipment." [*U.S. Dept. of Interior*, 2003b:14-15].

Additionally, the NPS will implement these standards as initial thresholds that will be necessarily superceded as technological improvements occur, and will actively employ resource inventory, monitoring, and adaptive management in order to assess and protect the long-term effects of management actions on park resources and values that include: air quality, wildlife, sound, water resources, safety, and visitor experience. Monitoring and/or adaptive management may lead the NPS to modify provisions of the FROD if it is found that they "have a greater or lesser effect on resource thresholds than predicted" [*U.S. Dept. of Interior*, 2003:13].

## 1.2 Previous Research

There are various environmental and health impacts associated with the use of snowmobiles in national parks, including air quality impacts from exhaust emissions. This section of the report presents current information from recent publications regarding the potential air quality impacts associated with snowmobile use in national parks. The research conducted to date, along with future assessments, will ultimately allow the NPS to make informed decisions regarding the use of snowmobiles in the National Park system. The NPS [2000c] has compiled an excellent summary of the current work performed and this review is intended to supplement this document.

### *1.2.1 Snowmobile Emissions and Air Quality*

To date, there have been several studies examining the emissions of snowmobile engines [*White and Carroll*, 1998; *Carroll and White*, 1999; *Morris et al.*, 1999; *Bishop et al.*, 2001; Southwest Research Institute, 2002]. The most recent mobile source emissions inventory based on fuel use for YNP shows that snowmobiles account for approximately 27% of the annual emissions of CO and roughly 77% of the annual emissions of hydrocarbons (HC) [*Bishop et al.*, 2001]. This study also investigated the effects of oxygenated (ethanol-blended) fuels on snowmobile emissions. The results indicated that a reduction in CO of 7±4% could be achieved in YNP using oxygenated fuels [*Bishop et al.*, 2001]. However, oxygenated fuels did not appear to reduce hydrocarbon emissions [*Bishop et al.*, 2001]. This study also attempted for the first time the real-time remote sensing of toluene, a major component of gasoline. Results from another study collected data at the West Entrance station over a 2-day period showed a mean toluene concentration of 1976 ppm in snowmobile exhaust [*Morris et al.*, 1999]. The toluene to hydrocarbon ratio measured in this study was consistent with toluene content of non-oxygenated fuels.

Research conducted by the Southwest Research Institute [2002] has shown that the specific technology incorporated into snowmobile engines can have a significant effect on the level of HC emissions. Specific findings based on laboratory tests of commercially available 2002 model 4-stroke snowmobiles, two 4-stroke machines entered in the 2002 SAE Clean Snowmobile Challenge, and a 2001 Polaris Sport Touring 2-stroke snowmobile included the following:

- "Commercially-available 4-stroke snowmobiles are significantly cleaner than 2-stroke sleds. Compared to previously tested 2-strokes, these 4-stroke sleds emit 95-98% less HC, 85% less CO, and 90-96% less PM [*particulate matter*]. Four-stroke snowmobile NOx, however, is considerably higher than from a 2-stroke, being increased by a factor of seven to twelve.
- The commercially-available 4-stroke snowmobiles emit roughly 90% less toxic hydrocarbons, such as 1,3-butadiene, benzene, formaldehyde, and acetaldehyde, than 2-stroke sleds.
- Use of a catalyst can further reduce snowmobile emissions. The University of Idaho CSC 2002 sled, that incorporates a 4-stroke, closed-loop controlled engine with catalyst, generated the lowest emissions of all sleds tested. Compared to the 4-stroke Arctic Cat sled, the Idaho sled emitted 64% less HC, 29% less CO, 99% less NOx, and 36% less PM.
- Operation on E10 [*10% ethanol fuel*] generally produced lower HC and CO emissions, but higher NOx emissions, compared to reference gasoline." [SWRI, 2002:viii-ix].

Measurements of snowcoach emissions by the SWRI team were less conclusive, but indicated that a Ford V-10 powered E-350 15 passenger van would emit approximately 37 times more HC, 130.53 times more CO, and 3.37 times more NOx operating in snowcoach-like conditions than would occur under normal highway driving conditions. These levels of emissions were all generally lower than emissions from the tested 2002 Arctic Cat 4-stroke snowmobile [SWRI, 2002].

Air quality studies at YNP have shown that the accumulation of a large number of snowmobiles in a small area, such as entrance stations and parking lots, can result in short-term exposures to very high levels of CO, PM, and HC (including toxic organics) [*Air Resource Specialists, Inc.*, 1996; *Kado et al.*, 1999]. These results indicate that there is a direct relationship between the number of snowmobiles, emissions and pollutant levels. Meteorology also plays an important role in that cold, stable atmospheric conditions with low wind speeds hinder the dispersion of air pollutants in the immediate area of their release [*National Park Service*, 2000c].

### *1.2.2 Snowmobile Emissions and Air Toxics*

Personal exposure measurements of VOCs were conducted for YNP employees during the winter of 1999. This study monitored a number of toxic compounds, including benzene, toluene, and formaldehyde [*Kado et al.*, 2001]. Of the VOCs measured in this study, toluene had the highest relative concentration. Also, the fixed-site VOC monitoring they performed showed similar types of gasoline-associated toxic compounds (*e.g.*, benzene and toluene) at each location, with highest levels prevailing at the West Entrance. The study indicated that the concentration of benzene for some employees could approach the Recommended Exposure Levels (RELs) as established by the National Institute for Occupational Safety and Health (NIOSH). The study supported "the hypothesis that Park employees and the surrounding environment are exposed to high levels of many toxic pollutants as a result of snowmobile use within the Park…" [*Kado et al.*, 2001]. These results indicate that levels of individual pollutants, including carcinogens such as benzene, resulting from snowmobile exhaust, can be high enough to be a threat to human health.

The CAA Amendments of 1990 provided the option of using oxygenated fuels during the winter months in approximately 40 areas throughout the U.S. that were not meeting the National Ambient Air Quality Standards (NAAQS) for CO. Methyl tertiary butyl ether (MTBE) and ethanol are two of several fuel additives used in oxygenated and reformulated gasoline to reduce CO emissions. Ethanol is used year-round in all gasoline powered NPS vehicles at YNP, including snowmobiles, and it is sold at West Yellowstone gas stations in the winter. Oxygenated fuels are not, however, available from commercial vendors located within the Park [*Bishop et al.* 2001]. Bishop et al. [2001] documented a statistically significant reduction in CO emissions from snowmobiles using fuels containing ethanol. Some small amounts of MTBE have been found in a few snowpack samples collected at YNP immediately adjacent to roadways [*Hagemann and VanMouwerik*, 1999]. This is thought to be the result of snowmobiles that have been transported with gasoline from locations that use MTBE. The extent to which MTBE additives are used in YNP is unknown.

In general, vehicle exhaust, including that from snowmobiles, contains numerous toxic compounds. The effects of these compounds are well documented and are discussed briefly. Exposure to air toxics contained in automobile and snowmobile exhaust can result in numerous respiratory and neurological effects. In addition, several of these air toxics have been shown to be carcinogenic.

- Acute exposure to acetaldehyde results in irritation of the eyes, skin, and respiratory tract in humans. Erythema, coughing, pulmonary edema, and necrosis may also occur and, at extremely high concentrations, respiratory paralysis and death are possible. The EPA classifies acetaldehyde as a probable human carcinogen of low carcinogenic hazard.
- Acute exposure to 1,3-butadiene results in irritation of the eyes and nasal passages, and causes neurological effects such as blurred vision, fatigue, headache, and vertigo. There is also a possible association between 1,3-butadiene and cardiovascular diseases. The EPA has classified this compound as a probable human carcinogen of medium carcinogenic hazard.
- Acute (short-term) inhalation exposure to benzene may cause drowsiness, dizziness, headaches, and unconsciousness in humans. These symptoms stop when exposure ceases. Exposure to benzene liquid and vapor may irritate the skin, eyes, and upper respiratory tract. Increased incidences of leukemia have been observed in humans occupationally exposed to benzene. The EPA and the International Agency for Research on Cancer (IARC) have classified benzene as a human carcinogen based on sufficient evidence from epidemiological studies [*U.S. EPA*, 1994; *IARC*, 1987].
- Toluene is an air toxic that can cause irritation of the eyes and upper respiratory tract, dizziness, headaches, anesthesia, and respiratory arrest. Acute and chronic exposures can

affect the central nervous system (CNS) producing CNS depression and loss of memory [*Irwin et al.*, 1998].

- MTBE in the air can cause headaches, dizziness, and eye irritation [*Keller et al.*, 1998].
- A report prepared for the Legislature and Governor of California [*Keller et al.*, 1998] states that 10% ethanol by volume in conventional gasoline can decrease emissions of CO (13% reduction), VOCs (16% reduction), and benzene (11% reduction). However, it can also increase exhaust emissions of NOx and acetaldehyde by 5% and 159%, respectively.
- Ethanol is known to have developmental and neurotoxicological effects, although the risk of exposure to ambient levels is not clear [*Keller et al.*, 1998].

Based on the types of air pollutants associated with snowmobile exhaust, as well as the quantities in which they are emitted, the cumulative damaging health effects of what could be a highly concentrated, multi-pollutant mixture in the vicinity of snowmobiles are likely to be high. This is particularly relevant for individuals who spend a significant amount of time in the vicinity of snowmobile exhaust, such as areas of traffic congestion (entrance stations, parking lots) and poor emission dispersion.

Another major concern is the accumulation of hydrocarbons and toxic organics in the snowpack. These pollutants may be flushed into nearby streams and water bodies during the spring snowmelt. The fate of these pollutants in the snowpack is under investigation. Potential water quality concerns from snowmobile use in parks have also been addressed in other reports [*Ingersoll et al.,* 1997; *Ingersoll,* 1999; *Hagemann and VanMouwerik*, 1999].

### *1.2.3 Wintertime Atmospheric Chemical Processing of VOCs*

With regards to the chemistry of the atmosphere, HOx (HO + $HO_2$) radicals, together with $H_2O_2$, play a major role in the oxidation processes of VOCs. However, during the late fall and winter, photolysis reactions slow down because of the limited amounts of solar radiation during daytime hours. Nonetheless, among various classes of atmospheric VOCs, alkenes are unique in exhibiting significant reactivity towards ozone as well as HO radicals. The reaction of ozone with alkenes is called ozonolysis and these reactions do not require any light to be initiated. Thus, they can occur throughout all hours of the day and all seasons of the year. These reactions are suggested to be competitive with the daytime HO initiated reactions and nighttime $NO_3$ radical reactions as a sink for alkenes [*Seinfeld and Pandis*, 1998]. It has been shown that ozonolysis reactions of anthropogenic alkenes can be more pronounced during the wintertime and can contribute significantly to HOx radical and peroxide formation during the late fall and winter months [*Ariya et al.*, 2000]. These results indicate that the additional HO radicals formed during ozonolysis could significantly augment atmospheric oxidation processes in YNP and its surrounding areas. Also, the oxidation products of $>C_6$ hydrocarbons could contribute significantly to secondary aerosol formation.

While the body of research into snowmobile-related air quality impacts in YNP is broad in scope, the majority of work has been focused on the emissions (and also noise) produced from snowmobiles employing different technologies, and the issue of human exposure to toxic air pollutants (i.e., VOCs, CO, and particulate matter). In response to the lack of knowledge concerning the spatial variation of snowmobile related air pollutants in YNP [*Institute for Environment and Natural Resources,* 2000] aside from two studies conducted by *Ingersoll et al.* [1997] and *Ingersoll* [1999] which relied on no more that six separate sample sites within the park itself, *Sive et al.* [2002] undertook to assess the spatial distribution of VOCs in the park in February, 2002, utilizing 96 whole air samples that were analyzed utilizing methods similar to those reported below. The intent of that investigation was to conduct a rigorous investigation of the spatial variation of snowmobile related VOCs in YNP under conditions of historically high levels of snowmobile usage. Furthermore, the study was designed to establish a set of baseline data associated with levels of oversnow travel that approximate historical peaks in order to document, through future studies, the effectiveness of any reduction in such travel owing to management decisions enacted by the NPS. Additionally, the investigation was intended to serve as a pilot-study designed to test the sampling and analytical methodologies for utilization in future studies to be conducted in the Park.

The investigators revisited YNP in February, 2003, to perform another iteration of the investigation conducted in 2002 but which included the following:

- implementation of an off-road/near-road sampling protocol to test the hypothesis that the sampling protocol requiring the acquisition of well-mixed ambient air samples upwind of oversnow routes produces no significant difference between samples acquired within 50 and 500 meters of the routes;
- the analysis of whole air samples for CO and $CH_4$;
- the monitoring of NO, NOy, CN and $O_3$;
- the importance of secondary organic aerosol formation;
- the inclusion of a control site at Snow Pass to the west of Mammoth Hot Springs;
- the acquisition of whole air sample in and around the community of West Yellowstone, MT, to determine VOC contributions from this potential source area;
- and the acquisition of atmospheric soundings via radiosonde equipped weather balloons to determine boundary layer depths.

### 1.3 Study Objectives

The primary objectives of the study being reported here include the following:

1. to monitor and determine the effects of snowmobile emissions on air quality in YNP and in the communities of Cooke City, Silver Gate, and West Yellowstone, MT.
2. to determine the mixing ratios and spatial variability of atmospheric VOCs, including nonmethane hydrocarbons (NMHCs), halocarbons, and alkyl nitrates.
3. to determine the mixing ratios and spatial variability of the air toxics benzene and toluene along with the criterion pollutant CO associated with oversnow vehicle traffic in YNP.
4. to characterize the nature of oversnow traffic as indicated by the VOC data.
5. to assess the diurnal variability of VOCs, NO, NOy, $O_3$, and CN in YNP during periods of moderate to high oversnow traffic.
6. to assess the potential for the formation of $O_3$ and secondary organic aerosols from VOCs in YNP during periods of moderate to high oversnow traffic.
7. to provide additional base-line data concerning these air pollutants that will supplement the data acquired in 2002 and aid the NPS in assessing the effect of management decisions concerning oversnow traffic in YNP.

## 2. Methods

As described in the research proposal submitted for approval by the YNP Research Permit Office, the investigators acquired whole air samples for analysis throughout the Park on

February 12 and 15, 2003. The dates selected (Wednesday and Saturday, respectively) were selected to coincide with both lower- and higher-traffic days associated with the President's Day Weekend which has historically represented a high- visitation period during the Park's winter season [*J. Sacklin*, Personal Communication, 2001]. A total of 218 whole air samples were collected and were distributed among morning, afternoon, and diurnal sample sets acquired for each day. The locations of the samples were registered with global positioning system (GPS) units, and their contents analyzed by gas chromatography using flame ionization and electron capture detection. In addition, 10 exhaust samples were collected from different oversnow vehicles including a snowcoach, a YNP snowcat along with 2-stroke and 4-stroke snowmobiles. The data were subjected to spatial analysis utilizing interactive graphical interpretation and mapping conducted with the use of a geographic information system (GIS). Discussions of the methodologies employed in the field and laboratory, the field conditions associated with data collection, the chemical and spatial analyses undertaken, and our findings are presented.

### 2.1 Study Area

Having a base elevation of 1620 masl[5] (5314 ft amsl[6]) where the Yellowstone River exits the Park on the north boundary, and having much of its area situated above some 2286 masl (7500 ft amsl), the Park is at high altitude. Its terrain is characterized as broad dissected plateau surfaces interrupted by several mountain ranges and containing notable volcanic and geothermal features. The high altitude and its situation within the Rocky Mountain system in the intermountain West give to the Park a winter climate that is characterized by significant periods of high atmospheric pressure associated with anticyclonic circulation which produce cold temperatures and strong inversions at or near the ground surface. These periods are regularly punctuated by mid-latitude cyclonic storms that originate in the northeast Pacific Ocean and bring significant amounts of snow to the Park.

### 2.2 Sample Collection

The assumptions which underlie the sampling of ground level atmospheric pollutants include the following: 1) emission plumes from non-stationary sources of air pollution become diffused in the lower atmosphere and combine to locally enhance background levels of pollutants in air masses that have entered the study area from the outside; 2) emission plumes from stationary and non-stationary sources are carried in a downwind direction by both surface and upper-level winds, but upper-level flows dictate the overall pattern of pollution at a landscape scale; and 3) volumetric samples of well-mixed ground level air acquired at any point on a given landscape will be representative of the "population" of such volumes surrounding that point.

Yellowstone N.P. and the surrounding communities of West Yellowstone, Silver Gate, and Cooke City, Montana constitute the study area. The Pahaska Teepee resort site adjacent to the Park's East Entrance was also included as a sample site to assess the quality of air on the lee side of the Absoroka Range that straddles the Park's eastern boundary. Given the general roadless nature of the Park, which is enhanced by wintertime road closures and off-road travel restrictions, it demonstrates a high degree of inaccessibility in the winter months which precludes the systematic acquisition of regular samples in the majority of the Park. Accordingly, a regular grid of 20 km$^2$ cells was superimposed over the Park to identify potential sample sites that correspond to wintertime accessible areas and to ensure adequate spatial coverage (Figure 1).

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[5] Meters above mean sea level.

[6] Above mean sea level

Eighteen primary sites were located utilizing this grid, and an additional control site was established at Snow Pass approximately 2 km to the southwest of Mammoth Hot Springs in order to determine the relative mixing ratios of the target gases in ambient air not subject to significant enhancement by oversnow traffic. In addition to those samples obtained within the Park's boundaries, samples were also acquired at Pahaska Teepee (WY) outside the Park's East Entrance, and on the afternoon of Saturday (February 15, 2003) and Sunday morning (February 16, 2003) in and around the community of West Yellowstone adjacent to the Park's western boundary (Figure 2). These additional sites were selected, respectively, to provide information concerning the potential for drift of VOCs under conditions associated with dominant westerly flow of air masses over the Park, and to assess the effect of oversnow traffic and other human activities on the mixing ratios of the target gases in these areas. Additional samples were collected on Sunday morning under the West Entrance roof enclosure and in both upwind and downwind directions (i.e., samples X14-X17 – See Figure 2). A diurnal site was established at Lake Ranger Station (R.S.) for the purpose of acquiring hourly whole air samples during the sample collection days beginning at 12:00 a.m. and ending at 11:59 p.m. (Figure 3). This site was selected because of its more interior position within the Park, its distance from the West Yellowstone-Old Faithful road segment, and because of the presence of NPS maintained air quality instruments including those for measurements of ozone and particles at site adjacent to the Ranger Station. Similar measurements, including ozone, particles (CN), NO and NOy were set up at the instrumentation site by the researchers to provide continuous data for a 96 hour period bracketing the sampling days (see Section 2.4.4 for instrument specifications).

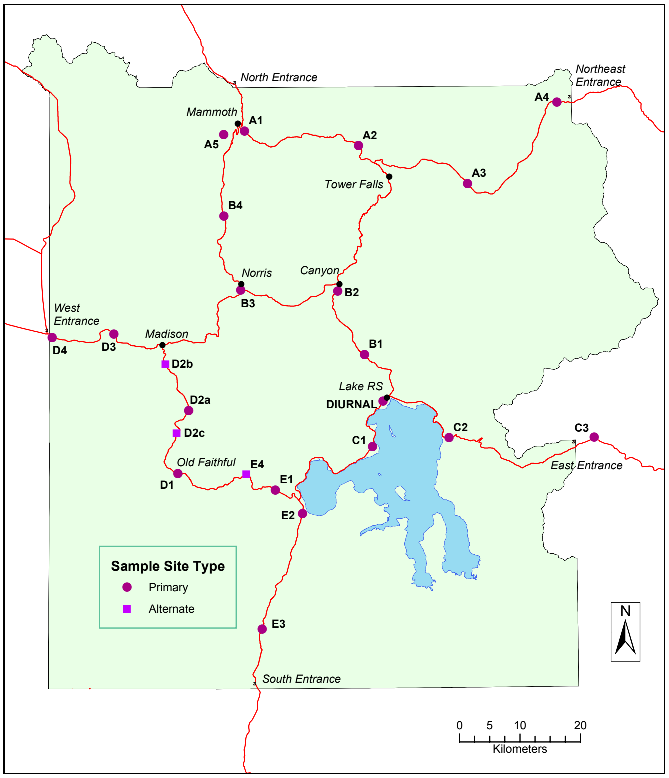

**Figure 1.** Sample sites within Yellowstone National Park.

Within each daily sample period, samples were to be acquired within a four-hour period of time. In order to test the efficacy of the sampling protocol which requires that well-mixed samples of air be acquired by field personnel, two separate samples were acquired at each sample site, both in an upwind direction of the nearest roadway. The first of these samples was taken some 500 m from the road (off-road) and the second some 50 m from the road (near-road). Samples were acquired in the early morning (AM), and again in the early afternoon (PM) at each sample site on both February 12 and 15, 2003. Diurnal data corresponding to the AM and PM sample periods on each day were added to their respective data pools providing an additional off-road observation for each period.

**Table 1.** Sample site locations.

| **Site Code** | **Description of Location** | **Latitude** | **Longitude** |
|---|---|---|---|
| A1 | 1.6 km E. of Mammoth H.S. | -110.68799 | 44.96468 |
| A2 | 5.2 km W. of Tower Junction | -110.44912 | 44.94196 |
| A3 | 1.3 km E. of Lamar R.S. | -110.22082 | 44.88471 |
| A4 | 2.5 km W. of NE Entrance | -110.03163 | 45.00433 |
| A5 | Snow Pass (W. of Mammoth H.S.) | -110.73149 | 44.96002 |
| B1 | Mud Pots, Hayden Valley | -110.43933 | 44.63043 |
| B2 | 1.2 km S. of Canyon Junction | -110.49446 | 44.72557 |
| B3 | Norris Geyser Basin | -110.69709 | 44.72739 |
| B4 | 0.5 km N. of Obsidian Cliff | -110.73192 | 44.83827 |
| C1 | 9.7 km S. of Lake R.S. | -110.42411 | 44.49314 |
| C2 | Lake Overlook | -110.26460 | 44.50531 |
| C3 | 0.5 km N. of Pahaska Teepee | -109.96237 | 44.50426 |
| D1 | Old Faithful | -110.82946 | 44.45407 |
| D2a | Fountain Paint Pot | -110.80663 | 44.54832 |
| D2b | Cascades of the Firehole | -110.85513 | 44.61731 |
| D2c | Midway Geyser Basin | -110.83187 | 44.51440 |
| D3 | 0.5 km E. of Madison Range Overlook | -110.96263 | 44.66211 |
| D4 | 0.6 km E. of West Entrance | -111.09125 | 44.65704 |
| DIURNAL | Lake R.S. | -110.40122 | 44.56050 |
| E1 | 5.3 km E. of West Thumb | -110.62634 | 44.42936 |
| E2 | 2.6 km E. of West Thumb | -110.57068 | 44.39393 |
| E3 | 10.5 km N. of South Entrance | -110.65546 | 44.22161 |
| E4 | 3.0 km E. of Craig Pass | -110.68698 | 44.45269 |

The sample dates February 12 and 15 (Wednesday and Saturday, respectively), 2003, were selected to assess the relative impact of differing levels of oversnow traffic on VOC distributions within the Park, specifically in order to develop a comparison of the spatial variability of VOCs associated with low-to-moderate and high visitation levels. Historically, the month of February is known for high wintertime visitation levels. In February, 1996, average daily visitation was in the range of 1500–1800 persons [*National Park Service*, 1999], and NPS documents consistently indicate that the vast majority of wintertime daily visitation is represented by snowmobile trips [*National Park Service*, 1999; 2000a; 2000b]. Furthermore, personal communication with YNP Planning Staff indicated that the President's Day weekend has historically constituted a high visitation period [*J. Sacklin*, Personal Communication, 2001]. Park entrance data for the previous year (i.e., the 2001-2002 Winter Season) show that moderate snowmobile visitation occurred on February 13, 2002, with 950 entries, and the month's and season's peak snowmobile visitation occurred on February 16, 2002, with 1515 entries (Figure 4). The majority of these vehicles are assumed to have been 2-stroke machines. The data also indicate that snowcoach entries into the Park on these days were slightly above the daily average for this month (Table 2).

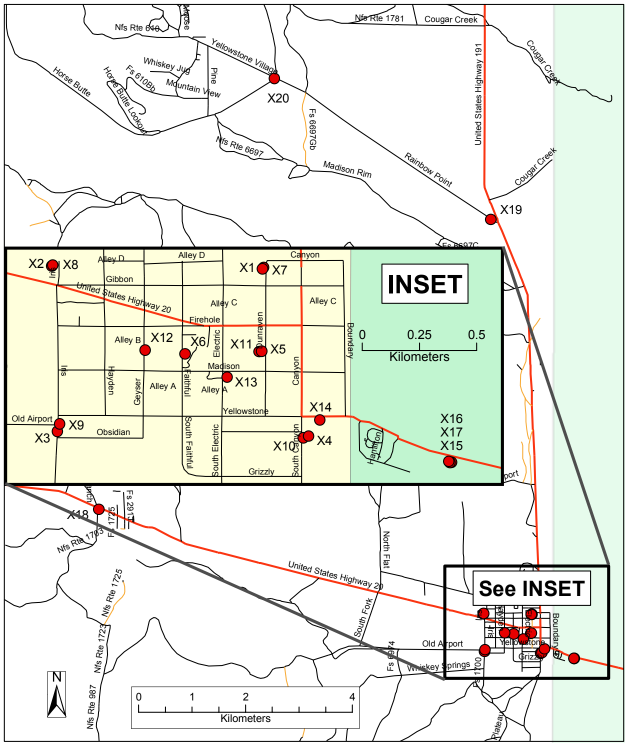

**Figure 2.** Sample sites within and around West Yellowstone, MT.

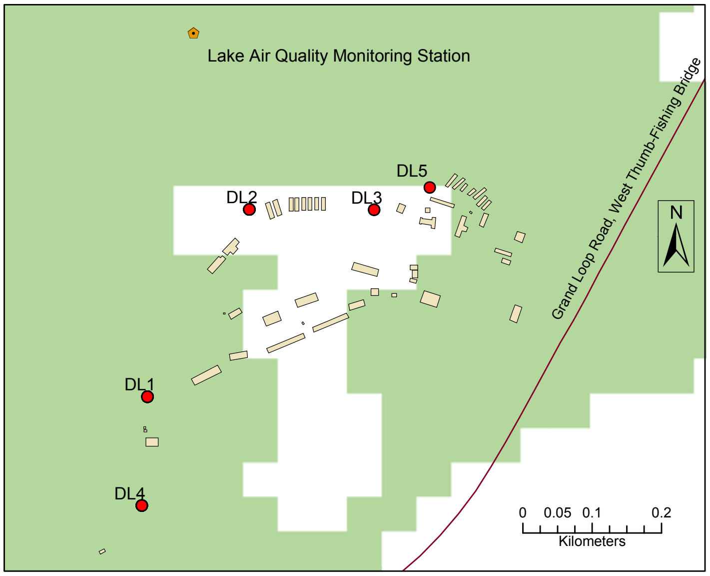

**Figure 3**. Lake R.S. Diurnal Site.

Two hundred and eighteen whole air samples were collected in 1-liter silica lined canisters (Entech Instruments, Simi Valley, CA) and 2-liter electropolished stainless steel canisters (University of California, Irvine, CA). Canisters were prepared at UNH and were first flushed with ultra-high purity (UHP) helium and then evacuated to 1 x $10^{-2}$ torr. The UHP helium was cold trapped cryogenically (passed through an activated charcoal/molecular sieve

(13X) trap immersed in liquid nitrogen) to ensure no contamination from the regulator attached to the cylinder. The canisters were then humidified with 10.0 torr of ultra-pure water vapor because low relative humidity air was expected to be sampled in the Park. Humidification of the sample canisters was necessary to alleviate/minimize surface adsorption of various gases under the low relative humidity conditions. The morning sample collection periods began at 5 a.m. prior to the initiation of significant oversnow travel and solar loading which can influence the photochemical processing of atmospheric trace gases. Afternoon sampling began at approximately solar noon (i.e., 12:00 p.m. Mountain Standard Time) and extended over a 4-5 hour period of time during which significant oversnow travel had occurred. Due to the apportionment of 3-4 sample sites per field sampler and the need for the acquisition of both off-road and near-road samples, each sample route or course required a maximum period of 5 hours to complete.

**Table 2.** Yellowstone N.P. Park snowcoach entry data, February 13 & 16, 2002.*

| **Date** | **N. Entrance** | **W. Entrance** | **S. Entrance** | **E. Entrance** |
|---|---|---|---|---|
| 2/13/2002 | **1** / 3.25 | **10** / 11.36 | **5** / 5.93 | **0** / 0 / 0 |
| 2/16/2002 | **0** / 3.25 | **13** / 11.36 | **5** / 5.93 | **0** / 0 / 0 |

*Figures reflect daily data / calculated daily average for February, 2002, based on monthly entrance data reported by the Visitor Services Office, Yellowstone National Park [Available: http://www.nps.gov/yell/stats/index.htm].

The protocol for the collection of well mixed whole air sample for trace gas analysis was carefully followed by each field sampler. All samples were to be collected following a period of several minutes after the shutdown of any research vehicle, and near-road samples were acquired at a distance of not less than 50+ m from upwind of all local vehicles and transportation routes. The upwind direction for sampling was determined by the field sampler at each of the sampling locations. The main objective for collecting upwind samples was to try and alleviate direct emission plumes on the roadways and to evaluate the large-scale impact of snowmobile emissions from samples representative of well mixed air masses. For each sample, the canister's valve port was flushed and the canister slowly filled in such a way as to ensure that the contents would be representative of the larger volume of ambient air surrounding the site. This required that the researcher slowly walk in an upwind direction with the canister held above eye-level to ensure that a fresh stream of ambient air be encountered by the valve port. At each site the location at which the valve was first opened was determined with the use of a Trimble® GeoExplorer3 Global Positioning System (GPS) receiver/data logger, and these data as well as other site and collection data were logged. The use of Lowrance® GlobalMap (Model No.100) GPS units permitted the acquisition of supplementary location data which were manually recorded on data forms together with the basic site data for backup purposes. The Lowrance units also permitted accurate determination of near-road and off-road distances from roads at each site. Off-road samples were acquired some 500 m in an upwind direction from transportation routes, and near-road samples were acquired at each site at a position within 100 m of the nearest road in order to assess the influence of distance from nearest road on pollutant levels. In the event surface winds were observed to have been moving parallel to the road adjacent to a sample site, the sample would have been acquired from a point 500 and 50+ m from the road, as indicated above, but in an upwind direction of the snowmobile utilized by the particular sampler.

## 2.3 Field Conditions

Ground surface conditions during the study period were characterized by snow cover at all but one site (A1). However, owing to warmer than average conditions during the weeks prior to and during this time large patches of snow free road surfaces were observed between Madison Junction and Old Faithful, Norris Junction and Mammoth Hot Springs, and on the north shore of Yellowstone Lake adjacent to geothermal features there. Snow depths ranged from 125 cm (50 in) at Snake River to patchy cover at Mammoth [*National Park Service*, 2003]. Due to the higher than average temperatures and associated snow losses on park roads, road closures on Saturday (2/15/2003) that would have severely limited oversnow travel in the West Yellowstone area were threatened. The closures were not implemented and significant oversnow traffic occurred but at levels considerably lower than for 2002 (Figure 5).

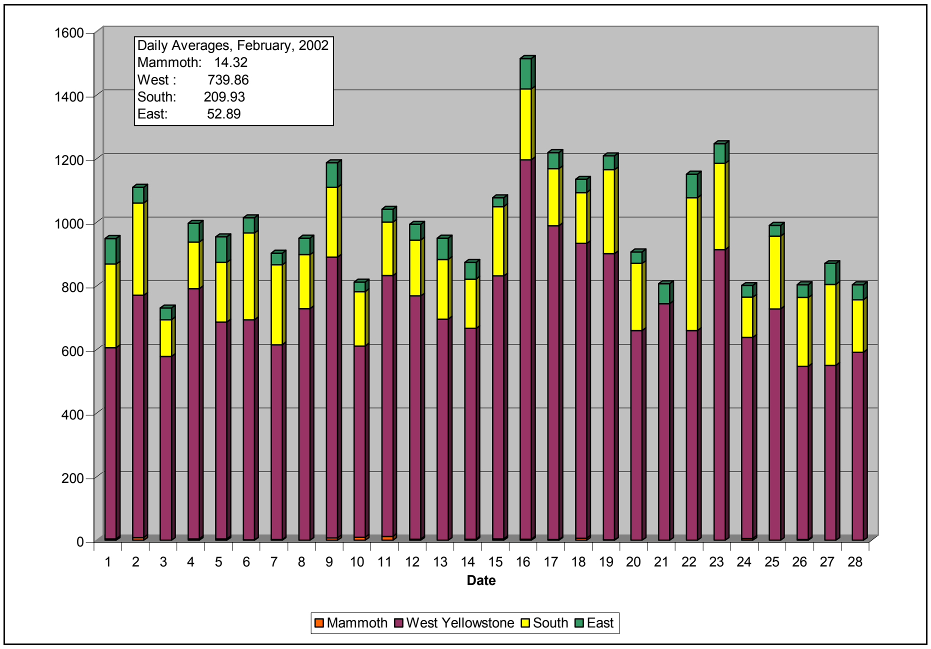

**Figure 4.** Yellowstone N.P. snowmobile entries, February, 2002.

The week bracketing the field sampling was dominated by high pressure in YNP. Upper air soundings to assess vertical stability of the atmosphere and potential for constraints on vertical mixing and air transport were acquired with the use of 2 meter diameter meteorological balloons equipped with radiosondes operating at 404.6 MHz during the sampling periods to determine boundary layer altitudes in the study area. The balloons, sondes (Model IS-5A-40XX), and receiver are instruments produced by Atmospheric Instrumentation Research, Inc., and the data were downloaded to a Compaq LTE Lite 4/33C laptop computer in carrier frequency mode.

Through the period 12:00 a.m. on Wednesday, February 12, to 9:00 p.m. on Saturday, February 15, surface temperatures ranged from -22.2 $^{o}$C (-8.0 $^{o}$F) to approximately 0 $^{o}$C (32 $^{o}$F) at the Yellowtone Lake National Weather Service monitoring station (KP60). Surface conditions on Wednesday were considerably colder than on Saturday owing to clearer skies that permitted the escape of long-wave radiation. Atmospheric conditions on Wednesday were characterized by thermally stable, anticyclonic conditions with a broad ridge over the western U.S. Satellite imagery indicated cloud free conditions in general with a small patch of low clouds in the northwest corner of the Park. The skies remained cloud free all day over the observation site at

Lake Ranger Station. The anticyclonic ridge extended throughout the depth of the troposphere with its northwest to southeast trending axis located to the west of the Park. This produced weak northwesterly winds over the area with the polar jet stream positioned well to the south over central Colorado. Surface winds during the day were almost entirely absent. Conditions on Sunday, February 16, in West Yellowstone were characterized by temperatures that were just below freezing and moderate velocity sustained winds associated with a weak winter storm that had developed that morning.

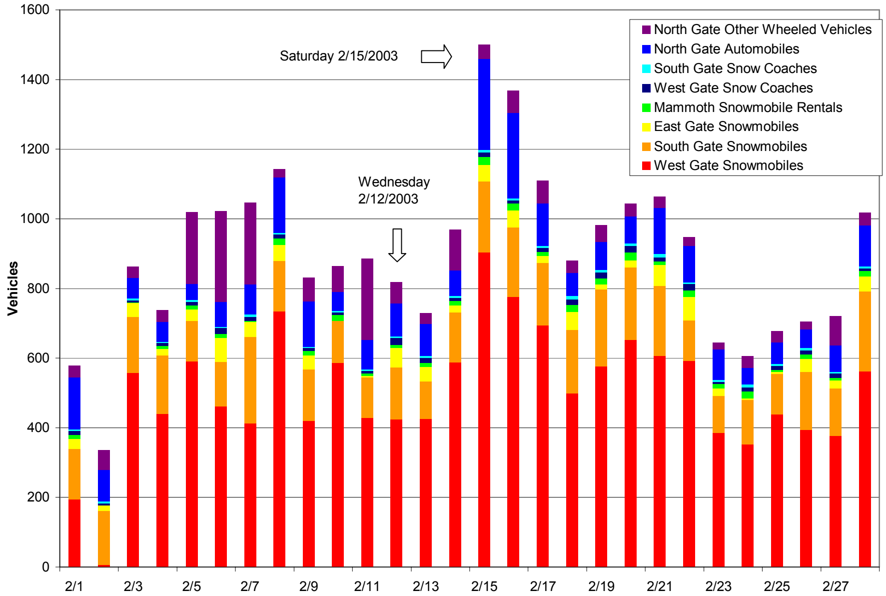

**Figure 5.** Yellowstone N.P. vehicle entries, February, 2003.

The upper air soundings are presented as graphs (Figures 6a-d) of potential temperature (PT) versus height above ground level in meters (m AGL). Temperature inversions are identified by a strong increase of PT with height. Soundings were made at 6:00 a.m., 1:00 p.m., and 4:00 p.m. to coincide with the collection of air samples. Equipment malfunction on Wednesday limited the collection of data to 1:00 p.m. only when a truncated sounding was made. Surface observations at Lake Ranger Station and a National Weather Service sounding taken at Riverton, WY (about 240 km southeast of Lake R.S.), both indicate the presence of a shallow but strong surface nocturnal inversion at 6:00 a.m. on Wednesday (2/12/2003). This was produced by strong radiative cooling under clear sky conditions at night. Significant surface warming took place in the morning during which time the surface temperature increased from -19.4 $^{o}$C (-3 $^{o}$F) at 6:00 a.m. to -4.4 $^{o}$C (24 $^{o}$F) at 1:00 p.m. This would allow for some vertical mixing to take place during the day. Vertical mixing in the boundary layer probably did not begin until about 12 noon owing to the extremely strong surface based inversion. Based on the vertical profile of PT the depth of the mixing layer was estimated to be about 100 m. If we allow for a 1.1 $^{o}$C (2 $^{o}$F) variation in surface temperature over the region, the mixing could have extended to a maximum height of 150 m AGL, but not beyond. At this elevation there was a shallow isothermal layer (where temperature is constant with height) which probably would have been sufficient to cap the warmest thermals leaving the surface. In the unlikely event that this cap was penetrated, the base of the subsidence inversion produced by the anticyclone was 257 m AGL. This would represent the absolute maximum depth of the mixing layer for the day. The Wednesday 1:00 p.m. sounding (Figure 6a) shows the temperature inversion near 250 m AGL that was produced by large scale subsiding air within the anticyclone. The base of the temperature inversion inhibits the vertical penetration of thermals leaving the surface, and thereby acts as a cap which acts to concentrate pollutants within the boundary layer (surface to inversion base).

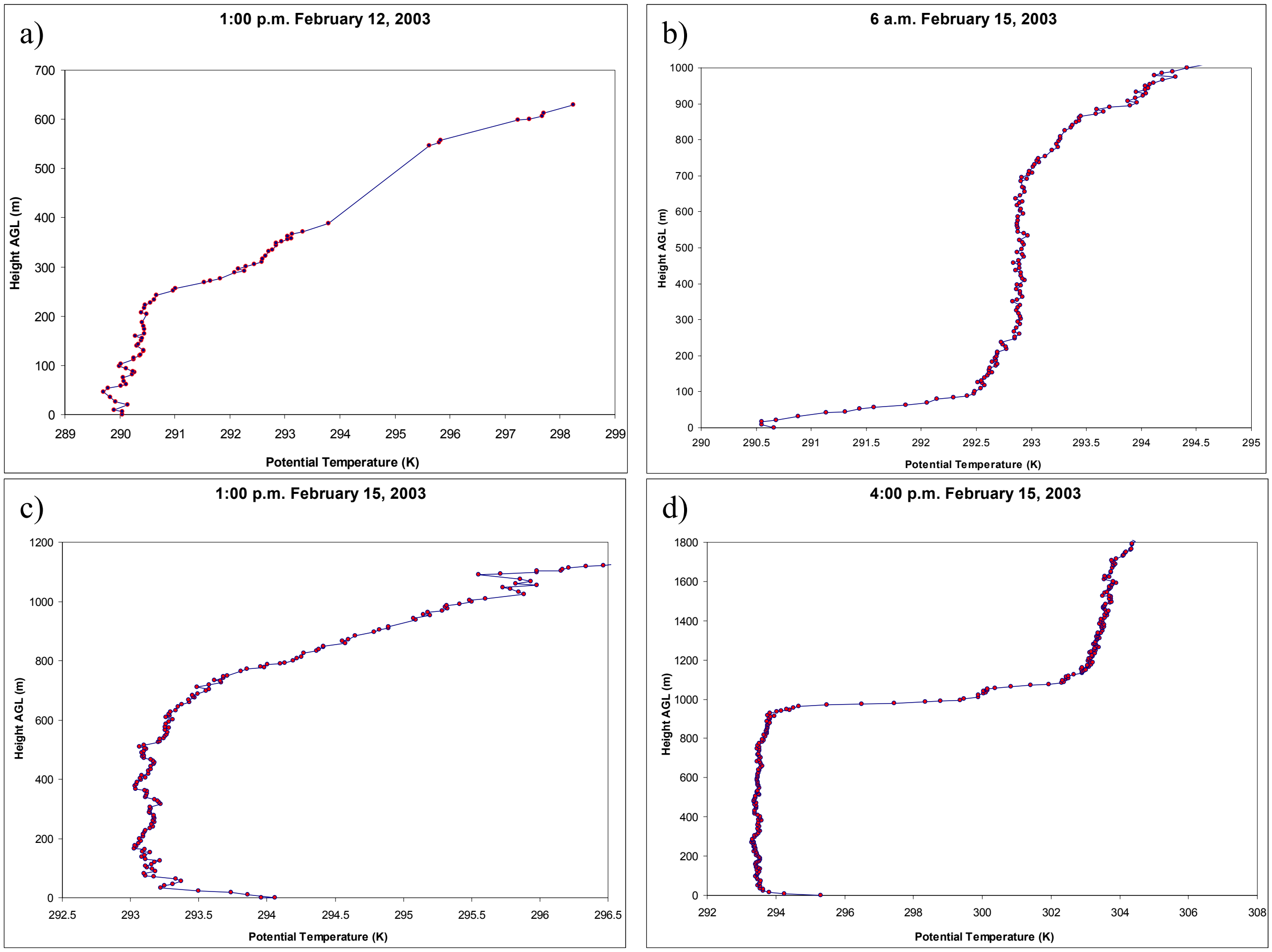

**Figure 6.** Atmospheric soundings, Lake R.S. (WED2003 & SAT2003).

Meteorology on Saturday was still dominated by the persistent upper ridge over the western US. The polar jet stream had shifted into Utah and central Arizona but winds throughout the troposphere over the study area remained weak. Windspeeds at the surface were generally less than 5 knots in strength. Skies were overcast throughout the region during the air sampling periods with satellite imagery indicating a shallow stratus cloud deck that was verified by ground observations in the Park. The cloud deck was capped by a subsidence inversion which is typical of anticyclonic conditions. Radiative cooling from the cloud top likely contributed to the partial breakup of the cloud deck, transforming it into a deck of shallow stratocumulus by 4:00 p.m. Soundings were taken at 6:00 a.m., 1:00 p.m., and 4:00 p.m. with a full retrieval of data. The temperature profiles were quite different from Wednesday due to the presence of the cloud cover which reduced the strength of the surface nocturnal inversion and significantly reduced the diurnal temperature range.

The profiles of PT for Saturday (Figures 6b-d) clearly indicate the subsidence inversion where the PT increases dramatically with height. They also indicate that the inversion increased in strength during the day as a result of the large scale subsidence. These soundings were checked for consistency with the National Weather Service soundings at Riverton, and with numerical forecast fields from the Eta model[7] for the region. All three sources confirmed not only the height but also the change in inversion strength throughout the day.

The profile for Saturday 6:00 a.m. (Figure 6b) shows a weak surface based inversion with a depth of 88 m. With calm winds at this time no vertical mixing would be expected to take place. The ceiling could not be visually estimated at this time of day but the sounding indicates a cloud top at 1230 m AGL with a jump in temperature, and a cloud base near 850 m AGL yielding a cloud depth of 380 m. By 1:00 p.m. the surface based inversion disappeared giving way to a nearly dry adiabatic (constant PT with height) sub-cloud layer. In the 1:00 p.m. sounding thermals leaving the surface would reach 720 m AGL. The ceiling was estimated visually at 763 m AGL. At 4:00 p.m. the sounding indicates that vertical mixing would extend to 995 m AGL which is the approximate level of cloud top at this time.

## 2.4 Trace Gas Measurements

### 2.4.1 Analytical System and Sample Analysis for NMHCs, Halocarbons and Alkyl Nitrates

Measurements of $C_2$-$C_{10}$ NMHCs, $C_1$-$C_2$ halocarbons, $C_1$-$C_5$ alkyl nitrates, CO and $CH_4$ were made from the whole air samples collected throughout the study region. The 218 whole air samples and 10 exhaust samples were collected in 1-liter silica lined canisters (Entech Instruments, Simi Valley, CA) and 2-liter electropolished stainless steel canisters (University of California, Irvine, CA). The canisters were filled to ambient pressure in the field and then were returned to the laboratory for analysis by gas chromatography using flame ionization and electron capture detection. The high-precision analytical system was capable of identifying and quantifying a large suite of compounds, with the 87 gases measured from the canisters listed in Table 3.

The analytical system utilized three Shimadzu GC17-A gas chromatographs (GCs). The samples were analyzed by trapping 1000 cc (STP) of air from the 2-liter canisters (650 cc (STP) of air for the 1-liter canisters) on a preconcentration loop, a 1/4-inch O.D. Silicosteel (Restek Corporation, Bellfonte, PA) loop filled with 1 mm diameter glass beads, immersed in liquid nitrogen. The 192 2-liter canisters were analyzed separately from the 26 1-liter canisters because of the difference in volume. The total volume sampled was measured by pressure difference using a capacitance manometer. After the sample was trapped, the preconcentration loop was isolated and warmed to 80 $^{o}$C. When the three GCs reached their initial temperatures, the sample was injected. Helium carrier gas flushed the contents of the loop and the stream was then quantitatively split into four, with each sub-stream feeding a separate GC column. One 25m x 0.53 mm I.D., 10 μm film thickness $A1_2O_3/Na_2SO_4$ PLOT column, one 30 m x 0.32 mm I.D., 0.25 μm film thickness Cyclodex-B, one 60 m x 0.25 mm I.D., 1 μm film thickness OV-1701 column and one 60 m x 0.25 mm I.D., 1.4 μm film thickness OV-624 columns were used for the trace gas separation. The OV-624 column was plumbed into an electron capture detector (ECD) and separated approximately 20 $C_1$-$C_2$ halocarbons. The OV-1701 column was also connected to an ECD and was used primarily for alkyl nitrate separation, but also provided duplicate measurements of several of the halocarbons. The PLOT column was connected to a flame ionization detector (FID) and separated the $C_2$-$C_6$ NMHCs while the Cyclodex-B column, also plumbed to an FID, was used for separating the $C_6$-$C_{10}$ NMHCs. It is also worth noting that the Cyclodex-B column is unique in its ability to resolve all three isomers of the xylenes as well as

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[7] The primary weather forecasting model developed by the National Oceanic and Atmospheric Administration.

the enantiomeric pairs of most chiral compounds [*Sive*, 1998; *Allahverdiev et al.*, 1999]. The gas separation was unique for each of the columns, and thus, any gases co-eluting on one column were usually resolved on another.

**Table 3.** The list of 87 gases quantified for the whole air samples collected in YNP.

| **NMHCs** | **NMHCs** | **Halocarbons** |
|---|---|---|
| ethane | trans-2-hexene | $CCl_2F_2$ (CFC-12) |
| ethene | cis-2-hexene | $C_2Cl_2F_4$ (CFC-114) |
| ethyne | methylcyclohexane | $CCl_2FCClF_2$ (CFC-113) |
| propane | 2,4-dimethylpentane | $CH_3Cl$ |
| propene | 2,3-dimethylpentane | $CH_2Cl_2$ |
| i-butane | 2-methylhexane | $CHCl_3$ |
| n-butane | 3-methylhexane | $CCl_4$ |
| 1-butene | n-heptane | $CH_3CCl_3$ |
| i-butene | toluene | $CHClCCl_2$ |
| trans-2-butene | n-octane | $CCl_2CCl_2$ |
| cis-2-butene | 2,2,4-trimethylpentane | $CH_3Br$ |
| cyclopentane | 2,3,4-trimethylpentane | $CH_2Br_2$ |
| cyclopentene | 2-methylheptane | $CHBr_3$ |
| i-pentane | 3-methylheptane | $CH_3I$ |
| n-pentane | p-xylene | $CHBrCl_2$ |
| 1-pentene | m-xylene | $CBrClF_2$ (H-1211) |
| trans-2-pentene | o-xylene | $CBrF_3$ (H-1301) |
| cis-2-pentene | ethylbenzene | $CBrF_2CBrF_2$ (H-2402) |
| 2-methyl-2-butene | styrene | **Alkyl Nitrates** |
| 3-methyl-1-butene | i-propylbenzene | $C_2H_5ONO_2$ |
| isoprene | n-propylbenzene | 1-$C_3H_7ONO_2$ |
| methylcyclopentane | 3-ethyltoluene | 2-$C_3H_7ONO_2$ |
| cyclohexane | 1,2,3-trimethylbenzene | 2-$C_4H_9ONO_2$ |
| 2,2-dimethylbutane | 1,2,4-trimethylbenzene | 2-$C_5H_{11}ONO_2$ |
| 2,3-dimethylbutane | 1,3,5-trimethylbenzene | 3-$C_5H_{11}ONO_2$ |
| 2-methylpentane | 1,3-diethylbenzene | $CH_3ONO_2$ |
| 3-methylpentane | 1,4-diethylbenzene | |
| n-hexane | $\alpha$-pinene | **Others** |
| 1-hexene | $\beta$-pinene | CO |
| benzene | n-decane | $CH_4$ |

For the standard analysis protocol, two different whole air working standards were assayed alternately every fifth analysis. The standards were used to monitor any drift of the analytical system and to quantify the gases reported in Table 3. The measurement precision for the $C_2$-$C_6$ NMHCs ranged from 0.4-3% while the precision for the $C_7$-$C_{10}$ NMHCs varied from 2-10%. For the halocarbons and alkyl nitrates, the measurement precision ranged from 1-10%.

Once the samples were assayed, the stored chromatograms were individually inspected and the reports from the chromatograms were summarized and checked for any inconsistencies. The data will be archived for public access on a website at UNH after manuscripts have been submitted for publication. However, the data is currently available for use by the NPS.

### 2.4.2 Standards and Calibrations for NMHCs, Halocarbons and Alkyl Nitrates

The preparation of standards for NMHCs and halocarbons has been discussed in detail in the Ph.D. dissertation of *Sive* [1998] and references therein. For the halocarbons, the mixing ratio range of the whole air standards used falls between 0.1 and 600 pptv (parts per trillion by volume). For the alkyl nitrate calibrations, the whole air standards used contain background levels of these gases and were calibrated against whole air standards at the University of California, Irvine (UCI) and synthetic standards prepared at the National Center for Atmospheric Research. The concentration accuracy for these gases are between 1-10%.

Calibration of the NMHC compounds has been achieved by employing Scott calibration gases available in the 1-100 ppmv mixing ratio range. A NIST propane standard with an absolute accuracy of 0.99±0.0l ppmv (parts per million by volume) was also used in the preparation of standards. In order to simulate whole air characteristics, a known amount of a particular calibration gas is added to a known amount of a previously assayed clean whole air sample. These samples contain background levels of ethane and are usually devoid of any other hydrocarbons, except methane. After adding the Scott standards, the augmented air sample concentrations are calculated. In this manner, standards have been prepared over a wide range of concentrations which are then used as primary standards for calibrating 36-liter pressurized whole air working standards collected at White Mountain Research Station, Bishop, CA. The overall accuracy of the $C_2$-$C_{10}$ NMHC calibrations are between 0.2-5%.

The Principal Investigator, B. Sive, has participated in all five tasks of the National Science Foundation sponsored Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE). Results from each task demonstrate that our analytical procedures consistently yield accurate identification of a wide range of unknown hydrocarbons and produce excellent quantitative results [*Apel et al.,* 1994, 1999, 2003; *Sive*, 1998]. For further information regarding the NOMHICE results, the public is encouraged to examine *Sive* [1998] (available upon request).

Each of the whole air working standards used in this project are part of a larger network of whole air standards maintained by B. Sive at UNH as part of the AIRMAP program (see http://www.airmap.unh.edu/). Additionally, these high-pressure pontoons are periodically compared with standards from D. Blake at UCI for NMHCs, halocarbons and alkyl nitrates. Comparing standards helps ensure that measurements from the different research groups will be on the same calibration scale, making it possible to meaningfully compare data sets obtained at YNP with other data sets generated by UCI and various other research groups throughout the world.

### 2.4.3 Methane and Carbon Monoxide

Two additional analyses were performed on the canister samples for $CH_4$ and CO by D. Blake at UCI. The following describes their analytical procedures.

The $CH_4$ mixing ratio within each sample was determined by gas chromatography (HP-5890A) using flame ionization detection. The use of primary calibration standards dating back to late 1977 ensures that our measurements are internally consistent. The $CH_4$ mixing ratios are reported for dry air, and are made relative to a primary standard purchased from the Matheson Gas Company in 1977 and to a National Bureau of Standards (now the National Institute of Standards and Technology (NIST)) standard purchased in August, 1982. The overall uncertainty in the NBS standard is ± 1%. The sample size for the $CH_4$ analysis was 5cc (STP). The analytical precision was determined from inter-sample comparisons that were obtained by alternating measurements of secondary standards with aliquots from an individual air sample. The analytical precision for the $CH_4$ analyses was better than 2 ppbv.

Carbon monoxide mixing ratios were determined by reducing CO to $CH_4$ using a heated Pt catalyst. The $CH_4$ was then detected by flame ionization on an HP-5890A GC. The sample size for ambient air was 50 cc (STP) and samples and calibration standards were run alternately. Each chromatogram was individually inspected to insure baseline integration was accurate. The primary standards were prepared by NIST and Scott Specialty Gases. The measurement precision for the CO analysis was ± 1% and the overall measurement accuracy was 5%.

### 2.4.4 Ozone, NO, NOy, and CN

Ozone was measured using a Thermo Environmental Instruments model 49C-PS which is based on UV photometric detection at 254 nm. The limit of detection was ~1.0 ppbv. Instrument calibration was achieved routinely utilizing an internal primary $O_3$ source. Total reactive nitrogen (NOy) and nitric oxide (NO) were measured using a custom modified Thermo Environmental Instruments model 42C. A molybdenum converter heated to 350 ± 0.5°C was used to reduce NOy compounds to NO, which was subsequently measured by $NO_2$ chemiluminescence. The conversion efficiency was found to be 100% for 50 ppbv $HNO_3$ added from an airborne quality permeation source [*Talbot et al.*, 2000]. In the field, conversion efficiency was checked by passing ~25 ppbv of isopropyl nitrate through the converter. This $NO_y$ compound is relatively difficult to convert and is a good overall check on converter performance [*Bradshaw et al.*, 1998]. Cylinders of previously analyzed ultra zero air were used for zeroing and dilution of a ~50 ppbv NO standard (Scott Marrin, Inc., ±2% NIST certified) to the 1-10 ppbv range for calibration. Zeroing and calibration procedures were conducted every 12 hours. Additionally, a TSI Model 3022A general-purpose Condensation Nuclei (CN) counter was used to detect airborne particles $\geq$ 7 nm in diameter and reported concentrations in particles/cm$^3$. All instrument operations and data acquisition protocols are controlled automatically using National Instruments hardware and software. One minute averaged data were obtained from the Lake R.S. site.

### 2.5 Spatial Analyses

The geographic locations of sample sites were logged with Trimble® GeoExplorer3 GPS devices. Positions constituting individual locations were downloaded into Trimble's® GPS Pathfinder Office software (Ver. 2.80) upon the completion of sample collection and were subjected to differential correction via post-processing utilizing base station data for the CORS site at Mammoth, WY (44º 58' 24.240000" N Lat.; 110º 41' 21.119998" W Long.), the Leon Johnson Hall Base Station at Montana State University's GPS Laboratory in Bozeman, MT (45º 40' 05.03467" N Lat.; 111º 02' 59.66511" W Long.) that were downloaded through the internet. The 68% (1 standard deviation) horizontal accuracy levels for all sample points generally fell under 2 m, and did not exceed 3.1 m. To permit the mapping and spatial analysis of air samples, VOC data for each day's AM and PM sample period were merged with the post-processed and spatially merged GPS data in the GIS environment (i.e., ArcGIS 8.3 published by ESRI®). All data were projected in Universal Transverse Mercator (1983 North American Datum) units for integration with existing YNP spatial data. The resultant maps (Figures 17-36) portray the mixing ratios in parts per trillion by volume (pptv) of the selected VOCs (exluding CO which is reported in parts per billion by volume (ppbv), and methane in parts per million by volume (ppmv)). Owing to the coarse spatial resolution of the data, VOC concentrations are portrayed cartographically with scaled or graduated point symbols rather than a continuous interpolated or geostatistical surface. Geostatistical surfaces were created in the lab for the gases CO and benzene using simple kriging techniques, however, the coarse resolution of the data and limited sample points produced surfaces that did not appear to represent the data well and these were not included.

## 3. Results and Discussion

A total of 218 whole air samples collected in YNP were analyzed for 85 different VOCs (60 NMHCs, 18 halocarbons, 7 alkyl nitrates) in addition to CO and $CH_4$. Additional measurements made by our research group included $O_3$, NO, NOy and particles (CN) at the Lake R.S. sampling site. In this section, we present our results from the work conducted in February, 2003.

### 3.1 Exhaust Samples

Exhaust samples were collected from various 2-stroke, 4-stroke and diesel engines in oversnow vehicles used throughout the Park in order to compare the composition of the exhaust emissions for the three different engine types. This type of source "fingerprinting" enables us to assess the influence of each engine type on the air mass composition for the ambient samples collected throughout the Park. A complete list of the oversnow vehicles sampled is listed in Table 4.

**Table 4.** Oversnow vehicles and conditions from which exhaust samples were collected.

| Collection Date | Sample Information | Engine Type |
|---|---|---|
| 2/14/03 | 2001 Polaris 550 fan cooled (Park Ranger), idle, hot engine | 2-Stroke |
| 2/16/03 | Polaris 550 Fan Cooled Super Sport, idle, hot engine | 2-Stroke |
| 2/14/03 | 1998 Summit X Ski-doo, water cooled, 3500 RPM | 2-Stroke |
| 2/14/03 | 2003 Polaris 500 Classic Touring Liquid Cooled, 3500 RPM | 2-Stroke |
| 2/14/03 | 1978 Bombadier snowcoach w/ 350 Chevy, idle | 4-Stroke |
| 2/15/03 | 2002 Polaris Fuel Injected 4-stroke; 3500 RPM | 4-Stroke |
| 2/16/03 | Polaris Frontier 4 Stroke Edge 136, idle, hot engine | 4-Stroke |
| 2/14/03 | Artic Cat 660, sample @ 3500 RPM | 4-Stroke |
| 2/16/03 | NPS Ford Power Stroke V-8 Sno-Van, 4000 RPM | Diesel |
| 2/15/03 | Lake Snowcat, idle | Diesel |

The exhaust samples were collected in 1-liter silica lined canisters from random snowmobiles that, in most cases, had just completed a transit from West Yellowstone to Old Faithful. For a portion of the snowmobiles (Table 4), the samples were collected at 3500 RPM, which corresponded to the estimated average revolutions per minute (RPM) for each engine during the transit. Although engine loading is not accurately simulated in this fashion, these samples are useful in determining relative emissions of speciated VOCs. Additionally, some samples were also collected from snowmobiles that were running idle with the engine still "hot" in order to determine if there was a difference in emissions between these conditions. These samples are significant and more accurately represent emissions when visitors in the Park pull over/stop to view the scenery and wildlife in the Park without turning off their oversnow vehicles. For idle sample collection, the canister was placed directly into the exhaust stream exiting the tailpipe of each engine and filled to ambient pressure while the engine was idling. For samples collected at 3500 RPM (4000 RPM in the case of the NPS Sno-Van), the brake was applied and the engine was held at the appropriate RPM while the canister was placed directly into the exhaust stream exiting the tailpipe and filled to ambient pressure A 0.5 $cm^3$ (STP) aliquot of each exhaust sample was analyzed by direct injection using the analytical system described previously. From the chromatographic data obtained for these samples, the mixing ratios for 60 different NMHCs were determined for each engine type. Results from the exhaust sample analyses indicate that the vehicles sampled had very different exhaust compositions for each of the different engine types. The emission ratios for a subset of the NMHCs (ppmv) relative to CO (ppmv) for the 2-stroke, 4-stroke and diesel engines are illustrated in Figure 7. Emission ratios relative to CO are commonly employed (i.e., *Blake et al.*,1996, *Lobert et al.*, 1991), and is appropriate for this analysis because of the inefficiency of the combustion processes associated with internal combustion engines where relatively large amounts of CO, $CH_4$ and NMHCs are produced/emitted in reduced chemical states.

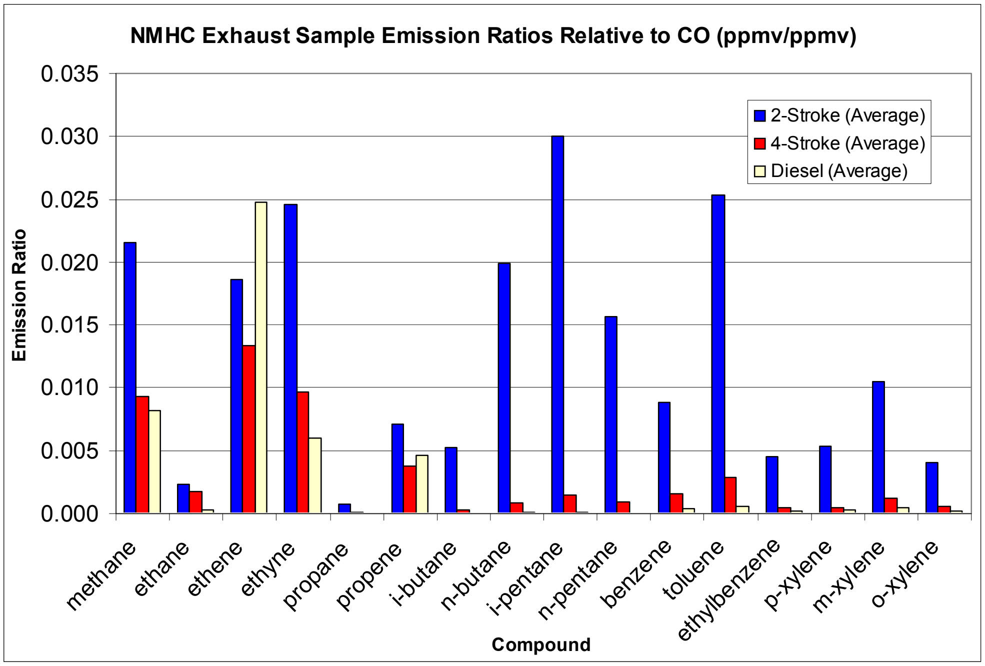


**Figure 7.** Average NMHC exhaust emission ratios relative to CO (ppmv/ppmv) for 2-stroke, 4-stroke and diesel engines.

The average emission ratios relative to CO for the 2-stroke engine are significantly larger for all of the reported compounds (Figure 7). Average emission ratios were used for this comparison because there were only very minor differences in the exhaust composition between samples collected from idling engines and the samples collected while the engine was revved to the appropriate RPM (not shown). Additionally, the composition of the exhaust sample from the Bombadier snowcoach sampled was similar to the 4-stroke snowmobiles and is included with the 4-stroke category. The i-pentane and toluene emissions dominated the 2-stroke engine exhaust samples (approximately 20 and 9 times larger than the four-stroke engine, respectively), but relatively large amounts of ethene, ethyne, n-butane and n-pentane were also present in the 2-stroke exhaust samples. For all three engine types, only a small fraction of the exhaust consisted of ethane, propane, propene and i-butane. With regard to air toxic emissions (i.e., benzene, toluene, ethylbenzene and xylenes), the 2-stroke engine emitted significantly larger quantities of these gases then either the 4-stroke or diesel engines. Additionally, the relative emission ratios in the exhaust samples collected in 2003 are consistent and show the same pattern as the exhaust samples collected by our research group in 2002.

### 3.2 General Distributions of VOCs

The distribution of VOCs observed in YNP during February 2003 provides striking evidence of the influence of anthropogenic emissions on the air quality throughout the Park region. This section presents and compares the general distributions and trends of NMHCs, halocarbons, and alkyl nitrates at 1) near-road and off-road sampling sites, 2) Lake R.S., and 3) West Yellowstone, MT. Additionally, air mass processing, hydroxyl radical (OH) reactivity, and diurnal trends are discussed. Finally, the results from the 2003 winter campaign are compared to the results obtained in 2002 as well as measurements from other remote sites along the U.S. west coast in March 2002 (data provided by D. Blake, UCI). The UCI data set represents background mixing ratios for the west coast during the same time of year and at similar latitudes as the Park. This data is included to serve as a comparison of well processed air to that of the air sampled in the Park, which should resemble a remote atmosphere.

In general, background mixing ratios of most reactive gases, particularly NMHCs, were lower during the 2003 sampling campaign as compared to the measurements made during 2002 in the Park. The seasonal mean geopotential heights at 850 mbar (not shown) and 500 mbar show that the winter trough over North America was markedly deeper and more distinct during the winter of 2003 (Figure 8). In 2003, the 500 mbar geopotential height contour of 5500 m extended southward to Washington D.C. (39ºN latitude) and then curved northward forming a ridge along the west coast of Canada. This positioning indicates strong meridional flow in the free troposphere in winter 2003, facilitating southward transport of Arctic air masses. The trough in winter 2002 was shallow without a ridge-trough pattern at 850 mbar or 500 mbar and the geopotential height contour of 5500 m at 500 mbar only reached central Massachusetts (42.5ºN latitude). Consequently, more zonal flow occurred reducing the possibility of a high latitude (>50ºN) influence on air masses sampled the previous year. In 2003, Yellowstone was located on the margin of the meriodional flow and was likely under the influence of more pristine Arctic air masses resulting in lower background mixing ratios for many of the shorter lived NMHCs than measured in 2002. Nonetheless, the west coast data from UCI (2002), in addition to our YNP 2002 data, provides useful information and insight with regard to remote samples and background mixing ratios for samples collected at similar latitudes.

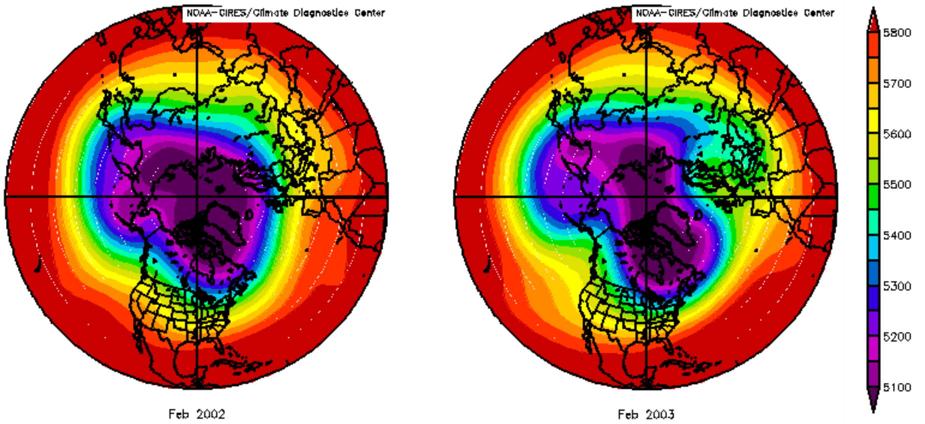


**Figure 8.** The 500 mbar composites for February 2002 and 2003 showing the winter troughs over North America.

### 3.2.1 Alkyl Nitrate Distributions

Alkyl nitrates ($RONO_2$) are photochemically produced compounds resulting from the oxidation of alkanes by OH in the presence of nitrogen oxides. Therefore, as photochemical processing of an air mass occurs and it becomes more "aged", alkyl nitrate mixing ratios will increase [*Bertman et al.*, 1993; *Simpson et al.*, 2003]. Alkyl nitrates provide information on the photochemical history of air mass as well as NMHC-$\mathrm{NO_x}$-$\mathrm{O_3}$ photochemistry [*Roberts et al.*, 1998; *Bertman et al.*, 1995; *Stroud et al.*, 2001; *Flocke et al.*, 1998]. This information is useful for analyzing the measurements from YNP because it can describe the influence of local and distant pollution sources, the relative age of emissions in the park, and the distribution and sources of the parent alkanes.

The most abundant alkyl nitrates throughout YNP on both February 12 and 15, 2003, were i-propyl nitrate (i-$\mathrm{PrONO_2}$) (mean = 5.6 pptv) and 2-butyl nitrate (2-$\mathrm{BuONO_2}$) (mean = 6.1 pptv) comprising approximately 60% of the total $\mathrm{RONO_2}$ ($\Sigma\mathrm{RONO_2}$) (Figure 9, Table 5). This is consistent with a predominantly anthropogenic source of alkyl nitrates. Propane, the parent alkane of i-$\mathrm{PrONO_2}$, is used throughout the Park as fuel for cooking and heating, while n-butane, the parent alkane of 2-$\mathrm{BuONO_2}$, is a major component of 2-stroke engine exhaust (Figure 7). In addition, i-$\mathrm{PrONO_2}$ and 2-$\mathrm{BuONO_2}$ have been found to be the most abundant alkyl nitrates in numerous other regions in the Northern Hemisphere, such as the North Atlantic [*Roberts et al.*, 1998], the eastern U.S. [*Bertman et al.*, 1995], Colorado [*Stroud et al.*, 2001], the western Pacific [*Simpson et al.*, 2003] and Germany [*Flocke et al.*, 1998]. Methyl nitrate ($\mathrm{MeONO_2}$) also represented a significant amount of $\Sigma\mathrm{RONO_2}$, ~ 15%. $\mathrm{MeONO_2}$ is typically associated with having an oceanic source [e.g. *Blake et al.*, 2003]. However, the enhanced $\mathrm{MeONO_2}$ observed in YNP points toward an anthropogenic source, particularly as is a component of 2-stroke engine exhaust. The remaining alkyl nitrates, ethyl nitrate ($\mathrm{EtONO_2}$), 2-pentyl nitrate (2-$\mathrm{PenONO_2}$), 3-pentyl nitrate (3-$\mathrm{PenONO_2}$), and n-propyl nitrate (n-$\mathrm{PrONO_2}$), each accounted for 10% or less of the total $\mathrm{RONO_2}$ ($\Sigma\mathrm{RONO_2}$). In addition, $\Sigma\mathrm{RONO_2}$ was, on average, 3-4% of $\mathrm{NO_y}$, which is consistent with several previous studies in continental regions [e.g. *Flocke et al.*, 1998; *Bertman et al.*, 1995; *Buhr et al.*, 1990; *Blake et al.*, 2003].

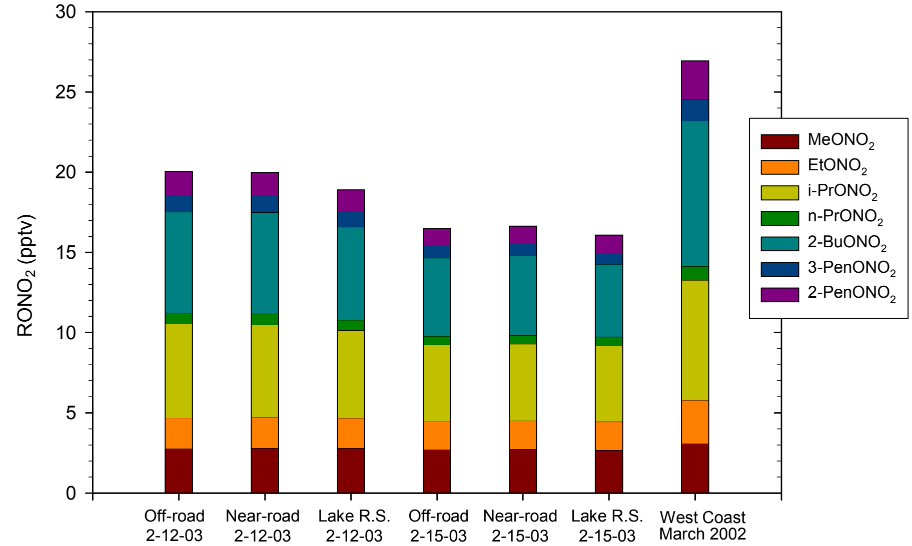


**Figure 9**. Median mixing ratios of alkyl nitrates at off–road sites, near–road sites, Lake R.S. (2003) and coastal sites during March 2002.

Alkyl nitrate mixing ratios were fairly uniform throughout YNP with median mixing ratios ranging from ~15-20 pptv on both 2/12/2003 (WED2003) and 2/15/2003 (SAT2003) (Figure 9, Table 5). The similarity between the distributions observed at the off-road, near-road, and lake sampling sites may be due to the lack of direct $\mathrm{RONO_2}$ sources and the relatively long $\mathrm{RONO_2}$ lifetimes (days-weeks) which allows them to become well-mixed [*Roberts et al.*, 1998;

*Flocke et al*., 1998]. The median total $RONO_2$ was 2-3 pptv larger on WED2003 compared to SAT2003. This very minor difference in mixing ratios was most likely a result of different meteorological conditions as well as the sampling of different air masses on each day. WED2003 was clear and sunny which may have resulted in more active photochemistry leading to the higher $RONO_2$ mixing ratios. In contrast, SAT2003 was generally overcast which would have suppressed the overall photochemical activity. In addition, the general direction of air mass transport was different on WED2003 and SAT2003. Three-day backward trajectories initiated at 3 different initialization altitudes were calculated every 4 hours using the NOAA HYSPLIT model. On WED2003, the trajectories indicate transport primarily from the northwest with the air masses originating 3 days earlier over western Canada (Figure 10a). This suggests that air sampled in YNP contained Arctic influence and was likely well processed. Figure 10b shows that air masses sampled on SAT2003 were transported from the west/northwest and closer to the surface. Additionally, these air masses may have contained more recent emission inputs which could also explain why the $RONO_2$ levels on SAT2003 were slightly lower.

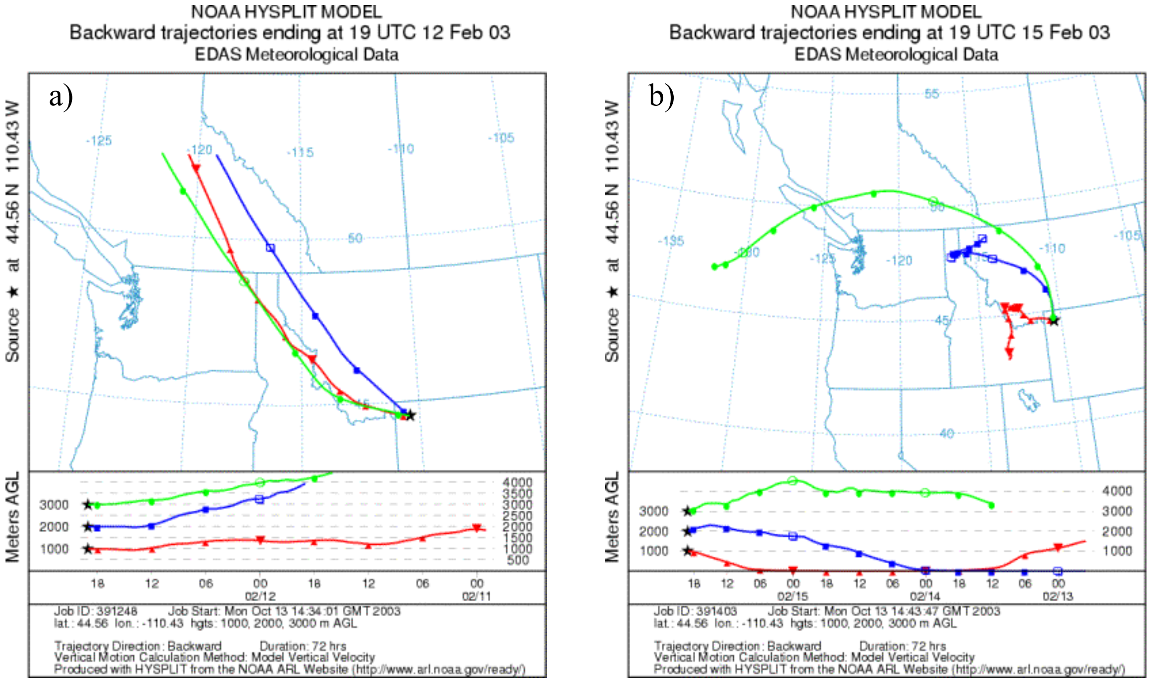


**Figure 10.** Three day backward trajectories for YNP on a) WED2003 and b) SAT2003.

The distribution of alkyl nitrates observed at four remote sites (Cape Blanco, OR, Cape Foulweather, OR, Ecola State Beach Park, OR, and Ocean Shores, WA) along the west coasts of Oregon and Washington state during March 2002 displayed the same general trends (Figure 9). The percentage of $\Sigma RONO_2$ that each individual alkyl nitrate accounted for was very similar to the distribution observed in YNP. The dominant alkyl nitrates at the remote coastal sites were also i-$PrONO_2$ and 2-$BuONO_2$ (28 and 33% of $\Sigma RONO_2$) followed by $MeONO_2$. The median $\Sigma RONO_2$ mixing ratio on the west coast was ~27 pptv. The higher mixing ratios of alkyl nitrates may reflect more processed air masses impacting these remote coastal areas in addition to local sources of gases with marine origin, such as $MeONO_2$. Furthermore, this suggests that the air masses affecting YNP were composed of local anthropogenic emissions that had not undergone significant photochemical processing.

The time evolution of alkyl nitrate/parent alkane ratios ($RONO_2$/RH) can be modeled using a method proposed by *Bertman et al.* [1995]. This ratio is useful for comparing ambient data with expected kinetic behavior. The photochemical age of an air mass can be estimated from the position of the $RONO_2$/RH ratio relative to a predicted photochemical production line. This ratio will increase as the air mass ages due to the production of alkyl nitrates from their parent hydrocarbons. Also, the extent of deviation from the predicted line is an indicator of potential contributions from additional sources of alkyl nitrates besides photochemistry [*Bertman et al.*, 1995; *Roberts et al.*, 1998]. The ratio of each alkyl nitrate species to its parent alkane is plotted against the ratio of 2-$BuONO_2$/n-butane (Figure 11). The 2-$BuONO_2$/n-butane ratio is used because 2-$BuONO_2$ is one of the most abundant alkyl nitrates, n-butane is one of the most abundant NMHCs emitted from continental sources, and OH oxidation and photolysis are roughly equal destruction processes of 2-$BuONO_2$ [*Roberts et al.*, 1998]. The "days" on Figure 11 represents the amount of time that the ratios have evolved since the alkanes were first injected into the air mass [*Bertman et al.*, 1995].

**Table 5.** Alkyl nitrate statistics on February 12, 15-16, 2003. Units are in pptv.

| Compound | Mean | Median | Max | Min | Std. Dev. | N | % of $\Sigma RONO_2$ |
|---|---|---|---|---|---|---|---|
| $MeONO_2$ | 2.9 | 2.8 | 8.9 | 2.4 | 0.6 | 210 | 14.6% |
| $EtONO_2$ | 2.0 | 1.9 | 10.4 | 1.4 | 0.7 | 211 | 10.1% |
| i-$PrONO_2$ | 5.6 | 5.4 | 40.9 | 3.8 | 2.8 | 208 | 28.7% |
| n-$PrONO_2$ | 0.7 | 0.6 | 5.0 | 0.4 | 0.3 | 210 | 3.3% |
| 2-$BuONO_2$ | 6.0 | 5.7 | 64.5 | 0.2 | 4.4 | 212 | 30.9% |
| 3-$PenONO_2$ | 1.1 | 0.9 | 16.0 | 0.5 | 1.1 | 212 | 5.4% |
| 2-$PenONO_2$ | 1.5 | 1.3 | 27.3 | 0.7 | 1.9 | 212 | 7.7% |
| $\Sigma RONO_2$ | 19.6 | 18.5 | 168.0 | 4.9 | 11.4 | 212 | |

The results from this method indicate that NMHC emissions of these gases were relatively recent, with the majority of the measurements lying between processing times of 1-5 days (Figure 11). Additionally, the relative air mass ages were similar at the different sampling locations throughout the Park. At the short reaction times (hours to ~2 days), the $EtONO_2$/ethane, i-$PrONO_2$/propane, and n-$PrONO_2$/propane ratios deviate strongly from the predicted photochemical line (Figures 11a, 11d, and 11e). However, these ratios also trend toward the predicted line at the longer processing times. These results suggest that there is an additional source, besides ethane and propane chemistry, that contributed to the formation of $EtONO_2$, i-$PrONO_2$, and n-$PrONO_2$. Additionally, these three ratios are predicted to approach steady state at long reaction times because the $EtONO_2$, i-$PrONO_2$, and n-$PrONO_2$ lifetimes are shorter than the lifetime of their parent alkanes [*Bertman et al.*, 1995; *Roberts et al.*, 1998]. The majority of the 2-$PenONO_2$/n-pentane, and 3-$PenONO_2$/n-pentane ratios fall at less than 2 days old and slightly below the line predicted for pure photochemical production (Figures 11b and 11c). The slopes of the 2-$PenONO_2$ and 3-$PenONO_2$/n-pentane ratios are consistent with the slope of the predicted line indicating a primarily photochemical source of the pentyl nitrates. Previous studies have suggested that large deviations from the photochemical line indicate that there is a primary source of the alkyl nitrate or that there is an additional source of the precursor peroxy radicals [*Bertman et al.*, 1995]. The decomposition of larger peroxy radicals (RO) is estimated to have a greater impact on the smaller radicals ($C_2$ and $C_3$) compared to the larger radicals ($C_5$) [*Bertman et al.*, 1995]. Therefore, this additional source may explain the larger deviations from the predicted line for the $EtONO_2$/ethane, i-$PrONO_2$/propane, n-$PrONO_2$/propane ratios observed at the short processing times compared to the larger pentyl nitrates. Additionally, the $RONO_2$/RH ratios for the remote west coast samples all indicate that the air masses ages were, in general, more than 2 days old (Figures 11a-e). The most aged point (~ 5 days or greater) for all the evolution plots in Figure 11 is from the west coast data. This substantiates that the samples collected along the west coast in March 2002 represent significantly processed air masses while that the air masses sampled in the Park had been augemented by local sources.

The $RONO_2$/RH ratios at West Yellowstone and at some of the near–road sites suggests a primary source of alkyl nitrates from oversnow vehicle emissions (Figure 11). This is particularly noticeable for the 2-$PenONO_2$/n-pentane and 3-$PenONO_2$/n-pentane ratios which indicate emissions less than 2 hours old. Furthermore, the highest alkyl nitrate mixing ratios (maximum $RONO_2$ = 168 pptv) were observed in West Yellowstone, MT on the morning of Sunday, February 16, 2003 (SUN2003 – see Table 5). This was likely caused by the large numbers of vehicles, specifically 2-stroke snowmobiles, present that morning providing evidence for a primary source of alkyl nitrates in vehicle exhaust.

The i-$PrONO_2$/propane and n-$PrONO_2$/propane versus 2-$BuONO_2$/n-butane ratios from the samples collected at Lake R.S. demonstrated unique behavior (Figures 11d and 11e). The ratios lie below the predicted line with relatively constant 2-$BuONO_2$/n-Butane ratios. Closer examination of exhaust samples revealed that i-$PrONO_2$, n-$PrONO_2$, and n-butane levels were relatively large while 2-$BuONO_2$ levels were lower than in ambient air samples. These results would decrease the 2-$BuONO_2$/n-butane ratio and could explain the behavior displayed in Figures 11d and 11e. Also, oxidation of propane used for heating and/or cooking at Yellowstone Lake could contribute an additional source of both i-$PrONO_2$ and n-$PrONO_2$.

### 3.2.2 NMHC and Halocarbon Distributions

The alkanes with the largest abundances in the atmosphere were ethane (>1 ppbv) and propane (0.5-1 ppbv) because of their long atmospheric lifetimes (Figure 12). The total amount of alkanes were approximately 2.5-3 ppbv. At Lake R.S., ethane and propane represented ~70% of the alkanes (Table 6) with the $C_4$ alkanes contributing ~300-400 pptv to the total. The levels of ethane observed during the 2002 sampling in the Park in addition to the remote west coast sites (March 2002) were a few hundred pptv higher, making the total alkanes slightly larger than at YNP during 2003. Also, the median propane mixing ratio was approximately twice as large at Lake R.S. on SAT2003 compared to the off-road and near-road samples from WED2003 and SAT2003 and the Lake R.S. samples from WED2003. These enhanced propane levels were presumably caused by the propane sources at/near the Lake R.S. site and may explain the larger i-$PrONO_2$ and n-$PrONO_2$ concentrations measured at Lake R.S. that were discussed previously.

The concentration of alkanes (~20 ppbv) was approximately a factor of 5-6 larger at West Yellowstone on SUN2003 compared to the levels observed on the other sampling days throughout the Park and compared to the high traffic day during the 2002 sampling campaign (not shown). This resulted from extremely high snowmobile traffic throughout all of West Yellowstone during the sampling in this location. The $C_4$ and $C_5$ alkanes dominated the distribution (~5 ppbv and 3.6 ppbv, respectively, Figure 12) which is consistent with 2-stroke exhaust emissions. The $C_4$ and $C_5$ alkanes comprised ~25% and ~18% of the total amount of alkanes, respectively (Table 6). Overall, the distributions of the alkanes, inside the Park and in West Yellowstone, are consistent with a primarily anthropogenic source of these gases.

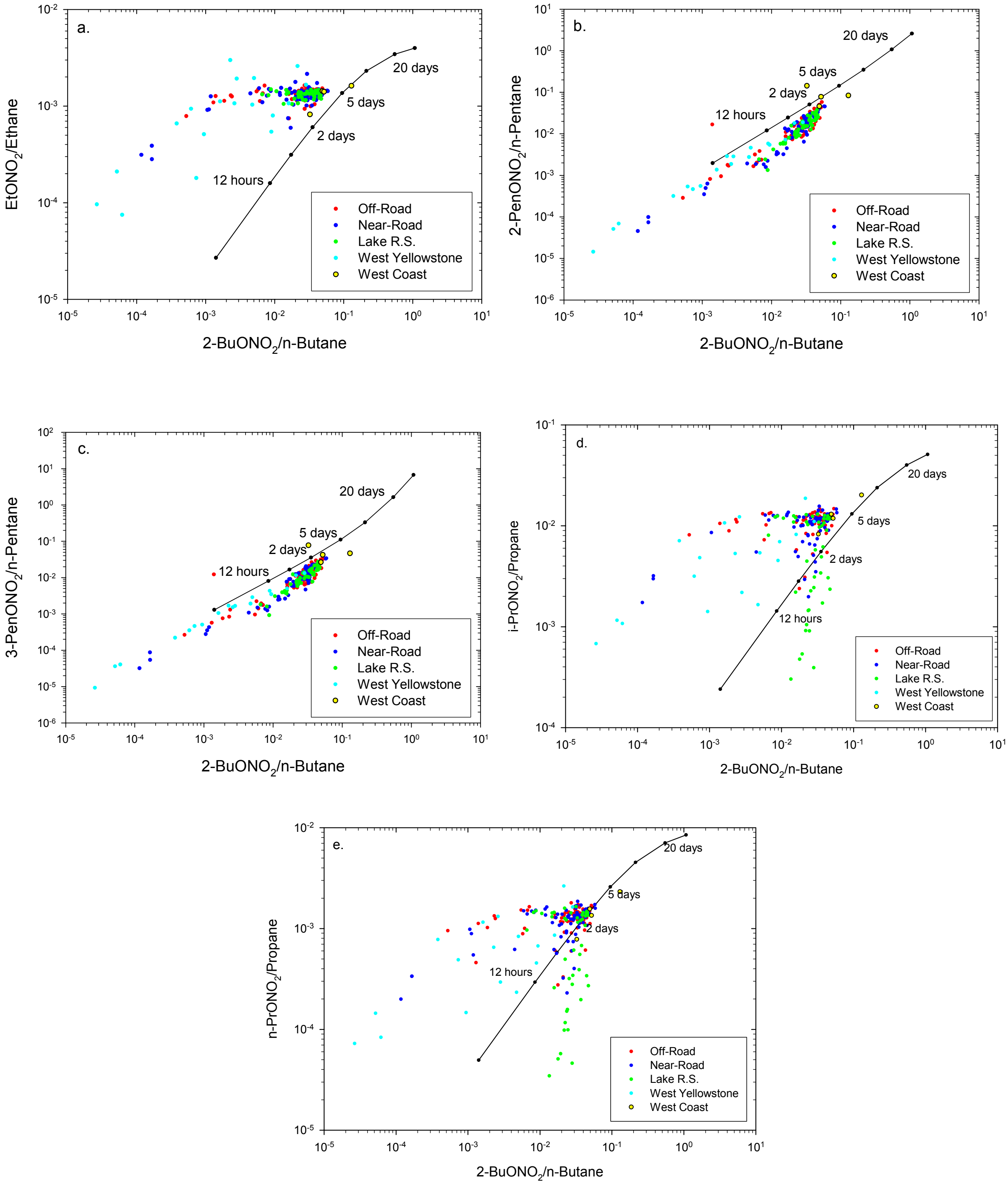


**Figure 11.** Time evolution of alkyl nitrate/parent alkane ratios (a) $EtONO_2$/ethane, (b) 2-$PenONO_2$/n-pentane, (c) 3-$PenONO_2$/n-pentane, (d) i-$PrONO_2$/propane, and (e) n-$PrONO_2$/propane.

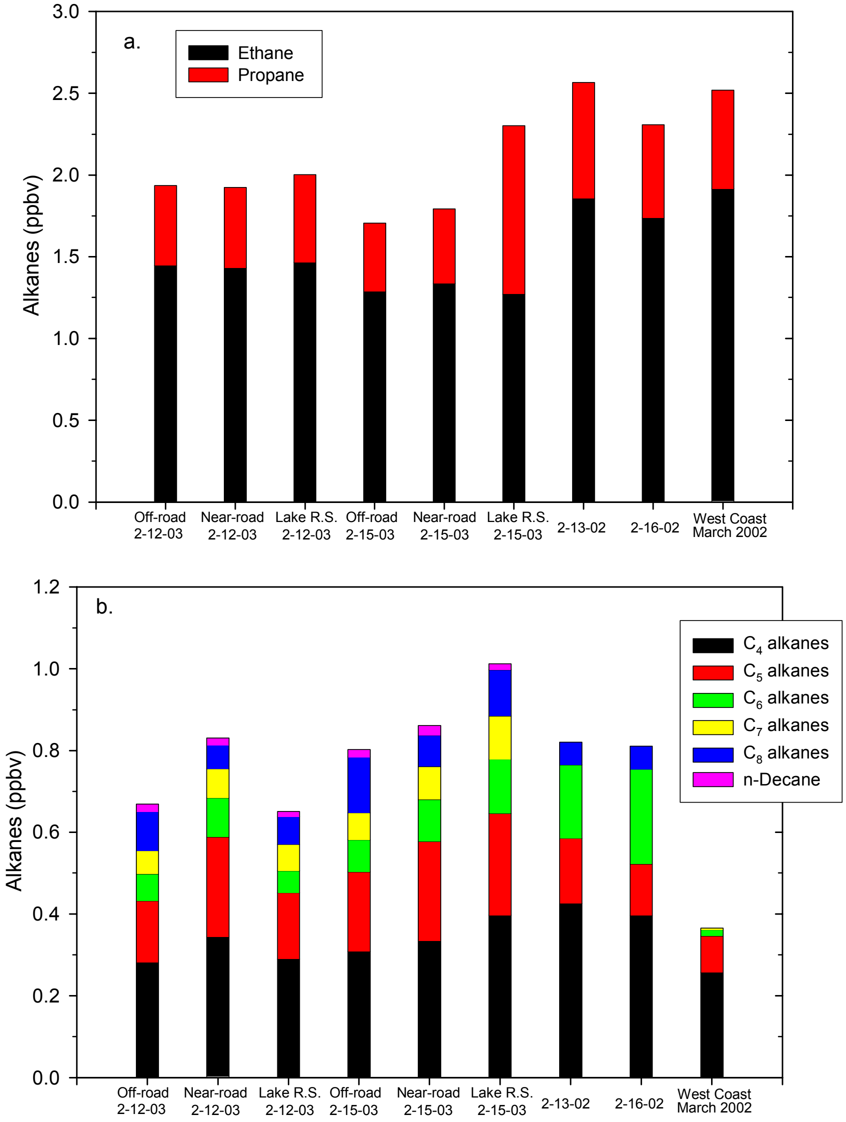


**Figure 12.** Median mixing ratios of a) ethane and propane and b) $C_4$-$C_{10}$ alkanes at off–road sites, near–road sites, Lake R.S. (2003), samples collected on low traffic and high traffic days in 2002 and coastal sites during March 2002.

At all sampling locations in YNP, the concentration of aromatics was dominated by benzene, toluene, and the xylenes with median mixing ratios of ~100-200 pptv each (Figure 13). Benzene accounted for the largest percentage (25%) of aromatics at Lake R.S., followed by toluene (24%), and the xylenes (17%) (Table 6). Similar trends for these species were also observed during the 2002 sampling campaign. The influence of 2-stroke exhaust in YNP during both the 2002 and 2003 sampling periods is readily apparent when these data are compared to the distribution of aromatics observed at remote west coast sites. Toluene, the xylenes, and ethylbenzene were approximately factors of 6-15 larger at YNP than at the remote sites (Figure 13). These results provide striking evidence of the differences in enhancements due to 2-strokes exhaust emissions. Furthermore, the high levels of the aromatics indicate that the atmospheric composition in YNP was not representative of a remote airshed, but largely impacted by local mobile source emissions consistent with 2-stroke exhaust.

At West Yellowstone (SUN2003), the total aromatics were an order of magnitude larger than all other sampling locations (not shown). Toluene and the xylenes, were the dominant aromatics with median mixing ratios of ~2 ppbv and represented 35% and 29% of the total aromatics, respectively (Table 6). Benzene and the trimethylbenzenes also made significant contributions of 11% and 9%, respectively. Evidence supporting a vehicular source of aromatics in West Yellowstone is provided by the strong correlations between ethyne and benzene, toluene, the xylenes, and ethylbenzene, along with CO for the same four species ($r^2$ = 0.75-0.98). Also, benzene, toluene, the xylenes, and ethylbenzene were correlated at the off-road sampling sites in the Park ($r^2$ > 0.85). At the near-road sites, these gases were also well correlated with ethyne ($r^2$ = 0.94). However, these correlations were weak at Lake R.S. ($r^2$ ~ 0.3-0.6). These strong correlations suggest that emissions consistent with 2-stroke exhaust were influencing the air quality in the Park.

The median mixing ratios of ethyne and the alkenes were ~350-400 pptv and ~200-300 pptv, respectively, at the near-road, off-road, and Lake R.S. sites. These levels are consistent with the mixing ratios observed on both the low and high traffic days during 2002 (Figure 14). Ethene, propene, and the $C_4$ alkenes accounted for 47%, 23% and 19% of the total alkenes at Lake R.S., respectively (Table 6). Similar to the alkanes and the aromatics, the alkenes were enhanced in West Yellowstone on SUN2003 (not shown). The median mixing ratios were factors of 10-30 larger compared to the mixing ratios observed on the WED2003 and SAT2003. The median ethene mixing ratio was ~ 2.5 ppbv, and it represented 52% of the alkenes (Table 6). The mixing ratios of propene and the $C_4$ and $C_5$ alkenes were fairly similar (600-700 pptv) and enhanced compared to their mixing ratios in the Park. Ethyne was ~3.4 ppbv at West Yellowstone, nearly an order of magnitude larger than its mixing ratios at the other sampling sites. The influence of recent and localized combustion sources is clearly demonstrated by the strong correlation between ethene and ethyne at West Yellowstone ($r^2$ = 0.96).

**Table 6.** Contribution of individual NMHCs to the total amount of alkanes, alkenes, and aromatics at (a) West Yellowstone and at (b) Lake R.S.

a. West Yellowstone

| Alkanes | | Alkenes | | Aromatics | |
|---|---|---|---|---|---|
| Ethane | 13.3% | Ethene | 51.8% | Benzene | 11.2% |
| Propane | 7.9% | Propene | 14.9% | Toluene | 35.0% |
| n-Decane | 0.5% | Isoprene | 1.2% | Xylenes | 29.1% |
| $C_4$ alkanes | 25.2% | $C_4$ alkenes | 14.1% | Styrene | 0.6% |
| $C_5$ alkanes | 18.3% | $C_5$ alkenes | 12.7% | Ethylbenzene | 6.3% |
| $C_6$ alkanes | 10.6% | $C_6$ alkenes | 5.3% | Alkyl benzenes | 7.2% |
| $C_7$ alkanes | 9.5% | | | Trimethylbenzenes | 8.9% |
| $C_8$ alkanes | 14.4% | | | Diethylbenzenes | 1.8% |

b. Lake R. S.

| Alkanes | | Alkenes | | Aromatics | |
|---|---|---|---|---|---|
| Ethane | 50.9% | Ethene | 46.6% | Benzene | 25.2% |
| Propane | 19.6% | Propene | 23.0% | Toluene | 24.1% |
| n-Decane | 0.5% | Isoprene | 1.8% | Xylenes | 16.7% |
| $C_4$ alkanes | 11.7% | $C_4$ alkenes | 18.5% | Styrene | 1.4% |
| $C_5$ alkanes | 8.7% | $C_5$ alkenes | 7.7% | Ethylbenzene | 4.3% |
| $C_6$ alkanes | 3.0% | $C_6$ alkenes | 2.3% | Alkyl benzenes | 9.7% |
| $C_7$ alkanes | 2.8% | | | Trimethylbenzenes | 13.7% |
| $C_8$ alkanes | 3.1% | | | Diethylbenzenes | 4.9% |

The mixing ratios of most halocarbons were fairly uniform throughout the study region (Figure 15). The median mixing ratios of several CFCs and methyl chloride (MeCl) are shown in 15a, while various other halocarbons are shown in 15b and15c. Many halocarbons are well mixed throughout the troposphere due to their long atmospheric lifetimes. However, short lived halocarbons, such as $C_2HCl_3$, are good markers of recent urban emissions and enable different source types to be deconvoluted from an air mass. Additionally, vehicular emissions of $CH_3Br$ have been observed and were shown to contribute to its global budget [*Chen et al.*, 1999]. Thus, investigating the distributions of this class of gases can provide useful information. The most abundant reactive halocarbon (halocarbons with atmospheric lifetimes that are less than ~6 months) was $C_2Cl_4$ with a median mixing ratio of ~7 pptv. These results are comparable to mixing ratios observed at the remote coastal sites in Washington and Oregon and to the $C_2Cl_4$ mixing ratios observed during the 2002 sampling period at YNP indicating the lack of local emission sources such as might be expected in urban settings. Further investigation of the $CH_3Br$ measurements are necessary to determine if there are impacts from 2-stroke snowmobile emissions on ambient mixing ratios in the Park.

### 3.2.3 NMHC Reactivity

The reactivity of a NMHC provides information on what can ultimately be considered the ozone production efficiency of the compound. Although NMHC reactivity may not be considered to be significant with regard to regulatory standards for ozone production in the wintertime, it is important to the chemistry, particularly oxidant balance and cycling, occurring in the Park and surrounding areas. This point is exemplified if ozone distributions on WED2003 and SAT2003 are compared (Figure 16). The WED2003 measurements of ozone show mixing ratios at about 50 ppbv, which is a typical background value for mid- to high-latitude measurements at this time of year. Comparing these measurements to those made on SAT2003, there is a more than twofold jump in noontime NO and that ozone values were significantly depleted overnight with values dropping to ~20 ppbv. This is likely the result of greatly increased amounts of NOx, which depleted ozone in the shallow nocturnal boundary layer. As the day progressed, the boundary layer height increased entraining clean free tropospheric air. As a result, ozone mixing ratios increased rapidly in the morning on SAT2003 – with mixing and chemistry both contributing to the afternoon ozone recovery (mixing being the dominant process, particularly due to the meteorological conditions on SAT 2003). However, because of the large amount of reactivity furnished by the 2-stroke exhaust, it is likely that ozone production is a factor and must be considered when evaluating regional oxidant balance as well as contributing to organic acid production and deposition [*Fehsenfeld et al.*, 1992].

The reactivity of a NMHC is determined from the product of its concentration with its rate of reaction with OH [e.g. *Young et al.*, 1997; *Biesenthal et al.*, 1998]. The peaks in the reactivity plots (Figure 17 and 18) correspond to the times when the maximum NMHC mixing ratios were observed on WED2003 and SAT2003 at Lake R.S. Overall, the alkenes made the largest contribution to the total reactivity of the NMHCs (Figure 17). They accounted for 14-63% of the total reactivity determined from the diurnal samples collected at Lake R.S. The alkanes and aromatics made similar contributions to the total reactivity, averaging 31% and 30%, respectively, while ethyne only accounted for a minor component of the NMHC reactivity (~ 3%). Furthermore, toluene, the xylenes, and the trimethylbenzenes made the most substantial contribution to the total aromatic reactivity (Figure 18). The trimethylbenzenes dominated thearomatic reactivity and accounted for 16-68% of the total. The xylenes and toluene accounted for 33% and 14% of the aromatic reactivity, respectively. These results suggest that the gases emitted by snowmobile exhaust may lead to $O_3$ production or particle formation in areas downwind of YNP, possibly impacting regional air quality.

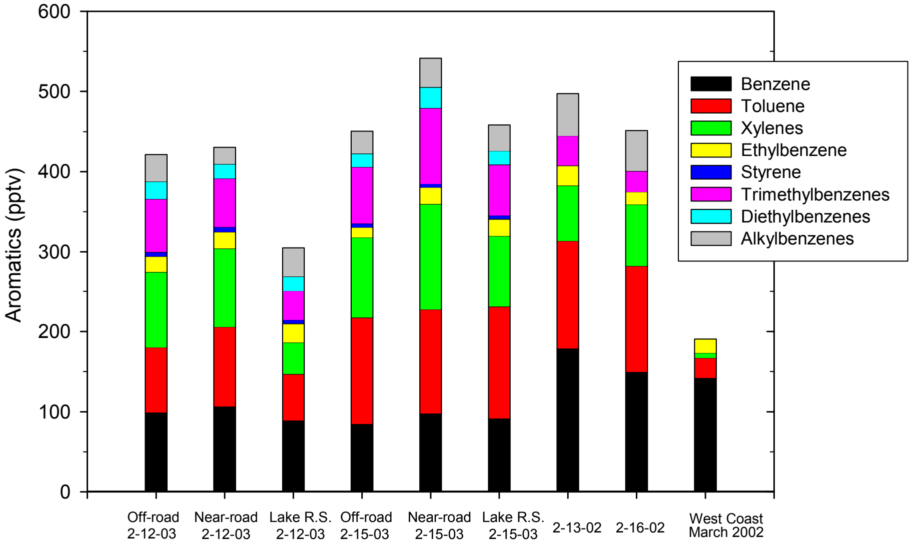


**Figure 13.** Median mixing ratios of aromatics at off–road sites, near-road sites, Lake R.S., YNP on 2/13/2002 and 2/16/2002, and coastal sites during March 2002.

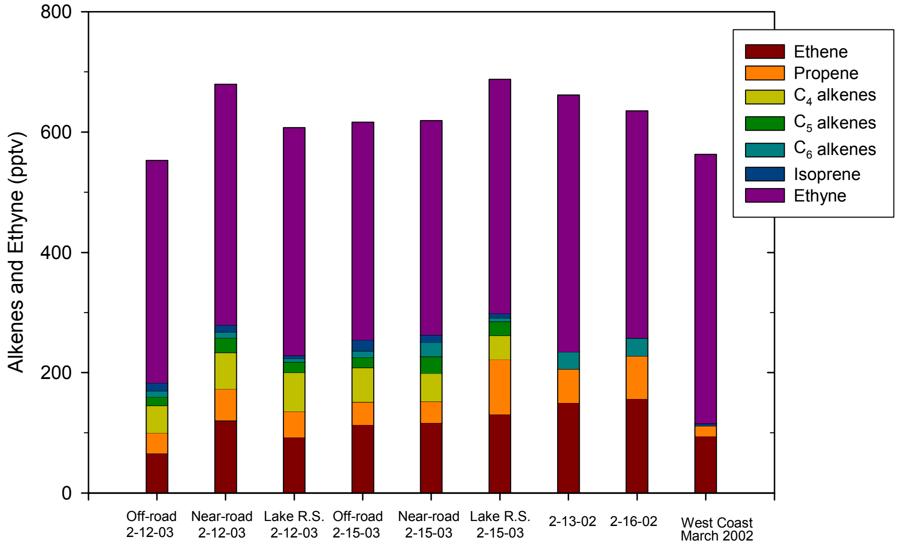


**Figure 14.** Median mixing ratios of alkenes and ethyne at off–road sites, near-road sites, Lake R.S., YNP on 2/13/2002 and 2/16/2002, and coastal sites during March 2002.

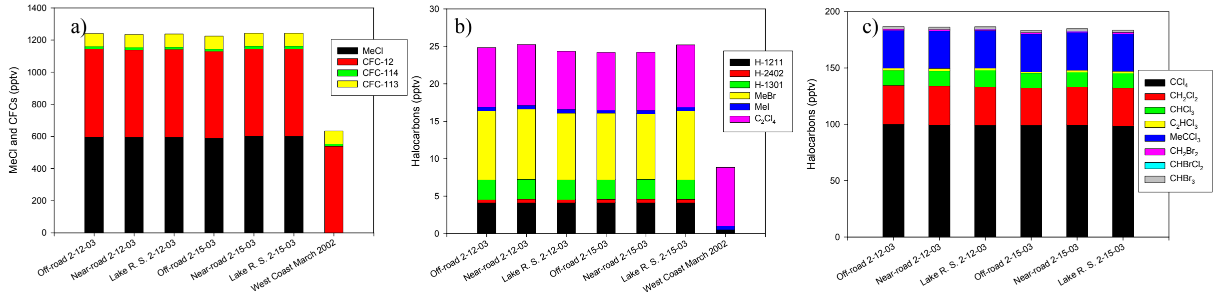


**Figure 15.** Median mixing ratios of a) CFCs and MeCl, b) and c) various other halocarbons.

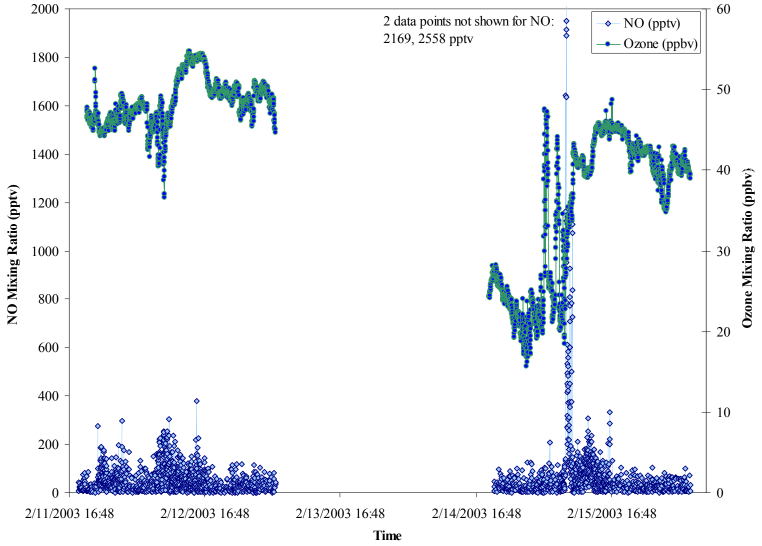


**Figure 16.** Measurements of ozone and NO at Lake R.S. on WED2003 and SAT2003.

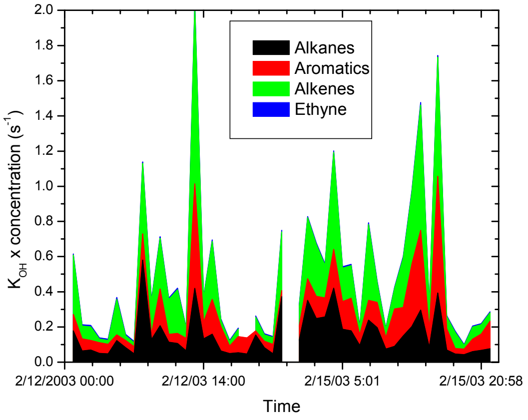


**Figure 17.** Reactivity of alkanes, aromatics, alkenes, and ethyne at Lake R.S.

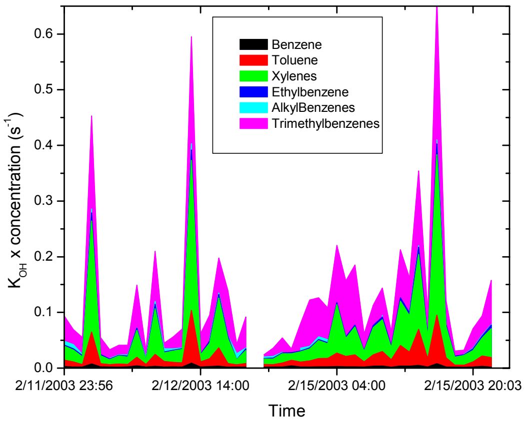


**Figure 18.** Reactivity of aromatics at Lake R.S.

### 3.2.4 Boundary Layer Dynamics

Boundary layer dynamics influence the distribution of trace gases in the atmosphere. Typically, NMHC mixing ratios decrease from morning to afternoon as a result of dilution caused by the increase in boundary layer height which entrains clean air from aloft. Various alkanes and alkenes exhibited this trend on WED2003 and SAT2003 suggesting that dilution was significant with regard to overall mixing ratios (Table 7, Figure 19). The median mixing ratios of ethane, propane, i-butane, n-butane, n-pentane, ethene, propene, ethyne, and $C_2Cl_4$ decreased by ~4-62% from the morning to the afternoon at all sampling locations. This behavior is consistent with the breakup of the nocturnal inversion layer in the morning and the subsequent dilution in the afternoon as was discussed in previous sections. The decrease for many of these gases was larger on SAT2003, suggesting that more dilution occurred between the AM and PM sampling periods. However, benzene, toluene, ethylbenzene, p-, m-, o-xylene, and i-pentane exhibited the opposite trend with larger median mixing ratios in the afternoon and evening (Table 7, Figure 19). The increase in mixing ratios ranged from 2-55 % for these particular gases. This trend is also apparent in the time series of the aromatics at the Lake R. S. (Figures 19f and 19g). On both WED2003 and SAT2003, the benzene, toluene, ethylbenzene, and xylene mixing ratios were factors of 3-4 larger in the afternoon compared to the morning. The aromatics, which are major components of 2-stroke engine exhaust, were too abundant to be sufficiently reduced by the dilution that occurred between sampling periods. Other gases that a major components of 2-stroke exhaust, such as n-butane, i-pentane, and n-pentane, also exhibited greatly enhanced mixing ratios at Lake R.S. on the afternoon of SAT2003 (Figure 19d). However, i-butane, which is not a major component of 2-stroke exhaust, did not have enhanced mixing ratios that afternoon. These results suggest that the anthropogenic influence in YNP was not restricted to a specific time during the day.

Boundary layer dynamics also strongly influenced the $O_3$ and $RONO_2$ levels. Total $RONO_2$ displayed the same trend as the NMHCs with larger mixing ratios over night due to the gases being trapped in the boundary layer. However, $O_3$ concentrations are typically lower at night due to surface deposition and/or titration by NO. An example of this behavior occurred on the morning of SAT2003 at Lake R.S. where $RONO_2$ and $O_3$ were ~20 pptv and ~20 ppbv, respectively (Figure 19a). The potential temperature profile from the morning of SAT2003 indicated a shallow, weak inversion layer, along with calm winds, that inhibited mixing throughout the morning (Figure 6b). The inversion layer had dissipated by 13:00 (local time) and the near neutral temperature profile suggests that mixing occurred throughout the afternoon (Figures 6c and 6d). The mixing and dilution caused $RONO_2$ mixing ratios to decrease to ~15 pptv following the increase in the boundary layer height, while $O_3$ mixing ratios increased due to $O_3$ enriched air from aloft mixing downward in addition to local photochemical production (see discussion in section 3.2.3). Other gases, such as $CH_4$, $C_2Cl_4$, and several alkanes, also exhibited enhanced mixing ratios on the morning of SAT2003 that decreased throughout the afternoon (Figures 19b, 19c and 19h). These gases are not associated with 2-stroke exhaust emissions and display trends consistent with atmospheric dynamics.

### 3.3 Overview of Spatial Distributions

The spatial distributions of 18 VOCs are shown in Figures 20-37. Each figure contains two sets of four maps corresponding to the morning and afternoon sampling periods for the near-road and off-road samples during the low and high traffic days (WED2003 and SAT2003). Mixing ratios are in pptv (except for $CH_4$ and CO, which are in ppmv and ppbv, respectively), and are designated by color-coding and symbol size. One feature worth noting before discussing the trace gas spatial distributions is that the road between Silver Gate and Mammoth Hot Springs is used primarily for automobile traffic, as opposed to the remainder of the park roads which are dominated by snowmobile traffic. Therefore, the samples collected in the northern region of the park were generally much cleaner, and the NMHC mixing ratios were only slightly enhanced above background northern hemispheric air.

In order to rule out the influence of urban emissions on the samples collected in the park, the spatial distribution of tetrachloroethene ($C_2Cl_4$) was first evaluated (Figure 20). For all AM, PM and diurnal samples, the mean $C_2Cl_4$ mixing ratio and $1\sigma$ standard deviation were $8.0 \pm 0.8$ pptv (the standard deviation at this mixing ratio level is dominated by the instrument's precision). This indicates that there was little or no influence on the air masses sampled in the park from urban areas directly upwind and that the NMHC enhancements observed were representative of local emissions.

The spatial distributions of methane, ethane and propane are shown in Figures 21-23. For all three of these gases, high concentrations were generally observed throughout the Park during the morning sampling periods. It is likely that these enhancements were a result of decreasing boundary layer height in addition to some minor local sources such as wood burning (used for home heating) and propane leakage in this area. The methane and ethane mixing ratios were essentially uniform indicating that the air masses sampled were well mixed throughout the park on both days, while the propane was patchy, indicating leakage of propane tanks at various locations throughout the Park. Overall, little variability was observed in the mixing ratios of these gases during both sampling periods.

Ethene and propene are useful indicators of fresh emissions from combustion sources because of their short atmospheric lifetimes, which are on the order of ~1.5 days and ~0.5 days, respectively. Both CO and ethyne are good indicators of combustion [*Blake et al.*, 1996b], but have different atmospheric lifetimes, with ethyne being somewhat shorter-lived. The spatial distributions of these four gases are shown in Figures 24-27. Large enhancements are observed throughout the loop road and southern route for these gases during the PM sampling periods on both days. A key feature to note is that the mixing ratios for these gases increased between the AM and PM sampling periods and that the values are consistent between near-road and off-road sampling sites. This indicates that local combustion sources are impacting the Park region. This is well demonstrated by CO with mixing ratios near background levels throughout the Park during the AM sampling periods except for site A4 near the West Entrance where high levels of

CO are commonly observed in the morning hours. Mixing ratios of CO are then observed to increase during the PM sampling periods that are characterized by increased levels of snowmobile traffic throughout the Park excepting along the Mammoth Hot Springs-Cooke City road along which snowmobile traffic is prohibited.

**Table 7.** Mean and median mixing ratios along with the percent difference in median values between morning and afternoon sampling times. Values are reported for all samples collected at off-road sites, Lake R.S., and near- road sites for WED2003 and SAT2003. Units are in pptv.

| Compound | Date | Location | Time | Mean | Median | % Difference |
|---|---|---|---|---|---|---|
| Ethane | 2/12/03 | off-road & lake | am | 1553.4 | 1483.9 | -8% |
| | | | pm | 1411.7 | 1379.7 | |
| | 2/12/03 | near-road | am | 1897.4 | 1473.7 | -8% |
| | | | pm | 1432.1 | 1365.1 | |
| | 2/15/03 | off-road & lake | am | 1446.7 | 1358.6 | -13% |
| | | | pm | 1247.9 | 1205.0 | |
| | 2/15/03 | near-road | am | 1810.4 | 1392.1 | -13% |
| | | | pm | 1579.0 | 1230.8 | |
| Propane | 2/12/03 | off-road & lake | am | 1447.4 | 561.3 | -23% |
| | | | pm | 1049.4 | 457.5 | |
| | 2/12/03 | near-road | am | 755.5 | 556.6 | -24% |
| | | | pm | 555.5 | 448.1 | |
| | 2/15/03 | off-road & lake | am | 2202.7 | 570.6 | -62% |
| | | | pm | 400.8 | 352.0 | |
| | 2/15/03 | near-road | am | 899.3 | 500.6 | -36% |
| | | | pm | 552.9 | 369.1 | |
| i-Butane | 2/12/03 | off-road & lake | am | 223.8 | 97.7 | -27% |
| | | | pm | 165.2 | 76.9 | |
| | 2/12/03 | near-road | am | 1086.3 | 121.8 | -36% |
| | | | pm | 252.4 | 89.8 | |
| | 2/15/03 | off-road & lake | am | 149.6 | 115.8 | -41% |
| | | | pm | 179.4 | 82.0 | |
| | 2/15/03 | near-road | am | 1198.5 | 117.0 | -10% |
| | | | pm | 577.9 | 106.3 | |
| n-Butane | 2/12/03 | off-road & lake | am | 538.5 | 166.9 | -9% |
| | | | pm | 373.5 | 153.8 | |
| | 2/12/03 | near-road | am | 3291.9 | 210.9 | -12% |
| | | | pm | 683.3 | 187.9 | |
| | 2/15/03 | off-road & lake | am | 228.1 | 213.6 | -25% |
| | | | pm | 574.1 | 170.7 | |
| | 2/15/03 | near-road | am | 4012.9 | 215.4 | -11% |
| | | | pm | 2234.8 | 194.3 | |
| i-Pentane | 2/12/03 | off-road & lake | am | 470.8 | 86.5 | 3% |
| | | | pm | 331.5 | 88.8 | |
| | 2/12/03 | near-road | am | 3144.7 | 122.8 | 22% |
| | | | pm | 759.3 | 156.8 | |
| | 2/15/03 | off-road & lake | am | 152.5 | 146.9 | -50% |
| | | | pm | 508.1 | 97.9 | |
| | 2/15/03 | near-road | am | 5308.0 | 145.0 | 9% |
| | | | pm | 2864.8 | 159.9 | |

**Table 7 (continued).**

| Compound | Date | Location | Time | Mean | Median | % Difference |
|---|---|---|---|---|---|---|
| n-Pentane | 2/12/03 | off-road & lake | am | 251.4 | 66.6 | -12% |
|  |  |  | pm | 172.9 | 59.7 |  |
|  | 2/12/03 | near-road | am | 1443.5 | 85.3 | 10% |
|  |  |  | pm | 455.5 | 94.9 |  |
|  | 2/15/03 | off-road & lake | am | 95.2 | 91.0 | -49% |
|  |  |  | pm | 265.2 | 61.2 |  |
|  | 2/15/03 | near-road | am | 3063.7 | 91.4 | -17% |
|  |  |  | pm | 1374.8 | 78.0 |  |
| Ethene | 2/12/03 | off-road & lake | am | 288.4 | 73.3 | 10% |
|  |  |  | pm | 301.2 | 81.7 |  |
|  | 2/12/03 | near-road | am | 2167.1 | 135.0 | -35% |
|  |  |  | pm | 363.9 | 100.0 |  |
|  | 2/15/03 | off-road & lake | am | 145.5 | 129.2 | -31% |
|  |  |  | pm | 355.5 | 98.3 |  |
|  | 2/15/03 | near-road | am | 2862.6 | 135.7 | -51% |
|  |  |  | pm | 3184.0 | 90.0 |  |
| Propene | 2/12/03 | off-road & lake | am | 130.6 | 36.6 | 3% |
|  |  |  | pm | 150.9 | 37.7 |  |
|  | 2/12/03 | near-road | am | 1021.2 | 61.9 | -46% |
|  |  |  | pm | 159.1 | 42.5 |  |
|  | 2/15/03 | off-road & lake | am | 129.1 | 44.6 | 3% |
|  |  |  | pm | 197.8 | 46.0 |  |
|  | 2/15/03 | near-road | am | 943.5 | 40.7 | -19% |
|  |  |  | pm | 2340.6 | 34.2 |  |
| Ethyne | 2/12/03 | off-road & lake | am | 872.5 | 373.3 | -5% |
|  |  |  | pm | 580.1 | 356.7 |  |
|  | 2/12/03 | near-road | am | 2719.4 | 408.3 | -6% |
|  |  |  | pm | 687.1 | 384.2 |  |
|  | 2/15/03 | off-road & lake | am | 381.6 | 374.2 | -11% |
|  |  |  | pm | 548.2 | 336.7 |  |
|  | 2/15/03 | near-road | am | 5324.2 | 365.7 | -7% |
|  |  |  | pm | 1365.8 | 343.3 |  |
| Benzene | 2/12/03 | off-road & lake | am | 260.1 | 94.3 | 11% |
|  |  |  | pm | 185.1 | 106.0 |  |
|  | 2/12/03 | near-road | am | 898.6 | 101.3 | 6% |
|  |  |  | pm | 259.0 | 108.0 |  |
|  | 2/15/03 | off-road & lake | am | 94.1 | 83.8 | 3% |
|  |  |  | pm | 213.7 | 86.4 |  |
|  | 2/15/03 | near-road | am | 1519.3 | 98.4 | -15% |
|  |  |  | pm | 874.4 | 85.2 |  |

**Table 7 (continued).**

| Compound | Date | Location | Time | Mean | Median | % Difference |
|---|---|---|---|---|---|---|
| Toluene | 2/12/03 | off-road & lake | am | 390.1 | 85.1 | 26% |
| | | | pm | 330.1 | 115.3 | |
| | 2/12/03 | near-road | am | 2622.7 | 74.8 | 45% |
| | | | pm | 598.9 | 134.9 | |
| | 2/15/03 | off-road & lake | am | 119.2 | 96.8 | 29% |
| | | | pm | 415.9 | 135.6 | |
| | 2/15/03 | near-road | am | 4269.6 | 127.5 | 24% |
| | | | pm | 2283.4 | 168.4 | |
| Ethylbenzene | 2/12/03 | off-road & lake | am | 77.1 | 23.6 | -2% |
| | | | pm | 75.3 | 23.3 | |
| | 2/12/03 | near-road | am | 420.6 | 18.1 | 35% |
| | | | pm | 102.2 | 28.0 | |
| | 2/15/03 | off-road & lake | am | 45.8 | 28.2 | 35% |
| | | | pm | 124.3 | 43.3 | |
| | 2/15/03 | near-road | am | 700.6 | 24.6 | 20% |
| | | | pm | 374.8 | 30.7 | |
| p-Xylene | 2/12/03 | off-road & lake | am | 99.7 | 36.0 | 18% |
| | | | pm | 108.7 | 43.7 | |
| | 2/12/03 | near-road | am | 568.9 | 33.9 | -26% |
| | | | pm | 116.2 | 27.0 | |
| | 2/15/03 | off-road & lake | am | 74.8 | 41.2 | 20% |
| | | | pm | 162.5 | 51.2 | |
| | 2/15/03 | near-road | am | 905.7 | 28.2 | 36% |
| | | | pm | 433.1 | 44.1 | |
| m-Xylene | 2/12/03 | off-road & lake | am | 153.8 | 20.1 | 55% |
| | | | pm | 127.8 | 44.5 | |
| | 2/12/03 | near-road | am | 1084.4 | 54.2 | 14% |
| | | | pm | 259.1 | 62.9 | |
| | 2/15/03 | off-road & lake | am | 34.2 | 25.0 | 43% |
| | | | pm | 179.1 | 44.1 | |
| | 2/15/03 | near-road | am | 1840.2 | 62.5 | 46% |
| | | | pm | 862.5 | 116.3 | |
| o-Xylene | 2/12/03 | off-road & lake | am | 78.3 | 11.0 | 43% |
| | | | pm | 64.5 | 19.3 | |
| | 2/12/03 | near-road | am | 524.9 | 14.4 | 48% |
| | | | pm | 123.7 | 27.6 | |
| | 2/15/03 | off-road & lake | am | 25.5 | 24.2 | 2% |
| | | | pm | 96.6 | 24.8 | |
| | 2/15/03 | near-road | am | 904.5 | 27.6 | 48% |
| | | | pm | 457.3 | 53.2 | |

**Figure 19.** Time series at Lake R.S. for (a) $RONO_2$ and $O_3$, (b) $CH_4$ and CO, (c) ethane and propane, (d) i-butane, n-butane, i-pentane, and n-pentane, (e) ethyne, ethene, and propene, (f) benzene, toluene, and ethylbenzene, (g) p-xylene, o-xylene, and m-xylene, and (h) $C_2Cl_4$ and $C_2HCl_3$.

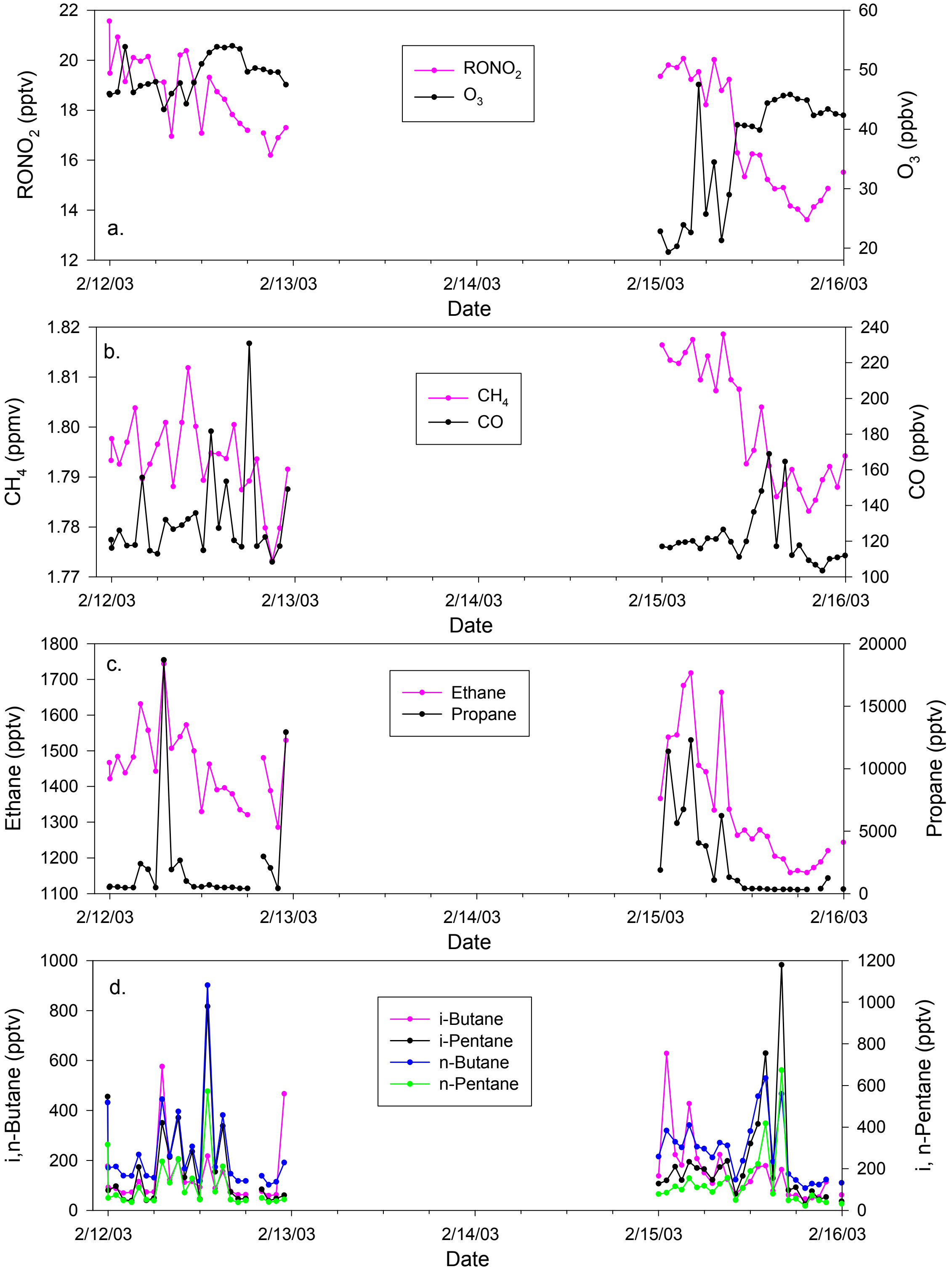
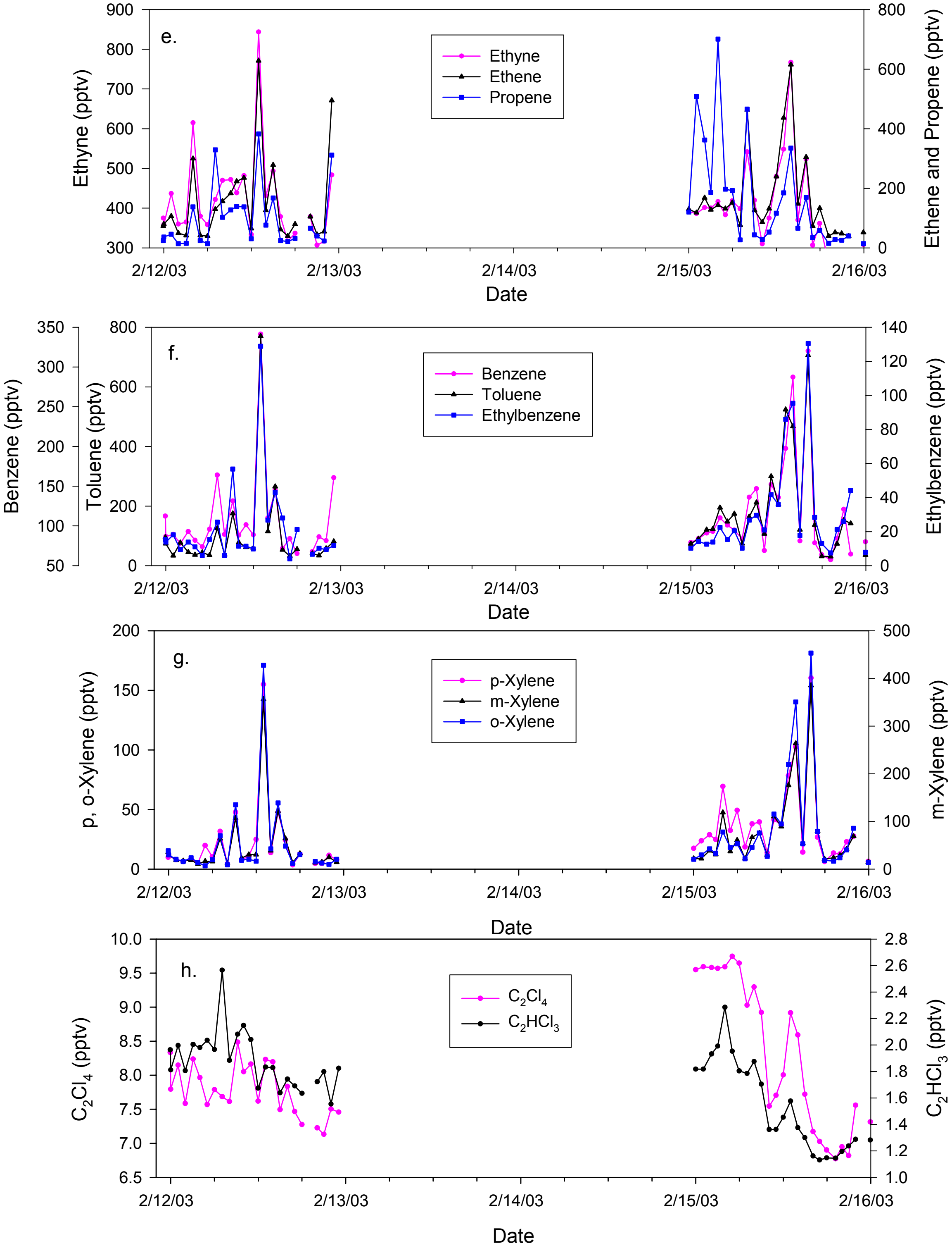


**Figure 19 (continued).**



The butanes (i-butane and n-butane) and pentanes (i-pentane and n-pentane) are indicators of fuel evaporation and are also emitted from combustion sources. The spatial distributions of these gases are shown in Figures 28-31. For i-butane, the overall difference between the morning and afternoon mixing ratios is small on both days. In contrast to i-butane, the n-butane, i-pentane and n-pentane show large enhancements between the AM and PM sampling periods on each day. The observed enhancements are a result of the increased snowmobile usage between the AM and PM sampling periods. However, because the road from Mammoth Hot Springs Silver Gate to is limited to automobiles, the mixing ratios of these gases remain essentially unchanged in this region for all sampling periods. The large enhancements observed for n-butane, i-pentane and n-pentane are consistent with the 2-stroke engine exhaust.

Similarly, benzene, toluene, ethylbenzene and the xylenes (m-, p- and o-) exhibit spatial distributions comparable to n-butane and the pentanes, with toluene emissions showing the greatest increases between the AM and PM sampling periods (Figures 32-37). The potential health hazards associated with exposure to these compounds are the primary reasons for controlling their emissions, thus their classification as federal hazardous air pollutants or air toxics (discussed further in section 3.6). The largest mixing ratios observed for each of these compounds were comparable to those found in a polluted urban environment [*Monod et al.*, 2001] illustrating the probable impact of 2-stroke snowmobile emissions on the Park airshed. To put these values into perspective, background mixing ratios from the west coast in March, 2002 were the following: benzene ~140 pptv; toluene ~30 pptv; ethylbenzene and the xylenes ~ 3 pptv.

The distributions of CO, benzene and toluene for samples collected in West Yellowstone, MT and surrounding areas are shown in Figures 38-40. Samples were collected late in the evening on SAT2003 and in the morning and afternoon on SUN2003. The scaling on the West Yellowstone maps are the same as the Park maps in order to directly compare the two locations and better see the effect of localized emissions for large numbers of snowmobiles. For the samples collected outside of downtown West Yellowstone (X18-X20), the mixing ratios are more representative of background type conditions. With the exception of two samples collected on the evening of SAT2003 (X2 and X3), all mixing ratios were extremely large (largest mixing ratio bin on the plots corresponding to the red dots) and were consistent with 2-stroke exhaust signatures. These extraordinarily large mixing ratios, which are comparable to polluted urban areas, are of concern because they are upwind of the Park. Ultimately, these compounds can be transported downwind in to the Park possibly adding to the wintertime air quality problems. However, it should also be noted that samples were collected during times in West Yellowstone when the snowmobile activity levels peaked (i.e., mid-morning).

The maps showing the spatial variation of mixing ratios for the selected gases demonstrate no observable gradients between observations acquired at numerous locations during a given sampling period. It is surmised that this results from the influence of local emission source areas that are smaller in scale, spatially, than the sampling grid was capable of resolving. These results hampered attempts to geostatistically model the spatial variability of pollutants across the Park and points to the need to utilize a finer spatial resolution in sampling specific areas of the Park in future iterations of the research.

In order to assess the strength of association between VOC emissions and differing levels of snowmobile traffic in the Park, correlation analyses (Pearson's Product Moment) were performed for four selected gases. Mixing ratios for near-road samples acquired in the PM sampling periods of Wednesday and Saturday were compared with average daily snowmobile use weighting factors derived from published values for YNP road segments contained in the "Winter Plans FEIS" [2000b]. Because VOC samples were not always acquired along the length of given road segments, those samples taken at segment endpoints (i.e., Norris Junction, Mammoth, Old Faithful, Canyon Village, and West Thumb) were combined with any intra-segment observations and averaged to produce representative values. Also, the road segment "Mammoth to Northeast Entrance" was eliminated from the analyses owing to the lack of snowmobile traffic there, as was the "Norris to Madison Junction" road segment owing to a lack of sample sites there.

The results of the correlation analyses (Table 8) show that there are only very weak correlations between snowmobile traffic and VOC mixing ratios in these segments, positive associations are indicated suggesting that the VOC values measured within the Park do vary as a function of differing traffic levels. It should be noted that the correlation results are affected by two important factors 1) the small number of road segments and corresponding VOC mixing ratios that serves to reduce the overall confidence in the reported correlation statistics, and 2) the snow conditions experienced in YNP in 2003 were different than average conditions which are characterized by a continuous snow surface on all road segments. Observations by field personnel in this year's sampling campaign indicated that the lack of snow cover in the Madison Junction-Old Faithful road segment was likely responsible for the reduced level of entries at the West Entrance, while improved snow and weather conditions on the West Thumb-South Entrance (Flagg Ranch) road segment led to increased traffic there rendering traffic patterns in YNP during the sampling periods different than the averages reported in the FEIS [2000b]. Lastly, it should be noted that a review of the weighting factors derived from average peak daily use values presented in the FEIS [2000b] revealed that these would not differ much from those computed for the average daily use values, therefore similar analyses were not performed for these.

**Table 8.** Correlation coefficients for YNP road segment-VOC concentrations.

| Sample Period | CO (ppbv) | Toluene (pptv) | i-Pentane (pptv) | Propane (pptv) |
|---|---|---|---|---|
| 2/12/2003 PM | 0.52 | 0.58 | 0.57 | 0.73 |
| 2/15/2003 PM | 0.56 | 0.57 | 0.57 | 0.61 |

### 3.3.1 Mixing Ratios Exceeding Maximum and Minimum Values in 2002

In comparing the maximum mixing ratios for the mapped gases, for all gases other than propane, all sampling sites produced values that exceeded the maximum values during 2002. The vast majority of these were located along the route from the West Entrance to West Thumb. Site D4 (see Figure 1), near the West Entrance, had 19 measurements that exceeded the 2002 mixing ratios for any given gas, while at D2 (well within the Park) 12 measurements showed higher values than at any location in 2002. The third site that had multiple observations (14) exceeding 2002 values was E1. Most of these maximum levels occurred at near-road locations. Ethyne, ethylbenzene and ethene were the gases with mixing ratios exceeding 2002 values at these sites. The only other sampling site to have any mixing ratio values that were higher than the 2002 values was B1.

Only four gases had mixing ratios that were less than the minimum values found in YNP during the 2002 sampling period. These were benzene with 40 measurements, ethene with 30, ethane with 19 and propene with only 5. Lower minimum mixing ratios were found throughout the Park in 2003, but were concentrated in its northern portion where snowmobiles are not allowed. The exception to this was shown in the new minimum values for ethane which were found more along the Loop Road.

## 3.4 Comparisons: Low and High Traffic Days and Near- and Off-Road Samples

Table 7 lists the median and mean mixing ratios in pptv, and percent difference in median mixing ratios between each sampling period (AM and PM) and location (near-road versus off-road) to assess the impact of increased snowmobile traffic in the Park.

The decrease in concentration of most gases between the AM and PM sample collections occurs regularly and is associated with the daytime heating of the earth's surface resulting in an increase in the planetary boundary layer height. This indicates that dilution is taking place with clean free tropospheric air mixing into the boundary layer. Even though air mass dilution is occurring, large enhancements in other trace gas mixing ratios associated with local snowmobile emissions were observed. Evaluating the percent difference of the median values for the samples collected on each day, the impact of the increased number of snowmobiles on the Yellowstone airshed can be assessed (median values are used for comparison rather than mean values so that the results are not skewed by samples with very high concentrations of NMHCs). Many of the compounds associated with 2-stroke engine exhaust, especially the aromatics, listed in Table 7 show enhancements in the percent difference of the median values between the low-traffic day and high-traffic. In general, the near-road samples also display larger enhancements. Overall, increased snowmobile usage resulted in an increase in median values for the reported trace gases.

**Table 9.** Results of *t*-Tests comparing off-road and near-road sample means (*t* critical value at 1.97756).*

| VOC | Off-Road Mean | Near-Road Mean | ǀTǀ | P-Value |
|---|---|---|---|---|
| Benzene | 198.8 | 893.4 | 1.64 | 0.10 |
| Methane | 1.804 | 1.806 | 0.89 | 0.37 |
| $C_2Cl_4$ | 7.9 | 8.0 | 0.45 | 0.65 |
| CO | 137.5 | 286.3 | 1.60 | 0.11 |
| Ethane | 1430.9 | 1677.8 | 1.85 | 0.07 |
| Ethene | 367.7 | 2130.9 | 1.69 | 0.09 |
| Ethylbenzene | 79.5 | 402.5 | 1.59 | 0.11 |
| Ethyne | 619.8 | 2567.5 | 1.42 | 0.16 |
| i-Butane | 211.1 | 785.3 | 1.59 | 0.11 |
| i-Pentane | 502.1 | 3016.6 | 1.64 | 0.10 |
| m-Xylene | 200.5 | 1019.5 | 1.57 | 0.12 |
| n-Butane | 592.8 | 2551.8 | 1.59 | 0.11 |
| n-Pentane | 261.1 | 1580.7 | 1.61 | 0.11 |
| o-Xylene | 98.2 | 513.4 | 1.58 | 0.12 |
| Propane | 565.4 | 695.3 | 1.61 | 0.11 |
| Propene | 176.5 | 1097.6 | 1.53 | 0.13 |
| p-Xylene | 96.3 | 373.0 | 0.95 | 0.34 |
| Toluene | 477.7 | 2469.3 | 1.59 | 0.12 |

*Note: Reported P-values are for a two-tailed rejection region.

The efficacy of the near-road (i.e., ~50 m upwind of nearest road feature) sampling protocol employed in the 2002 YNP air sampling campaign, and in countless other field campaigns of a similar nature, was tested in the field (WED2003 and SAT2003) by adding an additional off-road (i.e., >500 m) sample to that normally collected at each site. The mixing ratios of the near-road and off-road samples for all AM and PM periods on both sample days at each site were aggregated and then compared with the use of a *t*-Test for equal sample variances (Ho: Mean $_{\text{Near-Road}}$ = Mean $_{\text{Off-Road}}$) yielding the results shown in Table 9. These results indicate that there was no significant difference between the near-road and off-road sample means for each gas that was measured and subjected to this analysis (large ǀTǀ and P-values lead to the rejection of the null hypothesis or Ho). They do suggest, though, that the consistently lower mean values for the off-road samples as compared with the near-road observations is a function of distance. Based on these results the investigators will consider expanding the near-road sampling distance to ~100 m in future iterations of the study thus permitting the elimination of the 500 m off-road sites in the interest of shortening the length of the AM and PM sampling periods and dedicating canisters to additional sites and diurnal observations.

### 3.5 Secondary Organic Aerosol Formation

Many of the higher carbon-number compounds measured during this campaign have been shown to contribute to the formation of secondary organic aerosol (SOA). SOA forms when semi- or non-volatile oxidation products of gas-phase organics partition to the condensed phase. Of the compounds measured, >$C_8$ *n*-alkanes, and aromatic species are assumed to contribute to SOA formation [*Odum et al.*, 1996; *Odum et al.*, 1997; *Ziemann*, 2002; *Takekawa et al.*, 2003]. Because emissions rates of relevant species and a complete set of three-dimensional meteorological, initial, and boundary conditions are not available for this location and date, a full three-dimensional modeling simulation of SOA formation is not possible. However, the gas-phase measurements made allow for estimation of SOA formation rates as a function of time, as described below.

SOA yield, $Y_i$, for a given reactive organic gas (ROG) $i$ is defined as the concentration of SOA formed ($\mathrm{SOA}_i$) (µg m$^{-3}$) upon the oxidation of a certain concentration, $\Delta\mathrm{ROG}_i$ (µg m$^{-3}$), of ROG $i$ [*Pandis et al.*, 1991]. In relatively dry atmospheres with low concentrations of acidic aerosol species, such as would be expected in YNP in winter, this yield is expressed as

$$Y_i = \frac{\mathrm{SOA}_i}{\Delta\mathrm{ROG}_i} = \mathrm{OM}\sum_j \frac{\alpha_{ij} K_{ij}}{1 + \mathrm{OM} K_{ij}} \qquad (1)$$

where OM (µg m$^{-3}$) is the concentration of organic aerosol available to act as a partitioning medium for the secondary organic oxidation products, $K_{ij}$ (m$^3$ µg$^{-1}$) is the partitioning coefficient that describes the distribution between the condensed aerosol phase and the gas phase of product $j$ from parent ROG $i$, and $\alpha_{ij}$ is the mass-based stoichiometric coefficient for product $j$ from parent ROG $i$. This expression assumes that the dominant mechanism by which secondary organic oxidation products partition to the condensed phase is absorption into a pre-existing organic aerosol [*Pankow*, 1994]. OM is defined as being both SOA and primary organic aerosol (POA) (OM = POA + SOA). By definition, total SOA, $\mathrm{SOA}_\mathrm{T}$, is the sum of $\mathrm{SOA}_i$.

$$\mathrm{SOA}_\mathrm{T} = \sum_i \mathrm{SOA}_i = \sum_i Y_i \Delta\mathrm{ROG}_i \qquad (2)$$

If $Y_i$ and $\Delta\mathrm{ROG}_i$ values are available, it is thus possible to estimate the amount of SOA formed from a mixture of parent hydrocarbons. For the aromatic species (except styrene), $\alpha_{ij}$ and $K_{ij}$ values assuming a two-product model have been developed to fit experimental smog chamber data [*Odum et al.*, 1996; *Odum et al.*, 1997]. In this work, it was shown that aromatics could be classified structurally according to their SOA formation potential. Because of its functional side-chain, styrene is thus assumed to be a high-yield aromatic as described by *Odum et al.* [1997]. The partitioning coefficients used for the aromatic species were measured at over 300K, significantly higher than ambient temperatures observed during the campaign in YNP. Partitioning coefficients derived from the smog chamber experiments are therefore corrected for temperature using the Clausius-Clapeyron equation, as described by *Sheehan and Bowman* [2001]. Typically, OM contains both POA and secondary species, meaning that solution of equation (2) for SOA would require iteration if POA concentrations were known; however if OM is expected to consist mostly of POA (POA >> SOA such that OM ~ POA), the need for iteration is removed if OM is available. In this case, OM is assumed to be 0.4 μg $m^{-3}$ based on the average of 24-hour average filter samples taken in YNP for the IMPROVE network (http://vista.cira.colostate.edu/improve/) during February 2002. It should be noted that this methodology does not consider partitioning to the aqueous phase [*Pun et al*., 2002; *Griffin et al*., 2003] and the acid-catalyzed heterogeneous pathway of SOA formation recently postulated by *Jang et al*. [2002]. This assumption should not greatly affect presented results because of the low levels of particulate photochemically produced acids and dry conditions expected in a remote location in winter. For the alkanes considered, parameters for a two-product model are not available. Based on recent work [*Ziemann*, 2002; *Takekawa et al*., 2003]. However, it is assumed that *n*-decane has a yield three-quarters as large as toluene; *n*-octane has an assumed yield of half of that of toluene. By linking the yield of the alkanes to that of toluene, temperature-dependence of alkane yields is achieved.

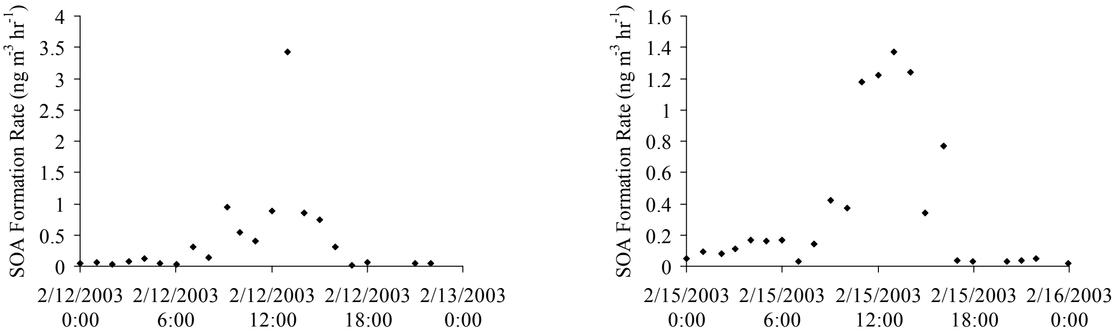
$\Delta\mathrm{ROG}_i$ values are estimated in the following manner. Hydroxyl radical is the primary oxidant leading to consumption of aromatics and alkanes in the atmosphere. Therefore, based on second order kinetics with an assumption of constant OH concentration over the time period of interest ($t_1$ to $t_2$, in minutes)

$$[\mathrm{ROG}_i]_{t_2} = [\mathrm{ROG}_i]_{t_1} \exp\left(-k_{\mathrm{OH},i}[\mathrm{OH}](t_2 - t_1)\right) \tag{3}$$

where $k_{\mathrm{OH},i}$ is the temperature-dependent reaction rate coefficient for species $i$ with OH ($\mathrm{ppm}^{-1}$ $\mathrm{min}^{-1}$) and the bracket notation represents concentration, in this case a mixing ratio (ppm). Subscripts on mixing ratios refer to temporal dependence. This allows for calculation of $\Delta\mathrm{ROG}_i$ over the period $t_1$ to $t_2$ assuming $[\mathrm{ROG}_i]_{t1}$ is that measured during sampling

$$\Delta\mathrm{ROG}_i = [\mathrm{ROG}_i]_{t_1}\left(1 - \exp\left(-k_{\mathrm{OH},i}[\mathrm{OH}](t_2 - t_1)\right)\right) \tag{4}$$

The difference between $t_2$ and $t_1$ is assumed to be two minutes, the length of the collection of samples for analysis. Reaction rate constants are taken from literature [*Calvert et al*., 2002; *Atkinson*, 2003]. [OH] values are estimated using a box-model version of the Caltech Atmospheric Chemistry Mechanism (CACM) with photolysis rate constants manipulated for application in YNP in winter [*Griffin et al*., 2002]. At each model time step, CACM calculates [OH] based on the concentration of other species present. CACM is initialized using observed organic mixing ratios for each sample as well as concurrent temperature, ozone, nitric oxide (NO), and reactive nitrogen ($\mathrm{NO_y}$) measurements. The difference between NO and $\mathrm{NO_y}$ is distributed among nitrogen dioxide, nitric acid, and peroxy acetyl nitrate based on the fractionation observed during the TOPSE campaign (http://topse.acd.ucar.edu/). CACM is run for two minutes of model time, and the average OH calculated by CACM over that time period is used in equation (4) above. $\Delta\mathrm{ROG}_i$ values are converted to μg $m^{-3}$ using measured ambient temperatures and the molecular weight of species $i$. Combination of the yields calculated above and the $\Delta ROG_i$ values described here allows for estimation of the concentration of SOA formed from each parent *i* over the two-minute period associated with a sample collection. The sum over all parent ROGs leads to the total concentration of SOA formed in that two-minute span. Dividing this value by 2 and multiplying it by 60 leads to an estimate of the hourly formation rate of SOA in this location. These values are shown for WED2003 and SAT2003 in Figure 41, respectively; corresponding values are given in Table 10. SOA formation rates peak in midday when both ROG and OH concentrations are highest. By summing over all of the available hours, the total amount of SOA formed in a day is found. For WED2003, this value is 9.1 ng m$^{-3}$ (noting that three hours did not have sufficient data to allow for SOA formation rate calculations); a corresponding value of 8.1 ng m$^{-3}$ is predicted for SAT2003 (with only one hour with data insufficient to allow this type of calculation). Given that it is expected that SOA will form on smaller particles [*Meng et al.*, 1998], it is not expected that a large fraction of these particles deposit or are transported out of the region within 24 hours. Therefore, dividing these values by the daily average 400 ng m$^{-3}$ gives an indication of the contribution of SOA to organic particulate levels in YNP in winter. The result is approximately 2%.



a b

**Figure 41.** SOA formation rates (ng m$^{-3}$ hr$^{-1}$) in YNP on a) WED2003 and b) SAT2003. *Note the difference in scale between parts a and b.

An investigation of the variables used to calculate SOA formation in this exercise indicates that the choice of a single value for OM is most likely the biggest assumption because daily average filter samples are unable to resolve diurnal patterns of OM concentrations. Given the importance of OM in determining SOA yield, it is of interest to see if changes in the value of OM used have large impacts on the estimate of SOA formation in YNP in winter. A value of 0.2 μg m$^{-3}$ for OM results in total SOA formed of 5.9 and 4.8 ng m$^{-3}$ for WED2003 and SAT2003, respectively. Corresponding values of 11.5 and 10.6 ng m$^{-3}$ are predicted for the case when OM is 0.6 μg m$^{-3}$. In any case, the amount of SOA formed in YNP in winter is on the order of 10 ng m$^{-3}$, typically only about 2-3% of total organic aerosol mass. The average total fine aerosol mass measured in February 2002 by the IMPROVE network was approximately 1.2 μg m$^{-3}$, indicating that SOA likely contributes less than 1% of the total fine aerosol mass in YNP in winter. However, POA material that is also likely derived from combustion sources is a significant fraction of fine particulate matter.

### 3.5.1 Possible Impact of Particle Emissions

Scattering of radiation by particles with sizes comparable to the wavelength of visible light is primarily responsible for visibility reduction. SOA formation could increase the number of particles in this size range and likely impact Park visibility. Therefore, it is important to first determine if SOA formation contributes to additional organic particle formation in the Park during periods of oversnow travel. From this work, we have determined that SOA formation does not contribute significantly to organic particulate levels in the Park. Ruling out SOA formation allows us to assume that the majority of organic aerosol in the Park is likely to be POAs, which can be emitted in large amounts by 2-stroke engines [*Carroll and White*, 1999] and diesel engines. Given the fact that the overall number of diesel vehicles in the Park is significantly less than 2-stroke snowmobiles, we must assume that the majority of particles measured at the Lake R.S. site are from 2-stroke snowmobiles. Figure 42 shows measurements of NO, NOy and particles (CN) from the Lake R.S. sampling site on SAT2003. A logarithmic scale has been used for displaying the CN values because of the large range of values observed. Strong correlations exist between NO, NOy and CN measured at the site (not shown) indicating a similar source – in this case, engine exhaust which is assumed to be predominantly 2-stroke based on the NMHC signatures. Additionally, enhancements are observed from the early morning through the end of the day when the majority of visitors are touring the Park, elevating particulate levels several orders of magnitude above background.

**Table 10.** SOA formation rates (ng $m^{-3}$ $hr^{-1}$) in YNP onWED2003 and SAT2003.

| Sample Time (February 12, 2003) | SOA Formation Rate | Sample Time (February 15, 2003) | SOA Formation Rate |
|---|---|---|---|
| 11:57PM (2/11/03) | 0.23 | 12:01AM | 0.05 |
| 12:01AM | 0.04 | 1:04AM | 0.09 |
| 1:02AM | 0.06 | 2:11AM | 0.08 |
| 2:01AM | 0.03 | 3:02AM | 0.11 |
| 3:05AM | 0.07 | 4:01AM | 0.17 |
| 4:01AM | 0.12 | 5:02AM | 0.16 |
| 5:01AM | 0.04 | 5:59AM | 0.17 |
| 6:01AM | 0.03 | 7:03AM | 0.03 |
| 7:04AM | 0.31 | 8:01AM | 0.14 |
| 8:04AM | 0.14 | 9:01AM | 0.42 |
| 9:12AM | 0.94 | 10:06AM | 0.37 |
| 10:01AM | 0.54 | 11:01AM | 1.18 |
| 11:01AM | 0.41 | 12:01PM | 1.22 |
| 12:00PM | 0.88 | 1:01PM | 1.37 |
| 1:01PM | 3.42 | 2:01PM | 1.24 |
| 2:01PM | 0.86 | 2:59PM | 0.34 |
| 3:01PM | 0.74 | 4:06PM | 0.77 |
| 4:01PM | 0.31 | 5:00PM | 0.04 |
| 5:01PM | 0.02 | 5:58PM | 0.03 |
| 6:01PM | 0.06 | 8:04PM | 0.03 |
| 9:01PM | 0.04 | 8:59PM | 0.04 |
| 10:00PM | 0.05 | 9:56PM | 0.05 |
|  |  | 11:58PM | 0.02 |

Particles in the range of 100-1000 nm in diameter are most effective, per unit mass, in reducing visibility [*Seinfeld and Pandis*, 1998]. *Carroll and White* [1999] performed a particle size analysis on the emissions of a Polaris 2-stroke snowmobile engine and determined that the particulate emissions were primarily composed of organics and were typically < 100 nm in size. Mean particle sizes ranged from 20-80 nm, depending on the engine speed and power conditions. Therefore, we estimate the average particle diameter emitted from a 2-stroke engine to be on the order of 40 nm. Because particles emitted from a 2-stroke engine have been determined to be primarily organic in composition, we can use this information to qualitatively assess both the mass scattering and absorption efficiencies. For mass scattering efficiencies at λ = 550 nm, particles composed of organics peak at ~200 nm in diameter with the low end of the distribution around 40 nm. This would suggest that the particles emitted in this size range would not have large light scattering efficiencies. However, mass absorption efficiencies peak for particles in the sub-100 nm size range, and as a result, overall light extinction by particles with diameters smaller than 100 nm is primarily due to absorption [*Seinfeld and Pandis*, 1998]. This would suggest that particulate emissions from 2-stroke engines may have adverse affects on visibility due to absorption of light by particles in this size range. Additionally, this does not include the fact that when particles are airborne, they may also aggregate and grow in size which would subsequently make light scattering a more important factor with regard to Park visibility.

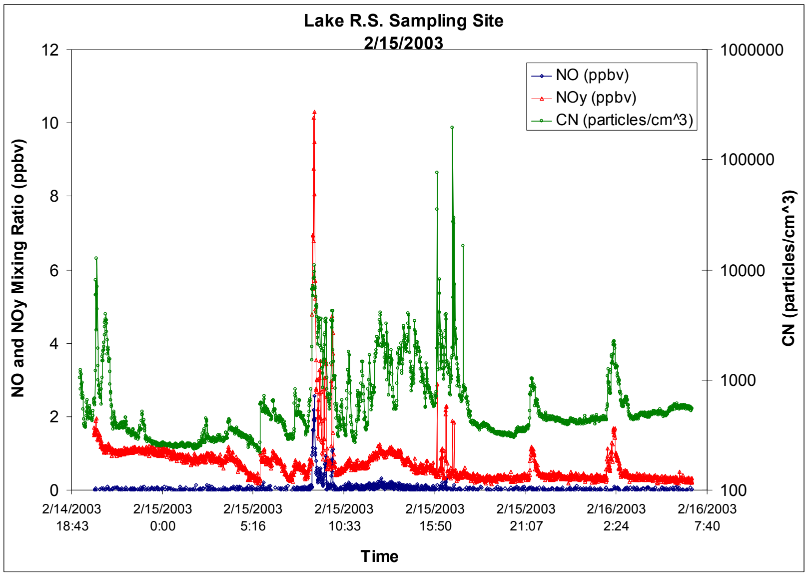


**Figure 42.** Measurements of NO, NOy and CN at the Lake R.S. sampling site on SAT2003. *NO and NOy values are reported in ppbv and are displayed on a linear scale. CN values are reported in concentration (particles/cm$^3$) and are displayed on a logarithmic scale.

The contribution of SOA formation to organic particulate levels in the Park was not significant during the period of this study. However, large enhancements of particles were observed at the Lake R.S. sampling site and we assume that these particles are POAs emitted directly from exhaust because of the robust correlations with NO, NOy in addition to the NMHC signatures. Because there were large enhancements of particles (several orders of magnitude above background) observed at the Lake R.S. sampling site, it is likely that there were visibility effects. This work is only a very general first-cut at addressing the issue of particles and how they affect visibility. However, to fully understand the impact of particles on visibility, further research with regard to particle size and composition measurements are critical.

### 3.6 Air Toxics and Hazardous Air Pollutants

Air toxics are pollutants in the air that cause adverse health effects. As a result of these effects, the U.S. EPA has focused considerable efforts on developing new field programs to deal with exposure to these compounds and the associated human health effects. Most air toxics have been identified through laboratory experiments in which animals receive very high doses of the compound being studied. Although humans almost never encounter the levels that animals are subject to in the laboratory, lower exposure levels can still pose severe health risks. Vehicular exhaust is a major source of toxic compounds to the atmosphere and evaluating the sources and distributions of these compounds is critical to protecting public health and the environment.

Vehicles, especially with 2-stroke engines, emit numerous pollutants that EPA has classified as known or probable human carcinogens. Benzene is a known human carcinogen, while compounds such as toluene, xylenes, and trimethylbenzenes are probable human carcinogens. The EPA estimates that mobile sources of air toxics account for as much as half of all cancer cases attributed to outdoor sources of air toxics. This estimate is based on models that predict the maximum number of cancer cases that could be expected from current levels of exposure to mobile source emissions. The models consider available health studies, air quality data, and other information about the types of vehicles and fuels currently in use. Non-road mobile sources (such as snowmobiles) emit significant amounts of air toxics as discussed previously.

Toxic compounds are also present in gasoline and are released to the atmosphere when gasoline evaporates or passes through the engine as unburned fuel. Benzene is a component of gasoline and vehicles emit it in various quantities in unburned fuel, or as vapor when gasoline evaporates. A significant amount of vehicular benzene comes from the incomplete combustion of compounds in gasoline, such as toluene and the xylenes, that are aromatic compounds and chemically very similar to benzene. These compounds, like benzene, occur naturally in petroleum and become more concentrated when petroleum is refined to produce high octane gasoline.

To date, there are no specific standards for air toxics emissions from motorized vehicles. However, the CAA (1990) does set specific emission standards for hydrocarbons and for diesel particulate matter. Air toxics are present in both of these pollutant categories and as vehicle manufacturers develop technologies to comply with the hydrocarbon and/or particulate standards (e.g., more efficient catalytic converters), air toxics will be reduced as well. Requirements under the Act for testing carbon monoxide emissions at cold temperatures will also have an indirect but important effect in reducing air toxics emissions in the critical first moments of vehicle operation or during cold weather operation.

### 3.6.1 Regulating Air Quality

The CAA (1990) requires the EPA to set National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment. The Clean Air Act established two types of national air quality standards. *Primary standards* set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. *Secondary standards* set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings.

The EPA Office of Air Quality Planning and Standards has set NAAQS for six principal pollutants, which are called "criteria" pollutants and are listed in Table 11. Units of measure for the standards are parts per million (ppm) by volume, milligrams per cubic meter of air (mg/m$^3$), and micrograms per cubic meter of air (μg/m$^3$).

Because of the possible adverse health effects from exposure to toxic compounds in the air, legal standards have also been implemented for workplace exposures by OSHA. These standards are known as Permissible Exposure Limits (PELs). Most OSHA PELs are for airborne substances with allowable exposure limits averaged over an 8-hour day, 40-hour week which is known as the Time-Weighted-Average (TWA) PEL. Adverse effects should not be encountered with repeated exposures at the TWA PEL. OSHA also issues Short Term Exposure Limit

(STELs) PELs. PEL STELs are concentration limits of substances in the air that a worker may be exposed to for 15 minutes without suffering adverse effects. The 15-minute STEL is usually considerably higher than the 8-hour TWA exposure level. Additionally, NIOSH has established Recommended Exposure Limits (RELs) and Short-Term Exposure Limits (STELs) for occupational exposure to hazardous or toxic compounds in the air. The NIOSH RELs are also based on an 8-hour time-weighted average and the NIOSH STEL is a 15-minute exposure limit that should not be exceeded during the workday. Table 12 lists the NIOSH RELs and STELs along with the OSHA PELs and STELs for selected VOCs.

**Table 11.** Selected National Ambient Air Quality Standards for criteria pollutants.

| **POLLUTANT** | **STANDARD VALUE** | | **STANDARD TYPE** |
|---|---|---|---|
| **Carbon Monoxide (CO)** | | | |
| 8-hour Average | 9 ppm | (10 mg/m$^3$) | Primary |
| 1-hour Average | 35 ppm | (40 mg/m$^3$) | Primary |
| **Nitrogen Dioxide ($NO_2$)** | | | |
| Annual Arithmetic Mean | 0.053 ppm | (100 μg/m$^3$) | Primary & Secondary |
| **Ozone ($O_3$)** | | | |
| 1-hour Average | 0.12 ppm | (235 μg/m$^3$) | Primary & Secondary |
| 8-hour Average | 0.08 ppm | (157 μg/m3) | Primary & Secondary |
| **Particulate (PM 10)** | *Particles with diameters of 10 micrometers or less* | | |
| Annual Arithmetic Mean | 50 μg/m$^3$ | | Primary & Secondary |
| 24-hour Average | 150 μg/m$^3$ | | Primary & Secondary |
| **Particulate (PM 2.5)** | *Particles with diameters of 2.5 micrometers or less* | | |
| Annual Arithmetic Mean | 15 μg/m3 | | Primary & Secondary |
| 24-hour Average | 65 μg/m3 | | Primary & Secondary |
| **Sulfur Dioxide ($SO_2$)** | | | |
| Annual Arithmetic Mean | 0.03 ppm | (80 μg/m$^3$) | Primary |
| 24-hour Average | 0.14 ppm | (365 μg/m$^3$) | Primary |
| 3-hour Average | 0.50 ppm | (1300 μg/m$^3$) | Secondary |

### 3.6.2 Maximum Levels of Toxic Compounds Observed in YNP

Table 12 lists a subset of gases that were measured in the study region that are considered to be hazardous air pollutants or air toxics. Several of the VOCs listed are halocarbons that are not directly emitted from vehicular sources. However, it is worth nothing that a number of these gases did, in fact, correlate with CO from the heavily polluted samples collected in West Yellowstone, MT. Nonetheless, the mixing ratios observed for the halocarbons were not significantly higher than background mixing ratios, and were well below any of the OSHA regulatory limits.

For two different ambient samples collected at the West Gate Entrance Station on SUN2003, adjacent to the main office (under the roof enclosure), extremely high levels were measured for most VOCs associated with snowmobile exhaust. Table 13 lists the mixing ratios in ppmv for selected gases. Although the timescale to fill the 1-liter sample canisters was on the order of 1 minute, benzene levels may have approached NIOSH STEL regulatory standards in both the morning and afternoon samples. Although we can not say that these levels persisted for a 15-minute duration in order to exceed the regulatory standard, it is likely that the area under the roof enclosure at the West Gate Entrance Station experienced elevated mixing ratios because of the sustained traffic through the Entrance Gate throughout the day. Additionally, it should be noted that Park employees working in this vicinity were likely exposed to significantly higher levels of toxic compounds, increasing their risk of possible health effects due to increased exposure.

**Table 12.** NIOSH RELs and STELs and OSHA PELs and STELs for selected VOCs.
*Cells containing no values do not have a set exposure limit.

| Compound | NIOSH REL (ppm) | NIOSH STEL (ppm) | OSHA PEL (ppm) | OSHA STEL (ppm) |
|---|---|---|---|---|
| CO | 35 | 200 | 50 | |
| Benzene | 0.1 | 1 | 1 | 5 |
| Toluene | 100 | 150 | 100 | 150 |
| Ethylbenzene | 100 | 125 | 100 | 125 |
| Xylenes | 100 | 150 | 100 | 150 |
| Styrene | - | - | 100 | - |
| 1,2,4-Trimethylbenzene | 25 | - | - | - |
| 1,3,5-Trimethylbenzene | 25 | - | - | - |
| n-Hexane | 50 | - | 500 | - |
| NO | - | - | 25 | - |
| $NO_2$ | - | - | - | 5 |
| $CH_3Cl$ | - | - | 100 | - |
| $CH_2Cl_2$ | - | - | 25 | - |
| $CHCl_3$ | - | - | 50 | - |
| $CCl_4$ | - | - | 10 | - |
| $C_2HCl_3$ | - | - | 100 | - |
| $C_2Cl_4$ | - | - | 100 | - |
| $CH_3Br$ | - | - | 20 | - |
| $CHBr_3$ | - | - | 0.5 | - |

From the samples collected throughout the Park, the maximum values for the toxic compounds were found on the route between the West Gate Entrance and Old Faithful. Mixing ratios for CO were in the 2-5 ppmv range and in the ~5-30 ppbv range for benzene, toluene, xylenes, ethylbenzene, n-hexane. Styrene and the trimethylbenzenes were in the ~ 500 pptv range. While these mixing ratios are significantly higher than background levels, they are considerably lower than the regulatory standards set by OSHA or NIOSH.

In summary, high levels of VOCs that are considered air toxics or hazardous air pollutants were observed in the vicinity of the West Gate Entrance Station and on the route between the West Gate and Old Faithful. Benzene levels for the samples collected at the West Gate Entrance Station were elevated to levels that approach those of regulatory standards, suggesting further investigation in this area of the Park is necessary to better determine what levels of Park workers are being exposed to. Additionally, high CO levels were measured just downwind of the West Gate Entrance Station. These results indicate that it is likely that Park personnel working in these areas are exposed to higher levels of toxic air pollutants and could experience increased health risks associated with exposure to these levels.

**Table 13**. Mixing ratios of selected VOCs collected at the West Gate Entrance Station on February 16, 2003.

| Collection Date<br>Sample Information<br>Compound | 2/16/03<br>West Gate Entrance Station, 10:34<br>Mixing Ratio (ppmv) | 2/16/03<br>West Gate EntranceStation, 15:44<br>Mixing Ratio (ppmv) |
|---|---|---|
| **CO** | 1.664 | 1.458 |
| **n-hexane** | 3.00 | 0.88 |
| **Benzene** | 2.88 | 1.02 |
| **Toluene** | 8.71 | 0.53 |
| **p-xylene** | 1.72 | 0.59 |
| **m-xylene** | 3.55 | 1.25 |
| **ethylbenzene** | 1.35 | 0.46 |
| **o-xylene** | 1.72 | 0.60 |
| **Styrene** | 0.08 | 0.03 |
| **1,3,5-trimethylbenzene** | 0.44 | 0.14 |
| **1,2,4-trimethylbenzene** | 1.61 | 0.52 |
| **1,2,3-trimethylbenzene** | 0.32 | 0.10 |

## 3.7 Discussion

The results produced from the February, 2003, air quality sampling campaign represent an important set of findings from a number of standpoints. First, important questions concerning the types, origins, and extents of wintertime air pollutants in YNP have been addressed. Second, these findings represent an important addition to those coming from the 2002 field campaign in YNP undertaken by the same research team, with important additional information concerning patterns of VOC distribution in West Yellowstone, MT, and the potential role of emission related secondary organic aerosols in reducing visibility in the Park. And last, these findings and the data on which they are based represent an important baseline against which the impacts of wintertime oversnow travel policies to be implemented by the NPS can be measured and assessed thus enhancing the opportunity for effective implementation of an adaptive management approach to winter planning.

Considerable discussion of the meaning and significance of the results has been provided in the previous sections, but in order to aide the interpretation of these results they are summarized as the following general observations:

- VOCs sampled in YNP during February, 2003, demonstrated both increased maxima and decreased minima over samples acquired during February, 2002. Higher values in 2003 were generally acquired along the loop road (especially along the southern route from Madison Junction to West Thumb), between the West Entrance and Madison Junction, and from West Thumb to the South Entrance (Flagg Ranch).
- Anthropogenic emissions in and around YNP produce enhanced levels of VOCs that negatively affects air quality in the Park and surrounding communities. This is demonstrated by mixing ratios for aromatic VOCs that are markedly different from air samples obtained at remote North American west coast sites at latitudes similar to that of YNP which are representative of background air quality in the northern hemisphere, and by the absence of enhanced levels of halocarbons that are associated with urban source areas.
- The data show that anthropogenic emissions in the communities of Cooke City and Silver Gate, MT, appear to have minimal impact on air quality in YNP owing to the prevailing westerly winds over the study area.

- Anthropogenic emissions, especially those from 2-stroke snowmobiles, in the community of West Yellowstone, MT, appear to have a strong negative impact on YNP air quality especially in the area just downwind of the West Entrance. Emissions from West Yellowstone likely exacerbate VOC mixing ratios experienced at the West Entrance Station, and contribute to the high values obtained for air toxics at this location. Based on the observations of field personnel, 2-stroke snowmobile use in the community of West Yellowstone during the President's Day weekend, 2003, was very high and exceeded the use of personal automobiles there. It must be noted that the samples acquired within West Yellowstone during this period show the effects of these levels of elevated/concentrated snowmobile use.
- Snow conditions within YNP have likely played an important role in influencing levels of snowmobile traffic in different areas of the Park and the resultant spatial patterns of associated VOC emissions. Furthermore, meteorological effects including the boundary layer depth can influence the mixing ratios of VOCs and allow pollutants to build up to high levels. Even though dilution occurs throughout the day, elevated levels of VOCs persist as a result of 2-stroke exhaust emissions.
- The limited number of exhaust samples that were obtained show that 2-stroke snowmobiles produce larger ratios of NMHCs (relative to CO, not including ethane) than 4-stroke snowmobiles, the Bombardier snowcoach, or the diesel vehicles. These results represent an important supplement to the findings of other recent tests concerned with snowmobile emissions.
- While there is no significant difference between the mean mixing ratios of gases measured from whole air samples acquired at near-road and off-road locations whose distance differed by an order of magnitude, statistical analyses indicate that there is a consistent negative relationship between distance from road and mixing ratio values for the sampled gases. Fifty meters represents a minimum acceptable off-road distance for such sampling.
- Primary organic aerosols (POAs) that are emitted from the exhaust streams of snowmobiles in YNP could likely play a dominant role in reducing visibility at a local scale rather than SOA formation, which appears to little or no effect due to the low production rate. More research is critical in order to understand the the role of organic aerosols in reducing visibility.

## 4. Conclusions

The research reported here indicates that the quality of wintertime air in YNP is clearly impacted by anthropogenic emissions, especially those coming from 2-stroke snowmobile use within the Park and in West Yellowstone, MT. The analysis of whole air samples acquired in the Park and in West Yellowstone in February, 2003, demonstrates this conclusively. The most abundant gases were ethene, ethyne, toluene, benzene, xylenes, trimethylbenzenes, ethane, propane, i-butane, n-butane, and i-pentane. These findings suggest a vehicular source of the pollution, with source fingerprints indicating 2-stroke engine exhaust. The median mixing ratios of gases observed at West Yellowstone on SUN2003 were much larger than the levels observed throughout the rest of the study region on WED2003 and SAT2003 because of widespread snowmobile usage during the sampling period. The distributions of alkyl nitrates, NMHCs, and halocarbons were relatively similar on the low traffic days. Also, the emissions were fairly recent (less than 5 days old). The relative age of the emissions in West Yellowstone were less than a day old suggesting that snowmobile exhaust is a primary source for the alkyl nitrates. The maximum $RONO_2$ mixing ratio was observed on the morning of SUN2003 providing further evidence of a source of alkyl nitrates in the exhaust of snowmobiles. Additional evidence of the anthropogenic impact in YNP is the significantly enhanced mixing ratios of toluene and the xylenes observed in the off-road and Lake R.S. locations compared to the levels observed at remote areas along the west coast during March 2002. Also important are the repeated spatial patterns that the NMHCs exhibited in the Park, and the fact that the gases were well correlated with one another spatially. Particular sites and areas within the Park consistently showed elevated mixing ratios of certain compounds while others showed mixing ratios that approach background levels. In general, the alkane, alkene, and alkyl nitrate distributions were similar to the findings from the 2002 sampling.

The findings suggest that reducing or holding overall levels of snowmobile usage steady, a reduction in the amount of 2-stroke snowmobile traffic will likely reduce NMHC emissions including the air toxics benzene and toluene. This scenario essentially represents the *Winter Use Plans Supplemental Environmental Impact Statement*'s [2003] Alternative 2. Alternatives 1a, 1b, and 3 would also have produced significant decreases in NMHC and air toxic levels in the Park. The preferred alternative, Alternative 4 identified in the SEIS [2003] and the associated ROD, will also produce similar decreases but will require their assessment, interpretation, and consideration in the context of planning for wintertime recreational use and visitation in the Park.

## 5. Management Alternatives and Implications

As noted previously, the NPS will implement a winter recreation management policy, Alternative 4, which provides for the development and implementation of daily snowmobile entry limits in addition to best available technologies (BATs) for these vehicles and snowcoaches together with monitoring and adaptive management, as the preferred alternative to be implemented beginning in the winter season of 2003-2004 [U.S. Dept. of the Interior, 2003b]. Beginning in December, 2003, all commercially guided recreational snowmobiles entering YNP must employ BATs, which in the year 2002 corresponded to two commercially available 2002 4-stroke machines produced by two separate manufacturers (i.e., the 2002 Arctic Cat 4-stroke, and the 2002 Polaris Frontier). As per FSEIS requirements, commercial outfitters will have to demonstrate that their 4-stroke fleets meet BAT standards before rental machines are permitted in the Park. Private riders will be exempt from these requirements, and other snowmobiles utilized by commercial outfitters and guides may gain access to YNP if it can be demonstrated that they meet the BAT requirements. Beginning in December, 2004, all snowmobiles entering YNP must meet BAT requirements.

Alternative 4 can be seen to be markedly different from the environmentally preferred alternative, Alternative 1b, which represented a deferred implementation of a no action alternative (i.e., Alternative 1a) which was the selected alternative coming from the 2001 ROD on the FEIS, albeit in a slightly modified form [*National Park Service*, 2003]. These alternatives, if selected, would have required the implementation of a complete phase-out of all snowmobile use in YNP and the development of an enhanced snowcoach fleet under NPS management to provide wintertime access to the Park for visitors. As noted in the 2003 ROD [*National Park Service*, 2003:7], the preferred alternative (Alternative 4) will take into account a broader set of factors than Alternative 1b, and provide the opportunity for monitoring and adaptive management that will be based on sound science and give consideration to emerging snowmobile BATs. This preferred alternative should not be viewed as a set of minimum standards because the NPS has spelled out its intentions to carefully monitor the effects of this management policy as initially conceived, and to modify it in any given direction should conditions merit so.

Given this state of affairs, the 2003 air quality study described herein suggests a number of implications for the implementation of Alternative 4. First, implementation of daily entrance limits and the phased implementation of BATs will almost certainly have an immediate and significant effect on air quality in the Park in the following ways:

- The vast majority of snowmobiles entering the Park during the winter 2003-2004 season will be BAT equipped, and the numbers of these machines entering through the most heavily utilized entrance (i.e., West) will be approximately half the number of machines that entered on SAT2003 when large-scale enhancements of VOCs were experienced throughout the Park and in adjacent West Yellowstone, MT. This translates into a large-scale reduction in VOC emissions, including air toxics, in the Park and a probable reduction of these compounds in West Yellowstone. Such a reduction will positively impact air quality in these areas, and will have important positive implications for Park personnel at the West Entrance Station who have in the past been exposed to air toxic levels that may approach regulatory limits. Wintertime air quality in YNP will approach that experienced in small- to moderate-sized urban communities in a similar geographic setting.
- Visibility in the Park is likely to be improved owing to the lower potential for primary organic aerosol emissions from 4-stroke engines.
- YNP is considerably less likely to experience the poor air quality conditions that have led to the development of a management approach that could circumvent potential regulatory enforcement procedures related to the CAA.

## 6. Recommendations

Based on the findings of this study and the consideration of the management approach to be implemented beginning in December, 2003, and the implications thereof, the following research-based and oriented recommendations are offered for the consideration of the YNP Planning and Center for Resources staff:

- YNP should present itself as a relatively “natural” or “high quality” environment in the context of human use and anthropogenic impacts. However, it is currently experiencing large-scale enhancements of anthropogenically generated VOCs whose signatures correspond to 2-stroke snowmobile engine emissions. To reduce or eliminate this condition will require the discontinuation of use of 2-stroke technology in the Park, as will occur with implementation of Alternative 4.
- Adherence to the initial requirements of Alternative 4, including entry limits and BATs, until the effects of the policies have been measured and ascertained will be critical in the safeguarding of the Park’s air quality and other resources. These standards should not be weakened until their effects have been properly studied.
- Require that snowmobiles motors be shut off rather than idled for any extended period of time beyond manufacturers recommendations by any commercially guided and/or private snowmobile riders when not in transit in the Park. This will likely have a small but measurable effect on air quality given that idling machines have VOC emission levels that can approximate those of machines under load.

- Begin to monitor snowmobile traffic levels more closely, perhaps using automated devices, in order to better understand the traffic dynamics within the Park. This will provide an improved understanding of the spatial distribution of snowmobiles in YNP and of associated VOC and particulate emissions, among other things. At a minimum, require all snowcoach operators, commercial guides of snowmobile visitors, and private riders to maintain a log of their activities within the Park, and to submit this to NPS personnel at the Entrance Stations upon their exit.

Specific recommendations related to future air quality research activities of a nature similar to the study reported here include:

- The establishment of a diurnal air sampling site at the West Entrance, which is equipped to monitor VOCs, particles, NOy, and $O_3$, will provide important data and information that will supplement that coming from the Lake R.S. sampling site as well as providing an important contrast with this more remote location.
- A summertime air quality study similar to this (i.e., spatial variation of pollutants including anthropogenic and biogenic VOCs) would provide an invaluable set of data that will allow comparison with the wintertime measurements of VOCs, CO, and particulate matter. Additionally, it would be beneficial to collect additional samples in December prior to the opening of the Park to the public for oversnow travel when all roads are closed. This would provide additional baseline data against which comparisons can be made.
- The incorporation of a 3 dimensional mesoscale pollutant transport model that will utilize meteorological data acquired in the field to model the dispersal of pollutants from sample source areas through the Park.
- A greater number of field personnel deployed in the sampling of VOCs throughout the Park as was accomplished in this study would reduce any given sample period and permit the acquisition of higher quality information. Given the high cost of transporting field personnel to YNP from University of New Hampshire and Central Michigan University, YNP staff might play an important role in assisting with the collection of field samples. Similarly, field personnel might be recruited from Montana State University in Bozeman, Montana.

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# 8. Appendices

## 8.1 Maps Showing Spatial Distributions of Gases

## 8.2 Glossary

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| **Acetaldehyde** | A colorless, volatile water-soluble liquid aldehyde used chiefly in organic synthesis. |
| **Acid** | A chemical species that donates protons or hydrogen ions and/or accepts electrons. |
| **Aerosol** | Non-gaseous substances, divided into solid particles or liquid droplets, held in suspension in the atmosphere. |
| **Airshed** | A geographic area that, because of its natural features such as topography or climate, is frequently affected by the same air mass. |
| **Aliquot** | Of, relating to, or denoting an exact divisor or factor of a quantity, especially of an integer. |
| **Alkane** | A compound in which each carbon atom is bonded to four other atoms. Each H is bonded only one C atom. |
| **Alkene** | An unsaturated hydrocarbon that contains one or more carbon-carbon double bonds. |
| **Alkyl** | A group of atoms derived from an alkane by the removal of one hydrogen atom. |
| **Ambient** | Surrounding (for example ambient air). |
| **Anthropogenic** | Relating to, or resulting from the influence of human beings on nature. |
| **Anticyclone** | An atmospheric circulation system in the troposphere with a descending and diverging air flow which appears to flow across the surface in the northern hemisphere in a clock wise manner. |
| **Aromatic** | An organic molecule containing a benzene ring. For example: benzene, toluene. |
| **Baseline** | A measurement calculation, or location used as a basis for comparison. |
| **Benzene** | A colorless liquid with a sweet odor which evaporates very quickly into the air. It is very flammable and is formed from both natural and human activities. Benzene is widely used and is a natural part of crude oil and gasoline. |

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| **Boundary Layer** | The region of the troposphere where surface effects are important. It's depth is of the order of 1 km, but varies significantly with the time of day and with meteorological conditions. The exchange of chemical compounds between the surface and the free troposphere is directly dependent on the stability of the boundary layer. |
| **Butadiene** | A colorless highly flammable, conjugated hydrocarbon obtained from petroleum. |
| **Butane** | Gaseous alkane, a hydrocarbon that is obtained from natural gas or by refining petroleum. It can be liquefied at room temperature by compression. There are two structural isomers of butane. |
| **Butyl** | Any of four isomeric univalent radicals derived from butane. |
| **Carbon Monoxide** | A colorless odorless toxic gas formed when carbon-containing compounds or fuels are burned with insufficient air; especially with incomplete burning of gasoline or oil. |
| **Carcinogen** | A substance that can cause cancer. |
| **Catalyst** | A substance that speeds up a chemical reaction without being consumed itself in the reaction. |
| **CFC** | Chlorofluorocarbons, human manufacturing of organic compounds that contain carbon atom attached to only chlorine and/or fluorine. |
| **Chemiluminescence** | Emission of light as a result of a chemical reaction, without producing heat. |
| **Chiral** | Optically active - a chiral molecule has a non-superimposable mirror image. |
| **Chromatogram** | A pattern or chart formed by substances that have been separated by chromatography. |
| **Chromatography** | A separation technique in which the mixture to be separated is dissolved in a solvent and the solvent passed through a column packed with an adsorbent stationary phase. |
| **Class One Air Shed** | As defined in the Clean Air Act, National Parks over 6,000 acres are included. |
| **Clean Air Act** | Originally passed in 1963 and modified several times including 1970 and 1990 is our national air pollution control program. |

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| **Climate** | The weather in some location averaged over some period of years. |
| **Condensation Nuclei** | Extremely small particles, with radii less than 0.01 um, they serve as a nucleus on which gases condense to form larger particles. |
| **dB(A)** | Decibel – the logarithmic ratio of amplitudes; for signals in volts. dB(A) is a sound level weighted with the A weighting network. The most commonly used measurement for noise abatement applications, since the A network gives a reasonable approximation of the human perception of loudness. |
| **Data Logger** | A device for recording information used with a gps system and from which information can be put into a geographic information system. |
| **Dimethylbenzene** | See xylene. |
| **Dynamometer** | an instrument for measuring mechanical power or force (as of an engine). |
| **Emissions** | Release of pollutants into the atmosphere from a source. |
| **Enantiomeric** | Either of a pair of chemical compounds whose molecular structures Have a mirror-image relationship to each other. |
| **Erythema** | abnormal redness of the skin due to capillary congestion. |
| **Ethane** | Gaseous hydrocarbon which is a continuous-chain alkane. As a constituent of natural gas it is used for fuel. It can also be prepared in the refining of petroleum. |
| **Ethanol** | A monohydric primary alcohol, commonly called grain alcohol or simply alcohol. |
| **Ethene** | Also known as ethylene. A gaseous unsaturated hydrocarbon. It is the simplest alkene. Because of the presence of the double bond in its molecule, it is very reactive. |
| **Ether** | A colorless volatile highly flammable liquid. |
| **Ethylbenzene** | Characterized as the most severe irritant of the benzene series. A component of automotive fuels. |
| **Ethyne** | Also known as acetylene or ethine, forms explosive mixtures with oxygen or air. A colorless gas produced by pyrolysis of natural gas. |

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| **Flame Ionization** | Pyrolysis of organic compounds at the temperature of a hydrogen-air flame to produce ionic intermediates which can be collected and the resulting ion current measured by gas chromatography. |
| **Formaldehyde** | The simplest aldehyde; it is a flammable, poisonous, colorless gas. |
| **Geographic Information System** | Is an integrated software package which is used for the input, management, analysis and display of spatial information. |
| **Georeferenced** | An established relationship between page co-ordinates on a planar map and known real-world co-ordinates. |
| **g/k W-hr** | Grams per kilogram produced during a watt hour. |
| **Grid** | Is a series of lines which are drawn on a map, usually at right-angles, to create reference areas for location purposed. |
| **Halocarbon** | Any of a class of compounds containing carbon, one or more halogens, and sometimes hydrogen. |
| **Hexane** | A colorless flammable liquid alkane derived from petroleum and used as a solvent. |
| **Hydrocarbon** | Any organic compound composed solely of the elements of hydrogen and carbon; examples methane or benzene. |
| **Hydroxyl Radical** | (OH) - a radical that is formed in the atmosphere from the photolysis of ozone in the presence of water vapor. OH controls the rate at which many trace gases are oxidized and removed from the atmosphere. |
| **Inversion** | In meteorology, a departure from usual (normal) decrease or increase in temperature with altitude of the value of an atmospheric property; also, the layer through which this departure occurs (the inversion layer). It prevents a mixing of air vertically. |
| **Isomer** | A compound that exists in forms having different arrangement of atoms but the same molecular weight. |
| **Isopropyl** | The alkyl radical isomeric with normal propyl. |
| **Isothermal Layer** | Relating to the equality of temperature. Having reference to the distribution of temperature in the atmosphere. A horizontal zone in the atmosphere where the thermal conditions are the same. |
| **Kriging** | Geostatistical mapping approach that relies on the variability of observations in designated neighborhoods of a given sampling region to |

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| | estimate values at unsampled cells. Analogous to interpolation but more robust. Kriging approaches include simple kriging, ordinary kriging, universal kriging, and probability kriging among other variants. |
| **Logarithmic Scale** | Is a type of scale in which a series of numbers increase by the multiple of its base, commonly logarithms to the base 10. |
| **Meteorology** | Science dealing with phenomena of the atmosphere; especially weather processes. |
| **Methane** | A colorless odorless flammable gaseous hydrocarbon that is a product of decomposition of organic matter and of the carbonization of coal, is used as a fuel and as a starting material in chemical synthesis, and is the simplest of the alkanes. |
| **m$^{-3}$** | Denotes a factor of $10^{-3}$, or 1/1,000. |
| **Methyl** | A hydrocarbon radical not existing alone but regarded as an essential residue of methane, and appearing as a component part of many derivatives; as methyl nitrate. |
| **Methyl Tertiary Butyl Ether** | An ether manufactured by reacting methanol and isobutylene. The resulting ether has a high octane and low volatility. It was one of the primary ingredients in reformulated gasoline and was permitted in unleaded gasoline up to a level of 15 percent. |
| **μm** | Micrometer - a unit of length equal to one millionth of a meter. |
| **μg** | Microgram - a unit of mass equal to one millionth of a gram. |
| **Mixing Ratio** | Expressed as parts per million, -billion, or trillion. The number of volumes of the pollutant found in $10^6$, $10^9$, or $10^{12}$ volumes of air; analogous to mole fraction. |
| **Necrosis** | Usually localized death of living tissue. |
| **Neurotoxicological** | The science that deals with the effects of poisons on the nervous system. |
| **ng** | Nanogram – a metric unit of mass equal to $10^{-9}$ gram. |
| **Nitric Acid** | A colorless, corrosive liquid, a toxic acid which can cause severe burns. At room temperature it gives off red or yellow fumes. Commonly used as a laboratory reagent. |
| **Nitric Oxide** | A colorless gas formed by the combustion of nitrogen and oxygen. Nitric oxide readily combines with oxygen or air to form nitrogen dioxide. |

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| **Nitrogen** | Gaseous chemical element; a colorless, odorless, tasteless diatomic gas. |
| **Nitrogen Dioxide** | Is an orange/brown gas, smells rather disgusting, and is poisonous. |
| **nm** | Nanometer – a metric unit of distance equal to $10^{-9}$ meter. |
| **NOx** | The sum of NO + $NO_2$. |
| **NOy** | Total reactive nitrogen, the sum of all oxidized nitrogen species. |
| **Organic** | Relating or belonging to the class of chemical compounds having a carbon basis. |
| **Oxygenated** | To add oxygen to something. |
| **Oxidation** | A chemical reaction in which oxygen unites or combines with other elements. |
| **Ozone** | A colorless gas, formed naturally in the atmosphere by photochemical reaction. It is a strong oxidizing agent; a criteria air pollutant and major constituent of smog in the lower atmosphere. It is a beneficial component of the upper atmosphere (where it acts as a screen for ultraviolet radiation). |
| **Ozonolysis** | The reaction of ozone with hydrocarbons. |
| **Particulate Matter** | A form of air pollution that includes fine divided solid particles that are suspended in the air and include such as soot, dust, dirt, and aerosols. It has readily apparent effects on visibility and exposed surfaces; less than 2.5 microns in diameter. |
| **Pentane** | Any one of the three metameric hydrocarbons of the paraffin series. They are colorless, volatile liquids, two of which occur in petroleum. So called because of the five carbon atoms in the molecule. |
| **Pentyl** | The univalent organic radical of pentane and certain of its derivatives in eight isometric forms. Same as Amyl. |
| **Peroxide** | In organic chemistry, peroxide is a specific functional group or a molecule containing that functional group. It contains two oxygen atoms, each of which is bonded to the other and to a radical or some element other than oxygen. They are powerful oxidizing agents. |
| **Peroxy** | Containing the peroxy group. |

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| **Peroxy Radical** | A combining form used in the names of chemical compounds in which the peroxy group is present. A prefix denoting the presence of an extra O atom. |
| **Photolysis** | Light-stimulated chemical decomposition; the irreversible decomposition of a chemical compound as a result of the absorption of electromagnetic radiation, especially visible light. |
| **Propane** | Colorless gaseous alkane which occurs in nature in natural gas and crude oil; it is also a byproduct of petroleum refining. |
| **Propene** | A colorless flammable gaseous hydrocarbon of the ethylene series, having a garlic odor. Also called propylene. |
| **Propyl** | Either of two isomeric chemical groups or radicals derived from propane. |
| **Pulmonary Edema** | Fluid in the lungs. |
| **Pyrolysis** | Is a form of incineration that chemically decomposes organic materials by heat in the absence of oxygen. |
| **Radical** | An atom or group of atoms that contains one or more unpaired electrons (usually very reactive species). |
| **Reactive** | Substances capable of changing into something else in the presence of other chemicals, usually violently or producing a hazardous by-product. |
| **Remote Sensing** | Is a study in which pictures and data about the earth is obtained from a distant location usually fro aircraft and spacecraft. |
| **Ridge** | An elongated anticyclone or high pressure cell. |
| **Radiosonde** | A miniature radio transmitter that is carried aloft by an unmanned balloon with instruments for broadcasting the temperature, humidity and pressure. |
| **Solar Loading** | Accumulation of the sun's energy at the earth's surface. |
| **Spatial** | Pertaining to or involving or having the nature of space. |
| **Tertiary** | Possessing some quality in the third degree; having been subjected to the substitution of three atoms or radicals. |
| **Thermal** | Column of vertically rising air as a result of heating below. |

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| **Titration** | The process of determining a concentration of a dissolved substance, in which a solution of one reactant, the titrant, is carefully added to a solution of another reactant, and the volume of titrant required for complete is measured. |
| **Toluene** | A clear colorless liquid which occurs naturally in crude oil and the tolu tree. It is also produced in the manufacture of gasoline. |
| **Toxics** | Chemical or physical items that, under certain circumstances of exposure can cause harmful effects to living organisms. |
| **Troposphere** | Lower part of the atmosphere, extending from the surface up to a height varying from about 7 to 9 km at polar regions to approximately 17 km in tropics. The troposphere is characterized by decreasing temperature with height, appreciable vertical wind motion, appreciable water vapor content, and weather. |
| **Volatile Organic Compound** | A compound that evaporates readily into the atmosphere.<br>They include substances such as toluene or ethene. |
| **Whole Air Samples** | Air collected in one or two liter canisters from ambient air. |
| **Xylene** | A colorless sweet smelling aromatic hydrocarbon that catches on fire easily. It occurs naturally in petroleum and is produced in forest fires. It is a mixture of three isomers that differ structurally from one another. |