

EFFECTS OF SNOWMOBILE USE ON SNOWPACK CHEMISTRY IN YELLOWSTONE NATIONAL PARK, 1998

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

	Multiply	By	To obtain
	meter (m)	3.281	foot
	kilometer (km)	0.6214	mile
	centimeter (cm)	0.3937	inch
	millimeter (mm)	0.03937	inch
	liter	1.057	quart

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

ADDITIONAL ABBREVIATIONS

ng/L	nanograms per liter
µeq/L	microequivalents per liter
mph	miles per hour
mL	milliliter

Effects of Snowmobile Use on Snowpack Chemistry in Yellowstone National Park, 1998

By George P. Ingersoll

Abstract

Snowmobile use in Yellowstone National Park has increased substantially in the past three decades. In areas of greatest snowmobile use, elevated levels of by-products of gasoline combustion such as ammonium and benzene have been detected in snowpack samples. Annual snowpacks and snow-covered roadways trap deposition from local and regional atmospheric emissions.

Snowpack samples representing most of the winter precipitation were collected at about the time of maximum annual snow accumulation at a variety of locations in and near the park to observe the effects of a range of snowmobile traffic levels. Concentrations of organic and inorganic compounds in snow samples from pairs of sites located directly in and off snow-packed roadways used by snowmobiles were compared.

Concentrations of ammonium were up to three times higher for the in-road snow compared to off-road snow for each pair of sites. Thus, concentrations decreased rapidly with distance from roadways. In addition, concentrations of ammonium, nitrate, sulfate, benzene, and toluene in snow were positively correlated with snowmobile use.

INTRODUCTION

Because wintertime visitors to Yellowstone National Park (fig. 1) consider clean air to be an important aspect of their experience in the park (Littlejohn, 1996) and because vehicle emissions degrade the air quality in Yellowstone, the park staff have become increasingly concerned (Wilkinson,

1995). The majority of winter visitors tour Yellowstone by motorized snowmobiles because unplowed snow-covered roadways preclude highway access by automobiles into much of Yellowstone throughout the snowfall season. The park is designated as Class I under the Clean Air Act of 1977, and degradation of air quality is prohibited. The quality of air is a growing concern because motorized winter visitation has increased nearly tenfold since 1968 (National Park Service, 1990; Craig McClure, National Park Service, written commun., 1996). Air-quality monitoring at the West Entrance during the winter of 1995 detected carbon monoxide (CO) levels potentially exceeding Federal air-quality standards, which raised concerns about employee and visitor exposure to snowmobile emissions (National Park Service, Air Quality Division, 1996). However, at this busiest entrance to the park, where over 1,000 snowmobiles have entered on peak traffic days, CO concentrations diminished at air-quality sampling sites 20 to 100 m away from the entry point.

Growing popularity of snowmobile use for winter recreation in the Yellowstone National Park area has resulted in increasing numbers of snowmobiles operating in the park in the past decade (National Park Service, 1990; Craig McClure, written commun., 1996). Local economies in towns adjacent to the National Park and National Forest lands benefit from the growing recreational attraction offered by snowmobile touring and are dependent upon revenues generated by accommodating snowmobile recreationists. However, snowmobile use in Yellowstone has become a controversial issue in recent years because of the noise, traffic congestion, and air pollution (Woodbury, 1997).

Increases in fossil-fuel combustion in the area could contribute to greater levels of emissions entering sensitive watersheds and animal habitats. Until recently, concentrations and the extent of dispersion of

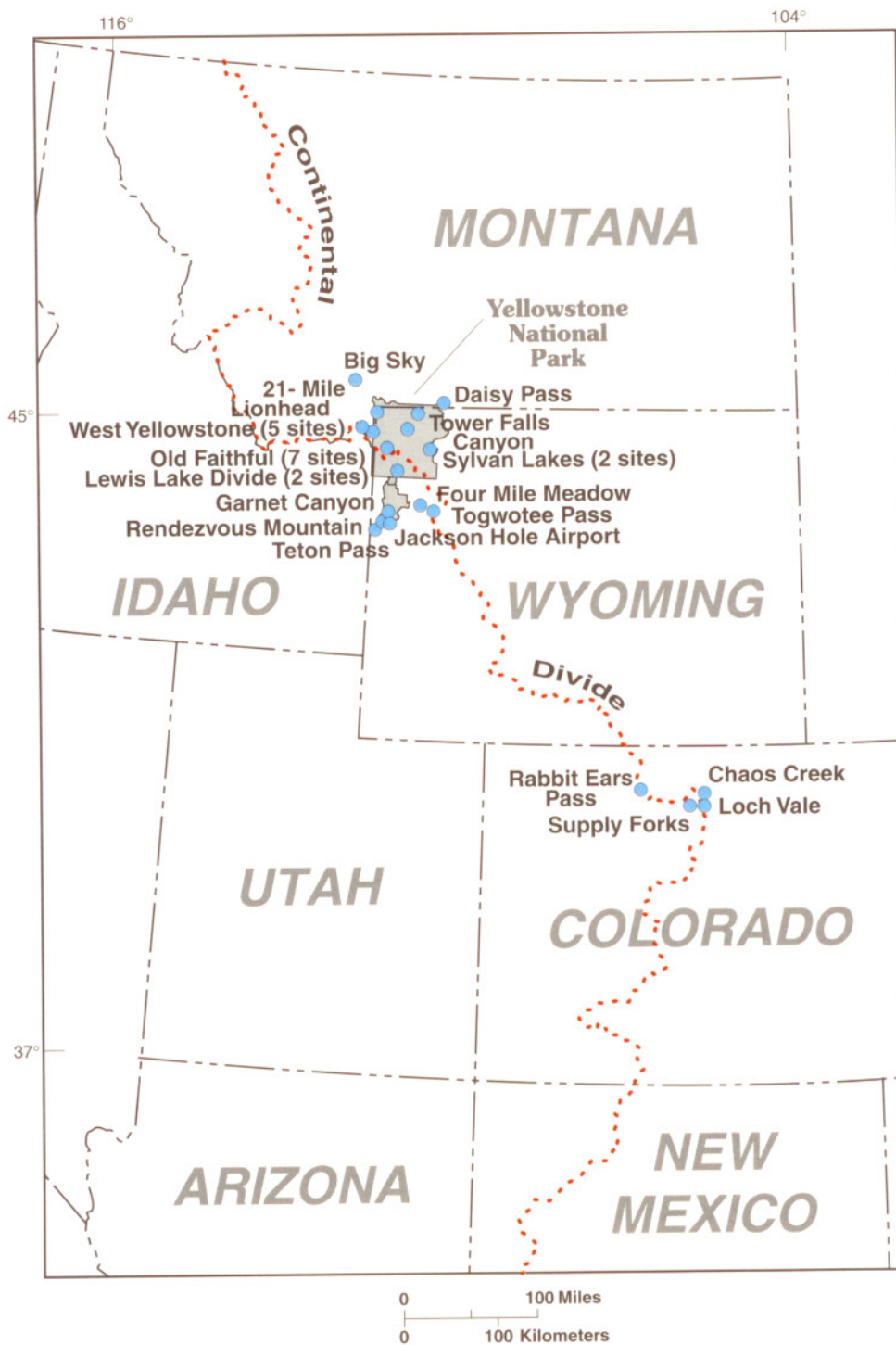


Figure 1. Location of snow-sampling sites in the Rocky Mountains in Western United States.

many emissions from wintertime snowmobile traffic in Yellowstone were unknown. High CO levels measured at the West Entrance, combined with increasing numbers of snowmobiles entering the park, raised the question of whether snowmobiles are causing increased levels of airborne emissions elsewhere in the park. If airborne snowmobile emissions are extensively distributed, at what distance from highway

corridors where snowmobiles operate are they detected?

Background

Early studies of the effects from snowmobile use in Minnesota (Wanek, 1971) and south-central

Canada (Neumann and Merriam, 1972) focused on ecological effects and indicated that physical damage to ecosystems occurred as a result of over-snow vehicular activity. As a result of the increased use of snowmobiles in the 1970's and 1980's, concerns about chemical emissions from a variety of mechanized equipment used outdoors, including snowmobiles, prompted extensive research of engine emissions (Hare and Springer, 1974; U.S. Environmental Protection Agency, 1991). Collins and Sell (1982) detected elevated concentrations of lead along a snowmobile trail in Wisconsin. Little work has been done, however, to evaluate chemical deposition in snowpack due to snowmobile use in the Western United States.

Numerous studies exist in the literature concerning the occurrence of hydrocarbons such as the benzene, toluene, ethylbenzene, xylenes (BTEX), and methyl tert-butyl ether (MTBE) compounds in precipitation, surface water, and ground water in urban hydrologic settings (Ayers and others, 1997; Bruce, 1995; Delzer and others, 1996) and in less densely populated areas, especially in the Central and Eastern United States (Fenelon and Moore, 1996; Terracciano and O'Brien, 1997; Reiser and O'Brien, 1998). However, comparatively few studies concerning hydrocarbons in precipitation and water have been done in the Rocky Mountain region (Dennehy and others, 1998), and even less is known about the occurrence of hydrocarbons in snowfall (Bruce and McMahan, 1996).

The U.S. Geological Survey (USGS) has been monitoring the chemical composition of annual snowpacks in Colorado since the mid-1980's. Elevated levels of emissions from atmospheric deposition held in seasonal snowpacks have been indicated by chemical concentrations of species associated with watershed acidification (including nitrate and sulfate) at alpine and subalpine sites in Colorado (Turk and Campbell, 1987; Campbell and others, 1991). Comparisons between chemical concentrations downwind of or nearer to possible emissions sources and those located crosswind or farther away from the source have revealed trends in snowpack chemistries in Colorado (Ingersoll, 1996; Turk and Campbell, 1997). At sites where atmospheric deposition was affected by local emission sources, concentrations of acidic species were higher than at locations more distant from the source (Ingersoll, 1995). This technique of using annual snowpack chemistry to identify

nearby emission sources has been successfully demonstrated in northwestern Colorado (Turk and others, 1992; Turk and Campbell, 1997).

The USGS, in cooperation with the National Park Service Air Resources Division, Denver, Colorado, and the National Park Service staff, Yellowstone National Park, Wyoming, has been monitoring atmospheric deposition to snowpacks in and around Yellowstone National Park annually since 1993. During 1993-98, chemicals in the snowpack, particularly acidic compounds, were monitored annually throughout a network of 50 to 60 sites in the Rocky Mountain region of the Western United States. The network includes several sites in and near Yellowstone National Park. Patterns emerging from preliminary, unpublished chemical analyses of the seasonal snowpacks in the Yellowstone National Park area during 1993-95 indicated that traffic volume of snowmobiles might positively correlate with chemical concentrations of ammonium, nitrate, or sulfate. Thus, a pilot study to test the hypothesis that snowmobile use results in increased emission deposition relative to background levels was begun in 1996. Results from the 1996 study of a small set of sites (three) demonstrated a positive correlation between the level of snowmobile traffic and chemical concentrations of ammonium and sulfate (Ingersoll and others, 1997). In a separate study, snowmobile engines were found to emit ammonia and sulfur dioxide in laboratory tests (White and Carroll, 1998).

Purpose and Scope

Building on the results of the 1996 pilot study, the USGS, in cooperation with the National Park Service, conducted a further investigation of the relation between snowmobile use and snowpack chemistry in Yellowstone National Park in 1998. The purpose of the 1998 study was to determine if emissions from snowmobile traffic are detectable in a larger sampling network of seasonal snowpack and to investigate whether emission levels tend to diminish rapidly with distance from the snowmobile thoroughfares as the emissions disperse into the surrounding watersheds. If dispersion is limited to a short distance from local sources such as snowmobiles, then two key results emerge. Watershed-scale effects from winter traffic are unlikely, and further identification of regionally

influenced deposition of emissions may be possible without interference from locally generated snowmobile emissions.

Knowledge of the extent of the deposition to annual snowpacks of acids and other compounds associated with fossil-fuel combustion is important to park preservation; it also is important to establish chemical baselines that can be used in evaluations that affect policy decisions controlling vehicle traffic in protected areas. Thus, snowpacks that represent a spectrum of snowmobile use at locations throughout Yellowstone were sampled during March 1998 to measure winter-time deposition of selected organic and inorganic by-products of gasoline combustion.

In this report, a method using snowpack chemistry as an indicator of snowmobile emissions is described. No permanent constructs, instrumentation, or maintenance were needed; data collection required minimal environmental impacts and required only one annual visit per site. A single snow sample from the annual snowpack provided data on the chemistry representing most of the yearly precipitation. With this method, a cost-effective sampling network was readily established to meet the objectives of the study, and the only constraints were that sampling sites were located where seasonal snowpacks persist and safe accessibility (low avalanche hazard) was likely.

Description of Study Area

The Yellowstone Plateau in southwestern Montana and northwestern Wyoming has a dry, mid-continental climate but frequently is in the path of the winter jet stream that brings abundant moisture, mostly from the Pacific, to the mountains (Martner, 1986). The area has strong winds and frequent storms that deliver precipitation preferentially to elevated areas; surrounding plains areas are dry by contrast. Annual snowpacks range in depth from 0.5 to about 4 meters. The high average elevation (more than 2,000 m) and latitude of the area maintain cool temperatures and cause most annual precipitation to fall as snow (Paulson and others, 1991). As in many subalpine continental settings in the Rocky Mountain region, snowcover is present about 6 months each year, generally from October until March or April.

The study area includes 28 snow-sampling sites at selected high-elevation locations in Yellowstone

National Park and nearby in Montana and Wyoming (fig. 1, table 1). Two additional sites in Colorado (Loch Vale and Supply Forks), where preliminary sampling and protocol development was done, also were selected to complement the study. Conifers dominate the mostly undeveloped mountainous landscapes at snow-sampling sites, facilitating sample collection at locations where snowfall tends to accumulate uniformly. Elevations of sampling sites range from 2,035 m above sea level at West Yellowstone, Montana, to about 2,570 m near Sylvan Lake in Wyoming. At these elevations, the seasonal snowpack is maintained throughout the winter into spring, and substantial snowmelt usually does not occur until spring runoff.

Acknowledgments

This research was made possible by the efforts of many from the National Park Service and Yellowstone National Park. The author also would like to express gratitude for the assistance with this project from Mary Hektner, Kristin Legg, Craig McClure, and John Sacklin of Yellowstone National Park; and Kristi Heuer and Kathy Tonnessen of the National Park Service, Air Resources Division, Denver, Colo.; and the District Ranger staff at Yellowstone National Park.

SAMPLE-COLLECTION LOCATIONS AND METHODS

Snow-sampling sites were carefully chosen at locations where the annual snowpack typically persists from October through March so that chemical solutes held in the snowpack structure that represent seasonal atmospheric deposition could be captured. Seasonal snowpacks provide a composite record of atmospheric deposition of airborne emissions throughout winter if no substantial melt occurs before sample collection. Obtaining snow samples before melt begins is crucial to preserving the chemical record of the snowpack because a concentrated elution, or ionic pulse, begins early in the annual snowmelt process (Campbell and others, 1995). Sampling within 2–3 weeks before melt begins permits data for most yearly snowfall to be collected in a single sample, and seasonal chemical deposition remains intact.

Table 1. Snow-sampling site locations and estimated snowmobile use levels in the Greater Yellowstone area and in northern Colorado

[Estimated use levels based on numbers of snowmobiles passing sites per day (ranging from 0 to over 1,000 snowmobiles per day), local observations, and restrictions. Categories from very low to high are estimated as less than 10, 10 to 99, 100 to 499, 500 or more snowmobiles per day for very low, low, moderate, and high levels, respectively; m, meters; km, kilometers]

Site name	Location (50- and 1,000-meter distances measured unless otherwise indicated; all other distances approximated)	Estimated level of snowmobile use
Big Sky	Big Sky ski area, Montana, mid-mountain, off-road	low
Biscuit Basin	3 kilometers north-northwest of Old Faithful geyser, 50 meters off-road	moderate-to-high
Biscuit Basin (in-road)	3 kilometers north-northwest of Old Faithful geyser, in snowpacked roadway paired with off-road site	moderate-to-high
Canyon	1 kilometer west of snowpacked roadway, and 3 kilometers south-southwest of Canyon, Wyoming, and about 50 meters off utilities service road	very low (if any)
Daisy Pass	200 meters south of Daisy Pass, Montana, and 100 meters west of snowpacked roadway	low
Four Mile Meadow	1 kilometer north of plowed US Highway 287 and 10 kilometers west of Togwotee Pass, Wyoming	low
Garnet Canyon	3 kilometers west of plowed Jenny Lake road and 25 kilometers north of Jackson, Wyoming	very low (if any)
Jackson Hole Airport	About 50 meters north of north edge of visitor parking lot and 100 meters east of active runway	very low (if any)
Lewis Lake Divide	5 kilometers south of Lewis Lake and 50 meters west of snowpacked roadway	moderate
Lewis Lake Divide (in-road)	5 kilometers south of Lewis Lake in snowpacked roadway paired with off-road site	moderate
Lionhead	2 kilometers northwest of Targhee Pass, Montana-Idaho and about 50 meters from snowmobiling area	low-to-moderate
Loch Vale	15 kilometers southwest of Estes Park, Colorado, and about 3 kilometers off-road	very low (if any)
Old Faithful (1,000 m)	1,000 meters south of Old Faithful, Wyoming, off-road along Fern Cascade trail	very low (if any)
Old Faithful Corrals	1 kilometer west of Old Faithful, Wyoming, and 50 meters off-road	low
Old Faithful East Lot	500 meters southeast Old Faithful geyser and 50 meters off-road	low
Old Faithful	300 meters southwest Old Faithful geyser and 50 meters off-road	high
Old Faithful (in-road)	300 meters southwest of Old Faithful geyser in snowpacked roadway paired with off-road site	high
Rendezvous Mountain	500 meters northwest of summit of Jackson Hole aerial tram, out of bounds	very low (if any)
Supply Forks	5 kilometers northwest of Grand Lake, Colorado, and 50 meters off-road	moderate-to-high
Sylvan Lake	1 kilometer west of Sylvan Pass, Wyoming, and 50 meters off-road	low
Sylvan Lake (in-road)	1 kilometer west of Sylvan Pass, Wyoming, in snowpacked roadway paired with off-road site	low
Teton Pass	2 kilometers west of summit of Teton Pass and about 50 meters off-road	very low (if any)
Togwotee Pass	25 kilometers west of Moran, Wyoming, and about 100 meters northeast of US Highway 287	low-to-moderate
Tower Falls	1 kilometer south of Tower Falls junction and about 50 meters east of snowpacked roadway	very low
21-Mile	About 21 miles (33 kilometers) north of West Yellowstone, Montana, and 150 meters west of plowed US Highway 191	very low (if any)
West Yellowstone	100 meters east of West Entrance, Yellowstone National Park, and 50 meters north of snowpacked roadway	high
West Yellowstone (in-road)	100 meters east of West Entrance, Yellowstone National Park in snowpacked roadway paired with off-road site	high

Table 1. Snow-sampling site locations and estimated snowmobile use levels in the Greater Yellowstone area and in northern Colorado—Continued

[Estimated use levels based on numbers of snowmobiles passing sites per day (ranging from 0 to over 1,000 snowmobiles per day), local observations, and restrictions. Categories from very low to high are estimated as less than 10, 10 to 99, 100 to 499, 500 or more snowmobiles per day for very low, low, moderate, and high levels, respectively; m, meters; km, kilometers]

Site name	Location (50- and 1,000-meter distances measured unless otherwise indicated; all other distances approximated)	Estimated level of snowmobile use
West Yellowstone (1,000 m)	100 meters east of West Entrance, Yellowstone, and 1,000 meters north of snowpacked roadway	very low (if any)
West Yellowstone, 8 km east	8 kilometers east of West Yellowstone, Montana, and 50 meters off snowpacked roadway	high
West Yellowstone, 8 km east (in-road)	8 kilometers east of West Yellowstone, Montana, and in snowpacked roadway paired with off-road site	high

Snowpack sampling sites along or near snow-packed routes were included in this study to represent various levels of over-snow traffic (fig. 1). Sites at West Yellowstone, Old Faithful, and Sylvan Lake were selected to repeat the pilot study of 1996. Additional sites were selected along the highway over Lewis Lake Divide where snowmobiles are typically operating at cruising speeds; along the roadway 3 km from Old Faithful and 8 km east of West Yellowstone where cruising speeds also are typical; and at a location about 20 km from snowmobile routes near Tower Falls. At snowpit-sampling locations a sample was taken at least 50 m off the nearest roadway in undisturbed forest, and at several sites the off-road sampling location was paired with a location in the active snow-covered roadway (West Yellowstone, 8 km east of West Yellowstone, Biscuit Basin, Old Faithful, Lewis Lake Divide, and Sylvan Lake). In-road snowpits were positioned directly in snow packed by snowmobile traffic. At about 1,000 m from snowmobile roadways, two additional off-road snowpits were established adjacent to snowpits that were 50 m off-road at West Yellowstone and Old Faithful.

Snowpacks in and near Yellowstone National Park were sampled during the period March 4–24, 1998, when snow-water equivalent values at snow-telemetry sites at sampling locations were 87 to 88 percent of the 30-year (1961–90) averages (Natural Resources Conservation Service, 1998). Snow depths at sampling sites ranged from 12 to 132 cm at in-road sites and 63 to 221 cm at off-road sites. Snow depths in packed roadways were substantially less than snow depths at unpacked off-road sites because of frequent compression from grooming machines and daily snowmobile traffic. Field sample collection was accomplished within just a few days of the season

closure dates for most segments of highways groomed for snowmobile traffic in the park.

During the 3 months before sampling the Yellowstone snowpack, sampling methods used in this study at Yellowstone were tested in Colorado in conditions similar to those at Yellowstone to identify potential sources of contamination during collection and transportation of snow samples. Two sites were selected: (1) Loch Vale in Rocky Mountain National Park, Colorado, representing background conditions where motorized travel is not permitted within 3 km, and snowmobile use is restricted to areas at least 10 km away, and (2) Supply Forks near Grand Lake, Colorado, where regular snowmobile use offers the opportunity to sample both the snow-covered roadway and directly adjacent off-road snowpacks using the methodology described in the pilot study of Ingersoll and others (1997). Certified blank waters (with documented low ionic strength) for both inorganics and organics analyses were used in field blanks, laboratory blanks, and trip blanks collected to measure contamination during collection of snow samples. Laboratory blanks are used to test for contamination during analytical processing; trip blanks are kept sealed in transit with samples to see if contamination of sealed samples might be occurring during transport. At both sites, replicate snow samples were collected to test reproducibility of results, and field blanks were collected by pouring certified blank water directly over locally cleaned sampling tools and into Teflon sample bags to check for contamination from collection equipment. Precautions were taken to prevent contamination because of the extremely dilute chemistry of snow. Further testing was done to detect possible corruption of samples due to nearby snowmobile use during snow sampling. Also, after investigators trav-

eled to the sampling sites by snowmobile, they donned Tyvek suits over their outer garments as an additional precaution against contamination. Workers wore latex gloves when collecting samples. The bottom few centimeters of the snowpack were not sampled to avoid inclusion of forest litter and soils in the samples. The top few centimeters of snowpack also were discarded to exclude snow contaminated by workers' activities resulting from transport to and preparation of the snowpit. Clean plastic shovels and scoops (scoured and rinsed with local snow) were used to collect a vertical snow column for each sample that represented the entire snowpack to be analyzed. Workers in the snowpits took precautions to avoid inclusion of foreign substances such as soils, tree litter, clothing, saliva, or perspiration when filling sample containers. The snow samples were cut and placed in 8-L Teflon bags that were prerinsed in pure (electrical resistance of 18 megohm/cm) deionized water (DI). Samples for analysis of organic constituents were collected in precleaned, 40-mL amber glass vials designed for collection of volatile organic carbon (VOC). These Teflon bags and vials were sealed against contamination in plastic bags and cases and transported frozen to USGS laboratories. Inorganic analyses were done at USGS Regional Research Laboratory in Boulder, Colorado, and organic analyses were done at the USGS National Water Quality Laboratory in Arvada, Colorado. Snow samples were kept frozen at -10°C to prevent chemical reactivity until the actual dates of laboratory analyses.

Snow samples were collected from snowpits prepared with a smooth, freshly cut, vertical face extending from the ground surface upward throughout the entire depth of the snowpack. Before snow samples were collected, physical measurements of the snowpack were made to ensure solute loss had not occurred. Full-snowpack temperature profiles were recorded at 10- or 20-cm intervals to ensure temperatures below zero degrees Celsius predominated among snow strata. Snow-crystal size, type, and hardness of all homogeneous strata were measured to document the history of the metamorphism of the snowpack during the winter. Further observations of a lack of evidence of melt, saturated wet snow, and soil moisture beneath the snowpack ensured snowmelt elution had not yet begun and that the snow to be collected maintained the seasonal atmospheric deposition in an ice phase. Snow samples from all sampling sites

presented in this report were collected before snowmelt began.

Snowmelt runoff was sampled at five locations during the first half of May 1998. Runoff from the melting snowpacks near snow-sampling sites was collected at West Yellowstone, Old Faithful, Lewis Lake Divide, Sylvan Lake, and Tower Falls. Snowmelt runoff samples for inorganics were collected in DI-rinsed, 2-L polyethylene bottles, refrigerated, and shipped overnight to the USGS laboratory in Denver, Colorado. Detection limits for inorganics in snowmelt-runoff samples were the same as mentioned above for snow samples except for ammonium ($2.0\ \mu\text{eq/L}$). Snowmelt runoff samples for organics were collected in precleaned and sealed, amber, 40-mL glass vials fit with caps designed for sampling VOC's.

ANALYTICAL PROCEDURES

Snow samples (8 L each) were allowed to melt in the Teflon collection bags and were processed within 12 hours by using a series of analytical procedures. Samples were kept cool by processing them soon after melting or refrigerating snowmelt aliquots reserved for subsequent analyses. Major cation concentrations were determined on filtered (0.45 mm), acidified aliquots by using two emission-spectroscopy techniques—inductively coupled plasma [for calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^{+})] and atomic absorption [for potassium (K^{+})]. Chloride (Cl^{-}) and sulfate (SO_4^{2-}) concentrations were determined on filtered (0.45 mm) aliquots by ion chromatography. Nitrate (NO_3^{-}) and ammonium (NH_4^{+}) ion concentrations were analyzed on filtered (0.45 mm), frozen subsamples by air-segmented, continuous-flow colorimetry. Detection limits were as follows, in microequivalents per liter ($\mu\text{eq/L}$): Ca^{2+} , 0.5; Mg^{2+} , 0.5; Na^{+} , 1.0; K^{+} , 0.3; Cl^{-} , 0.5; SO_4^{2-} , 0.4; NO_3^{-} , 0.2; and NH_4^{+} , 0.5. Specific conductance was measured in microsiemens per centimeter at 25°C with a platinum electrode; pH was determined in standard units with a combination glass electrode designed for low-ionic-strength waters. Alkalinity was determined using a Gran titration method.

Quality control involved systematically analyzing deionized-water blanks, an internal reference sample, and USGS standard reference water samples. Water from Chaos Creek in Rocky Mountain National Park, Colorado, was selected as the internal

reference sample to monitor instrument precision because of its similarity of ionic strength compared to snowmelt from the sites reported here. Approximately 40 percent of sample batch run time for the analytical instrumentation was dedicated to analyzing field blanks, laboratory blanks, trip blanks, duplicates, internal reference samples, and USGS standards. Calibration verifications were made with standards at the beginning and end of each batch of sample analyses. Processing blanks were analyzed to detect possible contamination from DI rinse water, filtering apparatus, and the Teflon collection bags. Charge balance was calculated between total anions and cations to check the quality of the analyses.

Analyses of the selected organics benzene, toluene, ethylbenzene, and xylenes (BTEX), and methyl tert-butyl ether (MTBE) were accomplished using purge and trap/selected ion monitoring and gas chromatography/mass spectrometry techniques. Snow samples were kept frozen in transit from sampling sites then allowed to melt in a refrigerator at 4°C. Liquid samples were then composited and acidified with 1:1 concentrated hydrochloric acid. Snow samples were analyzed within 14 days of melting. Field and laboratory blanks of certified, nitrogen-purged organics blank water, trip blanks, and field and laboratory replicates were analyzed for quality control and evaluation of the precision and contamination of sample-collection and analytical techniques. Numerous analyses of spiked reagent waters were done to evaluate instrument performance and establish method detection limits. Detection limits for organics analyses, in nanograms per liter (ng/L or parts per trillion), were 1.7 (benzene), 5.0 (MTBE), 4.8 (toluene), 3.8 (m- and p-xylene), and 1.6 (o-xylene). Minimum reporting levels for these organic compounds in this study are at least twice the method detection limits.

SNOWPACK CHEMISTRY

Major Ions

Ammonium and sulfate ion concentrations weakly correlate ($r^2 = 0.12$) in the Rocky Mountain region, but when snow samples from areas of high snowmobile use are included, the association becomes stronger ($r^2 = 0.56$) (fig. 2). Values for these samples

from the snow-covered roadway at four sites along snowmobile routes in Yellowstone form a distinct cluster in the upper right corner of the plot in figure 2 and demonstrate the elevated levels of these compounds in snow-packed roads in Yellowstone relative to 50 to 60 other snowpack-sampling sites in the Rocky Mountain region. Ammonium and sulfate were shown to be good tracers of snowmobile emissions in the pilot study of snowmobile effects on Yellowstone snowpack chemistry (Ingersoll and others, 1997). Concentrations of ammonium and sulfate in snow-covered roadways were well correlated in both high and low traffic levels in that study of the 1996 snowpack at three locations in the park.

Snow samples from the sites in Colorado that represent locations popular for snowmobile use were analyzed and compared to off-road, untracked snow during December 1997 and January 1998, before sampling began in Yellowstone in March 1998 (table 2). The Supply Forks site in Colorado proved to be a good site to test sampling protocols for detecting snowmobile emissions in snow because it is in a popular snowmobiling area, and the same pattern of emissions of ammonium and sulfate were observed there as in Yellowstone. Comparisons of the in-road samples at the Supply Forks site near Grand Lake, Colorado, to samples obtained 50 m off-road reveal a trend very similar to that seen in the 1996 Yellowstone pilot study. Elevated concentrations of ammonium (4.7 to 17.1 $\mu\text{eq/L}$) and sulfate (16.0 to 74.9 $\mu\text{eq/L}$) were detected in snow at the in-road site; consistently lower concentrations of ammonium (2.8 and 3.9 $\mu\text{eq/L}$) and sulfate (7.1 and 9.6 $\mu\text{eq/L}$) were detected in snow 50 m off-road and directly adjacent to the in-road sampling site. At the backcountry Loch Vale site in Colorado, about 3,000 m from wheeled-vehicle traffic and at least 10,000 m from snowmobile traffic, similarly low levels of ammonium (4.5 to 4.9 $\mu\text{eq/L}$) and sulfate (9.2 to 9.4 $\mu\text{eq/L}$) were detected. Nitrate concentrations were fairly consistent (14.3 to 17.1 $\mu\text{eq/L}$) in all in-road, off-road, and backcountry snow samples except for the "exhaust" sample (29.3 $\mu\text{eq/L}$), which was collected from the snow directly beneath (20 cm) the exhaust pipe of a snowmobile after its engine idled for 5 minutes.

The results for the inorganic major ion analyses exhibited higher concentrations of most constituents, especially ammonium and sulfate, in areas of high snowmobile use (fig. 3). A selected set of sampling

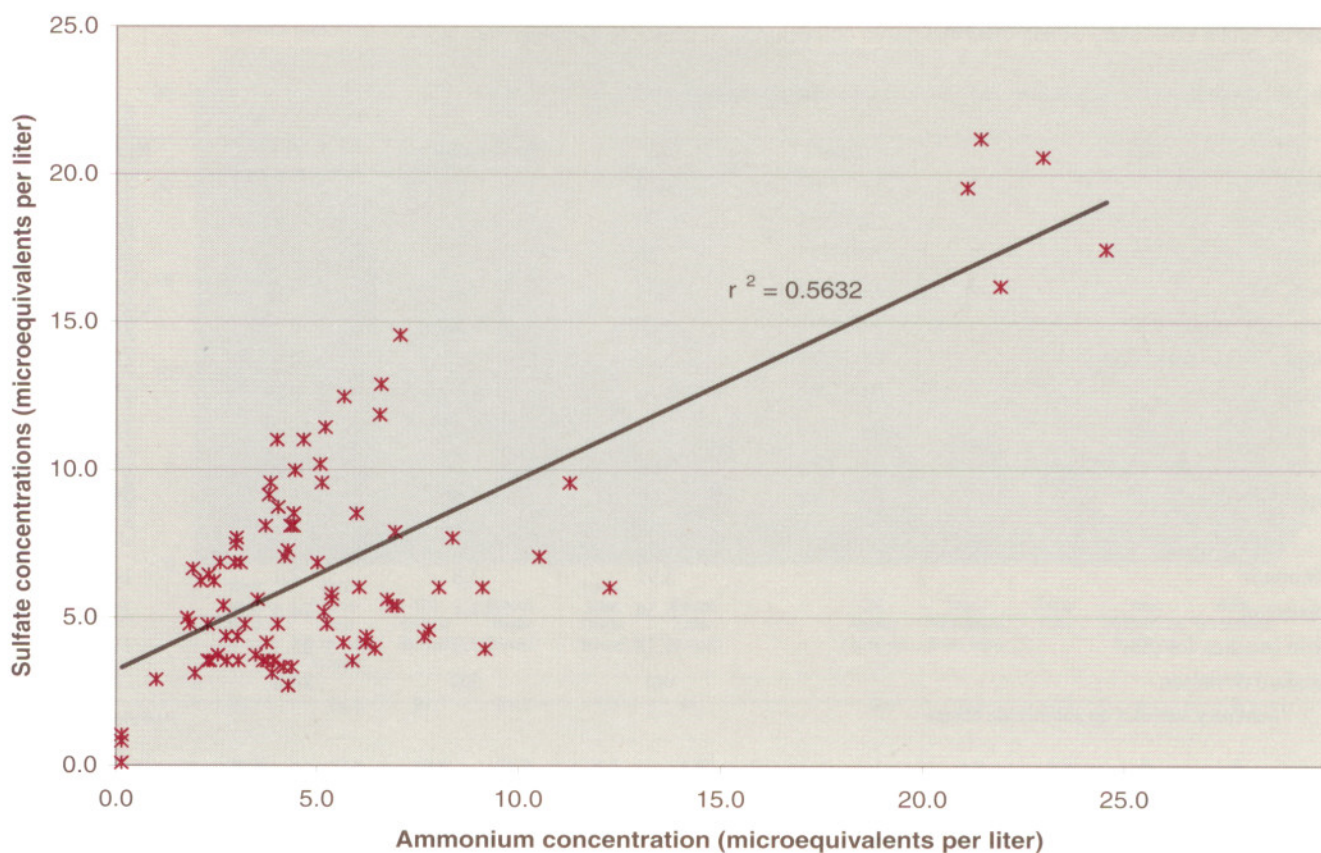


Figure 2. Relation between ammonium and sulfate in mountain snowpacks throughout the Rocky Mountain region, 1998.

sites where both inorganic and organic analyses were performed is shown in figures 3, 7, and 8. See table 3 for inorganic chemistry and table 5 for organic chemistry of sites not shown in figures 3, 7, and 8. Consistent with the results of the pilot study in 1996, similar patterns for ammonium, nitrate, and sulfate concentrations in snow emerged with analyses of the 1998 snowpacks. In-road snow samples were significantly higher in ammonium (4.0 to 24.5 $\mu\text{eq/L}$, $p = 0.007$) and sulfate (4.6 to 21.2 $\mu\text{eq/L}$, $p = 0.002$) than nearby (within 50 m) off-road concentrations of ammonium (4.4 to 9.1 $\mu\text{eq/L}$) and sulfate (3.3 to 6.0 $\mu\text{eq/L}$) (table 3). The p-values of 0.007 and 0.002 indicate 99.3 percent and 99.8 percent probability of the values being significantly higher, respectively. The original sample at West Yellowstone (in-road) is shown in figure 3; table 3 includes an additional replicate sample at that site which does not appear in figure 3.

Spatial patterns of concentrations of key major ions are shown in figures 4–6. Within the park boundary, six sets of in-road and adjacent off-road samples are shown (West Yellowstone, 8 km east of

West Yellowstone, Biscuit Basin, Old Faithful, Lewis Lake Divide, and Sylvan Lake). At the six paired sites where both in-road and off-road samples were taken, the in-road value is shown just below the corresponding off-road value. Traffic volumes were greatest at West Yellowstone, where 1,000 or more snowmobiles commonly enter the park daily; substantial numbers of those vehicles include Old Faithful as a destination. Concentrations of ammonium and sulfate in snowpacks generally were higher at the in-road sites between West Yellowstone and Old Faithful than elsewhere (figs. 4 and 6). On the West Entrance road, high traffic volumes typically result in much slower speeds (20–30 mph) and considerable acceleration and deceleration. In addition, groups stop on the snow road edge or in groomed turnouts to observe wildlife or the Madison River or to reorganize their party. On the South and East Entrance roads, lighter volumes mean that traffic moves more smoothly at higher speeds (35–45 mph). Visitors typically do not stop at Lewis Lake Divide or Sylvan Lake (John Sacklin, National Park Service, written commun., 1999). Considerably fewer

Table 2. Snow chemistry of selected inorganic compounds at protocol-development sites

[units: pH, standard; ammonium, sulfate, and nitrate, in microequivalents per liter; n/a, not applicable]

Site	Date	pH	Ammonium	Sulfate	Nitrate
Supply Forks	12/17/97	4.72	2.8	7.1	15.7
Supply Forks (in-road)	12/17/97	6.34	4.7	74.9	17.1
Supply Forks (field blank)	12/17/97	5.56	<0.2	0.6	<0.2
Loch Vale	12/16/97	4.84	4.5	9.2	14.3
Loch Vale (replicate)	12/16/97	4.80	4.9	9.4	15.0
Supply Forks (field blank)	01/15/98	5.56	<0.2	0.9	<0.2
Supply Forks	01/15/98	4.76	3.9	9.6	15.0
Supply Forks (in-road)	01/15/98	3.91	17.1	16.0	15.7
Supply Forks (in-road, replicate)	01/15/98	5.61	8.6	16.4	15.7
Supply Forks exhaust	01/15/98	4.07	12.1	58.2	29.3
Minimum ¹		3.91	2.8	7.1	14.3
Maximum ¹		6.34	17.1	74.9	29.3
Mean (median for pH) ¹		4.78	7.3	25.1	17.2
Standard deviation		n/a	5.0	26.2	4.9

¹Summary statistics do not include blanks

snowmobiles enter the park from the South or East Entrances and pass Lewis or Sylvan Lakes enroute to their destinations, which also is Old Faithful in most cases. During the sampling period of March 1998, snowmobiles during the day at Old Faithful commonly numbered in the hundreds, which was 5 to 10 times more than elsewhere in the park. In winter of 1998, 40,869 snowmobiles came in the West Entrance; 15,209 came in the South Entrance; 2,563 came in the East Entrance; and 1,469 came in the North (Mammoth Terraces) Entrance, for a total of 60,110 snowmobiles. Total recreation visitors in winter 1998 were 119,274, of which 72,834 came in on snowmobiles, 9,897 were in snowcoaches, and 40,101 were in automobiles (National Park Service, Yellowstone National Park, written commun., 1999). Nitrate concentrations (fig. 5) are minimally affected by snowmobile traffic and probably reflect regional deposition from sources other than snowmobiles.

Also worthy of note are the similarities in concentrations at the low- or moderate-traffic sampling sites at Lewis and Sylvan Lakes relative to other sites in and near the park in areas of reduced or restricted snowmobile use like Canyon, Tower Falls, and Big Sky ski area, where snowmobile travel is minimal. West of the park near Targhee Pass, the area around the Lionhead site has low-to-moderate snow-

mobile traffic. To the south, Garnet Canyon and Rendezvous Mountain in the Tetons and Four Mile Meadow and Togwotee Pass in the Wind River Range had background levels typical of off-road snowpacks where both local and regional emission deposition is minimal.

Selected Hydrocarbons

Benzene, toluene, and xylenes are VOC's and are by-products of gasoline combustion and have been detected in snowmobile emissions (White and Carroll, 1998; Morris and others, 1999). MTBE is a gasoline additive used in Colorado, but generally not found in gasoline used in the Yellowstone area. These hydrocarbons are common in urban areas (Lopez and Bender, 1998) but have been detected in this study far from urban development. Concentrations of these VOC's in seasonal snowpacks at the protocol-development sites in Colorado were higher for in-road snow samples than for off-road samples by factors of 2 to 1,000 (table 4). The range of in-road concentrations for benzene (37.4 to 1,820 ng/L), MTBE (10.1 to 374 ng/L), toluene (577 to 9,880 ng/L), m- and p-xylenes (640 to 14,100 ng/L), and o-xylene (377 to 7,380 ng/L) was substantially greater in most cases than the range of off-road sample concentrations of

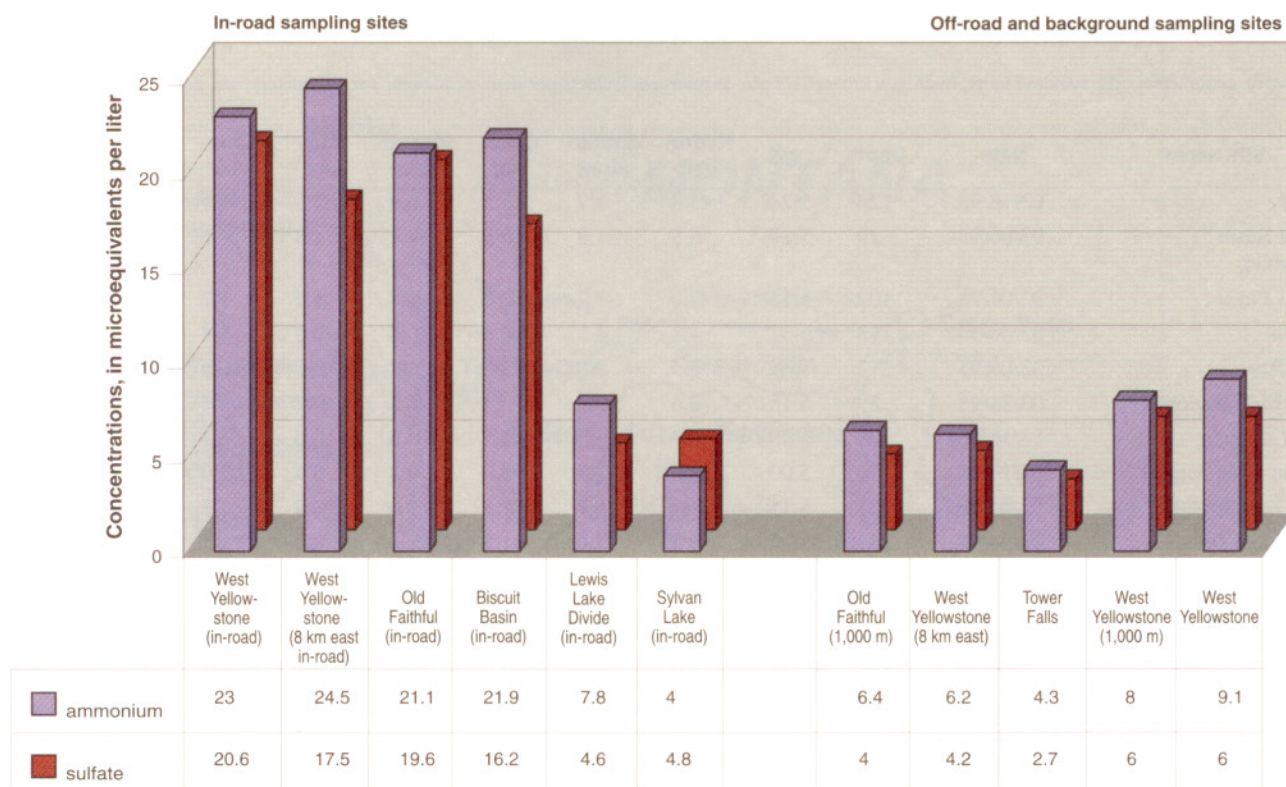


Figure 3. Ammonium and sulfate levels in snow at in-road and off-road sites in Yellowstone National Park, 1998.

benzene (less than 10 ng/L), MTBE (less than 10 to 10.1 ng/L), toluene (88.9 to 265 ng/L), m- and p-xylenes (13.7 to 22.8 ng/L), and o-xylene (5.4 to 12.9 ng/L).

Initial protocol development, including the processing of field blanks, laboratory blanks, and trip blanks, indicated a sensitivity to contamination near nondetect limits in three of six blanks, but inexplicably high contamination from toluene was detected in the field blank from 12/17/97 (1,570 ng/L) and a trip blank from 01/22/98 (1,400 ng/L). Many hydrocarbons are detected all over the world, including both poles and mid-latitude alpine zones of North America (Blais and others, 1998). Even though gasoline-powered vehicles were used to transport the sampling personnel and equipment for this study, these two toluene contamination levels are very high for blank samples. Anomalously high concentrations of toluene (relative to other hydrocarbons detected) are shown for three Yellowstone sites located 50 to 1,000 m off-road (fig. 8). The source of toluene contamination is currently under investigation.

A snow sample collected 5 m from an idling snowmobile at the Supply Forks site had a fairly elevated concentration of MTBE but relatively low

concentrations of other VOC's including toluene (65.3 ng/L). This indicates minimal interference from snowmobiles passing in-road sampling snowpits while samples were collected. Another exhaust sample (January 15, 1998) was collected in snow at the Supply Forks site directly beneath the exhaust pipe after a snowmobile engine had been running at about 2,000 revolutions per minute for 5 minutes. This direct deposition of exhaust emissions resulted in high concentrations of toluene and xylenes relative to other in-road samples shown in table 4. The Supply Forks in-road sample of January 15, 1998, also had relatively high concentrations for benzene, toluene, and xylenes. When that sample was collected, yellow and brown discoloration was observed in the snowpack, possibly due to spilled oil or fuel in the snowpacked roadway. Thus, contamination of that sample was likely, and concentrations of both inorganic (table 2) and organic compounds (table 4) may not reflect atmospheric deposition because of possible sampling of fuel spillage. Other in-road-sample concentrations of hydrocarbons at the protocol development site were similar to each other.

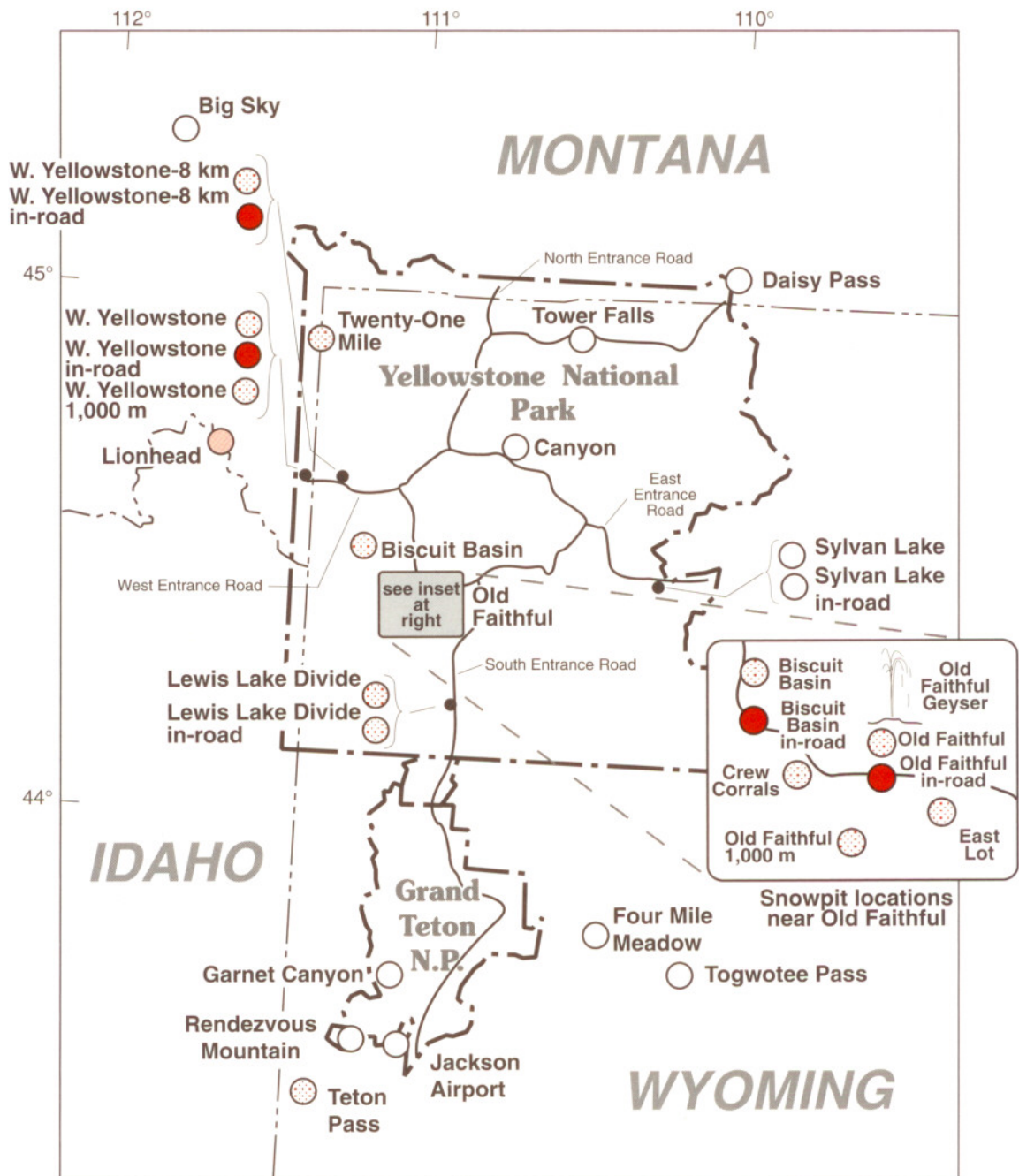
In the Yellowstone area in March 1998, samples collected for VOC analyses at 12 selected sites had the

Table 3. Snow chemistry of selected inorganic compounds in the Greater Yellowstone area

[units: depth, centimeters; pH, standard units; hydrogen through nitrate, in microequivalents per liter; m, meters; km, kilometers; n/a, not applicable]

Site name	Date	Depth	pH	Hydrogen	Ammonium	Calcium	Magnesium	Sodium	Chloride	Sulfate	Nitrate
Big Sky	03/18/98	128	5.24	5.8	3.7	3.5	0.8	0.9	0.9	3.5	5.4
Biscuit Basin (in-road)	03/06/98	29	5.19	6.5	21.9	10.5	4.1	4.8	7.6	16.2	10.0
Biscuit Basin Canyon	03/06/98	101	5.15	7.1	7.7	3.0	0.8	1.7	1.7	4.4	8.6
Daisy Pass	03/08/98	110	5.32	4.8	4.2	2.0	0.8	0.9	1.4	3.3	6.8
Four Mile Meadow	03/09/98	212	5.19	6.5	2.8	2.0	0.8	0.0	0.9	3.5	5.0
Garnet Canyon	03/24/98	89	5.18	6.6	2.5	3.5	0.8	2.2	1.4	3.7	6.2
Jackson Hole Airport	03/16/98	178	5.08	8.3	3.5	1.5	0.8	0.9	1.4	3.7	5.7
Lewis Lake Divide	03/19/98	70	5.00	10.0	2.3	5.0	0.8	0.4	2.0	3.5	8.4
Lewis Lake Divide (in-road)	03/04/98	221	5.15	7.1	5.9	1.5	0.0	0.9	1.1	3.5	6.3
Lionhead	03/04/98	132	5.17	6.8	7.8	1.5	0.0	0.0	1.1	4.6	5.3
Old Faithful (1,000 m)	03/07/98	144	5.03	9.3	10.5	2.5	0.8	1.3	2.3	7.1	10.9
Old Faithful Corrals	03/06/98	118	5.09	8.1	6.4	2.0	0.0	0.9	1.7	4.0	8.4
Old Faithful East Lot	03/06/98	85	5.23	5.9	9.2	2.0	0.8	1.3	1.7	4.0	9.7
Old Faithful	03/06/98	86	5.06	8.7	5.7	2.0	0.8	3.5	3.4	4.2	9.5
Old Faithful (in-road)	03/06/98	86	5.19	6.5	6.2	2.5	0.8	1.7	2.0	4.4	9.4
Rendezvous Mountain	03/06/98	12	4.94	11.5	21.1	13.0	2.5	5.7	7.3	19.6	10.6
Sylvan Lake	03/19/98	172	5.52	3.0	3.0	4.5	3.3	1.7	0.9	4.4	4.9
Sylvan Lake (in-road)	03/03/98	147	5.20	6.3	4.4	1.5	0.8	1.7	1.1	3.3	5.7
Teton Pass	03/03/98	96	5.04	9.1	4.0	1.0	0.8	2.6	1.4	4.8	6.2
Togwotee Pass	03/17/98	124	5.45	3.5	5.3	7.0	2.5	2.6	2.3	4.8	8.1
Tower Falls	03/24/98	179	5.31	4.9	2.3	3.0	0.8	3.0	1.1	3.5	4.7
Twenty-one Mile	03/10/98	63	5.10	7.9	4.3	1.5	0.0	0.9	1.4	2.7	7.4
West Yellowstone (blank)	03/07/98	130	5.06	8.7	7.0	1.5	0.8	2.6	2.3	5.4	9.7
West Yellowstone (1,000 m)	03/05/98	n/a	5.47	3.4	0.1	0.0	0.0	0.0	0.1	1.0	0.1
West Yellowstone 8 km east	03/05/98	85	4.85	14.1	8.0	2.5	0.8	3.0	2.5	6.0	12.4
West Yellowstone 8 km east (in-road)	03/06/98	64	4.94	11.5	6.2	1.5	0.8	1.7	1.7	4.2	11.2
West Yellowstone (in-road)	03/06/98	20	5.01	9.8	24.5	11.0	2.5	9.1	8.7	17.5	14.7
West Yellowstone (in-road)	03/05/98	73	5.00	10.0	9.1	3.0	0.8	3.0	2.5	6.0	13.1
West Yellowstone (in-road)	03/05/98	46	4.99	10.2	23.0	13.0	3.3	13.9	12.4	20.6	15.3
West Yellowstone (in-road) (replicate)	03/05/98	46	5.03	9.3	21.4	13.5	3.3	14.4	12.4	21.2	15.4
Minimum ¹		12	4.85	3.0	2.3	1.0	0.0	0.0	0.9	2.7	4.7
Maximum ¹		221	5.52	14.1	24.5	13.5	4.1	14.4	12.4	21.2	15.4
Mean (median for pH) ¹		105	5.10	7.9	7.9	4.1	1.2	3.0	3.1	6.8	8.8
Standard deviation		54.2	n/a	2.5	6.3	4.0	1.1	3.6	3.3	5.8	3.2

¹Summary statistics do not include blank.



EXPLANATION
 Ammonium ion concentration,
 in microequivalents per liter
 (minimum value 2.3; maximum value 24.5)

0 15 30 MILES
 0 15 30 KILOMETERS

- 2.3 - 4.9
- 5.0 - 9.9
- 10.0 - 14.9
- 15.0 - 19.9
- 20.0 - 24.5

Figure 4. Ammonium ion concentrations in snow in Teton-Yellowstone area, 1998.



EXPLANATION

Nitrate ion concentration,
in microequivalents per liter
(Minimum value 4.7; maximum value 15.4)

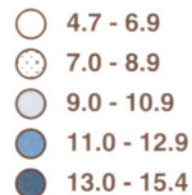
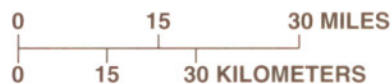


Figure 5. Nitrate ion concentrations in snow in Teton-Yellowstone area, 1998.

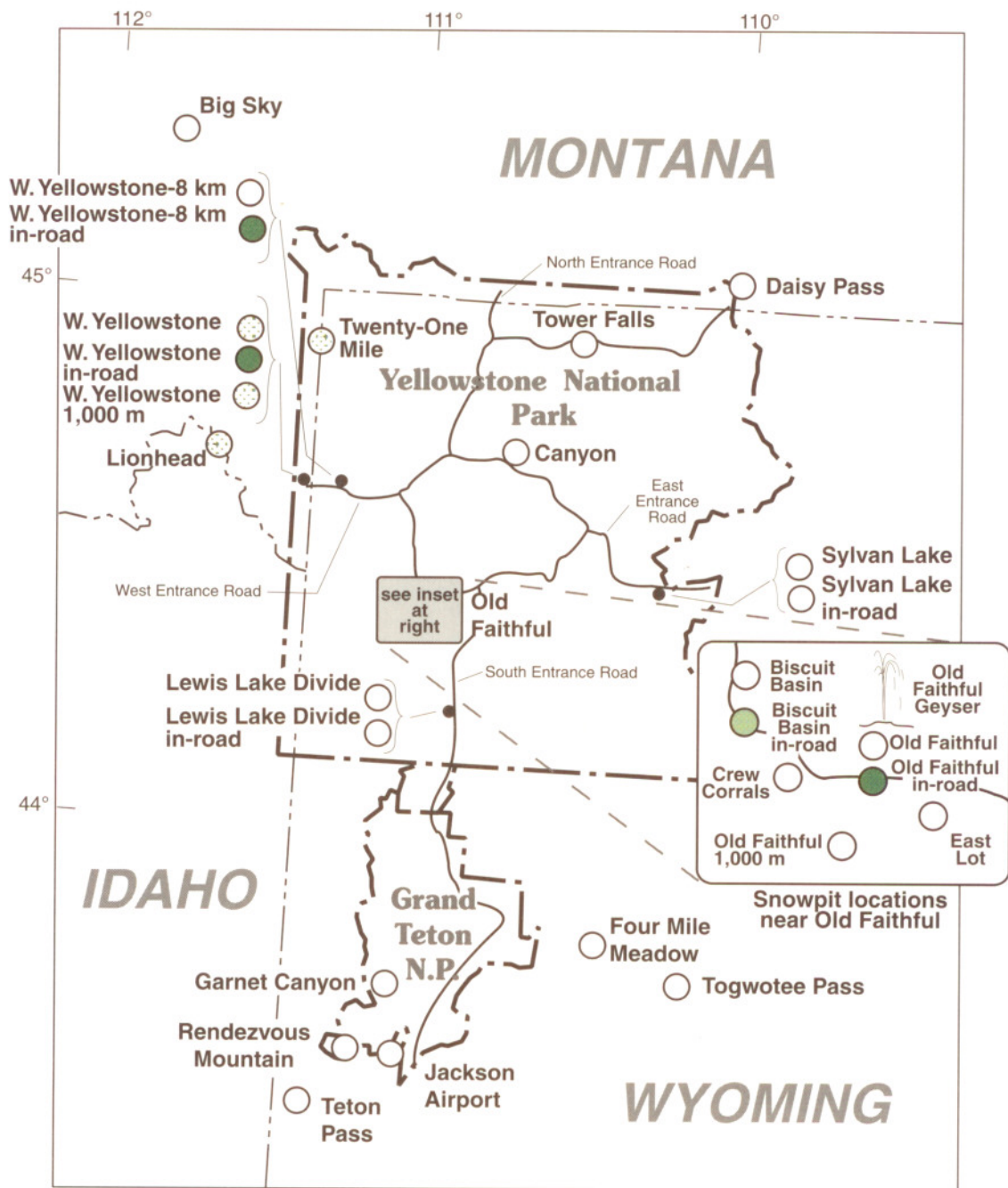


Figure 6. Sulfate ion concentrations in snow in Teton-Yellowstone area, 1998.

Table 4. Snow chemistry of selected volatile organic compounds at protocol-development sites

[MTBE, methyl tert-butyl ether; ng/L, nanograms per liter; <, less than]

Site and(or) sample name	Date	Benzene (ng/L)	MTBE (ng/L)	Toluene (ng/L)	m- and p-xylene (ng/L)	o-xylene (ng/L)
Field Blank	12/17/97	<10	<10	1,570	48.1	22.7
Field Blank	01/15/98	<10	46	<25	12	<5
Field Blank	01/22/98	<10	<10	<25	<10	<5
Laboratory Blank	01/28/98	<10	<10	<25	<10	<5
Trip Blank	01/15/98	<10	<10	<25	<10	<5
Trip Blank	01/22/98	15.8	<10	1,400	65	36.5
Loch Vale	12/16/97	<10	<10	91.5	14.9	9.8
Loch Vale (replicate)	12/16/97	<10	30.9	111	17.9	11.3
Supply Forks	12/17/97	<10	<10	265	22.8	12.9
Supply Forks (in-road)	12/17/97	37.4	10.1	577	640	377
Supply Forks	01/15/98	<10	10.1	88.9	13.7	5.4
Supply Forks (in-road)	01/15/98	1,820	374	9,880	14,100	7,380
Supply Forks (exhaust)	01/15/98	824	<10	7,860	32,100	20,900
Supply Forks	01/22/98	<10	<10	103	15.6	6.5
Supply Forks (5 meters-exhaust)	01/22/98	<10	200	65.3	16	7.2
Supply Forks (in-road)	01/22/98	182	298	1,100	1,390	765
Minimum ¹		<10	<10	65.3	13.7	5.4
Maximum ¹		1,820.0	374	9,880	32,100	20,900
Median ¹		<10	10.1	188	20.4	12.1

¹ Summary statistics do not include blanks.

same basic trends seen with major ions (fig. 7), particularly benzene. Other hydrocarbons such as MTBE, toluene, and the xylenes also showed similar positive correlations to snowmobile traffic patterns (fig. 8). Low concentrations of these VOC's generally occurred in the off-road and backcountry sites; much higher concentrations were noted at sampling sites nearer to snowmobile emissions (table 5). A replicate sample at the Old Faithful in-road site had concentrations similar to the original sample for all constituents analyzed. The VOC concentrations in snow samples at in-road sites also generally were lower at the low-traffic sites near Lewis and Sylvan Lakes. Squared Pearson correlation coefficients (r^2) for relations between VOC's shown in table 6 indicate that strong correlations ($r^2 = 0.44$ to 0.99) exist between all compounds except MTBE. Additionally, good correlations ($r^2 = 0.49$ to 0.80) between all hydrocarbons (except MTBE) and ammonium and sulfate support assertions that these inorganic and organic constituents are emitted from the same source. In general, when concentrations of ammonium and sulfate were highest

(at the high-use, in-road sites), toluene and xylene concentrations also were high. Although benzene and MTBE concentrations did not follow this pattern in each case, benzene concentrations were the highest at the high-use, in-road sites at West Yellowstone and Old Faithful, and lowest at off-road sites.

Snowmelt Runoff

Preliminary sampling of five snowmelt runoff sites near West Yellowstone, Old Faithful, Lewis Lake Divide, Sylvan Lake, and Tower Falls was undertaken as a first step in identifying whether local surface-water quality might be affected by elevated levels of emissions detected in snow near snowmobile traffic routes in the park. In this initial measure of stream chemistry after the onset of seasonal snowpack melting, only single grab samples were collected during May 1998. Those grab samples, a field blank, and a replicate were analyzed for major ions (table 7) and VOC's (table 8).

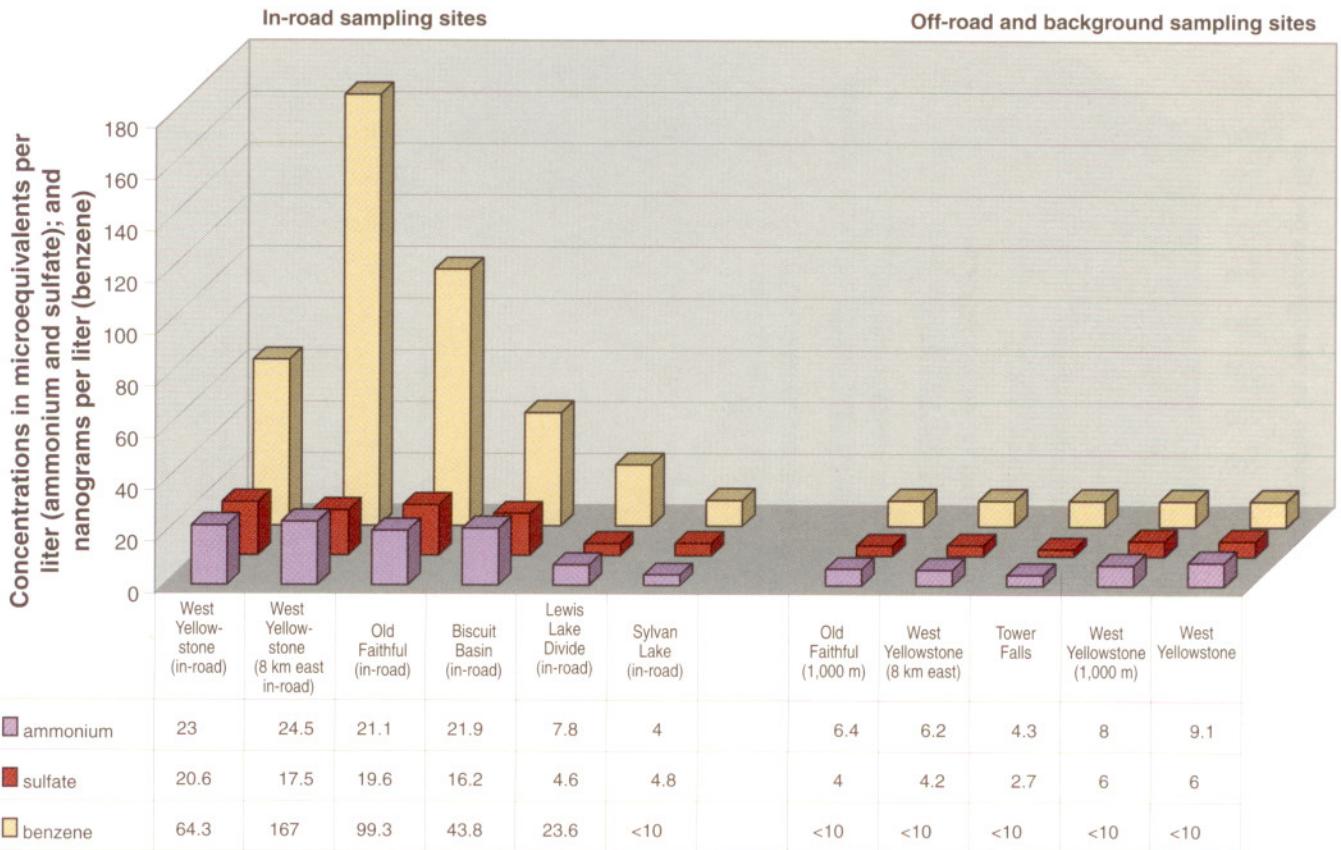


Figure 7. Ammonium, sulfate, and benzene levels in snow at selected sites in Yellowstone National Park, 1998.

Major ion chemistry generally indicated low concentrations of ammonium and nitrate (0 to 5.0 $\mu\text{eq/L}$), with much greater concentrations of sulfate (15.3 to 160 $\mu\text{eq/L}$) and calcium (121 to 432 $\mu\text{eq/L}$), magnesium (28.8 to 235 $\mu\text{eq/L}$), and sodium (102 to 359 $\mu\text{eq/L}$). The field blank showed normal low detections, but the replicate grab sample at West Yellowstone yielded a moderate sulfate concentration (18.3 $\mu\text{eq/L}$) compared to the high concentration (160 $\mu\text{eq/L}$) in the original sample. Free acidity in all stream waters sampled was very low (0.02 to 0.09 $\mu\text{eq/L}$ hydrogen ion concentration) relative to other streams in headwaters basins in the Rocky Mountain region (Campbell and others, 1991; 1995). The corresponding pH values ranged from 7.17 to 7.82 for these slightly basic surface waters. This low acidity is likely due to generally high cation concentrations that give the streams potential for neutralizing acidic snowmelt. Sodium concentrations are unusually high (102 to 359 $\mu\text{eq/L}$), especially at West Yellowstone and Old Faithful. Although pH and other major ion

levels are moderate to high relative to hundreds of other streams, ponds, lakes, and springs sampled in the Rockies, chemical concentrations in Yellowstone surface water (with the exception of sodium) are not unusually high (Musselman and others, 1996). Further monitoring and more intensive surface-water sampling are needed to verify and expand on this cursory, preliminary description of snowmelt-runoff chemistry.

If was noted
 VOC species tend to reach equilibrium with the atmosphere when liquid-phase species are allowed to interact with atmospheric gases (Rathbun, 1998). As snowmelt begins, hydrocarbons in solution mix readily with the atmosphere and tend to volatilize into the gaseous phase as they enter the atmosphere. All VOC's studied apparently exhibited this tendency except toluene; all other constituents registered below reporting limits while toluene persisted in snowmelt runoff waters (table 8). Additional monitoring and analyses are needed to verify the persistence of toluene in snowmelt runoff.

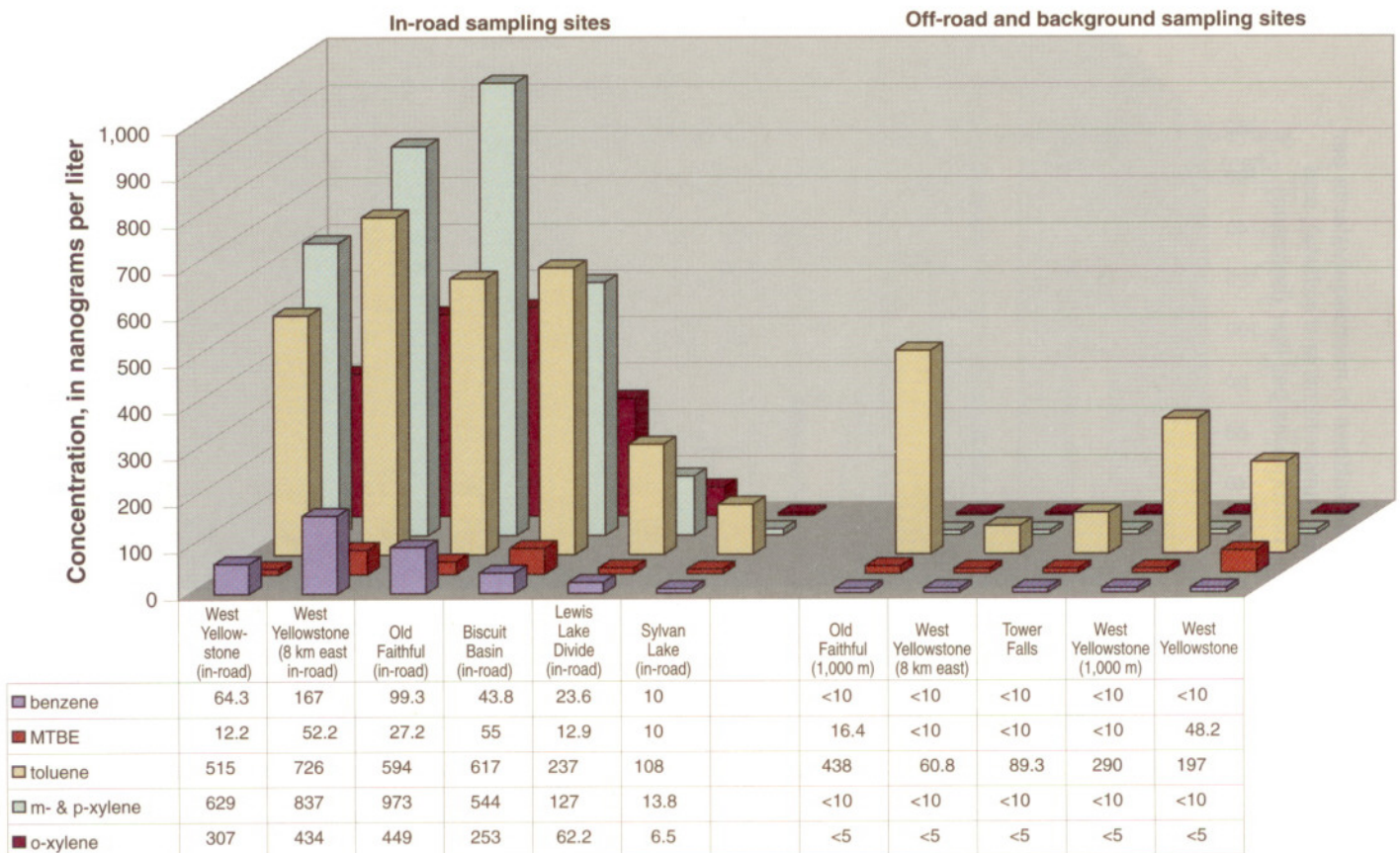


Figure 8. Hydrocarbons in snow on snowmobile-packed roads and off-road sites.



Table 5. Snow chemistry of selected volatile organic compounds in the Greater Yellowstone area

[ng/L, nanograms per liter; m, meters, km, kilometers; <, less than]

Site name	Date	Benzene	MTBE	Toluene	m- and p-xylene	o-xylene
Biscuit Basin (in-road)	03/06/98	43.8	55.0	617	544	253
Jackson Hole Airport	03/19/98	<10	<10	132	<10	<5
Lewis Lake Divide (in-road)	03/04/98	23.6	12.9	237	127	62.2
Old Faithful (in-road)	03/06/98	99.3	27.2	594	973	449
Old Faithful (in-road, replicate)	03/06/98	71.3	18.3	472	762	356
Old Faithful (1,000 m)	03/06/98	<10	16.4	438	<10	<5
Sylvan Lake (in-road)	03/03/98	<10	<10	108	13.8	6.5
Tower Falls	03/10/98	<10	<10	89.3	<10	<5
West Yellowstone	03/05/98	<10	48.2	197	<10	<5
West Yellowstone (1,000 m)	03/05/98	<10	<10	290	<10	<5
West Yellowstone, 8 km east	03/06/98	<10	<10	60.8	<10	<5
West Yellowstone, 8 km east (in-road)	03/06/98	167	52.2	726	837	434
West Yellowstone (in-road)	03/05/98	64.3	12.2	515	629	307
Minimum ¹		<10	<10	60.8	<10	<5
Maximum ¹		167	55.0	726	973	449
Median ¹		67.8	22.8	290	629	307

¹Summary statistics do not include blanks.**Table 6.** Squared Pearson correlation coefficients between selected organic and inorganic gasoline-engine-emission by-products

[MTBE, methyl tert-butyl ether; ng/L, nanograms per liter]

	Benzene (ng/L)	MTBE (ng/L)	Toluene (ng/L)	m- and p-xylene (ng/L)	o-xylene (ng/L)
Benzene		0.45	0.91	0.52	0.44
MTBE			0.30	0.06	0.03
Toluene				0.74	0.68
m- and p-xylene					0.99
o-xylene					
Ammonium	0.78	0.15	0.61	0.78	0.80
Sulfate	0.66	0.06	0.49	0.76	0.77

Table 7. Snowmelt runoff chemistry of selected inorganic compounds in Yellowstone National Park

[units: pH, standard; inorganic compounds, in microequivalents per liter; n/a, not applicable]

Site name	Date	pH	Hydrogen	Ammonium	Calcium	Magnesium	Sodium	Chloride	Sulfate	Nitrate
Lewis Lake Divide	05/09/98	7.17	0.07	0.0	121	28.8	116	16.6	15.3	4.3
Old Faithful	05/11/98	7.25	0.06	0.0	142	40.3	305	100	26.8	0.0
Old Faithful (field blank)	05/11/98	5.38	4.2	0.1	0.0	0.0	0.4	0.5	0.3	0.0
Sylvan Lake	05/19/98	7.42	0.04	0	432	104	102	5.2	150	2.3
Tower Falls	05/11/98	7.82	0.02	no data	398	235	261	15.8	42.3	5.0
West Yellowstone	05/04/98	7.24	0.06	1.4	219	54.3	358	0.0	160	0.8
West Yellowstone (replicate)	05/05/98	7.04	0.09	1.3	220	54.3	359	71.6	18.3	0.0
Minimum ¹		7.04	0.02	0.0	121	28.8	102	0.0	15.3	0.0
Maximum ¹		7.82	0.09	1.4	432	235	359	100	160	5.0
Mean (median for pH) ¹		7.25	0.06	0.5	255	86.1	250	34.9	68.8	2.1
Standard deviation		n/a	0.02	0.7	130	77.3	115	41.0	67.5	2.2

¹Summary statistics do not include blank.**Table 8.** Snowmelt runoff chemistry of selected volatile organic compounds in Yellowstone National Park

[MTBE, methyl tert-butyl ether; ng/L, nanograms per liter; <, less than]

Site name	Date	Benzene (ng/L)	MTBE (ng/L)	Toluene (ng/L)	m- and p-xylene (ng/L)	o-xylene (ng/L)
Lewis Lake Divide	05/09/98	<10	<10	<25	<10	<5
Old Faithful	05/11/98	<10	<10	<25	<10	<5
Old Faithful (field blank)	05/11/98	<10	<10	33.3	<10	<5
Sylvan Lake	05/19/98	<10	<10	<25	<10	<5
Tower Falls	05/11/98	<10	<10	252	<10	<5
West Yellowstone	05/04/98	<10	<10	80.2	<10	<5
West Yellowstone (replicate)	05/04/98	<10	<10	46.6	<10	<5
Minimum		<10	<10	<25	<10	<5
Maximum		<10	<10	252.0	<10	<5
Median ¹		<10	<10	80.2	<10	<5

¹Median values exclude field blank.

PATTERNS OF CHEMISTRY RELATIVE TO SNOWMOBILE USE

Although clear patterns have emerged to establish ammonium and sulfate as reliable indicators of snowmobile emissions in nearby snowpacks, particularly along the corridor from West Yellowstone to Old Faithful, nitrate concentrations are not much influenced by these local effects. With the exception of the extreme exposure of the direct exhaust sample at Supply Forks, snowpack concentrations of nitrate were relatively unaffected by snowmobile traffic.

Siting off-road sampling sites 50 m from snowmobile routes seems adequate to eliminate contamination from snowmobiles and allow observation of regional effects. Comparisons between chemistries at the West Yellowstone sites 50 and 1,000 m off-road show similar values for all major ions and also are similar to background levels elsewhere in the Rocky Mountain region; therefore, contamination from snowmobiles is less likely 50 m from highway corridors, especially when compared to in-road chemistry.

Furthermore, two sites 50 m off-road and a third site 1,000 m off-road around Old Faithful also had good agreement between major-ion concentrations and also were unaffected by snowmobile traffic, as shown by the in-road snow chemistry. Comparisons of these off-road and in-road sites in the Old Faithful area located within 2 to 3 km of the geyser also indicate negligible effects on sampling results from the geothermal activity.

Hydrocarbon levels in the snowpacks near snowmobile use were elevated relative to background snowpack chemistry in the study but were lower, in general, than concentrations at hundreds of locations nationwide representing a full spectrum of watershed settings ranging from subalpine to urban (Dennehy and others, 1998). Detectable concentrations of VOC's in Yellowstone ranged from 12.2 to 973 ng/L (table 5). VOC concentrations detected in urban stormwater in the United States have been found to range from 200 to 10,000 ng/L, with more concentrated levels observed less frequently (Lopez and Bender, 1998; Lopez and Dionne, 1998). In a variety of urbanized, forested, and agricultural settings in New Jersey (Reiser and O'Brien, 1998), median concentrations of seven streams detected for benzene (60 ng/L), MTBE (420 ng/L), toluene (60 ng/L), and o-xylene (10 ng/L) were markedly higher than concentrations in snowmelt runoff at Yellowstone except for

toluene (table 8). Little is known about levels of VOC's in Rocky Mountain snowpacks. Bruce and McMahon (1996) reported concentrations in snowfall collected in the Denver metropolitan area to be low.

Toluene concentrations in snowmelt runoff in Yellowstone (less than 25 to 252 ng/L; table 8) further indicate the potential sensitivity to contamination of snow and surface-water samples. Even at Loch Vale (table 4), the backcountry site in Colorado several kilometers from the nearest roadway, toluene concentrations were similar to those detected in the snow-packed roadway at Sylvan Lake (108 ng/L; table 5). Additionally, toluene concentrations in the snow-packed roadway at Old Faithful also were very similar to the concentration in snow 1 km off the highway (table 5). In some cases, there was a more clearly observable pattern, such as with comparisons between in-road and off-road sites at West Yellowstone and at the site 8 km east of West Yellowstone (West Yellowstone, 8 km east, table 5). The Tower Falls site, several kilometers from snowmobile traffic, had a low concentration (89.3 ng/L) similar to that detected in both the original (91.5 ng/L) and replicate (111 ng/L) snow samples at Loch Vale, Colorado (table 4). Oddly, the snowmelt runoff grab sample from the area near Tower Falls contained the highest concentration of toluene (252 ng/L). Clearly, more investigation is needed to determine whether these anomalously high values for toluene (relative to benzene, MTBE, and xylenes) in snowmelt runoff are due to the sampling methodology, other sources of contamination, analytical techniques, or ambient conditions. In spite of these uncertainties, the toluene snow chemistry positively correlates with other hydrocarbon and major-ion concentrations.

Drinking-water standards for benzene (5,000 ng/L), toluene (1,000,000 ng/L), and xylenes (10,000,000 ng/L) published by the U.S. Environmental Protection Agency (1996) far exceed any levels detected in either snow or snowmelt runoff at Yellowstone in this study. A drinking-water standard for MTBE has not yet been determined, but future regulation is planned. Even the highest detections of benzene in snow (167 ng/L at in-road site 8 km east of West Yellowstone) or snowmelt (less than 10 ng/L at all sites), or toluene in snow (726 ng/L at in-road site 8 km east of West Yellowstone) or snowmelt (252 ng/L near Tower Falls) at Yellowstone are far less than the established standards for water consumed by humans (less than 4 percent and less than 1 percent, respectively).

CONCLUSIONS

Snowpack-chemical analyses for ammonium and sulfate have proven to be repeatable indicators of snowmobile use in Yellowstone National Park and in Colorado, and the hydrocarbons benzene, toluene, and xylenes correlate well with patterns observed in 1998 for ammonium and sulfate in the park. Concentrations of ammonium and sulfate at the sites in snowpacked roadways between West Yellowstone and Old Faithful were greater than those observed at any of 50 to 60 other snowpack-sampling sites in the Rocky Mountain region and clearly were linked to snowmobile operation. Concentrations of ammonium, sulfate, and hydrocarbon compounds found in gasoline correlate with snowmobile use and traffic levels; where traffic volumes per day were greater, so were chemical concentrations. Thus, these combined analyses of chemistry of Yellowstone snowpacks are good indicators of the effects of high or low snowmobile traffic levels in the park. These chemical data establish important baselines for future evaluations. Further, these results indicate that snowmobile use along the routes originating at the South and East Entrances, and not including the immediate area (within 1 km) surrounding Old Faithful, may not be substantially affecting atmospheric deposition of ammonium, sulfate, and hydrocarbons related to gasoline combustion.

Preliminary analyses of snowmelt-runoff chemistry from five of the snow-sampling sites indicate that elevated emission levels in snow along highway corridors generally are dispersed into surrounding watersheds at concentrations below levels likely to threaten human or ecosystem health. Localized, episodic acidification of aquatic ecosystems in these high snowmobile-traffic areas may be possible, but verification will require more detailed chemical analyses of snowmelt runoff.

REFERENCES

- Ayers, M.A., Baehr, A.L., Baker, R.J., Hopple, J.A., Kauffman, and L.J., and Stackelberg, P.E., 1997, Design of a sampling network to determine the occurrence and movement of methyl tert-butyl ether and other organic compounds through the urban hydrologic cycle: American Chemical Society, v. 37, no. 1, p. 400-401.
- Blais, J.M., Donald, D.B., Kimpe, L.E., Muir, D.C.G., Rosenberg, B., and Schindler, D.W., 1998, accumulation of persistent organochlorine compounds in mountains of western Canada: *Nature*, v. 395, p. 585-588.
- Bruce, Breton, 1995, Denver's urban ground-water quality—Nutrients, pesticides, and volatile organic compounds: U.S. Geological Survey Fact Sheet FS-106-95, 2 p.
- Bruce, W.B., and McMahon, P.B., 1996, Shallow ground-water quality beneath a major urban center, Denver, Colorado: *Journal of Hydrology*, v. 186, p. 129-151.
- Campbell, D.H., Turk, J.T., and Spahr, N.E., 1991, Response of Ned Wilson Lake watershed, Colorado, to changes in atmospheric deposition of sulfate: *Water Resources Division*, v. 27, p. 2047-2060.
- Campbell, D.H., Clow, D.W., Ingersoll, G.P., Mast, M.A., Spahr, N.E., and Turk, J.T., 1995, Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains: *Water Resources Research*, v. 31, p. 2811-2821.
- Collins, B. J., and Sell, N. J., 1982, Lead contamination associated with snowmobile trails: *Environment Reservoir*, v. 27, p. 159-163.
- Delzer, G.C., Zogorski, J.S., Lopes, T.J., and Bosshart, R.L., 1996, Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-95: U.S. Geological Survey Water-Resources Investigations Report 96-4145, 6 p.
- Dennehy, K.F., Litke, D.W., Tate, C.M., Qi, S.L., McMahon, P.B., Bruce, B.W., Kimbrough, R.A., and Heiny, J.S., 1998, Water quality in the South Platte River Basin, Colorado, Nebraska, and Wyoming: U.S. Geological Survey Circular 1167, 38 p.
- Fenelon, J.M., and Moore, R.C., 1996, Occurrence of volatile organic compounds in groundwater in the White River Basin, Indiana, 1994-95: U.S. Geological Survey Fact Sheet FS-138-96, 2 p.
- Hare, C.T., and Springer, K.J., 1974, Exhaust emissions from uncontrolled vehicles and related equipment using internal combustion engines, Part 7, Snowmobiles: Southwest Research Institute, San Antonio, Texas, report no. SWRI-AR-946, 90 p.
- Ingersoll, G.P., 1995, Maximum-accumulation snowpack chemistry at selected sites in northwestern Colorado during spring 1994: U.S. Geological Survey Open-File Report 95-139, 14 p.
- Ingersoll, G.P., 1996, Snowpack chemistry at selected sites in northwestern Colorado during spring 1995: U.S. Geological Survey Open-File Report 96-411, 16 p.
- Ingersoll, G.P., Turk, J.T., McClure, C., Lawlor, S., Clow, D.W., Mast, M.A., 1997, Snowpack chemistry as an indicator of pollutant emission levels from motorized winter vehicles in Yellowstone National Park: Proceedings, 65th Annual Meeting, Western Snow Conference, May 4-8, Banff, Alberta, Canada, p. 103-113.

- Littlejohn, M., 1996, Yellowstone National Park visitors study, report 75: National Park Service Cooperative Park Studies Unit, Moscow, University of Idaho, January 1996.
- Lopez, T.J., and Bender, D.A., 1998, Nonpoint sources of volatile organic compounds in urban areas—Relative importance of land surfaces and air: *Environmental Pollution*, v. 100, p. 221–230
- Lopez, T.J., and Dionne, S.G., 1998, A review of semivolatile and volatile organic compounds in highway runoff and urban stormwater: U.S. Geological Survey Open-File Report 98–409, 67 p.
- Martner, B.E., 1986, Wyoming climate atlas: Lincoln, Nebr., University of Nebraska Press, 432 p.
- Morris, J.A., Bishop, G.A., and Stedman, D.H., 1999, Real-time remote sensing of snowmobile emissions at Yellowstone National Park—An oxygenated fuel study, 1999: Prepared for Western Regional Biomass Energy Program, P.O. box 95085, 1111 O Street, Suite 223, Lincoln, NB 68509, 40 p.
- Musselman, R.C., Hudnell, L., Williams, M.W., and Sommerfeld, R.A., 1996, Water chemistry of Rocky Mountain Front Range ecosystems: USDA—Forest Service, Research Paper RM–RP–325, 13 p.
- National Park Service, 1990, Winter Use Plan Environmental Assessment, Yellowstone and Grand Teton National Parks and John D. Rockefeller Jr. Memorial Parkway, Wyoming, Idaho, and Montana: U.S. Government Printing Office.
- National Park Service, Air Quality Division, 1996, Results of preliminary investigation of carbon monoxide and particulate matter levels at Yellowstone National Park West Entrance Station during 1995: Denver, Colo., National Park Service review draft, March 21, 1996.
- Natural Resources Conservation Service, 1998, Wyoming Basin outlook report, April 1, 1998: USDA-NRCS, Casper, Wyoming, p. 9–11.
- Neumann, P.W., and Merriam, H.G., 1972, Ecological effects of snowmobiles: *Canadian Field-Naturalist*, v. 86, p. 207–12.
- Paulson, R.W., Chase, E.B., Roberts, R.S., and Moody, D.W., 1991, National water summary 1988–89—Hydrologic events and floods and droughts: U.S. Geological Survey Water-Supply Paper 2375.
- Rathbun, R.E., 1998, Transport, behavior, and fate of volatile organic compounds in streams: U.S. Geological Survey Professional Paper 1589, 151 p.
- Reiser, R.G., and O'Brien, A.K., 1998, Occurrence and seasonal variability of volatile organic compounds in seven New Jersey streams: U.S. Geological Survey Water-Resources Investigations Report 98–4074, 11 p.
- Terracciano, S.A., and O'Brien, A.K., 1997, Occurrence of volatile organic compounds in streams on Long Island, New York, and New Jersey: U.S. Geological Survey Fact Sheet FS–063–97, 4 p.
- Turk, J.T., and Campbell, D.H., 1987, Estimates of acidification of lakes in the Mt. Zirkel Wilderness Area, Colorado: Water Resources Division, 23, 1757–1761.
- Turk, J.T., and Campbell, D.H., 1997, Are aquatic resources of the Mount Zirkel Wilderness Area in Colorado affected by acid deposition and what will emissions reduction at the local power plants do?: U.S. Geological Survey, Fact Sheet FS–043–97, 4 p.
- Turk, J.T., Campbell, D.H., Ingersoll, G.P., and Clow, D.W., 1992, Initial findings of synoptic snowpack sampling in the Colorado Rocky Mountains: U.S. Geological Survey Open-File Report 92–645, 6 p.
- U.S. Environmental Protection Agency, 1991, Non-road engine and vehicle emission study report: U.S. Environmental Protection Agency, Ann Arbor, Mich., Office of Mobile Sources, report no. EPA/460/3–91/02, 566 p.
- U.S. Environmental Protection Agency, 1996, Drinking water regulations and health advisories: Office of Water, U.S. Environmental Protection Agency, Washington, D.C., October, 1996, 15 p.
- Wanek, W.J., 1971, Observations on snowmobile impact: The Minnesota Volunteer, Minnesota Department of Natural Resources, v. 34, p. 1–9.
- White, J.J., and Carroll, J.N., 1998, Emissions from snowmobile engines using bio-based fuels and lubricants: Final report 08-7383, Southwest Research Institute, San Antonio, Texas, 184 p.
- Wilkinson, Todd, 1995, Snowed under—The roar of snowmobiles: *National Parks*, v. 69, Washington, D.C., p. 32–37
- Woodbury, Richard, 1997, Arctic cats and buffalo—Yellowstone may not be big enough for both its growing herds of snowmobilers and its bison: *Time*, v. 149, p. 62–3.



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