SNOWPACK CHEMISTRY AS AN INDICATOR OF POLLUTANT EMISSION LEVELS FROM MOTORIZED WINTER VEHICLES IN YELLOWSTONE NATIONAL PARK

by

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ABSTRACT

Wintertime visitors to Yellowstone National Park, Wyoming, consider scenery, wildlife, and clean air as three important qualities of their experience in the Park. Because the majority of winter visitors tour Yellowstone by motorized winter vehicles, and winter visitation has increased nearly tenfold since 1968, the effects of vehicle use are a growing concern for resource managers. The extent of effects on air quality and ecosystem health from increasing vehicular emissions throughout the Park is not fully understood.

Snowpack chemistry provides a composite record of atmospheric deposition of airborne pollutants throughout winter. Pollutant levels from vehicular emissions inside the Park were characterized by snowmelt-chemical data from three sites at a variety of high- and low-traffic locations. At each site snow samples representing most of the annual snowpack were collected at an off-road site 20 m to 100 m from motorized-traffic routes, and at a site directly in snow-packed roadways used by over-snow vehicles. Snowmelt chemistries were compared between these three pairs of samples collected in-road and off-road to determine whether concentrations decreased with distance from the source.

Concentrations of ammonium, nitrate, and sulfate in snowmelt positively correlated with vehicle usage. Ammonium and sulfate levels were consistently higher for the in-road snow compared to off-road snow for each pair of sites, but nitrate concentrations did not decrease within a distance of 100 m from the emission source.

This method demonstrates that snowpack chemistry can be used as a quantifiable indicator of airborne pollutants from vehicular traffic. A correlation was shown between pollutant levels and vehicle traffic. Additional results indicate the nitrate ion may be used to distinguish between local and regional emissions sources.

INTRODUCTION

Wintertime visitors to Yellowstone National Park, Wyoming, consider scenery, wildlife, and clean air as three important qualities of their experience in the Park (Littlejohn, 1996). The majority of winter visitors tour Yellowstone by motorized over-snow vehicles because unplowed snow-covered roadways prevent highway access by automobile traffic into large expanses 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. Air quality is a growing concern for resource managers as motorized winter visitation has increased nearly tenfold since 1968. Air-quality monitoring at the West Entrance during winter 1995 detected carbon monoxide (CO) levels exceeding Federal standards (National Park Service, Air Quality Division, Denver, Colo., 1996). However, at this busiest entrance to the Park, where 1,000 over-snow vehicles have entered on peak traffic days, CO concentrations diminished at air-quality sample-sites 20 to 100 m away from the entry point. Although CO concentrations decrease a short distance from the West Entrance, the extent of effects on air quality and ecosystem health from increasing vehicular emissions throughout the Park is poorly understood. Knowledge of the extent of other pollutants associated with fossil-fuel combustion is important to future Park preservation, and it is further important to establish chemical baselines that can be used in future evaluations that affect policy decisions controlling vehicle usage in pristine areas.

The term snowmachine used in this paper includes multi-passenger snowcoaches and other mechanized over-snow vehicles such as grooming machines and ambulances, but refers primarily to snowmobiles. Growing popularity of snowmachine usage for winter recreation in the Yellowstone National Park area has resulted in substantially increased numbers of snowmobiles operating in the Park in the past decade (National Park Service, 1990; Craig McClure, National Park Service, written Commun., 1996). Local economies in towns adjacent to the National Park and National Forest lands benefit from the growing recreational attraction offered by snowmachine touring, and are dependent upon revenues generated by accommodating over-snow recreation-alists. However, snowmachine usage in Yellowstone has in recent years become a controversial issue

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because of the noise, traffic congestion, and air pollution (Woodbury, 1997). Concerns about effects on area ecosystems from snowmachine usage include several biological and ecological considerations (Greater Yellowstone Coordinating Committee, 1996) ranging from disturbance of wildlife to human health effects. Of the many environmental affects of wintertime traffic through the Park, air pollution levels are increasingly worrisome to Park officials, and the visiting public (Wilkinson, 1995).

Increases in fossil-fuel combustion in the area could contribute to greater levels of pollutants entering pristine watersheds and animal habitats. Until recently, concentrations and the extent of dispersion of many emissions from wintertime snowmachine vehicular traffic in Yellowstone were unknown. High CO levels measured at the West Entrance, combined with increasing numbers of snowmachines entering the Park, raises the question of whether snowmachines are causing increased levels of airborne pollutants elsewhere in the Park. If airborne pollutants are extensively distributed, to what distance from highway corridors where snowmachines operate are they found? The study objectives are to determine if emissions from snowmachine traffic are detectable in the seasonal snowpack, and whether pollutant levels tend to diminish rapidly with distance from the snowmachine thoroughfares or disperse into the surrounding watersheds. If dispersion over a short distance from local sources such as snowmachines can be determined, then further identification of regionally-influenced deposition of pollutants may be possible without interference from local effects.

In this paper a newly-evolving method for analyzing snowpack chemistry is described for identification of emissions sources such as snowmachines that is flexible and cost-effective. No permanent constructs, instrumentation, or maintenance are needed; data collection is mostly free of environmental impacts and requires only one annual visit per site. A single snow sample from the annual snowpack provides a view of the chemistry representing the majority of yearly precipitation. With this technique, sampling networks are readily established to meet the objectives of a particular study with the only constraints being that sites are located where seasonal snowpacks persist, and safe accessibility (low avalanche hazard) is possible.

BACKGROUND

Early studies of impacts from snowmachine usage in Minnesota (Wanek, 1971) and south-central Canada (Neumann and Merriam, 1972) focused on ecological effects, and indicated physical damage to ecosystems occurred as a result of over-snow vehicular activity. As a result of the increased use of snowmachines in the 1970s and 80s, concerns about toxic chemical emissions from a variety of mechanized equipment used outdoors, including snowmachines, prompted extensive research of engine emissions (Hare and Springer, 1974; US Environmental Protection Agency, 1991). Collins and Sell (1982) found elevated concentrations of lead along a snowmobile trail in Wisconsin. But, little work has been done to evaluate chemical deposition in snowpack due to snowmachine use in the western USA.

The USGS has been monitoring the chemical composition of annual snowpacks in Colorado since the mid 1980s. Elevated levels of pollutants 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 et. al., 1991). Comparisons between chemical concentrations downwind of or nearer to possible emissions sources and those located crosswind or farther away from the source have shown trends in snowpack chemistries in Colorado. 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 chemistries to identify nearby emission-sources has been successfully demonstrated in northwestern Colorado (Turk and others, 1992).

During the years 1993-96, 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 that includes several sites in the Yellowstone National Park area. Snowmelt chemistries from this network of mountainous locations established normal, or background, levels of acidic ions deposited in the seasonal snowpack. In addition to normal chemical concentrations found in the region, elevated levels of pollutants in a given area are readily identifiable. Thus, emissions of chemical compounds such as ammonium, nitrate, and sulfate from local anthropogenic sources are discernible from normal background levels. Patterns emerging from chemical analyses of the seasonal snowpacks in the Yellowstone National Park area during 1993-95 indicated that traffic volume of snowmachines might positively correlate with chemical concentrations of ammonium, nitrate, or sulfate.

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 jetstream bringing abundant moisture, mostly from the Pacific, to the mountains (Martner, 1986). The area is the scene of strong winds and frequent storms that deliver heavy precipitation preferentially to elevated areas; surrounding plains areas are dry by contrast. The high average elevation (> 2000m) and latitude of the area maintain cool temperatures and cause most annual

precipitation to fall as snow (Paulson,et. al., 1991). As in many subalpine continental settings in the Rocky Mountain Region, snowcover is present about six months each year until March or April.

The study area includes three snow-sampling sites at selected high-elevation locations in Yellowstone National Park, Montana, and Wyoming (Fig. 1). These subalpine sites represent pristine snowpacks subjected to limited anthropogenic activity apart from being within 100 m of groomed snowmachine routes. 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 2035 m above sea level at West Yellowstone, Montana, to about 2570 m near Sylvan Lake, Wyoming. Old Faithful is at an intermediate elevation of about 2240 m. At these elevations the seasonal snowpack is maintained throughout the winter into spring and substantial melt usually does not occur until spring runoff. Accessibility to sampling locations requires snowmachines, but is simplified by travelling snowpacked roadways to within 100 m of sampling sites.
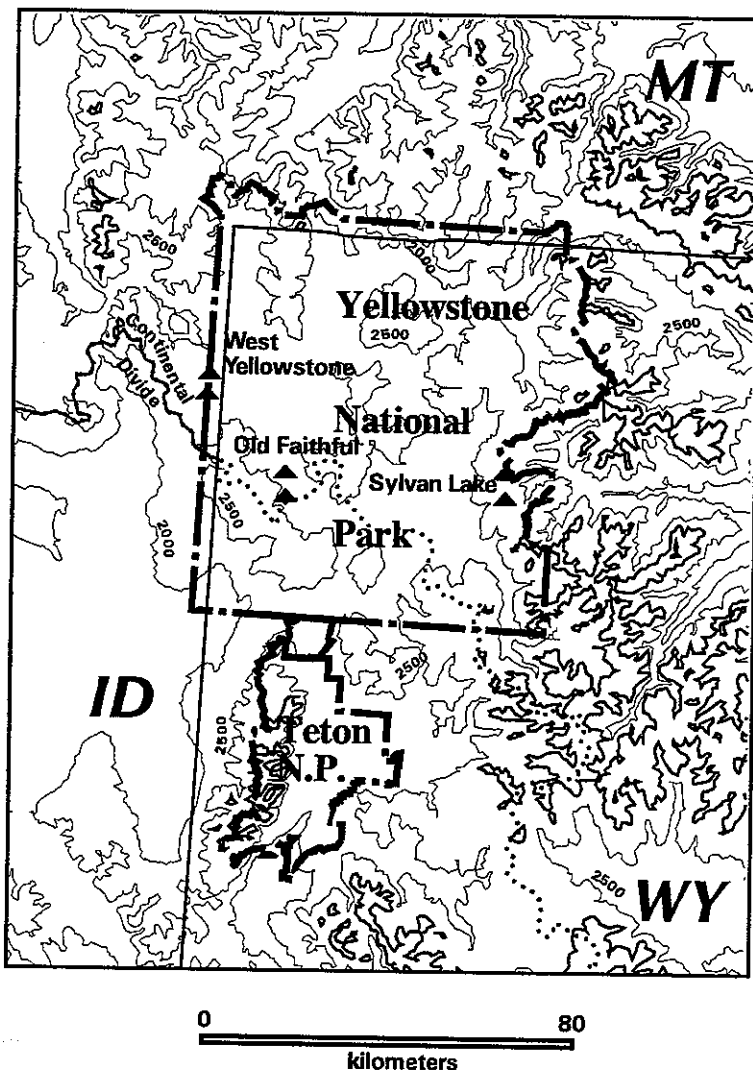
Figure 1: Paired snowpack sample sites in Yellowstone N.P., 1996. Contour interval is 500 meters; bold contours indicate elevations >3000 meters. Snake River Basin descends lower left edge of map.

METHODS

Sample Collection

Seasonal snowpacks provide a composite record of atmospheric deposition of airborne pollutants throughout winter if no substantial melt occurs before sample collection. 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. 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 et. al., 1995). By sampling within 2-3 weeks before melt begins, most yearly snowfall may be collected in a single sample and seasonal chemical deposition remains intact.

Three locations along snowpacked routes that represent variable levels of over-snow traffic were selected to observe differences in snowmelt chemistry at high-, moderate-to-high-, and low-use sites. At each of the 3 locations, West Yellowstone, Old Faithful, and Sylvan Lake, an off-road sampling site was paired with a site in the active snowpacked roadway. Off-road sites were established at distances from snowmachine roadways ranging from about 20 to 100 m. In-road sites were positioned directly in snow packed by snowmachine traffic.

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. Snow depths in the snow pits ranged from 0.6 to 1.7 m at in-road sites, and 0.9 to 2.2 m at off-road sites; snow depths in packed roadways were 60-80% of snow depths at unpacked off-road sites. Full-snowpack temperature profiles were recorded at 10- or 20-cm intervals to ensure temperatures below 0°C predominated among snow strata. Snow-crystal size, type, and hardness of all homogeneous strata were measured to document the history of the metamorphisms of the snowpack during the winter. Further observations of ice layers, evidence of melt, saturated wet snow, and soil moisture beneath the snowpack were recorded to ensure 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 the six snowpits were collected March 10-12, 1996 before snowmelt began at the sampling sites.

Snow samples were collected carefully to prevent several sources of contamination because of the extremely dilute chemistry of snow at sample locations. The bottom 10 cm of the snowpack were not sampled to avoid inclusion of forest litter and soils in the samples. Accordingly, the top 5 cm of snowpack were discarded to exclude snow contaminated by activities resulting from transport to and preparation of the snowpit. Latex laboratory gloves were worn, and clean plastic shovels and scoops 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, or perspiration when filling sample containers. The snow columns were cut and placed in 8-L Teflon bags that were prerinsed in pure (18 megohm-cm) deionized water (DI). These containers were sealed against contamination, and transported frozen to the USGS Regional Research Laboratory in Boulder, Colorado, for analysis. Snow samples were kept refrigerated to prevent chemical reactivity until the actual dates of laboratory analyses when they were batch-processed for major ions including ammonium, nitrate and sulfate.

Analytical Methods

Snow samples were allowed to melt in the Teflon collection bags and were processed within 12 hours by using a series of analytical procedures. Snowmelt-sample aliquots were refrigerated for subsequent analyses. Sulfate concentrations were determined on filtered (0.45 μm) aliquots by ion chromatography. Nitrate and ammonium ion concentrations were analyzed on filtered (0.45 μm), frozen subsamples by air-segmented, continuous-flow colorimetry. Detection limits were 0.4, 0.2, 0.5 μeq/L for sulfate, nitrate, and ammonium, respectively.

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 blanks, duplicates, reference samples, and 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. Quality control of field methods for snowpack sampling is not done at each sampling site; however, two snowpits, located side-by-side, were independently sampled at Rabbit Ears Pass, Colorado, to provide quality control for sampling at Yellowstone and other sites in the Rocky Mountain region. Charge balance was calculated between total anions and cations to check the quality of the analyses.

RESULTS AND DISCUSSION

Results of chemical analyses of the snowmelt from the 6 snowpits yielded two noteworthy relations. First, concentrations of ammonium, nitrate, and sulfate in snowmelt correlated positively with vehicle usage for both the off-road and in-road sites (Table 1, Fig. 2a-c). Snowmelt chemistry from both the off-road and in-road snowpits at Sylvan Lake show very similar low levels of all three constituents. This result is likely due to the low vehicle usage (about 5% of total Park traffic). These concentrations between 3.0 and 4.1 microequivalents per liter (μeq/L) for all three species at both Sylvan Lake snowpits are typical of regional background levels. The slight difference between the chemical levels in the snow on the roadway and off-road at Sylvan Lake suggests the low volume of snowmachine traffic on that highway corridor results in minimal chemical deposition in the annual snowpack. However, the higher-traffic sites exhibit a pattern of greater chemical deposition suggesting that in both the off-road and in-road sites consistently higher concentrations of all three constituents are due to the much higher over-snow vehicle traffic at Old Faithful and West Yellowstone.

Table 1: Snowmachine usage levels and chemical concentrations (microequivalents per liter) at snow-sampling sites

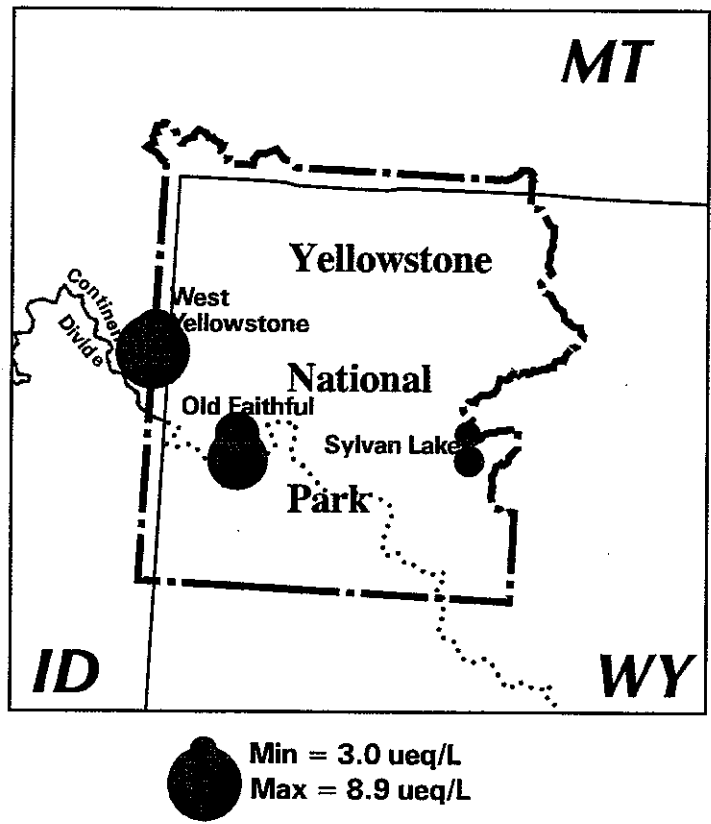| sitename	level of snowmachine use	ammonium	nitrate	sulfate
West Yellowstone (off-road)	high	5.1	7.9	4.2
West Yellowstone (in-road)	high	8.9	7.9	8.8
Old Faithful (off-road)	moderate-to-high	5.2	8.4	4.0
Old Faithful (in road)	moderate-to-high	7.2	8.4	6.2
Sylvan Lake (off-road)	low	3.0	3.9	3.3
Sylvan Lake (in road)	low	3.5	4.1	4.0

Figure 2a: Ammonium ion levels in Snowpack, 1996.

In—road levels shown below off—road levels.
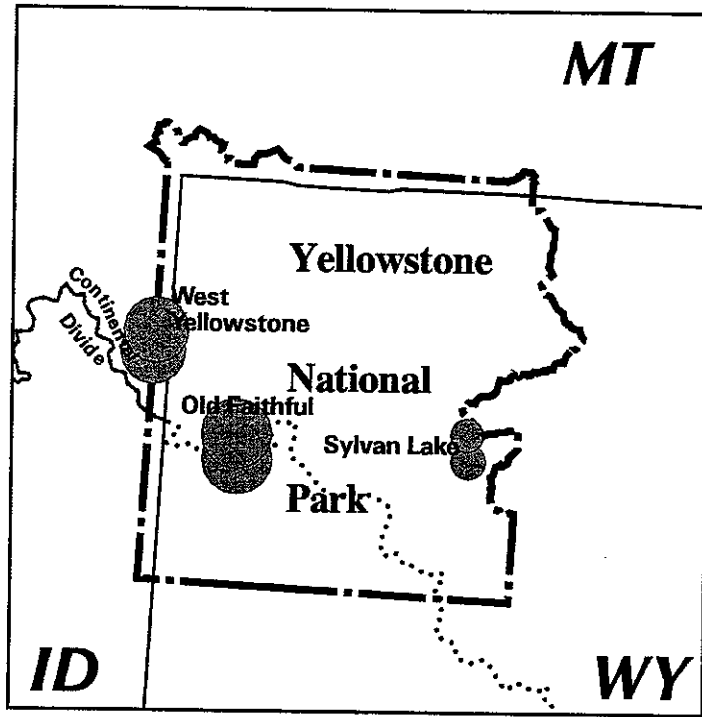
Figure 2b: Nitrate ion levels in Snowpack, 1996.

In–road levels shown below off–road levels.
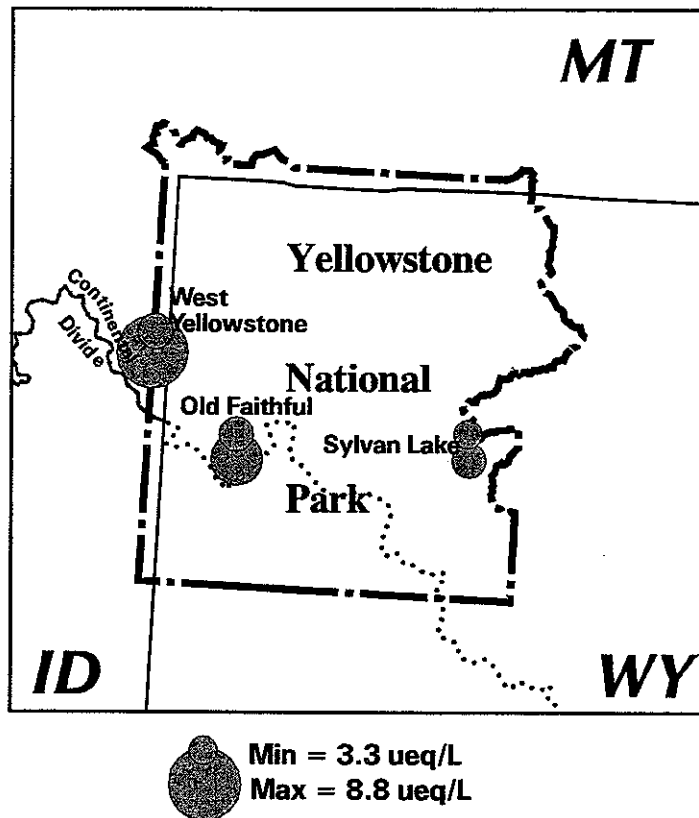
Figure 2c: Sulfate ion levels in Snowpack, 1996.

In—road levels shown below off—road levels.

The second result of the study illuminates an interesting variation in the dispersion of the three compounds studied, and contradicts the hypothesis that chemical concentrations of all three species are proportional to levels of snowmachine use. Comparisons between in-road and off-road chemical results at both Old Faithful and West Yellowstone show levels of ammonium and sulfate to be about 40 to 110% greater in the snowpacked road compared to the off-road snow. The same comparison for the pair of snow-chemistries at Sylvan Lake shows little differences, and probably is due to the much lower vehicular traffic. However, ammonium and sulfate concentrations decrease markedly over a short distance (20-100 m) between the in- and off-road sites (especially at the moderate-to-high- and high-traffic sites), but nitrate concentrations remain virtually unchanged over the same distance at all three pairs of snowpits (Figs. 2a-c). At Sylvan Lake the difference in nitrate concentration in the pair of snowpits is 0.2 μeq/L, and at Old Faithful and West Yellowstone the nitrate levels from the snowpit pairs are identical (Fig. 2b). Unlike ammonium and sulfate, nitrate concentrations did not exhibit a gradient over distance between any pair of snowpits regardless of traffic volume. This difference could suggest that nitrate ions disperse farther into surrounding watersheds than do ions of ammonium or sulfate. An analogous example is the atmospheric sampling of airborne gases and particulates near the snow surface in Greenland that indicate gaseous nitric acid concentrations to be greater than 10 times that of particulate, or aerosol, nitrate (Dibb, 1994). The same work showed sulfate to be more abundant in the heavier particulate phase, suggesting that sulfate levels might be expected to decrease over a short distance, and nitrate levels might not. Another possibility is that nitrate emissions from snowmachines may be small relative to other sources.

Perhaps the source of nitrates detected in the snowpack is not from snowmachines, but from regional influences such as agricultural production upwind in the Snake River basin of Idaho. Dust from nitrogen-bearing fertilizers used in large expanses of southeastern Idaho could be transported east toward southwestern Montana and northwestern Wyoming by prevailing westerly winds. Because the Continental Divide is relatively low where it traverses Yellowstone as compared to nearby mountain ranges to the north and south of the Park, eastbound airmasses preferentially pass onto the Yellowstone Plateau (Barry, 1992) and reach areas of popular snowmachine usage like West Yellowstone and Old Faithful.

In that case, a downwind gradient of declining nitrate concentrations from the source might result, especially after air masses undergo orographically-induced precipitation. For example, in a given airmass containing chemical constituents like nitrate, a finite number of airborne ions are present to bond with snow crystals during precipitation events. As the airmass proceeds upward over higher elevations and precipitation begins, it is possible that substantial amounts of airborne chemicals like nitrate could be removed from the atmosphere with falling snow before the airmass travels over the watershed divide. This process could result in higher concentrations of nitrate closer to potential sources, and at elevations below watershed divides where orographic precipitation fully develops. Under those circumstances, ions from a nearby source are removed readily from the airmass as they adsorb to snow crystals. During orographically-induced precipitation events, snowflakes form in about one-half hour (Barry, 1992). As the adsoption of airborne chemicals proceeds, progressively fewer ions are available to bond with snow forming in later hours as the airmass proceeds out of the watershed. Thus, chemical deposition via precipitation is likely greatest during early stages of these snowfall events.

In a comparable situation, observations of nitrate concentrations in snowpacks between a site in Colorado on the Continental Divide and a nearby lower-elevation site upwind show a relation supportive of this effect (Ingersoll, 1996). During 1993-96, seasonal-snowpack nitrate concentrations were consistently higher at the lower-elevation site (nearer to an emissions source) than at the higher-elevation site. Storms typically pass the lower site as they move up mountain slopes before reaching the higher site.

This similar observation would help explain why the Old Faithful and West Yellowstone sites, with their proximity to the agricultural areas of Idaho, have higher nitrate levels than the more distant Sylvan Lake site. In addition to being farther downwind from the other two sites, Sylvan Lake lies 500 m higher in elevation and is 50-80 km upslope on the Yellowstone Plateau. Thus, it could be expected that greater deposition of such regionally originated nitrate would be detected in snowpacks at Old Faithful (8.4 µeq/L) and West Yellowstone (7.9 µeq/L), than at Sylvan Lake (3.9-4.1 µeq/L). Preliminary snowpack-chemistry data from 1994 for other sites in the Yellowstone area (Fig. 3) support the assumption that the source of nitrate ion is less likely a result of local air-quality influences like snowmachines, and more likely caused by regional sources.
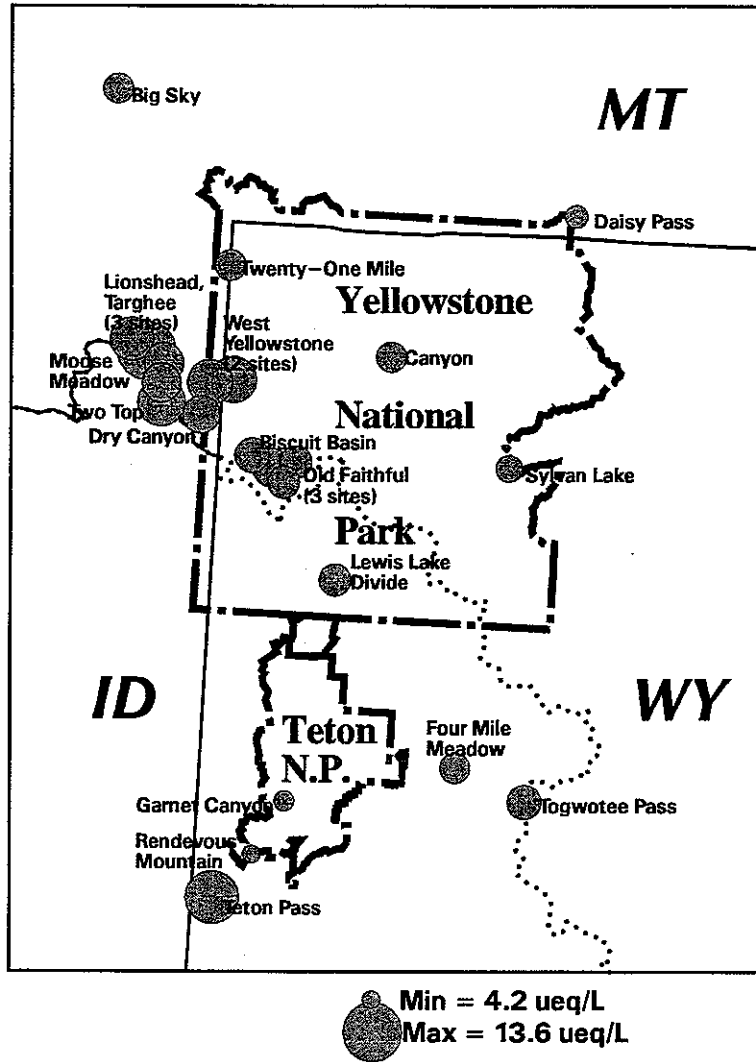
Figure 3: Nitrate ion levels in snowpack in the

Greater Yellowstone Area, 1994.

In summary, snowmelt chemistries for ammonium, nitrate, and sulfate from the 1996 annual snowpack indicated two important findings: 1) that ammonium and sulfate are quantifiable indicators of snowmachine use, and 2) that regional activities--not local snowmachine traffic--seem to be controlling nitrate deposition. Although chemical concentrations positively correlate with snowmachine traffic, and all three chemical levels generally decline a short distance (20 -100 m) from snowpacked highways, the decline with distance from snowmachine routes is not consistent for nitrate. Differences between ammonium and sulfate levels at the in-road and off-road sites show a decrease over a short distance from snowmachine traffic, but nitrate ion levels were virtually identical between paired snowpits at all three locations regardless of traffic levels. Further study duplicating the experiment presented here but incorporating the addition of snow-sampling locations several hundred meters to several kilometers from the busier snowmachine routes at West Yellowstone and Old Faithful might help distinguish between local and regional sources.

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