Effects of Snowmobile Emissions on the Chemistry of Snowmelt Runoff in Yellowstone National Park

Final Report

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Executive Summary

Created in 1872, Yellowstone National Park forms the core of the Greater Yellowstone Ecosystem, and is arguably the largest intact naturally functioning ecosystem remaining in the lower 48 United States. The park was created to protect the unique geothermal features and headwaters of the Madison, Snake, and Yellowstone rivers, while providing for the enjoyment of this unique environment by visitors. Approximately 44,000 hectares of lakes and 4,300 kilometers of streams exist in Yellowstone National Park, all which are classified as Outstanding Natural Resource Waters (Class I), meaning they must receive a very high level of protection against degradation.

More than three million people visit the park each year to engage in a wide range of recreational activities. Throughout the winter season (December–March), most park roads are closed to vehicular travel and are groomed and maintained for oversnow transportation. As a result, many visitors during winter months travel by snowmobiles. A significant increase in use of these machines was first documented in the late 1980s, when the numbers had increased nearly tenfold over that in 1968. By the mid-1990s the number of snowmobiles entering the park had increased to nearly 75,000 per year. During this time most snowmobiles had two-stroke engines, known to burn fuel inefficiently. Consequently, the steady increase in snowmobile use within the park was a concern to resource managers because of the potential that the increase in fossil-fuel combustion could result in greater levels of emissions entering the pristine surface waters of the park.

During late March through mid-April of 2003 and 2004 snowmelt runoff samples were collected from four sites along the heavily used road corridor between Yellowstone National Park's West Entrance at West Yellowstone, Montana, and the Old Faithful visitors area. Three of these sites were located immediately adjacent to the roadway in the vicinity of the West Entrance, Madison Junction, and Old Faithful. The remaining site was used as a control, located near Madison Junction approximately 100 meters from the roadway and away from the effects of snowmobiles. Each site was visited on 9–10 different days during the spring sampling period, with visits dependent on having a daily temperature >5^{o}C and good potential to obtain snowmelt runoff. *In situ* water quality measurements (i.e., water temperature, dissolved oxygen, pH, specific conductance, and turbidity) were collected. Snowmelt runoff samples were analyzed for nine volatile organic compounds (VOCs), including benzene, ethylbenzene, ethyl tert-butyl ether, isopropyl ether, *meta-* and *para*-xylene (m- and p-xylene), methyl tert-butyl ether, *ortho*-xylene (o-xylene), tert-pentyl methyl ether, and toluene. Of these nine compounds, only five were detected during any one sampling event. The detected compounds included benzene, ethylbenzene, m- and p-xylene, o-xylene, and toluene.

All *in situ* water quality measurements were within acceptable limits. The VOCs were most prevalent at the Old Faithful site, which receives extremely high use by snowmobiles each year. Fortunately, the concentrations of all VOCs detected each year were considerably below the U.S. Environmental Protection Agency's (USEPA) water quality criteria and guidelines for VOCs targeted in this study. During the course of the study, VOC concentrations of snowmelt runoff in Yellowstone National Park were below levels that would adversely impact aquatic systems. However, future research in Yellowstone National Park on snowmobile emissions should address the potential for another group of harmful chemicals known as the polycyclic aromatic hydrocarbons (PAH). The PAH tend to be more capable of persisting in the environment for longer periods than VOCs and are suspected at the Old Faithful site as it received runoff from a paved parking area.

INTRODUCTION

Over three million people visit Yellowstone National Park each year to engage in a variety of recreational activities, many of which include viewing wildlife, camping, hiking, fishing, and geyser watching. During the winter season, most roads are closed to wheeled vehicular travel, and are groomed and maintained for over-snow travel. Consequently, winter visitors can tour the interior of the park by snowmobiling, traveling in snowcoaches, cross-country skiing, and snowshoeing. A growing trend in the number of snowmobiles entering Yellowstone National Park was first documented in the late 1980s, during which time snowmobile numbers had increased nearly tenfold since 1968 (National Park Service 1990). By the mid-1990s the number of snowmobiles entering the park had increased to nearly 75,000 per year (National Park Service 2004). The burgeoning numbers of snowmobiles that enter the park each year are of particular concern because increases in fossil-fuel combustion could contribute to greater levels of emissions entering sensitive watersheds and animal habitats (Ingersoll 1999).

The increase in the number of snowmobiles entering the park prompted the National Park Service (NPS) to develop a winter use plan in 1990. In 1994, NPS and the U.S. Forest Service began work on a coordinated interagency report on winter visitor use management. In addition, the Greater Yellowstone Coordinating Committee, composed of National Park superintendents and National Forest supervisors within the Greater Yellowstone Area, met to specifically address the increasing number of snowmobiles that enter the park throughout the winter season (National Park Service 2002). In May 1997, the Fund for Animals and other organizations filed a law suit against the National Park Service alleging that the NPS failed to conduct adequate National Environmental Policy Act analysis when developing its winter use plan (National Park Service 2002). Under a Settlement Agreement, the NPS agreed to prepare an environmental impact statement (EIS) which was published in October 2000. Subsequently, a Winter Use Supplemental EIS (SEIS) was prepared in March 2002, to address new or additional information and data as provided by the public, cooperating agencies, and information regarding new snowmobile technologies (National Park Service 2002). This Winter Use SEIS identifies information needs as it relates to winter use activities and its impact on important park values such as air quality, soundscape, wildlife, aquatic resources, geothermal features, and visitor experience (National Park Service 2002).

In March 2003, a Winter Use Record of Decision (ROD) was completed to address future winter use activities in Yellowstone National Park. Two major components of the ROD were a reduction in the number of snowmobiles through daily limits and the use of snowmachines requiring best available technology (BAT). The SEIS and ROD led to changes in winter policies between the 2003 and 2004 winter seasons. During the 2003 winter season both two-stroke and four-stroke snowmachines were allowed in Yellowstone National Park with no limit to the number of snowmachines. By contrast, during the 2004 winter season a daily limit was placed on the number of snowmobiles that entered the park along with the requirement that all snowmobiles be BAT machines. The number of snowmobiles that entered the park during the 2003 and 2004 winter season were 47,799 and 22,423 respectively.

Obtaining baseline information on surface water quality as it relates to snowmelt runoff was identified as a priority in the Winter Use SEIS (National Park Service 2002). Specifically, snowmobile emissions could affect the overall surface water quality by changing pH, hydrogen, ammonium, calcium, sulfate, and nitrate levels and could also contribute harmful levels of volatile organic compounds (VOC). VOCs are hydrocarbons that are associated with crude oil and other petroleum products. They are of concern in Yellowstone National Park because they are produced by incomplete combustion of gasoline from two-stroke snow machines and can accumulate in snowpack (Ingersoll 1999). They are of particular interest because of their close association with gasoline exhaust and the possible adverse effects on human health and aquatic systems. In high concentrations, people exposed to VOCs can experience general symptoms such as headaches, dizziness, nausea, and throat and eye irritation (ATSDR 1997, ATSDR 1999); some VOCs, such as benzene, are known carcinogens (ATSDR 1997, USEPA 1980). VOCs can enter aquatic systems through precipitation or through snowmelt runoff. Concentrations of VOCs in snowmelt runoff and the effects they have on aquatic systems are poorly understood.

Over the past decade, many studies have been conducted to determine the occurrence of hydrocarbons in precipitation, surface water and ground water in urban settings (Bruce 1995, Delzar et al. 1996), in rural areas in the central and eastern parts of the United States (Fenelon and Moore 1996, Terracciano and O'Brien 1997, Reiser and O'Brien 1998), and within the Rocky Mountain region (Bruce 1995, Ingersoll 1999). Specific studies have been conducted in Yellowstone National Park to assess hydrocarbon concentrations in snowpack associated with snowmachine use (Ingersoll 1999, Tyler et al. 2001). These studies concluded that snowpack from roadways used by snowmachines contained detectable concentrations of several VOCs (i.e., benzene, methyl tert-butyl ether, m- and p-xylene, o-xylene, and toluene) while snowpack from off-road locations contained only trace amounts of toluene. In addition to snowpack chemistry, Ingersoll (1999) also collected samples (i.e., one sample visit) of snowmelt runoff during May 1998 where detectable concentrations of VOCs were limited to toluene.

The goal of the present study was to determine potential impacts of snowmobiles on the water quality of surface waters near roads in Yellowstone National Park. Specific objectives were to (1) examine snowmelt runoff for the presence of specific VOCs, (2) determine if concentrations of any VOCs exceed safe drinking water criteria, and (3) predict the potential for impacts by VOCs on the fauna of streams near roads heavily used by snowmobiles in the park.

Study Area

Yellowstone National Park encompasses approximately 898,321 hectares of pristine landscape in the northwest corner of Wyoming and portions of southwest Montana and eastern Idaho. It was created in 1872 as the nation's first national park, primarily to protect the unique geothermal features. Yellowstone National Park and adjacent wilderness areas form the headwaters of three major drainages, including the Snake River, the upper Missouri River system (Gallatin and Madison rivers), and the Yellowstone River. The park contains four large, high-elevation lakes (Yellowstone, Lewis, Shoshone, and Heart lakes) and more than 2,000 smaller lakes and ponds. In addition, Yellowstone National Park contains >10,000 geothermal features, which include geysers, hot springs, fumaroles and mud pots. All water bodies within the park are designated as Outstanding Natural Resource Waters (Class 1) and are given the highest level of protection possible (Wyoming Department of Environmental Quality 2001). As a result, preventing degradation of water quality and maintaining high water quality standards are a high priority for park resource managers. Roads receiving the greatest amount of use by snowmobiles each year and of greatest concern to managers were those between West Entrance and Old Faithful, in the west-central region of Yellowstone National Park (Figure 1).

Methods

To characterize snowmelt runoff in areas of heavy use by snowmobiles in Yellowstone National Park, we established four sites along the heavily used road corridor between West Entrance and Old Faithful (Madison/Firehole river drainage; Figure 1). Three sites were located adjacent to the roadway in the vicinity of West Entrance, Madison Junction, and Old Faithful. A fourth site was used as a control and located approximately 100 meters from the snowmobile traffic and the roadway near Madison Junction, (Figure 1). Samples from three sites (Madison, Old Faithful, and control) were collected from flowing water directly related to snowmelt runoff for both sample years. Conversely, soils near the West Entrance sample site are comprised of surficial glaciofluvial alluvium deposits which consist primarily of sands and gravels and a slope of less than 5 percent (Rodman et al. 1996). Consequently, flowing water near the West Entrance site was absent during both sampling periods. This resulted in snowmelt water being collected from pooled areas on or adjacent to the roadway. In 2003 the sample location at West Entrance was located approximately 5 meters from the main roadway within a group of pine trees. In 2004 the sample location was relocated to an area on the road surface near the West Entrance gate where water accumulated adjacent to a berm of snow. Distance between the 2003 and 2004 snowmelt sites was approximately 20 meters. Sample water from the Madison site was collected as it egressed from a culvert and before it entered the Madison River. In addition to snowmelt runoff from groomed road surfaces, water from the Madison site captured

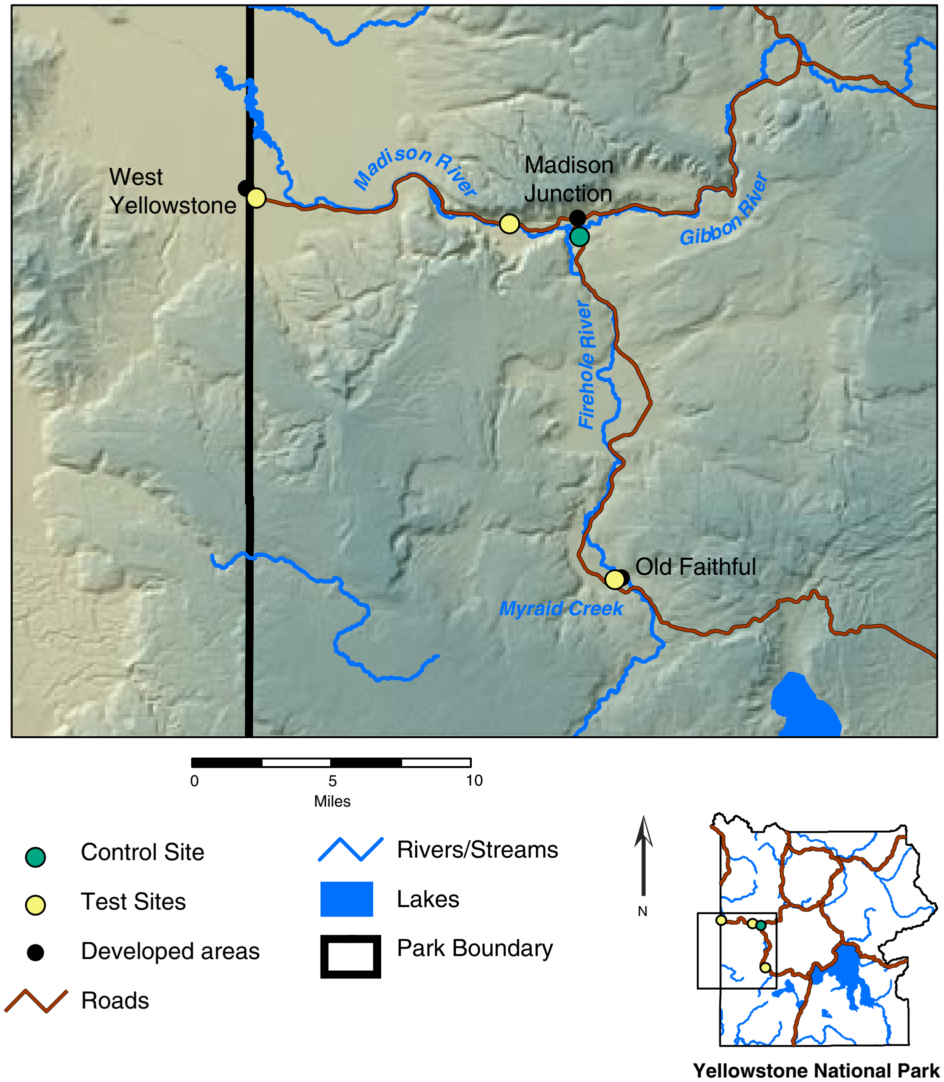

Figure 1. Study area within Yellowstone National Park with locations of sites where snowmelt runoff was collected in 2003 and 2004.

considerable amounts of snowmelt water from the adjacent hillside on the north side of the road. Samples from the Old Faithful area were collected from water flowing through a culvert that captured melt water drained from a large portion of a paved parking lot near the Old Faithful Visitor Center. This culvert directs the melt water into Myriad Creek whose confluence with the Firehole River is approximately 400 meters north of the sample site. In contrast to the Madison and Old Faithful locations, the control site near Madison Junction was located on a small intermittent stream that flowed through forested area that had been burned during the 1988 wildfires. All of the vegetation in this area was impacted by the 1988 fires and as a result, the site was characterized by abundant grasses, dead timber, and young lodgepole pine, *Pinus contorta*, approximately 3 meters in height.

During 2003 and 2004, sample collection began in mid-March after the end of the winter season when roads had opened for administrative travel by wheeled vehicles. Sampling generally took place when air temperatures were above 5°C with the sequence of site visits selected in random order. *In situ* measurements of water temperature, dissolved oxygen, pH, and specific conductance were made using a Hydrolab datasonde 4a multiparameter probe (Hach Environmental, Loveland, Colo.). In addition, a HACH 2100P (Hach Environmental, Loveland, Colo.) was used to measure turbidity. Instruments were calibrated twice daily (i.e., once prior to sampling and once after sampling was completed) following manufacturer instructions for calibration procedures.

Snowmelt runoff for VOC analysis was collected using USGS standard methods for determination of VOC compounds as described by Connor and others (1998). Water depth was too shallow to completely fill the sample vials; therefore a 2-liter opaque plastic bottle was used to collect snowmelt water from each site. Prior to collection, the bottle was rinsed with both deionized and sample water. The bottle was then submerged until approximately 500 ml of water was collected. Sample water was poured into four, 40-milliliter borosilicate U.S. Environmental Protection Agency (EPA) approved glass vials until a meniscus formed above the lip of each vial and all air bubbles were expelled. Each vial was immediately preserved by adding concentrated 1:1 solution of hydrochloric acid until a pH to 2 standard units (SU) was achieved. All vials were inspected for air bubbles and sealed with a cap having a Teflon-faced silicone septa. Each vial was labeled with a unique number that corresponded to the site data sheet.

In addition to sample vials, a set of two trip blanks were used to provide quality assurance/quality control information regarding sampling procedures and protocols. The trip blanks were provided by the U.S. Geological Survey (USGS), National Water Quality Laboratory, Denver, Colorado, and contained purified water. Trip blanks accompanied the field crew on randomly chosen sample dates. Analysis was conducted on these blanks to assure that no VOC contamination occurred during travel to and from the sample sites.

All sample vials and field blanks were shipped on ice to the USGS National Water Quality Laboratory, Denver, Colorado, for analysis. A gas chromatograph was used for VOC analysis (Connor et al. 1998). VOCs include a large list of hydrocarbons of which nine compounds were analyzed for this study including benzene, ethylbenzene, ethyl tert-butyl ether, isopropyl ether, *meta-* and *para-*xylene (m- and p-xylene), methyl tert-butyl ether, *ortho-*xylene (o-xylene), tert-pentyl methyl ether and toluene.

Results

Snowmelt Runoff in Spring 2003

In 2003, sampling began on 15 March and continued through 15 April. During this period, West Entrance, Old Faithful, and control sites were sampled nine days while the Madison site was sampled eight days. Summary statistics for all *in situ* water quality measurements are presented in Table 1. Water depth was quite shallow for all sites and ranged between 0.04 m and 0.13 m. Surface water temperatures ranged between 1.0°C and 11.8°C. The lowest mean water temperature of 3.94°C (range 1.3–7.1°C) was recorded at the West Entrance location; the highest mean water temperature of 7.09°C (range 5.2–9.4°C) was recorded for the control site. Individual measurements for pH ranged from 5.3 to 7.4 for all samples. The lowest mean pH value of 5.78 (range 5.3–7.0) was recorded at West Entrance and the highest mean pH value of 6.97 (range 6.8–7.1) at the control site. Snowmelt runoff typically has low specific conductance. Specific conductance was generally low for the three test sites which had ranges between 13 and 55 µSiemens cm^{-1} (µS) for all sample days combined. The lowest mean specific conductance of 21.44 µS (range 13–36 µS) occurred at West Entrance. Unlike the test areas, the control site exhibited the highest mean specific conductance of 144.78 µS (range 130–158 µS). Turbidity values, recorded in nephlometric turbidity units (NTU), were generally low for the West Entrance, Madison, and control locations with means of 14.01 NTU, 2.36 NTU, and 5.00 NTU respectively. The highest mean turbidity of 23.22 NTU (range 3.30–37.20 NTU) was recorded for Old Faithful (Table 1).

Of the nine VOC chemicals analyzed in snowmelt runoff, only five compounds were detected at least once during the 2003 sample season: benzene, ethylbenzene, m- and p-xylene, o-xylene, and toluene (Table 2). West Entrance and Old Faithful were the only two sites where all five compounds were detected during at least one sample event. Concentrations of benzene (0.0325 µg/L), ethylbenzene (0.0476 µg/L) and o-xylene (0.116 µg/L) were detected at West Entrance during one sample visit on 15 March 2003 (Figure 2). The presence of m- and p-xylene was detected during two visits to this site at concentrations of 0.1860 µg/L and 0.0105 µg/L, respectively, while toluene was detected in the snowmelt water collected from all nine visits (range 0.0243–0.1860 µg/L). In contrast, VOCs at the Madison site were not above the analytical detection limit (i.e., not detected) in any water samples collected during the sampling period (Table 2).

Volatile organic carbon compounds were most frequently detected at Old Faithful. The VOC

Table 1. Sample statistics for basic water quality measurements collected during the spring snowmelt runoff period of 2003.

[m, meter; °C, degrees celsius; mg/L, milligrams per liter; SU, standard units; µS, microSiemens; NTU, nephlometric turbidity units]

Site name	Sample statistic	Water depth (m)	Water temp. (°C)	Dissolved oxygen (mg/L)	pH (SU)	Specific cond. (µS)	Turbidity (NTU)
West Entrance	Mean	0.05	3.94	-	5.78	21.44	14.01
	Median	0.05	3.90	-	5.50	21.00	14.45
	Standard Error	0.00	0.63	-	0.63	2.34	1.82
	Std. dev.	0.01	1.90	-	0.53	7.02	5.14
	Range	0.01	5.80	-	1.70	23.00	15.70
	Minimum	0.05	1.30	-	5.30	13.00	6.80
	Maximum	0.06	7.10	-	7.00	36.00	22.50
	Num obs.	3	9	-	9	9	8
Madison	Mean	0.05	6.91	-	6.96	58.69	2.36
	Median	0.05	7.00	-	6.90	59.50	1.60
	Standard Error	0.00	0.39	-	0.05	1.17	0.47
	Std. dev.	0.01	1.09	-	0.14	3.31	1.33
	Range	0.01	3.50	-	0.40	8.50	3.20
	Minimum	0.04	4.80	-	6.90	55.00	1.20
	Maximum	0.05	8.30	-	7.30	63.50	4.40
	Num obs.	3	8	-	8	8	8
Old Faithful	Mean	0.06	7.00	8.17	6.86	27.44	23.22
	Median	0.05	8.00	7.80	7.00	24.00	26.70
	Standard Error	0.01	1.32	0.37	0.12	4.49	4.09
	Std. dev.	0.01	3.97	0.64	0.37	13.48	12.28
	Range	0.02	10.80	1.10	1.20	42.00	33.90
	Minimum	0.05	1.00	7.80	6.20	13.00	3.30
	Maximum	0.07	11.80	8.90	7.40	55.00	37.20
	Num obs.	3	9	3	9	9	9
Control	Mean	0.10	7.09	7.56	6.97	144.78	5.00
	Median	0.09	6.90	7.70	7.00	145.00	5.20
	Standard Error	0.01	0.53	0.11	0.03	3.07	0.58
	Std. dev.	0.02	1.60	0.25	0.10	9.22	1.73
	Range	0.05	4.20	0.60	0.30	28.00	5.80
	Minimum	0.08	5.20	7.20	6.80	130.00	2.60
	Maximum	0.13	9.40	7.80	7.10	158.00	8.40
	Num obs.	5	9	5	9	9	9

concentrations from this site were highest during a three-day sample period between 02 April and 10 April (Figure 3). During this time, concentrations of benzene ranged between 0.00992 µg/L and 0.0314 µg/L (Table 2). Highest concentrations of ethylbenzene (0.2740 µg/L), m- and p-xylene (1.4500 µg/L) and o-xylene (0.6920 µg/L) were detected during this period on 02 April 2003 (Table 2). Toluene was identified in the water from all nine site visits with a range between 0.0242 µg/L and 0.5890 µg/L. Snowmelt runoff from the control site, located approximately 100 meters from the roadway, surprisingly contained trace amounts of toluene during six of nine sample visits with a range from not detected to 0.0406 µg/L.

Snowmelt Runoff in Spring 2004

In 2004, snowmelt runoff samples were collected over a two-week period between 20 March and 03 April. Madison, Old Faithful, and control sites were sampled on ten days, and the West Entrance site was sampled on six days. Summary statistics for all *in situ* snowmelt water quality measurements are presented in Table 3. Water depth for all sites and sample dates combined ranged between 0.02 m and 0.10 m. Water temperatures ranged between 0.5°C and 11.6°C. The lowest mean water temperature of 4.12°C (range 1.0–9.3°C) occurred

Table 2. Summary of VOC concentrations at the four sample locations during the 2003 spring snowmelt runoff sample season.

[µg/L, micrograms per liter; e, estimated; <, less than reporting limit]

Site Name	Sample Date	Benzene (µg/L)	Ethylbenzene (µg/L)	m- and p-xylene (µg/L)	o-xylene (µg/L)	Toluene (µg/L)
West Entrance	03/15/03	e0.0325	e0.0476	e0.1860	0.116	0.1860
	03/30/03	<0.07	<0.06	<0.12	<0.14	e0.0243
	03/31/03	<0.07	<0.06	<0.12	<0.14	e0.0343
	04/01/03	<0.07	<0.06	<0.12	<0.14	e0.0557
	04/02/03	<0.07	<0.06	<0.12	<0.14	e0.0348
	04/09/03	<0.07	<0.06	<0.12	<0.14	e0.0797
	04/10/03	<0.035	<0.03	e0.0105	<0.07	e0.0566
	04/11/03	<0.07	<0.06	<0.12	<0.14	e0.0715
	04/15/03	<0.035	<0.03	<0.06	<0.07	e0.0259
Madison	03/31/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/01/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/02/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/09/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/10/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/11/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/14/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/15/03	<0.035	<0.03	<0.06	<0.07	<0.05
Old Faithful	03/15/03	<0.035	e0.0179	e0.0747	e0.0578	e0.0810
	03/30/03	<0.035	e0.0291	e0.1390	e0.0811	e0.0381
	03/31/03	<0.035	e0.0234	e0.1280	e0.0751	e0.0305
	04/01/03	<0.035	<0.03	<0.06	<0.07	e0.0242
	04/02/03	e0.0161	0.2740	1.4500	0.6920	0.6100
	04/09/03	e0.0314	0.1850	0.9840	0.5340	0.5890
	04/10/03	e0.00992	e0.0220	e0.0925	e0.0608	e0.0663
	04/11/03	<0.035	e0.0146	e0.0801	e0.0661	e0.0483
	04/14/03	<0.035	<0.03	<0.06	<0.07	e0.0283
Control	03/30/03	<0.035	<0.03	<0.06	<0.07	<0.05
	03/31/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/01/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/02/03	<0.035	<0.03	<0.06	<0.07	e0.0120
	04/09/03	<0.035	<0.03	<0.06	<0.07	e0.00997
	04/10/03	<0.035	<0.03	<0.06	<0.07	e0.0152
	04/11/03	<0.035	<0.03	<0.06	<0.07	e0.0150
	04/14/03	<0.035	<0.03	<0.06	<0.07	e0.0406
	04/15/03	<0.035	<0.03	<0.06	<0.07	e0.0212
Trip Blank	03/15/03	<0.035	<0.03	<0.06	<0.07	<0.05
	04/11/03	<0.035	<0.03	<0.06	<0.07	<0.05

at West Entrance; the highest mean water temperature of 7.89°C (range 5.3–10.4°C) occurred at Madison. Values for pH ranged from 5.3 to 7.4 for all sites combined and sample dates combined. The lowest mean pH of 6.49 (range 5.7–7.6) occurred at Old Faithful; the highest mean pH of 7.07 (range 6.3–7.4) occurred at West Entrance. The lowest mean specific conductance 16.5 µS (range 13–26 µS) occurred at West Entrance; the highest mean specific conductance value of 165.2 µS (range 156–174 µS) occurred at the control site. The lowest mean turbidity values were associated with West Entrance (5.3 NTU), Madison (2.75 NTU), and control sites (3.14 NTU) while the highest mean turbidity value of 35.21 NTU (range 5.3–250 NTU) was collected from the Old Faithful site.

Overall, presence of VOCs in snowmelt runoff illustrated similar patterns between the 2003 and 2004 sample years. Snowmelt runoff VOC concentrations

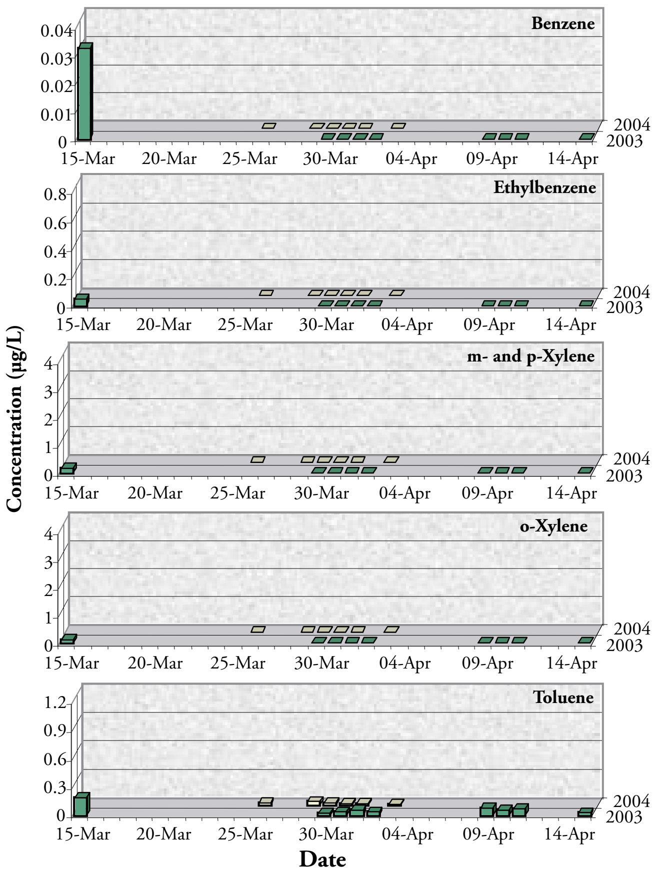

Figure 2. Concentration levels for five VOCs detected in snowmelt run-off at West Entrance, Yellowstone National Park, during spring 2003 and 2004 sample period. Note different concentration values for each compound. Values reported as zero were below detection limits.

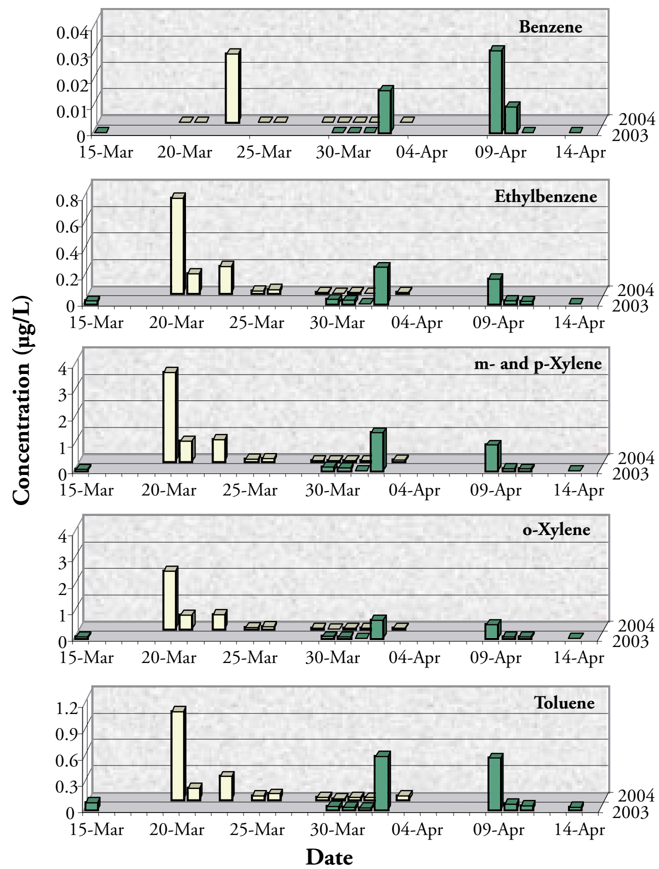

Figure 3. Concentration levels for five VOCs detected in snowmelt run-off at Old Faithful, Yellowstone National Park, during spring 2003 and 2004 sample period. Note different concentration values for each compound. Values reported as zero were below detection limits.

from spring 2004 are presented in Table 4. Six samples were collected from West Entrance and benzene, ethylbenzene, and o-xylene were not detected in any of the samples. Concentrations of m- and p-xylene were detected in two samples with concentrations of 0.007615 µg/L and 0.007854 µg/L collected on 31 March and 01 April, 2004, respectively (Table 4). Toluene was detected in water from all six site visits and ranged between 0.01183 µg/L and 0.03744 µg/L. The highest concentration was collected on 29 March with successive samples showing a general decreasing trend in toluene concentrations (Figure 2). Similar to the 2003 results, VOCs in water collected from the test site near Madison were below the analytical detection limit.

Samples from Old Faithful contained all five VOCs during the 2004 sample period. Benzene was detected from one sample with a concentration of 0.02631 µg/L on 23 March. At Old Faithful, the remaining four VOCs were collected at a greater frequency during 2004 compared to 2003 with the highest concentrations collected during the first three site visits (Figure 3). Ethylbenzene was found in eight of ten water samples, ranging from ND to 0.7202 µg/L; m- and p-xylene were found in ten samples, ranging from 0.01463 µg/L to 3.3650 µg/L; o-xylene was detected in nine water samples, ranging from ND to 2.1830 µg/L; and toluene was found in ten water samples, ranging from 0.01032 µg/L to 1.0080 µg/L (Table 4). Snowmelt runoff obtained at the control site once again contained trace amounts of toluene, but at a lesser frequency than the 2003 samples. Toluene concentrations ranged between ND and 0.01929 µg/L at the control site and were encountered early in the sample season during three sites visits (30 March and 02 April, 2004).

Table 3. Sample statistics for basic water quality measurements collected during the spring snowmelt runoff period of 2004.

[m, meter; °C, degrees Celsius; mg/L, milligrams per liter; SU, standard units; µS, microSiemens; NTU, nephlometric turbidity units]

Site name	**Sample statistic**	**Water depth (m)**	**Water temp. (°C)**	**Dissolved oxygen (mg/L)**	**pH (SU)**	**Specific cond. (µS)**	**Turbidity (NTU)**
West Entrance	Mean	0.08	4.12	-	7.07	16.50	5.30
	Median	0.08	3.45	-	7.15	14.50	3.15
	Standard Err.	0.01	1.32	-	0.16	2.05	1.78
	Std. dev.	0.02	3.24	-	0.39	5.01	4.36
	Range	0.06	8.30	-	1.10	13.00	10.70
	Minimum	0.04	1.00	-	6.30	13.00	1.80
	Maximum	0.10	9.30	-	7.40	26.00	12.50
	Num obs.	6	6	-	6	6	6
Madison	Mean	0.03	7.89	-	6.81	58.50	2.75
	Median	0.02	7.65	-	6.95	58.50	2.65
	Standard Err.	0.00	0.54	-	0.12	0.50	0.30
	Std. dev.	0.01	1.69	-	0.39	1.58	0.96
	Range	0.02	5.10	-	1.10	6.00	2.50
	Minimum	0.02	5.30	-	6.10	56.00	1.40
	Maximum	0.04	10.40	-	7.20	62.00	3.90
	Num obs.	10	10	-	10	10	10
Old Faithful	Mean	0.05	4.49	-	6.49	19.20	35.21
	Median	0.06	4.15	-	6.60	17.50	11.05
	Standard Err.	0.01	0.86	-	0.24	1.72	23.89
	Std. dev.	0.02	2.72	-	0.75	5.45	75.56
	Range	0.06	9.50	-	1.90	19.00	244.70
	Minimum	0.02	0.50	-	5.70	13.00	5.30
	Maximum	0.08	10.00	-	7.60	32.00	250.00
	Num obs.	10	10	-	10	10	10
Control	Mean	0.07	6.82	-	6.60	165.20	3.14
	Median	0.08	5.80	-	6.60	164.50	3.15
	Standard Err.	0.00	0.74	-	0.16	1.92	0.32
	Std. dev.	0.01	2.33	-	0.51	6.07	1.00
	Range	0.02	7.00	-	1.30	18.00	3.10
	Minimum	0.06	4.60	-	5.90	156.00	1.40
	Maximum	0.08	11.60	-	7.20	174.00	4.50
	Num obs.	10	10	-	10	10	10

Discussion

In general, most of the *in situ* water quality measurements are comparable between the two sample years and are within limits expected during a snowmelt runoff period on the Firehole and Madison rivers of Yellowstone National Park. Two exceptions however, were the lower pH values measured at West Entrance during spring 2003 and the high turbidity seen at Old Faithful during both sample years. Typically, snowmelt water is expected to have a pH near 7.0. The low mean pH for West Entrance (mean pH, 5.78) was most likely attributed to the physical area in which the water was obtained and not necessarily a characteristic of the chemical composition of the snowmelt run-off itself. Sample water from this site was collected from an off-road location within a group of lodgepole pine trees. Soils within a pine forest are naturally more acidic due to leeching of hydrogen ions from pine needles. This likely contributed to the lower pH values recorded at the West Entrance. By comparison, water samples collected from this area in 2004 were obtained directly from the paved road surface. The resulting mean pH value, when not in contact with forest soils, was 7.07.

High turbidities for the Old Faithful area are alarming because snowmelt run-off flows into Myriad Creek, a small tributary of the Firehole River. Sample water from this site reflects run-off that drains a paved

Table 4. Summary of VOC concentrations at the four sample locations during the 2004 spring snowmelt runoff sample season.

[µg/L, micrograms per liter; e, estimated; <, less than reporting limit]

Site Name	Sample Date	Benzene (µg/L)	Ethylbenzene (µg/L)	m- and p-xylene (µg/L)	o-xylene (µg/L)	Toluene (µg/L)
West Entrance	03/26/04	<0.021	<0.03	<0.06	<0.038	e0.02390
	03/29/04	<0.021	<0.03	<0.06	<0.038	e0.03744
	03/30/04	<0.021	<0.03	<0.06	<0.038	e0.02247
	03/31/04	<0.021	<0.03	e0.007615	<0.038	e0.01788
	04/01/04	<0.021	<0.03	e0.007854	<0.038	e0.01813
	04/03/04	<0.021	<0.03	<0.06	<0.038	e0.01183
Madison	03/20/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/21/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/23/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/25/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/26/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/29/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/30/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/31/04	<0.021	<0.03	<0.06	<0.038	<0.05
	04/01/04	<0.021	<0.03	<0.06	<0.038	<0.05
	04/03/04	<0.021	<0.03	<0.06	<0.038	<0.05
Old Faithful	03/20/04	<0.021	0.7202	3.3650	2.1830	1.0080
	03/21/04	<0.021	0.1493	0.7653	0.5019	0.1272
	03/23/04	e0.02631	0.2062	0.8113	0.5463	0.2634
	03/25/04	<0.021	e0.01822	e0.06662	e0.04316	e0.03967
	03/26/04	<0.021	e0.02782	e0.1087	e0.06731	e0.06515
	03/290/4	<0.021	e0.008128	e0.02824	e0.02128	e0.02670
	03/30/04	<0.021	<0.03	e0.01463	<0.038	e0.01032
	03/31/04	<0.021	e0.005851	e0.02332	e0.01493	e0.02351
	04/01/04	<0.021	<0.03	e0.01821	e0.01116	e0.02169
	04/03/04	<0.021	e0.008393	e0.03157	e0.01910	e0.04145
Control	03/20/04	<0.021	<0.03	<0.06	<0.038	e0.01538
	03/21/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/23/04	<0.021	<0.03	<0.06	<0.038	e0.01929
	03/25/04	<0.021	<0.03	<0.06	<0.038	e0.01143
	03/26/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/29/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/30/04	<0.021	<0.03	<0.06	<0.038	<0.05
	03/31/04	<0.021	<0.03	<0.06	<0.038	<0.05
	04/01/04	<0.021	<0.03	<0.06	<0.038	<0.05
	04/03/04	<0.021	<0.03	<0.06	<0.038	<0.05
Trip Blank	03/23/04	<0.021	<0.03	<0.06	<0.038	<0.05
	04/03/04	<0.021	<0.03	<0.06	<0.038	<0.05

parking lot with no soils or vegetation cover. As a result, runoff contained fine sand. This suspended material could have been produced from mechanical wear of the blacktop material in the parking lot. The material, as it enters the stream and is deposited, could have adverse affects on the chemical and physical properties of the water, as well as have harmful affects on the biological communities. During site sampling, a considerable amount of petroleum-like film was observed on the water's surface as it flowed from the culvert. This was probably a result of vehicular oil and petroleum products left on the parking area during the summer season and could have also been a factor with the higher turbidity measurements at this site.

At the Madison site no VOCs were detected in sample water during the two-year study period. Generally, snow from the plowed road surfaces in this area appeared to contribute minimal amounts of snowmelt to the overall sample. Most of the water volume appeared to originate from numerous freshwater springs flowing from the hillside adjacent to the roadway. If VOCs are introduced into the snowpack on groomed road surfaces, they are most likely diluted by the flux of water from these springs.

At West Entrance and Old Faithful, five VOC compounds were identified at least once during the two-year sample period. The highest concentration for benzene (0.0325 µg/L) was recorded at West Entrance on 15 March 2003, while Old Faithful had the highest frequency of occurrence for all VOCs with highest concentrations of ethylbenzene (0.2062 µg/L), m- and p-xylene (0.8113 µg/L), o-xylene (0.5463 µg/L), and toluene (0.2634 µg/L) on 23 March 2004. Although VOC concentrations were associated with areas having high volumes of snowmobile traffic, measurable amounts of VOCs remained considerably below EPA recommendation for VOCs in freshwater systems. The recommended freshwater acute criteria for benzene is 5,300 µg/L; for ethylbenzene, 32,000 µg/L; and for toluene, 17,500 µg/L (Rowe et al. 1997). Furthermore, aquatic toxicity information (Table 5) provides support that concentrations of VOCs measured during the 2003 and 2004 would have minimal, if any, affects on organisms within aquatic systems (Rowe et al. 1997).

The presence of toluene at our control site was not unusual and this VOC has been previously documented in the snowpack of off-road sites in Yellowstone National Park (Ingersoll 1999). The VOCs, including toluene, are produced as a byproduct of forest fires (Levine 1999). One possible explanation for the presence of low toluene levels at this our control site is that residual amounts of toluene exist within the burned timber that is abundant in the area around the control site. If toluene is contained within the cinders and charred wood, it could be released during the spring snowmelt period, producing detectable concentrations within the sample water. Additional monitoring needs to be conducted to confirm the persistence of toluene in snowmelt runoff at similar off-road locations.

Conclusion

Detectable concentrations of the five VOCs (i.e., benzene, ethylbenzene, m- and p-xylene, o-xylene, and toluene) were found in snowmelt runoff at the West Entrance and Old Faithful areas of Yellowstone National Park during 2003 and 2004. Both the West Entrance and Old Faithful areas receive high numbers of snowmobile use during the winter season. Additionally, trace amounts of toluene were detected at the control site, located away for roads and snowmobile traffic at Madison Junction. The highest frequency of VOCs occurred at the Old Faithful sample site however, these low VOC concentrations found within the snowmelt runoff would become more diluted as they entered a larger body of water such as the Firehole or Madison rivers, further limiting potential impacts to aquatic organisms. All detectable VOC concentrations were well below the EPA's recommended freshwater acute criteria for benzene, ethylbenzene, and toluene. Additional information regarding the toxicity of these five compounds on aquatic organisms provided further evidence that any impacts of VOCs found in snowmelt runoff on Yellowstone National Park's aquatic systems are likely negligible.

Although VOCs did not appear to be in high enough concentration to negatively impact aquatic systems, a concern arose during the study regarding the large amounts of petroleum based products that originated from snowmelt water observed at the Old Faithful site. These products could contain a different group of hydrocarbons, known as polycyclic aromatic hydrocarbons (PAH), which are much more persistent in the environment than VOCs. The PAHs do not easily dissolve in water and readily settle on the bottom of lakes and streams adhering to sediment particles (ATSDR 1995). In addition, PAHs can also accumulate in plant and animal tissues. Further studies are needed to identify concentrations of PAHs in effluent draining the Old Faithful area to determine possible affects on the aquatic environment there.

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Table 5. Aquatic toxicity information for selected volatile organic compounds measured by the U.S. Geological Survey (Rowe et. al. 1997).

[μg/L, micorgrams per liter; LC50, lethal concentration value; effective mean concentration]

Compound name	Taxonomic classification	Genus, species/ common name	Duration hours	Measures of toxicity (μg/L) LC50	EC50
Benzene	crustacean	*Gammarus fossarum*	120	66,007	
		Scud	96	68,283	
	crustacean	*Gammarus pulex*	48	42,000	
		Scud			
	crustacean	*Daphnia cucullata*	48	356,000	
		Water flea	48	390,000	
	crustacean	*Daphnia pulex*	96	15,000	
		Water flea	48	265,000	
	crustacean	*Daphnia magna*	1		6,300
		Water flea	24		10,000
	fish	*Salmo trutta*	1	12,000	
		Brown trout			
	fish	*Oncorhynchus mykiss*	96	5,300	
		Rainbow trout	96	5,900	
	fish	*Thymallus articus*	96	12,926	
		Artic grayling			
	insects	*Chironomus thummi*	48	100,000	
		Midge			
	invertebrates, misc	*Dugesia lugubris*	48	74,000	
		Turbellarian, flatworm			
o-Xylene	crustacean	*Daphnia magna*	24		1,000
		Water flea	48		3,185
	fish	*Oncorhynchus mykiss*	*96*	7,600	
		Rainbow trout	96	8,050	
m-Xylene	crustacean	*Daphnia magna*	24		4,700
		Water flea	48		9,556
	fish	*Oncorhynchus mykiss*	96	8,400	
		Rainbow trout			
p-Xylene	crustacean	*Daphnia magna*	24		3,600
		Water flea	48		8,494
	fish	*Oncorhynchus mykiss*	96	2,600	
		Rainbow trout			
Ethylbenzene	crustacean	*Daphnia magna*	48	75,000	
		Water flea	24	77,000	
	crustacean	*Daphnia magna*	24		1,810
		Water flea	24		1,930
	fish	*Oncorhynchus mykiss*	96	4,200	
		Rainbow trout	96	14,000	
Toluene	crustacean	*Daphnia magna*	24	310,000	
		Water flea	48	310,000	
	crustacean	*Daphnia magna*	1		
		Water flea	48		
	fish	*Oncorhynchus mykiss*	96	5,800	3,600
		Rainbow trout	96	24,000	6,000

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