

Potential Water Quality Concerns Related to Snowmobile Usage

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March 22, 2017

Introduction

Snowmobiles are powered by two-stroke engines which emit about 30 percent of the consumed fuel unburned via exhaust. Many different chemical compounds enter the environment from snowmobile emissions but the following organic compounds are widely recognized as the most toxic: benzene, toluene, ethylbenzene, and xylenes (BTEX); methyl tertiary butyl ether (MTBE); and polycyclic aromatic hydrocarbons (PAHs). Relative to MTBE and PAHs, BTEX will volatilize, biodegrade, and photo-oxidize more rapidly and therefore are less of an environmental concern. At least two inorganic compounds of potential concern, sulfate and ammonium, are found in snowmobile emissions.

MTBE is an animal carcinogen and suspected human carcinogen (Keller et al., 1998) and is discharged unburned via the exhaust where it is added to gasoline. Several PAHs are known human or animal carcinogens (Agency for Toxic Substances and Disease Registry, 1995); these are generated during the combustion process and discharged via the exhaust. It is possible that sulfate may contribute to acidification of water bodies and that ammonium also could degrade water quality.

Our review found, of the emissions from snowmobile exhaust, MTBE, PAHs, and possibly sulfate and ammonium are of greatest concern as potential threats to water quality in areas of heavy snowmobile use. This paper will show that there is a potential for snowmobile emissions to pose a risk to humans and aquatic life but this risk cannot be quantified because of a current lack of water quality data.

This report has been prepared by reviewing available literature on the subjects of snowmobile use, snowmobile engine emissions, and snowpack and water quality studies for the contaminants involved. Objectives of the report include:

- identifying compounds of snowmobile exhaust;
- discussing the potential for water quality degradation from snowmobile usage;
- identifying gaps in the availability of data that would allow us to document water contamination and predict risk to humans and aquatic life; and
- providing a list of references on this topic.

The information in this report is intended to contribute to a better understanding of the risk to natural resources stemming from snowmobile use in National Parks.

Engine Technology

Conventional Two-Stroke Engines

Nearly all snowmobiles are powered by two stroke engines. Also known as “two-cycle” engines, these motors intake a mixture of air, gasoline, and oil into the combustion chamber while exhaust gases are being expelled from the combustion chamber. Since the intake and exhaust processes are occurring at the same time, it is unavoidable that some of the unburned fuel mixture will escape with the exhaust. Based on average use, a typical conventional two-stroke engine will expel about 30% of the incoming fuel mixture, unburned, via the exhaust. Unburned fuel in the exhaust may contain MTBE which is added to gasoline in at least 16 states to improve air quality and potentially all states to enhance octane. PAHs are generated as fuel is burned. Total hydrocarbon emission levels for snowmobile engines range from approximately 140 grams per kilowatt-hour (kw-hr) to more than 290 grams per kw-hr (White and Carroll, 1998). The U.S. Environmental Protection Agency (EPA) has determined that hydrocarbon emissions, along with emissions of nitrogen oxides (NOX) and carbon monoxide (CO), from snowmobiles and other similarly powered equipment and vehicles, contribute significantly to air pollution (U.S. EPA, 1999).

PAHs have been measured in the emissions of two commonly used snowmobile engines, the fan-cooled Polaris 488-cc and the liquid-cooled Arctic Cat 440-cc (White and Carroll, 1998). PAH emissions vary with the fuel and lube oils used. Engine tests at five different speeds have found approximately 50% reductions in measured PAH emissions to occur using fuel with 10% ethanol, by volume (White and Carroll, 1998). There was no clear reduction in measured PAHs from using synthetic lube oils vs. conventional, mineral-based lube oils. These results are for particulate-phase PAHs only which made up 61% of PAHs emitted; vapor-phase PAHs made up 39% (White and Carroll, 1998).

Sulfur dioxide emissions have been measured in exhaust from the Polaris and Arctic Cat engines at rates of up to 2.75 grams per hour (White and Carroll, 1998). The emissions were said to be “low” by the authors. This was attributed to “low sulfur levels in the fuels” that were used in the test. Sulfur dioxide in the engine exhaust may react with moisture in the exhaust or other compounds in the atmosphere to form sulfate emissions.

Ammonia was measured in snowmobile exhaust from the Polaris and Arctic Cat engines (White and Carroll, 1998). Total ammonia was emitted at a rate of up to 3.2 grams per hour, a rate characterized as “fairly low” by the authors.

Direct-Injection Two-Stroke Engines

Direct-injection engines have concurrent intake and exhaust processes; however, unlike the conventional two-strokes, the intake charge is air only (no fuel is mixed into the intake charge). The fuel is injected directly into the combustion chamber only after the exhaust process has finished. This means that no unburned fuel escapes with the exhaust. This results in a four-fold decrease in smog-forming pollution in a typical 90-horsepower, two-stroke personal watercraft (PWC) engine, when compared to a conventional two-stroke (California EPA, 1999a). However, these emissions from direct-injected two-strokes are still four times higher than four-stroke engines with the same horsepower (California EPA, 1999a). There is also speculation that

although reductions in the emission of unburned fuel will significantly reduce MTBE emissions, PAH emissions will remain the same since the amount of burned fuel may not change.

These new direct-injection engines are now being introduced on PWC but are not available on snowmobiles. Some of the major manufacturers are reported to be studying the application to snowmobiles but do not appear to have formal plans to introduce direct-injection engines (Ed Klim, personal communication, 1999).

Status of Emission Regulations

At the present time, no regulations exist at the state or federal level to limit snowmobile emissions. Additionally, this review found no reports of snowmobile regulation at local or regional levels on the basis of water quality alone.

In a notice in the Federal Register, EPA has indicated its intent to write emission standards for snowmobiles and other all-terrain vehicles (ATVs) using engines rated above 25 horsepower (U.S. EPA, 1999). The basis for EPA's action is that these engines "contribute to ozone or carbon monoxide concentrations in more than one ozone or CO non-attainment area, and emissions of particulate matter from such engines cause or contribute to air pollution that may reasonably be anticipated to endanger public health or welfare." EPA estimated that snowmobiles and ATVs produce 1.1 million tons of hydrocarbons each year, or about 15% of all hydrocarbons emitted by mobile sources such as cars and lawnmowers; by 2010, EPA expects that share to rise to 19%.

Executive Orders and National Park Service Regulations

In 1972, President Nixon issued Executive Order (EO) 11644 concerning the use of off-road vehicles such as snowmobiles on public lands. The EO, amended in 1978 (EO 11989), instructs the National Park Service (NPS) to prohibit off road activities such as snowmobiling in National Parks if such use will "adversely affect their natural, aesthetic, or scenic values." Additionally, it requires the NPS, along with other public agencies, to "monitor the effects of the use of off-road vehicles." In 1974, in response to EO 11644, NPS issued a rule prohibiting snowmobiling in the National Parks absent special regulation (36 C.F.R. § 2.34, 1974). In 1979, NPS determined that snowmobiling must be "prohibited except where designated and only when their use is consistent with the park's natural, cultural, scenic and aesthetic values, safety considerations, park management, and will not disturb the wildlife or damage other park resources" (36 C.F.R. §2.18 (c), 1998).

The Potential for Contamination of Snow and Water

Introduction

Studies on emissions from PWC indicate that MTBE and PAHs are the two contaminants most likely to degrade water quality from snowmobile emissions. These contaminants are more likely than others to be found in water primarily due to their persistence in the environment. BTEX are much less persistent and less of a concern. One study at Lake Tahoe detected BTEX in the water; however, concentrations were over 1000 times lower than aquatic life protection levels, even during periods of high motorboat (including PWC) activity (Allen, et al., 1998).

According to EPA's Office of Mobile Sources, about 30% of U.S. gasoline supply currently contains oxygenates such as MTBE and ethanol to improve air quality. These oxygenates enhance octane level, increase burning efficiency, and reduce the emission of atmospheric pollutants. The most frequently used oxygenate is MTBE which is currently used in 16 states (CA, CT, DE, IL, IN, KY, MD, MA, NH, NJ, NY, PA, RI, TX, VA and WI) to meet air quality standards (National Science and Technology Council, 1997). In these states, MTBE is added to gasoline up to 15% by volume (National Science and Technology Council, 1997). In the remainder of the U.S., MTBE may be added at 2 – 8% by volume to boost octane. As a result, more than 10 billion kilograms (kg) of MTBE were used in U.S. gasoline in 1996 (U.S. EPA, 1998a), making MTBE the second most widely produced chemical in the U.S. (California EPA, 1999b).

PAHs occur naturally in crude oil. PAH molecules contain two to seven benzene rings. Their environmental fate, persistence, and toxicity are related to this molecular structure and to the number and configuration of attached alkyl groups (such as methyl (CH₃-) or ethyl (CH₃CH₂-) groups). Eighteen different PAHs, not including the 20 or so alkylated PAHs, have been found in snowmobile exhaust (White and Carroll, 1998). Nearly all the PAHs in snowmobile exhaust are created during the combustion process, although up to six have been found in unburned gasoline (Heath, et al., 1993).

A review of available literature revealed that no studies have been published to measure the presence of MTBE or PAHs in snow, surface water, or groundwater as a result of snowmobile use. Snowmobiles use virtually the same two-stroke engine and fuel mixture as PWC. The contamination of lakes and reservoirs with MTBE and PAHs has been documented where two-stroke PWC and outboard motors are used (Metropolitan Water District of Southern California, 1998; Reuter, et al., 1998; Mastran, et al., 1994; Oris, et al., 1998). Recreational use of these watercraft has been identified as a primary cause of this contamination. Because water quality degradation has been documented in association with two-stroke motor usage, it follows that water quality adjacent to areas of high snowmobile use also could be degraded by MTBE and PAH. One such high-use area is in Yellowstone National Park with nearly 54,000 visitors travelling via a single corridor from the West Yellowstone entrance in Montana during the winter of 1998/1999 (National Park Service, 1999).

Note: One study did find hydrocarbons—but not PAHs, specifically—in water and fish tissue in a Maine pond as a result of snowmobile use on a frozen pond surface (Adams, 1975). Hydrocarbon concentrations before and after the winter snowmobiling season increased from non-detect to 10 parts per million (ppm) in water, and from non-detect to 1 ppm in fish tissue. These increases were attributed to snowmobile emissions.

Sulfate and ammonium have been found in melted snow samples at Yellowstone National Park, where concentrations exceeded expected background levels (Ingersoll, 1997). Concentrations were consistently higher in samples from the snowmobile trail, decreasing as distance from the trail increased (up to 100 meters away), thus implicating snowmobiles as the source.

Potential for MTBE Contamination

MTBE may be imparted to snowpack in areas of snowmobile use through rain or snow precipitation, gravitational settling out of the air, or from the injection of tailpipe emissions into

deep snow. Given MTBE's affinity for water and evidence that it is not rapidly volatilized (National Science and Technology Council, 1997), it is likely that, once incorporated into the snow, it would remain there throughout the winter months. This would be especially likely if it were buried into the snowpack beneath snowmobile trails. Upon the melting of snow in the spring, MTBE would dissolve into the meltwater. When flowing over the ground surface and below ground as groundwater, MTBE would not be significantly retarded because it sorbs only weakly to soils and aquifer materials.

The State of California has adopted a public health goal (PHG) of 13 micrograms per liter ($\mu\text{g/L}$, or ppb) for MTBE in drinking water to prevent any significant risk to human health (California EPA, 1999c). This PHG is based on carcinogenic effects observed in experimental animals. California will likely set a drinking water standard at the level of the PHG in 1999. The EPA adopted an advisory level of 20-40 $\mu\text{g/L}$ for drinking water in 1997 (U.S. EPA, 1997). California's secondary maximum contaminant level (MCL) for MTBE is 5 $\mu\text{g/L}$ (California EPA, 1999c); this is to protect the public from MTBE concentrations in drinking water that can be smelled or tasted.

There is little known about the risk to aquatic organisms from MTBE. One of the most thorough studies to date found that there is little toxicity of MTBE to aquatic organisms (Johnson, 1998). The study found that adverse effects on rainbow trout are not expected until concentrations of MTBE in the water column reach 4,600 $\mu\text{g/L}$ to 4,700 $\mu\text{g/L}$. These levels are much greater than the human health standards for MTBE in drinking water supplies. Green algae have the lowest tolerance to MTBE but, according to this study, the results "indicate that there is low potential for adverse ecological effects from levels of MTBE currently in surface waters."

MTBE is theorized to be found in precipitation at maximum levels of 3 $\mu\text{g/L}$ (National Science and Technology Council, 1997). The highest concentrations in precipitation would be found where air concentrations of MTBE are high and where temperatures are cool (0 degrees Celsius). The U.S. Geological Survey sampled stormwater in 16 cities and metropolitan areas and found MTBE to be the seventh most frequently detected volatile organic compound (Delzer, 1996). MTBE ranged from 0.2 to 8.7 $\mu\text{g/L}$, with a median of 1.5 $\mu\text{g/L}$. The levels of MTBE in urban stormwater may be elevated above concentrations in precipitation as the water runs over paved surfaces and comes into contact with gasoline spills.

The highest value of MTBE in urban stormwater, 8.7 $\mu\text{g/L}$, is above California's secondary drinking water standard of 5 $\mu\text{g/L}$ but below the proposed California health-based drinking water standard of 13 $\mu\text{g/L}$ for MTBE. Maximum theorized levels of MTBE in precipitation are below any proposed primary or secondary drinking water standards and are well below levels that would affect rainbow trout. Levels of MTBE in excess of drinking water standards but well below levels that could effect rainbow trout have been found in lakes and reservoirs where PWC are used (VanMouwerik and Hagemann, 1999).

These studies indicate that the emission of MTBE from motor vehicles and incidental spillage have the potential to contaminate water. This contamination is most acute in lakes from the use of PWC where it is at levels that could pose a risk to human health. However, because no sampling has been conducted in the areas of snowmobile use, we cannot conclude for sure that MTBE is present or, if present, if it is in concentrations that would pose a risk to humans and

aquatic organisms that consume or contact water. The presence of MTBE and its potential risk in areas of snowmobile use can only be determined through snow- and water-sampling studies.

Potential for PAH Contamination

Deposition of airborne PAHs onto the ground is a commonly accepted phenomenon. Since PAHs are part of snowmobile emissions, deposition of PAHs in areas of high snowmobile use is expected. PAHs may also be imparted to snowpack from the injection of tailpipe emissions into deep snow.

Losses of PAHs from the snowpack should be minimal since degradation processes such as photo-oxidation and volatilization do not occur or are severely impeded (Boom and Marsalek, 1988). Indeed, studies have measured PAHs in snow from nearby automobile pollution and other point sources (Ettala, et al., 1986; Viskari, et al., 1997; Gjessing, et al., 1984). PAHs from nearby automobile pollution have also been found in surface water (Gjessing, et al., 1984). In the St. Lawrence River in Canada, springtime concentrations of PAHs were “most likely caused by snowmelt” from nearby urban, rural, and industrial areas (Pham, et al., 1993). Atmospheric PAHs deposited onto snow also were found in a karst groundwater system during and after snowmelt (Simmleit and Herrmann, 1986). The PAHs documented in these studies are found in snowmobile emissions. Levels of PAHs in excess of human health standards and levels that could harm aquatic life have been found in lakes and reservoirs where two-stroke engines are used (VanMouwerik and Hagemann, 1999).

PAH molecules preferentially bind to organic matter in soil. One study found “an essential part of the PAHs” in snowmelt drainage off of a highway to be retained in the soil surface layer (Gjessing, et al. 1984). However, the amount of PAH-contaminated meltwater that will pass over soil is difficult to predict; also, some deposition will occur directly onto snow-covered bodies of water. PAH-contaminated soil particles could also be carried with runoff meltwater into nearby water bodies whereby PAHs could contaminate water bodies by transferring from the soil particles to the water or by accumulating as sediment. (Some expect the possible effects of PAH-contaminated sediments to be a more serious, but currently less understood, risk to aquatic life than PAH-contaminated water.) Finally, PAHs could also be imparted to surface water bodies via overland flow during a rain-on-snow event.

One study found hydrocarbons in fish tissue as a result of snowmobile use on a Maine pond (Adams, 1975). Though PAHs were not specifically measured, it is quite possible they were part of the hydrocarbons found.

PAHs have recently been found to be toxic to aquatic life at very low concentrations due to their phototoxic effects (Oris, et al., 1998). PAH concentrations of 5-70 nanograms per liter (ng/L, or parts per trillion) were toxic to aquatic life, and calculated no-observed-effect-concentrations (NOEC) for PAHs were only 3, 7, and 9 ng/L for zooplankton reproduction, zooplankton survival, and fish growth, respectively (Oris, et al., 1998). Another recent study, based on toxicity tests, suggests a water quality standard for total PAHs of only 10 ng/L; this includes a safety factor of approximately 100x (Heintz et al., 1999).

PAH concentrations dangerous to human health are also very low. The lowest water quality standards for individual carcinogenic PAHs for the consumption of fish from a PAH-

contaminated water body is 49 ng/L, and for the consumption of both fish and drinking water it is even lower at 4.4 ng/L (U.S. EPA, 1998b).

These studies show that the emissions of PAHs from motor boats can contaminate water and that PAHs from motor vehicles can contaminate snow. The PAHs from motorboat pollution have been found at levels that pose a risk to aquatic life and human health. However, because no sampling for PAHs has been conducted in the areas of snowmobile use, we cannot conclude for sure that they are present or, if present, if they are in concentrations that would pose a risk to humans and aquatic organisms that consume or contact water. Snow and water sampling studies are needed to determine the presence of PAHs and their potential risk in areas of snowmobile use.

Potential for Sulfate Contamination

Sulfate in snowpack associated with snowmobile use (Ingersoll 1997) would be mobilized with the onset of snowmelt. Once sulfate reaches groundwater or surface water, acidification is possible in alpine areas where buffering potential is low because of thin soils and exposed rock (Corn and Vertucci, 1992). Pulses of acidity have been observed during spring snowmelt in lakes in the Rocky Mountains (Corn and Vertucci, 1992) and in southern Norway (Hagen and Langeland, 1973). During these intervals, the rapid decreases in pH may pose a risk to amphibian embryos in breeding habitats in the Rocky Mountains (Corn and Vertucci, 1992). The most acidic water bodies in the Rocky Mountains are thought to be influenced by point sources of atmospheric pollution (Corn and Vertucci, 1992; Ingersoll, 1997).

No water sampling for sulfate has been conducted in the areas of snowmobile use; therefore, we cannot document if acidification is occurring. The presence of sulfate or acidified waters and the potential for aquatic risk in areas of snowmobile use can only be determined through snow- and water-sampling studies.

Potential for Ammonium Contamination

Ammonium has been found in snowpack in association with snowmobile use (Ingersoll, 1997). In snow, it has been found to remain unchanged as ammonium (Don Campbell, personal communication, 1999). It is thought to dissolve into meltwater where it remains intact until it passes over soil or enters an oxygenated water body; at this point it can be used by terrestrial flora or be converted to nitrate in soil or in the receiving water. This could contribute to acidification, a decrease in dissolved oxygen, and eutrophication of receiving waters (Don Campbell and Dave Mueller, personal communication, 1999).

Conclusions

We have made the following conclusions on the basis our review of currently available literature:

- MTBE, PAHs, sulfate, and ammonium are the components of snowmobile exhaust which, in our opinion, have the highest potential to contaminate water resources;
- No data exist that would document the concentration of these or other potential contaminants in water as a result of snowmobile use;
- There is a potential for snowmobile emissions to pose a risk to aquatic organisms and humans in areas adjacent to heavy use; however, this potential can only be addressed through snow- and water-sampling research.

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