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ACID DRAINAGE AND AQUATIC RESOURCES

Dennis R. Neuman, Stuart R. Jennings, and James A. Jacobs

Evaluating acid mine drainage and the effects on fish health and ecology is an important aspect of environmental science and aquatic resources management. Resulting low-pH conditions from acid mine drainage mobilize metals from mining waste materials and pyrite-rich rocks and soils, usually resulting in degradation of water quality and impairment of aquatic health. Acid mine drainage and associated weathering products commonly result in physical, chemical, and biological impairment of surface water. Evidence from literature and field observations of practices to date suggests that large-scale mining or land development in sulfide-hosted rock imparts a substantial and unquantifiable environmental risk to surface water quality and fisheries (Jennings et al., 2008). Opportunities exist for significantly improved acid drainage prevention methods, remediation technologies, and environmental practices.

INTRODUCTION

Acidic drainage occurs when sulfide-bearing materials are exposed to water and oxygen, allowing mineral weathering reactions to proceed, including oxidation and hydrolysis. Mining increases the exposed surface area of sulfur-bearing rocks, allowing for accelerated sulfuric acid generation. If insufficient buffering capacity is present as neutralizing minerals such as calcite ($CaCO_3$), soil and water resources may become acidified. Collectively, the generation of sulfuric acid from pyrite and other sulfide minerals is termed *acid drainage* (AD).

Although other acid drainage conditions do exist in nature and as acid sulfate soils, or through other anthropogenic activities, such as development or farming, the majority of acid drainage is caused by mining activities. Having much greater surface area than in-place geologic material due to their smaller grain size, mine tailings and waste rock are more prone to generating acid drainage. Since large masses of sulfide minerals are exposed quickly during the mining and milling processes, the surrounding environment can sometimes not attenuate the resulting low-pH conditions. Metals that were once part of the host rock are solubilized and exacerbate the deleterious effect of low pH on terrestrial and aquatic receptors. Concentrations of common elements such as Cu, Zn, Al, Fe, and Mn all increase dramatically in waters with low pH. Logarithmic increases in metal levels in waters from sulfide-rich mining environments are common where surface water or groundwater pH is depressed by acid generation from sulfide minerals. These environmental, human health, and fiscal consequences, if not mitigated, can have long-lasting effects (U.S. EPA, 1995).

Acid mine drainage continues to emanate from mines in Europe established during the Roman Empire prior to A.D. 467 (Center for Streamside Studies, 2002). Georgius Agricola's *De Re Metallica* (1556), the first and seminal treatise on mining, exhibits detailed woodcut illustrations not only of the known mechanics of sixteenth-century mining, but also depictions of the devastation of streams. The cost of mitigation of environmental damage from acid mine drainage is great. In 1993, the U.S. Forest Service estimated that between 20,000 and 50,000 mines are currently generating acid on lands managed by that agency, with negative impacts from these mines affecting some 8000 to 16,000 km of streams (U.S. Department of Agriculture, 1993). Since that estimate, the numbers of mines generating acid mine drainage and the associated negative impacts on streams have grown significantly. Many of these mines are small abandoned facilities

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located in remote areas of the western United States and originating prior to modern environmental controls. However, several large-scale mines developed in the latter half of the twentieth century have declared bankruptcy and left taxpayers with the responsibility of treating acid waters in perpetuity. Examples include the Zortman Landusky mine in Montana, the Summitville mine in Colorado, and the Brohm mine in South Dakota. The largest and most expensive sites that the U.S. Environmental Protection Agency (EPA) has listed under the Comprehensive Environmental Resource Compensation and Liability ACT (CERCLA; a.k.a. the Superfund) are mining sites in the West, including the Iron Mountain mine in California, Bunker Hill in Idaho, and the Butte–Clark Fork River complex in southwestern Montana. Human health risks and ecological injury, chiefly from elevated metals, have been identified by the EPA and natural resource trustees at many of these mining Superfund megasites.

Acidic drainage has been identified as the largest environmental liability facing the Canadian mining industry and is estimated at \$2 billion to \$5 billion (MEND, 2001). In response to the challenge presented by mitigation of AD, 200 technology-based reports were generated to evaluate sampling, prediction, prevention, treatment, and monitoring of potentially acid-generating materials and locations. A 1986 estimate for Canada suggests that acid-generating tailings cover 12,000 ha, and an additional 350 million tons of mine waste rock was noted (Price, 2001).

EFFECT OF ACID MINE DRAINAGE ON AQUATIC RESOURCES

Once acid drainage is created, metals are released into the surrounding environment and become readily available to biological organisms. In water, for example, when fish are exposed directly to metals and H^+ ions through their gills, impaired respiration may result from chronic and acute toxicity. Fish are also exposed indirectly to metals through ingestion of contaminated sediments and food items. A common weathering product of sulfide oxidation is the formation of iron hydroxide [$Fe(OH)_3$], a red-orange precipitate found in thousands of miles of streams affected by acid drainage. Iron hydroxides and oxyhydroxides may physically coat the surface of stream sediments and streambeds destroying habitat, diminishing the availability of clean gravels used for spawning and reducing fish food items such as benthic macroinvertebrates. Acid mine drainage, characterized by acidic metalliferous conditions in water, is responsible for physical, chemical, and biological degradation of stream habitat. Two reports describe acid mine drainage on aquatic resources (Jennings et al., 2008; Neuman et al., 2009).

Water contaminated by acid drainage, often containing elevated concentrations of metals, can be toxic to aquatic organisms, leaving receiving streams devoid of most living creatures (Kimmel, 1983). Receiving waters may have a pH value as low as 2.0 to 4.5, levels toxic to most forms of aquatic life (Hill, 1974). Data relating to specific effects of low pH on growth and reproduction (Fromm, 1980) may be related to calcium metabolism and protein synthesis. Fromm (1980) suggested that a "no effects" level of pH for successful reproduction is near 6.5, while most fish species are not affected when the pH is in the range 5.5 to 10.5. Howells et al. (1983) reported that interactions of pH, calcium, and aluminum may be important to understanding the overall effects on fish survival and productivity. Several reports indicate that low-pH conditions alter gill membranes or change gill mucus, resulting in death due to hypoxia. Hatchery-raised salmonids can tolerate pH 5.0, but below this level, homeostatic electrolyte and osmotic mechanisms become impaired (Fromm, 1980).

A study of the distribution of fish in Pennsylvania streams affected by acid mine drainage (Cooper and Wagner, 1973) found fish to be affected severely at pH 4.5 to 5.5. Ten species revealed some tolerance to acid conditions of pH 5.5 and below; 38 species were found living in waters with pH values ranging from 5.6 to 6.4; and 68 species were found only at pH levels greater than 6.4. Further, these investigators reported complete loss of fish in 90% of streams with waters of pH 4.5 and a total acidity of 15 mg/L.

Healthy, unpolluted streams generally support several species and a moderate abundance of individuals, whereas streams affected are dominated by fewer species and often low-to-moderate numbers of organisms. Streams affected by acid mine drainage are poor in taxa richness and abundance. In older studies (Warner, 1971), more species of insects and algae were found in unpolluted West Virginia streams (pH $>$ 4.5) than in streams polluted by acid (pH 2.8 to 3.8). Reductions of benthic fauna in a West Virginia stream severely affected by acid mine water were reported by Menendez (1978). In more recent studies (Farag et al., 2003), some streams in the Boulder River watershed in Montana affected by nearly 300 abandoned metal mines are devoid of all fish near mine sources. Populations of brook trout *(Salvelinus fontinalis),* rainbow trout (*Oncorhynchus mykiss),* and cutthroat trout (*Oncorhynchus clarki)* were found farther downstream and away from sources of acid mine drainage. In a 2003 study evaluating the effect on the population structure of salmon of localized habitat degradation from a gold mine near the Yukon River in central Alaska, it was suggested that coho salmon (*Oncorhynchus kisutch)* may be at risk of losing genetic diversity due to localized habitat degradation (Olsen et al., 2004a,b). The abandoned Britannia copper mine in British Columbia, Canada has been releasing acid mine drainage into local waters for many years. Investigators compared fish abundance, distribution, and survival at contaminated and noncontaminated areas (Barry et al., 2000). Chum salmon (*Oncorhynchus keta)* fry abundance was significantly lower near the waters affected (pH $<$ 6 and dissolved copper

> 1 mg/L) than in the reference area. The investigators also reported that laboratory bioassays confirmed that acid mine drainage from the Britannia mine was toxic to juvenile chinook salmon (*Oncorhynchus tshawytscha)* and chum salmon. Chinook salmon smolt transplanted to surface cages near Britannia Creek experienced 100% mortality within 2 days (Barry et al., 2000).

The scientific literature is replete with studies designed to quantify the adverse environmental effects of acid mine drainage on aquatic resources. Most recent investigations focus on multiple bioassessments of large watersheds. These assessments include water and sediment chemistry, benthic macroinvertebrate sampling for taxa richness and abundance, laboratory acute water column evaluations, laboratory chronic sediment testing, caged fish within affected streams, and development of models to explain and predict the impact of acid mine drainage on various aquatic species Johnson et al., 1987; Woodward et al., 1997; Beltman et al., 1999; Hansen et al., 1999, 2002; Baldigo and Lawrence, 2000; Soucek et al., 2000; Kaeser and Sharpe, 2001; Maret and MacCoy, 2002; Schmidt et al., 2002; Griffith et al., 2004; Boudou et al., 2005; Martin and Goldblatt, 2007.

The ecological effects of acidic waters that are generated due to the oxidation of pyrite and related sulfide minerals, regardless of the source, are most clearly seen in aquatic environments such as streams, lakes, and marshes. In addition to the input from acid drainage, acid rain from atmospheric pollution is another source of acidity. Acid rain is formed from oxidized sulfur particles caused by the burning of coal and petroleum hydrocarbons containing high levels of sulfur. Most lakes and streams have a natural or background pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid drainage or acid rain. Although acid rain is a regional atmospheric environmental challenge and has caused documented fish kills and wildlife species endangerment, acid drainage tends to be much more localized and causing more impairment to specific aquatic species in the closest streams, rivers, lakes, and wetlands adjacent to sources of acid generation.

Fish and Aquatic Organisms in Acid Waters

Regardless of the source, sulfuric acid causes a cascade of effects that harm or kill individual fish, reduce or eliminate fish populations, and decrease biodiversity in the areas affected. As sulfuric acid from acid drainage (or acid rain) flows through soils in a watershed, aluminum and possibly other heavy metals are released from the soils into the streams, lakes, and rivers located in that watershed.

As pH in a water body decreases with the input of sulfuric acid, metals in sediments tend to solubilize and enter the water column. With increasing acidity levels, aluminum and other metal levels tend to increase, as does the toxicity of the aquatic environment to a large variety of organisms. Both low pH and increased aluminum levels are directly toxic to many fish species and other organisms. A gradual lowering of pH and gradual increase in aluminum levels cause chronic stress that may not kill individual fish, but leads to generally lower body weight and smaller size. These responses to gradual or seasonal environmental changes make affected fish less able to compete for food and habitat, causing declines in species diversity as well as abundance.

Some species or populations of plants and animals are able to tolerate acidic waters from acid drainage. Metal tolerance is known in both plants and animals. Others, however, are acid-sensitive. Generally, the young of most species are more sensitive than adults to environmental conditions. Rapid changes in pH and metal concentrations have a more pronounced negative result than does gradational or seasonal change. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die. Some acid lakes have no fish. Figure 12.1 shows that not all fish, shellfish, or the insects that they eat can tolerate the same amount of acid; for example, frogs can tolerate water that is more acidic (i.e., has a lower pH) than can trout.

Ecosystem Changes to Acid Waters

An ecosystem is a *biological environment* consisting of all the *organisms* living in a particular area, as well as all the nonliving, physical components of the environment with which the organisms interact, such as air, soil, water, and sunlight. The plants and animals living within an ecosystem are highly interdependent. For example, frogs may tolerate relatively high levels of acidity, but if their diet is made up of organisms intolerant of acidity, they may be affected because part of their food supply may disappear. Because of the connections between the many fish, plants, and other organisms living in an aquatic ecosystem, changes in pH or aluminum levels affect biodiversity as well. Thus, as lakes and streams become more acidic, the numbers and types of fish and other aquatic plants and animals that live in these waters decrease.

Acid Drainage and Fish Kills

There are thousands of site increases in acidity, and metal concentrations in surface water have killed fish on a large scale as a direct result of acid mine drainage. Following are three case examples.

Case Study 1: Leviathan Mine, Alpine County, California Prior to mining development in the 1870s, the Leviathan mine area was once known for Sierra trout fishing in the local mountain streams and creeks. Although the destruction of a once vibrant fish population in Leviathan Creek is just one casualty of acid drainage development, the case history of the Leviathan mine is common among inactive metals mines

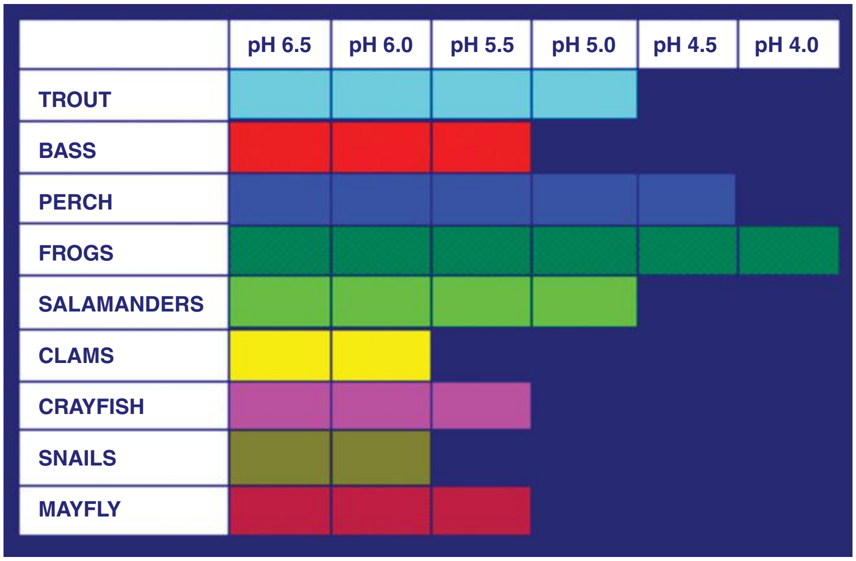

FIGURE 12.1 Estimated survival of various organisms related to pH. (From U.S. Environmental Protection Agency, 2010.)

in the western United States. According to the U.S. Environmental Protection Agency (2000), the Leviathan mine site is an abandoned sulfur mine located on the eastern slope of the Sierra Nevada in Alpine County, California at about 7000 ft above sea level. The mine began operations in 1863 for the extraction of copper sulfate for processing silver ore in the Comstock mining region of Nevada. Mining operations ceased in 1872, due to the high sulfur and low copper content of the ore. It is the high sulfur content that has since contributed to the massive acid mine drainage issue.

With larger equipment and different economics, in 1954 the Anaconda Company transformed the underground workings into an open-pit mine to extract the sulfur ore. Approximately 22 million tons of overburden and waste rock was removed to get to the sulfur ore. Anaconda placed the sulfur ore into and along the channels of Leviathan and Aspen creeks. In 1962 the Anaconda Company sold the mine to Alpine Mining Enterprises. The mine has not been active since 1962.

Infiltration of rainwater into and through the open pit and overburden piles created acid mine drainage that discharges directly into Leviathan Creek. Water contact with the mining waste piles located in the creek itself has also contaminated Leviathan Creek. The low-pH and high metals content of the acid mine drainage have eliminated aquatic life in Leviathan and Bryant creeks downstream of the mine. The release of acid mine drainage from the site has resulted in fish kills in Leviathan and Bryant creeks and the East Fork of the Carson River, which is 10 miles downstream of the site. The creeks and river downstream from the mine are historical habitat for the Lahontan cutthroat trout (*Onchorhynchus clarki henshawi*), a federally listed endangered species. Cutthroat trout still inhabit the East Fork of the Carson River (U.S. Environmental Protection Agency, 2000). Full remediation of Leviathan Creek and the inactive mine site are unfunded and decades away.

Health risks to wildlife in this case are not well documented. Risk assessments by the California Department of Health Services found that past and present consumption of water from the Leviathan, Aspen, and Bryant creeks and the River Ranch irrigation channel downstream of the Leviathan mine posed both cancer and noncancer health risks to humans from exposure to arsenic. Swimming and wading in these creeks pose human health risks due to arsenic exposure, which was mobilized by low-pH waters. A general lack of toxicological data exists and there are significant uncertainties regarding human consumption of fish, plants, and wild game collected near the Leviathan mine, or eating beef raised nearby. Inhalation of dust near the mine, and future exposure to surface water and sediments by drinking, swimming, and wading in affected water bodies are persistent concerns.

Case Study 2: Iron Mountain, Shasta County, California Chinook salmon runs have been documented historically and currently in surface waters near Mount Shasta, about 62 miles north of Redding, California. The Richmond mine at Iron Mountain is about 9 miles northwest of Redding. In more recent times, the Iron Mountain mine has shown the full extent of acid mine drainage characteristics and significant environmental degradation. In 1983, the Richmond mine at Iron Mountain was added to the U.S. Environmental Protection Agency (EPA) Superfund site list. Based on U.S. EPA documents (2010), from the 1860s through 1963, the

4400-acre Iron Mountain mine site was mined periodically for iron, silver, gold, copper, zinc, and pyrite. Although mining operations were discontinued in 1963, underground mine workings, waste rock dumps, piles of mine tailings, and an open mine pit remain at the site. Historic mining activity at the Iron Mountain mine has fractured the mountain, exposing pyrite to surface water, rainwater, and oxygen and leading to the formation of sulfuric acid. Biogeochemical research by Edwards et al. (2000) describes in detail the biological aspects of sulfide mineral dissolution that contribute to acid mine drainage at the Iron Mountain mine. Sulfuric acid flows through Iron Mountain and leaches out a variety of metals, including copper, cadmium, zinc, and other metals. High-concentration sulfuric acid flows out of seeps and portals at the mine.

Nordstrom et al. (2000) documented a pH of −3.6 in waters from the Richmond mine. Much of the acidic mine drainage is ultimately channeled into Spring Creek Reservoir by creeks surrounding the Iron Mountain mine. The Bureau of Reclamation releases the stored acid mine drainage periodically into Keswick Reservoir. Planned releases are timed to coincide with the presence of diluting releases of water from Shasta Dam. On occasion, uncontrolled spills and excessive waste releases have occurred when Spring Creek Reservoir reached capacity. Without sufficient dilution, harmful quantities of metals are introduced into the Sacramento River. Approximately 70,000 people use surface water within 3 miles of the Iron Mountain mine as their primary source of drinking water. The low pH level and companion metal contamination from the mine have caused the virtual elimination of aquatic life, including fish, in sections of Slickrock, Boulder, and Spring creeks. Since 1940, high levels of contamination in the Sacramento River have caused numerous documented fish kills. The continuous release of metals from the Iron Mountain mine has contributed to a steady decline in the fisheries population in the Sacramento River. In 1989, the National Marine Fisheries Service took emergency action to list the winter run chinook salmon as threatened under the Endangered Species Act and to designate the Sacramento River from the Red Bluff diversion dam to the Keswick dam as a critical habitat. In January 1994, the National Marine Fisheries Services issued its final rule, reclassifying the winter run chinook salmon as an endangered species.

Case Study 3: Blue Creek, Kanawha County, West Virginia
According to the local newspaper (McCoy, 2010) a spill of iron-laden acidic mine drainage has caused a fish kill along 9 miles of Blue Creek, a high-quality bass and trout stream in eastern Kanawha County in West Virginia. The spill began on October 2 or 3, 2010 in a small headwater tributary known as Morris Fork. Dead fish were documented in Blue Creek downstream of the town of Coco, West Virginia. A district fisheries biologist for the state Division of Natural Resources noted that it was a state-government attempt to clean up an abandoned coal mine that actually caused the spill. The hazmat workers tried to remediate an inactive mine water storage basin. According to reports, an underestimate of the total volume of the impounded water was the cause of the spill. Although the spilled water was not acidic when the release occurred, the water became more acidic over time as more water flowed out of the impoundment. It took a week before the leaking water started producing sulfuric acid and soluble iron to the extent that dead fish were observed and documented. An inventory of the dead fish was performed, and 13- to 15-in. smallmouth bass were among the dead fish. Other lost fish included rock bass as well as other assorted species. Blue Creek is reportedly stocked with brown trout fingerlings. Although dead trout were not found during the initial dead fish inventory, the trout were probably killed higher up in the watershed than in the area inspected by fish biologists. The acid drainage spill was stopped 9 miles downstream from the impoundment by placing limestone sand into the stream. The limestone buffered the sulfuric acid and prevented more fish from being killed.

NITROGEN AND ACID WATERS

Fish kills associated with acidic water can also occur when a body of water becomes eutrophic (oxygen depleted). Although the role of nitrogen in acid rain is well documented, the potential for nitrogen compounds to interact with acid drainage is also possible in areas where sulfuric acid is generated from pyrite oxidation and mixes with storm water runoff from nearby agricultural lands that may contain excessive fertilizers and nitrates. According to the U.S. EPA, storm runoff rich in nitrates represents 55 to 90% of the nitrogen produced by various human activities. This nitrate-rich runoff reaches estuaries and coastal ecosystems and is transported and deposited via surface waters and groundwater. Nitrogen introduced to water bodies as nitrates is an important factor in causing eutrophication of lakes and rivers. The symptoms of eutrophication include blooms of algae (both toxic and nontoxic), decline in the health of fish and shellfish, loss of seagrass beds and coral reefs, and ecological changes in food webs. Under certain unfortunate circumstances, nitrate-rich waters from agricultural tracts can mix with waters containing acid drainage to decrease the pH of the water and increase the potential for fish kills and significant environmental degradation.

PROBLEMS AND QUESTIONS

1. Describe the mechanism by which acid drainage develops and moves into an aquatic environment.
2. Based on Figure 12.1 is it likely that salamanders will survive at pH 4? Explain why.

3. Together, what are biological organisms and the environment called?
4. What causes death by eutrophication?
5. A gradual lowering of pH and gradual increase in aluminum levels in surface waters cause chronic stress that may not kill individual fish but lead to what physiological challenge for the fish?
6. Healthy, unpolluted streams generally support several species of fish or other organisms and moderate abundance of individuals. What dominates streams affected by acid drainage?

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