

EFFECTS OF SEASONAL AND CLIMATIC CHANGE ON WATER QUALITY FROM ACID ROCK DRAINAGE IN THE WESTERN UNITED STATES

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Abstract

Rainfall events cause both increases and decreases in acid and metal concentrations and their loadings from mine wastes, and unmined mineralized areas, into receiving streams in the western United States. Concentrations gradually increase during long dry periods and sudden large increases in concentrations are observed during the rising limb of the discharge following dry periods. By the time the discharge peak has occurred, concentrations have usually decreased, often to levels below those of pre-storm conditions, and then concentrations slowly rise again during the next dry period. These dynamic changes in concentrations and loadings are related to the dissolution of soluble salts and the flushing of waters that were concentrated by evaporation. These observations can be generalized to predict future conditions caused by droughts related to El Niño and climate change associated with global warming. Already, summer dry periods are lengthening in the western U.S. and rainstorms are less frequent and more intense when they occur. Consequently, flushing of inactive mine sites will tend to cause larger sudden increases in concentrations that will pose an increasing danger to aquatic life. Higher average concentrations will also tend to occur during longer low-flow periods. The predicted effects of global climate change suggest that remediation efforts will have to increase the capacity of engineered designs to deal with more extreme conditions, not average conditions of previous years.

Introduction

A general phenomenon that has been observed at several mine sites is the sudden increase in acid and metal concentrations during the early part of storm events, especially after a prolonged dry spell. This phenomenon has also been observed in mineralized but unmined areas. This increase in concentration is often attributed to the flushing of soluble salts. The purpose of this paper is to document these results for several sites in the western U.S., describe the processes causing it, and discuss the implications for continued global warming conditions.

Some historical notes (pre-1970)

The earliest civilizations of Sumeria, Assyria, and Egypt were familiar with soluble salts and those salts formed from the aqueous oxidation of pyrite and its evaporation (Karpenko and Norris, 2002). The Greek physicians Hippocrates (400 BCE) and Dioscorides (100 CE) mention the use of alum and “melanteria” for medical treatments. The salts alum, melanterite, and chalcantite were mentioned by the Greek philosopher Theophrastus (325 BCE). Pliny the Second (Caius Plinius Secundus, 23-79 CE) writes of “green vitriol” or melanterite and “blue vitriol” or chalcantite as well-known substances and these names continued to be used for most of the next two millenia. The toxicity of some of these salts was also established long ago. Agricola (1556) states “Since I have explained the nature of vitriol [sulfuric acid] and its relatives which are attained from cupriferous pyrites I will next speak of an acrid solidified juice . . . ; it is hard and white and so acrid that it kills mice, crickets, and every kind of animal.”

Although the rapid dissolution rate and high solubility of these salts has also long been known, the nature of their impact on receiving streams during storm events has rarely been mentioned or studied. Bandy (1938) provided some of the best descriptions of numerous soluble salts from the weathering of the copper deposits at Chuquicamata, Quetena, and Alcaparrosa, Chile. He briefly mentioned the rapid dissolution during rainfall and the re-formation during evaporating conditions. Nuhfer (1967) studied efflorescent salts forming from coal mines in West Virginia and noted how easily they can be dissolved and transported during rainstorms.

Iron Mountain, CA

During 1974-76, investigations by Nordstrom (1977) found both increases and decreases in acid and metals concentrations during rainstorms at the Iron Mountain site, California. Iron Mountain contains 3 massive sulfides emplaced under subaerial and partly submarine conditions in a Devonian rhyolite. During the monitoring phase of investigations at Iron Mountain, the concentrations of Cu and Zn increased as the mine effluent discharges increased in flow. This phenomenon occurred in the early part of the winter wet season for a short period of time. An example for the 1986-87 is shown in Figure 1 where substantial increases in Cu, Zn, and temperature occurred in November, 1986 coincident with rising discharge that followed major rainstorms. The temperature

rise is caused by flushing of high temperature waters (40-50°C) that have been found underground (Nordstrom, 1977; Nordstrom and Alpers, 1999) from the strongly exothermic oxidation of pyrite. Enormous quantities of soluble efflorescent salts have been found underground in the Richmond mine in association with waters of negative pH (Nordstrom and Alpers, 1999). These underground salts are periodically dissolved to some extent during the wet season. It has long been observed that large fish kills in receiving waters from Iron Mountain (the Sacramento River) are associated with major rainstorm events.

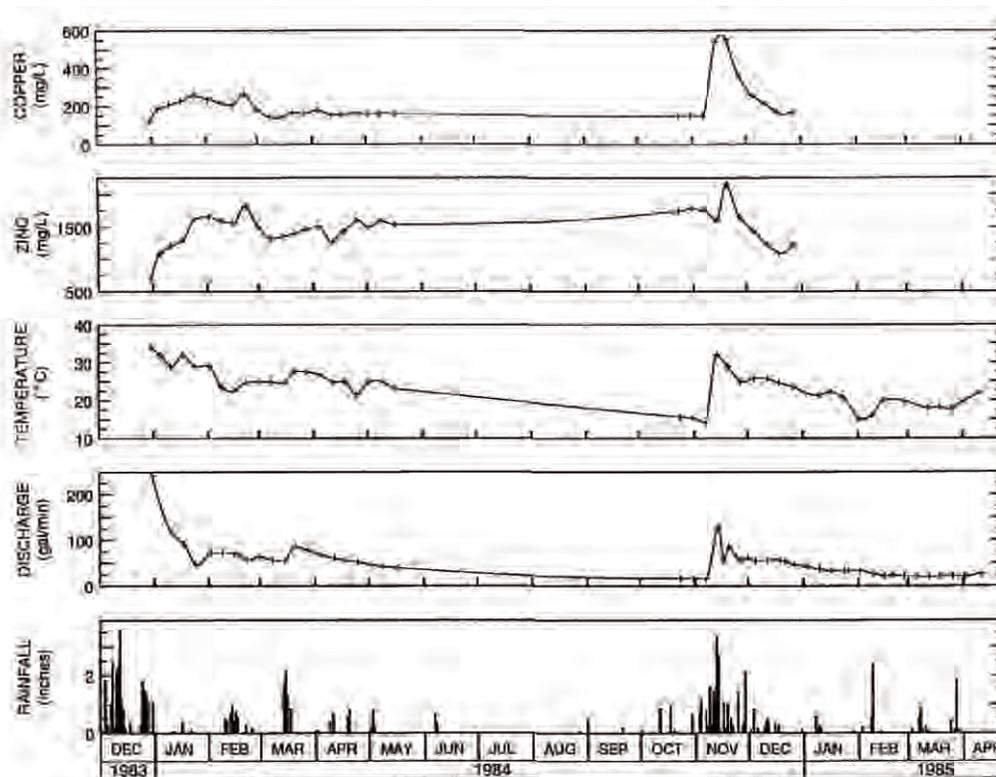


Figure 1. Copper and zinc concentrations, temperature, and discharge for Richmond mine effluent at Iron Mountain, CA with rainfall history at nearby Shasta Dam (from Alpers et al., 1992).

Contrary Creek, VA

Contrary Creek drains a gold-silver-copper deposit in the greenstone and biotite schists of the Piedmont region of central Virginia. Dagenhart (1980) identified the mineralogy and determined the chemical composition of efflorescent salts forming on mine wastes and tailings from the Sulphur, the Boyd Smith, and the Arminius mines. Melanterite, halotrichite-pickeringite, copiapite, and gypsum were found to be abundant. He then set up automated water sampling devices to collect samples during rainstorm events. He found distinct spiked increases in dissolved metal concentrations during the rising limb of the discharge as shown in Figure 2. The metal concentrations that increased the most could be related to the dissolution of efflorescent salts while those that increased very little, such as Mn, were not found in efflorescent salts. He made similar observations for other rainstorm events in Contrary Creek with the magnitude of the concentration peak related to the amount and intensity of the rainstorm and the length of the dry spell preceding the rainstorm.

Questa, NM

From 2001-2005, the US Geological Survey completed a study of surface and ground waters, mineralogy, and geology in the Red River Valley, northern New Mexico. The objective was to infer the pre-mining ground-water quality at an active mine site. The mine site is Molycorp's Questa molybdenum mine and is located along a caldera margin of hydrothermally altered volcanics (rhyolites and andesites). Areas of andesite that have been altered to quartz-sericite-pyrite (QSP) crop out to the east of the mine site. The topography is steep rising from the valley floor at about 2.3 km elevation to over 3 km at the ridge crest. One of these unmined catchments was chosen to study the geochemical processes that give rise to the ground-water composition as a proximal natural analog site. Ground waters in this valley are dominantly of two types: an acid water (pH = 3-4) found

predominantly in debris fans formed from rapid erosion of QSP altered rocks and circumneutral pH waters found in the less permeable volcanic bedrock

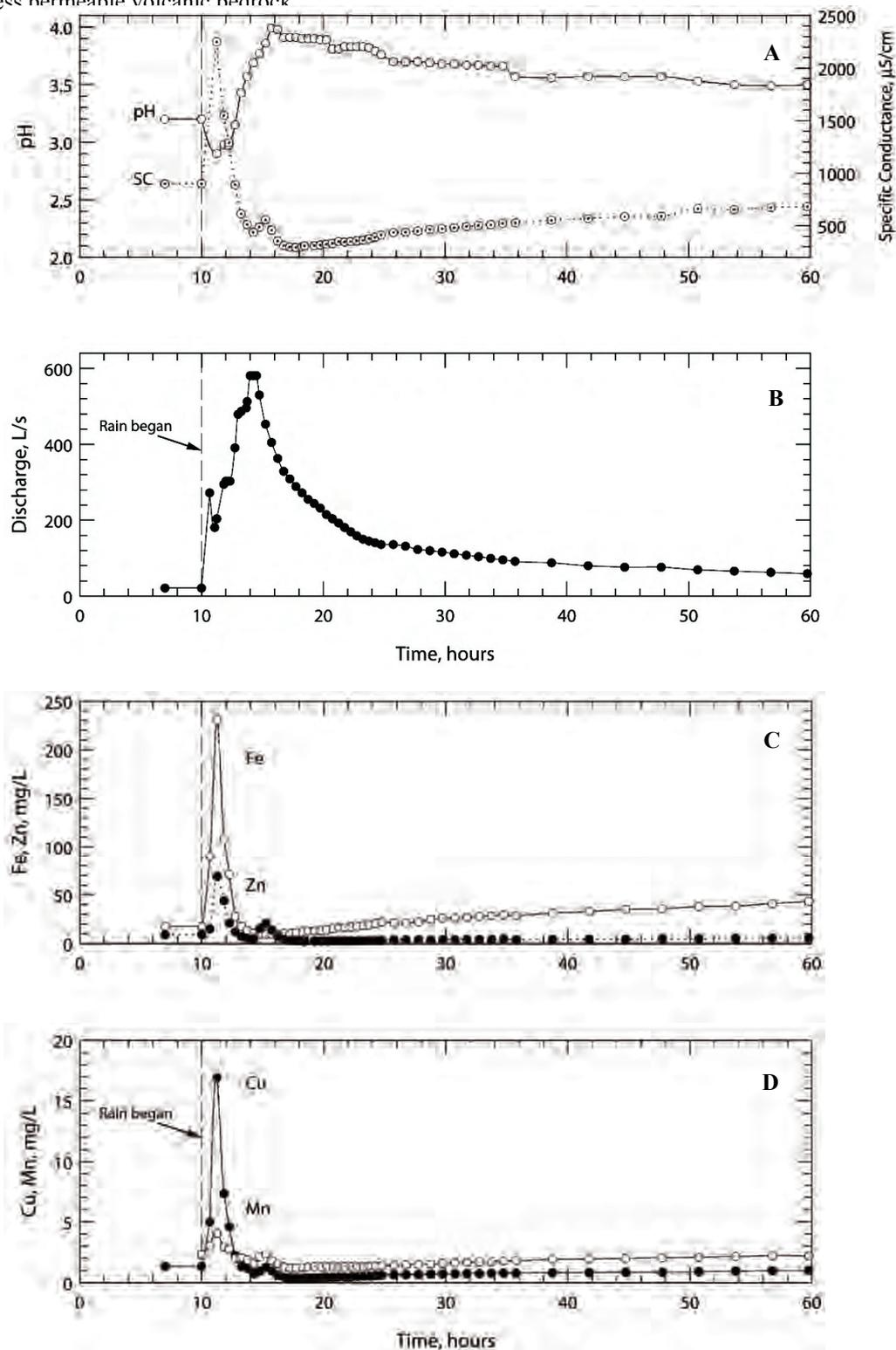


Figure 2. Specific conductance (A), pH (A), discharge (B), Fe, Zn (C), Cu, and Mn (D) concentrations in Contrary Creek during the rainstorm event of September 12-14, 1978 (modified from Dagenhart, 1980).

The upper reaches of the Red River are fed by carbonate-buffered springs and ground water, maintaining pH values of 7.5 to 8.5. Upon reaching the middle to lower portions of the Red River Valley, the water chemistry is

affected by acid drainage and mineralized water entering at several locations both along the mine site and above the mine site.

During the course of these investigations, monsoon rainstorms would wash clays from the debris material and acid water into the Red River, lowering the pH and raising the concentration of metals in the river. Furthermore, historical data collected by the U.S. Bureau of Land Management (BLM; compiled and summarized in Maest et al., 2004) demonstrated the severity of water-chemistry change as a result of these major rainstorm events. In Figure 3 the discharge and specific conductance are shown from monitoring by the BLM for 1982-1985. The discharge of the Red River responds regularly to snowmelt in late spring, causing the specific conductance to decrease as solutes are diluted. Following snowmelt the specific conductance gradually increases until the onset of the next snowmelt. During late summer rainstorms would occasionally cause some variations in this increase of conductance. If a peak in the hydrograph from snowmelt doesn't occur, as happened in water year 2002, the specific conductance continues to increase unabated (Verplanck et al., 2006). This pattern, only interrupted by infrequent monsoon rains, reflects the regular dilution of mildly mineralized water by snowmelt water.

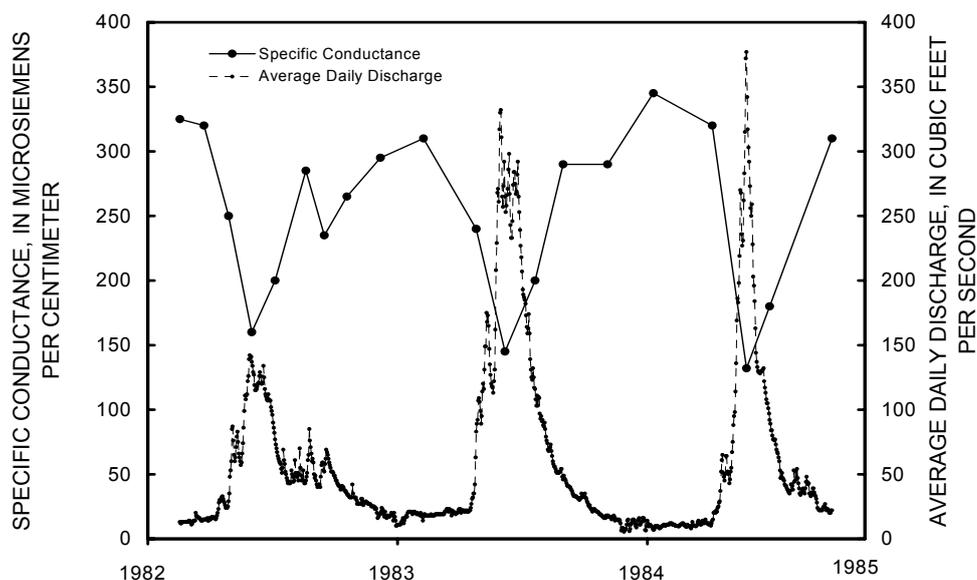


Figure 3. Changes in specific conductance with snowmelt (hydrograph peaks) in the Red River, NM for 1982-85 (from Maest et al., 2004).

The change in water chemistry from monsoon rains can be seen in Figure 4. In September of 1986, a heavy rain caused an abrupt rise in discharge simultaneously with an abrupt rise in specific conductance and drop in pH from 7.8 to 3.8. Dissolved zinc concentrations rose from about 0.2 mg/L to 2.6 mg/L.

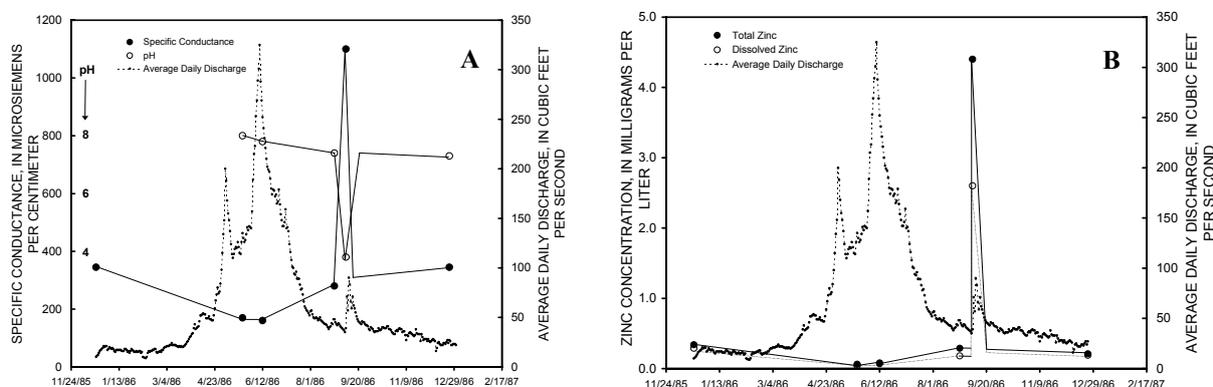


Figure 4. Change in water chemistry associated with a rainstorm event during September, 1986, in the Red River. A. Increase in specific conductance and decrease in pH shown corresponding to a peak in

storm-induced discharge. B. Increase in Zn concentrations corresponding to the increase in storm-induced discharge. Both plots from Maest et al. (2004).

A slightly more detailed look at changes in the water chemistry of the Red River can be seen in Figure 5 where a water sample was collected before, during, and after the storm. Figure 5 shows a spiked increase in dissolved manganese and sulfate and a spiked decrease in pH. The highest concentrations in metals and sulfate in the Red River occur when a major rainstorm hits the valley. This example shows that natural acid rock drainage can affect water quality as well as acid mine drainage.

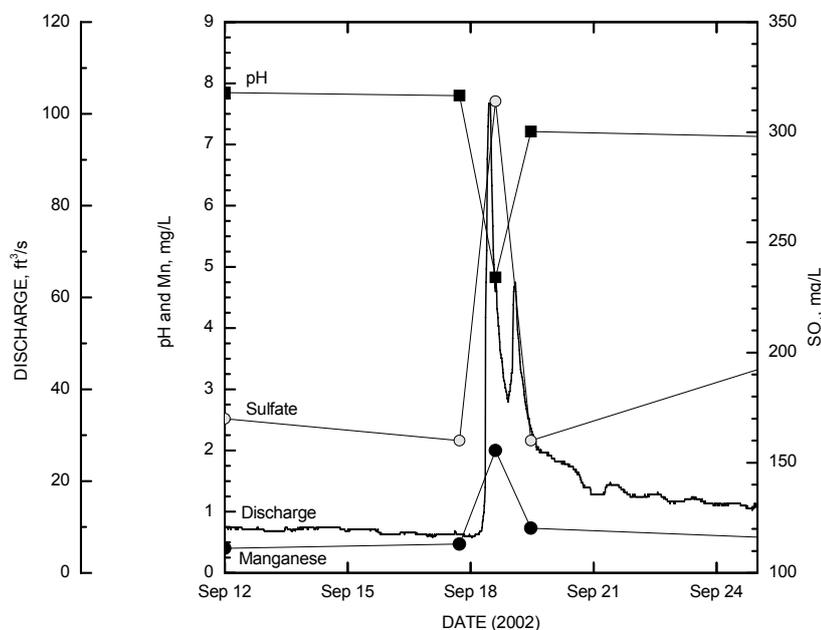


Figure 5. A rainstorm event on September 19, 2002, in the Red River Valley is shown by the rapid increase in discharge. Corresponding to a moment near the peak in discharge, a water sample was collected that records the decrease in pH and increase in manganese and sulfate concentrations (from Verplanck et al., 2006). A surge of acid water was traveling downstream because catchments containing natural acid drainage were being flushed out.

Changes in Climate for the Western United States

The patterns of climate change in the western US have been studied in relation to the Pacific Decadal Oscillation (PDO), El Niño Southern Oscillation (ENSO), North American Monsoon (NAM), and global warming (Hanson et al., 2006). Weather patterns on the scale of a few years are strongly influenced by ENSO and patterns on the scale of 1-2 decades are influenced by PDO. An important observation was the change in snowmelt streamflow timing by 1-4 weeks earlier by careful evaluation of data from the Sierra Nevada Mountains, the Rocky Mountains, and the Pacific Northwest for the period 1948-2000 (Dettinger and Cayan, 1995; Stewart et al., 2004, 2005). The shift in snowmelt runoff is only partly controlled by PDO. It is also controlled by longer term climate trends that can be related to global warming. This shift to earlier snowmelt prolongs the summer dry period, increases the accumulation of soluble salts, and residual evaporated vadose and ground waters will have increased in concentrations of soluble constituents. Furthermore, when rainstorms arrive, although they might be less frequent, they are likely to be more intense than averages based on historical records (Trenberth, 1999). This trend is a predicted aspect of global warming because warmer temperatures will cause more moisture to transfer to the atmosphere and when the dew point is reached, it has the potential to rain more intensely. Another trend with global warming is the change from snowfall to rainfall (Knowles et al., 2006). Although this trend is also partly caused by the PDO, it is also caused by longer-term climate shifts. Snowmelt does not cause sudden flush-out like rainstorms so this change would intensify the environmental effects.

Conclusions

Observed trends in the mobilization of acid mine waters and natural acid rock drainage in the western US indicate that large rainstorm events after extended dry periods result in sudden and dramatic increases in the concentration of acid and metals. Longer term (months long) trends indicate the metal concentrations of acid

drainage gradually increase during low-flow, summer dry periods and during droughts. Both long-term and short-term trends are predicted to be magnified with the predicted trends in weather patterns for the western US. These results have important consequences for remediation efforts. First, water quality is anticipated to worsen during global warming in the absence of any remediation. Second, remediation will have to consider more extreme conditions than those found in the historical record and the extremes in runoff and highest metal loads in the past may become typical of average conditions. Hence, remediation will become more expensive because the capacity of treatment plants and engineered plans (covers, dams, diversions, revegetation, etc.) will have to be enlarged or increased in size and strength.

Acknowledgements

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