Journal of Geochemical Exploration 100 (2009) 97–104

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

# Acid rock drainage and climate change

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ARTICLE INFO

*Article history:*
Received 2 February 2008
Accepted 3 August 2008
Available online 9 August 2008

*Keywords:*
Acid mine drainage
Acid rock drainage
Climate change
First flush
Flushing effect

ABSTRACT

Rainfall events cause both increases and decreases in acid and metals concentrations and their loadings from mine wastes, and unmined mineralized areas, into receiving streams based on data from 3 mines sites in the United States and other sites outside the US. Gradual increases in concentrations occur during long dry spells and sudden large increases are observed during the rising limb of the discharge following dry spells (first flush). By the time the discharge peak has occurred, concentrations are usually decreased, often to levels below those of pre-storm conditions and then they slowly rise again during the next dry spell. These dynamic changes in concentrations and loadings are related to the dissolution of soluble salts and the flushing out of waters that were concentrated by evaporation. The underlying processes, pyrite oxidation and host rock dissolution, do not end until the pyrite is fully weathered, which can take hundreds to thousands of years. These observations can be generalized to predict future conditions caused by droughts related to El Niño and climate change associated with global warming. Already, the time period for dry summers is lengthening in the western US and rainstorms are further apart and more intense when they happen. Consequently, flushing of inactive or active mine sites and mineralized but unmined sites will cause larger sudden increases in concentrations that will be an ever increasing danger to aquatic life with climate change. Higher average concentrations will be observed during longer low-flow periods. Remediation efforts will have to increase the capacity of engineered designs to deal with more extreme conditions, not average conditions of previous years.

## 1. Introduction

A general phenomenon observed at several sites affected by pyrite oxidation is the gradual increase in acid and metal concentrations during prolonged dry periods and the sudden increase in acid and metals concentrations during the early part of storm events, especially after a prolonged dry spell (Dagenhart, 1980; Maest et al., 2004; Miller and Miller, 2007). The sudden increase has been referred to as the "first flush" (Younger and Blachere, 2004). This phenomenon has also been observed in mineralized but unmined areas. This increase in concentration is often attributed to the dissolution and flushing of soluble salts. Shallow acidic groundwaters can also be pushed out into receiving streams by fresh infiltration. The purpose of this paper is to review these processes and consider the implications for surface waters receiving acid rock drainage under the expected conditions of climate change associated with global warming.

### *1.1. 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) mentioned the use of alum and "melanteria" for medical treatments. The salts alum, melanterite, and chalcanthite were mentioned by the Greek philosopher Theophrastus (325 BCE). Pliny the Second (Caius Plinius Secundus, 23–79 CE) wrote of "green vitriol" or melanterite and "blue vitriol" or chalcanthite as well-known substances and these names continued to be used for most of the next two millennia. The toxicity of some of these salts was also established long ago. Agricola (1556) stated "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 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.

The deleterious effects of copper mining at Iron Mountain, California on the Sacramento River water quality were recorded as far back as 1905 (Haywood, 1905). As early as 1939 copper and zinc

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0375-6742/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.gexplo.2008.08.002

toxicity studies on anadromous fish from the Sacramento River were done to determine the effect of Iron Mountain mine effluent discharges on fish in the Sacramento River (Shaw, 1940). "Freshets" or rapid flushing events from sudden rainstorms were thought to be the main cause of large fish kills, deaths estimated to be up to 100,000 fish during a single storm event (Nordstrom et al., 1977).

## 2. Dynamic rainstorm-runoff and "first-flush" events

Flushing out of soluble constituents from soils and sediments during rainstorm events, especially events preceded by a substantial dry spell, is a phenomenon noted by several researchers. Durum (1953) reported an increase in chloride during the early part of spring snowmelt for the Saline River, Kansas, caused by dissolution of salts found along the river banks. Hendrickson and Krieger (1960, 1964) noted annual increases in sulfate concentrations for some springs in Kentucky that were thought to result from increased recharge dissolving sulfate salts such as gypsum. The gypsum was derived from pyrite oxidation reacting with limestone dissolution. Gunnerson (1967) noted that seasonal changes in solute concentration with flow for the Columbia River Basin showed flushing of salts during seasonal increases in flow. Through weekly sampling of several rivers in Norfolk, UK, Edwards (1973) found that nitrate, sulfate, sodium, potassium, and chloride concentrations often increased with increasing discharge, especially at the beginning of the fall wet season because accumulated soluble weathering products were flushed from the soil. This phenomenon has been called the "flushing effect" by several authors (Edwards, 1973; Walling, 1974; Walling and Foster, 1975; Kennedy, 1971, 1978). The first major rainstorm following the dry season has been termed the "first flush."

The detailed study conducted by Kennedy (1978) on the geochemistry of the Mattole River, northern California, showed that different solutes bestowed different variations in concentration with changing discharge from storm events. Sulfate concentrations had the greatest range in concentration of any major solute (4.5–64 mg/L) during the 1966–67 water year. The largest increase in sulfate concentration occurred during the first major rainstorm of the wet season (November 12, 1966) as the discharge was increasing. The sulfate concentration peaked before the discharge peaked and then returned to the same concentration as observed before the rainstorm. After more storms had hit, the concentration continued to decrease to much lower concentrations than those before the first major rain. Kennedy (1978) also noted that sulfate concentration increased, almost linearly with time, during the dry season. This pattern reflects the decreasing proportion of runoff and delayed-storm flow and an increasing proportion of shallow groundwater with higher concentrations entering the river during prolonged dry periods. These results are from catchments that are not contaminated by acid mine drainage or other industrial effluents. An examination of what data exists for mine sites and mineralized areas with no mining or mineral processing activity should show a substantial magnification of these effects for sulfate, acidity, and metal concentrations.

Shanley and Peters (1993) studied a catchment in Georgia affected by acid rain, not acid mine drainage. They found that variations in sulfate concentrations with discharge were associated with relative contributions of rainfall, throughfall, soil solution, and groundwater depending on type of storm, and whether storms were winter or summer. These different sources of water and water chemistry have been termed "components" in models that attempt to simulate episodic events (Evans and Davies, 1998).

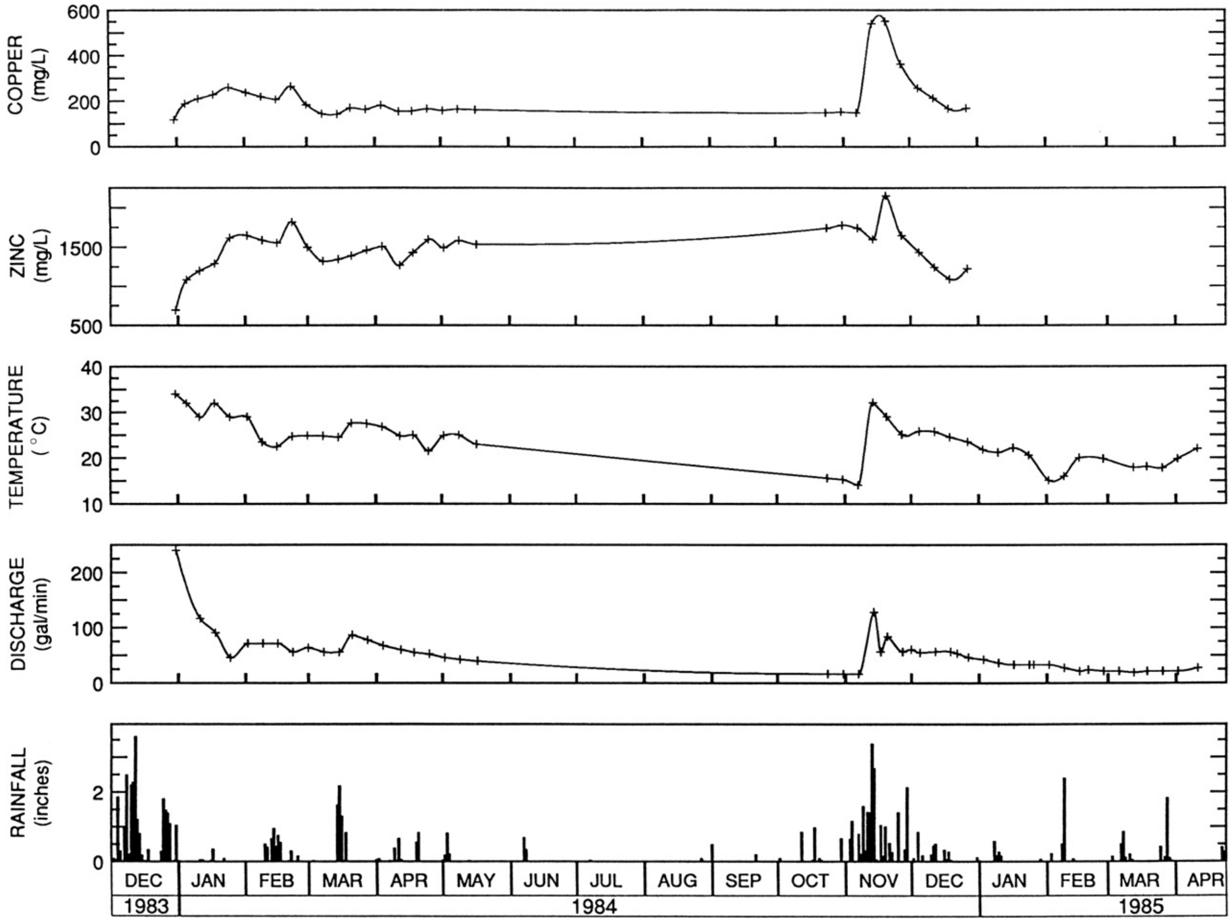

**Fig. 1.** Copper and zinc concentrations, temperature, and discharge for Richmond mine effluent at Iron Mountain, CA with rainfall history at nearby Shasta Dam (from Alpers et al., 1992).

Differences in solute concentration between rising and falling limb of the discharge causes a hysteresis effect when concentration and discharge are plotted. An example of this hysteresis was reported by Miller and Drever (1977) for the North Fork of the Shoshone River within the Shoshone National Forest, adjacent to Yellowstone National Park, and essentially absent of anthropogenic activities. Hendrickson and Krieger (1964) reported several examples of quite different hystereses for the Salt River, Kentucky using specific conductance with discharge. Although it falls outside the scope of this paper to discuss this phenomenon in detail, the advantage of such studies at mine sites or mineralized areas is that the cause of the spiked increase in solutes during the rising limb of the discharge can be directly related to the dissolution of salts and/or the flushing out of acid waters. These salts and evaporated acid waters are directly observable and available for analysis and the differences in endmember water compositions between meteoric input and mine water input is huge.

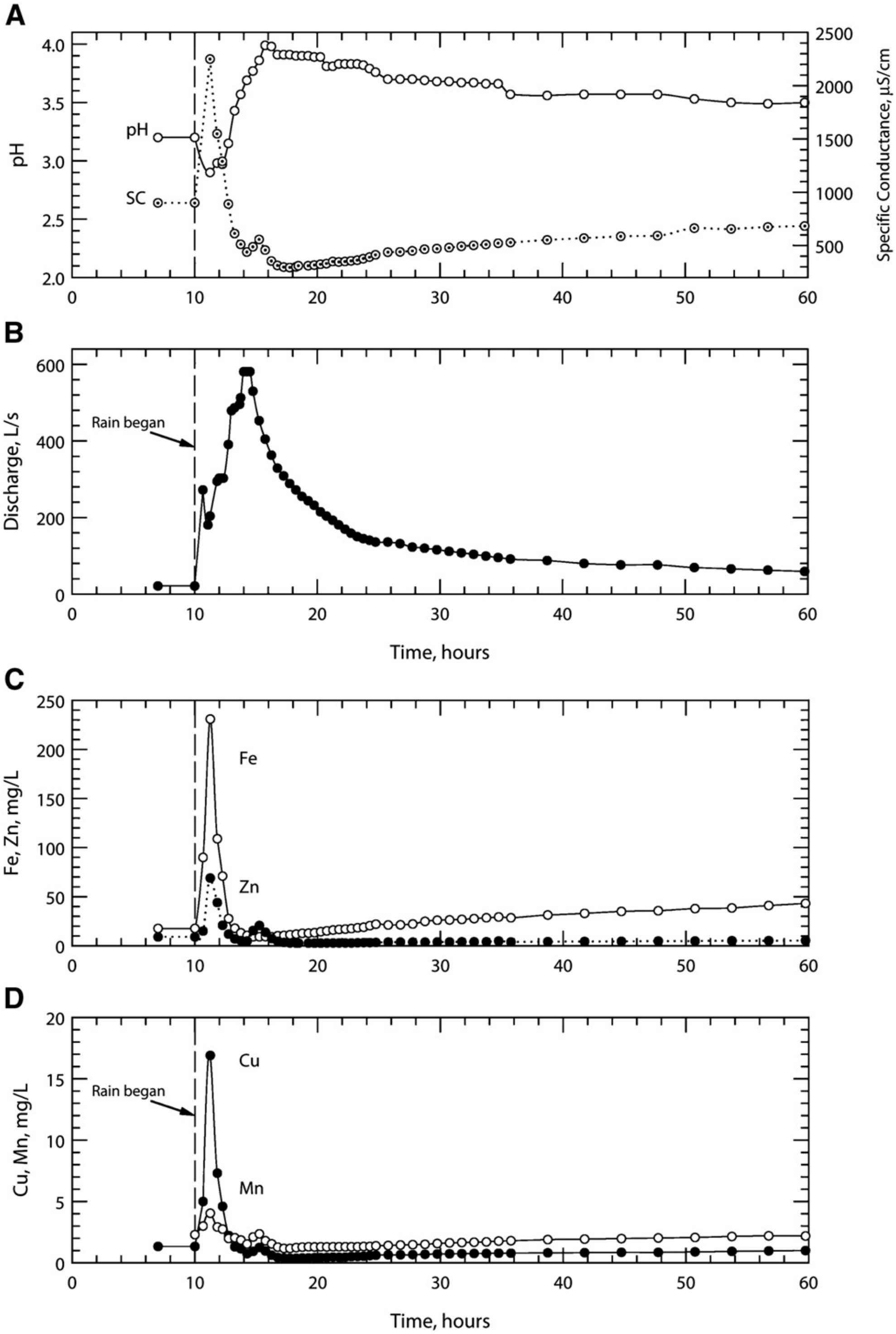

**Fig. 2.** Specific conductance (A), pH (A), discharge (B), Fe, Zn (C), Cu, and Mn (D) concentrations in Contrary Creek during the rainstorm event of September 12–414, 1978 (modified from Dagenhart, 1980).

## 3. Studies at mine sites

Three mine sites, two in the western US and one in the eastern US provide well-documented examples of flushing of high loads of metals, sulfate, and acid caused by rainstorm events.

### 3.1. 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. At one monitoring location, concentrations of acid and metals increased because the discharge of a contaminated tributary, Boulder Creek, increased more quickly than the clean waters of the upper main stream drainage, Spring Creek. At another location, the concentrations of acids and metals increased during the rainstorm because of the rapid dissolution of abundant soluble efflorescent salts in the catchment. At Iron Mountain, soluble metal sulfate salts effloresced abundantly on waste rock piles, tailings piles, on a copper cementation plant, and along the flume carrying highly concentrated acid mine drainage to the plant. Concentrations of sulfate and metals in the receiving stream, Spring Creek, consistently increased with the decrease in discharge during the dry season. This effect was very similar to that noticed in clean catchments noted earlier but with a much greater change in concentration, for sulfate, from 882 mg/L to 3090 mg/L from beginning to the end of the summer of 1975.

During the monitoring phase (remedial investigation) of Superfund (CERCLA or Comprehensive Environmental Response, Compensation, and Liability Act) investigations at Iron Mountain, the concentrations of Cu and Zn increased temporarily as the mine portal discharges increased in flow. This phenomenon occurred in the early part of the winter wet season for several water years. An example for the 1986–87 water year is shown in Fig. 1 where substantial increases in Cu, Zn, and temperature occurred in November, 1986 coincident with rising discharge that followed major rainstorms. Accumulations of chalcanthite are found a short distance along the main tunnel entrance to the Richmond mine from the Mattie deposit. These are easily solubilized during early rainstorm events and may explain why the Cu concentration peak precedes the Zn concentration peak. In addition, long-term records of Cu and Zn concentrations at Iron Mountain (Alpers et al., 1992) show systematic changes in Zn/Cu weight ratios with portal discharge, decreasing ratios during the wet season and increasing ratios during the dry season. Such changes are related to dissolution and precipitation of Zn- and Cu-bearing melanterite occurring in the underground mines (Alpers et al., 1994). Melanterite prefers Cu over Zn during formation and would leave the residual waters with increased Zn/Cu ratios whereas during the wet season, melanterite dissolution would decrease the Zn/Cu ratio. A clear pattern of increasing Zn/Cu ratios during the dry season and decreasing ratios during the wet season was also observed by Gray (1998) in acid drainage from a massive sulfide mine in Ireland.

The temperature rise during early flushing of the Iron Mountain mines is caused by high temperature subsurface waters (40 to >50 °C, Nordstrom and Potter, 1977; Nordstrom and Alpers, 1999a) 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, 1999b). These underground salts are periodically dissolved to some extent during the wet season. The dissolution of highly acidic waters and of efflorescent salts is also exothermic.

### 3.2. Contrary Creek, VA

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 along Contrary Creek, in central Virginia. He then set up automated

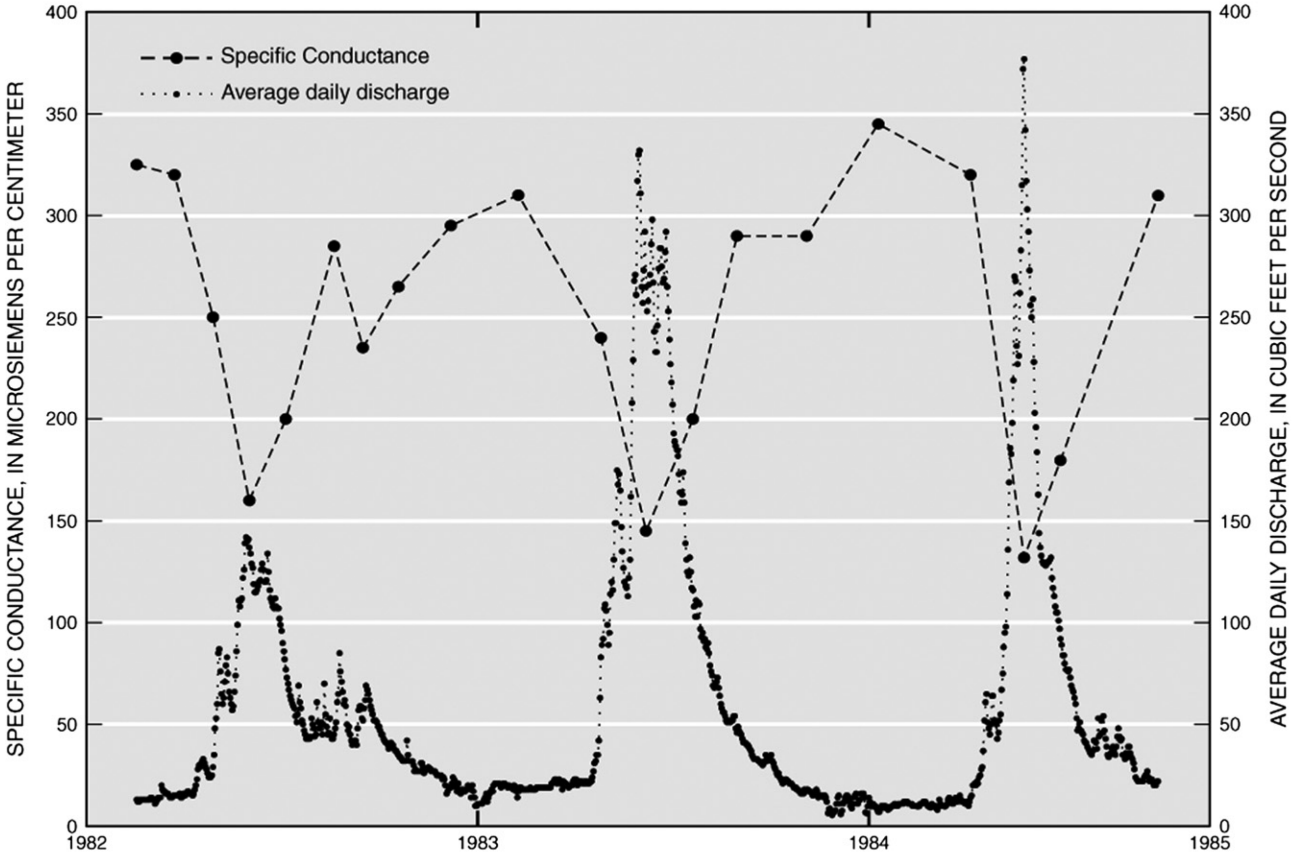

**Fig. 3.** Changes in specific conductance with snowmelt (hydrograph peaks) in the Red River, NM for 1982–85 (from Maest et al., 2004).

water-sampling devices to collect samples during rainstorm events. He found distinct spiked increases in metal concentrations during the rising limb of the discharge as shown in Fig. 2. These are some of the best documented examples of changes in receiving stream water chemistry from the flushing of metal mine tailings piles. 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. Again, the iron concentrations quickly recover from the dilution effect and begin increasing within a few hours of the discharge peaking and receding. The pH also quickly begins to decrease following cessation of the rainstorm.

### *3.3. 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 volcanic rocks (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. 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 anoxic waters found in the underlying and less permeable volcanic bedrock.

The upper reaches of the Red River itself are fed by carbonate-buffered springs and groundwater, 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 acid mineralized water entering at several locations both along the mine site and above the mine site.

During the course of these investigations, monsoon rainstorms profoundly affected the water chemistry of the Red River. Clays and acid water were washed from the debris material 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 Fig. 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 during the dry season 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.

The change in water chemistry from monsoon rains can be seen in Fig. 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 nearly 4.5 mg/L.

A slightly more detailed look at changes in the water chemistry of the Red River can be seen in Fig. 5 where a water sample was collected before, during, and after the storm. Fig. 5 shows a spiked increase in manganese and sulfate and a spiked decrease in pH. The highest concentrations in metals and sulfate in the Red River is when a major rainstorm hits the valley. The source of these acidic waters if from naturally mineralized areas devoid of any mining activities. This example shows that natural acid rock drainage can affect water quality as well as acid mine drainage.

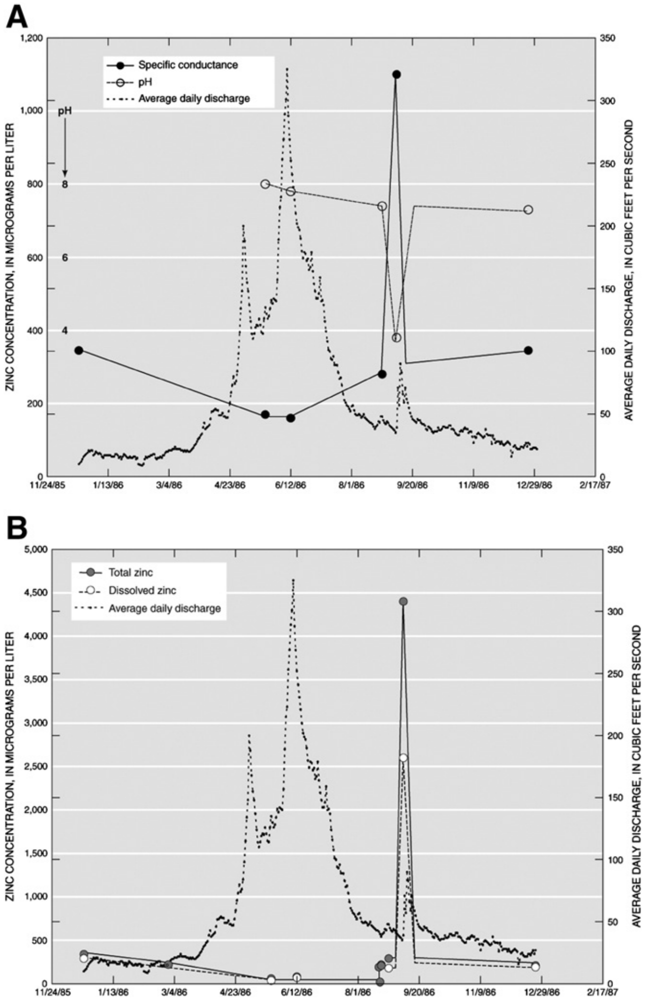

**Fig. 4.** Change in water chemistry associated with a rainstorm event during September, 1986, in the Red River. A. Increase in specific conductance and decrease in pH shown corresponding to a peak in discharge. B. Increase in Zn concentrations corresponding to the increase in discharge. Both plots from Maest et al. (2004).

### *3.4. Related studies*

Hart et al. (1982) reported increases in iron, manganese, copper, and zinc concentrations during the rising limb of the discharge for a flood event in Magela Creek, Northern Territory, Australia. They accepted the interpretation of Walling and Foster (1975), i.e. rapid dissolution or flushing of readily soluble salts in the surface soils.

Examples of first flush from mine workings, where concentrations of solutes have increased, have been described by Younger (1997, 2000) and Gzyl and Banks (2007). These examples are related to flooding of underground coal mines and the consequent dissolution of soluble salts. MacCausland and McTammany (2007) report increases in specific conductance related to acidic coal mine drainage both gradually during dry periods and rapidly during a first flush. They observed a noticeable decrease on the diversity of aquatic invertebrates with episodic flushing of coal mines.

A valuable overview of first flush, reverse first flush, and partial first-flush effects in mine site settings with examples and practical approaches to modeling was reported by Younger and Blachere (2004). These descriptions apply to complex mine workings in which unexpected water routing can occur if underground water tables and mine workings are not well understood. Reverse first flush occurs when clean water is produced first followed by increasing amounts of contaminant water caused by particular pathways of underground water routing. Partial first flush is a situation when the first flush does not follow expected phenomenological trends and model estimates because of dead-end storage underground. Empirical modeling presented by the authors demonstrate that these circumstances can be modeled with appropriate modifications.

Increases in acidity and metals during early stages of rising discharge, or first flush, in areas of acid sulfate soils has been noted by Green et al. (2006). They state that this increase in solute concentrations is caused by dissolution of soluble salts in the drainage area. Metal loading in the Merse River, Italy, was reported for pre-storm and storm conditions by Kimball et al. (2007). The basin has been affected by centuries of mining. They found that dissolved concentrations of metals did not change much from the storm but large increases in concentration and loading from colloids and other suspended sediment was readily apparent from the dynamic changes in flow. Total-recoverable (acid-soluble and unfiltered) iron load increased 21-fold while copper and manganese increased 8-fold and 7-fold, respectively during storm runoff.

Episodic flushing of mine sites has spurred research on the toxicity effects from such dynamic events (McCahon and Pascoe, 1990; Seager and Maltby, 1989). Mancini (1983) has proposed a method for calculating toxic effects for varying concentrations of contaminants.

## 4. Changes in climate for the western United States

The western US has experienced an increase in average temperature during the last 5 years that is 70% greater than the world as a whole (Saunders et al., 2008). 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 for the western US has several consequences. It prolongs the summer dry period, increases the accumulation of soluble salts, and residual evaporated vadose and ground waters will have increased 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. It is another reason why flush-out events mobilizing acid rock drainage could intensify with climate change.

These climate change patterns are not unique to the western US. Many parts of the world that have metal mines and their wastes will experience similar climatic conditions. The same consequences can be expected. Prolonged dry periods will cause increases in concentrations of metals, sulfate, and acidity because the proportion of surface runoff and shallow carbonate-buffered groundwaters will decrease. More intense rainstorms will dissolve more of the soluble salts more rapidly causing the spike in concentrations to be more pronounced. The toxic

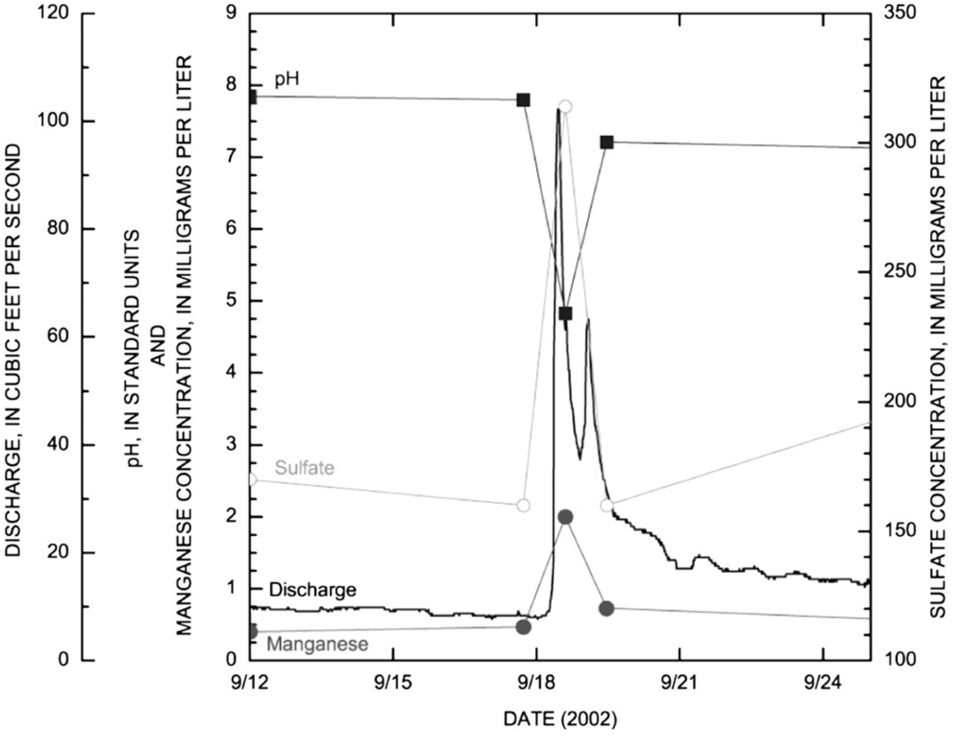

**Fig. 5.** A rainstorm event on September 19, 2002, in the Red River Valley is shown by the rapid increase in discharge. Corresponding to a moment near the peak in discharge, a water sample was collected that records the decrease in pH and increase in manganese and sulfate concentrations (from Verplanck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

effect on aquatic life will be more severe without proper remediation. Furthermore, remedial planning must account for worse extreme conditions than have been encountered normally in the past. Treatment plants will have to have greater capacities, passive treatment schemes must have greater capacities (wetlands, dams, diversions, revegetation, phytoremediation) and more resistance to erosion, and surface-water management must broaden its criteria. Finally, it becomes even more urgent to remediate mine sites, not only because we can expect these more extreme conditions, but also because the need for adequate supplies of water worldwide is increasing.

## 5. Conclusions

Although few water-chemistry studies have sufficient data to show how acidity and metal concentrations are mobilized during the transient events such as snowmelt, dry spells, and rainstorm events, the available data does show consistent trends from a variety of sites:

> Observed trends in the mobilization of acid mine waters and natural acid rock drainage in the western US during rainstorm events demonstrate sudden increases in the concentration of acid and metals during the rising limb of the discharge for early rainstorms in the wet season.
>
> The longer-term (months long) trends indicate the metal concentrations of acid drainage increase during summer dry periods and during droughts.
>
> Both long-term and short-term trends are predicted to be magnified with the estimated trends in weather patterns of climate change for the western US.

These results have important consequences for remediation efforts. First, water quality can anticipated to be worse without any remediation. Second, remediation will have to consider more extreme conditions than those found in the historical record, or, alternatively, 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

This work was supported by the National Research Program of the U.S. Geological Survey. I wish to thank Dr. K.J. Reddy, and the seminar series at the University of Wyoming, for encouraging me to consider the relationship between acid rock drainage and climate change. I am grateful to Dr. Rosa Cidu and the International Mine Water Association for inviting me to give a keynote lecture which was the basis for this paper.

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