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Review

# Baseline and premining geochemical characterization of mined sites

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ABSTRACT

A rational goal for environmental restoration of new, active, or inactive mine sites would be 'natural background' or the environmental conditions that existed before any mining activities or other related anthropogenic activities. In a strictly technical sense, there is no such thing as natural background (or entirely non-anthropogenic) existing today because there is no part of the planet earth that has not had at least some chemical disturbance from anthropogenic activities. Hence, the terms 'baseline' and 'pre-mining' are preferred to describe these conditions. Baseline conditions are those that existed at the time of the characterization which could be pre-mining, during mining, or post-mining. Protocols for geochemically characterizing pre-mining conditions are not well-documented for sites already mined but there are two approaches that seem most direct and least ambiguous. One is characterization of analog sites along with judicious application of geochemical modeling. The other is reactive-transport modeling (based on careful synoptic sampling with tracer-injection) and subtracting inputs from known mining and mineral processing. Several examples of acidic drainage are described from around the world documenting the range of water compositions produced from pyrite oxidation in the absence of mining. These analog sites provide insight to the processes forming mineralized waters in areas untouched by mining. Natural analog water-chemistry data is compared with the higher metal concentrations, metal fluxes, and weathering rates found in mined areas in the few places where comparisons are possible. The differences are generally 1–3 orders of magnitude higher for acid mine drainage.

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## 1. Introduction

Geogenic or 'natural background' substances in the environment are known to occur at concentrations in air, soils, and waters that are hazardous for most eukaryotic life forms. A well-known example is that of arsenic which, too often, occurs in groundwaters used for drinking water supplies at concentrations greater than the recommended drinking water limit of 10 µg/L (Nordstrom, 2002). Arsenic is not the only element that occurs naturally at dangerously high concentrations; a wide variety of elements are known to abide in groundwaters at concentrations hazardous for drinking especially where the soils, sediments, and bedrock are highly mineralized. These areas sometimes contained enough mineralization to be mined for their ores.

Hydrogeochemical characterization of a mine site for establishing background conditions should be done before mining begins. To define pre-mining conditions after a large mineralized area is already disturbed from underground excavations, open pits, waste piles, and tailings is fraught with considerable uncertainties. Distinguishing water contamination caused by natural mineralization compared to that derived from mining is, nevertheless, an important objective for environmental restoration. This chapter discusses the challenges of attempting to define pre-mining conditions for a site either after mining has begun (but may still be active) or after mining has ended (inactive) with the emphasis on mineral deposits that generate acid waters. Although doing a careful baseline study of conditions prior to mining is always preferable, there are approaches that can help constrain the range of likely pre-mining conditions in a post-mining setting.

Numerous mineralized areas undisturbed by mining are known to contain acid-sulfate waters with toxic concentrations of metals (Clarke, 1908; Eppinger et al., 2007; Falk et al., 2006; Graham and Kelley, 2009; Koyanagi and Panteleyev, 1993; Kwong et al., 2009; Mast et al., 2007; Plumlee et al., 1999; Posey et al., 2000; Runnells et al., 1992; Schwertmann et al., 1995; Stanton et al., 2000; Verplanck et al., 2009) and the February 2009 issue of Applied Geochemistry devoted a section to natural low-pH environments unaffected by human activity (Eppinger and Fuge, 2009). These conditions occur because the same geochemical and microbiological processes that produce acid mine drainage (AMD) also produce natural acidic water or natural acid rock drainage (NARD). The differences between AMD and NARD are that (a) mining increases the total mass amount of pyrite and other sulfides exposed to air and water, thereby increasing substantially the overall amount of metal-rich acid waters that can be produced, (b) mining greatly increases the surface area of pyrite and other sulfides exposed to air and water, thereby increasing substantially the rate of acidity produced, and (c) the increased acidity and water discharge from mining increases the mobility of heavy metals to waterways. Plumlee et al. (1999) has shown that NARD can contain orders of magnitude lower metal concentrations than AMD for similar mineralization and rock types. Hence, the risks to aquatic, terrestrial, and human health increase substantially from mining and mineral-processing activities compared to pre-mining conditions in the same areas, unless remedial measures offering environmental protection are incorporated into the mining plans.

Any attempt to determine pre-mining ground-water quality at older mine sites, whether active or inactive, must rely on indirect methods and scientific inference. Inference of groundwater quality constituents in a complex mineralized terrain of poorly known hydrology will always carry larger uncertainties than any direct methods of measuring groundwater quality, and the degree of uncertainty depends on the approach used. Before the 1970s, routine sampling and analytical techniques were not available to determine low concentrations of many trace elements in water samples. Concentrations and detection limits at the level of today's water-quality standards could not have been determined reliably, if at all, by routine analytical techniques at that time. Even if the effort was made to determine pre-mining conditions, there would have been analytical limitations.

The key to understanding pre-mining water-quality conditions at a disturbed site depends directly on understanding the processes that produce acid rock drainage in a given hydrogeological setting. Our understanding of rock weathering, pyrite oxidation, the inorganic and microbial processes that lead to the development of acidity, and processes affecting the mobility of metals in surface and ground waters has improved considerably over the last two decades (Blowes et al., 2003; Geller et al., 1998; Jambor et al., 2003; McLemore, 2008; Nordstrom, 2000; Nordstrom, 2008, 2011a,b; Nordstrom and Alpers, 1999; Plumlee et al., 1999). Continued work to document the geochemical weathering of unmined but mineralized areas will allow us to improve our confidence in characterizing the pre-mining conditions of already mined sites.

## 2. Natural background: definitions

There is a tendency to think of 'natural background' as unpolluted or pristine preindustrial conditions. Unfortunately, such concepts *in sensu stricto* are not helpful because (1) there are no water-quality data for such conditions because widespread global contamination by several trace constituents has occurred, (2) natural variations can be large and do not permit a simple, single analytical result for a given element or compound, (3) there is often a value judgment or anticipated 'use' judgment (water for drinking or for agriculture or for industry) associated with natural substances (rocks, soils, air, and water) that precludes a simple, unambiguous result, and (4) the effect of scale and study objectives play a very important role in the determination of background (Reimann and Garrett, 2005). This last comment applies to the spatial and temporal scale of the study area and that complexity increases with larger scales. The study objectives are also important because some criteria must be defined within which natural background is described and a different study may define these conditions differently. Anthropogenic contamination of our air, soil, and water resources by Pb, As, and Hg is well-documented, although the air, soil, and water themselves are 'natural.' One definition of natural background is the concentration of a hazardous substance consistently present in the environment that has not been influenced by localized human activities (Washington Department of Ecology, 2009). Bates and Jackson (1980) described a natural area as "An area of land or water that has retained its wilderness character, although not necessarily completely natural and undisturbed..." John Hem (1985) reminded us that "Natural waters need not be pristine—unaffected by the works of man. Indeed, probably few are completely free from such influences." A similar statement was made in the National Academies report on Alternatives for Ground Water Cleanup (National Academy Press, 1994). Hence, it is prudent to avoid the use of this word. Instead, the term 'baseline' is preferred to refer to conditions of water quality at the time of sampling and 'pre-mining' to describe those conditions that likely existed during the few hundred to few thousand years before mining took place. The time period must be constrained to the Holocene (the last 10,000 years). Earlier time periods would have had markedly different climatic conditions with different weathering rates. Even during the Holocene there have been substantial climate changes. Furthermore, some mineralized zones would have been deeper and less exposed to weathering in several areas that are in the weathering zone today. Baseline conditions may refer to current conditions either affected by mining or not affected by mining. Those areas not affected by mining could have been affected by anthropogenic activities such as exploration drilling, clearings for roads and power lines, and other structures, but not by the large-scale excavation of rock or the dumping of waste rock or tailings typical of metals extraction and concentration.

### 2.1. U.S. Environmental Protection Agency (USEPA) perspective

The USEPA (2002) has defined background as "Substances or locations that are not influenced by the releases from a site and are usually described as naturally occurring or anthropogenic: (1) Naturally occurring substances are present in the environment in forms that have not been influenced by human activity. (2) Anthropogenic substances are natural and human-made substances present in the environment as a result of human activities..." They refer to a background reference area in a similar manner as what is referred to here as a natural analog in this paper: "The area where background samples are collected for comparison with samples collected on site. The reference area should have the same physical, chemical, geological, and biological characteristics as the site being investigated, but has not been affected by activities on the site." They also add that "CERCLA [Comprehensive Environmental Response, Compensation and Liability Act] site activity (such as waste disposal practices) may cause naturally occurring substances to be released into other environmental media or chemically transformed. The concentrations of the released naturally occurring substance may not be considered as representative of natural background according to CERCLA 104(a)(3)(A)." CERCLA 104(a)(3)(A) refers to any naturally occurring substance as exempt from removal as long as its release is only from natural causes.

Breckenridge and Crockett (1995) discussed background concentrations for soils and sediments and pointed out that there are two issues to be considered when addressing background. "The first is whether the site and local area have a high natural variability in concentrations of inorganics. The second is to differentiate between natural and anthropogenic sources at a site with high background concentrations." Mineralized areas are notorious for having high natural variability because hydrothermally altered rock can change mineralogy and chemical composition radically over short distances. These authors went on to say that it is not feasible to establish a single universal background concentration for soils or sediments, it is only useful to discuss a range of concentrations for a particular contaminant. More than 50 years ago Hawkes and Webb (1962) called attention to the fact that natural background is a range and not a single value for each element.

### 2.2. European perspective

The problem of defining natural water quality was found to be both challenging and necessary by the European Union Water Framework Directive (Directive, 2000). The Groundwater Daughter Directive requires EU member states to establish thresholds for pollutants to identify groundwaters at risk of having poor quality (BRIDGE, 2006). For example, the natural concentrations of As and F in the Phlegrean Fields and Ischia Island in Campania, southern Italy, exceed substantially the reference values (Dulci and Sellerino, 2012). As Edmunds and Shand (2008a) pointed out, "...certain elements present naturally in groundwaters may breach guidelines for potable water quality. Baseline criteria are also needed as a reference to be able to assess quantitatively whether or not anthropogenic pollution is taking place." Concern for groundwater quality in Europe led to a Ministerial Seminar on Groundwater held in The Hague, November 26–27, 1991. Since then, Commissions and Directives have formed but throughout there have been different understandings of 'environmental quality' of groundwater depending on what country and what sector of society are being represented. Distinctions between 'natural' groundwater quality and groundwater quality designated for specific uses (industry, agriculture, drinking water supply) were never clearly made. Philippe Quevauviller (2008) stated, "The knowledge about 'natural quality' of groundwater is still very scarce, and ongoing exchanges among scientific and policy-making communities are needed to adopt a more detailed common methodology for groundwater threshold values and put it into practice."

Edmunds and Shand (2008a,b; Shand et al., 2002) have defined baseline concentration of a substance in groundwater as "the range of concentrations of a given element, isotope or chemical compound in solution, derived entirely from natural, geological, biological or atmospheric sources, under conditions not perturbed by anthropogenic activity." Of course, just to access groundwater we have to drill a well which is an anthropogenic activity that perturbs the groundwater chemistry. However, techniques have been developed to minimize or eliminate the effects of drilling and pumping on the water chemistry. These techniques include use of de-ionized drilling water, very slow-flow purging with continuous monitoring of sensitive parameters, and use of inflatable packers. Not all of these modifications are necessary for every sampling program; modifications depend on the objectives and the constituents of concern. If sampling is being done for major and some minor elements, these precautions may not be critical. For trace elements, these precautions and several others are critical.

Statistical analysis of analytical data has often been used when classifying geochemical and environmental data including efforts to identify natural background. The most widely used statistical techniques are all based on the assumption that the data follow a normal or lognormal distribution. However, Reimann and Filzmoser (1999) demonstrated that normal or lognormal distributions are the exception not the rule. Hence, biased or faulty conclusions may occur from statistical analyses without additional information. Non-parametric statistical methods are advocated instead. The approach used to define baseline by Edmunds and Shand (2008b) was a geochemical one, not a statistical one.

### *2.3. Variability of water compositions*

The definition of a water composition is not just a matter of analytical chemistry and a one-time sampling campaign. Water chemistry at any one location can vary from changing weather conditions (diel variations, storm events) and changing climate conditions (seasonal changes, long-term climate changes) as well as from anthropogenic pollution. Ancient civilizations were aware that natural water compositions varied considerably but it was not until the field of chemistry was on a more consistent basis that quantitative determinations of water composition were possible, from about the middle of the nineteenth century (Wanklyn and Chapman, 1868). Beginning with early compilations of water compositions such as Clarke (1908) and expanded upon by White et al. (1963), Barnes and Hem (1973), Kharaka and Hanor (2005), and Frape et al. (2005), it became clear that a great many geochemical and geological processes must have caused such a wide range of water compositions. Not only does the chemical composition of surface water and groundwater change with location and rock type but it can change at the same location over time because of both natural and anthropogenic activities. Consequently, deriving constant concentration values for any constituent to meet regulatory needs such as drinking water standards can be exasperating given the high variability of 'background.' A further complication arises when an anthropogenically contaminated aquifer is identified because it usually means that some obviously man-made compound such as MTBE (methyl tertiary butyl ether) or pesticides or tritium has been found. However, most of the major ions in the groundwater are often from geogenic sources, so it is really contaminated *with respect to specified constituents*, not everything. Then there are changes in groundwater composition caused by physical anthropogenic disturbances instead of chemical sources. High rates of pumping will contaminate deeper groundwaters with shallower groundwaters. Injecting clean water into aquifers for aquifer storage and recovery (ASR) can dissolve minerals that can contaminate an uncontaminated aquifer (Cavé, 1999; Price and Pichler, 2006; Vanderzalm et al., 2011). Such human activities that can cause the release and mobility of natural contaminants should not be considered as part of natural background.

## 3. Approaches to pre-mining characterization

During the late 1970's and the 1980's, B. Hanshaw, D.K. Nordstrom, and J.W. Ball (unpublished data) found several examples of NARD in the San Juan Mountains, Colorado. Many of these sites were later documented in Mast et al. (2007). From surveys of water chemistry in mineralized areas of Geneva Creek, CO, McHugh et al. (1988) found stream waters of low pH and elevated metal concentrations that were unaffected by mining. With these data, Bassett et al. (1992) developed a geochemical model based on inverse modeling, saturation indices, and mixing of waters to interpret a NARD setting. This example may have been the first to apply quantitative geochemical modeling to interpret a natural acid-sulfate weathering environment.

Runnells et al. (1992) documented NARD in mineralized and unmined areas and stressed the importance of natural background for determination of remediation goals and monitoring. They compiled 30 examples of water chemistry from areas of known mineralization but lacking any mining activity. They also suggested three methods for estimating natural background water chemistry: historical records, natural analog sites, and equilibrium geochemical modeling. Alpers and Nordstrom (2000) suggested additional geochemical tools for estimating pre-mining conditions such as use of stable isotopes, sediment geochemistry, inverse modeling, kinetic modeling, statistical analyses, mass balances on oxygen, and mass balances with age determination. They also pointed out that there can be both remote analogs and proximal analogs. Proximal analogs should have more similarities to the site under investigation and where proximal analogs are not possible, remote analogs of similar geological and hydrological conditions may provide useful information.

Yet another approach is to develop a reactive-transport model for a catchment through synoptic sampling and tracer-injection studies, subtract all mining-related inflows, and the difference should approximate pre-mining conditions. Synoptic sampling with continuous injection of a conservative tracer (such as bromide or chloride) allows a detailed and quantitative measure of the stream or river discharge. Concentrations of the naturally-occurring solutes can then be converted into mass fluxes. Mass flux profiles reveal inflows and outflows with their respective gains and losses of solutes and whether it is caused by base flow or surface flow (or a combination) or in-stream processes such as microbial activity, mineral dissolution/precipitation or sorption processes. Finally, a reaction-transport model can be developed for the stream. If inflows of contamination from mining or mineral processing activity can be clearly distinguished from natural inflows, then these can be sequentially removed in a remedial simulation scenario to determine what the downstream water quality effects would be. Advances in the application of tracer-injection with synoptic sampling (Kimball et al., 2002) and reactive-transport modeling (Kimball et al., 1994; Runkel et al., 1996a,b; Runkel et al., 1999; Runkel and Kimball, 2002; Kimball et al., 2003; Runkel, 2010) make this approach one of the most quantitative. The main difficulty is determining what is truly natural from what is anthropogenic in a given watershed where subsurface flows of mine waters are not always well defined. A secondary problem is that it still depends on modeling and important decisions are left to the modeler as to the appropriate reactions and their thermodynamic properties and their rates. Different mineral precipitates and their solubilities likely govern processes under more dilute and higher pH conditions than those under which the reactive-transport model was originally calibrated. Comparisons between this approach and actual analog sites that have been studied in detail should help to refine the method.

Pre-mining conditions can also be reflected in the sediment record when examined for trace elements, mineralogy, and processes of sediment dispersion (Helgen and Moore, 1996) or when sediments are dated and chemical changes with depth in buried sediment (Church et al., 2007a) are considered. Ferricretes are rocks formed by cementation of soils, alluvium, or colluviums with hydrous ferric oxides (primarily goethite) derived from acidic waters (Wirt et al., 2007). Several natural ferricretes have been studied and dated (Furniss et al., 1999; Verplanck et al., 2007) and even used to estimate pre-mining pH and dissolved copper concentrations (Nimick et al., 2009). When dealing with soils and sediments, the concept of natural background has been particularly elusive because it depends on local conditions, substantial natural variability, difficulties of knowing how much spatial, areal, and depth sampling is adequate to define conditions, and different statistical treatments have been used to define background from

**Table 1**
Summary table of locations where water chemistry data have been collected on mineralized and unmined areas, mined areas where comparisons are possible, and where pre-mining water chemistry studies have been conducted.

| Location | Water type | Number of samples |
|---|---|---|
| *San Juan Mountains, Colorado, USA* | | |
| Animas River | Springs, streams, AMD | 146 |
| Summitville | Springs, streams, AMD | 45 |
| Calico Peak | Springs, streams | 20 |
| Redcloud-Wetterhorn Peaks | Springs, streams | 41 |
| Red Mountain Creek | Stream | 1 |
| Geneva Creek, Colorado, USA | Springs, streams | 32 |
| Handcart Gulch, Colorado, USA | Springs, streams | 34 |
| East Alpine Gulch, Colorado, USA | Springs, streams | 19 |
| Redwell Basin, Colorado, USA | Stream | 37 |
| Red River Valley, New Mexico, USA | Springs, streams, groundwater | 168 |
| Robinson district, Ely, Nevada, USA | Groundwater | 44 |
| Phoenix mine, Battle Mountain, Nevada, USA | Groundwater | 551 |
| Coeur d'Alene, Idaho, USA | Streams | Unknown |
| Paymaster Creek, Blackfoot River, Montana, USA | Stream | 1 |
| Iron Mountain, California, USA | Pre-mining estimate, AMD | >500 |
| Wulik River basin, Alaska, USA | Springs, streams | |
| Red Mountain, Alaska, USA | Springs, streams | 36 |
| Bathurst Mining Camp, New Brunswick, Canada | Groundwater | 21 |
| Macintosh Creek, Yukon, Canada | Springs, streams | 9 |
| Colour Lake, Axel Heidelberg Island, Canada | Lake | 11 |
| Pfister Joch, Austria | Spring, stream | 1 |
| Arroyo del Val, Spain | Stream | 27 |
| Spence porphyry copper, Atacama Desert, Chile | Groundwater | 70 |
| Equatorial copper mine | Springs, streams | 8 |
| Lillesand, southern Norway | Highway rock pile | Hundreds |
| Kiiminki, Finland | Quarry lake | 23 |

these data. These challenges prompted a discussion by Matschullat et al. (2000) under the title "Geochemical background – can we calculate it?" Linear equations were derived among As, Cr, Co, Cu, Ni, Pb, Zn and Fe for Australian and southeast Asian soils to show that use of such correlations was a method of dealing with that large range of concentrations (Hamon et al., 2004). However, the correlations used log-log parameters and the $r^2$ values ranged from 0.50 to 0.71. The results are qualitative to semi-quantitative at best because of considerable dispersion in the data.

This paper presents pre-mining acidic water chemistry in mineralized areas from several examples of (1) analog sites, summarizing the range of water chemistry and what we know about the underlying processes and (2) reactive-transport simulations that have estimated pre-mining conditions for surface streams. Historical records can provide qualitative information but they lack the quantitative information needed for regulatory purposes. Geochemical modeling is very helpful to constrain the likely processes, to confirm geochemical reactions and hypotheses related to water flow, and to formulate hypotheses but it is too fraught with uncertainties to be the main approach *unless* supported by substantial field data that include water chemistry and discharge, isotopes, and substantial hydrologic and geologic characterization.

## 4. Natural analogs

Mineralized and unmined sites with water chemistry data have been reported from at least 20 sites or areas worldwide. These locations along with sites for which pre-mining estimates have been made are summarized in Table 1. All samples have been filtered through either 0.1 or 0.45 μm pore size filters.

### *4.1. San Juan Mountains, Colorado, USA*

The San Juan Mountains of southwestern Colorado are a large volcanic field composed of a thick sequence of lavas, ash, and pyroclastic debris with more than 15 eruptions between 40 and 18 million years ago (Blair et al., 1996; Yager and Bove, 2007). The rocks are andesitic to rhyolitic in composition. Hydrothermal mineralization accompanied this volcanic activity and produced some of the richest ore deposits in the State of Colorado. Despite numerous mines of various sizes, there are also many locations with sulfide mineralization without mining activity that produce NARD (see Fig. 1 for location and map of mine sites).

### *4.1.1. The US Geological Survey (USGS) abandoned mine lands initiative*

In 1997, the USGS began a 10-year initiative collecting extensive information on the geology, hydrology, mine sites, water chemistry, and aquatic and terrestrial ecology in the Animas River drainage basin in the heart of the San Juan Mountains (Church et al., 2007b). One of the more obvious signs of NARD in this investigation was the occurrence of ferricretes and their associated waters of acidic pH (Wirt et al., 2007; Verplanck et al., 2007). Mast et al. (2007) cataloged mines, collected water samples from mined drainages and unmined drainages, and compared the two sets of data using statistical techniques, mass balances, isotopes, and rare earth element signatures. Although there was some geographical overlap between mining-affected sites and those not affected by mining, the criteria used was simply whether there were any actual man-made disturbances upgradient from a site or not (other than small prospect pits). Using this criteria and with careful surveys on the ground and through available maps, 146 background water samples were collected. The chemical characteristics of these waters are summarized in Table 2.

Mast et al. (2007) concluded that although there was a tendency for metal concentrations to be lower in NARD than in AMD, there was also substantial overlap. The real issue in the Animas was that few of the 'mine' category sites actually ever produced ore. There was a lot of prospect mining (for example Paradise Portal where they went into ferricrete) in minimally mineralized areas that had to go under the "mine" category. Statistical tests were of two types, box-and-whisker plots and principal component analysis (PCA). Both tests could show a relation of water chemistry with degree of hydrothermal mineralization of the rock but they could not clearly distinguish between AMD and NARD. Mass balances were done on loadings from AMD versus NARD in the Middle Fork Mineral Creek and the results demonstrated that 56–90% of the metal loading was from NARD depending on which element was used. The inventory of water discharge indicated 78% of the water was from unmined sources. Strontium isotopes did not show any discrimination between AMD and NARD because the mined ore deposits did not differ in the range of isotopic composition from mineralized zones that were not economic to mine (Verplanck et al., 2001). Stable isotopes of sulfur and oxygen in dissolved sulfate did show some slight bias between AMD and NARD but there was also overlap for several samples that made this method unreliable (Nordstrom et al., 2007). What stable isotopes of sulfate did show was that there was a substantial amount of sulfate derived from gypsum or anhydrite dissolution in addition to pyrite oxidation. Rare earth element signatures did not show any discernible difference between AMD and NARD.

In this study another attempt to evaluate the Animas River Basin study is shown in the diagrams below. First, the water samples for mined and natural background sites were screened using

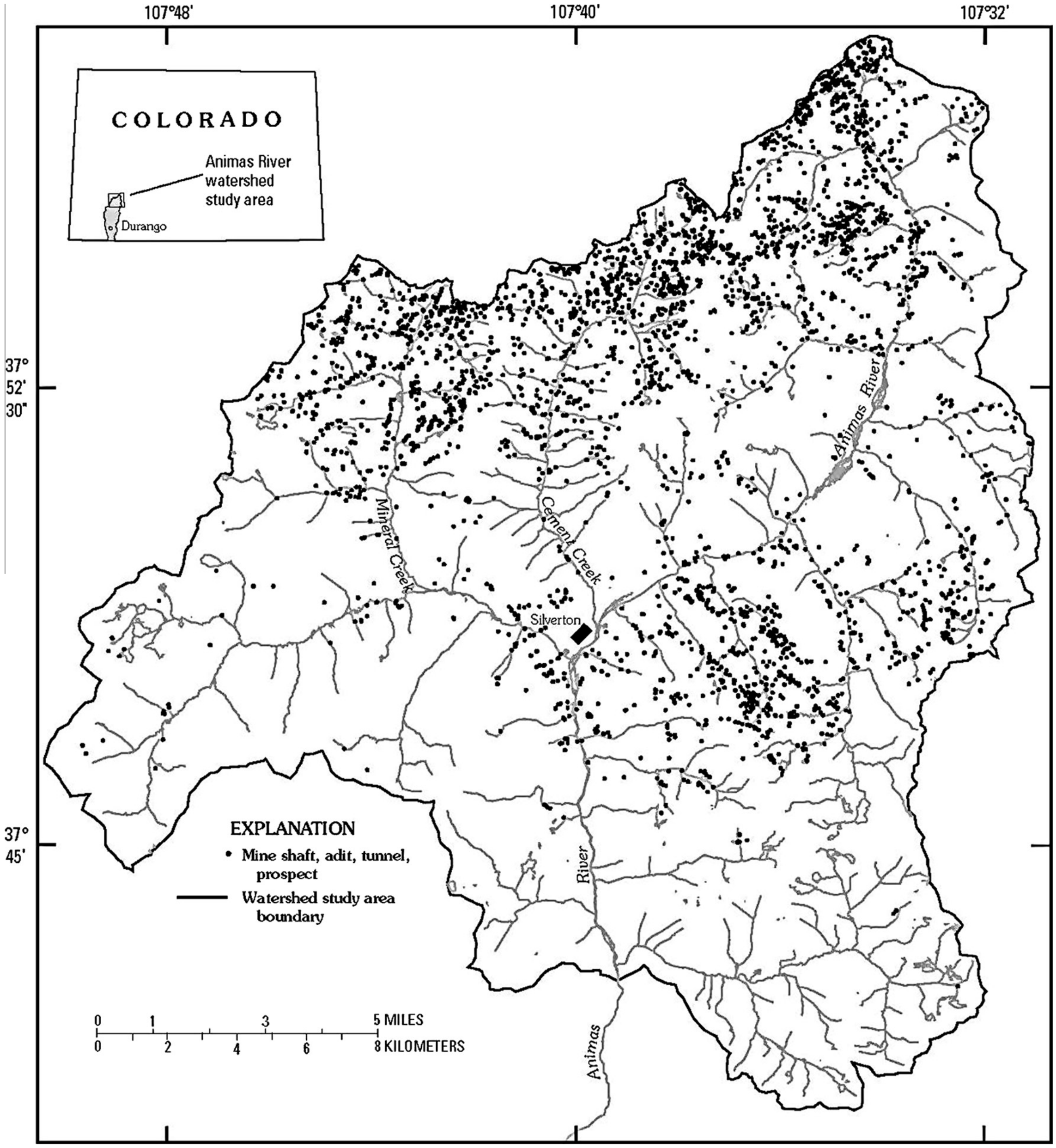

**Fig. 1.** Locations of 5397 mine shafts, adits, tunnels, and prospects in the Animas River drainage basin, Colorado (from Church et al., 2007b).

the categories developed by Mast et al. (2007) and those that were not distinctly mine drainage (category 4) or not distinctly natural (category 1) were eliminated. Next, metal concentrations were summed from the concentrations of Al, Fe, Mn, Cu, Pb, and Zn. Fig. 2 shows the relation between these summed metal concentrations and pH. Some separation of mined site samples from unmined site samples is evident at pH values above about 3.5 but convergence of values occurs at lower pH values. Consideration of the same metal concentration sum and its relation to sulfate concentrations is shown in Fig. 3a. Again considerable overlap occurs. However, sulfate concentrations were often found to be derived from gypsum or anhydrite dissolution as well as from pyrite oxidation for these samples (Nordstrom et al., 2007). A further screening was used to eliminate samples in which at least 60% of the sulfate concentration could be derived from gypsum dissolution. The samples were identified by simply looking at the molar ratio of calcium to sulfate and deleting data in which the ratio was greater than 60%. The result is Fig. 3b. Clearly a lot of the scatter in Fig. 3a was caused by samples with high concentrations of calcium. A stronger trend is now apparent and a more distinct separation between mine water samples and natural water samples can be seen.

### *4.1.2. Summitville*

Following the bankruptcy of Galactic Resources Limited and the emergency responses of the EPA, the Summitville mine became a superfund site and a series of studies were initiated for proper site characterization and consideration of remedial options. The drainage from Summitville enters the Alamosa River via the Wightman Fork tributary (Fig. 4). The occurrence of ferricrete (Logsdon et al., 1996) and existing natural acid springs and seeps (Miller and McHugh, 1994; Miller and McHugh, 1999) were clear evidence for NARD.

Water samples collected from the Stunner altered area (location of Iron, Bitter, and Alum Creeks in Fig. 4) were found to have pH values of 2.58–7.27 and metal concentrations tabulated in Table 2.

**Table 2**
Background water-quality statistics of samples from Colorado (**AR,** Animas River basin, Mast et al., 2007; **S,** Summitville, Miller and McHugh, 1994; **CP,** Calico Peak, Miller and McHugh, 1999); SC, specific conductance; alkalinity as $CaCO_3$; –, not reported.

| Solute (mg/L) | **AR** minimum | **AR** median | **AR** maximum | **S** minimum | **S** median | **S** maximum | **CP** minimum | **CP** median | **CP** maximum |
|---|---|---|---|---|---|---|---|---|---|
| Discharge (L/s) | 0.0283 | 7.08 | 211 | – | – | – | – | – | – |
| SC (μS/cm) | 12 | 270 | 2,180 | 80 | 340 | 2,400 | 36 | 122 | 316 |
| pH | 2.58 | 4.89 | 8.49 | 2.58 | 3.44 | 7.27 | 3.33 | 5.79 | 8.10 |
| Dissolved oxygen (mg/L) | 0.0 | 7.3 | 16.3 | – | – | – | – | – | – |
| Alkalinity | <0.5 | <0.5 | 69.0 | <1 | <1 | <1 | <1 | 6 | 132 |
| $SO_4$ | 1 | 90 | 1,300 | 10 | 95 | 1,250 | 7.1 | 27 | 63 |
| F | – | – | – | <0.1 | 0.3 | 1.5 | – | – | – |
| Ca | 0.8 | 27.6 | 550 | 7.7 | 12 | 150 | – | – | – |
| Mg | 0.1 | 3.2 | 34.0 | 1.5 | 5.7 | 122 | – | – | – |
| Na | <0.1 | 1.5 | 13.0 | 1.3 | 2.2 | 2.4 | – | – | – |
| K | 0.1 | 0.5 | 2.8 | <0.1 | 0.7 | 2.2 | – | – | – |
| $SiO_2$ | 0.8 | 5.8 | 53.0 | 8 | 27 | 62 | – | – | – |
| Al | <0.040 | 0.359 | 71.4 | <0.1 | 3.7 | 55 | <0.1 | 0.1 | 2.5 |
| Ba | <0.002 | 0.022 | 0.101 | – | – | – | – | – | – |
| Be | <0.001 | <0.001 | 0.065 | – | – | – | – | – | – |
| Cd | <0.002 | <0.002 | 0.0084 | <0.001 | 0.001 | 0.010 | – | – | – |
| Cr | <0.015 | <0.015 | 0.050 | <0.001 | <0.001 | 0.013 | – | – | – |
| Cu | <0.004 | <0.004 | 0.372 | <0.001 | 0.012 | 0.370 | <0.0006 | 0.001 | 0.350 |
| Fe | <0.030 | 0.049 | 117 | 0.12 | 3.1 | 141 | 0.01 | 0.05 | 1.48 |
| Pb | <0.030 | <0.030 | 0.141 | <0.001 | <0.001 | 0.004 | – | – | – |
| Li | <0.006 | <0.006 | 0.043 | – | – | – | – | – | – |
| Mn | <0.003 | 0.191 | 74.7 | 0.05 | 0.58 | 15 | 0.01 | 0.05 | 1.48 |
| Mo | <0.010 | <0.010 | 0.071 | – | – | – | – | – | – |
| Ni | <0.020 | <0.020 | 0.044 | 0.001 | 0.010 | 0.230 | – | – | – |
| Sr | 0.006 | 0.236 | 5.70 | 0.006 | 0.236 | 5.70 | – | – | – |
| Zn | <0.020 | 0.028 | 14.4 | 0.008 | 0.060 | 1.0 | <0.005 | 0.010 | 0.320 |

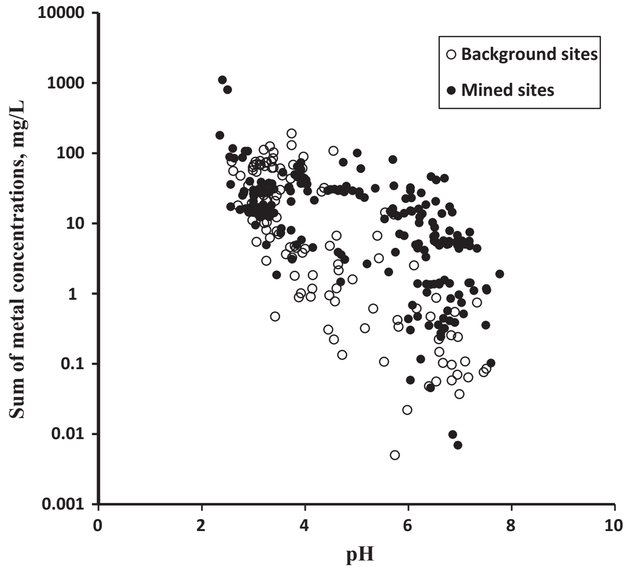

**Fig. 2.** Logarithm of the sum of Al, Fe, Mn, Cu, Pb, Zn concentrations relative to pH for unmined, background sites (open circles) and mined sites (closed circles) from data of Mast et al. (2007).

However, the Alamosa River just above the confluence with Wightman Fork has highly variable pH. Moran and Wentz (1974) measured pH values of 6.0 and 6.6 and an unpublished USGS measurement in 1999 was 5.87. Posey et al. (2000) compiled data from several sources to show major changes in chemistry with pH varying from 3.5 to 7 at this same location. Seasonal effects are very pronounced for this NARD and, consequently, no matter how much Summitville is remediated there will always be some NARD that will offset the Summitville restoration. The natural conditions limit the cleanup objectives.

Miller and McHugh (1999) estimated pre-mining baseline compositions of three surface waters just above points of confluence: Cropsy Creek above Wightman Fork, Wightman Fork above Cropsy Creek, and Wightman Fork above the Alamosa River. Cropsy Creek is a tributary of Wightman Fork that bounds the western edge of the mine site. They also considered a 'conservative scenario' and a 'most likely scenario' using similarities and differences in mineralization between the Summitville area and the Stunner altered area to help constrain their estimates. A similar comparison was done between Summitville drainage and drainage at Calico Peak (next section). However, as the data from Plumlee et al. (1995) and Posey et al. (2000) show, the natural variations in NARD for the Alamosa River just above the Wightman Fork confluence vary considerably and suggest there may be larger uncertainties than predicted by these pre-mining estimates.

### 4.1.3. Calico Peak altered area

Twenty water samples were collected and analyzed from the slopes of Calico Peak, northwest of Rico, CO (Table 2, Miller and McHugh, 1999). There has been minimal mining in this area and none of the mining was positioned to affect the water quality of the samples. Surface rocks and sediments were much lower in metal concentrations than those at Summitville, indicating less mineralization apparent in outcrops compared to Summitville.

### 4.1.4. Redcloud and Wetterhorn Peaks area

Redcloud Peak and Wetterhorn Peak are west to southwest of Lake City, CO, mostly within the Lake City caldera. McHugh et al. (1995) collected 33 water samples and Nordstrom and Ball (1980–82, unpublished data) collected 8 water samples (from Matterhorn Creek). No indication of mining could be found in any these drainages. Table 3 presents these results for selected constituents of interest.

## 4.2. Geneva Creek, Colorado, USA

The Geneva Creek area, in central Colorado's mineral belt about 75 km west-southwest of Denver, is underlain by Precambrian metamorphic and igneous rocks often containing substantial pyrite. In 1979, 32 water samples were collected and analyzed from

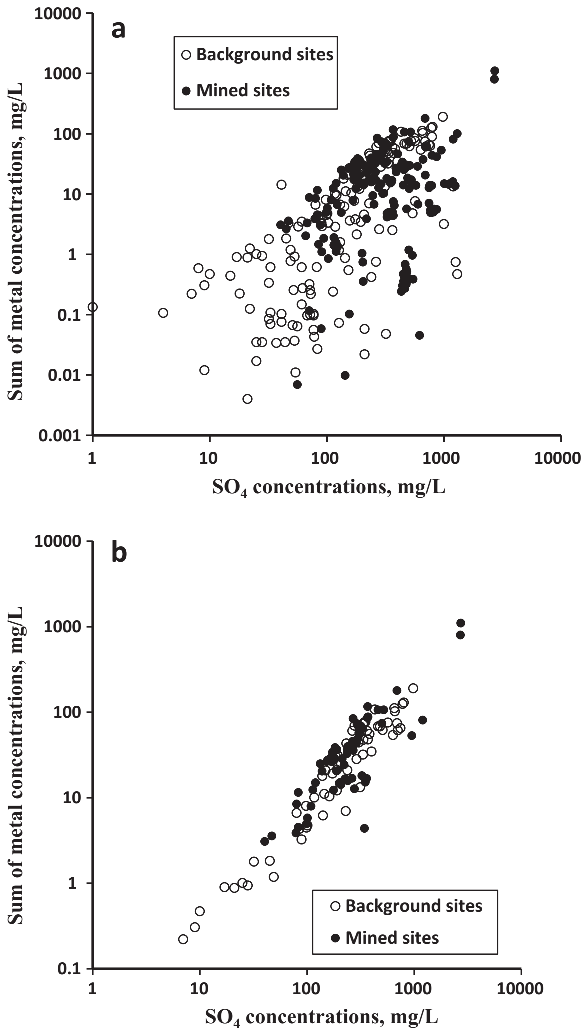

**Fig. 3.** **a.** Sum of metal concentrations for Al, Fe, Mn, Cu, Pb, and Zn plotted against $SO_4$ concentrations for water samples collected from the Animas River Basin, CO (data from Mast et al., 2007). Data only incudes those locations most clearly identified as not influenced by mining (background) or influenced by mining (mined). **b.** Same plot with all data points removed in which the calcium molarity makes up more than 60% of the $SO_4$ molarity.

areas unaffected by mining activities (McHugh et al., 1988). Water-quality results are shown in Table 3.

Bassett et al. (1992) used the data from Table 3 (less the trace metals) as a basis to calculate mass balances, using the inverse modeling approach (Konikow and Glynn, 2005; Plummer, 1984; Plummer and Back, 1980; Plummer et al., 1983), combined with saturation index calculations (Nordstrom and Munoz, 1994) and some assumed constraints on mineral precipitation reactions. Their results produced a 'most likely' reaction pathway for the chemical evolution of the water from snowmelt to the composition of Geneva Creek, shown in Table 4. Nearly a millmole of pyrite per kilogram of water could be oxidized along with dissolution of calcite, hornblende, biotite, sericite, plagioclase, and kaolinite. Precipitation of an iron oxide phase and a silica phase along with carbon dioxide loss was necessary for the mass balance model. They caution that there are actually several possible reaction model pathways.

These mineral mass transfer results are fairly typical for weathering of pyrite mineralized rock in the absence of mining activities. A large quantity of pyrite dissolves and most of the iron precipitates as hydrous iron oxides, silica dissolves in acid waters from kaolinite, feldspar, mica, and hornblende and most of it must precipitate as some form of silica, and if carbonates are present they dissolve to contribute divalent cations with a loss of $CO_2$.

### *4.3. Rocky Mountain sites, Colorado, USA*

In addition to summarizing data from the upper Animas River basin (data of Mast et al., 2007), Verplanck et al. (2009) documented three other sites of NARD in the Rocky Mountains of Colorado – Handcart Gulch, East Alpine Gulch, and Mount Emmons. These sites differ somewhat in geologic terrain but all have Tertiary porphyritic intrusions and the associated hydrothermal alteration. The Mount Emmons site is Redwell Basin which is mentioned below as a site where synoptic sampling with tracer-injection and reactive-transport modeling was obtained and mining-affected inflows were subtracted to simulate NARD. Data from Handcart Gulch and East Alpine Gulch are summarized in Table 3. Verplanck et al. (2009) compared pH, alkalinity, $SO_4$, Fe, and Zn concentrations for unmined sites of different degrees of hydrothermal alteration (propylitic, propylitic with veins, weak sericitic, and QSP [quartz–sericite–pyrite]) with those of mined sites by using box-and-whisker plots. There was substantial overlap between mined and unmined sites for all parameters but some indication of higher Zn concentrations for mined sites. In their plot of Cu with Zn concentrations reproduced here in Fig. 5, there is some separation of water chemistry from mineralized and unmined sites compared to mined sites. Certainly the highest concentrations are consistently from mined sites.

Water-chemistry data for Colorado streams from the early 1970's (Wentz, 1974a,b) might prove useful for comparison of water quality conditions today to document changes over decadal time periods.

### *4.4. Red River Valley, New Mexico, USA*

The USGS investigated acid groundwater systems in the Red River Valley in northern New Mexico as analogies to pre-mining groundwater conditions for the Questa molybdenum mine (Nordstrom, 2008). Most of the mineralized bedrock is hydrothermally altered Tertiary andesitic or rhyolitic volcanic rocks. Several small catchments contain NARD as both surface water and groundwater in poorly sorted debris fans that contain everything from clays to boulders. Quartz–sericite–pyrite (QSP) alteration is common and weathering of this rock produces surface waters with pH of 2.4–4.4 and groundwaters with pH of 2.99–4.0. Water-quality statistics for NARD of surface waters and groundwaters are shown in Table 5.

An inverse model was developed for median Straight Creek surface water (Nordstrom, 2008) much in the same manner as that for Geneva Creek. Two models were reported (Table 4) which seemed to be mutually exclusive, one that described the high Mg concentration as derived from chlorite dissolution and the other from hydrothermal dolomite dissolution. Both mineral sources are the most likely sources of Mg although dolomite would be more likely as a dominant source. Again, pyrite dissolution and goethite and silica precipitation dominate the mass transfer processes along with gypsum dissolution, which was lacking at Geneva Creek.

Groundwaters in the Red River Valley were either in debris fans and typically acidic or in crystalline bedrock and circumneutral in pH but contained high concentrations of $SO_4$ and Ca, and occasionally elevated concentrations of Fe, Mn, and Zn. The bedrock consists of all Tertiary volcanic rocks, either rhyolitic or andesitic and altered to various degrees but dissolved oxygen measurements indicated that the groundwater was anoxic. The range of groundwater compositions for debris-fan groundwaters (**DGW**) and bedrock groundwaters (**BGW**) are summarized in Table 5.

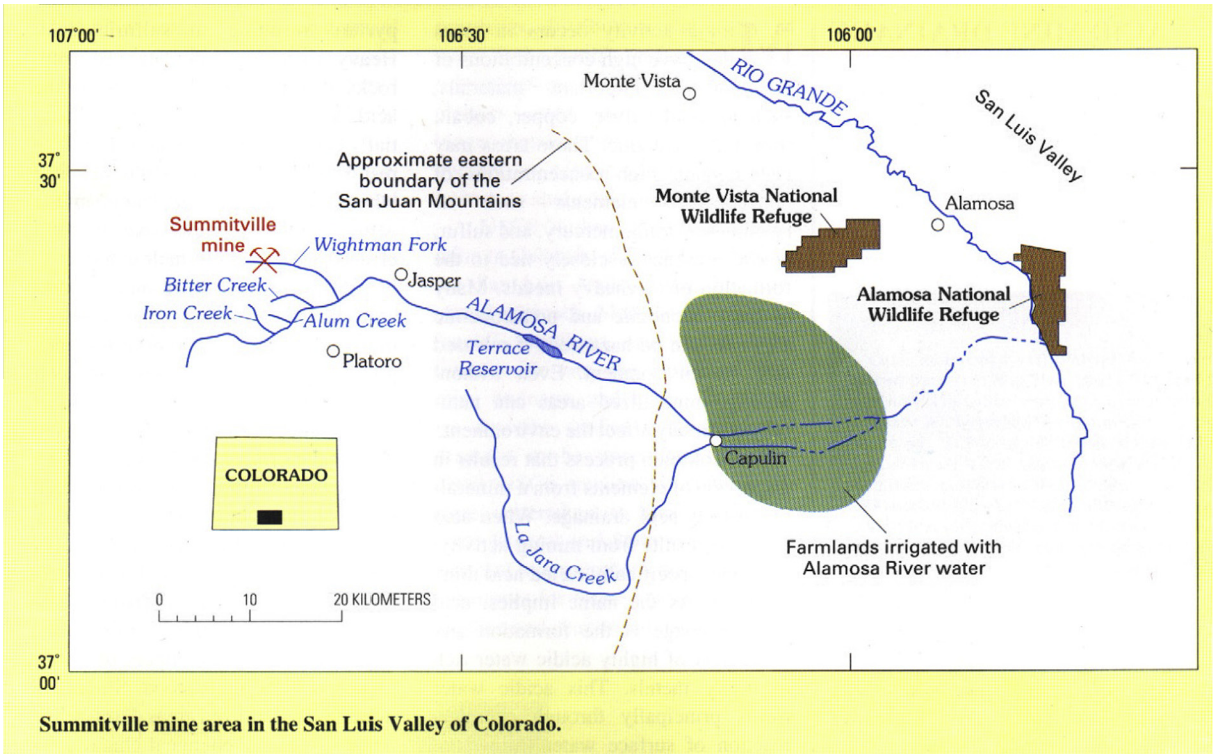

**Fig. 4.** Location of the Summitville mine relative to the Alamosa River, the San Luis Valley, and Terrace Reservoir. Along the Upper Alamosa River (above Wightman Fork inflow) several creek names indicate NARD such as Iron Creek, Alum Creek, and Bitter Creek. Cropsy Creek is located under the pick and hammer symbol designating the mine site.

**Table 3**
Background water-quality statistics of samples from Colorado, continued (**RW,** Redcloud Peak and Wetterhorn Peak, McHugh et al., 1995 and Nordstrom and Ball, unpublished data; **GC,** Geneva Creek, McHugh et al., 1988; **HC,** Handcart Gulch, Verplanck et al., 2009; **EA** East Alpine Gulch, Verplanck et al., 2009); SC, specific conductance; alkalinity as $CaCO_3$; –, not reported.

| Solute (mg/L) | **RW** minimum | **RW** median | **RW** maximum | **GC** minimum | **GC** median | **GC** maximum | **HC** Range | **EA** Range |
|---|---|---|---|---|---|---|---|---|
| SC (μS/cm) | 47 | 119 | 1,360 | 46 | 160 | 830 | – | – |
| pH | 3.29 | 7 | 7.92 | 3.10 | 4.64 | 7.30 | 2.69–6.77 | 3.15–7.83 |
| Alkalinity | <1 | 18 | 179 | <1 | <1 | 37 | – | – |
| $SO_4$ | 6.9 | 34 | 176 | 5.7 | 50 | 370 | 31–1010 | 6.6–3.23 |
| F | 0.05 | 0.16 | 1.08 | 0.05 | 0.30 | 3.10 | – | – |
| Ca | 6.3 | 15 | 85 | 2.0 | 6.5 | 17.8 | – | – |
| Mg | 0.5 | 1.8 | 10 | 0.59 | 2.3 | 10.1 | – | – |
| Na | 0.4 | 1.2 | 26 | 0.68 | 1.36 | 2.20 | – | – |
| K | 0.3 | 0.8 | 4.5 | 0.37 | 0.95 | 3.15 | – | – |
| $SiO_2$ | 3 | 9 | 29 | 4.2 | 13.0 | 38.0 | – | – |
| Al | <0.1 | <0.1 | 11.8 | 0.005 | 2.70 | 29.6 | – | – |
| As | <0.001 | <0.001 | 0.011 | <0.001 | <0.001 | 0.072 | – | – |
| Cu | <0.001 | <0.001 | 0.025 | <0.001 | 0.042 | 0.360 | <0.001–23 | <0.01 |
| Fe | 0.12 | 3.1 | 141 | 0.006 | 0.30 | 68.0 | – | – |
| Pb | – | – | – | – | – | – | – | – |
| Mn | <0.01 | <0.01 | 2 | 0.001 | 1.00 | 5.50 | – | – |
| Ni | – | – | – | – | – | – | – | – |
| Zn | <0.005 | 0.026 | 0.280 | <0.002 | 0.360 | 4.80 | 0.03–0.59 | <0.01–0.210 |

### *4.5. Robinson district, Ely, Nevada, USA*

The Robinson mining district consists of Paleozoic sedimentary rocks intruded by late Cretaceous to early Tertiary plutons near Ely, Nevada. Gold mineralization was the main target of mining. Davis and Newcomb (1998) used cluster analysis on the chemical composition of mining-affected and natural groundwater samples and were able to show that trace elements gave chemical signatures of these sources. Natural groundwaters were low in $SO_4$ concentrations and, consequently, had higher Ba concentrations than mining-affected groundwaters. Waste-rock seeps were distinguished by high scandium concentrations and pit lakes contained high rhenium and rubidium concentrations.

### *4.6. Phoenix mine, Copper Canyon district, Battle Mountain, Nevada, USA*

A study of mining-affected and natural groundwaters in and around the Phoenix mine discovered a strongly mineralized groundwater that appeared unaffected by mining (Davis et al., 2010). The district is located in the Basin and Range Province of the western US and consists of Paleozic sedimentary and volcanic

**Table 4**
Mineral mass transfer results for natural acid sulfate weathering at Geneva Creek (**GC,** Bassett et al., 1992) and at Straight Creek, New Mexico (**SC,** Nordstrom, 2008). Positive values denote dissolution, negative values denote precipitation or loss of gas from solution.

| Mineral or gas | **GC,** mass transfer, mmol/kg$_{H2O}$ | **SC,** mass transfer mmol/kg$_{H2O}$ – chlorite model | **SC,** mass transfer, mmol/kg$_{H2O}$ – dolomite model |
|---|---|---|---|
| Pyrite | 0.955 | 6.21 | 8.66 |
| Calcite | 0.157 | – | – |
| Dolomite | – | – | 4.64 |
| Chlorite | – | 0.93 | – |
| Gypsum | – | 8.51 | 3.78 |
| Hornblende | 0.0788 | – | – |
| Biotite/vermiculite | 0.0388 | – | – |
| Illite/Sericite ($K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}[OH]_2$) | – | 0.032 | 0.032 |
| Plagioclase ($An_{20}$) | 0.108 | 0.44 | 0.44 |
| Kaolinite | 0.159 | 0.47 | 1.40 |
| Sphalerite | – | 0.11 | 0.11 |
| Chalcopyrite | – | 0.029 | 0.029 |
| Fluorite | – | 0.20 | 0.20 |
| $CO_2$ | −0.157 | – | −9.26 |
| Goethite | −0.975 | −5.08 | −7.40 |
| $SiO_2$ | −0.869 | −3.82 | −2.89 |

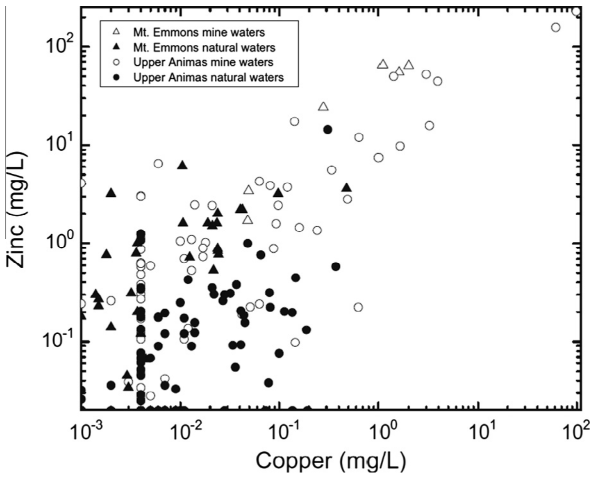

**Fig. 5.** Comparison of dissolved Zn and Cu concentration of surface waters from mines and natural springs and headwater streams in porphyry mineralized areas in the Upper Animas River and Mount Emmons study areas (Verplanck et al., 2009).

rocks intruded by quartz monzonite with consequent hydrothermal alteration and mineralization. The example well-water composition unaffected by mining is shown in Table 6.

### 4.7. Coeur d'Alene, Idaho, USA

The Coeur d'Alene mining district in northern Idaho is a site of hydrothermal mineralization of Precambrian quartzites and argillites related to the intrusion of two monzonite stocks during the Laramide orogeny (roughly 35–80 million years ago). Major ore zones carrying Pb, Ag, Zn were formed with lesser amounts of Au, Cu, As, and Sb. In the 1980's CERCLA had been initiated and by the 1990's mining had come to an end. A Natural Resource Damage Assessment was completed in 2000 (Stratus Consulting, Inc., 2000) which included estimates of soil, sediment, and water quality baselines. The baselines were developed from natural analogs, i.e., drainages that had similar geology, mineralization, and hydrology to mining-affected drainages. The water chemistry results were compiled in terms of medians, 25th percentiles and 75th percentiles for cadmium, lead, and zinc. The comparisons between baseline concentrations and mining-affected concentrations are shown in Table 7. They show between one and two-and-a-half orders magnitude greater concentrations for the mining-affected concentrations.

### 4.8. Wulik River basin, Alaska, USA

The Red Dog, Drenchwater, and Su-Lik deposits in the Wulik River basin southeast of Point Hope, AK, consists of massive sulfides in Mississippian to Pennsylvanian black shale in a thrust sheet containing zinc–lead–silver ore (Moore et al., 1986). A 16-month environmental baseline study was done before mining began on the Red Dog deposit (Dames and Moore, 1983). The lowest pH (2.8) and highest metal concentrations were found for Red Dog Creek near the headwaters. It should be noted, however, that the vast majority of surface waters and springs sampled in the district were of circumneutral pH. Only one sample indicated substantial acidity. For Drenchwater and Su-Lik, samples were collected by the USGS (Kelley and Taylor (1997) before mining with the lowest pH 2.8 and highest sulfate 1180 mg/L being found at Drenchwater. The pH range in the Su-Lik area was 6.2–8.3 because sufficient carbonates were present to neutralize the acidity but zinc and cadmium concentrations were similar regardless of pH. Graham and Kelley (2009) revisited the area and found naturally acidic drainage from a previously unsampled site, False Wager Creek. Concentrations, conductance, and pH are tabulated in Table 8 for the lowest pH samples found in these areas.

### 4.9. Red Mountain, Alaska Range, Alaska, USA

Exploration in the Alaska Range has revealed several massive or semi-massive sulfide deposits which have been exposed at the surface, giving rise to NARD because no mining had occurred when investigations began. Data collected from a massive sulfide in the Bonnifield district at Red Mountain found acid waters with substantial concentrations of metals. The host rocks are felsic metavolcanic rocks which have undergone extensive quartz–sericite–pyrite hydrothermal alteration. The deposit is classified as volcanogenic massive sulfide (VMS, Eppinger et al., 2007). About 40 water samples were collected from 33 sites and their range of composition is shown in Table 8.

### 4.10. Bathurst Mining Camp, New Brunswick, Canada

A detailed hydrochemical study at two undisturbed Ordovician massive sulfide (Zn–Pb) deposits at Bathurst Mining Camp found evidence for sulfide oxidation and mixing with saline water at one of the sites (Leybourne et al., 1998). The presence of saline water and the relatively low sulfate concentrations indicate there may not be much of a hydraulic gradient and/or there is a layer

**Table 5**

Background water-quality data from Red River Valley, New Mexico (Surface waters, **SW**: Nordstrom et al., 2005; Verplanck et al., 2006; Nordstrom, 2008; Debris-fan groundwaters, **DGW**: Naus et al., 2005; Nordstrom et al., 2005; Nordstrom, 2008; **BGW**, Bedrock groundwaters: Nordstrom, 2008; –, not detected).

| Solute (mg/L) | **SW** minimum | **SW** median | **SW** maximum | **DGW** minimum | **DGW** median | **DGW** maximum | **BGW** Range |
|---|---|---|---|---|---|---|---|
| SC (μS/cm) | 343 | 3085 | 10,480 | 1170 | 2375 | 2960 | 2480–3300 |
| pH | 2.44 | 2.98 | 7.71 | 2.99 | 3.45 | 4.04 | 5.88–7.52 |
| Alkalinity | 0.0 | 0.0 | 213 | – | – | – | – |
| $SO_4$ | 150 | 2030 | 13,500 | 653 | 1600 | 2180 | 1400–1920 |
| F | 0.506 | 7.71 | 28 | 2.49 | 3.24 | 10.1 | 0.74–6.58 |
| Ca | 19.8 | 349 | 540 | 76.8 | 296 | 469 | 481–548 |
| Mg | 10.0 | 113 | 920 | 36.1 | 61.4 | 138 | 37.4–215 |
| Na | 1.25 | 8.08 | 23.5 | 6.90 | 17.4 | 27.8 | 33–62.4 |
| K | 0.027 | 0.753 | 7.00 | 0.534 | 2.82 | 4.42 | 2.92–11.2 |
| $SiO_2$ | 6.7 | 74.2 | 112 | 50.0 | 76.3 | 103 | 18.1–25.4 |
| Al | <0.08 | 91.5 | 1300 | 38.3 | 52.0 | 104 | 0.004–5.38 |
| As | <0.0001 | 0.001 | 0.340 | <0.0001 | <0.0001 | 0.047 | <0.0001–0.002 |
| Ba | <0.0008 | 0.040 | 0.125 | <0.0008 | 0.005 | 0.025 | <0.0008–0.034 |
| Be | <0.00002 | 0.0005 | 0.350 | <0.001 | 0.011 | 0.030 | <0.001–0.041 |
| Cd | <0.00004 | 0.039 | 0.52 | <0.0002 | 0.012 | 0.054 | <0.0002–0.005 |
| Co | 0.00008 | 0.325 | 4.20 | 0.077 | 0.252 | 0.378 | <0.0007–0.323 |
| Cr | <0.00001 | <0.015 | 0.490 | <0.001 | <0.001 | 0.013 | <0.0005–0.008 |
| Cu | 0.0055 | 1.87 | 2.72 | 0.056 | 0.215 | 1.10 | <0.0005 |
| Fe | 0.010 | 65 | 540 | 0.042 | 21.2 | 93.4 | 0.468–58.9 |
| Pb | 0.000037 | 0.012 | 0.063 | <0.0003 | <0.0003 | 0.018 | <0.0003–0.011 |
| Li | <0.006 | <0.006 | 0.043 | 0.042 | 0.071 | 0.369 | 0.040–0.374 |
| Mn | <0.001 | 2.8 | 530 | 4.29 | 14.1 | 21.2 | 2.68–6.07 |
| Mo | <0.0005 | <0.007 | 0.210 | <0.007 | <0.007 | 0.018 | <0.007–0.024 |
| Ni | 0.0011 | 0.727 | 8.60 | 0.180 | 0.345 | 0.890 | 0.0012–0.430 |
| Sr | 0.006 | 0.236 | 5.70 | 0.006 | 0.236 | 5.70 | 1.15–11.9 |
| V | <0.000022 | <0.002 | 0.011 | <0.002 | <0.002 | 0.003 | <0.002–0.003 |
| Zn | 0.019 | 7.63 | 120 | 1.72 | 3.59 | 7.79 | <0.005–4.57 |

**Table 6**

Chemical composition of natural groundwater near the Phoenix mine, Nevada (Davis et al., 2010); groundwaters adjacent to an equatorial copper mine, undisclosed location (Davis, 2003); groundwaters near a porphyry copper mineral deposit, Atacama Desert, Chile (Leybourne and Cameron, 2006, 2008); and surface water in Arroyo del Val, Spain (**SW**, Gimeno, 1999); –, not reported.

| Constituent mg/L | Phoenix-F well | Equatorial | Porphyry, Chile | **SW**, Minimum | **SW**, Median | **SW**, Maximum |
|---|---|---|---|---|---|---|
| SC, μS/cm | | 150–430 | 1320–89,800 | 498 | 686 | 1800 |
| pH | 4.2 | 3.6–7.7 | 4.73–9.22 | 2.50 | 4.55 | 8.54 |
| $HCO_3$ | – | – | 29.6–629 | 0.0 | – | 106 |
| Cl | 35 | 10–13 | 47.0–80,500 | 1.6 | 6.0 | 22.0 |
| $SO_4$ | 2010 | 42–150 | 410–10,000 | 19 | 199 | 835 |
| F | 2.88 | – | – | 0.19 | 0.50 | 0.77 |
| Ca | 300 | 5–23 | 25–4020 | 15.2 | 26.7 | 54.0 |
| Mg | 202 | 2.2–17 | 2.7–1953 | 18.5 | 22.3 | 42.9 |
| Na | 119 | 11–21 | 165–53,000 | 8.0 | 10.0 | 19.0 |
| K | 8.3 | – | 12.6–718 | 1.0 | 1.5 | 2.5 |
| $SiO_2$ | – | – | – | 9.0 | 27.1 | 93.7 |
| Al | 25.9 | 0.4–3.6 | 0.020–0.860 | 0.1 | 1.5 | 14.8 |
| As | 0.0136 | <0.001–0.002 | <0.010–0.278 | – | – | – |
| Be | <0.002 | – | – | – | – | – |
| Cd | 0.508 | – | – | – | – | – |
| Cr | <0.006 | – | – | – | – | – |
| Cu | 9.45 | 0.001–0.660 | 0.009–0.564 | 0.01 | 0.02 | 0.07 |
| Fe | <0.06 | 0.02–7.7 | 0.004–54.50 | 0.11 | 0.25 | 5.95 |
| Pb | 0.122 | – | 0.0009–0.0238 | – | – | – |
| Mn | 2.98 | 0.013–0.390 | 0.001–3.95 | 0.02 | 0.84 | 2.13 |
| Ni | 0.999 | <0.002–0.008 | – | – | – | – |
| Se | 0.027 | – | 0.0021–0.797 | – | – | – |
| Zn | 10.6 | 0.006–0.191 | 0.005–0.131 | 0.05 | 0.62 | 1.67 |

**Table 7**

Median concentrations in μg/L for baseline and mining-affected surface waters (Stratus Consulting Inc., 2000).

| Area | Cd, baseline | Cd, mining-affected | Pb, baseline | Pb, mining-affected | Zn, baseline | Zn, mining-affected |
|---|---|---|---|---|---|---|
| Upper South Fork | 0.06 | 1.17 | 0.15 | 7.00 | 5.35 | 170 |
| Page-Galena Mineral Belt | 0.10 | 8.12 | 0.44 | 10.9 | 9.04 | 1,080 |
| Pine Creek drainage | 0.03 | 3.09 | 0.11 | 2.77 | 3.68 | 1,140 |
| Entire South Fork Coeur d'Alene Basin | 0.06 | 3.75 | 0.18 | 7.17 | 6.75 | 769 |

**Table 8**
Background water-quality data from Alaska (Dames and Moore, 1983; Kelley and Taylor, 1997; Graham and Kelley, 2009; Eppinger et al., 2007).

| Constituent (mg/L) | Red Dog | Drenchwater | Su-Lik | False Wager | Red Mountain |
|---|---|---|---|---|---|
| SC, µS/cm | – | 2150 | 210 | 980 | 515–4800 |
| pH | 2.8 | 2.8 | 6.2 | 3.2 | 2.39–7.8 |
| $SO_4$ | – | 1180 | 127 | 480 | 91–5600 |
| F | – | 0.52 | 0.19 | 0.28 | 0.1–80 |
| Ca | – | 21 | 27 | 23 | 32–190 |
| Mg | – | 5 | 4 | 8 | 12–340 |
| Na | – | 1 | 2 | 2 | 0.45–6.3 |
| K | – | 9 | <1 | 3 | 0.65–5.8 |
| $SiO_2$ | – | 4.3 | 17 | – | <0.2–64 |
| Al | – | 53 | 0.2 | 31 | 0.0003–300 |
| As | – | 0.026 | – | 0.0055 | <0.0002–0.0068 |
| Cd | 0.802 | 0.006 | 0.005 | 0.0078 | <0.00002–0.800 |
| Co | – | 0.048 | <0.003 | 0.0044 | <0.00002–1.00 |
| Cr | – | – | – | 0.059 | <0.001–0.015 |
| Cu | – | 0.260 | <0.010 | 0.120 | <0.0005–0.135 |
| Fe | – | 270 | 27 | 87.0 | <0.020–400 |
| Pb | 2.25 | 0.009 | <0.010 | 0.0025 | <0.00005–0.540 |
| Mn | – | 2.20 | 0.33 | – | <0.1–42 |
| Ni | – | 0.290 | 0.051 | 0.250 | <0.00005–0.540 |
| Se | – | – | – | – | <0.0002–0.056 |
| Sr | – | 0.090 | 0.22 | – | – |
| Zn | 272 | 2.00 | 2.00 | 2.60 | 0.001–280 |

**Table 9**
Range of groundwater compositions for sites in Canada. Halfmile Lake and Restigouche Sites at Bathurst Mining Camp. New Brunswick (**NB**, Leybourne et al., 1998 and Leybourne et al., 2002), Macintosh Creek, Yukon (**MC**, Kwong et al., 2009) and Colour Lake, Northwest Territories (**CL** Allan, 1986; Johannesson and Lyons, 1995; Johannesson and Zhou, 1999); –, not reported.

| Constituent (mg/L) | **NB** Range | **MC** Minimum | **MC** Median | **MC** Maximum | **CL** Minimum | **CL** Median | **CL** Maximum |
|---|---|---|---|---|---|---|---|
| SC, µS/cm | 15–41,600 | 91 | 580 | 770 | – | – | – |
| pH, standard units | 5.43–9.86 | 3.0 | 3.2 | 3.8 | 3.6 | 3.6 | 4.7[*] |
| $SO_4$ | 0.05–87 | 13 | 320 | 1600 | 206 | 270 | 354 |
| Ca | 0.36–790 | 1.4 | 4.7 | 19 | 41 | 58 | 102 |
| Mg | 0.121–320 | 0.97 | 7.2 | 30 | 11 | 15 | 18 |
| Na | 0.05–6200 | 0.25 | 0.45 | 0.63 | 7.1 | 7.8 | 9.0 |
| K | 0.073–19 | 0.40 | 1.3 | 12 | 2.7 | 4.7 | 7.4 |
| $SiO_2$ | 2.35–14.5 | 13 | 21 | 39 | 5.7 | 15 | 7.1 |
| Al | 0.0013–0.281 | 13 | 21 | 39 | – | 6.7 | – |
| As | 0.001–0.110 | 5.4 | 39 | 160 | – | – | – |
| Cd | 0.0005–0.006 | 0.009 | 0.036 | 0.13 | – | – | – |
| Co | 0.0002–0.0025 | 0.03 | 0.07 | 0.25 | – | – | – |
| Cu | 0.0005–0.012 | 0.002 | 0.23 | 0.69 | – | – | – |
| Fe | 0.003–1.6 | 0.11 | 29 | 300 | 0.35 | 0.49 | 15.1[*] |
| Mn | 0.005–0.580 | 0.04 | 0.27 | 1.1 | – | – | – |
| Mo | 0.0005–0.019 | – | – | – | – | – | – |
| Ni | 0.001–0.026 | 0.08 | 0.61 | 2.5 | – | – | – |
| Pb | 0.0002–0.530 | – | – | – | – | – | – |
| Zn | 0.002–2.30 | 0.12 | 1.5 | 5.0 | – | – | – |

[*] Fe concentration probably higher; loss occurred by oxidation during processing of sample.

protecting or reducing the amount of oxygen reacting with the sulfides combined with carbonates available for neutralization. Although the host rocks are similar to those in the Alaska Range, mostly felsic metavolcanics, these are groundwaters instead of surface waters and both the geology and mineralogy indicate limited throughput of oxygenated waters. Groundwater compositions shown in Table 9 are based on Leybourne et al. (1998, 2002). The dilute waters are from Halfmile Lake and the brackish to saline waters are from Restigouche.

### *4.11. Macintosh Creek, McMillan Pass, Yukon, Canada*

Located in easternmost Yukon, next to the border with the Northwest Territories, the Macmillan Pass area includes upper to middle Devonian black shale (Lower Earn Group) which produces acid water in the drainage where it crops out. Kwong et al. (2009) collected water samples in 1990 and 1991 and reported that acid waters were found in Macintosh Creek where no mining had occurred. They found any specific metal concentration to vary substantially depending on location along the creek. The water-quality data are shown in Table 9. Additional water samples from mineralized, unmined areas in the Yukon were collected from Engineer Creek and the Clear Lake Prospect but the analyses were not reported.

### *4.12. Colour Lake, Axel Heiberg Island, Northwest Territories, Canada*

During the spring snowmelt periods of 1983–85, the effect of snowmelt on the chemistry of Colour Lake in the high Arctic was monitored (Allan, 1986). This acidic lake was diluted substantially from annual snowmelt but otherwise maintains pH values of 3.6 (Johannesson and Lyons, 1995). The bedrock consists of considerable amounts of siltstones and marine and non-marine shales with some interbedded coal. It is not clear where the major inflow of acidic water originates because surface inflows are mostly circum-neutral pH with Gordon Creek, pH = 3.93 being the only exception

(Johannesson and Zhou, 1999) but the bedrock provides an adequate source of pyrite available for oxidation. Water-quality statistics from Johannesson and Lyons (1995) are shown in Table 9.

### 4.13. Pfister Joch, Austria

A stream named Rötlbach near the Pfitscher Joch in the Zillertaler Alpes of Austria contains the characteristic orange to red iron staining similar to ARD but it is NARD (Schwertmann et al., 1995). Rötlbach begins as a spring that drains schist in the Penninikum zone containing about 5% pyrite. A water analysis was not obtained but the pH was measured and found to be 2.3. The mineral schwertmannite was identified as a major component of the iron precipitate.

### 4.14. Arroyo del Val, north-central Spain

The Arroyo del Val, located in north-central Spain, southeast from Zaragoza, flows through a Silurian black shale (Bádenas Formation) and becomes acidic from pyrite oxidation with pH values near the headwaters as low as 2.5 (Auqué et al., 1993; Auqué et al., 1994; Gimeno, 1999). Chemical analyses are shown in Table 6.

### 4.15. Undisturbed Spence porphyry copper in Atacama Desert, Chile

During mineral exploration, an economic Cu porphyry deposit was discovered in the Atacama Desert by drilling and groundwater samples were collected from drillholes (Leybourne and Cameron, 2006, 2008). These groundwaters are mostly saline or brines and range in pH from 4.73 to 9.22. The range of concentration for both major and trace constituents are shown in Table 6.

### 4.16. Equatorial copper mine

The composition of several naturally mineralized seeps and springs were reported as part of a study to predict pit lake chemistry on closure of an equatorial copper mine (Davis, 2003). The copper ore minerals, primarily chalcopyrite and bornite, are found in a tonalite intrusive complex with diorite and andesite wallrock. The seeps and springs samples were collected before the area was mined. The range of compositions is summarized here in Table 6.

**Table 10**
Chemical composition of a natural proximal analog in the Red Mountain Creek basin, Colorado (**RM**, Runkel et al., 2007), a simulated water chemistry for Redwell Basin, Colorado (**RW**, Kimball et al., 2010), and Paymaster Creek chemistry, a stream unaffected by mining in the Heddleston mining district, Montana (**PC**, Nimick et al., 2009).

| Constituent (mg/L) | **RM** | **RW** | **PC** |
|---|---|---|---|
| pH | 3.08 | 5.12 | 3.44–4.04 |
| Cl | – | – | 0.464-0.531 |
| $SO_4$ | 315 | 25 | 42.8-72.2 |
| Ca | – | 7.7 | 3.70–5.00 |
| Mg | – | 1.23 | 3.23–3.73 |
| Na | – | – | 1.29–1.64 |
| K | – | – | 0.939–2.30 |
| Al | 29 | 0.140 | 1.46–2.45 |
| As | 0.00001 | – | – |
| Cd | 0.005 | 0.0085 | – |
| Cu | 1.6 | 0.0018 | <0.003–0.008 |
| Fe | 5 | 0.361 | 1.04–8.65 |
| Pb | 0.303 | 0.207 | – |
| Mn | – | 0.383 | 0.147–0.357 |
| Zn | 1.2 | 1.32 | 0.058–0.086 |

## 5. Pre-mining metal concentrations in streams from reactive-transport simulations by removal of mining influences

Kimball et al. (2006) pointed out three important steps in a process that could lead to responsible science-based decisions for remediation of mining-affected drainages: (1) determine metal sources and quantify loadings in a catchment to enable a ranking in terms of effects, (2) distinguish between natural and anthropogenic sources, and (3) optimize treatment alternatives for anthropogenic sources to achieve remediation goals. Determining metal sources and quantifying loads has been successful in a couple of dozen catchments in the western US (e.g. Kimball et al., 1999, 2007; Kimball and Runkel, 2007; Kimball et al., 2002, 2006). Distinguishing anthropogenic from natural sources can be challenging but it has been applied in at least two catchments in Colorado with reactive-transport modeling: Red Mountain Creek and Redwell Basin.

### 5.1. Red Mountain Creek, Colorado, USA

Red Mountain Creek drains the western part of Red Mountains #1, #2, and #3, south of Ouray, in the San Juan Mountains of Colorado. The rocks are hydrothermally altered rhyolitic and latitic flows, flow breccias, and pyroclastics. The upper 5.4 km of Red Mountain Creek was investigated by using tracer injection combined with synoptic sampling to obtain a spatially-detailed profile of concentrations, streamflows, and solute loads (Runkel et al., 2007). All possible inflows to the stream were sampled and their discharges measured. A reactive-transport model was developed for the reach using the OTEQ code (Runkel, 2010), which uses one-dimensional transport with equilibrium chemistry by combining the OTIS code (Runkel, 1998) with the MINTEQA2 speciation code (Allison et al., 1991).

During the study a tributary unaffected by mining, another natural analog, was found and its chemistry is tabulated in Table 10 to compare with other natural analog sites. This chemistry was used to substitute for inflows that were clearly mining related.

A calibration procedure was used to optimize the match between stream-water chemistry and modeled chemistry that included modification of the arsenic concentration at the upstream boundary condition and changing iron, arsenic, and sulfate concentrations of all inflows to account for inflows that could not be sampled.

The results from this study showed that pH values would be higher and metal concentrations lower under pre-mining conditions than those that exist today. The difference between pre-mining and current water chemistry varied considerably depending on the chemical element being considered. The pH increased by slightly more than a full pH unit and iron concentrations decreased by three orders of magnitude. However, most other metals decreased by less than an order of magnitude in concentration. One anomaly was the lead concentration data which were actually unchanged. The cause of the results for lead is the fact that the lead concentration at the proximal analog site is as high or higher than that for the mining-related inflows. The opinion was that the simulated lead concentrations were not representative of pre-mining conditions and further investigations were warranted.

### 5.2. Redwell Basin, Colorado, USA

Located in south-central Colorado, Redwell Basin contains metamorphosed Cretaceous marine shale intruded by a molybdenum-bearing granite porphyry of mid-Tertiary age (Thomas and Galey, 1982). Mineralization occurs within and beneath a rhyolitic breccia that rises above the granitic stock. A high-elevation, high-gradient stream drains the basin and only two inflows are identified as affected by mining. Consequently synoptic sampling with tracer-injection provides a relatively straightforward opportunity to apply reactive-transport modeling and subtract the loading of the two inflows. This analysis was achieved using the OTEQ code and resulted in pre-mining concentrations at a point in the stream about a kilometer downstream from the mining-affected inflows that are listed in Table 10 (Kimball et al., 2010). In-stream processes such as mineral precipitation and trace metal sorption were included in the simulation.

## 6. Pre-mining conditions averaged from Cu and Zn weathering and dating:Iron Mountain, California

Iron Mountain, located near Redding in northern California, hosts a group of mines that were active from the late 1870s to the early 1960s. The mineral deposit is classified as a type-I volcanogenic massive sulfide, similar to the Noranda deposit of Ontario, Canada. Three large, isolated blocks of sulfide mineralization contain 90–95% pyrite and a few percent chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) (Kinkel et al., 1956). Prior to mining, weathering converted parts of the massive sulfide to gossan consisting of hematite, goethite, and silica. Mining further exposed the pyritic masses to water and air, creating optimal conditions for sulfide oxidation and production of acid mine drainage. Because the acidic, metal-rich effluent reached the Sacramento River, the site has been one of the highest priorities on the US EPA's Superfund list since the early 1980s. A crucial area of scientific uncertainty that needed to be resolved was the magnitude of natural background metal flux. Paleomagnetic samples from the gossan were collected to determine the polarity of the Earth's magnetic field during pre-mining sulfide weathering (Alpers et al., 1999, 2007). Nineteen samples exhibited stable magnetic endpoints during thermal demagnetization; of these, four were of reversed polarity and the rest were of normal polarity. This result established that the gossan was already forming 780,000 years ago, and this information made it possible to estimate natural, pre- mining flux rates of Cu and Zn. Based on a minimum age of 780,000 years for the onset of gossan formation, pre-mining fluxes of Cu (1.1–3 wt.%) and Zn (1.3–3.5 wt.%) were estimated as 85–1000 kg per year for Cu and 100–1200 kg per year for Zn. The range of these estimates reflects uncertainties in both the metal content of the massive sulfide and the original size of the massive sulfide deposit. Post-mining (pre-remediation) fluxes of these metals have been about 45,000 kg per year for Cu and about 280,000 kg per year for Zn based on monitoring by USEPA (1983–2002; also see Alpers et al., 1992). Thus the overall effect of mining was to increase the annual metal loads by 1.5 to 3 orders of magnitude over the natural averaged weathering rate.

## 7. Road construction causing acid rock drainage

### 7.1. Southern Norway

Highway E18 between Grimstad and Kristiansand, southern Norway, constructed in the period 2006–2009, cuts through sulfide-bearing gneisses and granites. Because of the potential for the removed rock to produce acid drainage, it was stored in three separate locations and shell sand ± lime was added to neutralize any acidity. It was either added in the waste pile or in the discharge channel downgradient. One pile had no lime or shell sand mixed in. The mean metal concentrations before highway construction were monitored and could be compared to mean metal concentrations after construction (Hindar and Nordstrom, 2014). This comparison, in Table 11, shows a decrease in pH from 5.9 to 4.5 and substantial increases in Al, Cd, Co, Cu, Mn, Ni, and Zn concentrations. Concentrations of As and Cr did not change, concentrations of Fe decreased, and $SO_4$ concentrations increased considerably from 7.3 to 300–1000 mg/L.

This situation, in which drainages have been monitored before, during, and after highway construction through sulfide-bearing rock, has rarely been done. The mineralization is not economic as an ore deposit but the S content is comparable to some at 2 wt%. The rocks are not processed for metal extraction as an ore deposit would be, no crushing and milling is involved. It can be considered as an intermediate situation between a metal mine site and an undisturbed site. Pre-construction would be the natural undisturbed condition and by comparison the post-construction condition has increased sulfate and some metal concentrations by 1–3 orders of magnitude, similar to the effect of a mine site.

There are several examples of road construction through pyritic rock but often not well documented. In September of 2003, the Pennsylvania Department of Transportation discovered acid seeps and contaminated surface water from exposed rock and excavated pyritic sandstone from construction of Interstate Highway 99 at Skytop along Bald Eagle Mountain. The highway crew had actually

**Table 11**
Mean pH, sulfate, and metal concentrations (mg/L) for drainage waters from before and after highway waste rock was deposited in southeastern Norway (Hindar and Nordstrom, 2014) and water-quality statistics for gravel-pit lakes along Jolosharu esker, Finland (**JE**, Piispanen and Nykyri, 1997).

| Constituent | Pre-construction | Post-construction | **JE**, Minimum | **JE**, Median | **JE**, Maximum |
|---|---|---|---|---|---|
| SC, μS/cm | – | – | 91 | 580 | 770 |
| pH | 5.93 | 4.5 | 3.3 | – | 8.4 |
| $SO_4$ | 7.28 | 600 | 0 | 30 | 126 |
| Ca | – | – | 2.6 | 7.4 | 46.6 |
| Mg | – | – | 1.8 | 4.2 | 30.7 |
| Na | – | – | 1.0 | 4.9 | 6.8 |
| K | – | – | 0.8 | 1.9 | 4.9 |
| $SiO_2$ | – | – | 8.6 | 15 | 31.6 |
| Al | 0.232 | 25 | 0.2 | 0.3 | 2.9 |
| As | 0.00082 | 0.00072 | – | – | – |
| Cd | 0.00012 | 0.008.5 | 0.00001 | 0.00118 | 0.00528 |
| Co | 0.00149 | 0.401 | – | – | – |
| Cr | 0.00082 | 0.00097 | – | – | – |
| Cu | 0.0022 | 0.052 | <0.0001 | 0.0008 | 0.0073 |
| Fe | 1.35 | 0.712 | 0.10 | 0.9 | 4.1 |
| Pb | – | – | 0.01 | 0.09 | 0.19 |
| Mn | 0.058 | 4.47 | <0.1 | 0.4 | 0.9 |
| Ni | 0.0023 | 0.924 | 0.01 | 0.07 | 0.23 |
| Zn | 0.0184 | 1.05 | – | – | – |

exposed an unknown mineral deposit of ore grade. A geochemical investigation by Hammarstrom et al. (2005) explained the phenomenon and reported on the mineralogy, the metal and sulfide content of the sandstone, and the water chemistry of 4 surface drainages. The pH values were all similar, 2.0–2.3, and the sulfate concentrations were higher than many examples of AMD. These results are comparable to AMD not NARD.

### *7.2. Gravel lakes, Joloharu esker, Kiiminki, Finland*

Corrosion of aluminum boats and painful eye irritation for swimmers brought the attention of water-quality problems in several old gravel-pit lakes to Piispanen and Nykyri (1997) who found the source to be oxidation of sulfides in black schists that make up portions of eskers left from the last glaciation. Sulfide concentrations were found to be 1–3% in these schists. The resulting pH values were as low as 3.3 in some of the pit lakes. Water-quality data are summarized in Table 10. It is unclear to what extent the original development of gravel pits may have contributed to the acidification but it seems this situation is intermediate between mining with metal extraction and a natural undisturbed environment.

## 8. Nimick–Gurrieri–Furniss empirical method

An empirical method for estimating pre-mining pH and dissolved Cu concentrations was developed and tested by Nimick et al. (2009). For the method to work, there must be ferricrecte material in the catchment. The method is based on the statistically significant correlation between the pH, or the logarithm of the Cu concentration, and the logarithm of the Fe/Cu ratio in the ferricrete and is expected to vary between different catchments. There are several critical assumptions on which this method relies and most of the assumptions are discussed by Nimick et al. (2009) and found to have only minor effects, supported by laboratory data on sorption, precipitation, and aging studies on hydrous ferric oxides. One assumption not considered is the possible effect of differences in dissolved Fe/Cu ratios because of differences in the proportion of minerals contributing these metals to the water, other factors (such as pH) being constant. Drainages that have multiple upstream sources of Fe and Cu, with different Fe/Cu ratios and different pH values, might make this method untenable. Also, if pH and Fe/Cu ratios of the water are highly variable during the year, the results could be so dispersed as to be untenable. Nevertheless, this method shows promise and should be further tested, especially to define the limits of applicability in terms of Cu concentration and Fe/Cu ratio of ferricretes. One of the creeks studied, Paymaster Creek, was not affected by mining and the range of reported concentrations is reproduced in Table 10.

## 9. Mass fluxes

Metal concentrations are only part of the equation that quantifies field weathering rates. Other factors include the discharge, the surface area of reacting minerals exposed to water pathways, the relative reaction rates, the water sources and pathways, and processes that attenuate solutes such as adsorption, mineral precipitation, biological uptake, cation exchange, and oxidation–reduction. Field weathering rates have been estimated by several different techniques including the use of laboratory mineral dissolution rates, collecting surface drainage and chemistry and normalizing for catchment surface area, and measuring changes in mineral composition over time. These methods do not compare well and the very definition of weathering and weathering rate is not unambiguous.

**Table 12**
Mass fluxes of pyrite weathering compared to abiotic and biotic batch lab studies.

| Location | Rate (mmol $FeS_2$/h) | References |
|---|---|---|
| Lab microbial oxidation | 0.22 | Olson (1991) |
| Lab oxidation by Fe(III) | 0.2–20 | McKibben and Barnes (1986) |
| Straight Creek, NM (natural) | 5.46 | Nordstrom (2011a) |
| Leviathan, CA (mined) | 40 | Nordstrom (2011a) |
| Iron Mountain, CA (mined) | $17 \times 10^6$ | Nordstrom (2011a) |

During the weathering and oxidation of sulfide minerals, the production of acidity and the high metal concentrations overwhelm biological uptake, sorption, and cation exchange. Furthermore, redox changes and mineral precipitation are more quantifiable than other processes so that weathering rates are more quantifiable. In a review of hydrogeochemical processes that control solutes derived from weathering of mine wastes and unmined mineralized rock, Nordstrom (2011a) compared the mass fluxes of field sites where discharges had been measured and inverse modeling had been applied to quantify the amount of pyrite dissolved. These were referenced to the microbial rate of oxidation from an interlaboratory comparison by Olson (1991). Although the units are the same for the comparison (millimoles $FeS_2$/h), there are many orders of magnitude difference in the results with the natural weathering rate closest to the laboratory batch conditions (see Table 12). Mined sites are clearly much higher, by one to nearly six orders of magnitude. Of course, the mass flux in the field is not the same phenomenon as the rate from a batch lab experiment and rates were not normalized to catchment area unless the stored water during field oxidation is in a steady-state flow condition. Steady-state might be approximated for the Straight Creek drainage during low-flow conditions and this example is the closest to the batch lab results. It seems fruitful to compare mass fluxes from more natural and mined sites to see if this calculation provides better insight into the differences in rates between unmined and mined environments.

## 10. Conclusions

Water compositions from NARD can have a large range of metal and sulfate concentrations depending on the neutralization capacity of the host rock, style of mineralization, whether the water is a surface or groundwater, the residence time of the water in contact with sulfide minerals, the availability of oxygen, depth from surface, and ambient temperatures. The range of NARD compositions clearly overlaps with AMD in general, e.g. pH values are found as low as 2. However, for the few instances where direct comparisons could be made between NARD and AMD in a specific locale, the AMD can be 1–3 orders of magnitude greater than the NARD. This difference appears to hold regardless of whether it is stated in terms of concentrations, mass fluxes, or weathering rates. However, these comparisons are more meaningful in terms of mass fluxes, not concentrations, with appropriate inverse modeling (Nordstrom, 2011a). As more data of this type become available, especially when combined with discharge estimates, water flow paths, and detailed mineralogy, it should be possible to quantify additional factors that would allow us to model or simulate the range of likely water composition for a given hydrogeochemical terrain. A properly studied site with adequate natural background or pre-mining baseline data to compare with during and post-mining data has yet to be achieved.

For sites that have already been mined, natural analogs are essential to the interpretation of pre-mining water-quality conditions. Virtually every investigation compiled in this review had need of natural analog information even though quite different methods were occasionally employed. Monitoring of analog sites can help establish variability in composition and the processes that cause them, including the effects of climate change.

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