

CHARACTERISATION OF ACID MINE DRAINAGE USING A COMBINATION OF HYDROMETRIC, CHEMICAL AND ISOTOPIC ANALYSES, MARY MURPHY MINE, COLORADO

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Abstract. The legacy of mining continues to affect stream water quality throughout the western United States. Traditional remediation, involving treatment of acid mine drainage from portals, is not feasible for the thousands of abandoned mines in the West as it is difficult and expensive. Thus, the development of new methods to address acid mine drainage is critical. The purpose of this study was two fold; to identify and test new tools to identify sources of metal pollution within a mine and to identify low-cost treatment alternatives through the use of these tools. Research was conducted at the Mary Murphy Mine in Colorado, a multiple-level underground mine which produced gold, silver, copper, lead and zinc from 1870 to 1951. Source waters and flowpaths within the mine were characterised using analysis of hydrogen and oxygen isotopes of water (water isotopes) in combination with solute analysis and hydrometric techniques. Hydrometric measurements showed that while discharge from a central level portal increased by a factor of 10 during snowmelt runoff (from 0.7 to 7.2 L s⁻¹), Zn concentrations increased by a factor of 9 (from 3,100 to 28 320 µg L⁻¹). Water isotopes were used as conservative tracers to represent of baseflow and snowmelt inputs in a hydrologic mixing model analysis. The results showed that less than 7% of peak discharge was from snowmelt. Within the mine, approximately 71% of the high-flow Zn loading was caused by a single internal stream characterised by extremely high Zn concentrations (270 600 µg L⁻¹) and low pH (3.4). Somewhat surprisingly, hydrologic mixing models using water isotopes showed that new water contributed up to 79% of flow in this high-Zn source during the melt season. Diversion of this high-Zn source within the mine resulted in a decrease in Zn concentrations at the portal by 91% to 2,510 µg L⁻¹, which is lower than the base-flow Zn concentration. The results suggest that in some mines remediation efforts can be concentrated on specific areas within the mine itself. Using the characterisation techniques demonstrated in this study, problem areas can be identified and contaminated flows diverted or isolated. The results also suggest that it may be possible to dewater contamination areas, greatly reducing costs of remediation.

Key words: acid mine drainage, hydrochemistry, isotope hydrology, zinc

1. Introduction

Acid mine drainage (AMD) is a common problem at thousands of abandoned mine sites in the Rocky Mountains (Riebsame, 1997). The combination of low pH



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and high concentrations of metals associated with mine drainage can have severe toxicological effects on aquatic ecosystems. Acute exposure to high concentrations of metals can kill organisms directly, while long-term exposure to lower can cause mortality or other effects such as stunted growth, lower reproduction rates, deformities and lesions (Lewis and Clark, 1996). Contamination of fourth- and fifth-order river systems by trace metals is a common situation throughout the western United States (McKnight and Bencala, 1990), with concentrations exceeding aquatic standards for over 1,300 river miles in Colorado alone (Lewis *et al.*, 1992).

AMD is caused by the weathering of minerals such as iron disulphide (FeS_2), commonly known as pyrite, by water and oxygen (Singer and Stumm, 1970). When pyrite is exposed to water and oxygen, oxidation and hydrolysis reactions produce sulphuric acid (H_2SO_4) and free hydrogen ions (H^+), acidifying the water. Lower acidities allow other metals which are associated with mining, such as cadmium, copper, lead and zinc, to enter the solution phase and be transported from the system (Stumm *et al.*, 1996). These metals precipitate from the water column as pH increases, however the pH at which there is a potential for complete precipitation varies for different metals. For example, zinc precipitates at a minimum pH of 8.4 (Stumm *et al.*, 1996). Transport of zinc can occur over long distances, since the pH of many streams is less than 8.0. The rate of the AMD weathering reactions is limited by the surface area of ferrous iron exposed to weathering (Gray, 1997). The process of extracting ore from underground veins alters hydrologic processes by creating new pathways. As a result of mining activities, water and oxygen are able to infiltrate areas of high metal-sulphide mineral content at an increased rate, accelerating the natural acid-producing weathering processes.

The treatment of AMD has traditionally involved an end-of-the-pipe strategy, and is often conducted prior to a complete understanding of the processes involved in the contamination of water sources (Lanphear, 1995). Systems usually use inputs of lime artificially to raise the pH of the water, in order to precipitate metals. This type of treatment, however, is extremely expensive. For example, the system at the Argo mine in Idaho Springs, Colorado cost approximately \$6 million to design and build, and costs approximately \$1 million a year to operate (Scott, personal communication). Other treatment options include constructed wetlands, bactericides, grouting and dewatering (Frost, 1979; Michaud, 1994).

While the multiple methods of addressing AMD have met with some success, the initial and maintenance costs associated with after-the-fact treatment prohibit the cleanup of the majority of problem areas. In order to treat as many sites as possible, more efficient methods of preventing AMD are required.

A common method to characterise the sources and flowpaths of water through a hydrologic system is the use of the stable isotopes of water (^{18}O and Deuterium) as tracers (Pinder and Jones, 1969; Hooper and Shoemaker, 1986; Maulé and Stein, 1990). These isotopes are naturally occurring, do not decay over time to other isotopes, and are considered conservative in reactions with most catchment materials (Kendall and Caldwell, 1998). Distinct sources of water can have different isotopic

ratios determined by their past history of changes of state. Because the molecular bonds of heavier isotopes take more energy to break, lighter isotopes are preferentially selected in melting and evaporation, while heavier isotopes are preferentially selected in condensation and freezing, in a process referred to as fractionation. Simple mixing models parameterised with water isotopes can be used to quantify component sources of discharge, and to separate event-(snowmelt or rain inputs) from pre-event-(baseflow) water sources (Maulé and Stein, 1990; Stottlemyer and Toczydlowski, 1991).

The purpose of this study was two fold; to look for and test new tools to identify sources of metal pollution within mines and to identify low-cost treatment alternatives through the use of these tools. This study was conducted at the Mary Murphy Mine in Colorado. A combination of hydrometric measurements, isotopic study of water, and the analysis of dissolved solutes were used to address the following hypotheses:

- (1) water within the mine is primarily derived from channelised tributary streams; seepage from fractures is unimportant to discharge or concentrations of metals,
- (2) discharge is primarily from regional groundwater,
- (3) there is minimal event-water (direct input of snowmelt or rain) in the system,
- (4) sources of elevated metal concentrations in total discharge are confined to a small number of internal streams,
- (5) contaminated streams can be captured or diverted to improve the quality of targeted portal discharge, and
- (6) the source(s) of metal pollution can be isolated from the hydrologic system by capping or de-watering a portion of the mine.

2. Site description

The data reported here were collected at the Mary Murphy Mine in 1998 and 1999. The mine is located in Chaffee County, Colorado, approximately 19 km southwest of Buena Vista (Figure 1). The site is just east of the Continental Divide, in the Sawatch Range. Located in Chrysolite Mountain, the bottom of the mine is at approximately (3,139 m), with the mountain-top at approximately (3,810 m). The area receives an average of 460 mm precipitation annually, with a large portion falling as snow (SAIC, 1994). The snowmelt-dominated streamflow usually peaks in June, although the area can receive heavy precipitation at times in the summer as well (SAIC, 1994). Discharge in Chalk Creek is recorded by the State of Colorado Department of Water Resources at gauging station CHCRNACO (Chalk Creek near Nathrop, Colorado). Precipitation is measured approximately 20 km away at Taylor Park station number 58 184 (elevation 2,807 m) by the Colorado Climate Center.

The mine is located in a quartz monzonite batholith, intruded in the tertiary. Mining occurred primarily along veins of altered quartz monzonite. Plentiful in the sulphide minerals sphalerite (ZnS), galena (PbS), pyrite (FeS₂), and chalcopyrite (CuFeS₂), the Mary vein strikes north to north-east 35° and varies in width up to

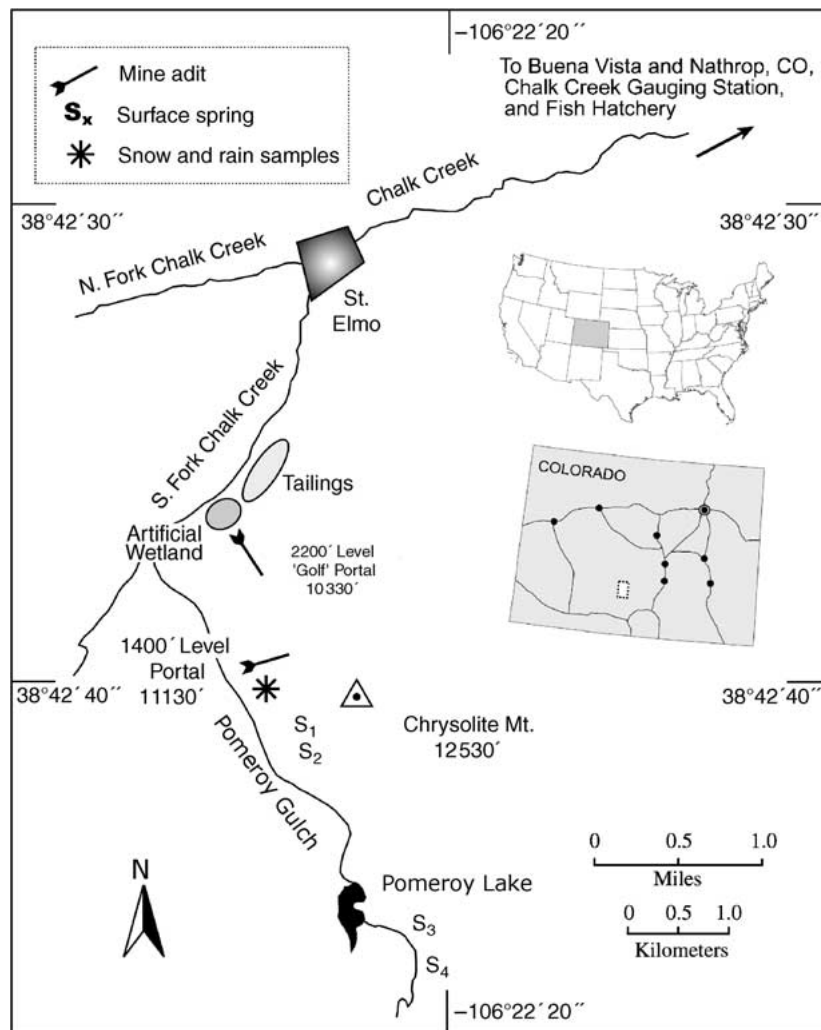


Figure 1. Location of the Mary Murphy Mine, near the former mining town of St. Elmo, Colorado (sampling was concentrated on the 1,400' Portal and nearby springs).

15 m (Dings and Robinson, 1957). Calcite is present in the ore veins (Dings and Robinson, 1957), and accounts for some neutralisation of drainage at the Mary Murphy Mine (Lanphear, 1995).

The mine drains high-zinc water from multiple portals into Chalk Creek about 32 km upstream from its confluence with the Arkansas River, and about 19 km upstream from the Colorado Division of Wildlife Chalk Cliffs Fish Rearing Unit. The site drew attention in 1986, after a fish-kill of 800 000 fingerling trout. In-stream concentrations of dissolved zinc and cadmium collected by the State of Colorado in August 1992 were as high as 929 and $3.5 \mu\text{g L}^{-1}$, respectively (SAIC, 1994). These concentrations were in exceedence of Colorado water quality standards for

aquatic life (at a hardness of 50, $65.0 \mu\text{g L}^{-1}$ is the acute exposure standard for zinc and $0.66 \mu\text{g L}^{-1}$ is the chronic exposure threshold for cadmium) (CDPHE, 1999). The mine site became part of the Nonpoint Source Program in 1990 (SAIC, 1994). Steps towards remediation began in the summer of 1991. Portals at the bottom of the mine '2,200' or 'Golf Portal' and centre of the mine '1,400' Portal' were opened and stabilised (Figure 1).

Previous work on metal concentrations at the Mary Murphy has focused on the Golf Portal and tailings piles along Chalk Creek (Lanphear, 1995; SAIC, 1994). Total Zn concentrations in drainage from the Golf Portal vary seasonally. They have been observed to be as high as $65\,150 \mu\text{g L}^{-1}$ in June 1994 and as low as $5,900 \mu\text{g L}^{-1}$ in September 1990 (SAIC, 1994). On average, in-stream concentrations of Zn below the Golf Portal and tailings piles were over $500 \mu\text{g L}^{-1}$, approximately 10 times the Zn concentrations in Chalk Creek above the Golf Portal drainage. The results of a geochemical analysis conducted by Lanphear (1995) suggested that the primary source of contamination in drainage from the Golf Portal was oxidised sulphide materials in the ore vein. Remediation at this location included consolidation of tailings piles and the construction of an artificial wetland to treat drainage from the Golf Portal (SAIC, 1994).

The 1,400' Portal (MM1400), which is the focus of this study, drains from the Mary Murphy Mine into Pomeroy Gulch on the west side of Chrysolite Mountain (Figure 1). Pomeroy Gulch enters Chalk Creek upstream from the Golf Portal source. Although less than 6% of total Zn load to Chalk Creek is derived from points upstream from the Golf Portal (Kimball, 1996), the flow from the 1,400' Portal is an important source of water with seasonally high zinc concentrations. Due to the stabilisation work at this level, the internal mine workings are accessible.

3. Methods

Collection of samples and measurements were designed to reveal the possible seasonal changes in discharge and chemistry. Sampling was concentrated on the 1,400' level of the Mary Murphy Mine (Figure 2).

Discharge at the 1,400' Portal (MM1400) was initially measured manually with a 10 cm cut-throat flume manufactured by Baski Water Instruments. On June 11, 1999, a permanent 5 cm Parshall flume with a data logger manufactured by Global Water was installed. Through October 12, 1999, discharge from the portal was recorded hourly, with a few periods missing due to human or natural disturbance. Discharge at points within the 1,400' level of the mine was measured manually at weekly to bi-weekly intervals using 5 cm and 10 cm cut-throat flumes to quantify inputs from distinct streams.

Grab samples for major solutes, isotopes ^{18}O and D of water, and trace metals were collected at six sites approximately every 2 weeks. Synoptic sampling at 12 locations was conducted on September 10, 1998 and June 10, 1999 in order to characterise baseflow and snowmelt conditions. On September 10, 1999, four

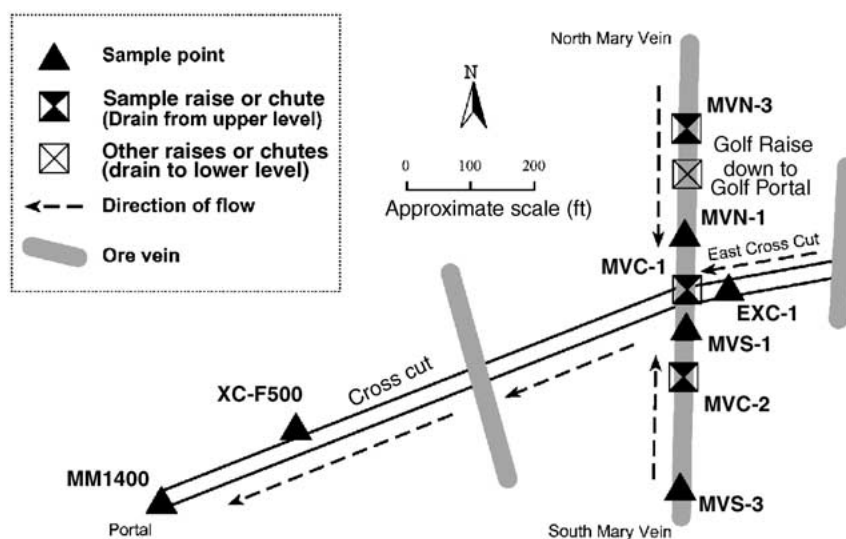


Figure 2. Schematic drawing of the 1,400' level of the Mary Murphy Mine, with locations of sampling points on the floor of the cross cut and vein and at inflow chutes and raises. The sampling location MM1400 is located at the outlet of the 1,400' level. XC-F500 is a seep draining into the crosscut. Sampling points XC-1, MVN-1, EXC-1 and MVS-1 are located along the floor of the cross cut, the north portion of the vein (north vein), the east extension of the cross cut, and the south portion of the vein (south vein), respectively. MVN-3, MVC-1 and MVC-2 are chutes draining water from upper levels of the mine. MVS-3 is located along the floor of the south vein, upstream from MVC-2. The unlabelled ore veins were partially mined.

nearby springs were sampled to provide a background comparison. Two of the springs drained from near the top of the catchment while two others drained from talus slopes slightly upslope from the mine (Figure 1). In addition, precipitation samples were collected near the 1,400' Portal. Three replicate samples of snow were collected on April 9, 1999 and rainwater samples were collected during storm events on August 24, 1999 and September 10, 1999.

Major solute samples were collected in 250 mL high-density polyethylene (HDPE) bottles that had been rinsed once with deionised water and three times with sample. Bottles for metal samples were acid-washed and acidified with 100 μ L of ultra pure HNO_3 per 50 mL of sample. Samples for the analysis of dissolved metals were filtered into the acidified bottles with a Gelman Acrodisc 0.45 μ m single-use filter. Isotope samples were collected in glass bottles with air-tight seals and kept at 5 $^\circ\text{C}$ until analysis could be performed.

Analysis of pH was conducted at the Kiowa Laboratory at the Institute of Arctic and Alpine Research (INSTAAR) following the protocol of Williams and Melack (1991). Analysis of metals concentrations from September 10, 1998 to April 9, 1999 and May 19, 1999 was performed by Analytica Environmental Laboratories in Broomfield, Colorado, and from the June 10, 1999 comprehensive sampling by the US EPA, Region 8 Technical Services Laboratory in Golden, Colorado, using

the US Environmental Protection Agency (EPA) method 200.7 for ICP (detection limit $5 \mu\text{g L}^{-1}$) (US EPA, 1983). Remaining metal samples were analysed for zinc only at the Limnology Laboratory at INSTAAR, using a flame atomic adsorption spectrophotometer (detection limit $1.5 \mu\text{g L}^{-1}$).

Isotope samples were analysed for ^{18}O and ^{16}O at the Stable Isotope Laboratory located at the Institute of Arctic and Alpine Research, University of Colorado, Boulder. Samples were run on a SIRA Series II mass spectrometer using a $\text{CO}_2/\text{H}_2\text{O}$ equilibration method, with a nominal precision of 0.1% . Analysis of Deuterium (^2H or D) was performed at the Cornell Stable Isotope Laboratory using a zinc reduction method described by Coleman *et al.* (1982) on a Finnigan MAT DeltaPlus isotope ratio mass spectrometer with a precision of 1.5% .

All isotopic ratios are expressed using the delta (δ) notation in which the numeric value of δ indicates how many parts per mil ($\%$) the difference between R_{sample} and R_{standard} is from the standard. δ was calculated using the following formula:

$$\delta = \left[\frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \right] \times 1000 \quad (1)$$

where R_{sample} and R_{standard} represent the isotopic ratio ($^{18}\text{O}/^{16}\text{O}$ or D/H) in the samples or the standard. The standard used was Vienna Standard Mean Ocean Water (V-SMOW).

3.1. HYDROGRAPH SEPARATION

Estimates of event and baseflow water mixing were made using a mixing model with isotopic ratios as a tracer (Pinder and Jones, 1969). Total discharge was assumed to be composed of two distinct sources, event water and baseflow water, each of which had a unique isotopic ratio. The following mass balance equation establishes the relationships between tracer concentrations and discharge:

$$Q_t C_t = Q_b C_b + Q_e C_e, \quad (2)$$

where

Q = discharge,

C = concentration of tracer ($\delta^{18}\text{O}\%$)

t = total stream discharge,

b = baseflow water,

e = event water.

From this relationship, the following equation was used to solve for the portion of baseflow water contributing to the total:

$$Q_b = Q_t * \left[\frac{C_t - C_e}{C_b - C_e} \right]. \quad (3)$$

The following specific assumptions were made:

- There were only two components contributing to flow; event and baseflow water.

- The tracer, $\delta^{18}\text{O}$, was conservative.
- The tracer, $\delta^{18}\text{O}$, was distinct in event and baseflow water.
- The mixing of event and baseflow water was complete.
- The variations in concentrations of the tracer over time were accounted for (the method of accounting for these variations is discussed below).
- Changes in $\delta^{18}\text{O}$ were due only to mixing of event and baseflow water.
- Atmospheric exchange or evaporation was negligible, and thus there was negligible fractionation.
- Surface storage waters contributed negligibly or not at all to discharge.

The model utilised knowledge of isotopic variation in snowpack and groundwater based on previous studies and observations of the system to make an empirical estimate of the end-members. The model was highly constrained by the minimal variation in the isotopic ratios in the mine system, which were close to the original baseflow ratios through the entire season.

The final model assumed that the $\delta^{18}\text{O}$ signature of snowmelt did not remain constant during the snowmelt season. Instead it was assumed that the snowmelt initially was lighter ($\delta^{18}\text{O}$ more negative) than the average snowpack, and then increased through the melt season as lighter atoms were preferentially selected through fractionation during the melt process. Maulé and Stein (1990) collected snowmelt in lysimeters in a watershed in Quebec and found a general trend towards heavier meltwater over time. Unpublished field data collected by one of the authors suggest that snowmelt is initially lighter in ^{18}O than the overall snowpack by approximately 2‰, and through the course of the melt season becomes heavier by approximately 2‰ (Williams, unpublished observations). This trend and magnitude are also supported by field observations of average isotopic ratios in a snowpack (Rodhe, 1981), as well as laboratory research on snowmelt (Herrmann *et al.*, 1981). A linear interpolation was used to estimate snowmelt $\delta^{18}\text{O}$ content around the measured snowpack $\delta^{18}\text{O}$ (Table I). The measured rain concentrations were used as the event input during the rain period.

The piecewise linear regression method of Hooper and Shoemaker (1986) was used to estimate baseflow $\delta^{18}\text{O}$ after the initial sampling on April 9. The trends and magnitude of the regressions were estimated from measurements at XC-F500, a fracture inflow to the 1,400' portal, which appeared to be relatively independent of the rest of the inflows in this study, and represented baseflow.

4. Results

4.1. HYDROMETRIC OBSERVATIONS

Precipitation peaked in early May, in the form of snowfall (Figure 3). Precipitation in the form of rain peaked during the week of July 7–14, but a series of large storms continued through July 29, followed by multiple smaller storms through the month of September.

TABLE I
Model definitions and results at MM1400

Date	Hydrologic period	Source end members		Model result event water
		$\delta^{18}\text{O}$ baseflow	$\delta^{18}\text{O}$ event	
9-Apr		-16.05	-22.199	0.0
19-May		-16.27	-20.22	1.0
10-Jun	Snowmelt	-16.396	-19.14	4.0
22-Jun		-16.46	-18.54	1.4
29-Jun		-16.50	-18.198	7.0
23-Jul			-16.63	0.23
5-Aug	Rain	-16.49	0.23	1.2
10-Sep		-16.47	-3.06	2.3
13-Oct		-16.44	-3.06	2.9

Parameters for other internal sampling points were developed from isotopic ratios using the same methods.

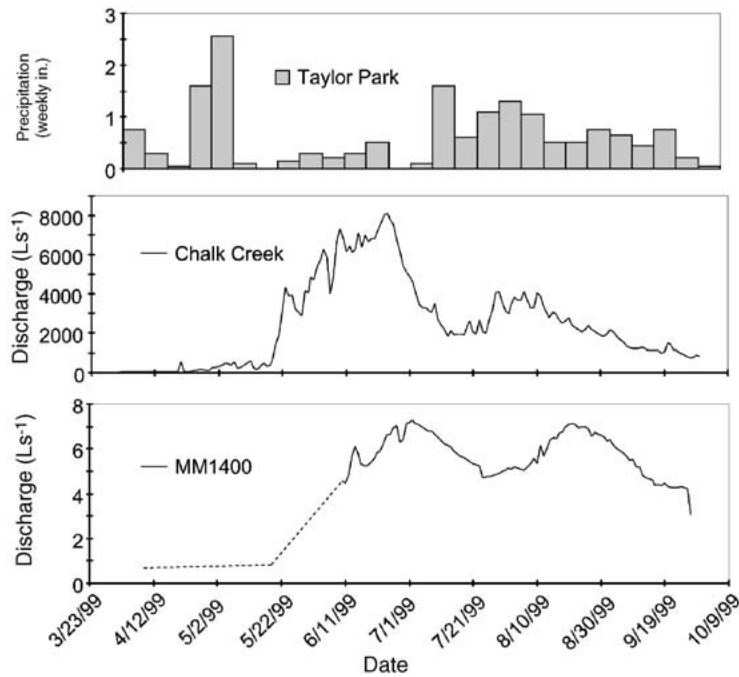


Figure 3. Weekly precipitation amounts (in.), discharge in Chalk Creek (L s^{-1}), and discharge from the 1,400' Portal of the Mary Murphy Mine (L s^{-1}). The dashed line in the plot of discharge at MM1400 indicates interpolation from three discrete measurements. After June 11, 1999, discharge was measured hourly and averaged to calculate a daily discharge value.

Streamflow measured in Chalk Creek showed a rapid response to snowmelt initiating in mid-May, peaking at $8,132 \text{ L s}^{-1}$ on June 24 (Figure 3). After snowmelt, discharge decreased until late-July, reaching a minimum of $1,813 \text{ L s}^{-1}$ on July 13. A second peak of $4,109 \text{ L s}^{-1}$ in response to rain storms was observed on August 6.

Discharge from the 1,400' Portal of the mine during baseflow conditions in April was very low, at 0.7 L s^{-1} (Figure 3). Discharge began to increase in late May, reaching a peak of 7.2 L s^{-1} on July 1, approximately 1 week after the streamflow peak. The rising limb of the hydrograph was followed by a steady decline in discharge through July 24 to 4.8 L s^{-1} .

Portal discharge rose steeply in response to summer rains, reaching a second peak of 7.3 L s^{-1} on August 19, 13 days after the streamflow peak. The average recession coefficients were similar (0.97 in the creek and 0.98 at the portal), the creek however showed more direct response to rain events than the delayed signal at the mine portal, suggesting a longer storage time and hence a groundwater dominated system within the mine.

Contributions to portal discharge from points within the mine were not uniform over time and space. At the baseflow comprehensive sampling on September 10, 1998, when the portal discharge was 2.1 L s^{-1} , contributions by distinct streams were fairly even (Figure 4). The largest component at this time was seepage, measured as gains along the length of the portal (0.9 L s^{-1} or 43% of total). Contributions by the central chute MVC-1 (0.5 L s^{-1} , or 24% of total) were second in importance. During baseflow conditions, 59% of discharge was measured as channelised flow along the floor of the 1,400' level of the mine.

During the comprehensive snowmelt sampling on June 10, 1999, the portal discharge had increased to 4.2 L s^{-1} . Although this was nearly double the discharge observed at the baseflow sampling, discharge from most of the contributing streams

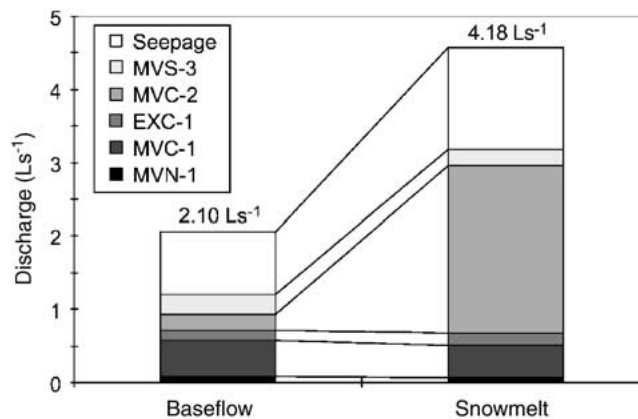


Figure 4. Internal water sources of the 1,400' level of the Mary Murphy Mine (L s^{-1}), at baseflow (September 10, 1998) and snowmelt runoff (June 10, 1999). The diversion of the flow at MVN-1 down the Golf Raise occurred after these samplings on August 4, 1999.

changed very little. Most of the change in discharge was due to a 10-fold increase in discharge at the south vein chute, MVC-2 (2.3 L s^{-1} or 50% of total). At this time, seepage increased in volume (1.4 L s^{-1}) but decreased in relative contribution (roughly 30% of total). Thus, during snowmelt runoff, the channelised portion of discharge increased to approximately 70%.

Over the season, the patterns of discharge at sampling points within the mine were not parallel. While the total discharge at the 1,400' Portal and MVS-1 peaked on July 1, discharge at MVN-1 was low during both low- and high-flow conditions. Discharge at MVN-1 did increase later in the season, from 0.07 L s^{-1} on June 10, 1999 to 0.24 L s^{-1} on August 4, 1999. Contributions to discharge from the 1,400' Portal from the north side of the vein measured at MVN-1 remained below 10% of the total portal discharge through the period of study. It should be noted that a percentage of water flowing along the north side of the vein flowed down the Golf Raise to the 2,200' level, and thus did not contribute to the flow at the 1,400' level (see Figure 2).

In light of this observation, on August 4, 1999 a small dam was built which would divert all water from the north portion of the vein down the Golf Raise to the 2,200' level (Figure 2). After the diversion, 100% of the north stream was directed to the Golf Portal, where a passive wetland was already in place to treat discharge. After this point in time all discharge and chemistry observations at MM1400 no longer incorporated inputs from the north stream.

Diversion of the north stream only minimally affected the volume at the portal. Over the period of this study the contribution measured at MVN-1 ranged between 0.1 and 0.2 L s^{-1} , smaller than the other tributary streams at all times. At its peak discharge on August 5, immediately after the diversion, the contribution by MVN-1 would have increased discharge at the portal by only 6%.

4.2. OXYGEN AND HYDROGEN ISOTOPES OF WATER

Measured $\delta^{18}\text{O}$ in the three snow samples collected on April 9 averaged -20.2‰ (Figure 5). Samples of rainwater collected on August 24 and September 10 were dramatically heavier, at 0.2 and -3.1‰ , respectively. This natural variation is due to the degree of isotopic fractionation in precipitation. The heavier values for rainwater are the result of warmer air temperatures and repeated recycling of water in local summer rainstorms (Ingraham, 1998).

There was little variation in the $\delta^{18}\text{O}$ of discharge at MM1400, which ranged from -16.1 to -16.6‰ (Figure 5a). The $\delta^{18}\text{O}$ of discharge measured at baseflow conditions was -16.1‰ . During snowmelt, discharge at MM1400 became isotopically lighter by 0.5 to -16.6‰ and during summer it became isotopically heavier, returning to -16.1‰ . Variation at most internal streams was also less than 1.0‰ (Figure 5b). Variation along the north stream however was about 2.0‰ greater. The north stream sampled at MVN-1 showed a more variable pattern than was seen at the portal. Initially this stream was heavier, at -15.4‰ , but decreased in June to

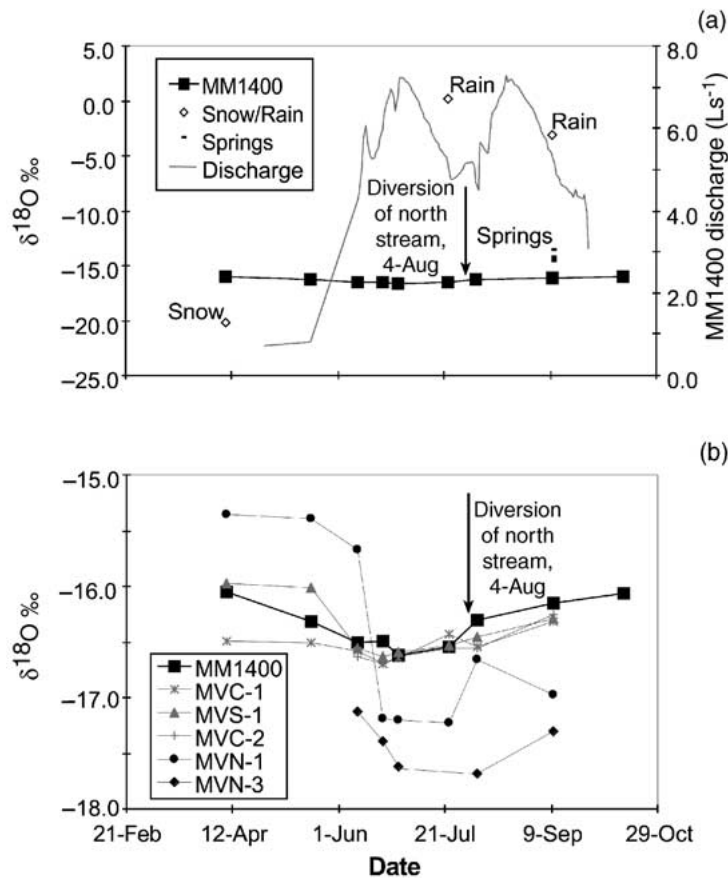


Figure 5. (a) $\delta^{18}\text{O}$ (‰) at MM1400 and in precipitation samples. The minimal variation at the portal suggests that the primary source of discharge is groundwater, which carries a volume weighted mean signal of local precipitation. (b) $\delta^{18}\text{O}$ (‰) at MM1400 compared with internal sampling points. Most sampling points exhibited a minimal response in $\delta^{18}\text{O}$ to snowmelt and rain inputs, but there was a greater range in the north side of the vein (MVN-1 and MVN-3).

-17.2 ‰. In comparison, the water sampled at nearby springs on September 10 was slightly heavier, averaging -14.1 ‰.

Samples from this study were compared to the Global Meteoric Water Line (GMWL), a globally averaged relationship between $\delta^{18}\text{O}$ and δD represented by the equation $\delta\text{D} = 8 * \delta^{18}\text{O} + 10$ (Craig, 1961). All of the mine samples for which both $\delta^{18}\text{O}$ and δD were measured fall along the line $\delta\text{D} = 7.35 * \delta^{18}\text{O} - 10.31$ ($r^2 = 0.88$) (Figure 6). While the mine samples fall below the GMWL, snow and nearby spring samples are consistent with mine samples, falling graphically along the same trendline. The lower slope and y-intercept of this Local Meteoric Water Line (LMWL) compared to the GMWL is indicative of a local system that has experienced some evaporative loss (Ingraham, 1998). However, none of the internal

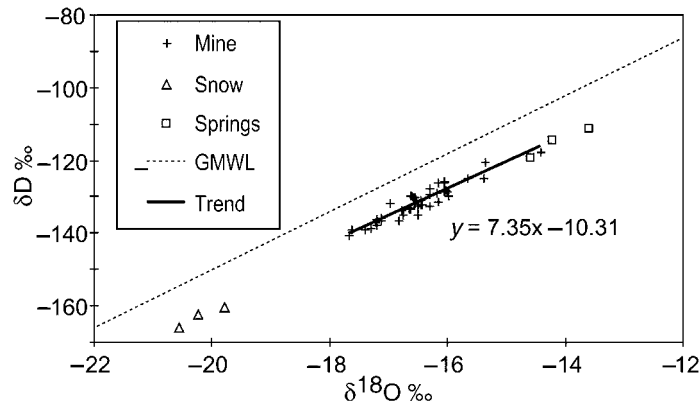


Figure 6. Comparison of the Local Meteoric Water Line (LMWL) with the Global Meteoric Water Line.

mine streams separate from others when δD is plotted against $\delta^{18}O$. Thus, there was no noticeable difference in evaporative influence between tributary streams within the mine, nor in snow and spring samples.

4.3. EVENT WATER ESTIMATION

Estimation of the contribution of event water on the basis of isotopic relationships shows that event water at the portal was extremely low (Figure 7). The results suggested that event water peaked at 7.0% on June 29, prior to the peak discharge, before dropping to 0.6% on July 23. During the rain period, event water also increased, but only reached a maximum of 2.9% on October 13. When discharge estimates were calculated using these results, event water reached a maximum contribution of 5.5 L s^{-1} on June 29, prior to the peak discharge from the portal. It reached a smaller peak during the rain period of 1.9 L s^{-1} .

When this model was applied to sampling points within the mine, using the same assumptions and parameterisation used at the portal, the results were illogical for certain dates. There were insufficient data to parameterise the model appropriately for each internal point. However, comparing the results offered insight as to differences of process within the mine.

Most of the sampling points showed similarly low estimates of event water, suggesting that source waters were the same (Figure 7). The model estimated dramatically higher event water concentrations at MVN-3 during the snowmelt season, up to 79% by June 29. As MVN-3 is a tributary to the stream measured at MVN-1, event water at MVN-1 also increased to over 50% in June. During the summer rainstorm period, the model predicted high negative percentages for event water at MVN-1 and MVN-3 suggesting that the parameterisation of the model was incorrect for these points. It is more reasonable to assume that snowmelt continued to be an influence at these points through the rain season.

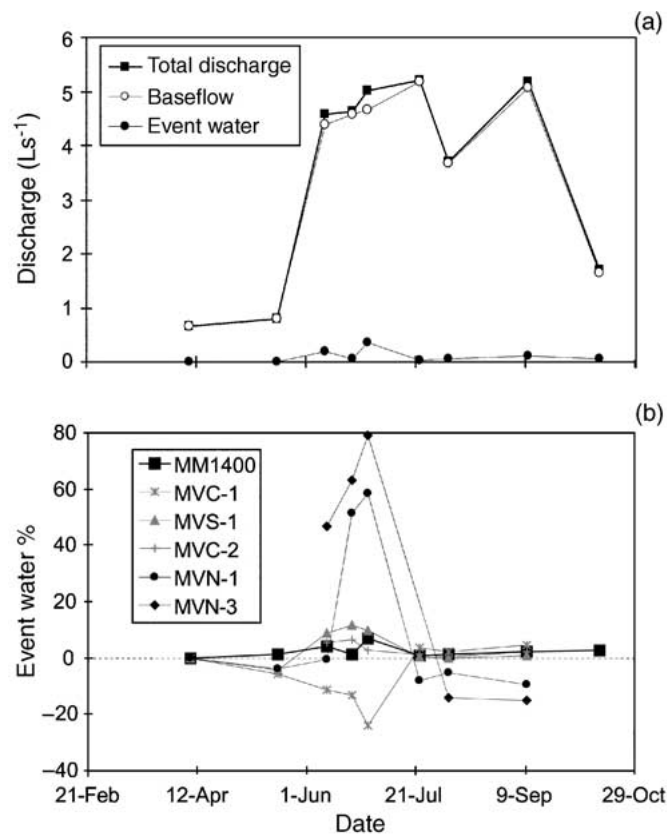


Figure 7. (a) Hydrographic separation at MM1400 for baseflow and event water components (L s^{-1}), using water isotopes as tracers and a two-component mixing model. (b) Model estimates of event water (%) for MM1400 and internal sampling points. Event water is low throughout the season at most points. In contrast, during snowmelt, event water is as high as 80% at MVN-1 and MVN-3.

4.4. CHEMISTRY

4.4.1. pH

The pH at the portal outflow remained neutral over the period of this study, but decreased somewhat by June 29, 1999 to 6.5 (Figure 8). This neutral pH can be explained by the presence of both calcite and rhodochrosite in the portals of the mine. Only a small amount of these minerals is necessary to neutralise the acid present in this system (Lanphear, 1995). Extremely acidic inputs were observed in the north stream, MVN-1, where pH dropped to 4.3 on June 29. While not as acidic, all points within the mine except for MVC-1 showed reduced pH with snowmelt. When MVN-3, the primary source of the north stream, was initially observed to be flowing in early June, its pH was recorded at 4.1. It dropped somewhat over the season to a measured low of 3.4 on September 10. The pH at MVN-1 was significantly different from that at MVC-1 and MVS-1 (T -test, α 0.05) which were both in the range of 6.3–7.4.

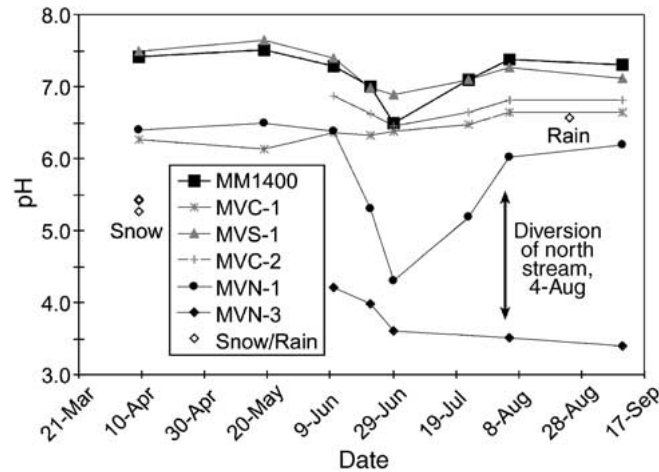


Figure 8. Time series plot of pH through the period of study at MM1400 and internal sampling points, with snow and rain for comparison. The pH remained neutral at the portal through the period of study. In contrast, the pH at MVN-1 and MVN-3 of ≈ 3.5 was extremely acidic. The diversion of this north stream on August 4 had no significant effect on the pH at the portal.

The natural neutralisation capacity in this hydrologic system was also reflected in the comparison of mine samples to precipitation inputs. All points except MVN-1 and MVN-3 showed a higher pH than the snowmelt inputs, the average pH of which was 5.4. Rain was less acidic, at a pH of 6.6. The pH measured at nearby springs was neutral, ranging from 7.2 to 7.6.

The diversion experiment appeared to have no significant effect on the pH at the portal. By August 4, the pH in the north stream was already increasing towards baseflow level, as was the pH at MM1400.

4.4.2. Zinc

Dissolved Zn represented approximately 100% of total Zn at all times and locations, so we present only the results for total Zn. Concentrations of total Zn at MM1400 ranged over nearly an order of magnitude from $3,100 \mu\text{g L}^{-1}$ on May 19, 1999 to $28,320 \mu\text{g L}^{-1}$ on June 29, 1999 (Figure 9). The relationship between discharge and zinc was complex at MM1400. Increased discharge initially diluted Zn concentrations, as total Zn dropped to its minimum on May 19 and remained low through June 10. However, the rapid increase to $28,320 \mu\text{g L}^{-1}$ on June 29 indicated that the supply of Zn had increased and greater discharge was no longer sufficient to keep concentrations low. Interestingly, the peak Zn concentration at the portal corresponded with the peak discharge observed only 3 days later on July 2. Zinc concentrations at the portal dropped to $2,510 \mu\text{g L}^{-1}$ after the diversion of the north stream, and remained at approximately this level as portal discharge slowly decreased.

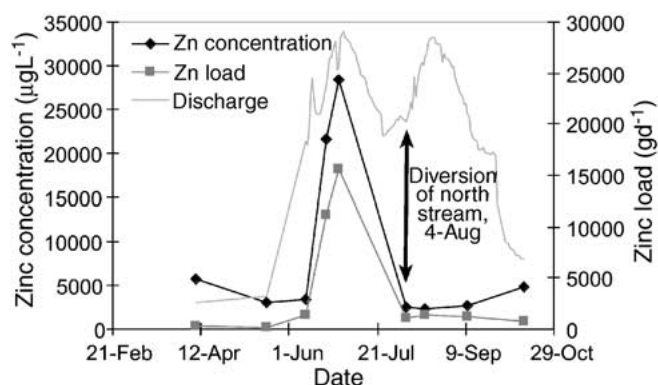


Figure 9. Zinc concentrations ($\mu\text{g L}^{-1}$) and loadings (g d^{-1}) at MM1400. Concentrations increased dramatically during snowmelt, from 3,100 to 28,320 $\mu\text{g L}^{-1}$, causing a 72-fold increase in daily Zn load (from 217 to 15 665 g day^{-1}). Discharge ($0.7\text{--}7.3 \text{ L s}^{-1}$) is superimposed on the hydrograph to illustrate timing.

Loadings of zinc at the portal were 72 times higher at their peak than at their lowest observed date (Figure 9). The lowest loading measured in this study, 217 g d^{-1} was observed to correspond with the lowest concentrations of Zn on May 19. The highest loading, 15 659 g d^{-1} , also corresponded with the highest concentrations of Zn on June 29.

In order to understand what was driving the flushing of zinc seen at the portal, it was also necessary to sample at points within the mine. Concentrations at MVC-1, MVS-1 and MVC-2 showed a dilution of Zn over the season, averaging 3,890 2,136 and 965 $\mu\text{g L}^{-1}$ respectively. In contrast, concentrations of Zn in the north stream increased with snowmelt (Figure 10). Concentrations at MVN-1 ($n = 8$) peaked at 190 200 $\mu\text{g L}^{-1}$ on June 10, and appeared to be driving the increase in Zn concentrations at the portal. Concentrations at MVN-3 ($n = 5$), the primary contributor to MVN-1, peaked at 270 600 $\mu\text{g L}^{-1}$ on June 22, 12 days later than that at MVN-1. Zn concentrations in the seepage along the portal averaged 30 $\mu\text{g L}^{-1}$, a comparatively insignificant contribution.

5. Discussion

The hydrological system in the Mary Murphy Mine can be defined as a channelised network of internal tributary streams. While seepage along the adit was detected, the majority of discharge enters the 1,400' Portal system at discrete and quantifiable points along the ore vein. The concentrations of metals in seepage samples are minimal and thus seepage is not important to metal loadings at the portal.

The steep rising limb of the hydrograph and 10-fold increase in discharge seen at MM1400 are characteristic of systems driven by snowmelt runoff (Caine, 1992). However, this hydrometric analysis alone could not determine whether the increase

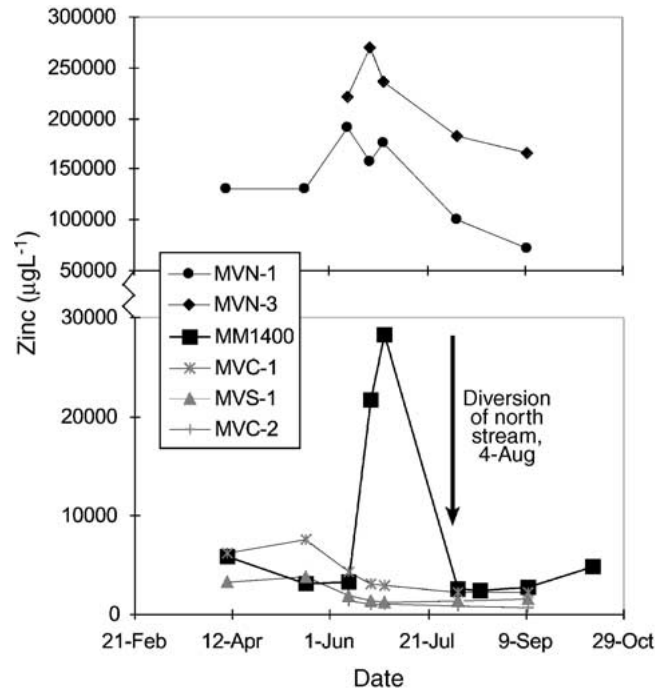


Figure 10. Zn concentrations ($\mu\text{g L}^{-1}$) at MM1400 and internal sampling points. The increase in concentrations seen at MM1400 appear to be caused by high concentrations in the north stream (MVN-1 and MVN-3). Other points within the mine experienced a dilution of Zn during snowmelt. After the diversion of the north stream, Zn at the portal dropped to below base-flow levels. Note that the scale on the graph is not linear, so as to show the high concentrations of inflows MVN-1 and MVN-3.

in discharge was due to direct snowmelt inputs or due to a displacement of pre-vent groundwater.

The average $\delta^{18}\text{O}$ signature of -16.3‰ at MM1400 is consistent with other systems in the Rocky Mountains (Alstad *et al.*, 1999; Welker, 2000), and represents a volume-weighted average of annual precipitation in the form of snow and rain. Although $\delta^{18}\text{O}$ in precipitation is highly variable in this region, variation in the $\delta^{18}\text{O}$ signature of groundwater is minimised by the size of the groundwater reservoir (Rodhe, 1998; Welker, 2000). Thus, the combination of hydrometric and isotopic evidence suggests that the increase in discharge seen at MM1400 during snowmelt is due largely to displacement of groundwater driven primarily by infiltration of snowmelt.

The relationship between $\delta^{18}\text{O}$ and δD can often yield additional insight into source waters. In this study, both precipitation samples and mine samples plot along the same regression line. This indicates that mine water is closely connected to meteoric recharge and that there is minimal evaporative difference between samples. Water which has interacted with pyrite can become isotopically enriched in $\delta^{18}\text{O}$

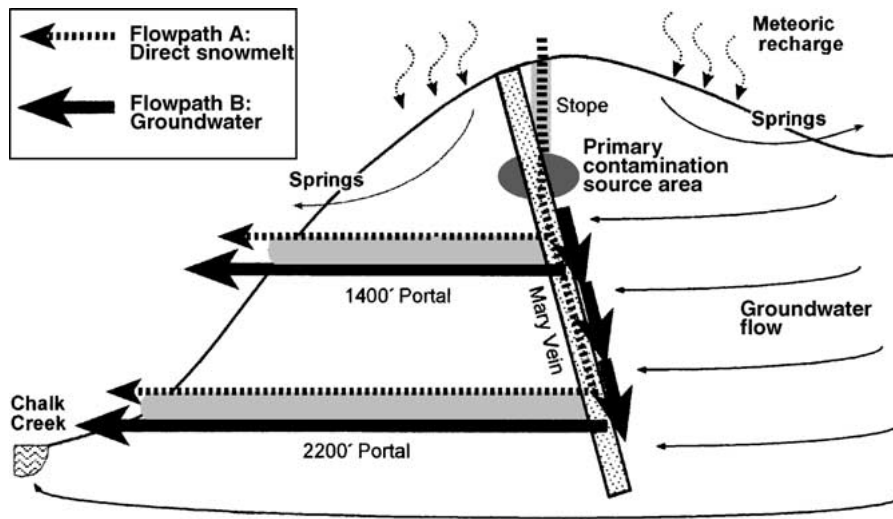


Figure 11. Conceptual diagram of two distinct flowpaths contributing to portal discharge. Flowpath A is a direct pathway for snowmelt to infiltrate into the mine workings. Flowpath B is a groundwater and fracture flow pathway where down-basin flow is intercepted by mine workings and channelised. Flowpath B represents a longer time scale than Flowpath A.

relative to δD (Taylor *et al.*, 1984; Ghomshei and Allen, 2000). In this study no mine samples show this shift to isotopically enriched $\delta^{18}O$ of water. Mine samples also do not show a difference in this relationship compared with unaffected spring samples, suggesting that the groundwater pool driving discharge from the mine is regional in scale.

In addition, the results of the hydrologic mixing model indicate that, overall, there is minimal event water discharged from the mine system. Hydrologic mixing models have commonly been utilised to separate event from baseflow waters on a catchment scale (Pinder and Jones, 1969; Hooper and Shoemaker, 1986; Kendall and Caldwell, 1998). In general, researchers have found that baseflow water represents a large component of seasonal increases in discharge (Dinçer *et al.*, 1970; Maulé and Stein, 1990; Wels *et al.*, 1990). Although event water is comparatively unimportant in this hydrologic system, this is to be expected as channelised flow is several hundred feet below the surface.

Event water at most internal sampling points is consistently low through the period of study. During snowmelt, however, event water is estimated to represent up to 80% of the discharge at MVN-3. The $\delta^{18}O$ results for MVN-3 indicate that there must be a source of snowmelt runoff contributing to discharge in this part of the mine. It is possible that there is a direct physical connection to the surface through large stopes (vertical shafts which open to the surface) where snow can collect and slowly melt into the north side of the mine. Assuming that snowmelt contributes to discharge in the north stream through September, back calculations from measured discharge and model results require approximately 122 m³ of liquid

water. Assuming a snow density of 50%, this would require roughly a cylindrical opening 5 m in diameter and 12.3 m deep. Stopes of this proportion have been observed at the Mary Murphy Mine (Stover, 1997).

Water sources for internal streams appear to be driven by two distinct hydrologic flowpaths through the mine system (Figure 11). Flowpath A is a pathway for snowmelt infiltration into the mine workings and represents only a small portion of the overall discharge from the mine. Residence time of water in flowpath A is thus on the order of weeks to months. Flowpath B is a groundwater pathway where down-basin flow is intercepted by mine workings and channelised. The groundwater reservoir is displaced and recharged by meteoric inputs during snowmelt, thus the hydrograph of flowpath B resembles a snowmelt-driven system. The residence time of water in flowpath B is greater than a year.

As hypothesised, metal concentrations are relatively low in most internal streams. Sources of seasonally elevated metal concentrations are confined to the event-water driven, low-volume stream draining the north side of the vein. The elevated metal concentrations measured in the north stream could be explained in several different ways. In their geologic survey of the mine, Dings and Robinson (1957) found that the ore in the veins is oxidised above the 400' level of the mine and partially oxidised above the 900' level. Most likely, this area is not saturated during baseflow conditions. During the period of infiltration by snowmelt, this localised source area may act as a 'coffee filter'. Infiltrating snowmelt reacts with the sulphide orebody, geochemical weathering is enhanced, and AMD is produced. It is also possible that event water from flowpath A displaces and mixes with water held by capillary tension, which was highly contaminated during its residence time. Some combination of these two mechanisms is also possible.

The interaction of internal streams is reflected in the pattern of Zn concentrations seen at the portal. Zn concentrations are diluted with increased discharge due to snowmelt, reflecting the dilution pattern at the majority of internal streams. However, at peak snowmelt, a flushing of Zn is observed, as the north stream begins to influence portal discharge more heavily. These results are consistent with other seasonal acid mine drainage research, which finds that discharge does not correlate well with metals concentrations, suggesting interactions of complex driving factors (Lewis and Clark, 1996; Stachler, 1997).

The diversion experiment indicates that, if an internal source can be isolated, it can be addressed separately to improve the quality of portal discharge. In this case study, metal concentrations were reduced to baseflow levels at the 1,400' Portal after the north stream was diverted down a raise and combined with drainage from the 2,200' Portal. Thus, point sources of AMD were effectively reduced from two to one at the Mary Murphy Mine. If desired, the contaminated stream could also be isolated from other contributing internal streams with a diversion pipe system which would allow for separate treatment of low-volume, high-metals discharge.

While the current diversion experiment is successful at reducing point sources, it does not represent a thorough preventative solution. To develop a preventative

solution, one of the three components of AMD (sulphur-bearing material, water and air) must be eliminated from the system (Singer and Stumm, 1970; Michaud, 1994). The identification of a direct snowmelt flowpath driving the seasonal flushing of Zn from the mine facilitates the identification and isolation of source areas. Existing technologies are available which could seal, divert, or collect direct inflows to avoid contact with contamination zones (Michaud, 1994; Banks *et al.*, 1997).

6. Conclusions

Using a combination of hydrometric, chemical, and isotopic analyses, we developed a method for characterisation of AMD sources within a mine. It was determined that the majority of flow in the mine was channelised along stopes and adits, enabling sampling and remediation within the mine. Increases in discharge were primarily driven by displacement of baseflow groundwater by meltwater and the majority of this groundwater was not a source of acid mine drainage. Metal loadings were concentrated in one low-volume internal stream. This channelised stream was driven by a distinct flowpath of direct snowmelt inputs. Upon diversion of this stream, water quality draining from this intermediate level of the mine improved significantly. This methodology can be applied in other abandoned mine systems to concentrate remediation efforts on specific sources, reducing volumes of water which require treatment, or enabling a preventative solution.

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