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Technical Article

Use of Pb, ^{18}O, and ^{2}H Isotopes in Mining-related Environmental Studies

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Abstract. An isotopic and geochemical study of surface water and groundwater was undertaken at the Sullivan Mine, a sediment-hosted Pb-Zn massive sulphide deposit with a well-defined homogeneous Pb isotopic composition. The Pb isotopic composition of surface water and groundwater samples from near the mine site define a mixing line between Sullivan Pb and at least one other end member. The δ^{18}O and δD isotopic results fall along an evaporation line that shows mixing between water from evaporative sources with water from meteoric sources.

Key words: British Columbia, Canada; groundwater; Pb isotopes; mining effluent; quality; stable isotopes of water; Sullivan Mine

Introduction

The variability of isotope ratios has proved valuable when studying a wide variety of geological and environmental problems. The study of Pb isotopes, in particular, has been applied to problems such as determining the source(s) and extent of anthropogenic Pb contamination in a variety of environments (Chow and Johnstone 1965; Patterson et al. 1976; Shirahata et al. 1980; Elbaz-Poulichet et al. 1986; Flegal et al. 1989; Hopper et al. 1991; Beck 1997; Wu and Boyle 1997). Some studies took an integrated approach and analyzed samples from several environmental media (e.g., Ault et al. 1970; Murozumi et al. 1996). Only limited work has been done using Pb isotopes to trace contamination from large scale mining operations, mostly on sediment samples (e.g., Abraham 1994: Church 1994). However, Gulson et al. (1989) used Pb isotopes in groundwater to investigate seepage from a uranium tailings pond.

Isotopes of the lighter elements, including hydrogen (Zimmermann et al. 1967; Michel et al. 1984), oxygen (Sklash et al. 1976; Veizer et al. 1997), carbon (Cerling et al. 1991; Wassenaar et al. 1991; Vogel 1993), nitrogen (Letolle 1980; Böttcher et al. 1990; Aravena et al. 1993), and sulphur (Nriagu and Coker 1978; Krouse 1980; Fry et al. 1988; Strebel et al. 1990) have also been used to help understand and to investigate a variety of environmental problems. The isotopes of two or more of these elements are frequently used in combination to solve an environmental problem (e.g., Toran and Harris 1989; Aravena et al. 1993; Fouillac et al. 1993; Taylor and Wheeler 1994; Mathieu and Bariac 1996).

The Sullivan Mine is located in Kimberley, British Columbia, Canada, approximately 32 km northwest of Cranbrook (Figure 1). The mine operated from 1900 until it was closed in 2000. The ore body consisted of beds of sulphide mineralization, including pyrrhotite, sphalerite, and galena, with minor pyrite. Environmental regulations did not exist when mining began at the Sullivan deposit; reclamation legislation was enacted in British Columbia in 1969, 60 years after Cominco Ltd. (currently Teck Cominco Ltd.) began mining the ore body. Cominco Ltd. began reclamation activities in 1972, following the implementation of this legislation. A major achievement was the commissioning of the drainage water treatment plant (DWTP) in 1979. In 1991, a comprehensive decommissioning and closure plan for the Sullivan Mine was submitted to the Ministry of Energy, Mines and Petroleum Resources. The plan addressed concerns relating to mine closure and reclamation, including providing possible solutions to each environmental issue identified.

As part of mine closure, Cominco Ltd. was required to ensure that all mine effluent water had been accounted for and that potential sources of contamination in the natural environment were identified. There are three acid rock drainage (ARD)-generating waste rock dumps in the area: the No. 1 Shaft waste rock dump, the Open Pit waste rock dump, and the Lower Mine Yard waste rock dumps (north and south). Both surface and ground water have been impacted by ARD. Cominco Ltd. currently carries out a water quality monitoring program at both the mine site and the mill/tailings area in compliance with mine reclamation regulations in British Columbia. Numerous piezometers have been installed around the mine site and are sampled twice yearly, along with surface waters. Thus, a significant geochemical database has been compiled. Water levels have been measured for most of the piezometers, and hydraulic conductivity values have been measured (by means of slug tests) for some of the piezometers.

One aspect of mine closure involved determining a background concentration of Pb to establish the level satisfactory for cleanup. Dissolved Pb concentrations

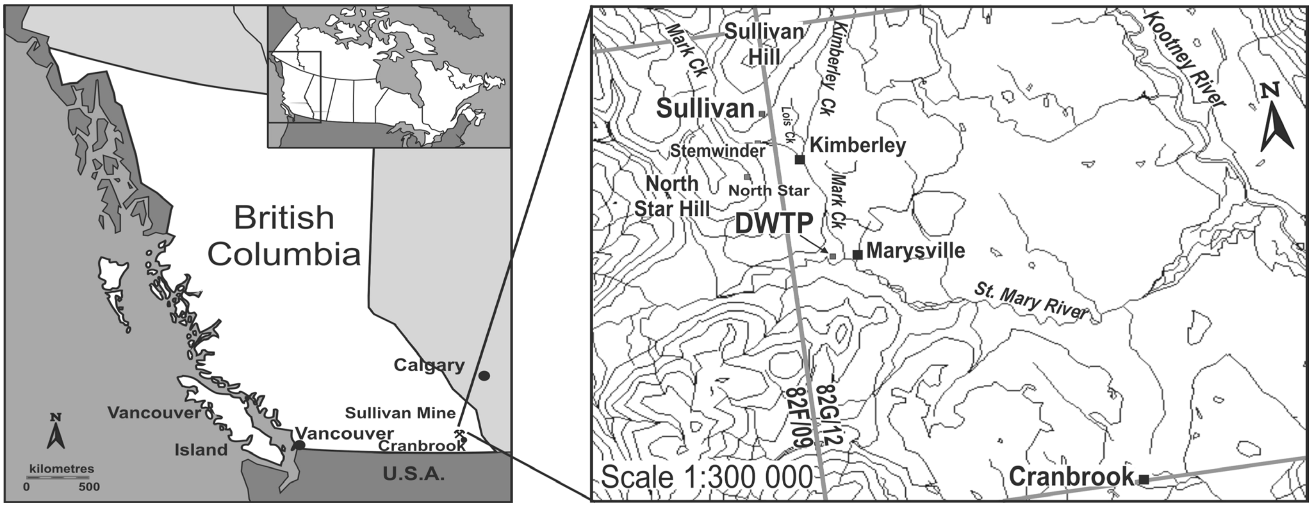

Figure 1. Location map for the Sullivan Mine and a topographic inset map showing the locations of rivers, creeks, towns, mineral deposits, and the drainage water treatment plant (DWTP) (topographic data from Land and Water BC)

in water at the mine site range from below the detection limit (<0.001 mg/L) up to 1.04 mg/L (Klohn-Crippen 2000). There was a question as to whether all of the dissolved Pb can be specifically related to mining activities. At the outset of the project, it was anticipated that Pb isotopes would possibly identify different sources of Pb within the mine area, and thus, determine the level of background Pb at the site.

The purpose of the research was to investigate the use of Pb, O, and H isotopes in an ARD study by undertaking a hydrogeochemical and isotopic investigation at the Sullivan Mine. The primary objectives were: (1) to characterize or differentiate possible sources of Pb (i.e., Pb from the ore rock versus Pb from other nearby deposits versus other sources of Pb, such as from deposition of aerosols), and (2) to use Pb, O, and H isotopes in combination with geochemical and hydrogeological data to better understand ARD and groundwater processes. This paper focuses on the Lower Mine Yard waste rock dumps. We describe the conjunctive use of Pb, O, and H isotopes to determine sources of both Pb and water in an area of the mine site that had been remediated, and thereby comment on the effectiveness of these remediation schemes. Lepitre (2001) provides results for the general mine site, and Lepitre et al. (2003) describe in detail the methodology employed for sampling and measuring Pb at the study site, and provide results for Pb in one area of the mine.

Pb, O, and H Isotopes

There are two possible mechanisms by which the isotopic abundance of elements may vary: 1) the decay of radioactive elements to their radiogenic daughter products, and (2) isotopic fractionation during physical, chemical or biological processes. For the heavier elements, such as Pb, fractionation is negligible because the relative mass difference between isotopes is small (roughly 1%). Rather, variations in isotopic ratios occur due to the addition of radiogenic daughter isotopes produced by radioactive decay. For the lighter elements, such as O, isotopic fractionation due to higher relative mass differences occurs.

Pb Isotopes

There are four naturally occurring isotopes of Pb: ^{204}Pb ^{206}Pb ^{207}Pb, and ^{208}Pb. ^{204}Pb is non-radiogenic; the other three isotopes are the radiogenic daughter products of ^{238}U, ^{235}U, and ^{232}Th, respectively, and thus accumulate through time.

Lead occurs in rocks as either common or radiogenic Pb. Russell and Farquhar (1960) defined common Pb, which includes all Pb-bearing ore minerals (e.g., galena), as being associated with insignificant or zero quantities of U and Th. The Pb isotopic composition of these minerals remains fixed because no further radiogenic Pb accumulates following crystallization. Therefore, the isotopic composition of Pb derived from deposits rich in galena is generally less radiogenic than background Pb in crustal rocks (Russell and Farquhar 1960). In contrast to ore deposits, most rocks incorporate minerals that contain both common Pb (representing the initial Pb isotopic composition) and minerals that contain U and/or Th; the Pb isotopic compositions of these have evolved through time to become increasingly radiogenic.

The differences in isotopic ratios between the sources of Pb in ore deposits and host rocks can thus be used to identify sources of Pb within geologic (e.g., Gulson 1986) and environmental systems (e.g., Sturges and Barrie 1987; Erel and Patterson 1994; Veron et al. 1994;

Tommasini et al. 2000). The Pb-bearing ore deposits have distinct isotopic signatures that enable the 'fingerprinting' of sources of Pb contamination (e.g., Rabinowitz and Wetherill 1972; Church 1994). Then, the Pb isotopic signature of a particular ore deposit can be used to trace transportation pathways of Pb contamination downstream from the deposit.

It is important to recognize that the isotopic composition of Pb contamination at a site may be due to mixing of multiple sources of Pb, such as Pb from host rocks, Pb from the ore deposit of interest, or Pb from aerosols deposited due to atmospheric Pb pollution. In the case of multiple sources of Pb, the different Pb isotopic compositions may be differentiated and the Pb isotopic composition of the contamination would be a composite of the different sources. The composite contamination would plot on a mixing line between the sources because Pb isotope ratios are linearly related (Russell and Farquhar 1960).

To summarize, common Pb in a deposit is normally less radiogenic than Pb in host rocks and Pb isotopes can be used advantageously to identify and trace contamination; mixing of Pb from the various sources can produce quasi-linear arrays on Pb isotope plots.

O and H Isotopes

Isotopes of light elements (environmental isotopes) can serve as tracers of water, carbon, nutrient, and solute cycling in the environment. For example, the amount of oxygen and hydrogen isotopic fractionation that meteoric waters undergo is a function of the temperature, the distance that precipitation occurs from the evaporative source (continental effect), and the altitude of the precipitation (Clark and Fritz 1997). Consequently, stable isotopes of O and H have been used widely to study a broad range of groundwater-related issues, such as groundwater recharge (Mathieu and Bariac 1996), groundwater velocities (Michel et al. 1984), and sources of groundwater contamination (Taylor and Wheeler 1994). However, research on the uses of these stable isotopes to study environmental problems affecting the mining industry is still in its infancy, and there are many unanswered questions related to the isotopic characteristics of ARD (Ghomshei and Allen 2000).

Stable isotopes are conventionally reported as the ratio of the second most abundant isotope to the most abundant isotope (Clark and Fritz 1997). For example, for oxygen, the ratio is $^{18}O/^{16}O$ and for hydrogen, the ratio is $^{2}H/^{1}H$ or $D/^{1}H$. The current standard is the Vienna Standard Mean Ocean Water (V-SMOW), and results are reported in parts per thousand or per mil ($^{0}/_{00}$) relative to V-SMOW using the delta (δ) notation (i.e., $\delta^{18}O$ and δD).

Although the values of $\delta^{18}O$ and δD of meteoric waters sampled worldwide varies over a large range, a linear relationship exists between $\delta^{18}O$ and δD, and is defined as the Global Meteoric Water Line (GMWL) (Craig 1961). Precipitation samples from a specific area normally have $\delta^{18}O$ and δD values that plot along a straight line specific to that area. Depending on the geographic location and climate of the area, the slope and intercept of the line differs slightly from that of the GMWL. Therefore, it is prudent to define a local meteoric water line (LMWL) for the study area. Processes affecting the water, such as evaporation or interaction with rocks, are referenced to the LMWL.

Frequently, groundwater samples from a particular aquifer fall in a tight cluster on the LMWL, indicating a relatively uniform source of recharge. Furthermore, because temperature varies both seasonally and with geographic location, O and H isotopes can provide information about sources (both temporal and geographic) for groundwater recharge. Mixed waters derived from two (or more) sources, each with a distinct $\delta^{18}O$ and δD compositions, can be identified on graphs of $\delta^{18}O$ versus δD, or $\delta^{18}O$ versus a conservative ion such as chloride (or possibly sulphate). Assuming simple mixing, mixed waters will fall on a mixing line between various end members. Therefore, O and H isotopes are useful for recognizing physical processes (such as evaporation) that have affected water, identifying source areas for groundwater recharge, and determining the proportion of water from multiple sources.

Geology and Hydrology

In the Kimberley area, most of the bedrock belongs to the Lower and Middle divisions of the Aldridge Formation. The Sullivan Deposit, a world-class sediment-hosted Fe-Pb-Zn stratiform massive sulphide (SEDEX) deposit, is hosted by the clastic sediments of the upper part of the Lower Aldridge Formation. Two smaller deposits, the Stemwinder and North Star Deposits, are situated 1.75 and 3.5 km south of the Sullivan Deposit, respectively. Unconsolidated surficial deposits in the area are mainly of glacial, glaciofluvial, and glaciolacustrine origin (Clague 1975).

Monthly average temperatures range from relatively cold in the winter (average daily minimum in January is -12.8ºC) to quite warm in the summer (average daily maximum in July is 25.7ºC) (Environment Canada 2001). Each spring, the melting of accumulated snow leads to a period of high run-off, an important source

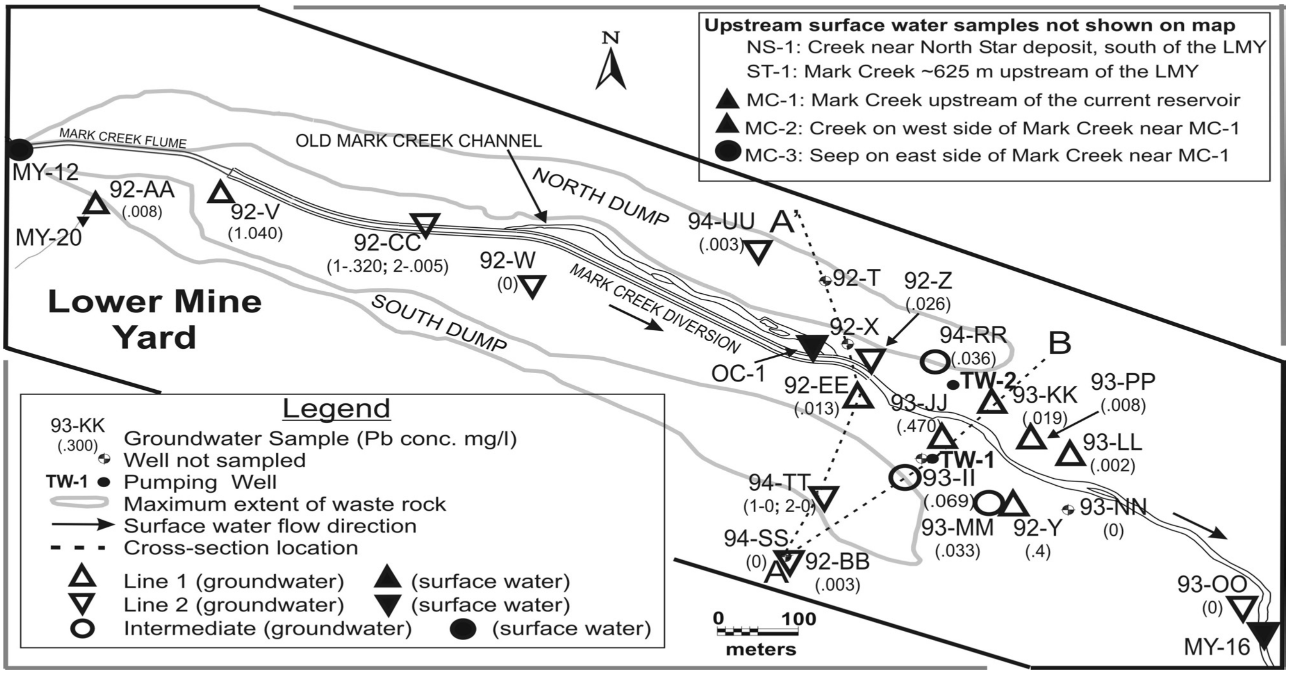

Figure 2. Groundwater and surface water sample locations in the Lower Mine Yard (LMY) at Sullivan Mine

of groundwater recharge. The surface drainage in the area generally drains towards the southeast (Figure 1). Mark Creek flows through the Lower Mine Yard (LMY) (Figure 2), ultimately draining into the St. Mary River approximately 7 km south of Kimberley. Water also enters the LMY via surface streams (several small creeks flow over both the north and south waste rock dumps and enter Mark Creek), and groundwater flowing towards Mark Creek from the steep slopes on both sides. The St. Mary River is tributary to the Kootenay River in the Rocky Mountain Trench to the east.

The hydrogeology of the mine site is largely governed by the presence of permeable units in the shallow subsurface, which overlie less permeable bedrock. The thin veneer of surficial material present over much of the mine site, and locally thick in valleys, is likely the dominant hydrostratigraphic unit through which groundwater and ARD is transported downstream, though ARD may enter and move through the groundwater system via fractures in the bedrock. The dominant unit in the area is a till, which despite its relatively low permeability, may act as an aquifer in the near surface because its permeability is likely higher than that of the bedrock. Primary aquifer units may include glaciofluvial sands and gravels, which allow ARD to discharge to the creeks, thus contributing to the degradation of surface water quality.

The Lower Mine Yard (LMY)

The LMY contains the two oldest waste rock dumps at the Sullivan Mine site (Figure 2). An estimated 4.1 million tons of waste rock were deposited in the LMY between 1909 and the mid-1960s. Waste rock was cascaded down both the north and south sides of the relatively steep slopes of the Mark Creek valley. Figure 3 shows two geologic cross-sections through the LMY, the locations of which are shown on Figure 2. The depth to bedrock decreases towards the western margin of the LMY, which is likely due to local bedrock irregularity associated with the Mark Creek valley. Bedrock is overlain by, from the bottom up, a gravel unit, a gravelly sand unit, a till unit with minor sandy lenses, and a silt/clay unit. Mark Creek has been cutting down through this stratigraphy following the retreat of the glaciers; more recently, waste rock was cascaded down both the north and south slopes of the valley, and therefore, cuts across the stratigraphy.

Prior to 1991, groundwater and surface water downstream of the LMY were contaminated by the oxidation of sulphides in the waste rock. In response, several mitigative measures were implemented. In 1991, the Mark Creek Diversion was constructed to eliminate ARD seepage to Mark Creek by isolating it from the waste rock. The Mark Creek Diversion consists of both a concrete flume at the upstream end (west) of the LMY where the creek was previously in direct contact with the waste rock, and a realignment of Mark Creek in a new channel located towards the centre of the valley. The old channel is used for collection of seepage, which is pumped to the DWTP. Two wells located at the downstream end of the LMY are pumped in order to collect ARD-contaminated groundwater. The first pumping well (TW-1) was drilled in 1993 at the toe of the south dump,

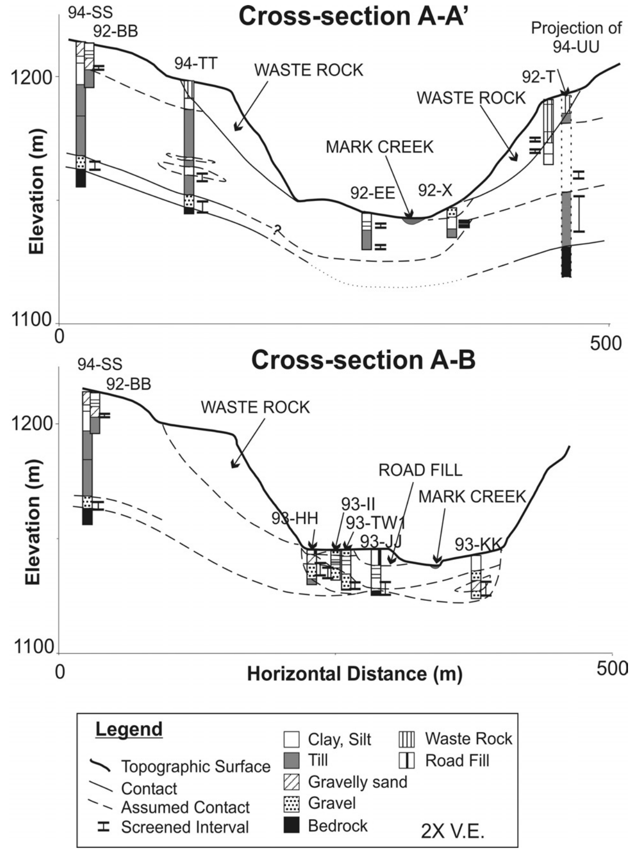

Figure 3. Cross-sections A-A' and A-B through the LMY

but it was found that the well was not collecting the entire plume; therefore, an additional well (TW-2) was drilled at the toe of the north dump in 1994. The water collected by the pumping wells is piped to the DWTP by means of the seepage collection system in the old Mark Creek channel. The south waste rock dump was capped with a layer of locally-derived silty till and revegetated in 1995. The north waste rock dump was reclaimed in a similar manner in 1997. The area within and surrounding the LMY has been instrumented with piezometers (Figure 2).

Suitability of the Site

In order to use Pb as a "fingerprinting" tool, certain criteria must be met: the Pb isotope composition of the main source(s) of Pb must be well defined and must be relatively homogeneous. The Sullivan deposit meets these criteria because: (1) the Pb isotopic composition has been well defined through the analysis of numerous samples of sulphide minerals from the deposit, particularly galena (i.e., LeCouteur 1973; Beaudoin 1997), which is the main Pb-bearing phase present, and (2) the Pb isotopic composition of the Sullivan deposit is homogeneous (Hamilton et al. 1982; Beaudoin 2001). The Pb isotopic composition of the ore is also significantly different from that of the host rocks (LeCouteur 1973). Most of the dissolved Pb in waters in the area is anticipated to be related to the Sullivan deposit. However, thick glacial overburden, which is a dominant hydrostratigraphic unit above the bedrock, may provide another potential source. If other sources of Pb are present, then these may be potential end members in chemical mixing and their Pb isotopic compositions should be determined.

Methodology

Fieldwork at the Sullivan Mine was completed over two field seasons. Most samples were collected during June, 1999; due to an unusually dry winter, some of the piezometers in the area were dry, and so the balance were collected in June, 2000. All samples were collected with minimal handling to prevent contamination of sample bottles by particulate matter (both surface and atmospheric). Sample bottles were sealed in plastic bags for transport to the laboratory. Groundwater was sampled from existing piezometers using dedicated pumps. Each piezometer was purged prior to sample collection by removing approximately 3 borehole volumes. Most of the surface water grab samples were collected at locations that were part of Cominco Ltd.'s water quality monitoring program. Samples of local till from near the Sullivan deposit and sulphide mineralization at two nearby, smaller mineral deposits (galena from the North Star deposit and pyrrhotite from the Stemwinder deposit) were collected to determine the Pb isotopic composition of other possible sources of Pb. Meteoric water samples, in the form of snow, were also collected and analyzed in order to establish the local meteoric water line.

All water samples were analyzed for dissolved Pb, Pb isotopes, and O and H isotopes. At sample sites not included in Cominco's monitoring program (Norecol, Dames & Moore 1994; Morrow Environmental Consultants 1999; Klohn-Crippen 2000), water samples were also collected for analysis of dissolved metals and major anions. Field parameters measured for each sample included: temperature, pH, conductivity, total alkalinity, and total dissolved solids.

Samples submitted for dissolved Pb analysis were filtered and acidified by a local analytical laboratory. Dissolved Pb concentrations (detection limit 0.001 mg/L) were determined by graphite furnace atomic absorption spectrophotometry. Bottle preparation, filtration, evaporation and isotopic analysis of Pb were undertaken in the clean lab facilities in the Geochronology Laboratory at the University of British Columbia (UBC). Pb isotopic ratios were measured on a modified, single collector VG-54R solid source, thermal ionization mass spectrometer equipped with a 16 sample turret and both Faraday and Daly collectors. The measured ratios were corrected for instrumental mass fractionation of 0.12%/amu (Faraday collector) or 0.43%/amu (Daly collector) per mass unit based on repeated measurements of the National Bureau of Standards SRM 981 Standard Isotopic Reference Material (common lead) and the values recommended by Todt et al. (1996). Errors were numerically propagated including all mass fractionation and analytical errors, using the technique of Roddick (1987); all errors are quoted at the 2σ level. The average total procedural blank on the trace lead chemistry was 110 picograms, measured on the laboratory blanks by isotope dilution mass spectrometry. Replicate samples from different Pb precipitates were run for approximately half of the Pb isotope samples and for one of the field blanks to assess the reproducibility of the analyses and to see if concentration was a factor in the reproducibility. Further details of the methodology followed for Pb isotopic analysis and quality control/quality assurance are described elsewhere (Lepitre et al. 2003).

Samples for oxygen and hydrogen isotopic analysis were sent to the Environmental Isotope Laboratory (EIL) at the University of Waterloo. Deuterium analysis was performed on hydrogen gas produced from water reduced on hot zinc, with a precision of ± 2 per mil (EIL 2000). Oxygen isotope analysis was done on CO_2 equilibrated with 2-8 ml water samples in a temperature controlled bath (EIL 2000). The EIL runs a quality assurance/quality control program that consists of analyzing duplicates (both O and H isotopes) on several submitted samples.

Results

Geochemistry

Figure 2 shows the locations of all ground and surface water samples in the LMY. The locations of sampling points off the map are described in the upper right left legend. Most of the geochemical data were obtained from Klohn-Crippen (2000) (Table 1). Of the 27 water samples with geochemical data from the LMY and vicinity, 21 samples have charge balance error (CBE) values less than 15%, and 17 samples have CBE values less than 10%. Samples 92-Y, 93-OO and MY-20 have CBE values between 15% and 20%. Samples 93-NN (24.52%) and MY-16 (29.18%) have even higher CBE values. The highest CBE value is from sample MY-12 (45.48%). While not excluded from the interpretation, samples with CBE values greater than 15% are considered suspect. These results are generally good, and the samples with very high CBE values can be explained, at least in part, by the low concentration of total dissolved solids.

The samples from the LMY and vicinity have been grouped into three categories, based on the location of the piezometer or surface water sample in the area (Table 2). Group 1 consists of samples from locations up-gradient of the LMY waste rock dumps. Group 2 consists of samples taken in the LMY either within or immediately down-gradient of the waste rock dumps. Group 3 consists of samples collected down-gradient of the LMY. Figure 4 is a Durov plot for the samples from the LMY, showing the relative abundances of the various ions. The cations (Ca, Pb, and Zn) and the anions (HCO_3, SO_4, and PO_4) are each normalized to 100% (in milliequivalents/L). Water chemistry for the LMY samples range from Ca-HCO_3 rich (background) to Zn-SO_4 rich (ARD). Samples that fall within the background area are mainly from Group 1 (MC-1, MC-3, ST-1, 92-BB, and 92-SS). Sample OC-1 also falls within the background range, although it is located within the LMY in the old Mark Creek channel. Several samples from Group 1 do not fall within the background category, including MY-12, MY-20, MC-2, 92-AA, and NS-1. The chemistry of sample MY-12 (taken from Mark Creek as it enters the LMY) may have been influenced by the presence of an exposed, oxidizing waste rock pile from the Stemwinder Pb-Zn deposit only 625 m upstream. Samples MY-20 (taken from a creek flowing from the south into Mark Creek), 92-AA (a shallow piezometer just above the waste rock), and NS-1 (taken from a surface seep on the North Star ski hill to the south of the LMY) are all downstream of the North Star Pb-Zn deposit that was mined in the early 1900s. It appears that all of these samples may be impacted by the North Star deposit rather than the LMY waste rock dump. The sample closest to the deposit (NS-1) shows the greatest contamination. Sample MC-2 was taken from a surface creek entering the side of Mark Creek opposite the Sullivan Mine. Therefore, although the source of the impact on the water chemistry is unknown, it is unrelated to Sullivan mining operations.

All but one sample (OC-1) that comprise Group 2 are characterized by relatively high dissolved Zn and SO_4 concentrations, and are associated with ARD from waste rock in the LMY. Group 3 samples plot similarly to Group 2 waters; however, there appears to be a trend of decreasing Zn levels in groundwater collected further downstream from the LMY. In fact, the two groundwater samples located furthest downstream of the LMY (93-NN and 93-OO) plot increasingly closer to background composition. This may be due to dilution of groundwater downstream.

Sample MY-16 (collected from Mark Creek, downstream of the LMY) appears to be a mixture of MY-12 and MY-20, which drains into Mark Creek downstream of MY-12. There is likely some inflow of groundwater to Mark Creek near MY-16. This is evidenced by the increase in Pb concentration (i.e., MY-12 has 0.051 mg/L dissolved Pb and MY-16 has 0.079 mg/L Pb), which cannot be explained by the inflow of the creek at MY-20 (which has <0.001 mg/L Pb). Therefore, it is suspected that Mark Creek at MY-16 is impacted by both the inflow of the creek at MY-20 and the inflow of ARD-contaminated groundwater from the LMY.

Although some samples have high Pb concentrations compared to other samples, this is not always obvious on a Durov plot because only the relative proportions

Table 1. Chemical data and isotopic data for Lower Mine Yard waters

Sample ID	**pH**	**HCO_3 (mg/L)**	**PO_4 (mg/L)**	**SO_4 (mg/L)**	**Ca (mg/L)**	**Zn (mg/L)**	**Pb (mg/L)**	**^{207}Pb / ^{206}Pb**	**^{208}Pb / ^{206}Pb**	**$\delta^{18}O$ ($^0/_{00}$)**	**δ^2H ($^0/_{00}$)**
92-CC1	3.7	0.00	15.944	480	98.3	21.1	0.320	0.9272	2.1784	-17.28	-141.3
92-CC2	4.6	7.08		104	20.5	4.7	0.005	0.9136	2.1627	-18.56	-145.1
92-CC2 r								0.9144	2.1643		
92-Z	3.2	0.00					0.026	0.8804	2.1210		
93-KK	3.9	0.00	0.460	1330	102	105	0.019	0.9198	2.1798		
93-LL	3.3	0.00	0.000	172	19.2	7.52	0.002	0.9189	2.1769		
93-PP	4.4	0.00	0.215	265	39.8	18.6	0.008	0.9188	2.1780		
93-PP r								0.9190	2.1759		
94-RR	3.8	0.00	0.000	2860	185	164	0.036	0.9156	2.1685	-17.75	-141.6
94-RR r								0.9185	2.1796	-17.87	-141.6
94-UU	6.7	705.60					0.003	0.9039	2.1510		
OC-1	7.4	196.80	0.000	44.9	58	0.069	0.004	0.9302	2.1814		
92-AA	4.8	48.00	12.265	29.1	24.9	0.26	0.008	0.9286	2.1836		
92-BB	4.9	246.00	22.383	58	94	0.15	0.003	0.8863	2.1199		
92-EE	4.2	0.00		280	49.4	18.7	0.013	0.9136	2.1751		
92-EEr								0.9132	2.1700		
92-V	2.5	0.00	0.920	1900	248	188	1.040	0.9354	2.1940		
92-V r								0.9352	2.1901		
92-W	5.4	53.40	4.906	420	139	18.4	<0.001	0.8660	2.0954		
92-W r								0.8667	2.1035		
92-Y	1.7	0.00	1.165	1400	334	780	0.400	0.9240	2.1791	-17.91	-144.2
92-Y r								0.9235	2.1789		
93-II	3	0.00		3800	152	410	0.069	0.9113	2.1624		
93-JJ	4.9	0.00		420	68.1	32.2	0.470	0.9229	2.1817		
93-MM	3.9	0.00	0.000	2100	221	58.5	0.033	0.9181	2.1704	-17.05	-138.7
93-NN	3.8	174.00	0.613	251	115	6.84	<0.001			-18.68	-144.6
93-OO	2.7	235.20	9.812	161	104	0.047	<0.001	0.9095	2.1458		
93-OO r								0.9077	2.1523		
94-SS	6.6	145.20	2.790	25.2	30	0.01	<0.001				
94-TT1	6	70.80					<0.001	0.8721	2.0981		
94-TT2	5.9	74.40					<0.001	0.8727	2.0909		
MY-20	6.2	55.56	0.000	24.8	22.2	1.33	<0.001				
NS-1	5.1	3.72	0.000	25.3	5.74	1.14	0.180	0.9378	2.1905		
NS-1 r								0.9269	2.1780		
MC-1	5.4	7.80	0.000	1.5	1.41	<0.005	<0.001	0.8737	2.1406	-16.20	-137.5
MC-1 r								0.8760	2.1419	-16.20	-137.4
MC-1 r2								0.8775	2.1432		
MC-2	6.5	14.28	0.000	10.1	5.06	<0.005	<0.001	0.9330	2.1895		
MC-3	6.8	85.56	0.245	11.3	20.6	<0.005	<0.001	0.9223	2.1744	-17.68	-143.0
MY-12	7.4	9.00	1.962	3.3	5.03	0.033	0.051	0.9176	2.1700		
MY-16	7.5	9.84	1.318	4.1	3.59	0.073	0.079	0.9131	2.1588		
ST-1	6.6	42.48	0.000	6.2	8.35	0.042	0.003	0.9365	2.1913		
NorthS								0.9393	2.1938		
StemW								0.9408	2.1987		
Till 1								0.8543	2.1139		
Till 2								0.9221	2.1963		
S-1										-21.78	-163.9
S-2										-19.85	-150.6

r – replicate analysis; r2 – rerun on replicate

Table 2. Division of LMY samples on the basis of sample location

Group #	Location	Samples
Group 1	Up-gradient of LMY waste rock dumps	MY-12, MY-20, MC-1, MC-2, MC-3, ST-1, 92-AA1, 92-BB, 94-SS, and NS-1
Group 2	Within or immediately down-gradient of LMY waste rock dumps	South side of Mark Creek: 92-V, 92-W, 92-EE2, 93-JJ, and 93-II; north side of Mark Creek: 92-CC1, 92-CC2, OC-1, and 94-RR
Group 3	Down-gradient of LMY pumping wells	South side of Mark Creek: 93-MM, 92-Y, 93-NN, 93-OO, and MY-16; north side of Mark Creek: 93-KK, 93-PP, and 93-LL

of the cations are plotted. For example, sample 92-V (1.04 mg/L) has approximately 13 times more Pb than MY-16 (0.079 mg/L). Although 92-V has significantly more Pb than MY-16, sample MY-16 has more Pb in relation to Zn and Ca than sample 92-V. Therefore, sample MY-16 plots closer to the Pb apex than sample 92-V. The reason that most of the samples plot along the Ca-Zn line is due to the low solubility, and therefore, low dissolved concentration of Pb in the water compared to Zn and Ca. Thus, Pb values on a Durov plot do not assist with the interpretation, but only serve as a third apex for completing the cation ternary diagram.

Only a few samples from the LMY have a relatively significant phosphate levels: MY-12, MY-16, 92-AA, and 92-BB. Samples MY-12 and MY-16 are located in Mark Creek, and samples 92-AA and 92-BB are shallow piezometers on the south side of the LMY. The phosphate is likely from septic tanks in the development just upstream from the sample sites.

In general, as the SO_4 concentration increases, a corresponding increase in the Zn concentration is observed (Figure 5). As expected, samples from group 1 have low Zn and SO_4 concentrations, whereas group 2 samples are relatively high in Zn and SO_4. The majority of group 3 samples have intermediate values of Zn and SO_4. However, sample 92-Y (past pumping well TW-1) shows a very high level of Zn and SO_4, indicating that ARD water has migrated downstream of the capture zone of the well. This may be due to the fact that the screened interval for 92-Y is in the high permeability gravel unit, below the upper layers that receive ARD waters directly from the waste rock. Samples 93-NN and 93-OO show decreasing Zn and SO_4 concentrations with increasing distance downstream.

Pb Isotopes

Dissolved Pb concentrations are provided in Table 1 and are also shown in brackets beneath the sample ID in Figure 2. Lead concentrations in water from the LMY range from below the detection limit (<0.001 mg/L) to 1.04 mg/L (Klohn-Crippen 2000). Lead isotopic ratios are provided in Table 1 and are displayed on a graph of $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$

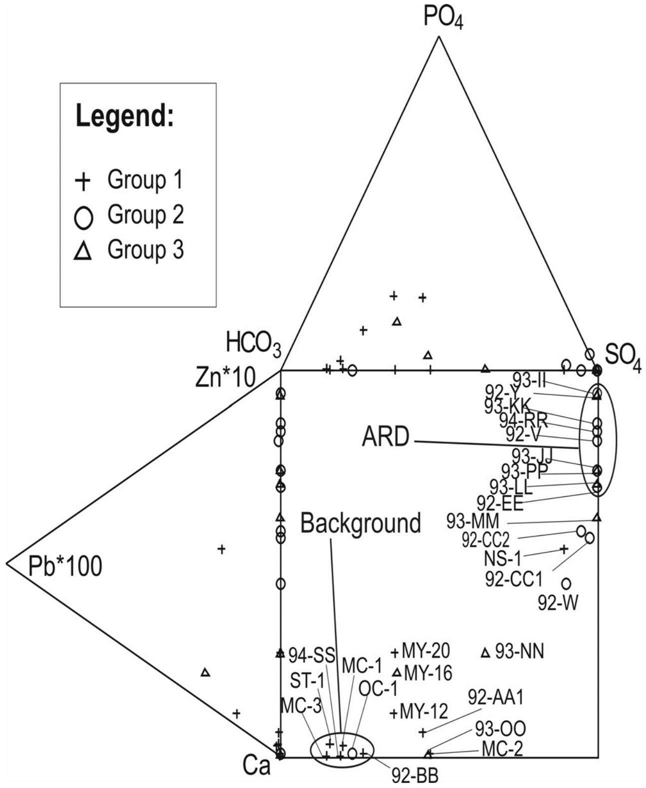

Figure 4. Durov plot showing the relative chemistry of all of the water samples from the LMY

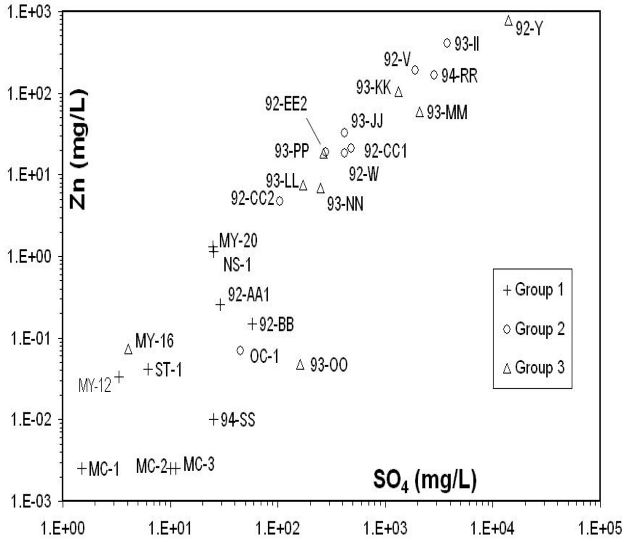

Figure 5. Zn versus SO_4 concentration for samples from the LMY and vicinity

(Figure 6). Note that Pb isotope data are available for all samples from the LMY, except for MY-20, 93-NN, and 94-SS.

Pb isotopic ratios for the LMY groundwater range from 2.035 to 2.194 for the $^{208}Pb/^{206}Pb$ ratio and from 0.817 to 0.936 for the $^{207}Pb/^{206}Pb$ ratio. The equivalent surface water sample ratios range from 2.064 to 2.191 ($^{208}Pb/^{206}Pb$) and 0.841 to 0.938 ($^{207}Pb/^{206}Pb$). Variability for replicates is due to a different precipitate being used. The Sullivan ore is characterized by a Pb isotopic composition of 2.183 to 2.194 for the $^{208}Pb/^{206}Pb$ ratio and 0.935 to 0.938 for $^{207}Pb/^{206}Pb$ ratio. The range in the Pb isotope ratios of Sullivan alteration spans a slightly larger range, with the $^{208}Pb/^{206}Pb$ varying from 2.167 to 2.209 and the $^{207}Pb/^{206}Pb$ varying from 0.923 to 0.945. The Pb isotopic results from samples from the nearby North Star and Stemwinder deposits (identified as NorthS and StemW in Table 1) plot close to that of Sullivan ore, although they plot slightly down and to the left of Sullivan Pb on Figure 6. The till samples, Till 1 and 2, have Pb isotopic compositions distinct from the Sullivan ore and from each other, and appear to be heterogeneous in composition.

The range in Pb isotopic ratios of water samples from the LMY defines what appear to be two mixing lines between Sullivan Pb and two other end members (Lines 1 and 2 on Figure 6). Therefore, the samples plot within a triangular area defined by three end members rather than along a single line. This indicates that not all of the dissolved Pb in waters collected in the study area originates from Sullivan ore or mining operations, as previously suspected.

Line 1 end members are Sullivan Pb and Pb with an isotopic composition similar to sample MC-1 background surface water). A surface water sample from another area of the mine site, reported by Lepitre (2001), plots near sample MC-1 (slightly above it and to the right) and serves to further constrain line 1.

Samples identified with an upright open (groundwater) or solid (surface water) triangle symbol in Figure 2 fall along line 1 (increasingly closer to the Sullivan Pb) and include: MC-1, 92-EE, 93-PP, 93-LL, 93-KK, 92-Y, 93-JJ, 92-AA, MC-2, and 92-V (although it is difficult to assign MC-2 and 92-V to line 1 due to their proximity to the Sullivan Pb). All of the groundwater samples (except 92-AA and 92-V) in this group are located close to the pumping wells. Therefore, it appears that surface water from Mark Creek with an isotopic composition similar to MC-1 is recharging the aquifer (with groundwater contaminated by the waste rock dumps) in the vicinity of the pumping wells.

End members for line 2 include Sullivan Pb and Pb characterized by a Pb isotopic composition more enriched in ^{208}Pb than MC-1 (i.e., passing through 94-TT1&2 and 92-W in Figure 6). Several samples fall along line 2, including (in order of increasing similarity to Sullivan Pb): 92-W, 94-TT2, 94-TT1, 92-Z, 92-BB, 94-UU, 93-OO, MY-16, 92-CC2, 92-CC1, and OC-1. These samples are identified with an inverted open (groundwater) or solid (surface water) triangle symbol in Figure 2. All of these samples are groundwater samples with the exception of MY-16 and OC-1. Sample MY-16 may be plotting on line 2 due to the inflow of groundwater at this point, as previously discussed and supported by the geochemical data.

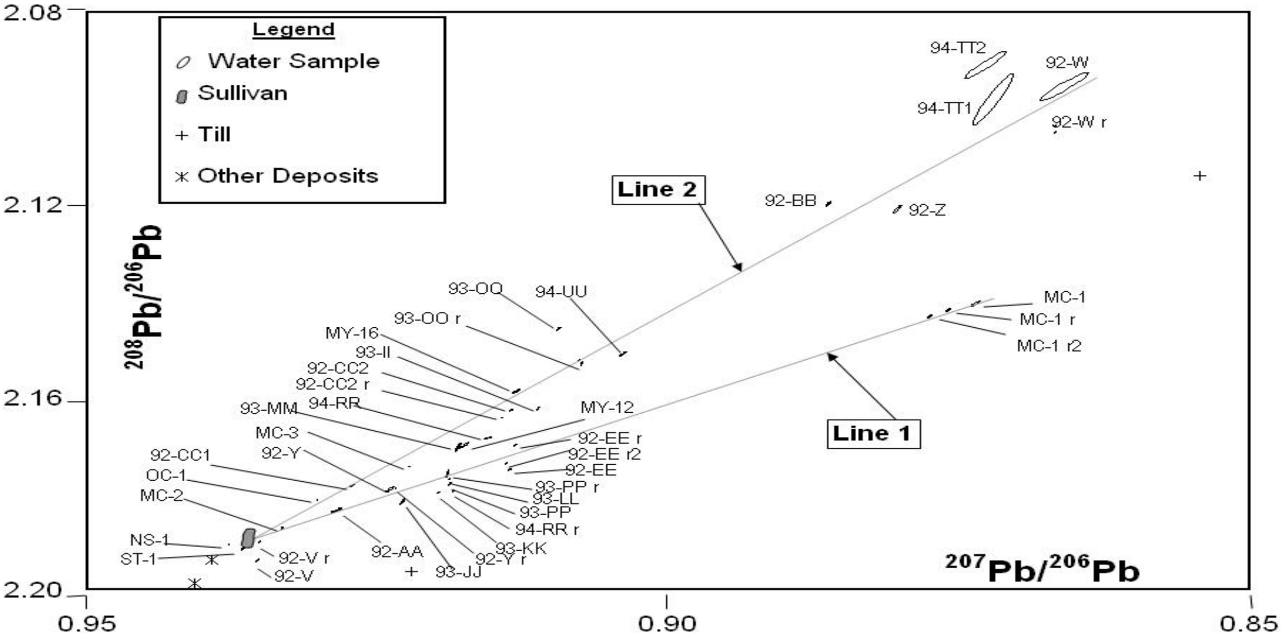

Figure 6. $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ for water samples from the LMY

This second end member for Pb in the groundwater samples is likely Pb contained within the local surficial deposits. Because of the heterogeneous isotopic composition of the tills sampled, it is unlikely that these constitute an end member. Rather, we propose that the Pb originates from the deposition of aerosols on the surficial deposits.

Several samples plot distinctly between the two mixing lines. These are represented by open circles (groundwater) or solid circles (surface water) in Figure 2. The data indicate that these samples contain a contribution of Pb from each of the three end members. These samples are: 93-II, 94-RR, MY-12, 93-MM, and MC-3 in order of increasingly similarity to Sullivan Pb. Samples 93-II, 93-MM, and 94-RR are all located near one of the two pumping wells. Therefore, although they are influenced by Pb from the local surficial deposits, there is also an influence of surface water from Mark Creek contributing some Pb. Sample MC-3 is a groundwater seep from a location on the Sullivan side of Mark Creek, near MC-1. Sample MY-12, expected to fall on line 1, is shifted towards line 2, possibly due to the influence of groundwater.

As expected, samples NS-1 and ST-1 plot very close to the isotopic composition of the sulphide mineralization from the North Star deposit and the Stemwinder deposit.

Water samples with elevated Pb concentrations were found to have Pb isotopic compositions indistinguishable from Sullivan ore, whereas water samples with low Pb concentrations display a range of Pb isotopic compositions. The threshold value of Pb is 0.001 mg/L, below which the source of Pb is not necessarily Sullivan ore. Thus, background Pb is associated with a concentration of 0.001 mg/L.

O and H Isotopes

The oxygen and hydrogen isotope data for samples from the LMY are reported in Table 1 and displayed on Figure 7. Only a subset (samples 93-NN, 92-CC2, 92-Y, MC-3, 94-RR, 92-CC1, 93-MM, and MC-1, listed in order of increasing enrichment in the heavy isotopes) of the samples from the LMY was sent for isotopic analysis. The GMWL is plotted with a dashed line on Figure 7 for reference (Craig 1961). A LMWL has been defined based on two local snow samples and duplicate analyses on the same samples; the isotopic results obtained are consistent with previous results for meteoric waters from south-eastern British Columbia (Ghomshei and Clark 1993). A linear regression through the points gives a LMWL of δD = 6.8135δ^{18}O – 15.453, which is similar to the LMWL defined by Allen and Voormeij (2002). In Figure 7, the oxygen and hydrogen isotopic results for samples collected from the LMY and vicinity plot along a trajectory (with a lower slope) to the right of the LMWL. The trajectory has an equation defined by δD = 3.9076δ^{18}O – 73.027 (with an R^2 value of 0.9905), and likely represents an evaporation trend. The evaporation line is constrained by a sample taken from a standing pool of water in the open pit (OP-1), which has definitely undergone evaporation. Also, the slope of the evaporation line agrees with slopes of evaporation lines (between 3 and 5 in δ^{18}O–δD space) found by previous researchers (Ghomshei and Clark 1993; Ghomshei and Allen 2000).

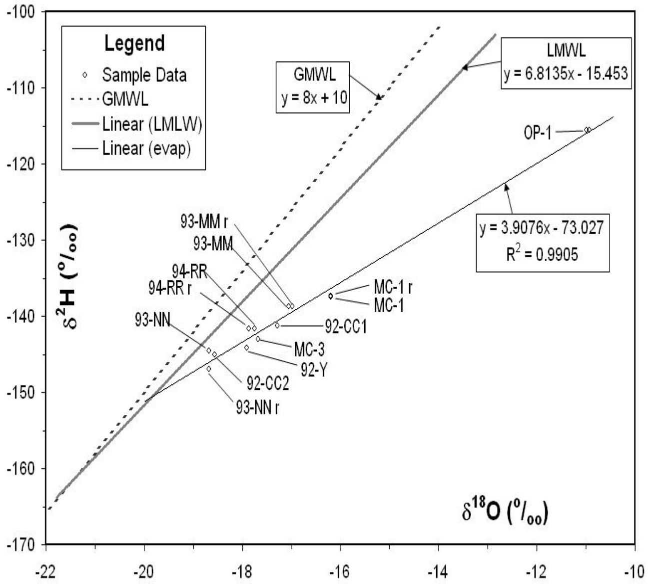

Figure 7. δD versus δ18O for all samples from the LMY

Surface water samples MC-1 and MC-3 have likely undergone evaporation, leading to enrichment in the heavy isotopes. The remaining samples are all groundwater, but do not plot as a cluster on the LMWL as is typical for groundwater recharged from meteoric sources. Rather, they fall at varying distances along the evaporation line. Several of the samples are taken from piezometers located near the two pumping wells, including 93-MM, 92-Y, and 93-NN on the south side and 94-RR on the north side of Mark Creek. On the south side, there is a trend of increased enrichment in the heavy isotopes closer to the pumping well. This suggests that an increasingly higher proportion of the surface water is contributing to these samples. Unfortunately, there are not enough data from the north side to decipher a similar trend. Sample 94-RR is closest to one of the pumping wells, but is not as strongly influenced by an evaporative source. This is probably due to the fact that this piezometer is completed at a greater depth than the other piezometers, and therefore, is less influenced by surface water recharge. The other enriched samples include 92-CC1 (11.15m) and 92-CC2 (6.55m), which are located on the north side of the LMY. It is unclear why these two samples are enriched in the heavy isotopes, and are more enriched with increasing depth.

Discussion

The geochemical, Pb isotopic, and stable O and H isotopic data provide a means of evaluating mitigation of down-gradient contaminant movement by the LMY pumping well system. The geochemical results indicate that some ARD-contaminated groundwater is escaping downstream of the two pumping wells in the LMY, particularly in the shallow subsurface. However, the results also show that groundwater samples plot increasingly closer to background composition down-gradient from the waste rock. This may be due to dilution of the groundwater with increased distance. In addition, the geochemical results show that there is minimal contamination of the surface water downstream of the LMY. The reason that the surface water shows minimal impact from the ARD is likely due to remedial activities, such as the isolation of Mark Creek from the LMY waste rock (Mark Creek Diversion).

The geochemical data are supported by the Pb isotopic data since the samples become increasingly more radiogenic (i.e., further from the Sullivan signature) down-gradient of the LMY. The Pb isotope data may also provide evidence that the reclamation of the LMY waste rock dumps (by capping with silt till) has had some success. Piezometers 94-TT2 (south) and 94-UU (north) are similar in their depths of completion and in their geology. Both are completed approximately 40 m below the ground surface in a sand and gravel till underlying a layer of waste rock. Sample 94-TT2 has a much more radiogenic Pb isotopic signature (i.e., plots further from Sullivan Pb) than the sample from 94-UU. The south dump was reclaimed 2 years earlier than the north dump; therefore, infiltration has potentially been reduced for a longer period of time on the south dump, and the Pb isotope ratios are within the background range.

Oxygen and hydrogen isotopes showed that Mark Creek water is recharging the groundwater in the vicinity of the pumping wells. These data also suggest that the pumping well 93-TW1 is effective at inducing recharge to the lower aquifer (i.e., 93-MM in the deeper gravel aquifer is more enriched in the heavy isotopes compared to 92-Y in the shallow gravel aquifer). Thus, the stable isotope results suggest that the surface water and shallow groundwater regimes are highly connected and interact across the site, and that there is a high incidence of recharge by surface waters (particularly by Mark Creek water in the LMY).

The implication of significant contributions of evaporated surface water to the groundwater regime is that the surface water and groundwater systems cannot be evaluated separately. Any activities related to water diversion either on the surface or at depth (i.e., through pumping) must take into consideration the effects on the entire hydrologic system. Furthermore, the use of stable isotopes may provide a useful tool for evaluating the contributions of surface water to groundwater systems, and surface waters may serve as an isotopic fingerprint for identifying potential evaporative sources of contaminated water.

Conclusions

Geochemical data from samples from the LMY demonstrate the mixing of background waters with ARD waters. Of the 10 samples collected up-gradient of the waste rock dumps, five do not plot as background waters, indicating that there are sources of heavy metal contamination up-gradient of the LMY. The most likely source of this contamination is old workings from two nearby mineral deposits that were mined in the early 1900’s. The geochemical results also indicate that some ARD-contaminated groundwater is escaping downstream of the two pumping wells in the LMY, and that there is minimal contamination of the surface water downstream of the LMY. The reason that the surface water shows minimal impact from the ARD is due to the isolation of Mark Creek from the LMY waste rock, through remedial activities.

Mixing between Sullivan and at least two distinct end members was observed. Therefore, dissolved Pb in water near the LMY waste rock dumps originates from a variety of sources including mining operations, potentially the ore itself, and background sources. Pb at concentrations at or below 0.001 mg/L can be associated with a variety of sources; however, further sampling of local surficial deposits and background surface waters is needed to better constrain the Pb isotopic ratios of these end members. Pb isotopic data add another perspective to the traditional geochemical data. For example, sample ST-1 (up-gradient of the LMY) has a background geochemical signature; however, the Pb isotopic ratio indicates that ST-1 is not background, but rather a mixture of Sullivan and Stemwinder Pb. The Pb isotope data may also assist in evaluating the efficiency of the silt till capping of the waste rock dumps.

Oxygen and hydrogen isotope data from water samples from the LMY plot along an evaporation line. The surface waters have undergone evaporation and therefore enrichment in the heavy isotopes. Most of the other samples are groundwater samples located near the two pumping wells. These samples plot along the evaporation line, possibly due to induced recharge of the groundwater by Mark Creek water.

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