THE INFLUENCE OF SURFACE MINING ON HYDROLOGY IN ELK VALLEY, B.C.

# THE INFLUENCE OF SURFACE MINING ON RUNOFF TIMING AND FLOW PATHWAYS IN ELK VALLEY, BRITISH COLUMBIA

By

Nadine J. Shatilla, B.Sc

A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Science

McMaster University

© Copyright by Nadine J. Shatilla, September 2013

McMaster University MASTER OF SCIENCE (2013) Hamilton, Ontario (Earth Science)

TITLE: The influence of surface mining on runoff timing and flow pathways, Elk Valley, British Columbia AUTHOR: Nadine J. Shatilla, B.Sc. (McMaster University) SUPERVI-SOR: Professor Sean K. Carey NUMBER OF PAGES: 73

#### Abstract

Surface mining is a common method of accessing coal. In high-elevation environments, vegetation and soils are typically removed prior to the blasting of overburden rock thereby allowing access to mineable ore. The removed waste rock is deposited in adjacent valleys where it may bury existing streams. Previous research, predominantly in Appalachia, has focused on downstream water quality impacts with less focus on how streamflow response and flow pathways are affected by surface mining. This study reports on how surface mining affects streamflow hydrological and chemical responses at the headwater catchment scale in the Elk Valley, British Columbia. A paired catchment approach was utilized between May and October 2012, where a reference catchment (Dry Creek - DC) was compared to an impacted catchment (West Line Creek -WLC), whose area is 30% covered by deposited waste rock. Hydrometrically, WLC had considerably lower flows and exhibited a damped, slower response to precipitation events than DC. Dissolved ions were an order of magnitude greater in WLC, with conductivity (SpC) ranging between 400  $\mu$ S/cm at high flow to 1300  $\mu$ S/cm at low flow. A strong hysteretic pattern was observed between SpC and flow and with specific ions at WLC, suggesting dilution or changing flowpaths as the season progressed. In contrast, patterns of SpC and flow at DC did not exhibit hysteresis. Major ion hydrochemistry at WLC shows dilution affecting ion concentrations whereas results at DC are consistent with chemostatic behavior. Stable isotopes were more depleted at DC compared with WLC, suggesting different sources and timing of water contributing to streamflow. Future research will work towards a conceptual model of surface mining impacts on catchment scale processes in montane environments through increased understanding of residence time and flowpath distributions at a number of impacted and reference catchments.

## Acknowledgements

I'd like to express my gratitude to my supervisor, Dr. Sean Carey, for his immense patience and support during trivial and somewhat less trivial 'crises'. His experience and advice were (surprisingly) invaluable. I'd also like to thank Dr. Mike Treberg and Dr. Gordon Drewitt for help in the field, and with instrumentation and analysis. In particular, I'd like to thank Mike Treberg for graciously permitting me to drive when he could have done it better. Another thank you to Krysha Dukacz for encouraging me to think in a broader, more spatial sense and for assembling maps of study sites.

Teck Resources Limited provided me with an amazing opportunity and a beautiful study location. Special thanks to Rob Klein from Line Creek Operations for being extremely generous with his time and ensuring that I understood and followed site procedures and protocols. I appreciate the loan of many pairs of safety glasses and a toque or two. I'd also like to say that my experience with the project was enriched by the presence and guidance of Clara Qualizza. Clara, thanks for your encouragement, trust and kind words.

Year "Zero" of this project owes a lot to Dr. Tyler Birkham, Stu McPhee and Sebastian Lamoureux from O'Kane Consulting for equipment installs, a little bit of babysitting and a lot of support in the first few weeks of the field season.

This project involved the collaboration of many researchers from University of Saskatchewan that were led by Dr. Jim Hendry, Dr. Lee Barbour and Virginia Chostner. Thank you to Jim and Lee for 'divining' the West Line Creek rock drains and directing me towards them, and thank you to Virginia for a lot of coordination and hard work in organizing the analysis of geochemical samples.

A key part of this thesis was based on results of stable isotope analysis from Dr. Carl Mitchell at the University of Toronto Scarborough. I really appreciated the quick turnaround and clear communication.

To my family and friends, I'm surprised that you all continue to tolerate my quick temper and limited patience.

One last thank you to Nikolas Gazo for his inimitable skill with LATEX.

# Table of Contents

A	bstra	ct	iii					
Acknowledgements								
Ta	ble c	of Contents	v					
Li	st of	Figures	vii					
Li	st of	Tables	viii					
1	<b>Intr</b> 1.1 1.2 1.3 1.4	oduction and Background    Hydrological Regimes of Mountain Catchments    Stable Isotopes and Stream Hydrochemistry in Catchment    Hydrology    Paired Catchment Studies    Research Objectives	<b>1</b> 2 4 6 7					
2	Site 2.1	Description and Methods    Site Description    2.1.1  Climate    2.1.2  Soils and Geology    2.1.2.1  Coal Spoil	<b>8</b> 8 9 9					
	2.2	2.1.3  Ecology  Ecology  Ecology    Field Methods  Ecology  Ecology  Ecology    2.2.1  Stream discharge  Ecology  Ecology    2.2.2  Weather and Precipitation  Ecology  Ecology    2.2.3  Water Samples  Ecology  Ecology	10 11 11 11 11					
		2.2.3  Water Samples    2.2.3.1  Isotopes    2.2.3.1.1  Precipitation samples    2.2.3.1.2  Stream samples    2.2.3.2  Geochemistry (Major Ions)    2.2.4  High Frequency Monitoring (Conductivity Tomporature and Water)	12 12 12 13 13					
		2.2.4  Ingli Frequency Montoring (Conductivity, Temperature and Water Level)    2.2.4.1  West Line Creek (WLC)    2.2.4.2  Line Creek 1 (LC1)    2.2.4.3  Line Creek 3 (LC3)    2.2.4.4  Dry Creek (DC1)	14 14 14 14 15					
	2.3	Laboratory Methods	15 15 15 16 16					

3	Res	ults		17					
	3.1	Field (	Observations	17					
		3.1.1	Climate	17					
		3.1.2	Discharge	18					
		3.1.3	Specific Conductance	19					
	3.2	Hydro	chemistry	19					
		3.2.1	Time Series of Major Ions	19					
			3.2.1.1 Dry Creek (DC1) $\ldots$	20					
			3.2.1.2 West Line Creek (WLC) $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	21					
	3.3	Stable	Isotopes	22					
		3.3.1	Local Meteoric Water Line	22					
		3.3.2	Streams	22					
			3.3.2.1 Dry Creek (DC1) $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	23					
			3.3.2.2 WLC	24					
			3.3.2.3 General Observations of Enrichment	24					
<b>4</b>	Disc	cussion	1	26					
	4.1	Hydro	metric Response	27					
	4.2	Hydro	chemical Response	28					
		4.2.1	Specific Conductance and Discharge (Q)	29					
		4.2.2	Log-log C-Q Relationships	32					
	4.3	Stable	Isotopes	33					
	4.4	Summa	ary	35					
<b>5</b>	Con	clusior	ns	37					
Figures									
rigures									
Appendix									
References									

# List of Figures

1	Map of Elk Valley, B.C.	39
2	Map of Study Sites	40
3	Boxplots of Mean Monthly Air Temperature	41
4	Boxplots of Mean Monthly Precipitation Partitioned into Rain and Snow	42
5	Isotope Precipitation Gauge (Photo)	43
6	Mean Daily Air Temperature and Precipitation at 1300m and 1850m $\ .$	44
7	Mean Daily Precipitation at 1300m and Discharge at WLC and DC1 $\ .$	45
8	Time Series of Specific Conductance and Discharge at WLC and DC1 $\hdots$	46
9	Time Series of Major Ion Concentrations and Selenium	47
10	Stable Isotopes of $\delta^{18}{\rm O}$ and $\delta^2{\rm H}$ from Elk Valley plotted along Calgary LMWL	48
11	Stable Isotopes of $\delta^{18}$ O and $\delta^{2}$ H from WLC and DC1 Streams	49
12	Stable Isotopes of $\delta^{18}{\rm O}$ and $\delta^{2}{\rm H}$ from Precipitation and Streams at WLC and	
	DC1	50
13	Enrichment of Stream $\delta^{18}$ O and $\delta^{2}$ H $\ldots$	51
14	Discharge Normalized to Catchment Area at Sites Along Line Creek	52
15	Discharge versus Specific Conductance	53
16	Discharge versus Specific Conductance on Logarithmic Axes	54
17	C-Q Relationships of Major Ions	55
18	Aerial Photo of West Line Creek Catchment (1986)	56
19	Aerial Photo of Dry Creek Catchment (2011)	56
20	DEMs of WLC Pre- and Post-Mining Impacts	57

# List of Tables

1	Summary Statistics of Stable Isotopes	58
2	Log-log Slopes and Significance Tests for Major Ions	58

## 1 Introduction and Background

Surface mining is a common practice for accessing coal in alpine environments in British Columbia, Canada. This type of mining involves the removal of vegetation at high-elevation, and the use of explosives to blast the rock overlying the coal-bearing lithology in successive layers (Palmer et al., 2010). Each layer of excess rock (called overburden or waste rock) is removed and transported to an end-dumping location. The overburden is then pushed into adjacent valleys where it buries existing streams and rivers (Palmer et al., 2010; Swanson et al., 2011). This overburden is known as coal spoil and typically contains a heterogeneous collection of overburden, waste rock and lower quality coal (Dickens et al., 1989; Wayland & Crosby, 2005). In British Columbia, coal spoils can be up to several kilometers long and several hundred meters thick (Line Creek Phase II Expansion EA Review, 2013).

Surface mining for metallurgical coal has been ongoing in Elk Valley, British Columbia, since 1897, yet increased in scale substantially beginning in the late 1960s (Line Creek Phase II Expansion EA Review, 2013). There are currently five open-pit coal mines in this region of southeastern British Columbia, all operated by Teck Resources Ltd., with an annual production volume of approximately 20 million tonnes of metallurgical coal (Teck Resources Limited Quarterly Report, 2012).

Surface mining operations alter the physical composition of the landscape and increase the volume and surface area of geologic material available for weathering and erosion processes (Dickens et al., 1989; Guebert et al., 2001). This newly fractured and unconsolidated material is exposed to aerobic conditions and water, accelerating reaction rates and the release of solutes into surface waters (Swanson et al., 2011). Recent studies of mine affected rivers in central Appalachia in West Virginia as well as Elk Valley in British Columbia have reported ion concentrations elevated above expected background conditions (Kennedy et al., 2000; Chapman et al., 2007; Murphy et al., 2012). In Elk Valley, considerable attention has been given to increasing concentrations of selenium (Se), a trace metalloid present in natural freshwater systems in concentrations ranging from 0.1 to 1  $\mu$ g/L (Kennedy et al., 2000; Lussier et al., 2003; Wayland & Crosby, 2005; Chapman et al., 2007).

Despite concerns about rising Se concentrations in Elk Valley, there is limited understanding of Se release and mobilization from waste rock (Jayaweera, 1996; SRK Consulting (Canada) Ltd, 2010; Swanson et al., 2011; Murphy et al., 2012). Geochemical analyses of Se have shown that the metalloid is more readily transported in the soluble forms selenate and selenite signifying a tight coupling between the movement of water and Se (Ryan & Dittrick, 2000; Kennedy et al., 2000; MacDonald & Strosher, 2001; Hamilton, 2004; Chapman et al., 2007). Any attempt to limit the mobilization of Se first requires a conceptual model of how the coal spoil deposited in alpine watersheds has altered the hydrological regime and runoff generation processes.

## 1.1 Hydrological Regimes of Mountain Catchments

The hydrological regime of mountainous catchments in interior continental regions of North America is characterized by strong seasonal signals in precipitation and temperature, which lead to high-energy stream responses typically dominated by snowmelt freshet (Hoeg & Uhlenbrook, 2000; Becker, 2005). In northern latitudes, annual low flows often occur during winter when most precipitation falls as snow and direct water inputs to the catchment are small (Moore & Wondzell, 2005). Snow typically accumulates throughout the winter season and snowmelt or freshet results in annual peak flows in spring or early summer (Moore & Wondzell, 2005; Stewart, 2009). Meltwater production in alpine catchments depends on variations in topographic shelter, elevation, slope, aspect and vegetation characteristics can depend on the amount of snow accumulated, the snow covered area as well as climatic factors that control the melt regime (Moore & Wondzell, 2005; DeBeer & Pomeroy, 2009). High elevation areas with significant snow accumulation are linked to longer periods of snowmelt and delayed peak flows (Liston, 1999; Stewart, 2009). Occasionally, high magnitude summer rain events can lead to greater runoff than the stream freshet response (Moore, 1991). Typically, discharge is low beginning in late summer and during the onset of the winter season (Moore & Wondzell, 2005).

At present, our scientific understanding of high altitude areas is comparatively poor due to the many logistical challenges related to access and human hazards (Burns et al., 2001). Additionally, runoff generation processes in alpine environments are extremely complex, difficult to monitor and highly variable in space and time (Anderson & Burt, 1990; Bonell, 1993; Hoeg et al., 2000; Beldring et al., 2000; Carey & Woo, 1999; 2001; Becker, 2005; McCartney et al., 2006; McGuire et al., 2007). Runoff in mountain catchments is often controlled by non-linear relationships and interactions among soils and geology, climate and vegetation (Hoeg et al., 2000; Becker, 2005; Bales et al., 2006). The combination of these factors determines the relative influence of each component of the water balance including storage and soil moisture dynamics, evapotranspiration and the resultant runoff (McNamara et al., 2005). Runoff in these environments is often difficult to accurately assess because of the predominance of subsurface flow pathways (Harr, 1977; Jones & Grant, 1996; Anderson et al., 1997; Hoeg et al., 2000; McGuire et al., 2007).

In terms of stream water composition, alpine areas are often characterized by dilute runoff owing to the rapidity of hydrological processes caused by high hydraulic gradients, high flow velocities and the transmission of pressure-induced pulses (Silar, 1990). There is also a potential, dependent on the permeability of the bedrock geology, for subsurface flow to bypass the basin outlet (Moore & Wondzell, 2005). Hydrometrics and stream chemistry reported at the watershed outlet are an integrative measure of diverse runoff generation processes and associated flow pathways as well as different water sources (McDonnell & Stewart, 1991; Peters & Ratcliffe, 1998; Joerin et al., 2002; Majone et al., 2010; McGuire et al., 2005; Peters et al., 2010). Over the past several decades, the coupled hydrometric and chemical signature of streams (which includes stable isotopes of water) have been used to infer the mixing and movement of waters (e.g. Sklash & Farvolden, 1979; Buttle, 1994; Kirchner et al., 2001; Joerin et al., 2002; Carey & Quinton, 2005; Tetzlaff et al., 2008; Dincer et al., 2010; Kendall et al., 2011; Soulsby et al., 2011; Carey et al., 2013).

# 1.2 Stable Isotopes and Stream Hydrochemistry in Catchment Hydrology

Stable isotopes are naturally occurring conservative tracers that have a wide variety of applications but are primarily used for two purposes in watershed hydrology: (1) identifying temporal variations in water sources during baseflow and individual storms, and (2) determining the source of water during and between events (McGuire et al., 2007; Roa-García & Weiler, 2010). Commonly used isotope tracers are  $\delta^{18}$ O and  $\delta^2$ H which are calculated as the ratio of heavy to light isotopes relative to a standard isotopic ratio (McDonnell, 1998).  $\delta^{18}$ O and  $\delta^2$ H values are calculated relative to Vienna-Standard Mean Ocean Water (V-SMOW) which was adopted as the freshwater standard by the IAEA in 1967 (eds. Kendall & McDonnell, 1998). The concentration of isotope ratios is expressed in per mil values using the equations:

$$\left(\frac{\frac{{}^{18}O}{{}^{16}O}_{sample} - \frac{{}^{18}O}{{}^{16}O}_{standard}}{{}^{18}O\over{}^{16}O}_{sample}}\right) \times 1000 \tag{1}$$

$$\left(\frac{\frac{^{2}H}{^{1}H}_{sample} - \frac{^{2}H}{^{1}H}_{standard}}{\frac{^{2}H}{^{1}H}_{sample}}\right) \times 1000$$
(2)

The conservative nature of stable isotope tracers means that changes in their composition can only result from mixing with other sources of water (eds. Kendall & McDonnell, 1998) and fractionation processes such as evaporation and condensation (Gat, 1969). Groundwater has a relatively consistent  $\delta^{18}$ O value and tends to dampen the highly variable isotopic values of precipitation and snowmelt (Rodhe et al., 1981; eds. Kendall & McDonnell, 1998). Stable isotopes have been used in hydrology to identify water sources and the mixing of precipitation with water that exists within the catchment at depth and near the surface. The most common application is isotopic hydrograph separation, which separates stormflow response into water that existed in the catchment that reports to the outlet (often termed pre-event or old water) and water that is derived directly from the precipitation event (often termed event or new water). There have now been hundreds of papers utilizing hydrograph separation, which is limited by several well-documented assumptions (Sklash & Farvolden, 1979; Buttle, 2004). In most cases, streamflow is dominated by water that existed within the catchment prior to the event, as displacement of water predominates over direct delivery of precipitation. Other uses of stable isotopes are evaluation of residence times, the time it takes for a molecule of water to transit the catchment (see McGuire et al., 2006 for review) and in the general mixing of waters from different sources (McDonnell et al., 1991; Kendall et al., 1999; Dincer et al., 2010).

Stable isotopes are effective in identifying water sources but are less informative concerning flow pathways and runoff mechanisms (Kendall et al., 2002). In contrast, variation in the timing and fluxes of solutes are used to identify flow pathways as it is assumed that stream hydrochemistry reflects the path taken by water through the catchment (Laudon, 1997; Engstrom et al., 2000; Hoeg et al., 2000; Scanlon & Raffensperger, 2001, McGuire et al., 2005; McGuire et al., 2007). Chemical weathering results from the interaction between water and the underlying soil or geology (Dickens et al., 1989; McGuire et al., 2005; Godsey et al., 2009). High concentrations are considered to reflect long residence times while low concentrations result from short contact times (Buttle, 1994; Hornberger et al., 2001; Burns et al., 2001; McGuire et al., 2005; Moore & Wondzell, 2005). The transport of dissolved solutes in catchments is tightly coupled to hydrology and leads to patterns between stream discharge and dissolved ion concentrations (Kirchner et al., 2000; Scanlon et al., 2001; Godsey et al., 2009). These concentration-discharge (C-Q) patterns can be used to infer catchment behaviour (Godsey et al., 2009). Analyses of C-Q relationships focus on the development of mixing models of different source areas (Capell et al., 2011), the determination of the relative timing of mixing based on hysteresis (Williams, 1986; Evans & Davies, 1998), and the assessment of dilution and chemostatic mechanisms of solute release (Godsey et al., 2009).

Investigations that combine hydrometric, isotopic and hydrochemical methods are effective in identifying sources, residence times and flow pathways (Wels et al., 1991; Carey & Quinton, 2005; Tetzlaff et al., 2007; Tetzlaff & Soulsby, 2008; Soulsby et al., 2009; Carey et al., 2013).

## **1.3** Paired Catchment Studies

Paired catchment studies, where certain watersheds remain undisturbed while others undergo some form of treatment or disturbance have a long history in hydrological research (Bormann et al., 1970; Harr, 1977; Hewlett & Doss, 1984; Hornbeck et al., 1997; Martin et al., 2000; Likens & Buso, 2006; Naranjo et al., 2011). For example, classical studies in the Hubbard Brook Research Watersheds in New Hampshire have used manipulation of small watersheds to understand the response of a treatment such as the addition of  $CaCO_3$ , forest harvest practices and other management techniques on watershed hydrology and biogeochemistry. In the west coast mountain ranges of North America, both Canadian and United States forestry services have used paired catchment approaches to establish the effect of forest practices, fire and other disturbances such as forest disease on hydrological response. While there are considerable shortcomings in paired watershed approaches, largely due to the statistical limitations (Alila & Beckers, 2002), they remain a powerful and widely used approach in hydrology to understand the impact of disturbances and change on the hydrology of systems. In this thesis, to develop a conceptual model of the influence of spoils on streamflow response and chemistry, the paired catchment approach was used pairing a surface mining affected catchment and an adjacent natural catchment.

## 1.4 Research Objectives

Using a paired catchment approach, the objective of this thesis is to understand how coal spoil affects the rate, timing, magnitude and chemistry of runoff from a watershed affected by surface mining.

To answer this objective, two instrumented watersheds were established: a mine affected catchment (West Line Creek) and a natural reference catchment (Dry Creek). West Line Creek is influenced by approximately 2.10 x  $10^8$  cubic metres of deposited coal spoil, whereas Dry Creek is presently not influenced by spoil but some forestry activity has occurred. For each catchment, precipitation and discharge were measured along with major ion hydrochemistry, stable isotope tracers ( $\delta^{18}O, \delta^2H$ ) and high frequency specific conductance at basin outlets. Concentrations of major ions and temporal patterns of flow and conductivity were used to provide insight into flow pathways and runoff mechanisms, while stable isotopes  $\delta^{18}O$  and  $\delta^2H$  were used to understand sources of runoff. Results of this thesis will provide an improved understanding of how coal spoil influences the hydrology of alpine catchments, which provides a direct benefit to operators facing water quality issues due to surface mining as well as communities who depend on the surface water downstream of mining activities.

## 2 Site Description and Methods

## 2.1 Site Description

Field research was conducted in Elk Valley, British Columbia from April 19th to September 19th, 2012. Elk Valley is located in the Kootenay region of southeastern British Columbia on the west side of the Alberta Rockies (Figure 1). Geologically, the coal-bearing Mist Mountain Formation from the Jurassic and Cretaceous periods is found within this region (Ryan & Dittrick, 2000). The Mist Mountain Formation comprises the Crowsnest Coalfield where five mines owned and operated by Teck Coal Limited are located (Ryan & Dittrick, 2000). These mines produce over 20 million tonnes of coal annually, which has resulted in approximately 4.63 x 10<sup>9</sup> cubic metres of coal spoil over the last 3 decades (Teck Coal Ltd Spoil Volume Estimates, 2010).

Research focused on two Elk Valley watersheds: West Line Creek (WLC) catchment (10.7 km<sup>2</sup>) and Dry Creek (DC) catchment (25.9 km<sup>2</sup>) (Figure 2). WLC is part of the larger Line Creek watershed and approximately 30 percent of the catchment's total area is covered by waste rock (known as coal spoil) from Line Creek Operations (LCO). LCO has been placing waste rock into the valley of WLC since 1984 and the coal spoil in WLC now measures approximately 3.5 km in length and is up to 1 km wide, covering a surface area of 2.7 km<sup>2</sup> (SRK Consulting (Canada) Ltd, 2010) (Appendix, Figure 18). The total volume of the WLC coal spoil is approximately 2.10 x  $10^8$  cubic metres (Teck Coal Ltd Spoil Volume Estimates, 2010). The catchment ranges in elevation from 1450 m at the outlet to approximately 2650 m at the peaks of the Witsukitsak range at the western edge. The slopes of the watershed are south and east facing.

Dry Creek (DC) is a catchment directly adjacent to the north of WLC that has not been disturbed by mining operations and is used as the reference catchment in this study. While DC is currently unaffected by mining or coal spoil, there has been forestry activity in the watershed with roads and cutblocks cover approximately 20% of the catchment area (Appendix, Figure 19).

#### 2.1.1 Climate

The study area has a humid continental climate characterized by low relative humidity, highly variable temperature and precipitation. The mean annual temperature is approximately 5°C. Summer mean temperatures range from 9°C to 15°C and winter mean temperatures range from -2°C to -7°C (Figure 3). Summer and winter extreme temperatures of 36°C and - 38°C, respectively, have been recorded. Mean annual precipitation at lower elevations ranges from 600 mm to 800 mm and approximately 55% of precipitation falls as snow (Figure 4). Precipitation is predominantly frontal, but convective storms are common in late summer. As in most alpine environments, precipitation is highly variable and there is considerable measurement uncertainty. Records from 2012 suggest that between 1300 m and 1850 m, the proportion of snow to rain varied from 28% to 66% snow.

#### 2.1.2 Soils and Geology

The study area is located within the Northern Continental Divide Ecoregion, which can be further specified as the Elk Valley Ecosection using the designations from the B.C. Government. This Ecosection is described as being predominantly comprised of a wide valley, with soft sedimentary rocks that are bounded by ridges of limestone and dolomite. The high relief and rugged topography implies a complex geology and a heterogeneous distribution of soil types. Common parent materials in this area are deep and shallow colluvium, glacial till, fine and coarse textured fluvial fans and floodplains. In mountain valleys, remnants of silty lacustrine terraces are found. In dry valleys, thin layers of sands and silts are common. The predominance of sedimentary limestone and dolomite suggests that most soil materials in this area overlie calcareous parent materials. Sedimentary and metamorphic rocks (e.g. shales and siltstones) result in fine textured soil parent materials, which are prone to mass wasting. Conglomerate, sandstone and quartzite bedrock leads to coarser textured and more stable soils. Detailed information about the geology of the Elk Valley and surrounding areas can be found in Gibson (1979), Gibson and Hughes (1981) and Vessey and Bustin (2000).

#### 2.1.2.1 Coal Spoil

The excess rock that is blasted to access buried coal in surface mining is commonly referred to as coal spoil. Coal spoil consists of some coal from seams that are too narrow or of poor quality to exploit, and mudstone and siltstone interburden (Lussier et al., 2003). Coarse and fine refuse is sometimes placed in coal spoils rather than being disposed of in tailings ponds. The coal spoil volume at WLC was estimated from historical records of mining production at a maximum 2.10 x  $10^8$  cubic metres. Using volumetric estimates based on the 2010 and the pre-mined topography, the coal spoil volume was estimated at  $1.87 \times 10^8$  cubic metres. The difference between these estimates is due to uncertainties in historical reports as well as difficulties in accounting for backfilling, and spoil compression and compaction over time.

#### 2.1.3 Ecology

Vegetation varies widely due to the rugged topography, elevation, as well as the resultant heterogeneity in precipitation, soil type and soil moisture. The Elk Valley Ecosection is comprised of 4 main ecosystems: (1) Western Hemlock and Western Red Cedar in the lower vegetation zone; (2) Subapline fir and Engelmann spruce in the subalpine vegetation zone; (3) The Interior Mountain-Heather Alpine vegetation zone is mainly bare rock with patches of grass-sedge meadows; (4) Whitebark Pine and Alpine Larch sometimes occurring at the timberline. The understory of the lower vegetation zone is composed of Douglas-fir, Western Larch, Grand Fir, Lodgepole Pine with common plants such as blueberries, devil's club, oak fern and mosses. Understory plants in the subalpine vegetation zones are white-flowered rhododendron, black gooseberry, false azalea, twisted stalk, Sitka valerian, bunchberry, and dense moss. Avalanche chutes are common to most alpine catchments in the area and are dominated by Sitka alder and herbs (Jones and Annas, BC Government Soils - Section 1.4 Vegetation).

## 2.2 Field Methods

The field season began on April 19th and ended on September 19th, 2012. The methods used to measure stream discharge, meteorological parameters, water quality parameters and water chemistry are outlined below.

#### 2.2.1 Stream discharge

Solinst leveloggers were installed on 19 April at the outlets of WLC and DC watersheds to measure stage at 15-minute intervals. These instruments are pressure transducers that measure temperature, specific conductivity and pressure. The pressure is converted into water level by correcting for atmospheric pressure using a barometric logger. Water level must be converted to stage using a calculated offset that relates the staff gauge and the water level measured by the pressure transducer. Pictures of the staff gauges at DC1 and WLC were taken at each site visit and these were used to make a record of staff gauge height. Discharge was measured using an acoustic Doppler velocity current meter (SonTek FlowTracker) and the velocity-area method (Dingman, 2002) was referenced to the staff gauge height at the time of measurement. Over the study period, the relationship between the staff gauge height and stream discharge (stage-discharge curve) was strengthened. The equation of this curve is specific to each stream, and was applied to convert the stage measured at high frequency to stream discharge.

#### 2.2.2 Weather and Precipitation

Air temperature was measured at a former Environment Canada weather station in Elkford, B.C. (50°01.200N, 114°55.200W) (Figure 1). The outlets of DC and WLC are both within 100 m of elevation in relation to the Elkford meteorological station (1300 m). Precipitation and temperature data were also collected at a higher elevation site at Greenhills Operations (GHO) ( $50^{\circ}05.498$ 'N,  $114^{\circ}52.518$ 'W, 1830m). Precipitation was recorded by a Geonor total precipitation gauge located  $\sim 9$  km and  $\sim 15$  km from the outlets of DC and WLC catchments, respectively. Local stations within DC and WLC with less contiguous data were used to check consistency of precipitation values with the Elkford and GHO stations.

### 2.2.3 Water Samples

#### 2.2.3.1 Isotopes

#### 2.2.3.1.1 Precipitation samples

A total of 93 rainfall samples (54 field replicates) were collected using a precipitation sampler (Figure 5) built according to IAEA standards to prevent fractionation from occurring between the rain event and sample collection (Groning et al., 2012). This gauge consists of a 1000 mL HDPE Nalgene bottle, a PP 108 mm outer diameter funnel connected to the bottom of the Nalgene with a PVC tube and 7.6 mm of 4.8 mm outer diameter Tygon pressure/vent tubing. The outer casing that held the bottle and attached funnel was constructed from white 4" PVC pipe. Connectors for the vent tube and funnel tube were all Swagelok bulkhead connectors. It was estimated that a rain event of 4.5 mm or greater was necessary to fill the bottle of the bottle to reach the funnel tube ( $\sim$ 1 mm) and seal the precipitation gauge.

Rain found in the gauges was collected in 7 mL or 20 mL HDPE scintillation vials 24-48 hours after each event. Each vial was air-tight and minimal headspace was ensured. After each rain event, the 1000 mL HDPE Nalgene bottle in each gauge was replaced. The isotope samples were brought back to McMaster University in late August 2012 and were then sent to the Mitchell Research Group at University of Toronto and run on a Los Gatos Liquid Water Isotope Analyser through February 2013.

#### 2.2.3.1.2 Stream samples

A total of 668 isotope samples were taken from the outlets of DC (60 grab samples, 22 integrated over 24 hours, 215 high-frequency) and WLC (53 grab samples, 70 integrated over 24 hours, 238 high-frequency) over the course of the study period. All samples were collected in 20 ml HDPE scintillation vials with displacement caps to minimize headspace. Three types of samples were collected:

- (1) Point or grab samples Samples were collected from the stream at a given point in the day. This type of sample was taken several times a week at each outlet when site visits were conducted.
- (2) Daily integrated samples A 1000 mL sample comprised of a 250 mL sample taken every 6 hours was subsampled. These samples were primarily taken over weekends when site access was not possible.
- (3) High-frequency integrated samples A 900 mL sample made up of 300 mL samples taken every hour was subsampled. This type of sample was collected during rain events.

Integrated samples were collected using a Teledyne ISCO autosampler located within 5m (WLC) or 25m (DC) of each outlet sampling location. All isotope samples were brought back to McMaster University in late August 2012. Samples were then sent to the Mitchell Research Group at University of Toronto and run through February 2013.

#### 2.2.3.2 Geochemistry (Major Ions)

Water samples for chemical analysis were collected from the outlets of DC and WLC in 500mL PETG bottles. These bottles were brought kept cool and filtered through a 0.7 um glass fiber filter 6-36 hours after collection. Each  $\sim$ 500 mL of filtrate was separated into a 60 mL HDPE amber bottle, two 20 mL HDPE scintillation vials and the filter was placed in

a petri dish and wrapped in parafilm. The HDPE bottles were refrigerated until they were shipped for major ion analysis.

#### 2.2.4 High Frequency Monitoring (Conductivity, Temperature and Water Level)

Solinst pressure transducers and Hobo conductivity sensors were installed at the outlets of each watershed. These instruments provided redundant measurements of temperature and conductivity at 15-minute intervals. Pressure head, which was later converted to water level, was also recorded every 15 minutes by Solinst Leveloggers.

#### 2.2.4.1 West Line Creek (WLC)

One Solinst pressure head and conductivity sensor and one Hobo conductivity sensor were installed 2m upstream of an existing nitrogen bubbler pressure transducer and weir at the outlet of West Line Creek. The instruments were secured to an aluminum rod that was driven into the creek bed and a wooden stake was attached. Each logger was enclosed in a PVC or ABS pipe with holes drilled into the plastic to allow the flow of water across the sensor. A Solinst Barologger was installed in the nearby Teck datalogger enclosure. In addition to gauges at the basin outlets, discharge was also recorded at a number of other locations within the Line Creek and Dry Creek watershed.

#### 2.2.4.2 Line Creek 1 (LC1)

A pressure transducer was installed at this site by Kerr Wood Leidal Associates Ltd in 2010 (KWL Hydrometric Report, 2010). This section of Line Creek is located upstream of existing LCO operations.

#### 2.2.4.3 Line Creek 3 (LC3)

One Solinst pressure head and conductivity sensor was installed at LC3 located downstream of the WLC dump, near the existing Teck Coal Ltd staff gauge. The transducer was encased in a PVC pipe casing to avoid damage with drilled holes allowing flow of water across the sensor. Rebar was driven into the creek bed and used to anchor the sensor.

#### 2.2.4.4 Dry Creek (DC1)

A Solinst Levelogger and Hobo conductivity sensor were installed in Dry Creek outlet near the existing Teck monitoring station. Sensors were encased in PVC and ABS pipe casings with drilled holes to allow the flow of water across the sensors. The sensors were attached to two rebar rods driven into the creek bed (O'Kane Consulting Ltd LCO Fieldwork Summary, 2012).

## 2.3 Laboratory Methods

#### 2.3.1 Isotopes

Water samples were analyzed for isotopes of  $\delta^2$ H and  $\delta^1$ 8O by the Mitchell Research Group at University of Toronto using a Los Gatos Research (LGR) Water Isotope Analyzer. The LGR Liquid Water Isotope Analyzer requires 1 µL of sample and runs up to 150 samples bracketed by 30 standards (LGR Liquid Water Isotope Analyzer (LWIA-24d) Datasheet, 2013). The duplicate precision for 86 random samples of  $\delta^2$ H and  $\delta^1$ 8O was 0.72‰ (SD: 0.56‰) and 0.13‰ (SD: 0.12‰), respectively.

#### 2.3.2 Major ions

All analyses of major ions were conducted at the University of Saskatchewan under the supervision of Dr. Jim Hendry. Analytical procedures were adapted from EPA Method 300.1 quality assurance (QA)/quality control (QC) guidelines.

#### 2.3.2.1 Cations

Water samples were analyzed for cations using a Metrohm 861 Advanced Compact Ion Chromatograph coupled to a Metrohm 868 Advanced Sample Processor. Common inorganic cations ions were separated in a Metrosep C4 150/4.0 cation exchange column with a 1.7 mM nitric acid and 0.7 mM dipicolinic acid eluent. IC Net® chromatography software was used to control the equipment and analyze the output. Nine standards and one lab reagent blank (LRB) were prepared and standards were run at the beginning and end of each 135 sample batch (all information provided by the Hendry Lab at University of Saskatchewan). Duplicates and fortified samples were prepared for 10% of samples. Measured cations include total lithium (Li<sup>+</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), magnesium (Mg<sup>2+</sup>), and calcium (Ca<sup>2+</sup>).

#### 2.3.2.2 Anions

Water samples were analyzed for common inorganic anions using a Dionex IC25 ion chromatograph coupled to a Dionex As50 Autosampler. Anions were separated using a Dionex IonPac AS9-HC 4x250 mm anion exchange column with a 9 mM sodium carbonate eluent. After a Dionex Anion Regenerating Suppressor (ASRS 300, p/n 064554) was used to suppress conductivity of the eluent solution, a DS3-1 D conductivity detector (Detection Stabilizer) was used. PeakNet® chromatography software was used to control the equipment and record conductivity. For every batch of 34 samples, ten standards and one laboratory reagent blank (LRB) were run at the beginning and at the end. Duplicates and fortified samples were prepared for 10% of samples (all information provided by the Hendry Lab at University of Saskatchewan). Measured anions include fluoride ( $F^-$ ), chloride ( $Cl^-$ ), nitrite ( $NO_2^-$ ), bromide ( $Br^-$ ), nitrate ( $NO_3^-$ ), phosphate ( $PO_4^{3-}$ ), and sulfate ( $SO_4^{2-}$ ).

## 3 Results

## 3.1 Field Observations

The data presented in this section were collected during the study period of April 19th (DOY 110) to September 19th, 2012 (DOY 263). Throughout the results, day of year (DOY) will be used instead of calendar dates.

#### 3.1.1 Climate

Air temperature and precipitation was measured at both both Elkford and Greenhills Operations (an adjacent Teck Coal mine) weather station (Figure 6). Daily mean air temperature at Elkford was 2.5°C on the first day of the study period and gradually increased throughout the study period to a maximum of 21.5°C on DOY 194. Average daily air temperature followed the seasonal trend yet had notable 5-10°C variability on a week-by-week basis. Following DOY 194, temperatures gradually decreased to 13.7°C on DOY 263. Compared with the climate normal for the nearby town of Sparwood (11.3°C), the study period in 2012 was considered average in terms of air temperature (10.8°C).

In total, 251.4 mm of rain fell over the study period, which was 40.1 mm less than the climate normal (1971-2000). Smaller precipitation events were common at the beginning of the study period, followed by a dry period between DOY 123 and DOY 155. There were two large precipitation events in the middle of the study period, a 25.6 mm rain event on DOY 158 and a 24.8 mm rain event on DOY 178. The rain event on DOY 178 was followed by three relatively dry weeks and then a rain event of 16.5 mm on DOY 197. Seven rain events greater than 5.0 mm occurred over the remainder of the study period when flows were receding in both catchments. Total precipitation throughout the study period in 2012 was  $\sim$ 4 mm less than averages calculated from the Sparwood Environment Canada station. All precipitation at 1300m in 2012 was identified as rain whereas climate normals for 1980-2007

showed that 17% of precipitation fell as snow at a similar elevation. In the months preceding the study period, there were large differences in precipitation totals and partitioning between rain and snow compared to climate normal. In 2012, total precipitation between January and the end of April was 248.5 mm which was approximately 95 mm greater than the historical average for those months. Additionally, 65% of precipitation during this period was rain in comparison to the longterm average value of 29%.

#### 3.1.2 Discharge

Discharge measurements at both sites were normalized to mm/d to account for catchment area (Figure 7). Dry Creek exhibited much higher flows and variability than WLC over the course of the study period. DC1 discharge first rose to 12 mm/d on DOY 110 before declining sharply to less than 5 mm/d in 6 days. A sharp spike to 11 mm/d followed by a 1 mm/d decline over the period of one day was followed by a rise to 23 mm/d (DOY 141) in another 2 days. This peak marked the highest flows of Dry Creek in 2012 as measured at the outlet. By DOY 150, DC1 flows declined over several days before rising to 20 mm/d by DOY 160. Discharge at DC1 reached a minimum of 6 mm/d before rising slightly on DOY 187, after which, discharge steadily decreased to 2 mm/d rest of the study period.

West Line Creek had a longer record of discharge that preceded the field investigation, and showed much lower flows and much less variation than DC over the course of the year and throughout the study period. Discharge at WLC was low (1 mm/d) until DOY 137, when water levels showed a steep increase. The hydrograph showed three distinct peaks, the first on DOY 141 (2 mm/d), the second on DOY 159 (3.1 mm/d) and the third on DOY 181 (2.7 mm/d). WLC discharge decreased from 2.7 mm/d to below 0.5 mm/d between DOY 181 and the end of the study period. This recession was marked by small diurnal fluctuations but no discernible increase in discharge associated with rainfall.

### 3.1.3 Specific Conductance

Specific Conductance (SpC) was measured at the outlets of DC and WLC every 15 minutes throughout the study period (Figure 8). The first recorded SpC at DC1 prior to freshet was 179.1  $\mu$ S/cm. SpC values reached their lowest values ~100  $\mu$ S/cm at DC1 on DOY 136 and on DOY 158, which corresponded to the dilution of stream water in response to early snowmelt in mid-May, and to the largest rain event of the study period (25.6 mm) in early June. Local minima were observed on DOY 123 and DOY 178. Low SpC on DOY 123 was linked to snowmelt, and a 24.8 mm rain event occurred on DOY 178. SpC at DC1 showed diurnal variability with values fluctuating by 5-11  $\mu$ S/cm. The last recorded value at DC1 was 205.3  $\mu$ S/cm, which was 26  $\mu$ S/cm higher than the pre-melt conductivity.

The pre-melt value at WLC was 1330  $\mu$ S/cm. SpC decreased over the next several weeks before reaching a local minimum value of ~720  $\mu$ S/cm on DOY 144. There was a slight increase in SpC over the next several weeks before the minimum value of 525  $\mu$ S/cm occurred on DOY 175. This minimum persisted for 3 days before beginning to rise on DOY 178. SpC continued to increase for the remainder of the study period with a small decrease on DOY 200. The last reliable recording at WLC was 945  $\mu$ S/cm on DOY 238, which was 385  $\mu$ S/cm lower than the pre-melt value.

### 3.2 Hydrochemistry

#### 3.2.1 Time Series of Major Ions

Stream waters at the outlets of DC and WLC were analyzed for all major ions as well as selenium (Figure 9). The concentrations of nitrate  $(NO_3^-)$ , sulphate  $(SO_4^{2-})$ , calcium  $(Ca^{2+})$ , magnesium  $(Mg^{2+})$ , potassium  $(K^+)$ , sodium  $(Na^+)$  and selenium (Se) were all above the limit of detection of the analyzer at both DC1 and WLC. A large proportion of the results of chloride  $(Cl^-)$  analysis from samples at DC1 were below the limit of detection (not shown in

Figure 9). A total of 25 samples were collected by Teck Coal Ltd personnel for compliance monitoring purposes and were included in analysis.

In this study, concentration is reported as opposed to load as the focus is on flow-chemistry interactions related to hydrological flow paths, not downstream delivery of contaminants to receiving water bodies. Concentrations of all major ions and Se were higher, and often considerably higher, in WLC compared with DC1. Concentrations of weathering ions  $Ca^{2+}$  and  $Mg^{2+}$  at WLC were an order of magnitude higher than DC1 while Se concentrations were two orders of magnitude higher.

## 3.2.1.1 Dry Creek (DC1)

Major ions and elemental Se collected at DC1 did not display the same patterns as solutes collected from WLC. Less samples were collected at DC1 and many of these samples were below their respective limits of detection (LOD). Analysis of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> did not provide many samples above LOD and no meaningful patterns were observed. Ca<sup>2+</sup> concentrations ranged between 10-50 mg/L. Concentrations were low at the beginning of the study period and showed a large degree of variability between DOY 160 and DOY 180 before gradually increasing towards the end of the study period. Mg<sup>2+</sup> followed the same pattern as Ca<sup>2+</sup> as low initial ion concentrations showed high variability and an increasing trend between DOY 160 and DOY 180 before reaching maximum concentrations around DOY 255. K<sup>+</sup> concentrations were lowest between DOY 145-160 and increased by 0.5 mg/L between DOY 205-240.  $SO_4^{2-}$  concentrations showed a pattern distinct form all other ions at DC1 and WLC. Initial concentrations of  $SO_4^{2-}$  were low but increased by 10 mg/L before reaching a maximum of 19 mg/L by DOY 160. This maximum was followed by a decrease to minimum on DOY 227 after which concentrations increased until the end of the study period.

Se concentrations were very low ( $\sim 0.00137 \text{ mg/L}$ ) at the beginning of the study period

and remained stable before showing a ten-fold increase by DOY 210 (0.0104 mg/L). A large degree of variability was observed in the latter half of the study period. Unlike at WLC, Se concentrations at DC1 were below the Canadian Water Quality Guideline of 10 micrograms per liter (0.0100 mg/L), with one exception on DOY 210, and closely conformed to expected background concentrations.

#### 3.2.1.2 West Line Creek (WLC)

Initial concentrations of  $Ca^{2+}$  were ~310 mg/L and gradually decreased to 150 mg/L between DOY 175 and DOY 180. Mg<sup>2+</sup> concentrations at the beginning of the study period were 220 mg/L and decreased to 5mg/L on DOY 158. Na<sup>+</sup> at WLC showed no distinct temporal trend during the study period. Concentrations decreased to a minimum by DOY 140 and remained low before beginning to increase slightly on DOY 210. Ions more closely linked with surface and soil processes, NO<sub>3</sub><sup>-</sup> and K<sup>+</sup>, reached maximum concentrations that were greater than those at DC1 by a factor of 2. NO<sub>3</sub><sup>-</sup> and K<sup>+</sup> concentrations showed minimum values around DOY 180 and a local minimum in NO<sub>3</sub><sup>-</sup> on DOY 220 and in K<sup>+</sup> on DOY 230. Cl<sup>-</sup> concentrations followed a similar trajectory to NO<sub>3</sub><sup>-</sup> and K<sup>+</sup> with initially high concentrations reaching a minimum on DOY 180 and a local minimum around DOY 220.

 $SO_4^{2-}$  concentrations were an order of magnitude higher in WLC compared with DC1 and high concentrations at the beginning of the study period declined to a minimum on DOY 180 before returning to near-initial values by the end of the study period. Elemental Se concentrations were an order of magnitude higher in WLC than at DC1. Se concentrations at the beginning of the study period were approximately 50 times higher than expected background concentrations and decreased to a minimum by DOY 162. Concentrations of Se remained relatively low (~0.1mg/L) for several days before beginning to increase on DOY 180.

## 3.3 Stable Isotopes

#### 3.3.1 Local Meteoric Water Line

The local meteoric water line (LMWL) describes the best-fit linear relationship between in  $\delta^{18}$ O and  $\delta^2$ H and is typically specific to a region (Craig, 1961, eds. Kendall and McDonnell, 1998). Cooler precipitation is more depleted (more negative) in heavy isotopes, whereas warmer precipitation is more enriched (less negative). Deviations from the slope of the LMWL indicate evaporation and other fractionation processes (Dansgaard, 1964). In this study, the Calgary LMWL was used as a proxy LMWL in the absence of a fully developed Elk Valley LMWL. Rain samples collected in Elk Valley throughout the study period are displayed in addition to the  $\delta^{18}$ O and  $\delta^2$ H data from WLC and DC1 (Figure 10). The data from the Elk Valley precipitation isotopes collected between April and the end of August fit along the Calgary LMWL and coincide with Calgary precipitation when temperature was greater than 0°C. The samples from WLC and DC1 are located along the LMWL, which suggests that the stream water has not undergone significant evaporation or other fractionation effects (Dansgaard, 1964).

Summary statistics for isotope samples taken from stream water and precipitation gauges at WLC and DC catchments showed that stream samples from WLC were more enriched in  $\delta^{18}$ O and  $\delta^{2}$ H than samples from DC1 (Table 1).

#### 3.3.2 Streams

Analysis of stable isotopes indicated that the  $\delta^{18}$ O and  $\delta^{2}$ H values measured at DC1 and WLC were distinct from one another. DC1 values of  $\delta^{18}$ O ranged from -20.91 to -17.04‰ while  $\delta^{2}$ H values ranged from -151.14 to -137.72‰.  $\delta^{18}$ O values at WLC ranged from -20.79 to -16.25‰ and  $\delta^{2}$ H values from -147.34 to -121.86‰. Despite the overlap in the ranges of  $\delta^{18}$ O and  $\delta^{2}$ H values from DC1 and WLC, the majority of isotope data from each site

clustered in separate regions of the  $\delta^{18}$ O -  $\delta^{2}$ H plot. A Mann-Whitney Rank Sum test was run on values of  $\delta^{18}$ O and  $\delta^{2}$ H (p<0.001, M-W U ( $\delta^{18}$ O) = 13856, M-W U ( $\delta^{2}$ H) = 6309) and it was concluded that these stream waters are isotopically distinct.

Samples of stream isotopes were integrated over a 24-hour (daily) period, and collected in situ as point measurements at DC1 and WLC (Figure 12). These samples are a subset of the stream samples shown previously, which also included high-frequency isotope samples (Figure 11). Integrated daily samples at DC1 and WLC were collected between storms while point samples were collected every 2-3 days.

Precipitation data collected over the 2012 study period at both sites had no significant difference in means for either  $\delta^{18}$ O or  $\delta^{2}$ H (t-test, t = -0.111, 2-tailed P-value = 0.912). Towards the beginning of the study period, samples from precipitation gauges indicated rain was slightly more enriched in heavy isotopes at WLC compared to DC1 (Figure 12). After DOY 160, the majority of precipitation samples from WLC were more depleted than those collected at DC1.

#### 3.3.2.1 Dry Creek (DC1)

There was a close relation between patterns  $\delta^2$ H and  $\delta^{18}$ O, so descriptions of isotope patterns will be restricted to  $\delta^{18}$ O. Stream values of  $\delta^{18}$ O at DC1 were measured starting on DOY 134 (-19.23‰) and ending on DOY 238 (-18.52‰) (Figure 12). Rainfall events at DC1 caused enrichment in  $\delta^{18}$ O on the order of 1-3‰ depending on the isotopic composition of the rain composition and amount. Rainfall events of comparable magnitudes occurred on DOY 158 (weighted average  $\delta^{18}$ O = -20.43‰) and DOY 178 ( $\delta^{18}$ O = -14.08‰). The heavier rain signal from DOY 178 led to stream isotopic enrichment of 3‰, which was three times greater than the compositional change related to the event on DOY 158. Subsequent rain events were much smaller in magnitude and, despite being enriched in  $\delta^{18}$ O, caused stream enrichment of approximately 1‰. Prominent depletions in stream isotopic composition occurred on DOY 150 ( $\delta^{18}O = -20.19\%$ ) and 153 ( $\delta^{18}O = -19.79\%$ ) and DOY 170 ( $\delta^{18}O = -20.58\%$ ). The first depletion episode was caused by the first pulse of snowmelt as depleted meltwater was delivered to the stream. The second depletion episode on DOY 170 occurred during conditions of high antecedent moisture (an accumulation of 75.5 mm of rain over the previous two weeks) and reflected the initiation of a second peak in freshet due to a rain-on-snow melt event.

#### 3.3.2.2 WLC

Stream values of  $\delta^{18}$ O at WLC were measured starting on DOY 144 ( $\delta^{18}$ O = 19.26‰) and ending on DOY 239 ( $\delta^{18}$ O = -18.21‰) (Figure 12). The first depletion occurred on DOY 152 ( $\delta^{18}$ O = -19.12‰) and was followed by episodes on DOY 158 ( $\delta^{18}$ O = -19.29‰), DOY 171 ( $\delta^{18}$ O = -18.92‰), DOY 189 ( $\delta^{18}$ O = -18.85‰) and DOY 229 ( $\delta^{18}$ O = -18.43‰). The first depletion episode occurred on DOY 152 and is linked to early snowmelt. The second depletion of stream isotopic composition on DOY 158 was closely linked to two very enriched  $\delta^{18}$ O values and the largest rain event of the study period. The episode on DOY 166 followed an accumulated rainfall of 60.4 mm (mean  $\delta^{18}$ O = -14.65‰) and occurred just after the recession of the peak annual flow in the. The last two depletions occurred on DOY 189 ( $\delta^{18}$ O = -18.85‰) and DOY 229 ( $\delta^{18}$ O = -18.43‰) as discharge at WLC decreased to the end of the study period. Enrichment and depletions in the isotope composition of WLC was not tightly linked to precipitation in most cases but a 6-8 day lag following high magnitude events on DOY 158 and DOY 178 were observed.

#### 3.3.2.3 General Observations of Enrichment

Seven rain events occurred between DOY 180 and DOY 240 with a mean  $\delta^{18}$ O value of -11.85‰. Stream isotopic composition from of both types of samples at WLC and DC1 show enrichment over the course of the study period (Figure 13).  $\delta^{18}$ O was relatively depleted at WLC at the beginning of the study period, and became gradually enriched over the course of

the study. Daily integrated samples displayed lower variability than point samples. Trends showing enrichment of  $\delta^{18}$ O in both streams showed that isotopic stream composition at WLC varied much less than at DC1.

## 4 Discussion

The objective of this study was to understand how waste rock (coal spoil) from surface mining affects the hydrology of headwater catchments in Elk Valley, British Columbia using a paired catchment approach. Large volumes of coal spoil are deposited in the valleys of montane watersheds as a result of surface mining in this region, yet limited information exists on the subsequent effects on downstream areas and the hydrological processes that occur within these catchments. Higher than background concentrations of the trace metalloid selenium as well as sulfate, nitrate and other solutes have been reported downstream of mined catchments throughout Elk Valley (Lussier et al., 2003). These higher concentrations are stressors to the aquatic biota living downstream and have the potential to impact human health and recreation (Lussier et al., 2003; Wayland & Crosley, 2006; Jones et al., 2009).

The mechanisms of chemical release and transport from coal spoil to the aquatic environment largely depend on the hydrology of the system, and understanding their interaction aids in the development of conceptual models of the influence of surface coal mining on hydrology. Paired catchment studies are frequently used in hydrology to provide insight into impacts related to land use change as well as the effects of other stressors on hydrology (Verry & Lewis, 1983; Martin et al., 2000; Moore & Wondzell, 2005).

The results of the 2012 study period showed marked differences in (1) the flow magnitude and stream response, (2) the runoff hydrochemistry, and (3) the stable isotope signature of waters in the stream. WLC was much less productive than DC1 based on runoff normalized to catchment area measured at both outlets. The magnitude of streamflow response to precipitation events was also much more muted at WLC than at DC1 and peaks were attenuated. Concentrations of weathering ions at WLC were up to an order of magnitude higher than at DC1. The isotope signal at WLC was significantly more enriched at WLC than at DC1 although the tight clustering of isotopes from each site implies source waters were well mixed and showed evidence of evaporation (little deviation from LMWL). The following sections will highlight the key functional differences between WLC and DC1, and provide information towards an improved conceptual of the impact of surface mining on headwater function and response.

## 4.1 Hydrometric Response

Discharge measured at WLC and DC1 exhibited substantial differences in both magnitude and timing. Dry Creek catchment is approximately 2.5 times larger than West Line Creek, and was expected prior to the study to have attenuated flow timing and volume due to longer flowpath lengths and routing times. However, measurements made during the 2012 study period showed that DC1 was much more productive in terms of total runoff volume and more 'flashy' than WLC (Figure 7). During the 2012 study period, which was 153 days long, 663 mm of water was reported at DC1 outlet compared with 182 mm at WLC, and the peak flows were approximately 20 days earlier.

DC1 had high amplitude flow peaks in response to rain events as well as considerable variability in discharge throughout the field season. In contrast, WLC had attenuated peaks and its response to snowmelt and rain events showed substantial lags in comparison to DC1 (Figure 7). The lags in timing and muted stream response to precipitation at WLC can be linked to the presence of large volumes of coal spoil. In WLC, a waste rock volume of 2.10 x  $10^8$  cubic metres was deposited over the pre-mined catchment in an area previously disturbed by forestry activity (Teck Coal Ltd Spoil Volume Estimates, 2010). Results suggest that this porous material, along with changes to the catchment morphometry, acts to delay the response of streamflow compared with undisturbed catchments (Appendix, Figure 20). The travel times of water from surface input to the sub-spoil drainage network are likely considerable as networks can be several hundred meters below the surface.
Although the timing of high and low flows in the discharge record can be related to coal spoil affecting pathways and rates of water transport, the low streamflow productivity at WLC is not directly attributable to mining activities and the resultant spoil. This suggests that runoff in mine affected catchments will be dominated by throughflow leading to peaks in stream response being attenuated whereas overall productivity will not necessarily be affected. Discharge records from the study period in 2012 as well as previous years indicate that WLC yields much less water per unit area than other sites affected by mining located in the Line Creek watershed (Figure 7). WLC is part of the larger Line Creek catchment and its low productivity is anomalous when compared to mine affected sites like LC, LC1 and LC3, which remain more productive despite the presence of large volumes of coal spoil. Each of these sites has distinct basin and bedrock characteristics, which may account for the local variability in water yield. A highly permeable bedrock could lead to subsurface flow unreported at the basin outlet as well as attenuated streamflow responses, which is plausible in this calcareous bedrock regime. Reports from drilling and sediment cores taken from WLC suggest that the underlying bedrock is highly fractured (SRK Consulting (Canada)) Ltd, 2012). However, despite large differences in productivity between WLC and other sites, the timing and overall shape of the hydrographs were similar despite dissimilar basin characteristics. No measurements of DC1 discharge from 2011 were available.

#### 4.2 Hydrochemical Response

Stream hydrochemistry can be used to improve understanding of the flow pathways of water as it moves through the catchment (Buttle, 1994; Scanlon et al., 2001). In this study, specific conductance and major ion concentrations were used to assess differences in flow pathways between Dry Creek and West Line Creek. Data from previous studies indicates that streams affected by coal spoil have higher concentrations of weathering and surface-derived ions than natural catchments (Lussier et al., 2003; Wayland & Crosley, 2006; Jones et al., 2009). These higher concentrations are primarily due to surface mining exposing deep geologic layers that were buried under soil and vegetation for millions of years to aerobic conditions (Dickens et al., 2012). Additionally, blasting processes used in mining increases the surface area of previously intact layers and thus the extent of the available contact area between air, water and the newly exposed rock (Dickens et al., 2012). In active mining areas, operations are ongoing and the volume of coal spoil increases by up to tens of millions of cubic metres per vear, which inhibits the system from reaching a chemical or weathering equilibrium (or a steady state), which leads to consistently increasing ion concentrations in downstream locations (Kennedy et al., 2000; Lussier et al., 2003; Chapman et al., 2007; Dessouki, 2010; Dickens et al., 2012). Previous research by Murphy et al. (2012) in Appalachia focused on the relationship between ion concentrations and stream flow to gain insight into hydrologic processes in a landscape affected by mining. Results of comparisons between historical and post-mining conditions at two sites downstream of surface mining operations showed high concentrations of dissolved ions which peaked and then decreased over time as well as a shift from more chemostatic behaviour to a more predominant dilution mechanism (Murphy et al., 2012).

#### 4.2.1 Specific Conductance and Discharge (Q)

Concurrent with previous studies in Elk Valley that reported elevated ion concentrations (Chapman et al., 2007; Dessouki, 2010), the results of the 2012 study period showed that specific conductance (SpC) was an order of magnitude higher at WLC than at DC1 (Figure 8), and WLC had a much higher ionic load compared to DC1 (Figure 9). Values of specific conductance (SpC) are related to total dissolved solutes (TDS) using a simple linear conversion in most cases and represent an integrated measure of ionic behaviour (Thomas, 1986; Liu et al., 2013). Relationships between stream discharge and SpC are often heterogeneous and exhibit hysteresis through time (Thomas, 1986; Williams, 1989; Evans & Davies, 1998; Kirchner et al., 2000; Seeger et al., 2004, McDonnell & Weiler, 2006) and these patterns

are typically used to assess changes in water quality and catchment function subsequent to urban or agricultural land use change (Rose, 2003; Liu et al., 2013). The shape and direction (clockwise or counterclockwise) of hysteretic loops that occur during snowmelt and rain events can be used to infer runoff generation processes associated with solute behaviour in the catchment (Walling & Webb, 1986; Evans & Davies, 1998; Scanlon et al., 2001).

These hysteresis loops are classified and interpreted according to contributions of different components of runoff associated with a particular event or season (Walling, 1975; Williams, 1989; Evans and Davies, 1998; Scanlon et al., 2001; Rose, 2003; Seeger et al., 2004; Liu et al., 2013). Hysteresis loops proceeding in the clockwise direction suggest the rapid delivery and depletion of a readily available source of dissolved solutes to the stream (Scanlon et al., 2001; Seeger et al., 2004) and the activation of the transmissivity feedback (Hornberger et al., 1994; McDonnell & Weiler, 2006; Kendall et al., 2011). Essentially, the timing of peaks in solute concentrations in the stream are congruent or lag slightly behind peaks in the hydrograph (Williams, 1989). Counterclockwise hysteresis loops are quite common and occur when solute transport precedes streamflow response (Williams, 1989). This type of hysteresis loop is associated with flushing via the vertical-lateral preferential flow conceptual model (McDonnell et al., 2006). In this case, threshold antecedent moisture conditions facilitate rapid water and solute transport from the hillslope to the stream, and flushing is dominated by hillslopes rather than riparian areas (McDonnell & Weiler, 2006).

Plots of instantaneous discharge versus SpC from data collected over the study period in 2012 provided insight into differences in the hydrochemical behaviour of both catchments (Figure 8). The relationship between SpC and discharge at DC1 was similar to those observed in undisturbed catchments and did not exhibit a very dynamic response to individual events (Rose, 2003; Liu et al., 2013). Over the course of the study period, SpC declined as discharge increased and this pattern repeated several times in response to fluctuations in discharge caused by rain events and subsequent recessions. Natural catchments often exhibit hysteretic patterns related to interactions with wetting and drying of soil horizons and shifting runoff pathways, but this was not observed at DC1.

There was a large-scale clockwise pattern of hysteresis at WLC with higher concentrations on the rising limb and lower concentrations on the descending limb. This characteristic hysteretic pattern indicates possible flushing of available solutes (Walling & Foster, 1975; Scanlon et al., 2001) or the activation of different flow pathways during events (Hooper et al., 1990). 'Flushing' is a phenomenon commonly observed in catchments impacted by urban and agricultural land use as dissolved solutes are introduced into the system in higher than background concentrations (Rose, 2003; Liu et al., 2003). Like urban and agricultural systems, surface mining increases the availability of readily available dissolved solutes (Kennedy et al., 2000; Lussier et al., 2003; Chapman et al., 2007; Dickens et al., 2012; Murphy et al., 2012; Line Creek Phase II Expansion EA Review, 2013) and the initiation of flushing responses appears likely.

At both catchments, rain events occurring on DOY 154-160 led to notable differences in the relationship between SpC and Q (indicated in red, Figure 8). On DOY 158 - 159, the pattern at DC1 shifted from its typical trajectory (indicated in red) and initiated a counterclockwise hysteresis loop. Loops proceeding chronologically in the counterclockwise direction that result from a single event are a well-known phenomenon (Williams, 1989; Evans and Davies, 1998). This type of loop is initiated when peaks in solute delivery and discharge are tightly coupled or as a peak in discharge preempts a peak in solute delivery (Williams, 1989). The current hypothesis is that the large rain event on DOY 158, in conjunction with an accumulated 58.9 mm of rain and snowmelt runoff, led to high soil moisture, flood conditions and the incorporation of sediment sources across the catchment (Williams, 1989; Seeger et al., 2004; Capell et al., 2011). This divergence from the expected relationship occurred over 36 hours before the previously observed pattern was reestablished and continued throughout the rest of the study period. At WLC, the large rain event on DOY 158 was related to a clockwise loop, which is expected under 'normal' conditions in response to rain events (Seeger et al., 2004). Solutes were quickly removed, transported to the stream and the source was depleted (Williams, 1989; Seeger et al., 2004).

#### 4.2.2 Log-log C-Q Relationships

Further hydrochemical analysis was undertaken by combining ion concentrations and discharge in log-log C-Q plots to understand how individual ions contributed to the observed patterns in SpC (Figure 15). Major ion chemistry displayed in C-Q plots provided the opportunity to determine geologically different source areas and explore the impact of land use changes on solute concentrations under diverse flow conditions (Kirchner et al., 2000; Capell et al., 2011; Godsey et al., 2009; Liu et al., 2013).

C-Q plots often exhibit power law relationships between concentration (C) and discharge (Q), which are identifiable by their linear pattern on log-log axes (Kirchner et al., 2000; Godsey et al., 2009). The linear slope of C-Q plots with log-log axes, or the exponent of the power law  $Q = aC^b$ , indicates the behaviour of a particular solute (Kirchner et al., 2000; Godsey et al., 2009). A slope of 0 indicates that the system behaves chemostatically, meaning that the solute concentration remains constant as discharge increases or decreases. Conversely, a slope of -1 suggests that solute concentrations vary inversely to discharge as if dilution of a finite solute source is occurring. Slopes across and within watersheds typically follow a range of values between 0 and -1. This range is due to the distinct basin and bedrock characteristics of each watershed as well as variability in available flowpaths. Linear regressions of log-log plots of discharge versus SpC at DC1 and WLC were -0.159 and -0.271, respectively (Figure 16). Slopes of the majority of ions at DC1 tended to be closer to 0 (with the exception of NO<sub>3</sub><sup>-</sup>), whereas slopes at WLC were typically steeper (Figure 17).

The slopes of weathering ions  $Ca^{2+}$  and  $Mg^{2+}$  (summarized in Table 4.1) were similar at DC1 and WLC although concentrations were an order of magnitude higher at WLC than at DC1. Both catchments are underlain by the same limestone and dolomite geology (rich in calcium and magnesium) but the material exposed as coal spoil at WLC may differ. The causes of the higher ionic concentrations at WLC were discussed previously as the result of the exposure waste rock to oxygen and water.

Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup> and K<sup>+</sup> all showed behaviour that was more chemostatic at DC1 while slight dilution behaviour predominated at WLC. While most ions showed similar concentrations, SO<sub>4</sub><sup>2-</sup> was an order of magnitude higher at WLC and elemental Se was several orders of magnitude higher than at DC1. The slope of NO<sub>3</sub><sup>-</sup> was relatively steep at DC1 and demonstrated a stronger than average dilution relationship with discharge at WLC. Peaks in NO<sub>3</sub><sup>-</sup> concentrations have been hypothesized to occur due to concentration from evapotranspiration and decomposing organic matter (Petrone et al., 2006), 'flushing' of near surface soils (Anderson & Burt, 1982) or the movement of groundwater through till (Weiler & Mc-Donnell, 2006). The possible explanations behind the behaviour of NO<sub>3</sub><sup>-</sup> at WLC, however, are further complicated by the use of N-based explosives in blasting during surface mining. These explosives contain high levels of nitrate, which could be obscuring the temporal trends in NO<sub>3</sub><sup>-</sup> as well as be contributing to the ionic load at WLC.

#### 4.3 Stable Isotopes

As reported in Chapter 3, precipitation isotope samples, which were largely rainfall, collected during the study period in 2012 at DC1 and WLC showed that  $\delta^{18}$ O and  $\delta^{2}$ H values were not significantly different. However, stream water isotopes collected over the same period indicated that the isotope signals from WLC and DC1 were significantly different from one another, with WLC being more enriched in heavy isotopes than DC1.  $\delta^{18}$ O and  $\delta^{2}$ H values of stream water at WLC and DC1 were located on the Calgary LMWL, which appears similar to the local Elk Valley MWL, indicating that evaporation or other fractionation processes did not have a large influence on stream water sources (Figure 10).

Over the course of the study period,  $\delta^{18}$ O and  $\delta^{2}$ H values of stream water from each site showed muted responses to snowmelt (depletion) and rain events (enrichment) (Figure 7). The subdued isotopic response to snowmelt at WLC and DC1 is in contrast to other studies in alpine environments that showed the arrival of meltwater causing a deflection of stream  $\delta^{18}$ O to more depleted values (Carey et al., 2013). Minimal deflection during freshet suggests that even at this time, meltwater at WLC and DC1 is primarily derived from displaced water at depth, likely storage in large alluvial aquifers, as opposed to surface or near-surface runoff sources (eds. Kendall and McDonnell, 1998).

With regard to rain events, both streams showed slight enrichment and greater variability in  $\delta^{18}$ O during and subsequent to rain events although the timing of isotopic enrichment at WLC was not always in direct correspondence with rain events. One exception to the generally lagged response of WLC occurred on DOY 158 and was hypothesized to have resulted from the quick delivery of surface water to the stream. Between rain events, point and daily-integrated values of  $\delta^{18}$ O displayed little variation (Figure 12) with enrichment occurring throughout the study period as less depleted rainwater became a greater influence on stream water discharge (Figure 12). The muted seasonal signal of stream isotopes suggests that residence times in both catchments are long (McGuire et al., 2006) and that the primary pathways of runoff generation involve considerable mixing.

The lack of variability evidenced during the study period as well as the statistically significant difference between stream isotope signals at DC1 and WLC implies that stream water from each site was derived from two distinct but well-mixed sources (Kendall & McDonnell, 1998). WLC had a more enriched signal than DC1 indicating that the stream is comprised of predominantly warmer water. This enriched signal could be attributed to two possible scenarios: (1) large differences in the source (precipitation) signals, or (2) more of the heavier water delivered during warmer seasons making its way to the stream. The lack of a significant difference between  $\delta^{18}$ O and  $\delta^{18}$ H values from precipitation samples at each site appear to refute the first scenario. Instead, it was hypothesized that the lack of vegetation and soil cover on the coal spoil at WLC led to less interception, decreased evaporation, and increased percolation to depth over the study period, particularly during the summer months. The combination of this influx of water enriched in heavier isotopes and decreased soil storage (presence of coal spoil over 30% of the catchment area) leads to the water reporting at the outlet to be dominantly 'warm'. One inconsistency between this hypothesis and the observed results is that WLC as recorded at the outlet had much less discharge compared with DC1, yet is believed from previous reports and regional observations that WLC is anomalous in its low runoff coefficients and hydrogeological investigation in 2012 suggests that the watershed may have considerable leakage at depth.

#### 4.4 Summary

Our current conceptual understanding of how coal spoil influences the hydrology of montane headwater catchments is based on a relatively short period of time and a limited data set. However, the preliminary investigation of discharge timing and magnitude, hydrochemistry and stable isotopes has elucidated some aspects of how mine affected catchments differ from natural headwater catchments in this area and led to some hypotheses as to the causes. In comparison to DC1, WLC displayed:

- Delayed and attenuated responses in stream discharge to freshet and rain events due to the considerable storage associated with coal spoil.
- (2) A large scale pattern of hysteresis in specific conductance (a metric for the total dis-

solved ionic load) related to a flushing response or changing pathways over the study period and during events.

- (3) Order of magnitude higher concentrations in weathering ions (Ca<sup>2+</sup> and Mg<sup>2+</sup>) and  $SO_4^{2-}$  ascribed to water-rock interaction within the spoil.
- (4) Slightly steeper slopes on log-log C-Q plots indicating that weathering ions (Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>) and most surface ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>) are subject to dilution processes operating within with spoil.
- (5) Limited variability in isotope values of  $\delta^{18}$ O associated with water reporting at the outlet being derived from a well-mixed source. This indicates that in both catchments, water spends considerable time traversing flow pathways before reaching the stream.
- (6) A more enriched (heavier) stream isotope signal attributed to bare spoil allowing greater than average percolation of warmer water (heavier water from summer rain events). This more enriched water is a source distinct from that of DC1.

In summary, a relatively short study period over the summer season in 2012 has demonstrated that the presence of coal spoil has altered the hydrology of West Line Creek as outlined above. Relationships between changes in catchment characteristics, processes and the resultant behaviour have been hypothesized. Further research is required across a range of natural and spoil-influenced catchments in the area to validate or refute the above preliminary conceptual understanding and provide more data to develop conceptual models on the impact of surface mining on hydrology.

### 5 Conclusions

This research examined the impact of surface mining on runoff timing and pathways in Elk Valley, British Columbia. Five open-pit mines operate in this region of southeastern British Columbia, Canada and produce over 20 million tonnes of steelmaking coal annually (Teck Coal Quarterly Report, 2012). This type of mining involves the removal of vegetation and soils, the blasting of successive geological layers to access buried coal and the placement of blasting debris (waste rock) into adjacent valleys. Waste rock, commonly known as coal spoil, buries existing streams and alters catchment morphometry and landscape characteristics.

Coal spoil is a heterogeneous mix of waste rock and lower quality coal that becomes exposed to aerobic conditions and water during surface mining operations. This exposure leads to downstream influences on stream biota and water quality due to increased weathering and transport of dissolved solutes. One water quality parameter of particular interest in Elk Valley is selenium (Se). Increases in Se concentrations are linearly correlated with increases in spoil volume upstream of tributaries to major rivers in this area. The mobilization and release of Se into the aquatic environment is dependent on water movement. Any attempt to understand and limit Se release first requires a conceptual understanding of the hydrological regime of mine affected alpine catchments.

A paired catchment approach was used to investigate how coal spoil affects the rate, timing, magnitude and chemistry of runoff from a watershed affected by surface mining. Based on the results of field, isotopic and hydrochemical observations, the presence of coal spoil at WLC has led to lagged and attenuated responses in streamflow to both snowmelt freshet and rain events, delayed isotopic enrichment of stream water due to precipitation, increased percolation of rainwater, and order of magnitude concentrations of weathering ions and sulfate as well as flushing responses that indicate the predominance of a transmissivity feedback. Additionally, DC1 showed ion concentrations resulting from dilution mechanisms while WLC exhibited more chemostatic behaviour. Future research is required to assess if: (1) conclusions drawn from one year of data are accurate in representing the behavior of these two catchments, and (2) if WLC and DC are representative basins and the conclusions drawn from this study have broader applicability.

## Figures



Figure 1: Study area map of Elk Valley. Study sites are located near Line Creek Operations (LCO). Five open-pit coalmines in this region are owned and operated by Teck Resources Limited. Inset shows the location of Elk Valley within southeastern British Columbia, Canada 39



Figure 2: Map of Dry Creek (DC1) and West Line Creek (WLC). Red points represent distributed sampling locations where surface waters samples were collected. Yellow points indicate the locations of catchment outlets (ISCO autosamplers, flow monitoring stations, isotope precipitation gauges).



Month

Figure 3: Mean monthly air temperature in Elk Valley (1980-2007).



Figure 4: Mean monthly precipitation in Elk Valley (1980-2007).



Figure 5: (a) Isotope precipitation gauge at WLC, and (b) close-up of isotope precipitation gauge (1000mL Nalgene, Swagelock fittings, funnel and tubing).



Figure 6: (a) Mean daily air temperature, (b) mean daily precipitation at Elkford meterological station, and (c) mean daily precipitation at higher Greenhills Operations (GHO) meteorological station. Green represents GHO measurements while Elkford's are shown in black. Measurements of mean daily air temperature and daily precipitation totals at the Elkford meteorological station represent conditions at DC1 and WLC.



Figure 7: (a) Mean daily precipitation at Elkford meteorological station, (b) Dry Creek outlet (DC1) hydrograph throughout the study period, and (c) West Line Creek outlet (WLC) hydrograph throughout the study period. Discharge was normalized to catchment area and is expressed in millimetres per day.



Figure 8: Specific conductance (SpC, solid line) and discharge (Q, dashed line) for Dry Creek (DC, top) and West Line Creek (WLC, bottom).



Figure 9: Time series of concentrations of  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and Se throughout the study period. WLC is West Line Creek and DC1 is Dry Creek oulet. Concentrations are in milligrams per liter for all dissolved solutes.



Figure 10:  $\delta^{18}$ O and  $\delta^{2}$ H values from precipitation and stream isotopic composition of WLC and DC1 and precipitation from Calgary, AB.  $\delta^{18}$ O and  $\delta^{2}$ H values are expressed as per mil concentrations relative to the V-SMOW standard.



Figure 11:  $\delta^{18}$ O and  $\delta^{2}$ H values collected from WLC and DC1 streams over the course of the study period.  $\delta^{18}$ O and  $\delta^{2}$ H values are expressed in per mil concentrations relative to the V-SMOW standard.

M.Sc. Thesis - N.J. Shatilla; McMaster University - School of Geography and Earth Sciences



Figure 12: (a) Daily precipitation totals and isotopic composition, (b) daily average discharge at DC1 and stream isotopic composition, and (c) daily average discharge at WLC and stream isotopic composition.



Figure 13: Daily integrated samples of stream  $\delta^{18}$ O at DC1 and WLC. Point measurements of stream  $\delta^{18}$ O from DC1 and WLC.



M.Sc. Thesis - N.J. Shatilla; McMaster University - School of Geography and Earth Sciences

Figure 14: Discharge records from LC, LC1, LC3 and WLC. Discharge was normalized to catchment area and expressed in millimetres per day



Figure 15: Specific conductance-discharge (SpC-Q) relationships at DC1 and WLC. Responses to a 25.6mm rain-on-snow event are indicated in red.





Figure 16: Specific conductance-discharge (SpC-Q) relationships plotted on logarithmic axes.



Figure 17: Concentration-discharge (C-Q) relationships for  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  at DC1 and WLC. Concentration and discharge (Q) axes are logarithmic. Concentrations that result from dilution processes should closely follow a log-log slope of -1 (indicated by the dashed diagonal line) while less steep slopes indicate that concentrations resulted from more chemostatic behaviour (log-log slope of 0).

# Appendix



Figure 18: Aerial photo of WLC spoil (1986).



Figure 19: Aerial photo of Dry Creek catchment (2011).



Figure 20: DEMs of WLC catchment (a) pre-mining and (b) post-mining.

Site	DC1					WLC		
Source	Q (n = 280)		P~(n=23)		Q~(n=352)		P(n = 16)	
	$\delta^2 \mathrm{H}~(\%)$	$\delta^{18}$ O (‰)	$\delta^2 \mathrm{H}~(\%)$	$\delta^{18}$ O (‰)	$\delta^2 \mathrm{H}~(\%)$	$\delta^{18}$ O (‰)	$\delta^2 \mathrm{H}$ (‰)	$\delta^{18}O$ (‰)
Mean	-145.63	-19.02	-107.32	-13.82	-140.91	-18.30	-106.08	-13.68
Std Dev	2.08	0.54	24.65	3.29	2.78	0.56	28.71	3.73
25%	-146.92	-19.29	-123.99	-16.26	-142.43	-18.62	-124.57	-16.21
75%	-144.56	-18.71	-87.62	11.01	-139.55	-18.03	-81.48	-10.31
Minimum	-153.24	-20.91	-165.13	-21.75	-147.34	-20.08	-165.63	-21.36
Maximum	-137.72	-17.04	-66.94	-9.64	-119.13	-15.68	-61.56	-8.42

Table 1: Summary statistics of stable isotopes in precipitation and streamflow at DC1 and WLC. Q is discharge and P is precipitation.

Table 2: Log-log slopes of discharge versus major ion concentration.

Site	DC1		WLC	
	Linear Regression Slope	Wilcoxon Signed Rank Test Significance	Linear Regression Slope	Wilcoxon Signed Rank Test Significance
Chloride	-0.0681	Z = -1.726 P = 0.091	-0.3764	$egin{array}{llllllllllllllllllllllllllllllllllll$
Nitrate	-1.523		-0.5139	$egin{array}{llllllllllllllllllllllllllllllllllll$
Sulphate	0.0928	${ m Z} = 4.577 \ { m P} = < 0.001$	0.6275	${ m Z} = 5.373 \ { m P} < 0.001$
Sodium	-0.0693	${ m Z} = 1.680 \ { m P} = 0.097$	-0.1537	
Potassium	-0.1038		-0.0403*	$egin{array}{llllllllllllllllllllllllllllllllllll$
Calcium	-0.1400	$egin{array}{llllllllllllllllllllllllllllllllllll$	-0.3311	Z = 2.245e-314 P = 1.000
Magnesium	-0.1644	$egin{array}{llllllllllllllllllllllllllllllllllll$	-0.4492	${ m Z} = 4.541 \ { m P} < 0.001$

## References

Alila, Y., & Beckers, J. (2002). Using numerical modelling to address hydrologic forest management issues in British Columbia. *Hydrological Processes*, 15(18), 3371-3387. doi:10.1002/hyp.1038

Anderson, S. P., Dietrich, W. E., Montgomery, D. R., Torres, R., & Conrad, M. E. (1997). Subsurface flow paths in a steep, unchanneled catchment. *Water Resources Research* 33 (12): 2637-2653.

Anderson, M.G., Burt, T.P. (1982). The contribution of throughflow to storm runoff: an evaluation of a chemical mixing model. *Earth Surface Processes and Landforms* 33 (1): 211-225.

Bales, R. C., Molotch, N. P., & Painter, T. H. (2006). Mountain hydrology of the western *Water Resources Research* 42: 1-13.

Becker, A. (2005). Runoff processes in mountain headwater catchments: recent understanding and research challenges. *Global Change and Mountain Regions* 23: 283-295.

Beldring, S., Gottschalk, L., & Rodhe, A. (2000). Kinematic wave approximations to hillslope hydrological processes in tills. *Hydrological Processes* 14: 727-745.

Bishop, K., Seibert, J., Kohler, S., Laudon, H. (2004). Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrological Processes* 18 (1): 185-189.

Bormann, F. H., Siccama, T. G., & Likens, G. E. (1970). The Hubbard Brook Ecosystem Study: Composition and Dynamics of the Tree Stratum. *Ecological Monographs* 40 (4): 373-388.

Burns, D. A., McDonnell, J. J., Hooper, R. P., Peters, N. E., Freer, J. E., Kendall, C., & Beven, K. (2001). Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA). *Hydrological Processes* 15 (10): 1903-1924. doi:10.1002/hyp.246

Capell, R., Tetzlaff, D., Malcolm, I. A., Hartley, A. J., & Soulsby, C. (2011). Using hydrochemical tracers to conceptualise hydrological function in a larger scale catchment draining contrasting geologic provinces. *Journal of Hydrology* 408 (1-2): 164-177. doi:10.1016/j.jhydrol.2011.07.034

Carey, S. K., & Quinton, W. L. (2005). Evaluating runoff generation during summer using hydrometric, stable isotope and hydrochemical methods in a discontinuous permafrost alpine catchment. *Hydrological Processes* 19 (1): 95-114. doi:10.1002/hyp.5764

Carey, S. K., Boucher, J. L., & Duarte, C. M. (2013). Inferring groundwater contributions and pathways to streamflow during snowmelt over multiple years in a discontinuous permafrost subarctic environment (Yukon, Canada). *Hydrogeology Journal* 21 (1): 67-77. doi:10.1007/s10040-012-0920-9

Carey, S. K. & M-K. Woo. (1999). Hydrology of two slopes in subarctic Yukon, Canada. *Hydrological Processes* 13: 2549 - 2562.

Chapman, P. M., Berdusco, R. J., & Jones, R. (2007). Update on the status of selenium investigations in the Elk River Valley, B.C.

Dansgaard, W. (1964). Stable isotopes in precipitation. Tellus XVI (4): 436-468.

DeBeer, C. M., & Pomeroy, J. W. (2009). Modelling snow melt and snowcover depletion in a small alpine cirque, Canadian Rocky Mountains. (J. Buttle & B. Branfireun, Eds.) *Hydrological Processes* 23 (18): 2584-2599. doi:10.1002/hyp.7346

Dessouki, T. (2010). Canada-British Columbia Water Quality Monitoring Agreement. 1-55.

Dickens, P. S., Minear, R. A., & Tschantz, B. A. (1989). Hydrologic Alteration of Mountain Watersheds from Surface Mining. *Journal (Water Pollution Control Federation)* 61 (7): 1249-1260.

Dingman, S. L. 2002. Physical hydrology. Prentice-Hall, Upper Saddle River, New Jersey.

BC Government (2013). Ministry of Environment Comments on Line Creek Phase II Expansion EA Review. (A. J. Downie, Ed.): 1-47.

Gat, J. R., E. Mazor and Y. Tzur. The stable isotope composition of mineral waters in the Jordan Rift Valley, Israel. *Journal of Hydrology* 7 (3): 334-352.

Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration-discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes* 23: 1844-1864. doi:10.1002/hyp.7315

Groning, M., Lutz, H. O., Roller-Lutz, Z., Kralik, M., Gourcy, L., & Pöltenstein, L. (2012). A Simple Rain Collector Preventing Water Re-Evaporation Dedicated for Delta<sup>18</sup>O and Delta<sup>2</sup>H Analysis of Cumulative Precipitation Samples. *Journal of Hydrology* 448-449 (C): 195-200. doi:10.1016/j.jhydrol.2012.04.041

Harr, R. D. (1977). Water flux in soil and subsoil on a steep forested slope. *Journal of Hydrology* 33: 37-58.

Hewlett, J. D., & Doss, R. (1984). Forests, Floods, and Erosion: A Watershed Experiment in the Southeastern Piedmont. *Forest Science* 30 (2), 424-434.

Hoeg, S., & Uhlenbrook, S. (2000). Hydrograph separation in a mountainous catchment - combining hydrochemical and isotopic tracers. *Hydrological Processes* 14: 1999-1216.

Hornberger, G.M., T.M. Scanlon and J.P. Raffensperger. (2001). Modelling transport of dissolved silica in a forested headwater catchment: the effect of hydrological and chemical time scales on hysteresis in the concentration-discharge relationship. Hydrological Processes (Special Issue: Hydrology and Biogeochemistry of Forested Catchments) 15 (10): 2029-2038.

Jayaweera, G. R. (1996). Role of Redox Potential in Chemical Transformations of Selenium in Soils. *Soil Science* 60: 1056-1063.

Jones, J., & Grant, G. (1996). Peak flow responses to clear-cutting and roads in small and large basins, western Cascades, Oregon. *Water Resources Research* 32 (4): 959-974.

Jones, R. G., Brienne, S. H., Jensen, S. E., & Tompkins, A. N. (2009). Selenium Release from Coal Mines in the Elk Valley, and Treatment R&D Plans: 1-10.

Jones and Annas - BC Government Soils - Section 1.4. Valentine, K.W.G., Sprout, P.N., Baker, T.E., Lawkulich, L.M. (Eds.), 1978, The Soil Landscapes of British Columbia. BC Ministry of Environment, Resource Analysis Branch. 197p.

Kendall, C., & McDonnell, J. J. (Eds.). (1998). *Isotope Tracers in Catchment Hydrology*. Elsevier Science.

Kirchner, J. W., Feng, X., & Neal, C. (2001). Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations. *Journal of Hydrology* 254(1-4): 82-101. doi:10.1016/S0022-1694(01)00487-5

Laudon, H. (1997). Hydrograph separation using stable isotopes, silica and electrical conductivity: an alpine example. *Journal of Hydrology* 201: 82-101

Likens, G. E., & Buso, D. C. (2006). Variation in Streamwater Chemistry Throughout the Hubbard Brook Valley. *Biogeochemistry* 78: 1-30.

Liston, G. E. (1999). Interrelationships among Snow Distribution, Snowmelt, and Snow Cover Depletion: Implications for Atmospheric, Hydrologic, and Ecologic Modeling. *Journal of Applied Meteorology* 38 (10): 1474-1487. doi:10.1175/1520-0450(1999)038

Liu, S., Wang, Y., Yu, L., & Oakey, J. (2006). Volatilization of mercury, arsenic and selenium during underground coal gasification. *Fuel* 85(10-11): 1550Đ1558. doi:10.1016/j.fuel.2005.12.010

Lussier, C., Veiga, V., & Baldwin, S. (2003). The geochemistry of selenium associated with coal waste in the Elk River Valley, Canada. *Environmental Geology* 44 (8): 905-913. doi:10.1007/s00254-003-0833-y

Martin, C. W., Hornbeck, J. W., Likens, G. E., & Buso, D. C. (2000). Impacts of intensive harvesting on hydrology and nutrient dynamics of northern hardwood forests. Can. J. Fish. Aquat. Sci. 57 (Suppl. 2): 19D29.

McDonnell, J., & Stewart, M. (1991). Effect of catchment-scale subsurface mixing on stream isotopic response. *Water Resources Research* 27(12): 3065-3073.

McGuire, K. J., McDonnell, J. J., Weiler, M., & Kendall, C. (2005). The role of topography on catchment-scale water residence time. *Water Resources Research* 41: 1-14.

McGuire, K. J., Weiler, M., & McDonnell, J. J. (2007). Integrating tracer experiments with modeling to assess runoff processes and water transit times. *Advances in Water Resources* 30 (4): 824-837. doi:10.1016/j.advwatres.2006.07.004

Moore, R. D., & Wondzell, S. M. (2005). Physical Hydrology and the Effects of Forest Harvesting in the Pacific Northwest: A Review. *JAWRA Journal of the American Water Resources Research* 41(4): 763-784.

Murphy, J. C., Hornberger, G. M., & Liddle, R. G. (2012). Concentration-discharge relationships in the coal mined region of the New River basin and Indian Fork sub-basin, Tennessee, USA. *Hydrological Processes*. doi:10.1002/hyp.9603

Naranjo, J. A. B., Stahl, K., & Weiler, M. (2011). Evapotranspiration and land cover transitions: long-term watershed response in recovering forested ecosystems. *Ecohydrology* 15, 3461-3473. doi:10.1002/eco.256

Palmer, M. A., Bernhardt, E. S., Schlesinger, W. H., Eshleman, K. N., Foufoula-Georgiou, E., Hendryx, M. S., et al. (2010). Mountaintop Mining Consequences. *Science*, 327(5962), 148Đ149. doi:10.1126/science.1180543

Peters, N. and E. Ratcliffe. (1998). Tracing Hydrologic Pathways Using Chloride at the Panola Mountain Research Watershed, Georgia, USA. Water, Air, and Soil Pollution 105, (1-2): 263-275.

Roa-García, M. C., & Weiler, M. (2010). Integrated response and transit time distributions of watersheds by combining hydrograph separation and long-term transit time modeling. *Hydrology and Earth System Sciences* 14(8): 1537-1549. doi:10.5194/hess-14-1537-2010

Rose, S. (2003). Comparative solute Đ<br/>discharge hysteresis analysis for an urbanized and a "control basin" in the Georgia (USA)<br/> Piedmont. Journal of Hydrology 284(1-4): 45-56. doi:10.1016/j.j<br/>hydrol.2003.07.001

Ryan, B. D., & Dittrick, M. (2000). Ryan: Selenium in the Mist Mountain Formation *Geological Fieldwork*.

Scanlon, T. M., & Raffensperger, J. P. (2001). Modeling transport of dissolved silica in a forested headwater catchment: Implications for defining the hydrochemical response of observed flow pathways. *Water Resources Research* 15: 2029-2038.

Seeger, M., M.-P. Errea, S. Beguería, J. Arnaez, C. Mart and J.M. García-Ruiz. (2004). Catchment soil moisture and rainfall characteristics as determinant factors for discharge/suspended sediment hysteretic loops?in a small headwater catchment in the Spanish pyrenees. *Journal* of Hydrology 288: 299-311.

Soulsby, C., D. Tetzlaff and M. Hrachowitz. (2009). Tracers and transit times: windows for viewing catchment scale storage? *Hydrol. Process.* 23: 3503-3507.

SRK Consulting (Canada) Ltd. (2010). Selenium Geochemistry and Water Quality Predictions Phase 3 - Implementation 2009 Status Report DRAFT. (D. M. MacGregor & S. Day, Eds.) (pp. 1-377).

Stewart, I. T. (2009). Changes in snowpack and snowmelt runoff for key mountain regions. (T. D. Prowse, Ed.)*Hydrological Processes* 23(1): 78-94. doi:10.1002/hyp.7128

Swanson, S., Abbott, R., Funk, W., Kirk, L., McKenna, G., Ohlendorf, H. M., & Sandy, T. (2011). Building stakeholder engagement in sustainable solutions: the strategic advisory panel on selenium management, 1-8.

Tetzlaff , D. and C. Soulsby. (2008). Sources of baseflow in larger catchments - Using tracers to develop a holistic understanding of runoff generation. *Journal of Hydrology* 359 (3-4): 287-302.

Tetzlaff, D., Soulsby, S. Waldron, I. A. Malcolm, P. J. Bacon, S. M. Dunn, A. Lilly and A. F. Youngson. (2007). Conceptualization of runoff processes using a geographical information system and tracers in a nested mesoscale catchment. *Hydrological Processes* 21: 1289-1307.

Verry, E., & Lewis, J. (1983). Aspen Clearcutting Increases Snowmelt and Storm Flow Peaks in North Central Minnesota. *JAWRA Journal of the American Water Resources Association* 19 (1): 59-67.

Walling, D.E. and I.D.L. Foster. (1975). Variations in the natural chemical concentration of river water during flood flows, and the lag effect: Some further comments. *Journal of Hydrology* 26 (3-4): 237-244.

Wayland, M., & Crosley, R. (2006). Selenium and Other Trace Elements in Aquatic Insects in Coal Mine-Affected Streams in the Rocky Mountains of Alberta, Canada. Archives of Environmental Contamination and Toxicology 50 (4): 511-522. doi:10.1007/s00244-005-0114-8

Weiler, M., & McDonnell, J. J. (2006). Testing nutrient flushing hypotheses at the hillslope
scale: A virtual experiment approach. Journal of Hydrology 319: 339-356. doi:10.1016/j.jhydrol.2005.06.040

Wels, C., R. J. Cornett, and B. D. Lazerte. (1991). Hydrograph separation: A comparison of geochemical and isotopic tracers. *Journal of Hydrology* (122) 253-274.