Journal of Hydrology 534 (2016) 616–629

Contents lists available at ScienceDirect

Journal of Hydrology

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

High-resolution profiling of the stable isotopes of water in unsaturated coal waste rock

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ARTICLE INFO

Article history:
Received 8 October 2015
Received in revised form 7 January 2016
Accepted 20 January 2016
Available online 29 January 2016
This manuscript was handled by Peter K. Kitanidis, Editor-in-Chief, with the assistance of Massimo Rolle, Associate Editor

Keywords:
Stable isotopes of water
Mine waste rock
Unsaturated soils
Net percolation

SUMMARY

Characterization of the rate of water migration through unsaturated mine waste rock dumps is an essential element in assessing the chemical loading from these landforms; yet our understanding of how water moves into, through and out of waste rock is incomplete. To further understand the rates and magnitude of percolation through waste rock, deep high-resolution (every 0.1–4.5 m) depth profiles of the stable isotopes of water (δ^2H and δ^{18}O) at two coal waste rock dumps and a natural alluvial deposit down-gradient of one of the dumps were collected in the Elk Valley, British Columbia, Canada. The profiles were generated using vapor equilibrium techniques applied to continuous core samples collected using dry sonic drilling methods. Elevated core temperatures (up to 80 °C) were measured during sonic coring. The isotopic values of pore waters measured in the core samples were corrected for water loss to the atmosphere attributed to the elevated core temperatures. The average isotopic composition of the core samples were compared to water collected from rock drains discharging from the base of the dumps. The results indicate that high-resolution profiles of δ^2H and δ^{18}O can be measured to depths of 86 m in coal waste rock dumps and, based on the seasonal cycles in the isotopic composition of recharging water, can be used to characterize the migration of recharge water within these dumps. These profiles also suggest that recharge into these dumps occurs from both rain as well as snow melt and may be as high as 400–600 mm/yr (60–75% of annual precipitation). Combined with the relatively low volumetric water contents of these dumps (5–10%) the rates of water migration through the dumps are tens of meters each year.

1. Introduction

Characterizing the volumes and rates of water migration through unsaturated mine waste rock dumps is foundational to an evaluation of chemical loading associated with the flushing of constituents of interest (CI) from these waste deposits. Few large-scale investigations of flow through mine waste overburden dumps have been conducted, and there has been limited success in relating the timing and volume of net percolation (recharge) to rates of water migration through the dump (Anterrieu et al., 2010; Azam et al., 2007; Nichol et al., 2005; Poisson et al., 2009).

Natural stable isotopes of water such as deuterium (^{2}H) and oxygen-18 (^{18}O) have been used as tracers to measure recharge and flow rates in natural profiles of deep unsaturated soil. The isotopic composition of infiltrating meteoric water varies seasonally (wetter vs. drier, colder vs. warmer) while remaining on a local meteoric water line (LMWL). These seasonal cycles in the stable isotope of water signature of infiltrating meteoric water have been used to track recharge (i.e. net percolation) in natural soil profiles (Adomako et al., 2010; Allison et al., 1994; Barnes and Allison, 1988; Gazis and Feng, 2004; Mathieu and Bariac, 1996). Yet the number of studies in which deep (>10 m) profiles of stable isotopes of water have been studied are limited (Bath et al., 1982; Cheng et al., 2014; DePaolo et al., 2004; Gaye and Edmunds, 1996).

There are two particular challenges associated with estimating net percolation rates from deep isotopic profiles: the first is the shift in the signature of recharging water relative to meteoric water as a result of surface evaporation (Allison, 1998; Barnes and Allison, 1988; Melayah et al., 1996) and the second is the loss (dampening) of the seasonal signal as water moves downward through the unsaturated soil profile (Bath et al., 1982). DePaolo et al. (2004) and Singleton et al. (2004) show that in semi-arid

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http://dx.doi.org/10.1016/j.jhydrol.2016.01.053
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zones (i.e. high evaporation relative to net percolation) the stable isotope profile in finer textured soils (e.g. clayey silt and silty sand) may only propagate to depths of a few meters, after which the profile tends to become uniform with depth and shifted relative to meteoric water as a result of the fractionation by evaporation during dry seasons. However, in sandy soils under greater rates of net percolation (e.g. >200 mm/y) the seasonal cycles in the isotopic composition of infiltrating water are propagated to greater depths and without a significant (i.e. relative to analytical error) shift in the isotopic profile relative to meteoric water. Cook et al. (1992) and Bath et al. (1982) show that the seasonal fluctuations of isotopic signatures may propagate to great depths (and consequently are representative of sources of surface recharge over a greater time) if the recharge rates are high (>100–200 mm/y) and the volumetric water content within the profile is relatively low (e.g. 0.05–0.1). It is hypothesized that these restrictions are met during the recharge of meteoric waters into waste rock dumps in subhumid regions of western Canada.

The other major challenge in applying the stable isotopes of water to trace net percolation in mining waste rock dumps is the assumption that flow through these deposits is dominated by preferential flow through the coarser rock and gravel which segregates from the finer matrix of sandy material during placement of the waste rock by dumping. For example, in waste rock dumps associated with coal mining in the Elk Valley of southern British Columbia, the focus of this paper, the predominant dump construction method is by end or push dumping. These methods tend to create particle segregation in which the largest particles (boulders) move to the base of the slope with a mixture of finer and coarse particles retained over much of the slope length (Morin et al., 1991). Piteau (1999) noted that for Elk Valley waste rock dump heights greater than 20 m, a coarse rubble zone is formed at the base of the dumps. The basal rubble zones act as ‘rock drains’, collecting water draining from the dump as well as water moving laterally into the dump from adjacent natural watersheds, and channeling this water to adjacent surface drainage (Lighthall et al., 1985). Textural breaks can also be created by the layers of coarser and finer material running parallel to the slope as illustrated for a gold mine waste rock dump by Azam et al. (2007). Similar breaks can also be formed as a result of compaction associated with trucks and dozers working along the top of dump surfaces.

It is often assumed that water migration through unsaturated mine waste rock is dominated by non-capillarity or macro-pore dominated water migration (Beven and Germann, 1982). There is, however, evidence that even relatively coarse textured soils will exhibit ‘soil-like’ capillarity depending on gradation. A commonly used threshold for this behavior is given by a soil having greater than 20% by mass finer than 2 mm (#10 U.S. Standard sieve) or 40% finer than 4.75 mm (#4 U.S. Standard Sieve) (Holmquist et al., 1983; Smith et al., 1995; Strohm et al., 1978). Recent studies by Nichol et al. (2005), Neuner et al. (2013), and Blackmore et al. (2014) as well as literature recently synthesized by Amos et al. (2014), highlight that in waste rock dumps comprised of these ‘soil-like’ textures, the dominant mass transport is through matrix flow with relatively high levels of leaching efficiency. The qualitative definition of leaching efficiency being used here is the proportion of a conservative Cl, initially contained within the pore water, that is removed by the first pore volume of flushing.

In dumps in which water migration occurs primarily through matrix flow, deep profiles of the stable isotopes of water should provide valuable information on the source, distribution and rate of water movement through the dumps. The application of stable isotopes of water to track water migration has seen limited use in waste rock dumps. Marcoline et al. (2006) applied a ^{2}H spike to the top of a 5 m high test pile constructed earlier by Nichol et al. (2005) in order to track water movement by collecting samples by trenching and hand sampling. The results were difficult to interpret; however, due to the small volume of the spike water addition, fractionation due to evaporation during sampling, and dump heterogeneity. Sracek et al. (2004) collected water samples from a full-scale dump (30–35 m) using suction lysimeters installed in the dump and from a water well in the underlying saturated zone. These isotope data suggested an equal contribution of snowmelt water and spring rainfall to recharge. One observation of particular interest was the apparent fractionation due to evaporation that occurred at depth in the dump. This internal evaporation was suggested to be due to the convective flow of atmospheric air into the dump near the toe of the slope.

As surface mining has continued to expand, there have been increasing calls to understand the fundamental hydrology of waste rock dumps and how they interact with the surrounding catchment hydrologic and hydrogeologic systems (INAP, 2009, 2015). The goal of this study is to apply isotopic hydrological approaches to better understand water migration in and through mine waste rock. The specific objectives of this work are as follows:

1. Develop field sampling methods to measure high spatial resolution profiles of the stable isotopes of water through coal mine waste rock and natural alluvial deposits down gradient of a waste rock pile.
2. Evaluate the accuracy of these profiles by comparing the average isotopic composition of the water in the waste rock to that measured in adjacent natural soil profiles using coring and water well samples, as well as the isotopic composition of effluent collected from rock drains.
3. Estimate the magnitude (volume) of annual recharge and the rate of water migration through coal mine waste rock based on the patterns (seasonality and magnitude) of the high spatial resolution profiles of the stable isotopes of water.

2. Study sites

The sites for this study are located at two Teck Resources mines along the Elk River watershed (Fig. 1) in southern British Columbia, Canada: the West Line Creek (WLC) watershed and waste rock dump at the Line Creek Operation (LCO-WLC); and the Bodie dump at the Elk View Operation (EVO-BRD). These mines extract coal from the Mist Mountain formation which is comprised of siltstones, mudstones, and sandstones with coal seams up to 18 m thick (Gibson, 1985; Ryan and Dittrick, 2001).

Teck Resources initiated a multi-disciplinary research and development program in 2012 based on the recommendations of a Strategic Advisory Panel (SAPSE, 2010). This ongoing research has been incorporated into the Elk Valley Water Quality Plan as approved by the provincial government (EVWQP, 2014). The focus of this research program is to find methods of managing water quality, including methods of controlling water and chemical migration from waste rock dumps. This paper presents work undertaken to characterize the source, distribution and rate of water movement through coal waste rock dumps.

The WLC watershed is approximately 10 km^{2} in area (Shatilla, 2013; Wellen et al., 2015) and ranges in elevation from 1450 to 2650 m. The dump covers approximately one quarter (2.7 km^{2}) of the eastern flank of the watershed (Fig. 2a). The dump was constructed over the last 35 years and has surface elevations ranging from 1500 m in the south to more than 2140 m in the north, with a maximum waste rock thickness of approximately 255 m and an average dump thickness of approximately 115 m. The dump extends from the north of the watershed to within 0.5 km of the southern end of the watershed where the rock drain and creek drain into Line Creek. The Bodie dump (Fig. 2b) covers approximately 1.22 km^{2} of the original Bodie Creek pre-mining watershed,

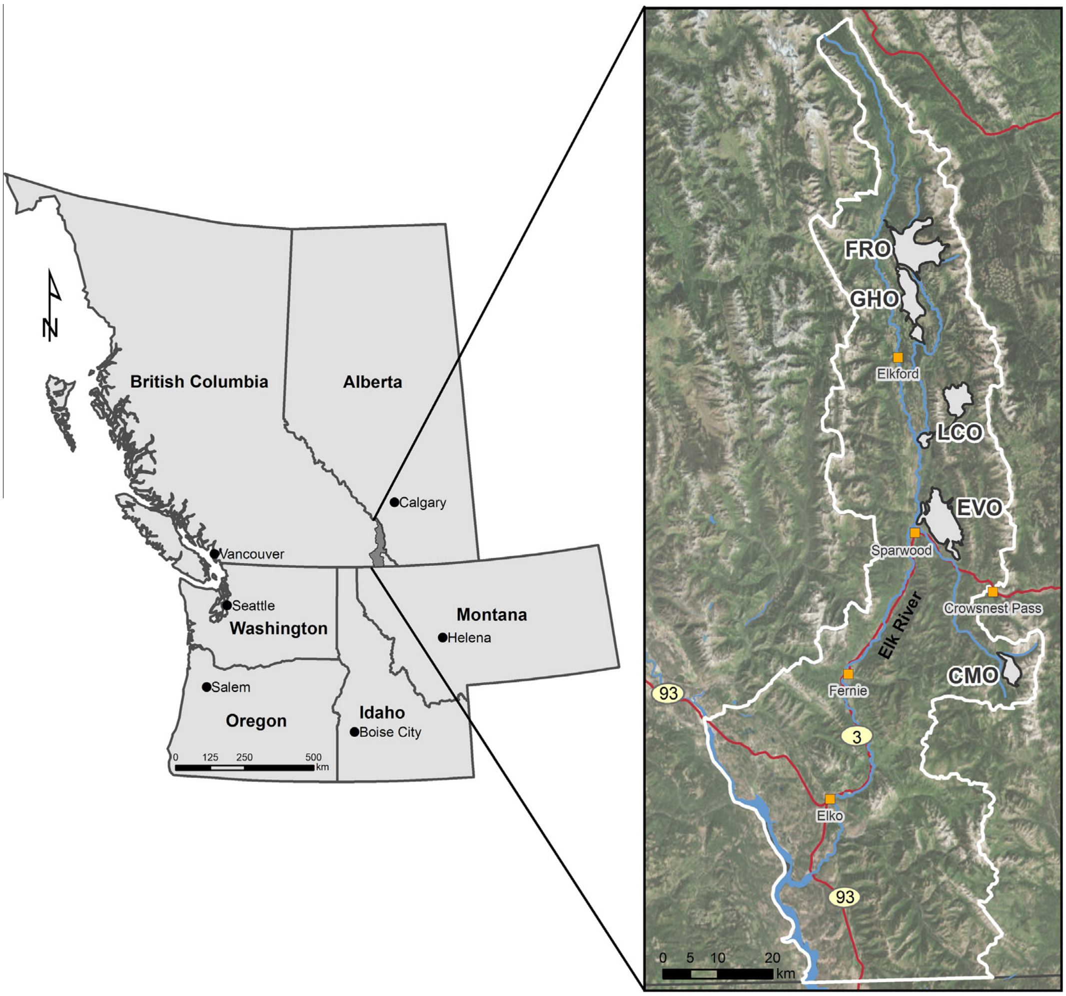

Fig. 1. Location map showing the Elk Valley, British Columbia, Canada and regional coal mining operations (FRO, GHO, LCO, EVO, and CMO). The limits of the Elk River watershed boundary are delineated with a solid white line.

extending from the crest of the pit to the southernmost extent of the dump. A boulder rock drain was constructed over the original Bodie Creek thalweg to collect and release water at the toe of the dump. The Bodie dump was constructed over 6 years (1996–2002). It has surface elevations of 1290–1545 m, a maximum thickness of approximately 190 m and an average thickness of approximately 70 m. Water from the mine pits to the northeast of the dump is occasionally discharged into the most northerly portion of the dump above Bodie Creek.

The general hydrological context for the WLC watershed and the Elk Valley is summarized by Shatilla (2013) and Wellen et al. (2015), respectively. The physical and chemical conditions in the alluvial aquifer system downstream of the waste rock dump is presented in Szmigielski (2015). These studies are the source of the hydrological information presented below and are also drawn upon later in the paper to establish the hydrological and hydrogeological context for interpretation of the stable isotopes of water.

The Elk Valley has a humid continental climate characterized by low relative humidity, highly variable temperature and precipitation. The mean annual temperature is approximately 4.4 °C as reported at Sparwood, BC (Environment Canada, 1981–2010 Climate Normal, elevation: 1138 m). Summer mean temperatures range from 9 °C to 15 °C and winter mean temperatures range from −2 °C to −7 °C. Mean annual precipitation is 613 mm, with considerable inter-annual variability. At Sparwood, approximately 67% of precipitation falls as rain, although the fraction of snow increases dramatically with elevation and is highly variable as with most alpine environments. A local temperature and precipitation lapse rate is approximately −0.48 °C/100 m and +21 mm/100 m.

Shatilla (2013) compared the hydrology of two paired watersheds; one with no waste rock (Dry Creek) in the same region as the waste-rock influenced catchment outlined here (WLC). Wellen et al. (2015) expanded this work to assess the broader influence of waste rock on flow and streamflow chemical regimes (specifically Selenium) throughout the Elk Valley. Shatilla (2013) observed that the presence of waste rock within the watershed dampens the hydrograph response, delaying snowmelt freshet and buffering streamflow response to summer precipitation events. Total ionic load (expressed as electrical conductivity) in watersheds with waste rock is typically an order of magnitude greater than watersheds without waste rock.

The groundwater flow system down-gradient of the waste rock dump at LCO-WLC was studied by Szmigielski (2015), who observed this system to be comprised of an upper perched aquifer with direct hydraulic connection to the creek, underlain by an unconfined aquifer within alluvial sediments and the upper weathered bedrock surface. The migration of CIs from the waste rock dump in the groundwater system was primarily along the lower, unconfined alluvial aquifer which later discharges into the Line Creek alluvium. The chemistry of the groundwater reflects that of waste rock effluent and showed a seasonal cycle controlled by seasonal mixing and dilution of waste rock

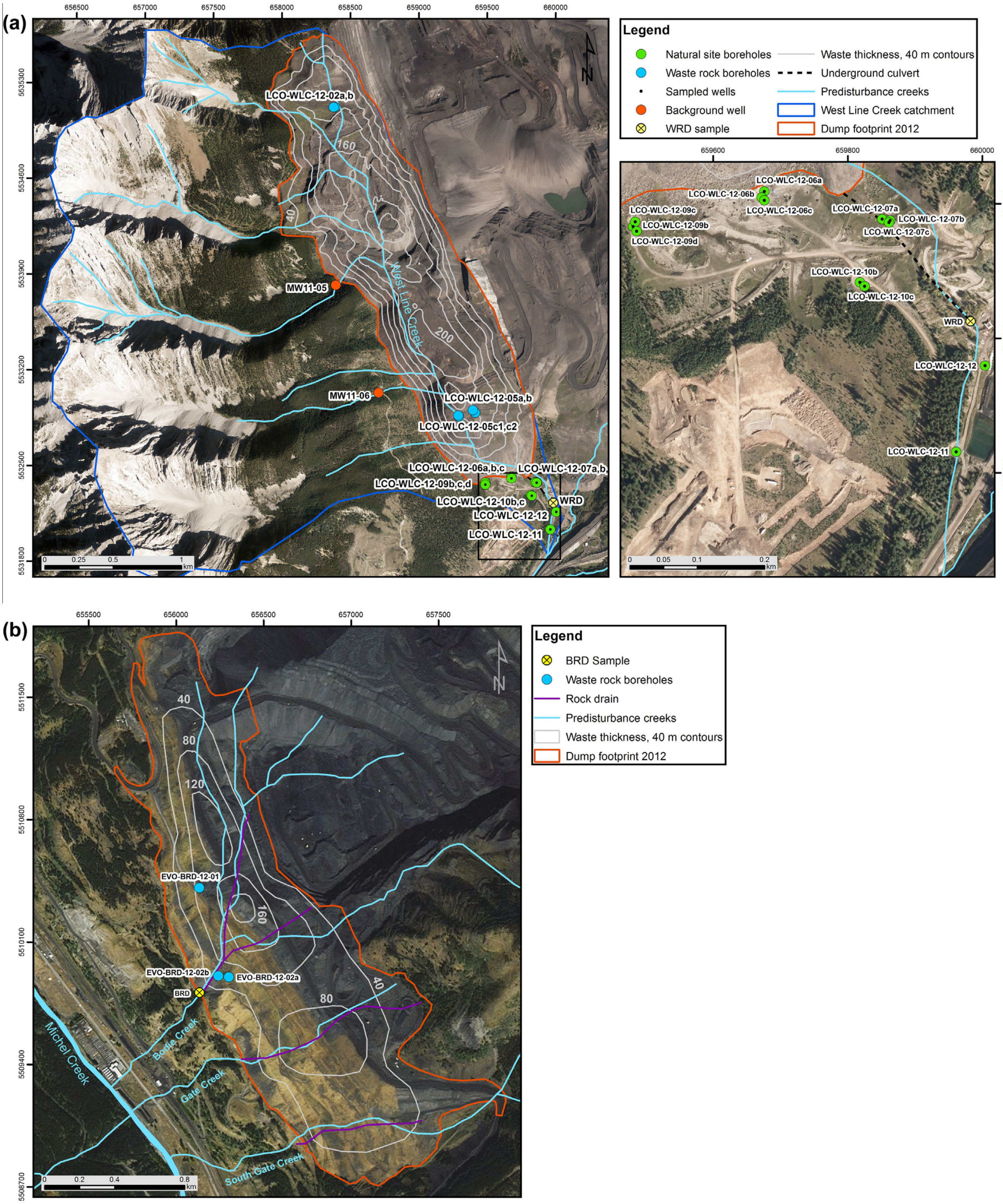

Fig. 2. Map of (a) LCO-WLC and (b) EVO-BRD study areas with location of boreholes, rock drain/creek monitoring locations and waste rock thickness contours.

effluent by natural waters. Szmigielski (2015) estimated that the lowest (winter) discharge through this aquifer was approximately $0.4 \times 10^6\ \text{m}^3/\text{y}$ with an average discharge through the aquifer of approximately $0.45 \times 10^6\ \text{m}^3/\text{y}$. The average flows represent approximately 22% of the annual flows from West Line Creek ($2.2 \times 10^6\ \text{m}^3/\text{y}$ from 2009–2014; ranging from $0.95 \times 10^6\ \text{m}^3/\text{y}$ in the winter to $16 \times 10^6\ \text{m}^3/\text{y}$ during peak spring flow).

3. Materials and methods

Drilling of the waste rock dumps and natural profiles was undertaken from July to September of 2012. To help the reader distinguish between waste rock and natural site profiles in the text, an asterisk ($*$) is added to the end of waste rock profile identifiers (e.g. LCO-WLC-12-02a*). A total of 19 holes were drilled at 5 different mine sites; however, only the holes drilled at LCO-WLC and EVO-BRD are discussed in this paper. Water samples from wells installed downstream of the waste rock dump at a number of the WLC natural sites and from the West Line Creek rock drain (WRD) as well as the Bodie rock drain (BRD) are also presented. Location maps with sample locations at the LCO-WLC and EVO-BRD sites are shown in Fig. 2.

All holes were drilled with a truck mounted sonic drill rig using a 152.5–177.8 mm (6–7″) casing with either a 120 mm (4.75″) or 152 mm (6″) sampling core barrel. The coring barrel was typically advanced 3.05 m (10 feet) ahead of the casing followed by casing advance and core retrieval. Both 'dry' and 'wet' sonic methods were evaluated. In the wet method, water was added to the hole to help reduce friction along the casing. In order to evaluate the potential for core contamination a ^{2}H spike was added to the drilling water. A comparison of the results from the 'wet' and 'dry' drilling method is reported in Hendry et al. (2015b). Only the core samples from the dry coring method are discussed in this paper.

The core was placed in a plastic sleeve after retrieval and the sleeve knotted at each end to seal the bag. A 133 mm (5.25″) sleeve was typically used for the 120 mm core and a 184 mm (7.25″) sleeve for the larger 152 mm core. The core was then placed in a PVC half pipe for transfer to a sampling area near the drill rig. The plastic bag was then split open to expose the core for logging and sampling. The outer 1–5 mm of the core was removed using a sterilized scraper and the core temperature was measured with a Taylor 9840 digital thermometer inserted 1–2 cm into the core. The time between the end of core drilling and obtaining temperature readings ranged between 5 and 15 min depending on the drilling depth. A section of approximately 2 kg of core was selected from within each meter of retrieved core and the depth interval recorded. This sample was then homogenized and approximately 500 g was sub-sampled to provide samples for geochemical and stable isotope of water analyses. Geochemical core data associated with the distribution of selenium (Se) within the waste rock is presented by Hendry et al. (2015a). The approximately 500 g of sample was placed in a medium Ziplock® bag (17.7 cm × 19.5 cm) and the air in the headspace was removed by squeezing and the bag was sealed. A second larger Ziplock® bag was then used to double seal the bag prior to shipping to a field isotope laboratory.

The stable isotopes of water in the pore water of the samples were measured using the vapor equilibration method described by Wassenaar et al. (2008). At the laboratory, the medium size Ziplock® bag was inflated with dry air and the inflated bag was placed in a large, Ziplock® bag which was evacuated and sealed. After equilibrating for three days the vapor phase was analyzed using a Picarro Cavity Ringdown Spectrometer L2130-i. The stable isotope values of the vapor were corrected for machine drift and equilibration fractionation (vapor to liquid) to obtain the corresponding pore-water values. This correction was undertaken using standard water samples of stable isotope concentrations that bracketed the composition of the core samples. The standards were well established laboratory standards (Birsay, Saskatchewan glacial aquitard water; δ^2H and δ^{18}O of $-178.7‰$ and $-22.86‰$ respectively; Saskatoon Tap Water, δ^2H and δ^{18}O of $-130.2‰$ and $-15.96‰$ respectively). The analytical error associated with this method is ±0.4‰ and ±2.1‰ for δ^{18}O and δ^2H, respectively (Hendry et al., 2015b).

Water samples were collected from the rock drains (WRD and BRD) on a daily basis from June through August 2012 after which the sampling frequency was decreased to weekly samples until October 2012. Sampling was not conducted during the winter of 2012/2013. Sampling was targeted on a weekly basis over the summers of 2013 and 2014. During the winter sampling period site access was limited and sampling was reduced to monthly samples for the 2013/2014 and 2014/2015 winter seasons. Sampling consisted of rinsing a clean one liter collection bottle in the drain water prior to filling the bottle. The capped bottle was labeled and transported back to the field lab where the water sample was filtered using a 0.45 μm paper filter into a 30 mL HDPE scintillation vial. The scintillation vial was capped and stored at room temperature before analysis. Analysis was conducted with the Picarro Cavity Ringdown Spectrometer L2130-i combined with an autoinjector and vaporizer. The isotope analysis was conducted using the methodology developed by IAEA Water Resources Programme using U.S. Geological Survey standards USGS-46 (δ^2H and δ^{18}O of $-235.8‰$ and $-29.80‰$ respectively) and USGS-48 (δ^2H and δ^{18}O of $-2.0‰$ and $-2.224‰$ respectively). The analytical error associated with this method is ±0.3‰ and ±0.8‰ for δ^{18}O and δ^2H, respectively (Lis et al., 2008).

The gravimetric water contents of the core samples were measured based on the method described by ASTM D2216-10 (2010). Particle size analyses of waste rock was carried out at the Geotechnical Laboratory, University of Saskatchewan in accordance with ASTM D422-63 (2007). Loss on ignition (LOI) was measured on nine samples from LCO-WLC-12-05a* using the procedure detailed in ASTM D7348-08 (2008). A representative portion of each particle size was subjected to a temperature of 550 °C in a muffle furnace for 5 h. The mass loss on ignition for each particle range was then determined. The sample was subsequently analyzed a second time for particle size analysis according to ASTM D422-63 (2007). Particle size analysis of the natural sites was performed in the Cameco Chair Geochemistry lab at the University of Saskatchewan using the laser diffraction method (LDM) outlined by Sperazza et al. (2004) and the sieve-hydrometer method in accordance with ASTM D422-63 (2007). LDM analysis was performed using a Mastersizer 2000 with wet dispersion (i.e. hydro MU) on ~3 g of oven dried, crushed sample sieved through a 2 mm sieve at a laser obscuration of 10–15%, dispersion pump speed of 2200 rpm and ultrasonic tip displacement of 3 μm for 60 s prior to data collection. Samples were measured in triplicate for 20 s; grain sizes were reported as the average of three successive analyses (Sperazza et al., 2004). Results of the LDM particle size analysis were calibrated to the sieve-hydrometer method using the method outlined in Eshel et al. (2002).

As one of the objectives of this paper was to provide an overview of the distribution and composition of the stable isotopes of water within the waste rock and adjacent natural geologic profiles as compared to precipitation, data collected as part of an ongoing research program on the hydrology of the study watersheds was utilized. A portion of this work is reported in Shatilla (2013). A total of 313 precipitation samples were used to characterize the local isotopic meteoric water line (LMWL) of the Elk Valley. All precipitation samples were analyzed on a Los Gatos DLT-100 Liquid Water Isotope Analyzer at the University of Toronto. Rainfall samples (249 with 35 field replicates retrieved within 48 h of events) were collected using a series of five samplers built after Gröning et al. (2012). Snow samples were collected at three sites within WLC and at five sites in the Elk Valley ranging in elevation from 1394 to 2147 m. Snow pits were excavated in late March in 2012 and 2013 and average volume-weighted values were determined from melted samples.

4. Results and discussion

4.1. Local meteoric water line

The LMWL for the Elk Valley established was: $\delta^{2}H = 7.6\ \delta^{18}O - 2.1‰$, similar to the LMWL reported for Calgary, Alberta by Peng et al. (2004). The volume-weighted $\delta^{2}H$ and $\delta^{18}O$ for precipitation were −130.4‰ and −17.4‰, respectively, with volume weighted averages for rain of −114.4‰ and −14.6‰, respectively and for snow of −155.7‰ and −20.5‰, respectively. These values and the LMWL are for an average elevation of 1450 m with total precipitation of 678 mm (350 mm rain and 328 mm snow). An isotopic gradient for $\delta^{18}O$ of −0.25‰ per 100 m was observed, consistent with that reported by Clark et al. (1982) at Mount Meager in the Coast Range of British Columbia and by Gammons et al. (2006) in the Rocky Mountains near Butte, Montana.

4.2. Isotopic fractionation correction for the drill core samples

A compilation of depth profiles of measured data from the core samples at five waste rock sites, two at EVO-BRD and three at LCO-WLC (Fig. 3), and four natural profile sites at LCO-WLC (Fig. 4) are presented with the field generated core descriptions. The data includes: $\delta^{2}H$ and $\delta^{18}O$ for pore water, gravimetric water content, *d*-excess relative to the local meteoric water line, and core temperature measured at ground surface. Pore gas oxygen and in situ temperature measurements from gas monitoring ports within the dump are also available at various sites and are also plotted on these figures.

The use of dry sonic drilling provided near continuous core samples (>90% recovery) of the coarse, unsaturated, waste rock and alluvial soils; however, the drilling method resulted in heating of the cores above in situ temperatures with core temperatures generally increasing with depth and greater in coarser (drier) soils. In situ temperatures measured in two waste rock boreholes ranged between 0.1 and 29 °C (see Fig. 3 profiles LCO-WLC-12-05a* and EVO-BRD-12-02b*) with the largest fluctuations and highest temperatures generally being measured near the surface. The maximum core temperatures reached 80 °C as measured within the core after retrieval. Condensation of water vapor on the inner surface of the plastic sleeve was often observed following core retrieval. Since the relative humidity within the bags was close to 100%, water vapor was released from the bag when it was opened. This loss of water can lead to fractionation of the stable isotopes of water within the remaining pore water.

Evaporation of water from a soil or water body will cause the stable isotope of water composition to plot below the LWML along an evaporation fractionation line (EL) (Clark and Fritz, 1997). The high rates of recharge that are likely given the climate and coarse textured nature of this waste rock suggests that the water within the core should be near the LMWL as represented by low negative values of *d*-excess relative to the LMWL. However; as shown in Fig. 5, typical sets of isotope values from core taken from two waste rock sites (LCO-WLC-12-05a* and EVO-BRD-12-01) and a natural profile (LCO-WLC-12-06a) show some shift below the LMWL. The observed *d*-excess values for uncorrected isotope analyses ranged from −20‰ to −40‰ throughout much of the WLC waste rock profiles becoming more depleted in zones of higher core temperature. The natural profiles (LCO-WLC-12-06a, -09b, -12) generally have much smaller negative *d*-excess values, in the range of 0 to −10‰, despite the fact that the core temperatures reach similar values as those for the waste rock. The reason for this smaller amount of fractionation as a result of core heating and vapor loss is attributed to the generally higher water contents associated with the natural profiles.

Although fractionation due to evaporation at surface is likely to be low due to the expected high rates of recharge, there could be zones of 'internal' evaporation associated with the convective ingress of drier atmospheric air, similar to that observed by Sracek et al. (2004). This convective air flow may be produced by heating within the dump as a result of exothermic reactions associated with sulfide oxidation (Lefebvre et al., 2001) but can also be created as a result of differences in internal dump temperatures

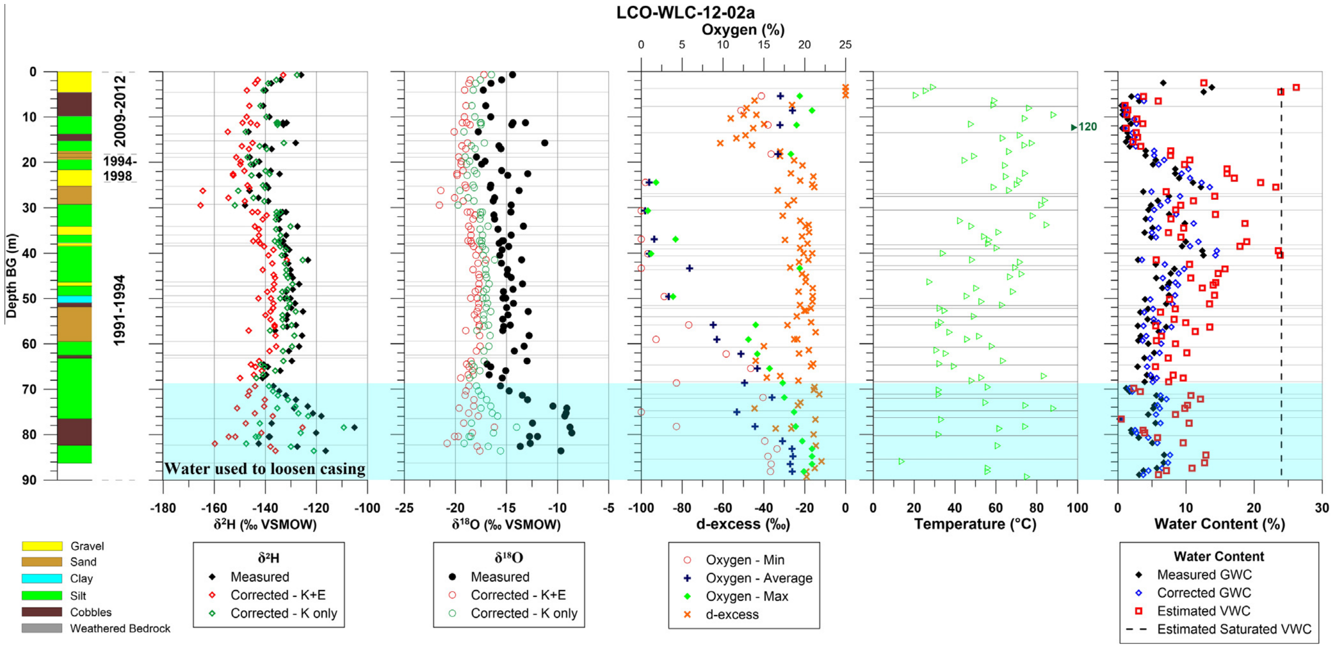

Fig. 3. Core data from waste rock sites (LCO-WLC-12-02a, 12-02b, 12-05a and EVO-BRD-12-01, 12-02b). Data includes depth profiles below ground (BG) of measured and corrected (kinetic (*K*) and equilibrium (*E*)) stable isotopes of (i) $\delta^{2}H$, (ii) $\delta^{18}O$, (iii) *d*-excess and in situ oxygen gas content (where measured), (iv) measured core temperature and in situ temperature (where available), and (v) measured and corrected gravimetric water content (GWC) and estimated volumetric water content (VWC, where measured). The date ranges indicate when the waste rock was placed.

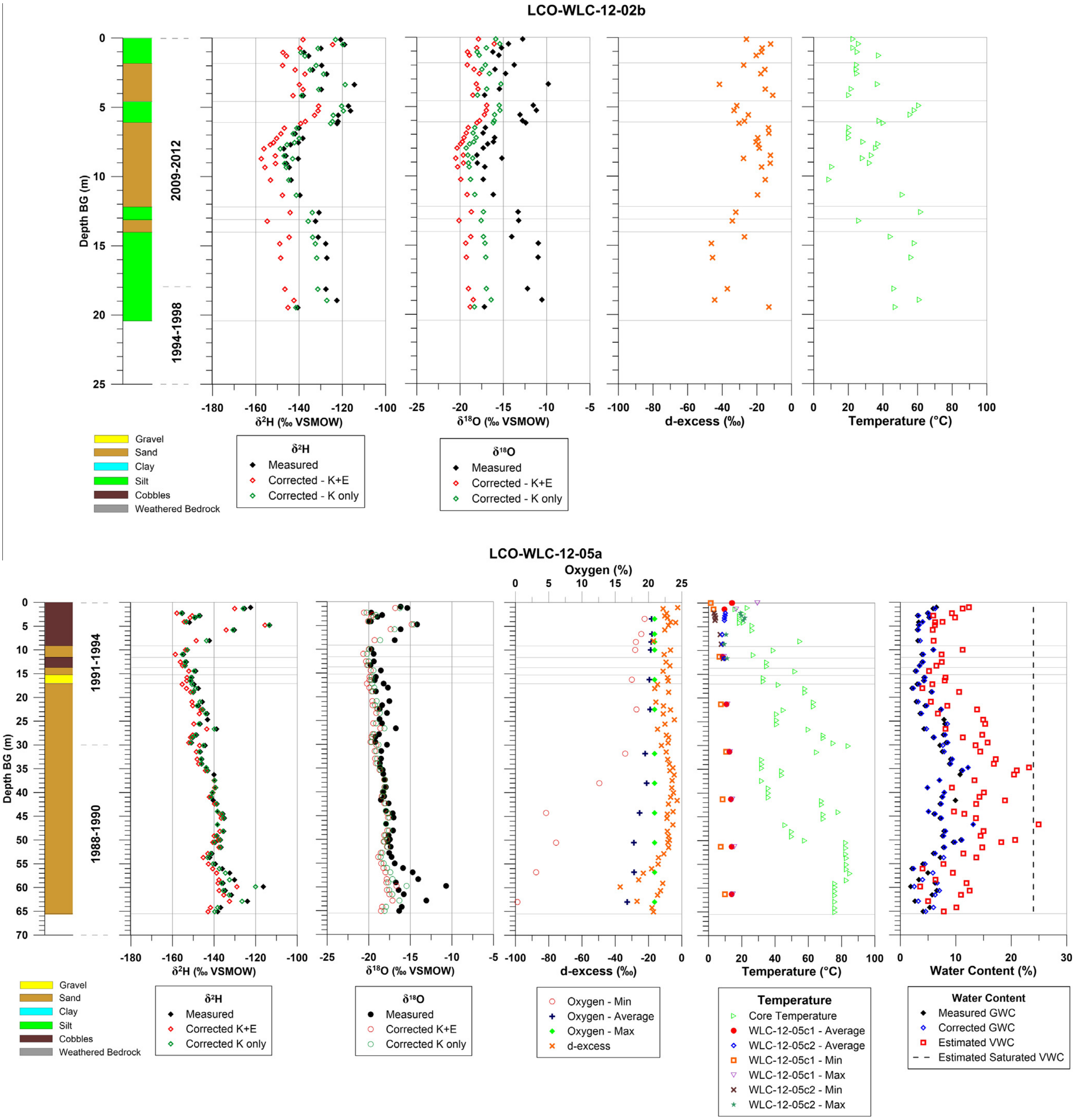

Fig. 3 (*continued*)

relative to seasonal air temperature fluctuations (Goering and Kumar, 1996).

It is not possible to separate out the impact of fractionation due to sample water loss from internal evaporation. However, there were locations where larger negative values of *d*-excess were observed in zones associated with dropping oxygen levels (e.g. upper 20 m of LCO-WLC 12-02a*, lower portion of LCO-WLC 12-05a*) which could be associated with oxygen consumption by sulfide oxidation (exothermic heating) and convective air flow. In addition, the bottom portion of EVO-BRD-12-02b* is of particular note in this regard, since although oxygen levels remain high, the internal dump temperatures are close to zero from depths of 45–60 m with *d*-excess values as low as −60‰. This suggests strong inward convection of dry winter air flow leading to freezing at the toe of the dump.

In an attempt to correct the profiles for the effect of water loss and fractionation during sampling the measured isotopic values were adjusted by moving them back to the LMWL along an expected evaporation line. This correction was applied to all samples for the purpose of consistency; however, it should be noted that in the case of internal evaporation due to convective air flow this correction would not be appropriate.

For simplicity, a Raleigh distillation fractionation calculation was applied as follows (Clark and Fritz, 1997; Gat, 1996):

$$\delta = \left(\left(\frac{\delta_o}{1000}+1\right)f^{(\alpha-1)}-1\right)*1000 \qquad (1)$$

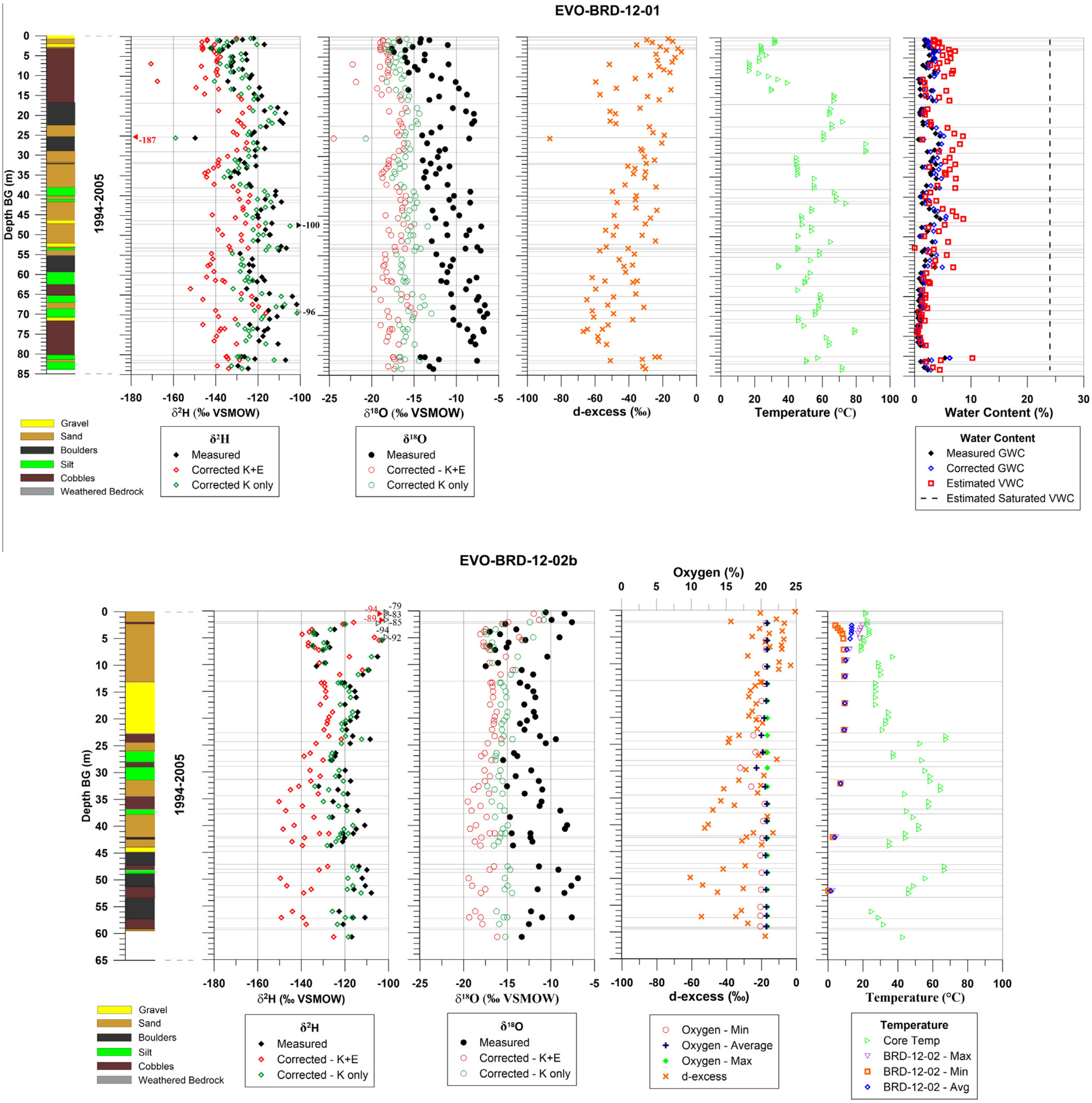

Fig. 3 (*continued*)

where δ_o is the initial isotope composition of the pore water, δ is the isotopic composition following fractionation, f is the fraction of the water remaining in the sample, and α is the equilibrium fractionation factor. The equilibrium fractionation factor is expressed as the ratio of the isotopic composition of the vapor to the liquid phases (R_v/R_L) which can also be expressed as:

$$\alpha = \frac{\delta_v - 1}{\delta_l - 1} \quad \text{or} \quad \varepsilon = (\alpha - 1)1000 \tag{2}$$

where ε is the enrichment factor.

Fractionation is assumed to occur as a result of equilibrium fractionation of the porewater under the elevated core temperature (equilibrium fractionation) combined with kinetic (transport) fractionation as a result of evaporative water loss from the sample.

The equilibrium fractionation factor was calculated from the equations given by Majoube (1971) as follows:

$$\text{Deuterium}: \ln(\alpha_e) = \frac{24844}{T^2} - \frac{76.248}{T} + 0.052612 \tag{3}$$

$$\text{Oxygen} - 18: \ln(\alpha_e) = \frac{1137}{T^2} - \frac{0.4156}{T} - 0.0020667 \tag{4}$$

where T is the temperature of the core in degrees Kelvin, and α_e is the equilibrium fractionation factor.

The kinetic fractionation due to evaporation of water from the cores was described using the equations described by Gat (1996) or Clark and Fritz (1997):

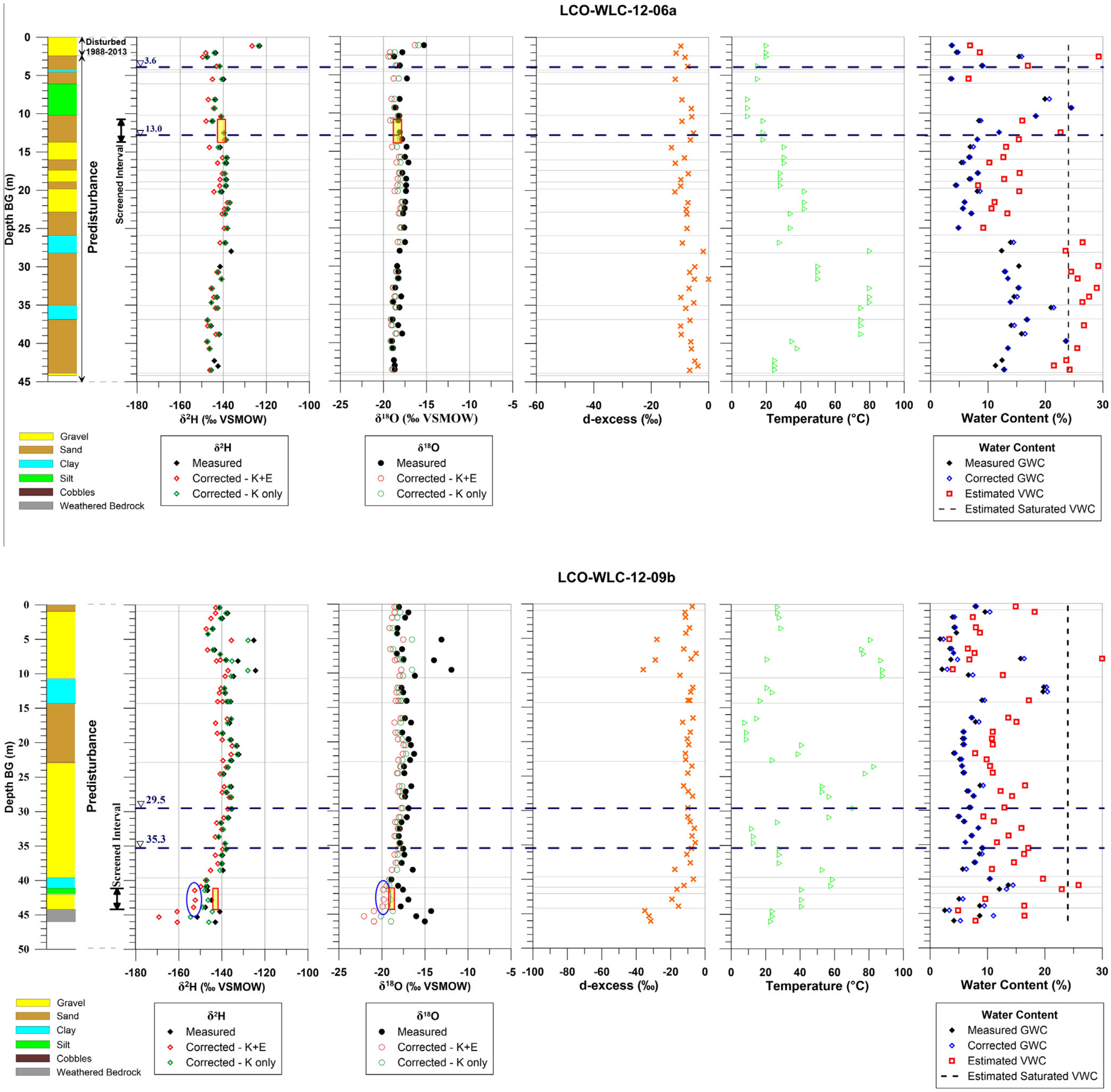

Fig. 4. Core data from natural sites (LCO-WLC-12-06a, 12-09b, 12-10b, 12-12). Data includes depth profiles below ground (BG) of measured and corrected (kinetic (K) and equilibrium (E)) stable isotopes of (i) δ^2H, (ii) δ^{18}O, (iii) d-excess and in situ oxygen gas content (where measured), (iv) measured core temperature and in situ temperature (where available), and (v) measured and corrected gravimetric water content (GWC) and estimated volumetric water content (VWC, where measured). Also shown is the depth of the screened interval, the range in water level measured in the well (dashed blue lines), and range in stable isotopes measured from well samples (yellow box). Blue circles on LCO-WLC-12-09b are estimated values because temperature measurements were missing.

$$\Delta\varepsilon_k = (1-h)\theta n C_d \quad [‰] \tag{5}$$

where h is relative humidity of the air, θ is a weighting term which can be taken equal to one for a small evaporating body, n is a weighting term related to whether evaporation is turbulent (open water) or through a stagnant layer as through a soil profile. For the latter case, n is taken equal to unity, C_d is taken to be 28.5‰ for ^{18}O and 25.1‰ for ^{2}H (Gat, 1996).

A total fractionation factor was calculated assuming that equilibrium and kinetic fractionation are additive (Clark and Fritz, 1997). The isotopic composition of the pore water within the sample prior to water loss was then calculated using:

$$\delta_c = \left(\frac{\left(\frac{\delta_m}{1000}+1\right)}{f^{(\alpha-1)}} - 1\right) * 1000 \tag{6}$$

where δ_m is the measured isotopic composition of the sample and δ_c is the corrected isotopic composition of the sample.

Air temperature and relative humidity were not recorded on site during drilling so these parameters were estimated from nearby monitoring stations. There was one climate monitoring station on the Bodie waste rock dump at the time of drilling with an additional five stations installed at Teck operations proximal to the drill sites in August 2012: two on the WLC dump, two on reclaimed

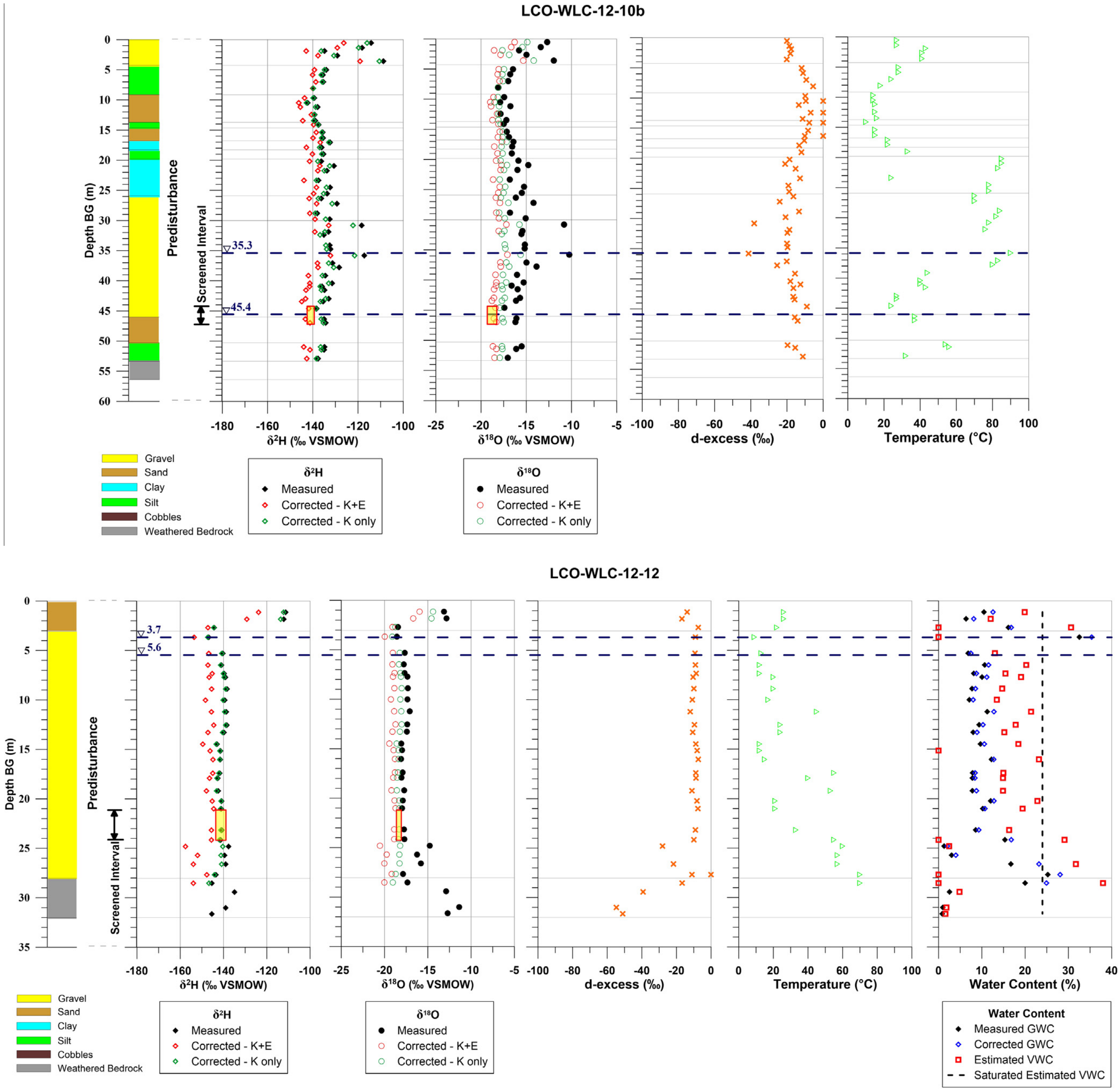

Fig. 4 (*continued*)

waste rock at GHO and one at FRO (see Fig. 1). The daily air temperature and vapor pressure at these sites, along with the Environment Canada station at Sparwood, British Columbia, were compared to the Bodie monitoring station. The data showed a strong correlation with elevation ($R^2 > 0.97$) for both vapor pressure and air temperature. Consequently, these correlations were used to estimate the air temperature and relative humidity at each drill site for each specific drilling date based on the monitoring data at the Bodie station and the elevation of the drill site.

An iterative method was used to solve Eq. (6) by adjusting the value of f until the corrected δ^2H and δ^{18}O values fell on the LMWL. The calculated values of 'f' were then used to determine corrected gravimetric water contents (ω) from the measured water contents. The corrected isotope profiles along with the corrected water contents are presented in Figs. 3 and 4 for the waste rock and selected natural sites. The corrected ω values were also multiplied by an assumed dry density (ρ_d) to calculate volumetric water contents (θ). In these calculations, ρ_d was assumed to be 1900 kg/m^3, similar to that reported by Dawson (1994) and Dawson et al. (1998) for Elk Valley coal waste rock. This ρ_d would result in a total porosity (n) of about 0.24 based on a particle density (specific gravity) of 2.5. Comparing the estimated θ values to the dashed line representing the estimated n provides a visual indication of the variation of the degree of saturation (θ/n) with depth.

4.3. Interpretation of corrected isotopic composition of pore-water

The uncorrected isotopic values (Figs. 3 and 4) for the core samples can be compared with corrections for only kinetic (K) fractionation (only relative humidity correction) or for both kinetic and equilibrium ($K + E$) fractionation (relative humidity and temperature corrections). The correction for kinetic fractionation alone is

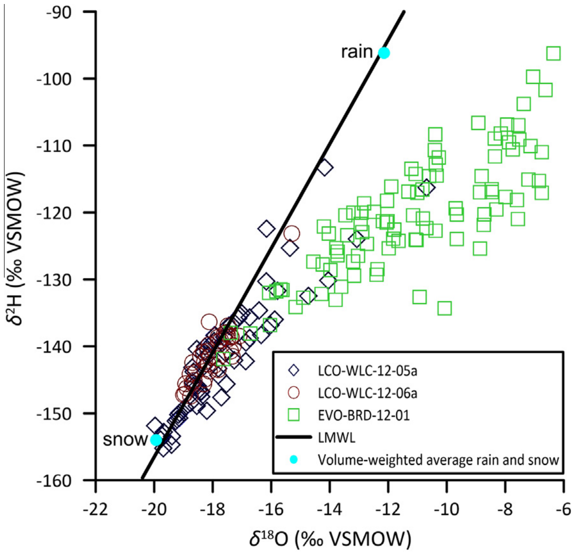

Fig. 5. Uncorrected isotope pore-water measurements from core samples plotted with LMWL and volume-weighted rain and snow values for the Elk Valley: LCO-WLC 12-05a*, LCO-WLC 12-06a and EVO-BRD-12-01*.

similar to the combined kinetic plus equilibrium fraction for many of the sites; however, in the case of low water content sites (e.g. EVO-BRD) the addition of equilibrium fractionation appears to produce a more monotonic profile with isotopic values which are in agreement with values measured in the rock drain as described in the following section.

There are a few indirect methods by which to check the method used to correct the isotopic composition of the cores. The range of isotopic values obtained for groundwater samples taken from wells installed at a number of the natural site profiles are highlighted by a yellow box in Fig. 4. In most cases there was very little variation in the isotopic composition of these samples over the course of the year. In general, the results from the corrected core data correspond well with those obtained by direct sampling of the groundwater.

The other check on the corrected isotopic values is to compare the average isotopic composition of the corrected drill core samples to that measured from the rock drains. Table 1 provides a statistical comparison of the distribution of the isotopic composition of pore water from the waste rock and natural sites and volume weighted averages from the rock drains. At both LCO-WLC and EVO-BRD the core data corrected for both equilibrium and kinetic fractionation is in better general agreement with the observed rock drain isotopic composition, although some differences of note can be observed.

The mean isotopic composition of the WRD from July 2012 to December 2014 was a δ^2H of −141.3‰ and δ^{18}O of −18.5‰, lying on the LMWL. These are very similar to the valley wide volume-weighted precipitation values noted earlier (−130.4‰, −17.4‰) which, when adjusted for differences in elevation (valley wide elevation of 1450 m to the WLC average elevation of 2050 m), become (−145.7‰, −18.9‰). At BRD, the average composition of the rock drain water (May 2012–May 2013) was (−134.4‰, −17.3‰). These values are similar to the valley wide volume-weighted precipitation values adjusted for elevation (−133.6‰, −17.3‰).

The flow rates at WRD show high seasonal variability which is related to the hydrology of the WLC watershed with a pronounced hydrograph of peak flow during the spring freshet (e.g. peak flows in the order of 0.48 m^3/s) followed by much lower winter base flows (e.g. 0.03 m^3/s). BRD is completely covered by waste rock and has a similar flow rate throughout the year. From May 2012 to May 2013 the annual flow rate at BRD ranged between approximately 0.01 and 0.03 m^3/s with no discernible pattern in isotopic composition of the water.

The WRD collects waters originating from both the dump and the natural watershed. The flows from the dump will be due to snow melt and summer rainfall but are heavily buffered by storage within the dump, while the flows from the natural watershed are dominated by a large rapid release of water from snowmelt. Fig. 6 illustrates that during winter or low flow conditions (i.e. base flow) the isotopic composition of the WRD water becomes enriched (i.e. warmer) with peak values of −18 to −17.8‰ for δ^{18}O, and total dissolved solid (TDS – sum of measured anions and cations) concentrations increasing to ~2000 mg/L at the lowest observed flow rates. The reason for this shift is interpreted to be the increasing contribution of dump effluent to the rock drain, which is supported by the increasing TDS of the effluent during this low flow period (Fig. 6). The presence of this 'warmer' water reflects the greater proportion of recharge water into the unvegetated dump from summer precipitation as compared to the vegetated natural slopes. The work of Shatilla (2013) made a similar observation when comparing WLC (waste rock present) and Dry Creek (no waste rock present). The WLC hydrograph was heavily buffered as compared to Dry Creek when normalized for water-

Table 1
Summary statistics on stable isotope composition of creek, rock drains, waste rock and natural profiles. Note: K+E is for kinetic and equilibrium fractionation, K is for kinetic only fractionation and NC means no correction. *Note:* K+E is for kinetic and equilibrium fractionation, K is for kinetic only fractionation and NC means no correction.

	Rock drain		Dry Creek
	BRD	WRD	
δ^2H mean (‰)	−134.4	−141.3	−145.4
δ^{18}O mean (‰)	−17.3	−18.5	−19.0

	Waste rock														
	EVO-BRD-12-01			EVO-BRD-12-02b			LCO-WLC-12-02a			LCO-WLC-12-02b			LCO-WLC-12-05a		
	K + E	K	NC	K + E	K	NC	K + E	K	NC	K + E	K	NC	K + E	K	NC
δ^2H mean (‰)	−136.9	−124.7	−120.9	−131.6	−119.7	−116.9	−143.6	−135.6	−133.2	−144.8	−134.6	−132.4	−144.3	−142.1	−141.3
δ^{18}O mean (‰)	−17.7	−16.1	−11.2	−17.0	−15.4	−12.3	−18.6	−17.6	−14.5	−18.8	−17.4	−14.6	−18.7	−18.4	−17.6

	Natural sites																	
	LCO-WLC-12-06a			LCO-WLC-12-07a			LCO-WLC-12-09b			LCO-WLC-12-10b			LCO-WLC-12-11			LCO-WLC-12-12		
	K + E	K	NC	K + E	K	NC	K + E	K	NC	K + E	K	NC	K + E	K	NC	K + E	K	NC
δ^2H mean (‰)	−143.1	−141.7	−141.3	−149.8	−137.6	−135.3	−143.2	−139.7	−138.9	−139.5	−134.2	−133.0	−146.2	−140.0	−139.7	−146.3	−139.7	−139.1
δ^{18}O mean (‰)	−18.6	−18.4	−18.0	−19.5	−17.8	−14.8	−18.6	−18.1	−17.0	−18.1	−17.4	−15.7	−19.0	−18.1	−17.5	−19.0	−18.1	−16.7

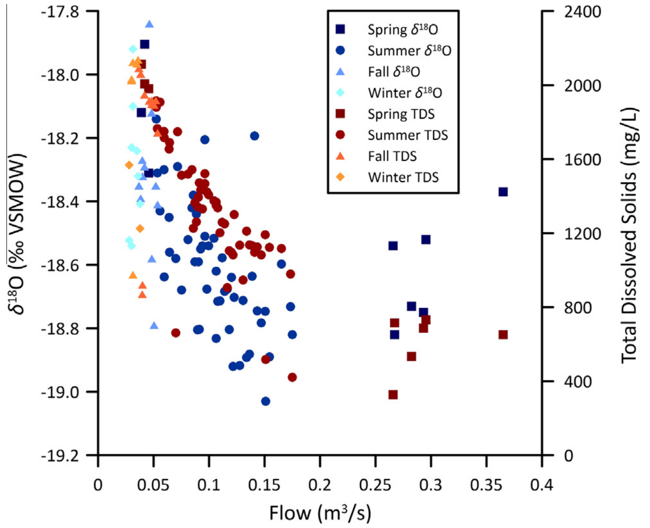

Fig. 6. $\delta^{18}O$ and TDS values for WRD water showing a seasonal pattern. Results divided into Spring (April–June), Summer (July–September), Fall (October–December) and Winter (January–March).

shed area and the δ^2H and $\delta^{18}O$ signatures for WLC were approximately +4‰ and +0.7‰, respectively, warmer than Dry Creek.

The mean isotopic values in the WLC waste rock, natural profiles and rock drain are similar although the ranges are different. The waste rock profiles have a larger range in values (e.g. differences in maximum to minimum δ^2H range from 33‰ to 71‰) relative to the natural profiles (e.g. differences in maximum to minimum δ^2H range from 9.1‰ to 34.1‰). Mueller et al. (2014) observed that profiles with a Coefficient of Variation (CV) of greater than 1.5% show distinct seasonal cycles that can be associated with net percolation estimates. Values of CV for the waste rock samples are generally >5% (ranging from 4.8 to 9.2%) while the natural profiles are <5% (ranging from 2 to 5%), although still greater than the 1.5% threshold proposed by Mueller et al. (2014).

The isotopic profiles (Figs. 3 and 4) in both the waste rock and natural profiles are generally monotonic, suggesting a level of continuity in water migration with depth. The monotonic nature of the isotope profiles in the waste rock are consistent with similar deep profiles in capillarity dominated pores from the literature (e.g. Bath et al., 1982, for unsaturated chalk). A commonly held assumption is that water and chemical transport through waste rock is preferential, macropore dominated flow rather than flow and transport through the matrix pores as governed by capillarity and described by Richards' equation. There are some distinct breaks in the profiles, often associated with changes in water content associated with textural heterogeneity. There is also increasing scatter within these profiles near surface (LCO-WLC 12-2b*, LCO-WLC 12-05a*) where flow rates would be the highest and consequently preferential flow may be more dominant.

The ranges of measured waste rock particle sizes (including coal particles) are summarized in Table 2. The amount of coal (based on LOI) measured on nine samples from LCO-WLC-12-05a* ranged from 1% and 8% with an average of 3.4%. The core samples do not include larger particles which could not be captured within the core barrel; however, in general the observed particle size distribution is consistent with those reported for the Elk Valley by Dawson et al. (1998) and Smith et al. (1995). Based on these measurements, even the coarsest waste rock at EVO still contains more than 20% of particles finer than 2 mm (or 40% finer than 4.75 mm), reflective of soil-like behavior as described earlier. This is also consistent with the high leaching efficiencies observed for waste rock of similar textures as summarized by Amos et al. (2014).

The isotope profiles also show cyclic depth profiles consistent with seasonal oscillations in the composition of recharging water and these patterns appear to be persistent with depth, particularly for the coarser, drier, EVO sites. Although these cyclic patterns are present for both the uncorrected and corrected data; the patterns in the corrected data are more monotonic with less drift to more ^2H and ^{18}O enriched values with depth – with the exception of LCO-WLC-12-05a*.

The natural profiles are typically more uniform with depth with the exception of a small deviation as the profile enters the underlying bedrock at the base of LCO-WLC-12-09b where Szmigielski (2015) also noted a distinct shift in geochemistry. There are several possible reasons for the differences in patterns between the waste rock and natural sites. The primary reason is likely that the water migration through the waste rock profiles is predominately vertical, gravity driven water movement as a result of surface recharge and consequently these profiles more clearly reflect seasonal cycles in the isotopic composition of snow melt and rain water. The natural profiles act as unconfined or perched aquifer systems, as reflected in the water tables marked on the summary profiles. Consequently, they receive much of their water from lateral flow through the alluvial deposits; water that is contributed from both the upstream watershed unaffected by waste rock placement as well as water that has migrated through the waste rock. The seasonal range of isotopic composition observed within wells constructed by Szmigielski (2015) at the various natural sites is also shown on those depth profiles by yellow shading. This data highlights that there is little seasonal variation in the isotopic composition of the well water at these sites although LCO-WLC-12-09b did exhibit greater seasonal variations in isotopic composition. This well is located near the corner of the waste rock dump close to the natural watershed.

A second reason for the differences is likely due to the differences in particle size (texture) and consequently water contents within the profiles. The average texture of the waste rock and natural profiles summarized in Table 2 shows that while the gravel/sand/silt and clay fractions of the waste rock were approximately 36%/54%/10% for EVO-BRD-12-01* and 44%/50%/7% for LCO-WLC-12-05a*, the same fractions in the natural profiles were 51%/21%/27%. This difference in texture is evident in the higher volumetric water contents of the natural profiles including zones of saturation below the water table. The average volumetric water content for the waste rock sites ranged from approximately 5% (EVO) to 10% (WLC) while the natural profiles were closer to 20%. The actual field volumetric water contents may be lower than estimated due to the exclusion of particles from the core that are larger than the core diameter (i.e. oversize fraction). For example, if we assume that the oversize fraction is 20% (Golder Associates, 1987; Dawson, 1994; Smith et al., 1995) then the in situ volumetric water contents would be reduced to 4% (EVO), 8% (WLC) and 16% (Natural profiles).

The impacts of these differences in water content are also evident in the magnitude of the oscillations in the waste rock isotope profiles. Sites that are finer textured and have slightly higher water contents (e.g. LCO-WLC-12-02*, -05a*) have smaller oscillations in the isotopic profiles while sites that are coarser and have lower water contents (e.g. EVO-BRD-12-01*, -02*) have greater oscillations in the isotope profiles. This is consistent with the observations and inferences pointed out by Cook et al. (1992) and Bath et al. (1982) that the seasonal fluctuations of isotopic signatures may propagate to great depths (tens of meters) only if recharge rates are high (>100–200 mm/y) and the volumetric water content within the profile is relatively low (e.g. 0.05–0.1).

The location of peaks and troughs in the isotope profiles can be combined with the estimates of volumetric water content to obtain average rates of recharge through each of the waste rock dumps.

Table 2
Statistical comparison of textural data from waste rock and combined natural profile core without the coal particles removed by combustion.

	EVO-BRD-12-01			LCO-WLC-12-05a			Natural profiles combined		
	% Gravel	% Sand	% Silt/clay	% Gravel	% Sand	% Silt/clay	% Gravel	% Sand	% Silt/clay
Mean	36.0	53.9	10.02	43.8	49.6	6.64	51.2	21.4	27.4
Standard error	1.89	1.36	0.84	1.55	1.43	0.56	1.82	0.96	1.40

Rigorous modeling of the spatial and temporal (i.e. annual climate) variability of these profiles is underway; however, for the purpose of illustration the approximate 'peak to peak' depths were selected from visual observation as follows: 5–10 m at LCO-WLC-12-02b* and LCO-WLC-12-05a* and 15-20 m at EVO-BRD-12-01* and BRD-EVO-12-02b*. If we assumed the depth averaged volumetric water contents (corrected for a 20% missing oversize fraction) at these two sites was 4% (EVO) and 8% (WLC) this would suggest an upper limit of recharge rates at WLC of 400–800 mm/y and at EVO of 600–800 mm/y. If this water migration acted to move chemicals through the dump by piston flow the initial pore-volume of water held within a 100 m high dump could require as little as 5 years to flush (EVO) or as much as 20 years to flush (WLC).

The average precipitation at the WLC and Bodie dumps (based on Elk Valley station and observed lapse rates) would be in the order of 700–800 mm/y and 650–700 mm/y, respectively. If an average winter base flow rates (0.027–0.037 m^3/s) and the estimated low flow discharge through the alluvial aquifer at WLC (0.4×10^6 m^3/y, approximately) are assumed to be due to net percolation through the waste rock, then the average water release from LCO-WLC of approximately 255 mm/y (2009–2014 data) would be apportioned as 460–580 mm/y of recharge through the waste rock and only about 180–130 mm/y through the undisturbed portions of the watershed. If we assume that the observed low flow rates at Bodie (0.01–0.015 m^3/s) plus an assumed groundwater discharge equal to 1/3 of the surface flow (0.003–0.05 m^3/s) are all due to recharge through the dump overlying the original Bodie watershed then the annual recharge rates through the dump would be approximately 350–520 mm/y.

5. Conclusions

This work highlights the feasibility and value of developing high-resolution profiles of stable isotopes of water within waste rock dumps. The methods of sample collection, isotope analyses, and the fractionation correction for evaporative water loss from the core water provide a potentially valuable method for measuring stable isotope profiles in mine waste.

The data set presented in this paper provides new insights into the nature of recharge and water migration processes within coal waste rock dumps in the Elk Valley which should be broadly applicable to mine waste rock worldwide. The high resolution profiles highlight that the seasonal oscillations of pore water that are well documented within the literature for natural profiles are also seen within waste rock, and in fact appear to propagate to greater depths than have generally been observed in the literature for natural, unsaturated soil profiles. This is consistent with the postulation made by Cook et al. (1992) that oscillations should be identifiable to great depths (and consequently reflect antecedent recharge events over many years) under conditions of relatively high recharge rates (e.g. 100s mm/y) into lower water content soil profiles (e.g. <10%).

The range of the observed stable isotopes of water within the dump suggests that the dumps are being recharged by both snow melt, typical of natural systems in the region, but also by summer rainfall events. The contribution of summer rainfall to recharge into the dump is also highlighted by the 'warmer' isotopic composition of the WLC rock drain during the winter as the flows decrease toward base flow conditions. The relative amount of water associated with these two sources of recharge is expected to be similar; however, the variation in these values from year to year remains to be determined.

Based on the interpretations presented in this paper, it is expected that these waste rock dumps will undergo greater rates of recharge (relative to the natural profiles) with water residence times of 5–20 years for a 100 m high dump. The leaching efficiency associated with these rates of water migration is currently being studied using the long-term water quality monitoring in rock drains in the Elk Valley (Kuzyk et al., 2014).

Acknowledgements

Financial support was provided by Teck Resources Ltd. and funding through a Cameco-NSERC Industrial Research Chair (MJH) as well as a Syncrude-NSERC Industrial Chair (SLB). SC acknowledges the support from the NSERC-CRD program. The assistance of O'Kane Consultants with field instrumentation and monitoring assistance and from SRK Consulting in leading field drilling and sampling programs is gratefully acknowledged.

References

Adomako, D., Maloszewski, P., Stumpp, C., Osae, S., Akiti, T.T., 2010. Estimating groundwater recharge from water isotope (delta H-2, delta O-18) depth profiles in the Densu River basin, Ghana. Hydrolog. Sci. J. 55, 1405–1416.

Allison, G.B., 1998. Stable isotopes in soil and water studies. In: Causse, C., Gasse, F. (Eds.), Hydrologie et Géochimie Isotopique. ORSTOM, Paris, pp. 23–38.

Allison, G.B., Gee, G.W., Tyler, S.W., 1994. Vadose-zone techniques for estimating groundwater recharge in arid and semiarid regions. Soil Sci. Soc. Am. J. 58, 6–14.

ASTM D422-63, 2007. Standard test method for particle-size analysis of soils, in: Annual Book of ASTM Standards, West Conshohocken, PA.

ASTM D7348-08, 2008. Standard Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues. In: Annual Book of ASTM Standards, West Conshohocken, PA.

ASTM D2216-10, 2010. Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock. In: Annual Book of ASTM Standards, West Conshohocken, PA.

Amos, R.T., Blowes, D.W., Bailey, B.L., Sego, D.C., Smith, L., Ritchie, A.I., 2014. Waste-rock hydrogeology and geochemistry. Appl. Geochem. 57, 140–156. http://dx.doi.org/10.1016/j.apgeochem.214.06.020.

Anterrieu, O., Chouteau, M., Aubertin, M., 2010. Geophysical characterization of the large-scale internal structure of a waste rock pile from a hard rock mine. Bullet. Eng. Geol. Environ. 69, 533–548.

Azam, S., Wilson, W., Herasymuik, G., Nichol, C., Barbour, S., 2007. Hydrogeological behavior of an unsaturated waste rock pile – a case study at the Golden Sunlight Mine, Montana, USA. Bullet. Eng. Geol. Environ. 66, 259–268. http://dx.doi.org/10.1007/s10064-006-0077-7.

Barnes, C.J., Allison, G.B., 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. J. Hydrol. 100, 143–176.

Bath, A.H., Darling, W.G., Brunsden, A.P., 1982. The stable isotopic composition of infiltration moisture in the unsaturated zone of English chalk. In: Schmidty, H.L. (Ed.), Stable Isotopes. Elsevier, New York.

Beven, K., Germann, P., 1982. Water flow in soil macropores. Water Resour. Res. 18, 1311–1325.

Blackmore, S., Smith, L., Mayer, U.K., Beckie, R.D., 2014. Comparison of unsaturated flow and solute transport through waste rock at two experimental scales using temporal moments and numerical modeling. J. Contam. Hydrol. 171, 49–65.

Cheng, L., Liu, W., Li, Z., Chen, J., 2014. Study of soil water movement and groundwater recharge for the Loess Tableland using environmental tracers. Trans. ASABE 57, 23–30.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. CRC Press/Lewis Publishers, Boca Raton, FL, 328 pp.

Clark, I.D., Fritz, P., Michel, F.A., Souther, J.G., 1982. Isotope hydrogeology and geothermometry of the Mount Meager geothermal area. Can. J. Earth Sci. 19, 1454–1473.

Cook, P.G., Edmunds, W.M., Gaye, C.B., 1992. Estimating paleorecharge and paleoclimate from unsaturated zone profiles. Water Resour. Res. 28, 2721–2731.

Dawson, R.F., 1994. Mine Waste Geotechnics, Ph.D. Dissertation, Department of Civil Engineering, University of Alberta, 239 pp.

Dawson, R.F., Morgenstern, N.R., Stokes, A.W., 1998. Liquefaction flowslides in Rocky Mountain coal mine waste dumps. Can. Geotech. J. 35, 328–343.

DePaolo, D.J., Conrad, M.E., Maher, K., Gee, G.W., 2004. Evaporation effects on oxygen and hydrogen isotopes in deep vadose zone pore fluids at Hanford, Washington. Vadose Zone J. 3, 220–232.

Eshel, G., Levy, G.J., Mingelgrin, U., Singer, M.J., 2002. Critical evaluation of the use of laser diffraction for particle-size distribution analysis. Soil Sci. Soc. Am. J. 68, 736–743.

EVWQP, 2014. Elk Valley Water Quality Plan, Teck Resources Limited, July 22, 2014, 290 pp.

Gammons, C.H., Poulson, S.R., Pellicori, D.A., Reed, P.J., Roesler, A.J., Petrescu, E.M., 2006. The hydrogen and oxygen isotopic composition of precipitation, evaporated mine water, and river water in Montana, USA. J. Hydrol. 328, 319–330.

Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. Annu. Rev. Earth Pl. Sc. 24, 225–262.

Gaye, C.B., Edmunds, W.M., 1996. Groundwater recharge estimation using chloride, stable isotopes and tritium profiles in the sands of northwestern Senegal. Environ. Geol. 27, 246–251.

Gazis, C., Feng, X., 2004. A stable isotope study of soil water: evidence for mixing and preferential flow paths. Geoderma 119, 97–111.

Gibson, D., 1985. Stratigraphy, sedimentology, and depositional environments of the coal-bearing Jurassic-Cretaceous Kootenay Group, Alberta and British Columbia. Geol. Surv. Canada 357.

Goering, D.J., Kumar, P., 1996. Winter-time convection in open-graded embankments. Cold Reg. Sci. Technol. 24, 57–74.

Golder Associates, 1987. Regional study of coal mine waste dumps in British Columbia, Stage II. Supply and Services File #23440-6-9188-01SQ.

Gröning, M., Lutz, H., Roller-Lutz, Z., Kralik, M., Gourcy, L., Pöltenstein, L., 2012. A simple rain collector preventing water re-evaporation dedicated for δ^{18}O and δ^{2}H analysis of cumulative precipitation samples. J. Hydrol. 448–449, 195–200. http://dx.doi.org/10.1016/j.jhydrol.2012.04.041.

Hendry, J.M., Biswas, A., Essilfie-Dughan, J., Chen, N., Day, S.J., Barbour, S.L., 2015a. Reservoirs of selenium in coal waste rock: Elk Valley, British Columbia, Canada. Environ. Sci. Technol. 49, 8228–8236. http://dx.doi.org/10.1021/acs.est.5b01246.

Hendry, M.J., Schmeling, E., Wassenaar, L.I., Barbour, S.L., Pratt, D., 2015b. Determining the stable isotope composition of pore water from saturated and unsaturated zone core: improvements to the direct vapor equilibration laser spectroscopy method. Hydrol. Earth Syst. Sci. Discuss. 12, 6241–6274.

Holmquist, D.V., McOmber, R.M., Roberts, J.M., 1983. Engineering and Design Manual for Disposal of Excess Spoil. Denver, CO: U.S. Department of the Interior, Office of Surface Mining, Technical Services & Research, 294 pp.

INAP, 2009. The Global Acid Rock Drainage Guide. Prepared for the International Network for Acid Prevention. <http://www.gardguide.com>.

INAP, 2015. Global Cover System Technical Design Guidance Document. Prepared for the International Network for Acid Prevention by O'Kane Consultants Inc.

Kuzyk, T., Barbour, S.L., Hendry, M.J., 2014. A conceptual model for the flushing of coal waste rock piles in the Elk Valley, British Columbia, Canada. 2014 GSA Annual Meeting in Vancouver, British Columbia, Poster Presentation, Abstract No. 249669, GSA Abstracts, vol. 46, no. 6.

Lefebvre, R., Hockley, D., Smolensky, J., Lamontagne, A., 2001. Multiphase transfer processes in waste rock piles producing acid mine drainage: 2. Applications of numerical simulation. J. Contam. Hydrol. 52, 165–186.

Lighthall, P., Sellars, C., Burton, W.D., 1985. Design of waste rock dumps with flow-through rock drains. In: Proceedings of the 9th Annual British Columbia Mine Reclamation Symposium, Kamloops, BC, pp. 55–68.

Lis, G., Wassenaar, L.I., Hendry, M.J., 2008. High-precision laser spectroscopy D/H and 18O/16O measurements of microliter natural water samples. Anal. Chem. 80, 287–293.

Majoube, M., 1971. Fractionnement en oxygene-18 et en deuterium entre l'eau et sa vapeur. J. Chim. Phys. PCB 68, 1423–1436.

Marcoline, J.R., Smith, L., Beckie, R.D., 2006. Water migration in covered waste rock, investigations using deuterium as a tracer. 7th ICARD. ASMR, 1142–1155.

Mathieu, R., Bariac, T., 1996. An isotopic study (^{2}H and ^{18}O) of water movements in clayey soils under a semiarid climate. Water Resour. Res. 32, 779–789.

Melayah, A., Bruckler, L., Bariac, T., 1996. Modeling the transport of water stable isotopes in unsaturated soils under natural conditions: 2. Comparison with field experiments. Water Resour. Res. 32, 2055–2065.

Morin, K.A., Gerencher, E., Jones, C.E., Konasewich, D.E., 1991. Critical literature review of acid drainage from waste rock. MEND Rep. 1 (11), 1.

Mueller, M.H., Alaoui, A., Kuells, C., Leistert, H., Meusburger, K., Stumpp, C., Weiler, M., Alewell, C., 2014. Tracking water pathways in steep hillslopes by δ^{18}O depth profiles of soil water. J. Hydrol. 519, 340–352.

Neuner, M., Smith, L., Blowes, D.W., Sego, D.C., Smith, L.J.D., Fretz, N., Gupton, M., 2013. The Diavik waste rock project: water flow through mine waste rock in a permafrost terrain. Appl. Geochem. 36, 222–233. http://dx.doi.org/10.1016/j.apgeochem.2012.03.011.

Nichol, C., Smith, L., Beckie, R., 2005. Field-scale experiments of unsaturated flow and solute transport in a heterogeneous porous medium. Water Resour. Res. 41, W05018. http://dx.doi.org/10.1029/2004WR003035.

Peng, H., Mayer, B., Harris, S., Krouse, H.R., 2004. A 10-yr record of stable isotope ratios of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada. Tellus B 56, 147–159.

Piteau Engineering Ltd., 1999. Mined Rock and Overburden Piles. Rock Drain Research Program, Final Report, February 1999.

Poisson, J., Chouteau, M., Aubertin, M., Campos, D., 2009. Geophysical experiments to image the shallow internal structure and the moisture distribution of a mine waste rock pile. J. Appl. Geophys. 67, 179–192.

Ryan, B., Dittrick, M., 2001. Selenium in the Mist Mountain Formation of Southeast British Columbia. British Columbia Geological Survey, Geological Fieldwork 2000, Paper 2001-1.

SAPSE, 2010. A strategic plan for the management of selenium at Teck Coal operations. Strategic Advisory Panel on Selenium Management, June 30, 2010, 233 pp.

Shatilla, N.J., 2013. The influence of surface mining on runoff timing and flow pathways in Elk Valley, British Columbia. Master's thesis, McMaster University, Hamilton, Ontario, Canada, 73 pp.

Singleton, M.J., Sonnenthal, E.L., Conrad, M.E., DePaolo, D.J., Gee, G.W., 2004. Multiphase reactive transport modeling of seasonal infiltration events and stable isotope fractionation in unsaturated zone pore water and vapor at the Hanford site. Vadose Zone J. 3, 775–785.

Smith, L., Lopez, D., Beckie, R., Morin, K., Dawson, R., Price, W., 1995. Hydrogeology of Waste Rock Dumps. Contract No: 23440-4-1317/01-SQ Final Report, Department of Natural Resources Canada.

Sperazza, M., Johnnie, M.N., Hendrix, M.S., 2004. High-resolution particle size analysis of naturally occurring very fine-grained sediment through laser diffractometry. J. Sediment. Res. 74, 736–743.

Sracek, O., Choquette, M., Gélinas, P., Lefebvre, R., Nicholson, R.V., 2004. Geochemical characterization of acid mine drainage from a waste rock pile, Mine Doyon, Quebec, Canada. J. Contam. Hydrol. 69, 45–71.

Strohm, W.E., Bragg, G.H., Ziegler, T.W., 1978. Design and construction of compacted shale embankments. Volume 5: Technical guidelines. Final Report, Federal Highway Administration, Report No. FHWA-RD-78-141.

Szmigielski, J., 2015. Characterizing a groundwater system downgradient of a coal mine waste rock dump, Elk Valley, British Columbia, Canada. M.Sc. Thesis. Department of Geology, University of Saskatchewan.

Wassenaar, L.I., Hendry, M.J., Chostner, V.L., Lis, G.P., 2008. High resolution pore water δ^{2}H and δ^{18}O measurements by H_2O(liquid)-H_2O(vapor) equilibration laser spectroscopy. Environ. Sci. Technol. 42, 9262–9267. http://dx.doi.org/10.1021/es802065s.

Wellen, C., Shatilla, N.J., Carey, S.K., 2015. Regional scale selenium loading associated with surface coal mining, Elk Valley, British Columbia, Canada. Sci. Total Environ. 532, 791–802. http://dx.doi.org/10.1016/j.scitotenv.2015.06.040.