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Potential impacts to perennial springs from tar sand mining, processing, and disposal on the Tavaputs Plateau, Utah, USA

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HIGHLIGHTS

- The potential water quality impacts of the first US tar sand development are considered.
- Analyses of perennial springs in adjacent canyons indicate hydrologic connection to the site.
- Enhanced bitumen dissolution into water is expected based on chemical thermodynamic estimations.

GRAPHICAL ABSTRACT

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ABSTRACT

Similar to fracking, the development of tar sand mining in the U.S. has moved faster than understanding of potential water quality impacts. Potential water quality impacts of tar sand mining, processing, and disposal to springs in canyons incised approximately 200 m into the Tavaputs Plateau, at the Uinta Basin southern rim, Utah, USA, were evaluated by hydrogeochemical sampling to determine potential sources of recharge, and chemical thermodynamic estimations to determine potential changes in transfer of bitumen compounds to water. Because the ridgetops in an area of the Tavaputs Plateau named PR Spring are starting to be developed for their tar sand resource, there is concern for potential hydrologic connection between these ridgetops and perennial springs in adjacent canyons on which depend ranching families, livestock, wildlife and recreationalists. Samples were collected from perennial springs to examine possible progression with elevation of parameters such as temperature, specific conductance, pH, dissolved oxygen, isotopic tracers of phase change, water-rock interaction, and age since recharge. The groundwater age dates indicate that the springs are recharged locally. The progression of hydrogeochemical parameters with elevation, in combination with the relatively short

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groundwater residence times, indicate that the recharge zone for these springs includes the surrounding ridges, and thereby suggests a hydrologic connection between the mining, processing, disposal area and the springs. Estimations based on chemical thermodynamic approaches indicate that bitumen compounds will have greatly enhanced solubility in water that comes into contact with the residual bitumen–solvent mixture in disposed tailings relative to water that currently comes into contact with natural tar.

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1. Introduction

The area of study lies on the Tavaputs Plateau, which forms the southeastern rim of the Uinta Basin, approximately 145 km (90 miles) south of Vernal, UT (Fig. 1). This area is poised to become the first tar sand mine in the United States, operated by US Oil Sands (USOS), which operates mining and processing of tar sands deposits in Athabasca, Canada. The tar sand development site exists on the northwest–southeast trending Seep Ridge, which is the high point of the Tavaputs Plateau in this area (Fig. 1). USOS will remove overburden (surface mine) to expose subsurface tar sand, and will extract bitumen from crushed mined rock on-site using a citrus-based organic solvent (D-limonene). Tailings will be disposed of directly on the excavated land surface following removal of bitumen-equilibrated solvent to soil moisture contents between 10% and 20%. In 2008, a permit was granted to conduct mining, processing, and disposal on approximately 0.25 km^2 (63 acres) in the Seep Ridge area (Figs. 1 and SI-1) on the basis of an expected *de minimus* effect of the project on groundwater quality (Allen, 2012). The permitted area was recently increased to 0.93 km^2 (230 acres). Multiple perennial springs exist nearby and directly below the site (~100 to 300 m vertical) in adjacent canyons. These springs support aspen groves and lush meadows, and are used by ranching families, livestock, wildlife and recreationalists. A small reservoir in Main Canyon is fed by the springs (Figure SI-2), and is located approximately three miles from the initial permitted tar sand development site.

Expert witness testimony (Allen, 2012, and contributing documents), noting the lack of "significant" water in ridgetop boreholes, attributed the springs to two possible sources: 1) a regional aquifer that is pressurized due to recharge in distant mountains, e.g. the Uinta Mountains (Fig. 1); 2) local recharge via snowmelt and precipitation directly onto the surface of the alluvium in the canyon bottom, the areal extent of which is approximately 0.4 km^2 (100 acres) (Figure SI-1). However, neither of these attributed potential sources was substantiated via data or other objective methods; hence, the source of the springs was previously unknown. The goal of this study is to provide needed hydrogeochemical data to determine the source of the canyon springs, which is critical to understanding whether tar sand mining, processing, and disposal activities at the ridgetops have potential to impact springs, and more generally groundwater resources, in the adjacent canyons. In addition to a hydrologic connection between the ridgetops and the springs, any concern for potential impacts to spring water quality related to tar sand mining, processing, and disposal should address how (and whether) such activities pose potential water quality impacts that exceed those posed by the natural tar sands through which any water recharging at ridgetops would currently pass prior to emission at the springs. This possibility is examined using chemical thermodynamics approaches (e.g., Schwarzenbach et al., 1993) to determine whether bitumen compounds in residual bitumen–solvent mixture in disposed tailings have significantly greater propensity to dissolve in water relative to that propensity of bitumen compounds in the natural tar.

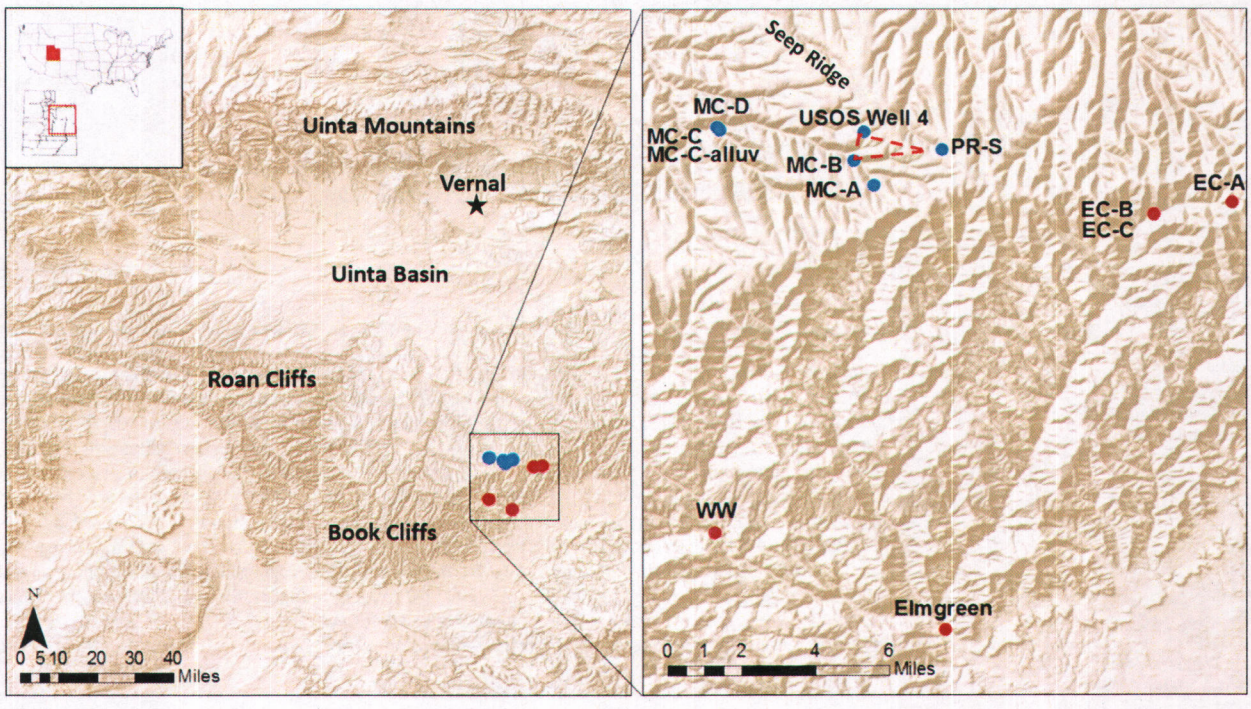

Fig. 1. Relief maps with general location (left) and detailed locations (right) of springs and wells sampled. Blue dots correspond to Main Canyon area, red dots correspond to Book Cliffs area. The southern rim of the Uinta Basin forms a topographic divide between the Main Canyon and Book Cliffs areas. The permit for tar sand mining, processing and disposal activities concerns the area bounded by PR-S, MC-B, and USOS Well 4, and roughly outlined in red dashed lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The Tavaputs Plateau ranges in elevation from 2150 m to 2750 m (7000 to 9000 ft) ASL, and is bounded on the south by the Roan and Book Cliffs, and to the north by the Uinta Basin. The Uinta Basin has an annual average precipitation of less than 21 cm (8.5 in.) (Fuller, 1994; Jensen et al., 1990) and the higher elevation plateau has an annual precipitation of approximately 20 to 50 cm (8 to 20 in.) (Utah Division of Water Resources, 2006; Western Regional Climate Center, 1997). The maximum and minimum mean daily temperatures for the region are 14 °C and 1 °C, respectively (PRISM Climate Group, 2006). Geologically, the study area is the southern rim of the Uinta Basin synclinal trough, and is comprised of Tertiary sedimentary units of lacustrine Green River (Eocene) and sandstone-dominated Wasatch (Paleocene–Eocene) Fms., spanning 66 to 33.9 Ma (Byrd, 1970). These units outcrop on the south-facing Roan and Book Cliffs of southeastern Utah (Fig. 1), and dip slightly (a few degrees) northward. The uppermost unit in the study area, the Parachute Creek Fm., contains bituminous sands (tar sands), and is underlain by the Douglas Creek member of the Green River Fm., and Eocene Renegade Tongue of the Wasatch Fm. (Kimball, 1981; Lindskov and Kimball, 1985; Holmes and Kimball, 1987). The Douglas Creek and Renegade Tongue outcrops are significant because both formations contain a large freshwater aquifer, the Douglas Creek aquifer, where they exist at depth to the north (Holmes and Kimball, 1987). The water budget for the Douglas Creek aquifer is estimated to be 2.5E7 m^3/yr (20,000 acre-ft/yr) with recharge via precipitation and stream infiltration (Holmes and Kimball, 1987). Existing investigations of the water resources specific to the study area are sparse (Price and Miller, 1975; Byrd, 1970). They describe the rim of the plateau in this location as an area where water, in the form of precipitation, stream or overland flow, or snowmelt, enters the subsurface and recharges the underlying shallow unconfined aquifer. This reflects the fact that the Tavaputs Plateau is the highest physiographic feature in the region, other than the Uinta Mountains approximately 160 km (100 miles) to the north, or the much smaller (in area) La Sal Mountains to the southeast (Fig. 1).

2. Methods

2.1. Approach

The isotopic and chemical characteristics of spring and well samples were evaluated in order to determine the likely sources of recharge. In addition to conventional field parameters such as dissolved oxygen (DO), pH, temperature, specific conductance, and alkalinity; additional parameters reflecting phase change, water-rock interactions, and age related to recharge and transport were also measured. The stable isotopes of hydrogen and oxygen were measured, as these values are a function of the elevation of recharge and may further distinguish waters that have experienced significant evaporation prior to recharge. Strontium (Sr) isotope ratios ($^{87}Sr/^{86}Sr$) were examined since they are proven tracers of water–rock interaction along groundwater flow paths, since Sr^{2+} is a divalent cation that readily substitutes for Ca^{2+} in minerals such as calcite, gypsum, and feldspars.

Tritium (^3H), a radioactive isotope of hydrogen with a half-life of 12.3 years, was sampled to evaluate groundwater residence time. ^3H occurs naturally due to interactions between cosmic rays and atmospheric gases, but concentrations were increased in the global atmosphere during nuclear weapons testing in the 1950s and 1960s, peaking in 1963. As such, it is a qualitative tracer of groundwater age, since waters absent tritium reflect pre-1950 recharge age. Because the decrease in atmospheric ^3H has approximately followed the decay curve from 1963 to 2005, it is difficult to use ^3H as an absolute dating tool during this period, but it is very effective at distinguishing pre-bomb (pre-1960s) from post-bomb recharge, and can be used for absolute dating for water that recharge since 2005.

Sulfur hexafluoride (SF_6), a relatively inert gas that is widely used in industrial processes, was also used to investigate groundwater age. Since about 1970, the atmospheric mixing ratio of SF_6 has been increasing by about 7% each year with its current value (2014) being 8.2 pptv. This monotonic increase in the atmospheric mixing ratio results in a unique SF_6 concentration in groundwater recharge each year and hence its application in groundwater dating (Busenberg and Plummer, 2000). The dissolved concentrations of SF_6 in groundwater were converted to atmospheric mixing ratios using Henry's law and compared to observed atmospheric mixing ratios to provide an estimate of year in which the water was last in contact with the atmosphere (Busenberg and Plummer, 2000). Measurements of Ne in selected samples indicated only a modest amount of excess air, which can form during transient recharge events (water table rise), and is a concern since air bubbles that become entrapped below the water table will drive dissolution of atmospheric gases and modify the SF_6 age (Heaton and Vogel, 1981; Aeschbach-Hertig and Solomon, 2013). Terrigenic SF_6 contributions were assumed negligible in these sandstone-dominated strata; however they are produced in fluorite-rich terranes (Harnisch and Eisenhauer, 1998), and terranes having volcanic activity and igneous intrusions (Busenberg and Plummer, 2000; Goody et al., 2006; Koh et al., 2007; Darling et al., 2012; Friedrich et al., 2013).

To aid the evaluation of potential water quality impacts from mining, processing, and disposal activities, selected springs were sampled for diesel range organics (DROs) and gas range organics (GROs) potentially emanating from natural tar. Batch equilibration studies between collected tar-rich sandstone samples and pure water (Milli-Q) were performed in order to determine concentrations of DRO/GRO in water equilibrated with tar sand.

2.2. Sampling

Springs were sampled during several field campaigns over the period spanning July 2013 to December 2014. The locations of sampled springs are provided in Fig. 1. Two focus areas were examined: Main Canyon adjacent to the permitted tar sand development site; and a set of springs/wells on the Book Cliffs side of the plateau rim, in order to determine similarities and contrasts between these two areas (Fig. 1). PR Spring (PR-S in Fig. 1), is a landmark on regional maps, and serves as the name of the general area of USOS proposed tar sand development. PR-S emits via pipe from a cistern built into the adjacent hillside, from which flow is driven by gravity upon release of a valve at the pipe exit. In contrast, all other springs emitted from continuously flowing pipes that long ago had been driven into adjacent hillsides (MC-C, East-A), or as natural flowing pools (MC-B & MC-D, East-B, WW) or flows directly from rock strata into small pools (MC-A, East-C). Several feet lateral to the discharge of MC-C, a 4-inch diameter screened PVC well was installed to a depth of 0.6 m in the alluvium (MC-C-alluvium), and was sampled using a peristaltic pump. USOS Well 4 and the Elmgreen wells were drilled ~670 m and ~24 m into the subsurface, respectively. PR-S flows at a high rate (>5 gpm) with no detected depletion of available water volume in the cistern over hour-long flow periods, indicating rapid refill of the cistern via groundwater seepage. Likewise, the two sampled wells discharged water at high rates in response to turning on the dedicated well pump (estimated to be hundreds of gpm) with no detected decrease in flow over hour-long sampling periods.

During sampling, the springs and wells were characterized in the field for temperature, conductivity, dissolved oxygen (DO) and pH using a multi-parameter water-quality probe (YSI Inc.). Measurements were performed by placing the field probe in either: 1) the flowing natural pool where the spring emits (MC-B & MC-D, East-B, WW); 2) In an over-flowing 1-L Nalgene reservoir filled from: a) the discharging pipe (PR-S, MC-C, East-A, USOS Well 4, Elmgreen); or b) Teflon tubing driven via peristaltic geopump (MC-A, East-C, MC-C-alluvium). All parameters were recorded after stabilization to constant values. Alkalinity was measured in filtered samples (0.45 μm) in the field using a portable titration kit (Hach Analytics).

Samples for major ion analysis were filtered (0.45 μm) in the field, collected in 100 mL HDPE bottles without headspace, and refrigerated until analysis. Samples for stable isotopes of hydrogen and oxygen were filtered to 0.25 μm and collected in 4 mL glass vials with minimal/no headspace. The vials were capped and double- sealed with parafilm and refrigerated until analysis. Samples for strontium and other ICP-MS analytes were filtered (0.25 μm) into a 100 mL acid-washed bottles preserved with 2.4% nitric acid. Sample used for ^3H analysis were collected in 1-L Nalgene bottles with minimal/no head space. SF_6 samples were collected in duplicate 1-L amber bottles filled using a copper tube in the bottle bottom to minimize atmospheric contact and allowed to overflow for at least two bottle volumes before closing with a polyseal cone lined cap, that was further sealed with electrical tape. Samples for excess air (Ne analysis) were collected at selected sites by drawing sample through copper tubes (using a peristaltic pump) ensuring removal of air bubbles. The copper tubes were sealed with pinch clamps that were subsequently enclosed in plastic caps filled with sample. DRO/GRO samples were collected in triplicate 40 mL glass vials containing a preservative (Chemtech-Ford Laboratories, Sandy, Utah), sealed with a teflon-lined cap and stored in ice-packed coolers in the field and in transport. Replicate 150 g of crushed (1 cm) tar-rich rock samples were equilibrated (seven days) with Milli-Q (350 mL) under ambient laboratory conditions. The supernatant was then collected and analyzed as described below.

A continuous record of temperature and conductance was obtained at spring MC-C to allow identification of potential excursions from baseline (or lack thereof). This record allows comparison to surface temperature variations and to precipitation events to infer the degree of insulation of the groundwater from surface influences, and ultimately the average depth of the groundwater flow path to that spring (as described in the Discussion section). For this purpose, a probe for continuous (15 minute interval) collection of water temperature and conductivity (Aqua TROLL 200, In-Situ Inc.) was deployed at the pipe exit of MC-C for nearly one year. An accompanying probe for air temperature and atmospheric pressure (BaroTROLL, In-Situ Inc.) was deployed in a nearby barn for the same time period. Both probes were calibrated prior to deployment, and during each data retrieval. Monthly precipitation data was retrieved from a remote automated weather station (RAWS) located in upper PR Canyon 3.5 miles northeast of the USOS mine site at an elevation of 2500 m (Western Regional Climate Center, 2013). Snow depth and snowfall was retrieved from the East Willow Creek Utah SNOTEL Site located 14 miles southwest of the USOS mine site at an elevation of 2531 m, thereby allowing differentiation of rainfall and snowfall events.

2.3. Analysis

Major anion samples were analyzed within two weeks of collection by ion chromatography (883 Basis IC plus, Metrohm). Deuterium (^2H) and oxygen (^{18}O) isotopes were analyzed using cavity ring-down spectrometer (Picarro L-2130i) at the University of Utah SPATIAL laboratory. Data are reported in delta notation ($\delta = R_{sample}/R_{standard} - 1$, where $R = [^2H]/[^1H]$ or $[^{18}O]/[^{16}O]$) relative to the VSMOW standard. Instrument operation, calibration, and data reduction protocols were reported in Good et al. (2014). External precision for the analyses, estimated based on the between-run standard deviation of a quality-control water, was 0.40‰ for $\delta^{18}H$ and 0.06‰ for δ^2O.

Sr concentration and isotope analysis was performed at the ICP-MS Laboratory at the Department of Geology & Geophysics, University of Utah. Strontium concentrations were measured using an Agilent 7500ce quadrupole inductively coupled plasma mass spectrometer (ICPMS). The limit of detection was 0.04 parts per billion (ppb). Standard Reference Material 1643e (Trace Elements in Water, National Institute of Standards and Technology, USA) was used to assess the accuracy of the method. SRM 1643 was run together with samples and the value obtained differed by 1.4% from the certified value. For the Sr concentration, the estimated maximum laboratory uncertainty is 5%. The isotopic analysis of strontium was performed using a Thermo Neptune multi-collector ICP-MS with an in-line strontium purification method (Brennan et al., 2014). SRM 987 (Strontium carbonate, National Institute of Standards and Technology, USA) was run together with samples and the measured average value was 0.71029 ± 0.00001 (1 s, N = 8).

Tritium (^3H) analyses were performed at the University of Utah Dissolved Gas Laboratory using a Helix SFT sector-field mass spectrometer in accord with the helium ingrowth method (Clarke et al., 1976). The detection limit for this method at the University of Utah is about 0.05 TU with typical uncertainties of about 3%.

SF_6 analysis was performed at the University of Utah Dissolved Gas Laboratory using a custom purge and trap gas chromatographic system (Shimadzu GC8A electron-capture detector) similar to that described by Busenberg and Plummer (2000). Calibration was performed using a 150 parts per trillion (ppt) SF_6 standard. Determination of recharge age requires an estimate of recharge elevation, which fortunately is not a sensitive parameter; i.e., an error of 300 m in recharge elevation yields an error of about 0.5 year in the SF_6 recharge age, with overestimation of the recharge elevation resulting in a younger apparent age (Busenberg and Plummer, 2000). The detection limit of SF_6 is 0.01 femtomole (fmol)/L in water. Neon was measured using a quadrupole mass spectrometer after cryogenic separation from other gases at a precision of about ±2%.

3. Results

Whereas the currently-permitted tar sand mining, processing, disposal site lies adjacent to Main Canyon on the north side of the plateau rim, we also examine results for springs on the southern side of the plateau rim (Book Cliffs) to serve as a contrast, as well as a baseline, since future development will potentially encompass the plateau rim.

3.1. Field parameters (dissolved oxygen, pH, temperature, conductance) and major ions

The water temperatures of the springs ranged from approximately 4 to 16 °C (Fig. 2a), whereas the temperature of MC-C-alluvium was significantly outside the observed range for the Main Canyon springs. The temperature of USOS Well 4 was 27 °C, which was likely influenced by kinetic energy imparted by the high capacity pump installed in the well, and so it is not shown. The trend of groundwater temperature as a function of elevation (Fig. 2a) generally matched the expected relationship between elevation and mean annual ground surface temperature for Central Utah (black line) (Powell et al., 1988), for both Main Canyon and Book Cliffs springs/wells (excepting USOS Well 4).

Specific electrical conductance increased with decreasing elevation for both Main Canyon and Book Cliffs springs (Fig. 2b). Values ranged from approximately 700 to 2600 (μS/cm). While the precise relationship between conductance and salinity or total dissolved solids (TDS) depends on ion valence, a rough generalization is that TDS (in mg/L) is approximately 64% of specific conductance (μS/cm) (Atekwana et al., 2004). Hence, based on specific conductance, the waters range from approximately 470 to 1740 mg/L TDS, which spans the range from freshwater to slightly brackish, the latter corresponding to MC-C-alluvium, USOS Well 4, EC-A, EC-B, WW, and Elmgreen. For a given elevation, the specific conductance values were generally higher for the Book Cliffs sites relative to the Main Canyon sites, possibly reflecting differences in lithologic units and aridity among the two areas. Dissolved oxygen (DO) (temperature compensated) generally decreased with decreasing spring elevation, although the relationship showed significant variability (Fig. 2c). For pH as a function of elevation, two opposing weak trends were observed for Book Cliffs versus Main Canyon (Fig. 2d). Notably, USOS Well 4 shows a much higher pH relative to springs/wells in Main Canyon and the Book Cliffs. Alkalinity increased

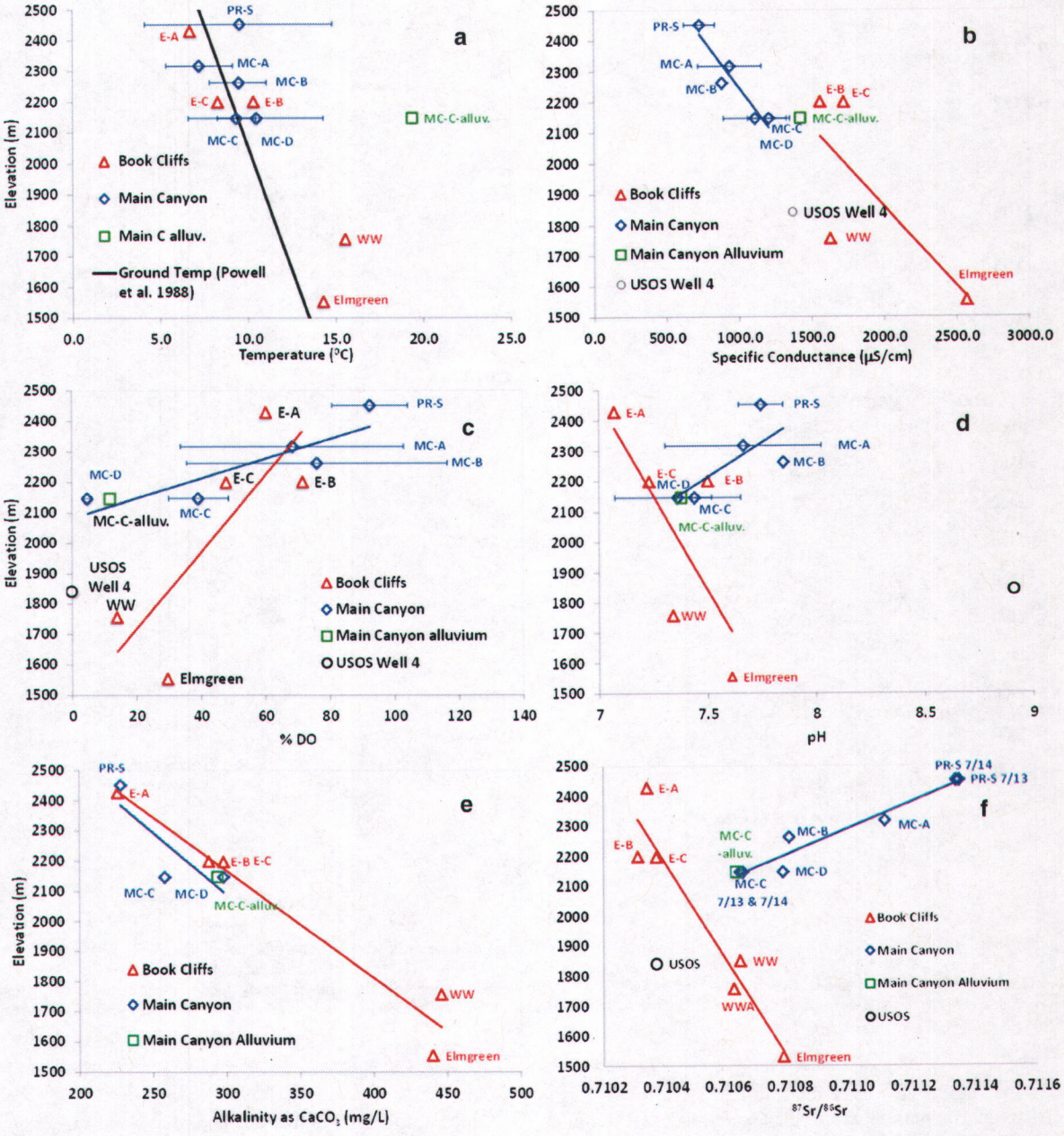

Fig. 2. The relationship between elevation and temperature (a), specific conductance (b), dissolved oxygen (DO) (c), pH (d), alkalinity (e), and $^{87/86}Sr$ (f) for springs and wells in Main Canyon and the Book Cliffs areas. Error bars represent standard deviations around mean values for replicate measurements over the year-long study (where available). The black line in (a) represents ground surface annual mean temperature as a function of elevation (Powell et al., 1988). Red and blue trend lines are fit to Book Cliffs and Main Canyon data, respectively. Alkalinity was not measured at USOS Well 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with decreased spring/well elevation, with equivalent trends for the Main Canyon and Book Cliffs areas (Fig. 2e).

3.2. Sr isotopes

Sr concentration and $^{87}Sr/^{86}Sr$ isotopes ratios showed distinct trends as a function of elevation for Main Canyon and Book Cliffs springs/wells that were also distinct from USOS Well 4 (Fig. 2f). Notably, $^{87}Sr/^{86}Sr$ was inversely correlated to Sr concentration in both Main Canyon and the Book Cliffs, yielding opposing trends between Main Canyon and the Book Cliffs for both Sr concentration and $^{87}Sr/^{86}Sr$ (Supporting Information SI-4). Plotting $^{87}Sr/^{86}Sr$ as a function of inverse strontium concentration (1/Sr) yielded nearly equivalent trends among the Main Canyon and Book Cliffs springs, that again were distinct from the value at USOS Well 4 (Fig. 3a). However, the elevation trends between the two series remained opposed, with the highest elevation springs having the highest versus lowest $^{87}Sr/^{86}Sr$ (and 1/Sr) values in Main Canyon versus the Book Cliffs, respectively.

3.3. Oxygen-deuterium values

Sample δ^2H and $\delta^{18}O$ values span a range of ~10‰ and 1.8‰, respectively (Fig. 3b). Values for the Main Canyon samples span a relatively narrow range of values, with four of the six sites clustering within 2‰ (δ^2H) and 0.3‰ ($\delta^{18}O$) of each other. MC-B exhibits the highest and most variable values in Main Canyon, and MC-C has δ^2H values similar to, but $\delta^{18}O$ values about 0.4‰ higher than, the main cluster of MC samples. In contrast, samples from the Book Cliffs springs spanned the

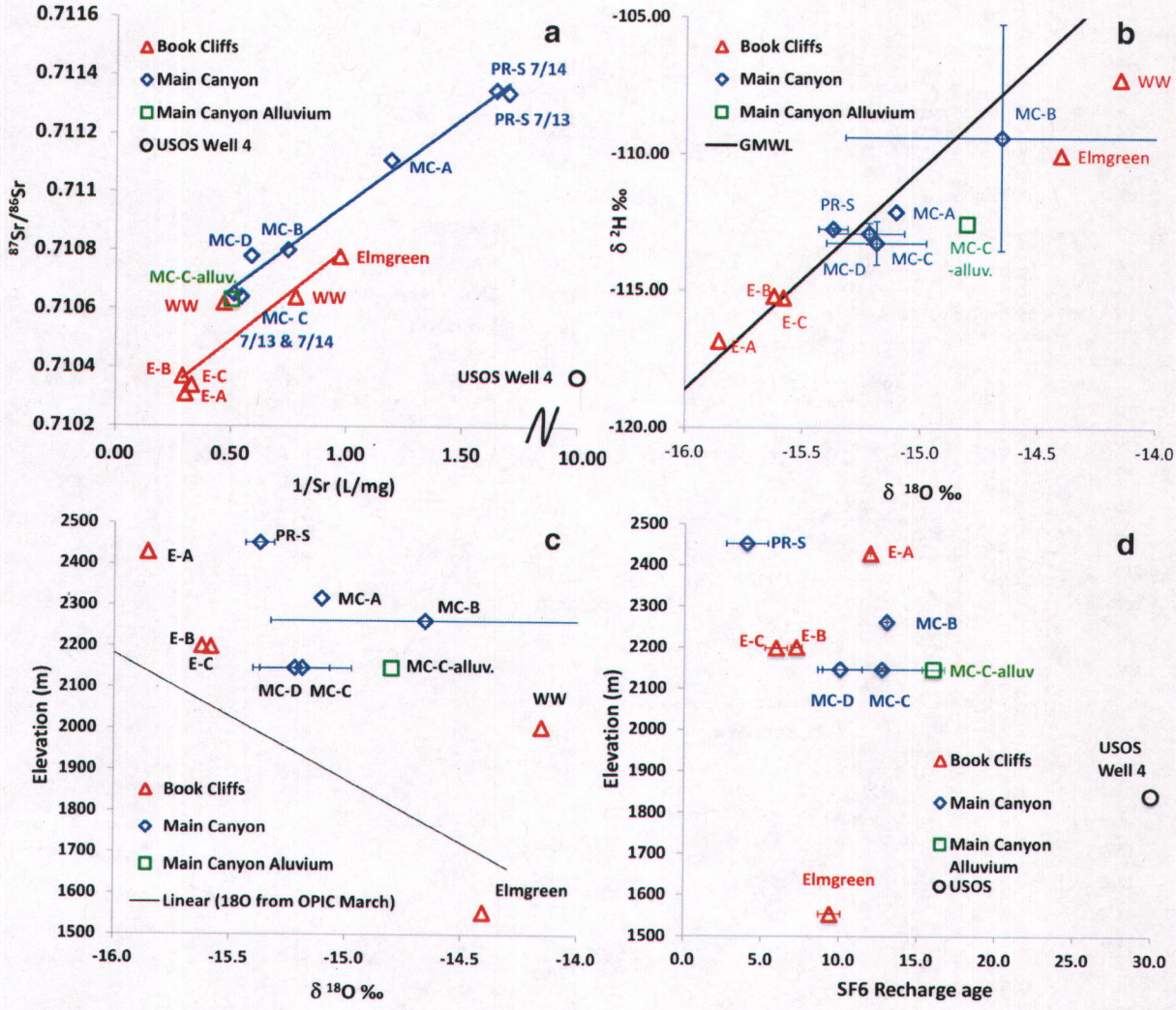

Fig. 3. Relationships between: (a) $^{87}Sr/^{86}Sr$ versus inverse Sr concentration, (b) δ^2H vs. $\delta^{18}O$ with global meteoric waterline (GMWL) shown in black, (c) $\delta^{18}O$ values as a function of elevation with black trend line for estimated ^{18}O as a function of elevation as calculated using the Online Isotopes in Precipitation Calculator (OPIC) (Bowen, 2014), (d) SF_6 recharge ages as a function of elevation. Error bars represent standard deviations around mean values for replicate measurements over the year-long study (where available). Red and blue trend lines in (a) are fit to Book Cliffs and Main Canyon data, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

full range of observed stable isotope values. The majority of the samples cluster along the Local Meteoric Water Line (LMWL, $\delta^2H = 7.6 \times \delta^{18}O + 3.9$) determined from annual precipitation estimates at the sampling sites using the Online Isotopes in Precipitation Calculator (OIPC; Bowen et al., 2005; Bowen, 2014), a spatial precipitation isotope model that assimilates global monitoring data. The LMWL which reflects the approximate expected relationship between δ^2H and $\delta^{18}O$ values for precipitation-derived waters that have not been subjected to appreciable evaporation. Samples from MC-C-alluvium, MC-B, and the two lower Book Cliffs samples (Elmgreen well and Westwater stream) are well below the LMWL, suggesting some evaporative loss from these samples. Notably, Elmgreen well lies in the floodplain of Westwater stream (approximately 500 m from the stream) and is expected to include flow contribution from the stream.

Water isotope ratios of continental precipitation typically decrease with elevation, and predicted regional precipitation values from the OPIC suggest a $\delta^{18}O$ range of >2‰ for local precipitation across the elevation range of the samples collected here (Fig. 3c). Samples from the Book Cliffs sites parallel the predicted precipitation trend. In contrast, the Main Canyon samples exhibit a weak elevation trend, supported only by the data from the MC-C-alluvium sample and one of the three replicates from MC-B.

3.4. Groundwater dating

Concentrations of sulfur hexafluoride (SF_6) range from 2.8 to 0.2 femtomole/L and these correspond to apparent ages (transit times) of near 0 to more than 30 years (Fig. 3d). These apparent ages were computed using modest (0 to 1 ccSTP/kg) excess air as confirmed by several measurements of dissolved Ne (data not shown). Neon is typically used to evaluate excess air as its solubility in water is not very sensitive to temperature and there is no significant subsurface source (Aeschbach-Hertig and Solomon, 2013). The lowest value of 0.2 femtomole/L is from USOS Well 4 and is very near the analytical detection limit. We interpret this sample as having a transit time that is older than 30 years, consistent with the ^3H measurement.

The tritium (^3H) values for all springs and wells sampled are consistent with post-1960s recharge except for USOS Well 4 (Fig. 4). USOS Well 4 has a tritium value that was significantly lower than the others and near the detection limit, indicating that recharge of USOS Well 4 groundwater occurred prior to the 1950s. The ^3H results in Main Canyon show a significant correlation of decreasing concentration with decreasing elevation (Fig. 4). This trend may reflect groundwater transit times that increase as water moves from recharge areas beneath the ridge tops to discharge points progressively deeper in the system. The

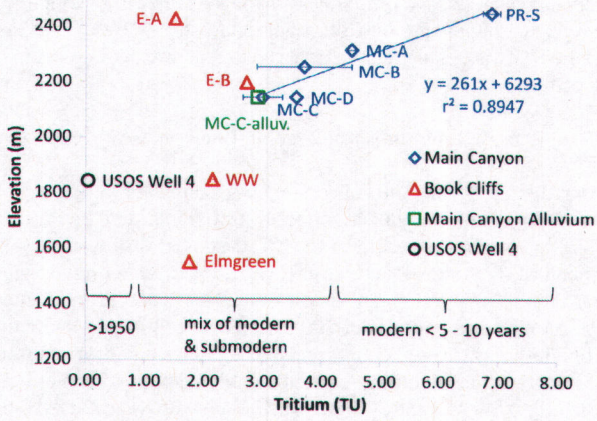

Fig. 4. ^{3}H prevalences as tritium units (TU). Error bars represent standard deviations around mean values for replicate measurements over the year-long study (where available). The apparent age (transit time) was computed using the radioactive decay equation with the assumption that the tritium value in precipitation returned to the pre-bomb natural value of about 7 TU near the start of the 21st century (Morgenstern et al., 2010; Thatcher, 1962). Blue trend line is fit to Main Canyon data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

apparent age (transit time) of the Main Canyon springs can be computed using the radioactive decay equation with the assumption that the tritium value in precipitation returned to the pre-bomb natural value of about 7 TU near the start of the 21st century (Morgenstern et al., 2010; Thatcher, 1962). Apparent ages for the Main Canyon springs ranged from <1 year for the highest elevation samples to 15 years for the lowest elevation sample. Samples from the Book Cliffs had tritium values ranging from 2.9 to 1.5 TU and did not correlate with elevation. The results from Book Cliffs are consistent with these samples representing mixtures of old (pre-bomb) and modern water. The absolute age of these samples cannot be computed using tritium alone because they recharged during a period of time when the value in precipitation was decreasing at approximately the same rate as radioactive decay. Apparent ages from ^{3}H are generally similar to those from SF_6, with values from Main Canyon correlated with elevation.

3.5. Continuous record of temperature & conductance at MC-C

The water temperature in MC-C was relatively stable over the nearly year-long period from October 2013 through September 2014, with minimum and maximum water temperatures of 6.8 °C and 11.0 °C, respectively (Figure SI-3a), yielding an amplitude of 2.1 °C for MC-C water temperature over the year of study. Diurnal air temperature fluctuations during this period were typically greater than 5 to 10 °C, with a minimum and maximum average daily air temperatures over the year of −5 °C and 20 °C, respectively, yielding an annual amplitude of 12.5 °C for the average daily air temperature at MC-C over the study period. From November 2013 through May 2014, the conductance record at MC-C was near 1050 μS/cm (Figure SI-3b). This steady conductance persisted regardless of precipitation events; however, the precipitation events were mainly snow. From May through August 2014 there was a sustained increase with significant variability in conductance that reached a maximum value of 1300 μS/cm in August. The initiation of this steady increase may correspond to infiltration of surface-equilibrated snowmelt during ground thaw. The variability of the conductance in summer may reflect the influence of precipitation events.

3.6. DRO/GRO analyses

All field samples showed non-detection for both DROs and GROs, with reporting limits of 0.24 mg/L (GROs) and 5.0 mg/L (DROs). The tar sand-equilibrated water samples (batch samples) yielded non-detect for GROs, and 9.0 mg/L DROs.

4. Discussion

4.1. Significance of measured groundwater ages

With respect to the possibility that the springs represent a regional aquifer recharged at distant mountains (as postulated by expert testimony), the ^{2}H and SF_6 ages (Figs. 3d and 4) are too young (at most two-to-three decades) to represent what are reasonably expected to be many-decade to centuries transport times required for groundwater to travel from the Uinta Mountains to Main Canyon (~160 km). The increase in conductance observed at MC-C in spring, presumably in response to infiltration of snowmelt and precipitation, also could not be propagated from the Uinta Mountains in the time frame of weeks as observed in the data. The measured ages require that the recharge occurs locally, as originally concluded by early hydrologic assessments of the area (Price and Miller, 1975; Byrd, 1970). It should be noted that USOS Well 4 showed distinct hydrogeochemistry relative to both Main Canyon and the Book Cliffs for pH (Fig. 2d), Sr concentration, $^{87}Sr/^{86}Sr$ ratios, (Figs. 2f & 3a), SF_6 age (Fig. 3d), and ^{3}H age (Fig. 4). These distinctions, along with the fact that the bottom of USOS Well 4 is 500 m deeper than the lowest springs measured in Main Canyon, as well as the distinct geographic unit of USOS Well 4 relative to the Book Cliffs, all strongly indicate that USOS Well 4 reflects an aquifer system that is distinct from groundwater in the Main Canyon and Book Cliffs areas studied here.

4.2. Significance of observed temperatures

The indicated local nature of recharge to the springs raises the issue of whether they are recharged via infiltration of snowmelt and precipitation across a landscape that includes the adjacent ridges, or whether recharge is restricted to infiltration of snowmelt and precipitation solely onto the alluvial surface (Figure SI-1). The depth of the groundwater flow path leading to discharge at MC-C can be inferred from the continuous temperature record (Figure SI-3) based on the fact that the ground surface temperature amplitude produces a corresponding (albeit phase-lagged) temperature response at depth, that decays as a function of depth, as detailed in the Supporting Information. The amplitude of the annual temperature variation at MC-C (2.1 °C), relative to that at the ground surface (12.5 °C), indicates an average depth of ~6 m for the groundwater flow path that discharges at MC-C. It should be noted that this is the minimum depth of the flow path, because it is not known how much of the temperature variation in MC-C is amplified by ambient temperature and sunlight heating effects on spring water as it transits the discharge pipe. Only a small fraction of the pipe cross-sectional area is filled with flowing water (<20%) yielding significant water to pipe contact during its approximately 30-m transport distance. Subtraction of an assumed 1 °C enhancement of the amplitude from ambient temperature and sunlight effects yields an average flow path depth of 7.6 m. Subtracting two degrees yields a 15-m average depth of flow path. Hence, the analysis demonstrates that the flow path depth is significant, but since the depth of the alluvium is not precisely known, this finding alone does not rule out the possibility that flow paths occur solely through the alluvium.

4.3. The volume of alluvium

The volume of the alluvial fill can be roughly calculated by assuming that the cross-sectional shape of the alluvial fill in the subsurface is approximated by an isosceles right triangle, consistent with the typical shape of a stream cut canyon. This yields the assumption that the depth of the alluvium is about 1/2 the width of the alluvial fill across the canyon. As detailed in the Supporting Information, the approximate

0.4 km^2 (100 acres) area of the alluvial surface, combined with an average plan-view width of the alluvium equal to approximately 120 m (400 ft), yields a maximum depth in the alluvium of approximately 60 m (200 ft). The volume of water that can be held in the alluvium is 7.3E6 m^3 (6000 acre-feet), assuming a sediment porosity of 0.3. Assuming that 20% of snow and rain fall infiltrates into the subsurface (McMahon et al., 2011), the residence time of water in the alluvium that would result from recharge directly to its surface ranges from 180 to 440 years for the observed range of precipitation rates, 50 and 20 cm/year, respectively. Since the shortest estimated residence time (highest precipitation rate) is approximately ten times greater than the measured ages of water in the springs (<20 years) (Figs. 3d and 4), the analysis argues against the possibility that the springs represent recharge solely to the surface of the alluvium, and indicates that the springs represent recharge at both the alluvium surface and the surrounding ridges.

4.4. Significance of observed progressions with elevation

The possibility that spring waters in Main Canyon reflect recharge to the adjacent ridges is also strongly supported by the observed progression in several hydrogeochemical parameters as a function of elevation including: 1) specific conductance (Fig. 2b); 2) alkalinity (Fig. 2e); 3) Sr concentration and $^{87}Sr/^{86}Sr$ ratio (Figs. 2f & 3a); 4) ^{18}O and ^{2}H (Fig. 3b & c); 5) ^{3}H concentration (Fig. 4). Notably, PR-S and MC-A contribute to trends in the above parameters as a function of elevation despite having elevations higher than the alluvial fill. This indicates that the recharge zones to the springs extend above the alluvial fill onto the surrounding ridges. Furthermore, from a water budget perspective, the limited areal extent of the alluvium in Main Canyon relative to the large areal extent of the surrounding ridges (Figure SI-1) suggests that snowmelt and precipitation (in excess of evapotranspiration) on the non-alluvial (higher elevation) surface should contribute to recharge in the canyon springs. The progressions of hydrogeochemical parameters with elevation in Main Canyon, and the relative areas of alluvial and non-alluvial surface in Main Canyon, indicate that recharge driving the springs in Main Canyon is derived from both the surrounding ridges and the alluvial surface.

Notably, the trends of $\delta^{18}O$ versus elevation and ^{3}H ages versus elevation differ between Main Canyon and the Book Cliffs, with ^{3}H in the Book Cliffs lacking a progression with elevation (Fig. 3c), and Main Canyon showing increasing age with decreasing elevation (Fig. 4). In contrast, $\delta^{18}O$, which should be a largely conservative tracer of recharge source water isotope ratio, declines with elevation in the Book Cliffs, but not in Main Canyon (Fig. 3c). The $\delta^{18}O$ versus elevation trend for the Book Cliffs springs is similar to the OPIC trend, which explicitly accounts for elevation-driven trends in estimated precipitation isotope ratios (Bowen et al., 2005), and suggests that the Book Cliffs capture progressively lower-elevation recharge at progressively lower elevation springs. The lowest elevation Book Cliff springs also exhibit isotopic evidence for evaporation during recharge or discharge, which may in part account for their higher isotope ratios. Although it is possible that these waters could have been derived from higher-elevation recharge and subsequently subject to evaporation, estimation of the un-evaporated source water compositions assuming a typical soil-water evaporation line slope (2.5) to back-project to the LMWL suggests recharge $\delta^{18}O$ values 0.3 to 1.0‰ higher than observed for the other samples, consistent with somewhat lower-elevation recharge. The similar $\delta^{18}O$ values regardless of spring elevation for Main Canyon (Fig. 3c) suggest that these waters were predominantly recharged at the same elevation, i.e., the top of the system (the ridgetops). These findings are consistent with the fact that the Book Cliffs are a major south-east facing topographic feature that can be expected to exert topographic influence on isotopic fractionation of precipitation (Fig. 1), and for which the sampled springs/wells aggregate multiple drainages over a large area. In contrast, Main Canyon is narrowly incised into the rim of the plateau, yielding a recharge zone primarily at the highest elevation (ridge top) from which groundwater flow propagates downward (Figs. 1 and SI-1) and for which the sampled springs reflect different distances along similar flow paths.

4.5. Significance of contrasting results at MC-C-alluvial well

That the springs in Main Canyon reflect groundwater recharge from both the ridges and the alluvial surface is further indicated by contrasting hydrogeochemical results at the MC-C-alluvial well relative to its neighbor MC-C, as shown for $\delta^{18}O$-$\delta^{2}H$ (Fig. 3b & c), water temperature (Fig. 2a), and DO (Fig. 2c). These results likely reflect capture of lower elevation recharge (e.g., direct infiltration of precipitation/snowmelt on alluvium), warming, and associated evaporative alteration and microbial respiration during residence in the alluvium. Furthermore, the slightly greater ^{3}H and SF_6 ages of MC-C-alluvium (Figs. 3d & 4) suggest that the alluvial water includes groundwater flowpaths through the surrounding ridges in addition to flow in the alluvium. Notably, MC-B also showed evidence of evaporation, as well as variable $\delta^{18}O/\delta^{2}H$ (Fig. 3b & c), and variable ^{3}H results (Fig. 4), consistent with the water at MC-B representing variable contributions of alluvial and ridge block ground waters, the predominance of which varied with season, as is reasonably expected based on its location in a channel in the alluvium.

4.6. Significance to potential impacts on springs

Concerns for impacts to springs in adjacent canyons from mining, processing, and disposal activities on the ridgetops are potentially mitigated by a lack of apparent groundwater (reported by drillers) in hundreds of boreholes (6.4 cm diameter) that were drilled in the areas of the permitted site, ranging in depth from 43 to 79 m (Allen, 2012). However, it should be noted that the maximum depth of 143 documented bore holes (~93 m) (US Oil Sands Inc., 2011) corresponds to an elevation that is higher than all but one of the perennial springs in adjacent canyons (Fig. 5). Hence, the apparent lack of groundwater in the 143 documented bore holes likely reflects the zone of downward transport into the ridge (the unsaturated zone) (US Oil Sands Inc., 2011), and does not indicate the absence of a groundwater system recharged at the ridgetops.

The apparent hydrologic connection between the ridgetops and the springs in adjacent canyons, as suggested by the hydrogeochemical data, indicates that further evaluation is warranted of potential impacts

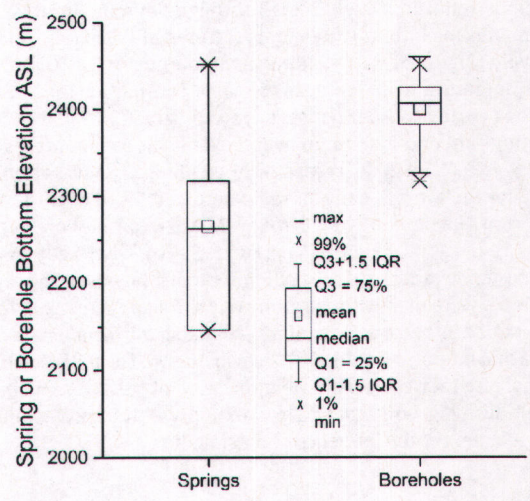

Fig. 5. Bottom elevations of the ^{18}O USOS-drilled boreholes relative to the elevations of the 5 perennial springs in adjacent canyons (PR and Main Canyons). IQR = interquartile range = Q3–Q1.

from ridgetop mining, processing, and disposal activities on groundwater availability and quality in adjacent Main Canyon. Evaluation of potential water availability impacts might entail hydrogeologic investigation of recharge rates at the ridgetops, as well as monitoring of flows in springs in adjacent canyons, which is beyond the scope of this paper. Assessment of potential water quality impacts might include the fate and transport of bitumen compounds, as we examine briefly below.

Detectable GRO and DRO concentrations in the sampled springs would potentially indicate that water recharged at the ridgetops equilibrated (at least partially) with bitumen-bearing units during downward transport. Notably, DRO and GRO concentrations in sampled spring waters were below detection. This observation does not; however, disprove that recharge occurred at the ridgetops, since sorption and dispersion of these highly hydrophobic compounds during transport between tar-rich strata and the springs will potentially reduce the GRO concentrations below detection (e.g. Johnson and Amy, 1995). For example, 1:1 batch equilibration of pure water (Milli-Q, 150 mL) with tar-rich (via visual inspection) rock samples (150 g) from the site showed detectable DRO concentrations in duplicate samples (9.0 and 9.9 mg/L), that would likely be driven below the reporting limit (5.0 mg/L) by sorption and dilution during transport over km-scale distances (e.g., Johnson and Amy, 1995). The absence of DRO in the spring waters despite likely equilibration with bitumen-bearing units during downward transport from the ridgetop suggests that sorption and dilution during transport to the springs may be sufficient to remove dissolved bitumen compounds that will potentially emanate from disposed tailings. However, an important water quality concern is the potential influence of the extraction solvent (D-limonene, a small non-polar terpene) in facilitating the transfer of tar compounds to water.

Bitumen compounds in ambient tar sands have low solubility in water; whereas, when they exist in a mixture with D-limonene, their solubility in water may be enhanced by two potential mechanisms: 1) the much greater solubility in water of D-limonene (13.8 mg/L at 25 °C, Massaldi and King, 1973) relative to bitumen compounds (μg/L range at 25 °C, Schwarzenbach et al., 1993) enhances the water solubility of bitumen compounds via partitioning to dissolved D-limonene in water, 2) because D-limonene ($T_{melt} = -75$ °C, USEPA, 1998) is liquid at ambient temperature, residual bitumen compounds that would normally be solid phase at ambient temperature (T_{melt} > ambient) exist in the sub-cooled liquid state when dissolved in D-limonene, thereby increasing their solubility in water since this solubility is higher for the liquid relative to the solid phase; an exception to point (2) above occurs, for example, at tar seeps, where sufficient content of liquid phase petroleum compounds exist to allow the ambient tar to exist as a liquid.

The enhanced concentration of an organic compound in water in the presence (C^*_w) versus the absence of D-limonene (C_w) can be determined using multiple methods to reflect the above two mechanisms. This simplest method considers the impact of dissolved D-limonene in water solely as a co-solvent that produces enhanced concentration (C^*_w) relative to normal concentration (C_w) of the bitumen compounds in water, reflecting only mechanism (1) of the above-described influences of D-limonene. The enhanced transfer to water by this mechanism occurs as a function of the concentration of dissolved D-limonene in water (C^{DL}_w) and the distribution constant for the bitumen compound between water and D-limonene (K_{DL}) (Schwarzenbach et al., 1993):

$$C^*_w = C^{sat}_w\left(1 + K^{B(a)P}_{DL} C^{dl}_w\right). \tag{1}$$

The enhanced solubility effect is demonstrated here with the arbitrary (but reasonable) assumption that benzo(a)pyrene (B(a)P) is a representative bitumen compound, and scenario where the concentration of D-limonene in water is approximately half its normal solubility of 13.8 mg/L (Massaldi and King, 1973; USEPA, 1998). The value of $K^{B(a)P}{}_{DL}$ is well approximated by the equilibrium partition constant for B(a)P between water and octanol ($K^{B(a)P}{}_{ow}$), where octanol is an alcohol that is commonly used as a surrogate organic solvent for many environmental contaminants (Schwarzenbach et al., 1993), and the value of which is $10^{6.5}$ (Schwarzenbach et al., 1993). Substituting these values yields and converting units yields:

$$\frac{C^*_w}{C^{sat}_w} = \left(1 + \left(\frac{10^{6.5}\ \mathrm{mL}_w}{\mathrm{mL}_{DL}}\right)\left(\frac{6.9\ \mathrm{mg}_{DL}}{\mathrm{L}_w}\right)\left(\frac{\mathrm{L}_w}{10^3\ \mathrm{mL}_w}\right)\left(\frac{\mathrm{mL}_{DL}}{0.84\ \mathrm{g}_{DL}}\right)\left(\frac{1\ \mathrm{g}_{DL}}{10^3\ \mathrm{mg}_{DL}}\right)\right) = 26 \tag{2}$$

where the density of liquid D-limonene is 0.84 (USEPA, 1998). The enhanced solubility of B(a)P resulting from D-limonene in water is predicted by this method to be 26 times greater than the normal water solubility of B(a)P. In reality, the concentration of D-limonene expected in water is impacted by its mole fraction in the residual bitumen–solvent mixture, and concentration of B(a)P in water is impacted by the phase change from semi-solid B(a)P in the ambient tar to sub-cooled liquid B(a)P in the bitumen–solvent residual. A more comprehensive estimation method recognizing these impacts is given by (derivation is provided in the Supporting Information):

$$\frac{C_{w-DL}}{C_w} \approx \left(1 - X^{DL}_{ext}\right)\left(\frac{\gamma_w}{\gamma_{w-DL}}\right)\left(\frac{P^0(L)}{P^0(S)}\right) \tag{3}$$

where $X^{DL}{}_{ext}$ is the mole fraction of D-limonene in the residual bitumen-D-limonene mixture, $P^0(L)$ and $P^0(s)$ are the vapor pressures of the pure liquid and solid compound, respectively, and γ_o and γ_w are the activity coefficients of the compound in the organic and water phases, respectively.

The value for the liquid/solid vapor pressure ratio for B(a)P is equal to the ratios of its pure liquid and solid solubilities, which are 1.52 and 49.2 μg/L, respectively (Schwarzenbach et al., 1993):

$$\frac{P^o_{(L)}}{P^o_{(S)}} = \frac{C^{sat}_w(L)}{C^{sat}_w(S)} = \frac{49.2}{1.52} = 32. \tag{4}$$

The value for γ_w, the activity coefficient of B(a)P in water, is estimated from the pure liquid solubility (Schwarzenbach et al., 1993):

$$\gamma_w = \frac{1}{C^{sat}{}_w(\mathrm{L})}\frac{1}{V_w} = \frac{1}{\frac{49.2E{-}6\ \mathrm{g}}{\mathrm{L}}\frac{1\ \mathrm{mol}}{252.3\ \mathrm{g}}}\frac{1\mathrm{mol}}{0.018\ \mathrm{L}} = 10^{8.45} \tag{5}$$

The value for $\gamma_w{}^{DL}$, the activity coefficient for B(a)P in water plus D-limonene, is estimated using a system of water with octanol ($\gamma_w{}^{oct}$). The activity of B(a)P in the water plus octanol) ($\gamma_{w\text{-}DL}$) relative to that in a pure octanol droplet (γ_{oct}) is given by (Schwarzenbach et al., 1993):

$$\frac{\gamma^{DL}_w}{\gamma_{oct}} = K_{ow}\frac{V_{oct}}{V_w} = \frac{10^{6.5}}{2}\frac{0.16}{0.018} = 10^{7.15} \tag{6}$$

where V_{oct} is the molar volume of octanol (0.16 L/mol), V_w (0.018 L/mol) approximates the molar volume of water with dissolved octanol at solubility, and $\gamma_{oct} \sim 2$ rather than unity to reflect the slight incompatibility of the polar alcohol group in octanol with non-polar D-limonene (Schwarzenbach et al., 1993).

Assuming for the sake of similarity to the preceding estimation that D-limonene comprises half of the residual bitumen–solvent mixture, and substituting the values into (1) yields:

$$\frac{C_{w-DL}}{C_w} \approx (0.5)\left(\frac{10^{8.45}}{10^{7.15}}\right)(32) \approx 320 \tag{7}$$

which indicates that D-limonene will enhance the transfer of B(a)A compounds to water by a factor in the range of 300. The two methods used above estimate a large (factors of multiple tens to hundreds) increase in the water solubility of this representative compound as

result of changing its environment from ambient tar to residual bitumen–solvent extract. Similar enhancement of solubility will occur for the other compounds in the bitumen, of which there are hundreds to thousands, to extents depending on their relative compatibilities with water (uniformly low) and D-limonene (uniformly high).

It is notable that recently reported (Gross, 2015) synthetic precipitation leaching protocol (SPLP) tests indicate that DRO concentrations up to 9.2 mg/L were achieved in water (2 L, pH 5) equilibrated with USOS tailings (25 g). At first glance, the generation of 9.2 mg/L of DRO in the SPLP leachate from the tailings appears similar to our above-described result from equilibrating water with ambient tar-rich rock (9.0 to 9.9 mg/L), which seems to indicate that tailing disposal presents no greater potential impact than does the natural tar-bearing rock. However, the water:solid mass ratio in the SPLP test was 80; whereas this ratio was 1 for the tests examining natural tar-bearing rock, which indicates that the propensity of bitumen compounds to dissolve into water from the residual bitumen–solvent mixture was on the order of 80 times greater relative to their propensity to dissolve into water from the ambient tar. This comparison is not precise since the residual content of the disposed tailings (stated as 10 to 20%) was not quantitatively compared to ambient tar content of the rock in our studies (estimated at 20–30% based on visual inspection). Nevertheless, the finding is qualitatively consistent with expectations from chemical thermodynamic estimations, indicating that the SPLP test corroborates our expectation that replacing the ambient tar with residual bitumen–solvent mixture may significantly increase the transfer of bitumen compounds into water (e.g. precipitation and snowmelt) that contacts the disposed residual. This result suggests the need for further investigation of potential water quality impacts to springs that may result from decades of residual disposal on adjacent ridges.

5. Conclusions

The above findings indicate that there is a hydrologic connection between the ridgetops and the springs in adjacent canyons. The spring ages are likely too young to represent water recharged in distal mountains, a possibility that was raised in expert testimony. That local recharge includes contributions from local surrounding ridges (in addition to recharge through the alluvial surface) is supported by multiple independent analyses; including observed groundwater temperatures, which indicate the depth of groundwater flow to the springs is greater (possibly far greater) than 6 m. Ground water contribution from the surrounding ridges is also supported by the fact that recharge solely through the alluvial surface, given the modest precipitation rate, would produce order of magnitude greater measured ages relative to what was observed. The observed progression with elevation of specific conductance, alkalinity, Sr concentration, $^{87}Sr/^{86}Sr$ ratio, $\delta^{18}O$, and ^{3}H concentration also indicate that ground water flow paths to the springs include flow through the ridges. The contrasting hydrogeochemical parameters observed in water specifically collected from the alluvium versus water collected from flowing springs indicate that the perennial springs are not derived solely from alluvial water, and indicate contribution from the surrounding ridges. Chemical thermodynamic estimations indicate enhancement of water concentrations of bitumen compounds by factors of multiple tens to hundreds resulting from replacing the ambient tar environment with residual bitumen–solvent mixture. This expectation is qualitatively corroborated by a recent SPLP leaching test. Both results suggest that the potential for water quality impacts to springs from decades of residual bitumen–solvent disposal on adjacent ridges should be further investigated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2015.05.127. These data include Google map of the most important areas described in this article.

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