Solute sources and water mixing in a flashy mountainous stream (Pahsimeroi River, U.S. Rocky Mountains): Implications on chemical weathering rate and groundwater–surface water interaction

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Identifying solute sources and mixing processes between various water types is challenging in geologically diverse, fractured rock settings, where various minerals contribute to solute loads and mixing between groundwater and surface water can occur at difficult-to-delineate point locations. In such regions, chemical indicators that allow constraining characteristic mineral fingerprints of drainage lithology or aquifer end-members are critical. This study assesses solute sources and water mixing in the Pahsimeroi River, a small stream with highly variable discharge draining two heavily deformed mountain ranges of the U.S. Rocky Mountains. Solute inputs to the main stream were estimated using an end-member mixing model with 87Sr/86Sr and Na/Sr ratios as tracers considering that these depict the compositional variability pertaining to the various carbonate and silicate lithologies of the basin. Our results show that the mean solute input from carbonate-dominated terrains decreases from 54.4% in the headwaters to about 36.4% in the lowlands while the corresponding inputs from volcanic and metapelitic sources increase from 3.63% to 51.0% and 0.45% to 12.6%, respectively. Data further indicate highly variable chemical weathering rates with highest values observed in the steeper uplands. Calculated CO2 consumption rates (mean value: 0.14 Mmol km−2 a−1) are lower than the reported continental average (0.21 Mmol km−2 a−1) possibly due to lower than average streamflow at the time of sampling and significant input of carbonate solute-enriched baselaw in the downstream sections where the basin shallows and decreases in width. The herein delineated gaining stream segments are consistent with those deduced from downstream seepage runs which suggests that groundwater sustains perennial flow in the agriculturally developed lowlands.

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1. Introduction

Assessing the long term reliability of water resources associated with Rocky Mountain streams is important because they comprise sensitive ecosystems and also supply water for hydroelectric power, irrigation and potable usage. Robust information about stream water availability and quality is critical for sustainable management of these resources. In general, the availability of stream water depends upon components specific to the watershed’s water budget; particularly precipitation, evapotranspiration as well as the degree to which streams are discharging to or are fed by local groundwater (baselaw). Stream water quality and ability to provide potable supply or to support wildlife, in turn, depend upon the watershed geology, climate, and land use regime(s) as well as the degree of mixing between surface and groundwater reservoirs. Climate change and increasing water usage since the early to mid-20’s century caused a significant decline in streamflow in watersheds of the western U.S. and the Rocky Mountains in particular (Rood et al., 2005; Luce and Holden, 2009; Luce et al., 2013). Given that continuing decline in future decades is likely, assessments of sustainable limits for water extraction are critical. Such assessments require a detailed understanding of water mixing and solute sources.

Documenting water mixing in streams is challenging given that it can vary seasonally between wet and dry periods, and also spatially depending on local hydrogeologic conditions. For instance, in sedimentary systems where surface runoff as well as diffuse recharge from local groundwater can contribute to streamflow (Winter et al., 1998; Lamb, 2004; Langhoff et al., 2006; Anibas et al., 2011), numerical models relying on extensive climatic and hydrogeological parameters are commonly applied to quantify the contributions of various tributaries and baselaw to streamflow. These methods, however, are subject to uncertainty particularly in crystalline (i.e., fractured) rock settings where mixing can occur at difficult-to-delineate point locations along fractures or fault planes (Winter et al., 1998; Sophocleous, 2002). In
such regimes, hydrochemical surveys can provide valuable information on solute sources and water mixing if reliable source end-members can be established.

Water mixing in streams has been analyzed using various tracers including major ions, trace compounds (e.g., CFCs), stable (O and H) isotopes and radioactive (e.g., $^{14}$C, $^{3}$H, $^{222}$Rn) isotopes (Genereux and Pringle, 1997; Negrel et al., 2003; Negrel and Peteet-Giraud, 2005; McCallum et al., 2010; Cartwright et al., 2011; Guida et al., 2013). However, selecting appropriate tracers for a specific setting is not straightforward, considering that there can be site specific limitations. For example, the applicability of $^{18}$O and D tracers is compromised when various source waters (e.g., surface runoff, baseflow) and stream water display overlapping values because they are derived from the same meteoric water source. $^{222}$Rn values, which have been successfully used to quantify baseflow contributions due to the $^{222}$Rn gradient between groundwater (high values due to prolonged water–rock interactions) and surface water (low values due to shortened water rock-interactions) may be unsuitable in turbulently flowing river segments characterized by significant $^{222}$Rn degassing (Cartwright et al., 2014) or when infiltrating rainwater exhibits $^{222}$Rn concentration similar to river water values (Stellato et al., 2008). There may also be problems when $^{222}$Rn values of local aquifer end-members cannot be reliably constrained, particularly when multiple, mineralogically distinct aquifers contribute to baseflow. In such cases, $^{87}$Sr/$^{86}$Sr ratios can facilitate refined assessments as $^{87}$Sr/$^{86}$Sr values specifically reflect chemical weathering input of Sr-bearing minerals (i.e., carbonates yielding high Sr contents but low $^{87}$Sr/$^{86}$Sr values, K-silicates yielding low Sr contents but high $^{87}$Sr/$^{86}$Sr ratios and Ca/Na plagioclase yielding intermediate Sr contents and low $^{87}$Sr/$^{86}$Sr ratios) (Negrel et al., 1993; Galy et al., 1999; Grosbois et al., 2001; Harrington and Herzeg, 2003; Wu et al., 2009; Hagedorn et al., 2011). Additionally, major ion data – if corrected for atmospheric input and apportioned among appropriate chemical weathering reactions (Galy and France-Lanord, 1999; Spence and Telmer, 2005; Ryu and Jacobson, 2012) – may provide additional constraints on chemical weathering and water solute sources.

This study applies $^{87}$Sr/$^{86}$Sr ratios and major ion systematics to understand the contribution of water originating from mineralogically distinct sub-basins to the Pahsimeri River in the Idaho Rocky Mountains. The river is a major tributary of the Salmon River and has become increasingly exploited for local agriculture irrigation. It drains two heavily deformed mountain ranges (Fig. 1) which are characterized by diverse mineralogies and numerous normal faults that juxtapose impermeable bedrock with pervious alluvial sediments. As a result, groundwater discharges into the river via springs or baseflow at multiple locations causing various high-flow and low-flow segments along the river reaches (Liberty et al., 2006). Because of increasing levels of groundwater extraction in the watershed, there is a need for an understanding of the dominant water source(s) along the entire reaches of the Pahsimeri. Unlike many water resources in the western U.S., there is the opportunity to use results to understand the hydrochemistry of the stream ahead of major development. Such studies can thus be implemented in other areas where broad-scale watershed studies have identified that there is a high risk of streamflow and water quality change developing in the future.

2. Local physiographic setting

The Pahsimeri River Watershed is located in the central Idaho Rocky Mountains covering a total area of approximately 2150 km$^2$. The Pahsimeri River is about 95 km long and flows in a northwesterly direction between the Lemhi Range to the northeast, and the Lost River Range to the southwest. Altitude changes from ~3180 m above sea level (asl) in the headwaters of the Lost River Range to ~1490 masl at the confluence with the Salmon River near the small community of Ellis (Fig. 1). The watershed is characterized by deeply incised, steep mountain terrain and narrow stream channels in the uplands and more gently dipping slopes in the central portions of the valley.

Precipitation is highest from November through February and lowest from June through September and is mainly received as snow in the highlands (WRCC, 2014). Spatially, precipitation varies strongly with elevation with annual means as high as 1000 mm in the mountains and as low as 250 mm/yr in the central valley (PRISM, 2010). Mean air temperatures in Challis (located approximately 24 km southwest of Ellis) vary between −5.6 °C in January and 20.3 °C in July (WRCC, 2014) and generally decrease at a mean lapse rate of about 0.4 °C per 100 m elevation increase (Blandford et al., 2008). Because the short annual growing season in the valley (mid-June to the end of August) coincides with the annual dry period, approximately 0.15 km$^3$ of water is diverted annually within the basin to irrigate about 120 km$^2$ (Williams et al., 2006).

The study area is only sparsely populated with most of the populace (~100 people) concentrated in May and Ellis. Land cover in the valley comprises shrub/rangelands (55%), grass/pasture/hay lands (19%), natural forest (17%), water/wetlands (7%) and grain crops (2%) (NPRC, 2008). The Pahsimeri is an important anadromous fish spawning stream (Maret et al., 2005) and alike other rivers in the Rocky Mountains, it has experienced significant declines in resident fish (i.e., trout and salmon) populations; arguably caused by water diversions and climate change-induced changes in water temperature (Rieman et al., 2007; Rieman and Isaak, 2010). This has led to concerted efforts to minimize out-of-stream diversions particularly in the upper reaches of the river, the main juvenile fish rearing space (SOI-DFC, 2014).

2.1. Local geology

The study area is located in the heavily deformed Basin and Range Province of the western U.S.; a region that experienced multiple lithospheric extension events and associated volcanism since the late Paleogene. The general stratigraphy in the region as mapped by Fisher et al. (1992), McIntyre and Hobbs (1987) and Janecke (1993) is summarized from oldest to youngest as: (1) Precambrian (Belt Supergroup) metamorphic basement (quartzites and metagreywackes), (2) Paleozoic limestone and dolomite containing varying amounts of interbedded siltstone, shale and lithic fragments, (4) Paleogene Challis volcanics (intermediate lava flows and associated sediments); and (5) recent basin fill deposits (alluvial and fluvial gravel, sand and silt) (Fig. 1). The basement rocks cover large proportions of the Lemhi Range and comprise the Mid-Proterozoic Swauger Formation containing mainly fluvi-lacustrine feldspathic arenites (~80% quartz, <12% K-feldspar; <1% lithic fragments) (Connor et al., 1991). Carbonate rocks occur mainly in the southwestern parts of the watershed in the Lost River Range as thick limestone and dolomite banks (Fisher et al.,...
1992; Link and Janecke, 1999). Volcanic rocks comprise intermediate lavas and associated pyroclastic rocks (McIntyre and Hobbs, 1987). Rhydacites occur in the northern section of the Lost River Range, whereas the western flanks mainly comprise K rich trachyandesites and to a lesser extent latites (McIntyre et al., 1982; Moye et al., 1988; Norman and Mertzman, 1991). Sulfides (mainly pyrite) occur as minor accessory phases within most lithological units, either as a primary phase in the igneous rocks or as diagenetic phase in the (meta)sedimentary rocks.

Basin fill deposits comprise laterally discontinuous gravel, sand and silt layers of eroded drainage materials. Seismic surveys indicate a fairly symmetrical drainage basin geometry with greatest depths (~2000 m) in the southern central portions at McCoy Lane (Fig. 1) and shallowest parts (~200 m) towards the northwest at Dowton Lane (Liberty et al., 2006). Numerous northwest–southeast trending normal faults along the valley boundaries and in its interior (e.g., Goldburg Fault) (Liberty et al., 2006) document the local extensional history. Springs occur along these faults and form bordering wetlands (Fig. 1). These springs reportedly comprise the main source of streamflow in the watershed (Williams et al., 2006).

2.2. Local hydrology

Streamflow changes with season with highest values in late fall/early winter due to surface runoff pulses as well as irrigation return flows. These characteristics are common in mountainous watersheds in the area (Tang et al., 2012); as is the typical El Niño–Southern Oscillation pattern in discharge records with peak flows in Ellis (lowland gage; Fig. 1) occurring in the wet years 1984, 1998 and 2010 (Fig. 2).

Groundwater movement in the area generally follows topography and occurs down-valley to the northwest. However, a lack of concurrent water level and well construction data for the Pahsimeroi Basin prohibits a detailed evaluation of hydraulic gradients. Mean depth to groundwater data for 10 shallow wells (data from USGS National Water Information System) varies between 5.56 m and 32.1 m over short (10s of meters) lateral distances indicating significant vertical gradients reflective for semi-confined conditions which are characteristic for laterally discontinuous fluvial sand/silt units. Meinzer (1924) reported that depth to the water table along the Pahsimeroi River fluctuates >3 m over the course of a year with the largest fluctuations occurring around irrigated tracts near McCoy Lane and Ellis. Seasonally, the water table rises rapidly in spring due to streamflow contributions and irrigation and is highest in June and September and lowest in February and early May (Meinzer, 1924). Based on the generalized water budget by Williams et al. (2006; and references therein), groundwater underflow through the mouth of the Pahsimeroi Basin indicating that groundwater flow through the basin outlet is minimal with respect to the annual water budget.

In an effort to better understand the hydrology of the Pahsimeroi Watershed, Williams et al. (2006) conducted seepage runs along the entire length of the river in August (irrigation season) and November (post irrigation season) of 2005 (Fig. 3). They characterized four primary reaches (in order of occurrence) as: (1) a losing upper reach from the headwaters and downstream for approximately 28.8 km, (2) a 9.17 km long gaining reach of extensive springs and wetlands in the vicinity of McCoy Lane, (3) a mid-valley 12.7 km long losing/sink reach, and (4) a lower 29.8 km long gaining reach towards the outlet. The average gain/loss of streamflow estimated during the 2005 seepage runs is highly variable ranging from ~−100 to +300 L/s/km (Williams et al., 2006; Fig. 3b). That there is an overall trend of increasing baseflow contribution towards the lower reaches suggests that at least beyond Furey Lane, where the basin shallows and decreases in width, groundwater sustains perennial flow.

The picture that emerges is that the Pahsimeroi Watershed is located in a complex geologic setting where water from 3 lithologic regimes contributes to streamflow: (1) the carbonate dominated portions of the Lost River Range, (2) the volcanic dominated portions of the Lost River Range, and (3) the metamorphic (quartzite)-dominated sections of the Lehmi Range. While sub-basin runoff and spring water sampled within the respective mountain ranges are likely characterized by watershed lithology-specific chemical fingerprints, water derived from within the basin depocenter is expected to represent an integrated average of the chemical heterogeneity of bedrock formations. In the following sections, geochemical tracers will be applied to characterize each of these potential sources and assess their contribution to streamflow.

3. Materials and methods

Water from rivers, springs, precipitation and shallow domestic wells was collected during eight sampling campaigns carried out between February 2006 and October 2007 (Appendix A). Surface water was sampled at approximately 20 cm water depth during broad daylight. All wells except the Sulfur Creek Well were equipped with subsensible
Fig. 3. (a) Map of Pahsimeroi Basin showing the sinks and spring complex areas, and gaining and losing segments of the Pahsimeroi River as observed during seepage runs in August and November of 2005 (after Williams et al., 2006). (b) Distributed gains and losses observed along the Pahsimeroi River stretches during August and November 2005 seepage runs (after Williams et al., 2006).
pumps and were sampled at hose bibs. The Sulfur Creek Well was sampled with an ABS pipe bailer. Rain and snow was collected from rain gages from February to September 2007.

Collected samples were filtered through 0.45 μm membrane filters, acidified (with 1% HNO₃) for cation analysis and stored in HDPE bottles (for major ions) and glass VOA vials (for D and ¹⁸O samples) free of headspace below 4 °C. Water pH, temperature and electrical conductivity were measured immediately after collection using portable YSI probes that were calibrated before each sampling campaign. Alkalinity was determined in the field via Gran titration using Hach digital titrators and reagents. Major ions were analyzed at the University of Hawaii by ion chromatography (Dionex) for anions and by ICP-OES and AAS for cations. The precision of major ions in dilute waters based on repeat analyses was generally better than ±15%. The major ion charge balance error (CBE) is generally better than ±10% (mean and median values of 3.7% and 0.4%, respectively). Some samples show an excess of cations which most likely reflect inaccuracies in the titration of HCO₃ particularly in dilute (EC < 50 μS/cm) waters.

Stable O and H isotopes were measured at the SIRFER Laboratory of the University of Utah using a Finnigan MAT 252 mass spectrometer and an automated Finnigan MAT H/Device. δ¹⁸O and δD values were measured relative to internal PLRM and SLRM standards that were calibrated against accepted NIST and/or IAEA water reference materials. 

δ⁸⁷Sr/⁸⁶Sr values were analyzed on a VG Sector thermal ionization mass spectrometer (TIMS) at the SOEST Isotope Laboratory of the University of Hawaii at Manoa. All samples were dried down on a hotplate and re-dissolved in 3.5 M HNO₃, and Sr was separated using standard ion exchange techniques. Measured δ⁸⁷Sr/⁸⁶Sr ratios were corrected for instrumental mass fractionation using δ⁸⁷Sr/⁸⁶Sr of 0.1194. The total procedural blanks for Sr varied between about 1 and 3 ng compared to sample strontium loads of several micrograms. Reproducibility and accuracy of Sr isotope runs have been periodically checked by running the Standard Reference Material NBS 987, with a mean δ⁸⁷Sr/⁸⁶Sr value of 0.710238 ± 0.000014 (2σ standard deviation).

4. Results and discussion

4.1. Basic hydrochemical patterns

Appendix A lists the geochemistry of the main stream Pahsimeroi River (MSPR) waters subdivided according to sampling locations (Fig. 1) into headwaters (sampled about 60 km southeast of the confluence), upper reaches (sampled at McCoy Lane, about 40 km southeast of the confluence), mid reaches (sampled between Hooper Lane and Dowton Lane, between 11 and 20 km southeast of the confluence) and lowland (sampled between Burststed Lane and Ellis, between 3.8 and 0.2 km from the confluence). The dataset also incorporates the chemistries of tributaries/springs sampled within the metamorphic rock-dominated Lemhi Range (source waters — metamorphics) and the carbonate/volcanic rock-dominated Lost River Range (source waters — carbonates, source waters — volcanics), respectively. Also included are precipitation data as well as tributary, spring and groundwater samples collected within the alluvial plains.

4.1.1. Stable isotopes (δD, δ¹⁸O)

Values of δD and δ¹⁸O of sampled waters range from —128.5‰ to —152.2‰ and from —17.2‰ to —19.6‰, respectively (Fig. 4). All points align close to the global meteoric-water line (Craig, 1961) as well as within the local precipitation (rain and snow) range indicating a local meteoric water origin and a lack of significant evaporation or oxygen isotope exchanges between water and bedrock material. Seasonal changes are most pronounced in rainfall samples illustrated by the Whittier Ranch samples that display a shift of δD and δ¹⁸O from —24.5‰ and —187.6‰ in February 2007 to —13.0‰ and —110.0‰ in June 2007. Compared to precipitation, variability of δD and δ¹⁸O values of surface water, spring water and groundwater samples is relatively muted and samples plot over a narrow range indicating a majority of water input from summer precipitation (Fig. 4) and some degree of mixing and homogenization affecting these waters along their flow paths. There is no correlation between altitude and δ¹⁸O values of spring water and precipitation even if we subdivide the dataset into smaller

Fig. 4. δ¹⁸O vs. δD values of sampled waters along with the Global Meteoric Water Line (GMWL; data from Craig, 1961) and Local Meteoric Water Line (LMWL) which is based on local precipitation data.
4.1.2. Major ion systematics

There are no significant seasonal electric conductivity variations (Appendix A) in the MSPR; there is however a consistent downstream trend towards increasing electric conductivity values (Fig. 5a) possibly reflecting the combined effects of progressive chemical weathering and water mixing. Only two out of a total of 76 samples exhibit nitrate levels higher than EPA’s maximum contaminant level (MCL) of 10 mg/L (EPA, 2014). These samples came from an unused groundwater well (Sulfur Creek Well) located in a pasture with an open borehole covered by a sheet of plywood. The NO₃ is likely introduced through the borehole and the samples were excluded from further analysis. Overall, however, agricultural (i.e., fertilizer) contamination does not appear to significantly affect waters in the basin and solute loads are mainly attributed to precipitation, chemical weathering and mixing. Ionic ratios (Ca/Na vs. Mg/Na; Fig. 6) of MSPR headwater and carbonate tributary samples align close to the theoretical carbonate lithology end-member indicating a dominant contribution of water derived from the carbonate portions of the Lost River Range (e.g., Grouse Creek and/or Leatherman Lake Spring) to the headwaters. There is also an increasing input from silicate weathering in the MSPR mid reach to lowland samples implying that the contribution from the volcanic and/or metamorphic terrains increases downstream. MSPR upper reach waters sampled near McCoy Lane plot significantly closer to the silicate end-member than the alluvial spring samples (e.g., Lone Pine Spring, Baldwin Spring) that were collected in close proximity to these waters (Fig. 6). This would per se imply that the contribution of groundwater to streamflow near McCoy Lane was only minor at the time of sampling. However, in this case, the discrepancy could also be ascribed to inflow from the Goldburg Creek tributary which originates in the metamorphic Lemhi Range and is hence more influenced by a silicate major ion fingerprint. These competing major ion signatures (e.g., carbonate dominated spring vs. silicate dominated tributary waters) make a quantitative MSPR solute source assessment challenging. Given that aside from the carbonate tributary waters, all tributary, ground- and spring waters exhibit more or less overlapping major ion compositions, refined mixing assessments and a clear water and solute source distinction cannot be reliably conducted on the basis of cationic ratios alone.

4.1.3. Strontium isotopes

⁸⁷Sr/⁸⁶Sr values in the Pahsimeroi Watershed range from 0.70797 (IDFG Well#2) to 0.75596 (Patterson Creek). There are no significant seasonal variations, as illustrated by the MSPR headwater and outlet samples which vary by only 0.00175 between August 2006 and February/May 2007. In agreement with major ion trends discussed above, increasing ⁸⁷Sr/⁸⁶Sr values in downstream MSPR samples imply increasing silicate weathering inputs (Fig. 5c). Spatially, ⁸⁷Sr/⁸⁶Sr are highest (>0.72) in waters of the metamorphic Lemhi Range and lowest (<0.72) in waters of the carbonate/volcanic rock dominated Lost River Range. There is a relative depletion of ⁸⁷Sr/⁸⁶Sr in MSPR and adjacent spring water and groundwater samples collected from the gaining stretches of the Pahsimeroi (Fig. 7a). This indicates that groundwater and spring water derived from the Lost River Range recharge the river and dilute the silicate weathering signature in the MSPR waters. A lack of correlation between ⁸⁷Sr/⁸⁶Sr and 1/Sr (R² < 0.2; relationship not shown), however, militates against simple binary (carbonate–silicate) mixing in the system.

Plots of ⁸⁷Sr/⁸⁶Sr vs. (Ca + Mg)/(Na + K), Ca/Sr and Na/Sr (Fig. 8a–c) provide more useful information on mixing as they are capable of depicting the compositional variability pertaining to the various carbonate and silicate lithologies (Negrel et al., 1993; Hagedorn et al., 2011). High ⁸⁷Sr/⁸⁶Sr values (>0.73) coupled with generally low (Ca + Mg)/(Na + K) ratios, such as those observed for the metamorphic source waters, imply high contributions from K silicates; particularly orthoclase, biotite and other micas that contain elevated contents of incompatible Rb. Intermediate ⁸⁷Sr/⁸⁶Sr values (<0.73, >0.71) and highly variable (Ca + Mg)/(Na + K), Ca/Sr and Na/Sr ratios in the volcanic tributary samples suggest input of less radiogenic Sr from plagioclase of the
volcanic rocks which exhibit quite variable Ca and Na compositions in the area (McIntyre et al., 1982; Norman and Mertzman, 1991). As Sr is excluded from the carbonate lattice during water rock interaction, dissolution of carbonate will lead to elevated Ca/Sr ratios. Thus, high Ca/Sr combined with low \(^{87}\)Sr/\(^{86}\)Sr values (<0.71) and low Na/Sr, such as observed for the carbonate source waters and MSPR headwater samples, are consistent with primary (marine) limestone weathering. Even though solute input of accessory calcite with relatively high \(^{87}\)Sr/\(^{86}\)Sr values has been shown to be significant in metamorphic basemant systems (Galy et al., 1999), like the one under consideration in the present study, the observation that metamorphic source waters display the lowest overall Ca/Sr values militates against more than minor solute contributions from these sources. However, accessory calcite derived from igneous sources may very well exhibit the \(^{87}\)Sr/\(^{86}\)Sr, Na/Sr, Ca/Sr and (Ca + Mg)/(Na + K) patterns of Ca-plagioclase and may – as such – bias the signal of the volcanic source waters towards a calcite weathering fingerprint. While the relative contribution of igneous rock-derived secondary calcite cannot be fully ruled out, a lack of macroscopic secondary calcite deposits in the field suggests its solute contribution to be only of secondary importance in the volcanic source waters.

MSPR and tributary samples exhibit distinct \(^{87}\)Sr/\(^{86}\)Sr vs. (Ca + Mg)/(Na + K), Ca/Sr and Na/Sr trends reflective of the solute contributions of the dominant lithologies as well as atmospheric precipitation. In its headwaters, the MSPR retains a signature reflective for mainly carbonate rocks. This signature becomes increasingly mixed with silicate derived solutes as the waters drain the alluvial sediments of the basin’s depocenter. Tributary inflow from the metamorphic Lehmi Range (e.g., Patterson Creek) and the volcanic sections of the Lost River Range (e.g., Morgan Creek) combined with baseflow input further homogenizes the solute content of MSPR waters particularly in the gaining segments near McCoy Lane and in the lowlands.

### 4.2. Chemical weathering rates

Chemical weathering of silicates by atmospheric H\(_2\)CO\(_3\) and the subsequent riverine transport of dissolved HCO\(_3\) to the ocean is an important control on atmospheric CO\(_2\) levels over geologic time (Berner et al., 1983). Modeling studies using runoff and bedrock geochemistry input data predict that rivers draining the U.S. Rocky Mountains, on a continental and global scale, exhibit very high CO\(_2\) consumption rates due to the combined effects of runoff and lithology exposure (Amiotte-Suchet and Probst, 1995; Amiotte-Suchet et al., 2003; Moosdorf et al., 2011; Li et al., 2014). Given the abundance of silicate lithologies in the Pahsimeroi Watershed, these high CO\(_2\) consumption rate predictions should be reflected in the collected geochemistry data. To estimate CO\(_2\) consumption in this study, solute contents were apportioned among specific weathering reactions using major ion inversion techniques similar to those described in previous studies (Stallard and Edmond, 1981; Galy and France-Lanord, 1999; Spence and Telmer, 2005; Ryu and Jacobson, 2012). Such techniques require the following assumptions: (1) dissolved cations are not fractionated during dissolution, (2) all Cl is derived solely from evapotranspiration of precipitation, (3) there is no major ion input from anthropogenic sources, and (4) the only acids that contribute to mineral weathering are carbonic acid (derived from atmospheric or soil CO\(_2\)) and, to a lesser degree, sulfuric acid (derived from oxidation of sulfide minerals). Given these constraints and the local lithologic setting, the following four weathering reactions are considered to contribute to solute yields in the Pahsimeroi Watershed: (1) carbonic acid–carbonate weathering (CACW), (2) carbonic acid–silicate weathering (CASW), (3) sulfuric acid–carbonate weathering (SACW), and (4) sulfuric acid–silicate weathering (SASW). The herein presented major ion inversion techniques have generally only been applied to surface (stream) water samples. Here, spring waters and groundwater are included in the analysis assuming they are derived from local mountain front recharge and are not significantly affected by secondary (e.g., ion exchange) reactions.

As a first step, we filtered out the atmospheric solute input via:

\[
i^*_W = i_W - Cl_W (i/Cl)_P
\]

where \(i^*_W\) is the corrected concentration of solute \(i\), and \((i/Cl)_P\) correspond to the measured concentration of \(i\) and Cl in the collected water (W) and precipitation (P) sample, respectively. The ID03 precipitation data used here comprises the geometric mean major ion value of precipitation that was collected at an elevation of 1807 m asl about 140 km southeast of Ellis between 1980 and 2013 (NADP, 2014). This data is considered a valid long-term proxy of mountain front precipitation chemistry in the study area.
Fig. 7. Natural neighbor interpolation of measured $^{87}\text{Sr}/^{86}\text{Sr}$ (a) and calculated mean CWR$_{\text{Carb}}$/CWR$_{\text{Sil}}$ (b) values in Pahsimeroi waters. Depicted gaining and losing stream segments are taken from Williams et al. (2006).
where $R$ refers to the ratio of carbonic acid consumed by silicate weathering to carbonic acid consumed by carbonate weathering (2). Because SACW generates a $\text{Ca, Mg vs. SO}_4$ ratio of 2, cations derived by SACW were calculated as:

$$\text{Ca}_{\text{SACW}} + \text{Mg}_{\text{SACW}} = 2\text{SO}_4_{\text{SACW}}.$$  

SASW-derived cation yields were then calculated as:

$$\text{Na}_{\text{SASW}} = \text{SO}_4_{\text{SASW}}(\text{Ca}/\text{Na}_{\text{sil}} + \langle \text{Mg}/\text{Na}_{\text{sil}} \rangle + 0.5(K'/Na')_{W} + 0.5)^{-1}$$

$$K_{\text{SASW}} = \text{Na}_{\text{SASW}}(K'/Na')_{W}$$

$$\text{Ca}_{\text{SASW}} = \text{Na}_{\text{SASW}}/(\text{Ca}/\text{Na}_{\text{sil}})$$

$$\text{Mg}_{\text{SASW}} = \text{Na}_{\text{SASW}}/(\text{Mg}/\text{Na}_{\text{sil}}).$$  

Crucial input parameters in the calculation of weathering rates in inverse modeling studies are the silicate-bedrock $\text{Ca}_{\text{Na}_{\text{sil}}}$ and $\text{Mg}_{\text{Na}_{\text{sil}}}$ ratios. Uncertainties in these ratios can impart a significant error in the weathering yield estimates, particularly in basins that are not large enough to average the chemical heterogeneity of bedrock formations [Hren et al., 2007]. Most past studies applied mean Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios taken from whole rock chemical analyses. However, these can be uncertain because fractionation caused by weathering itself [Negrel et al., 1993] or inadequate study area coverage. It is therefore important to apply Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios of watershed-representative and relatively unaltered silicate bedrock samples. To account for uncertainty in the calculated chemical weathering rates, we utilize two sets of Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios: (1) values of 0.63 ($\text{Ca}_{\text{Na}_{\text{sil}}}$) and 0.92 ($\text{Mg}_{\text{Na}_{\text{sil}}}$) corresponding to the geometric mean ionic ratios of silicate bedrock samples (equal proportions of volcanic and metamorphic rocks) collected in Central Idaho [data from McIntyre et al., 1982; Connor et al., 1991], and (2) values of 1.50 ($\text{Ca}_{\text{Na}_{\text{sil}}}$) and 2.06 ($\text{Mg}_{\text{Na}_{\text{sil}}}$) which correspond to the geometric mean $\text{Ca}$ and $\text{Mg}$/Na$_{\text{sil}}$ values of the volcanic and metamorphic source waters in the study area. These are assumed to be influenced only by silicate weathering without major contribution from secondary calcite dissolution or atmospheric precipitation (mean precipitation $\text{Ca}$/Na and $\text{Mg}$/Na = 0.17 and 0.30, respectively). The latter approach allows for a more localized end-member identification that takes into account local ionic and isotopic considerations (Fig. 9a, b). Subsequent calculations of chemical weathering and CO$_2$ consumption rates are based on both end-member ranges of Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios.

Cation yields from CASW and CACW were computed as:

$$\text{Na}_{\text{CASW}} = \text{Na'}_{W} - \text{Na}_{\text{SASW}}$$

$$\text{Ca}_{\text{CASW}} = \text{Na}_{\text{CASW}}/(\text{Ca}/\text{Na}_{\text{sil}})$$

$$\text{Mg}_{\text{CASW}} = \text{Na}_{\text{CASW}}/(\text{Mg}/\text{Na}_{\text{sil}}).$$

From these estimates, the chemical weathering rate (CWR) of carbonates (carb) and silicates (sil) were approximated by the total mass of cations as:

$$\text{CWR}_{\text{carb}} = (\text{Ca} + \text{Mg})_{\text{SACW}} + (\text{Ca} + \text{Mg})_{\text{CASW}}$$

$$\text{CWR}_{\text{sil}} = (\text{Ca} + \text{Mg} + \text{Na} + \text{K})_{\text{SASW}} + (\text{Ca} + \text{Mg} + \text{Na} + \text{K})_{\text{CASW}}$$

and the CO$_2$ consumption rate from carbonic acid weathering was calculated as:

$$\text{CO}_2_{\text{carb}} = (2\text{Ca} + 2\text{Mg} + \text{Na} + \text{K})_{\text{CASW}}Q/A$$

where $Q$ is the Pahsimeroi River discharge at Ellis and $A$ is the total watershed area (data from USGS National Water Information System).

CWR$_{\text{carb}}$ and CWR$_{\text{sil}}$ values range from 0.04–2.48 mmol/L and 0.04–1.45 mmol/L, respectively, using the whole rock Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios, and from 0–2.36 mmol/L and 0.07–2.58 mmol/L, respectively, using the water chemistry-deduced Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ values. Mean CWR$_{\text{carb}}$/CWR$_{\text{sil}}$ ratios (Fig. 7b) are generally highest (~1) in the carbonate-dominated southwestern portion of the watershed and lowest (~0.1) in the metamorphic eastern portions of the watershed. Similar to the $^{87}$Sr/$^{86}$Sr distribution, mean CWR$_{\text{carb}}$/CWR$_{\text{sil}}$ values exhibit decreased silicate weathering rates in MSPR and adjacent spring water and groundwater sampled along the gaining stretches of the river. This confirms an earlier hypothesis that northeasterly flowing groundwater dilutes the MSPR silicate weathering signatures derived from Lehmi Range tributaries. There is also a particular trend towards lower mean CWR$_{\text{carb}}$/CWR$_{\text{sil}}$ at higher elevations (and channel slopes) in the Lehmi Range stream waters, supporting observations by Hren et al. [2007] that for monolithic regimes, CWR$_{\text{sil}}$ fluxes are highest in areas of highest topographic drive.

Calculated CO$_2$ consumption rates (Eq. (16)) at the MSPR outlet range from 0.074–0.117 Mmol km$^{-2}$ a$^{-1}$ using the whole rock Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios and increase to 0.147–0.232 Mmol km$^{-2}$ a$^{-1}$ if the water chemistry-deduced Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios are applied. The high sensitivity of calculated rates to the Ca$_{\text{Na}_{\text{sil}}}$ and Mg$_{\text{Na}_{\text{sil}}}$ ratios underscores the need for an accurate understanding of the lithologic composition in the study area for reliable weathering rate assessments. The herein presented rates are up to an order of magnitude higher than those of other rivers draining orogenic settings on the continent such as the Yukon (0.019–0.023 Mmol km$^{-2}$ a$^{-1}$) and the Mackenzie (0.0004–0.067 Mmol km$^{-2}$ a$^{-1}$) [Millot et al., 2003]. These discrepancies likely relate to the latitudinal effect (colder climate) and geologic setting with both the Yukon and Mackenzie draining vast areas of stable basement shields constituted of resistant shales. More CO$_2$ consumption data from smaller scale watersheds in the Rocky Mountains are needed to systematically evaluate the controlling factors on CO$_2$ consumption in the area.

The herein reported CO$_2$ consumption rates are similar to, if not slightly lower than the North American average of 0.21 Mmol km$^{-2}$ a$^{-1}$ (Moosdorf et al., 2011) which is based on an empirical forward model that relates measured bicarbonate fluxes induced by rock-weathering to catchment lithology and land cover. This is surprising given that regional forward models predict relatively high CO$_2$ consumption rates in Rocky Mountain streams. Given the methodological differences between forward and inverse modeling approaches and the different datasets underlying both, it is not possible to reliably discern the causes...
for this discrepancy. Lower than average streamflow during the sampling campaigns (Fig. 2) could be one explanation; carbonate solute-enriched baseflow input at the Pahsimeroi outlet could be another. In any case, the overall high variability in CWR and \(^{87}\text{Sr}/^{86}\text{Sr} \) values throughout the watershed highlights the small scale variability of chemical weathering (and \( \text{CO}_2 \) consumption) that can occur at the watershed scale and this variability needs to be taken into consideration when extrapolating weathering rates to continental or even global scales (Hagedorn and Cartwright, 2009; Peucker-Ehrenbrinck and Fiske, 2014). Further research should hence address \( \text{CO}_2 \) consumption prediction model calibration. One means to achieve this goal could be using the outputs of local inverse modeling studies as calibration targets for larger scale \( \text{CO}_2 \) consumption models.

4.3. Quantifying the solute contribution of waters from volcanic, metamorphic and carbonate terrains

To estimate the relative solute contributions of various lithologic regimes to the Pahsimeroi River, we linked chemical weathering fingerprints in MSPR waters to the various local bedrock end-members. To achieve this, a mixing model was established using (a) \(^{87}\text{Sr}/^{86}\text{Sr} \) and (b) \( \text{Na}/\text{Sr} \) ratios as tracers. We considered these appropriate for this task because they highlight the compositional variability of the individual carbonate and silicate solute sources in the watershed. The observation that these tracers span a ternary domain that basically encompasses MSPR samples, spring waters and groundwater (Fig. 8c) supports this hypothesis. Assuming that atmospheric precipitation
affects all water samples to the same degree and the solute load of the Pahsimeroi River is only controlled by input of metamorphic-, volcanic- and carbonate source waters, the contribution of each to the total solute load can be calculated following Liu et al. (2004) as:

\[
f_1 = \frac{(C_{\text{river}} - C_1^1)}{(C_2^1 - C_1^1)} - \frac{(C_2^1 - C_1^1)}{(C_3^1 - C_1^1)} \quad (17)
\]

\[
f_2 = \frac{C_{\text{river}} - C_1^1}{C_2^1 - C_1^1} - \frac{C_1^2 - C_1^1}{C_2^1 - C_1^1} f_1 \quad (18)
\]

\[
f_3 = 1 - f_1 - f_2 \quad (19)
\]

where \(f_1\), \(f_2\) and \(f_3\) are the solute contributions from metamorphic, volcanic and carbonate sources, respectively, and \(C\) corresponds to the tracer concentration. The C superscript highlights the specific tracer \(^{87}\text{Sr}^{86}\text{Sr}\) for \(1\) and \(\text{Na/Sr}\) for \(2\) and the subscript denotes the component (i.e., \(\text{river}\) for the river sample, \(1\) for the metamorphic, \(2\) for the volcanic and \(3\) for the carbonate end-member). Of all MSPR samples, only one headwater sample plots outside the triangular domain possibly reflecting analytical error and/or end-member uncertainty. For this outlier, a two end-member mixing solution solving the Pythagorean Theorem (Liu et al., 2004) as:

\[
\frac{C_1}{C_0} = \frac{C_{\text{river}} - C_1}{C_{\text{river}} - C_2} \quad \frac{C_2}{C_1} = \frac{C_{\text{river}} - C_2}{C_{\text{river}} - C_3} \quad \frac{C_3}{C_2} = \frac{C_{\text{river}} - C_3}{C_{\text{river}} - C_1}
\]

The results of this study show that the mean solute input from carbonate terrains decreases from about 95.9% in the headwaters to about 36.4% in the lowlands while the corresponding input from volcanic and metamorphic sources increases from 3.63% to 51.0% and 0.45% to 12.6%, respectively. This indicates a clear dominance of water precipitated over the Lost River Range on contributing to streamflow in the basin. Although both bounding mountain ranges receive comparable annual precipitation (PRISM, 2010), the Lost River Range area is significantly greater than that of the Lehmi Range and thus likely dominates precipitation, runoff and recharge volume. The herein presented data could hence be useful for validating watershed models aimed at simulating the amount of streamflow generated from precipitation over the Lost River vs. the Lehmi Ranges.

Seasonally, volcanic source input in the MSPR outlet samples is lower in summer (mean for June, August and September samples: 38.0%) than in winter (90.0% in February), a trend that is reversed for the metamorphic (~15.0% vs. 5.68%) and carbonate (~47.1% vs. 4.39%) input. These seasonal patterns likely reflect the corresponding variations in baseflow and sub-basin runoff. The increased metamorphic and carbonate source contributions in summer (when MSPR streamflow is low) could be indicative for increased baseflow input of groundwater from fractured carbonate and, to a lesser degree, metamorphic rock aquifers. The increased volcanic rock solute source input in winter (when MSPR streamflow is higher) could be due to increased components of surface runoff enriched in solutes derived from weathering of volcanic rock which make up the largest lithologic proportion of the watershed. However, more time-series geochemical data particularly for the transitional spring and autumn months could strengthen our understanding of the hydrogeological controls on water and solute transport.

### 4.4. Assessing baseflow

There is a remarkable heterogeneity in alluvial spring and groundwater chemistry in relation to landscape position and aquifer
mineralogy. Church Well (sample 43 in Fig. 1), for example, is located at the mountain fronts of the Lemhi Range and sampled groundwater displays $^{87}\text{Sr}/^{86}\text{Sr}$ vs. (Ca + Mg)/(Na + K), Ca/Sr and Na/Sr values much different to groundwater or spring water sampled closer to the Lost River Range (e.g., IDPerG Well 2, sample 39 in Fig. 1). Sulfur Creek Pump (sample 42 in Fig. 1), which is located in the basin interior and in close proximity to the MSPR exhibits intermediate values (Fig. 8a-c) consistent with mixing and homogenization of carbonate and metamorphic mountain front end-members.

The overall variability of groundwater and spring water samples prohibits a direct quantification of baseflow input to the Pahsimeroi based on simple end-member mixing analysis. Nonetheless, observed trends allow some qualitative assessment of the extent of groundwatersurface water interaction in the basin. Upper reach to lowland MSPR samples show distinct $^{87}\text{Sr}/^{86}\text{Sr}$ vs. (Ca + Mg)/(Na + K), and Na/Sr values aligning over a relatively narrow range bracketed by the Circle Pt Upper Spring (sample 34 in Fig. 1), Dowton Spring (sample 32 in Fig. 1) and Sulfur Creek Pump end-members (Fig. 8). This suggests a common solute source and/or ongoing mixing with baseflow starting at least at McCoy Lane. This also confirms the seepage runs by Williams et al. (2006) that characterized gaining segments upstream of McCoy Lane and Furey Lane (Fig. 3). MSPR headwater samples, on the other hand, plot outside the alluvial spring water/groundwater range (Fig. 8) which is indicative for a lack of hydraulic communication between surface water and groundwater (losing segment) and also consistent with Williams et al.’s (2006) observations. That these distinct signatures of the headwater samples are not fully reflected in the $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Sr plot is likely due to the overlapping Ca/Sr values of waters characterized by carbonate and Ca-silicate weathering. Unfortunately, no MSPR data was collected from the second reported losing segment of the MSPR between McCoy and Furey Lane, so the nature of this segment cannot be confirmed in the present study. However, unlike the gaining stretch upgradient of Furey Lane which is ascribed mainly to topographic control (baseflow input increases as the basin shallows and decreases in width), the gaining stretch at McCoy Lane occurs where the basin is widest and deepest. Liberty et al. (2006) linked this segment to the Goldburg Fault (Fig. 1) forcing easterly flowing groundwater upwards when it encounters impervious material at the footwall. This general conceptual model is depicted in Fig. 11. More spatially distributed data particularly from the upper reaches of the Pahsimeroi would allow better constraining the location and time at which MSPR $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Na/Sr and (Ca + Mg)/(Na + K) values align outside of the alluvial spring and groundwater range which would indicate a change from gaining to losing conditions.

5. Conclusions and implications

Geochemical data indicate that the Pahsimeroi’s solute content is mainly derived from the volcanic-rock dominated sections of the Lost River Range making these sections and the tributaries that drain them most important with regards to anthropogenic (e.g., fertilizer-derived) contamination. The question whether the inflow component of the volcanic source waters reflects increased tributary/baseflow input from the respective sub-watersheds or a clear dominance of volcanic rock-derived sediments in the basin depocenter needs to be further investigated. Tributary flow data from the various sub-watersheds and petrographic information on basin fill sediments could potentially shed more light on the respective controls on the stream solute load.

In agreement with previously performed seepage runs, geochemical data depict a trend towards increasing downstream baseflow inputs that sustain perennial flow downward of McCoy Lane. Quantitative baseflow estimates, however, cannot be provided due to the chemical variability of alluvial groundwater and spring water samples. $^{222}\text{Rn}$ information may provide useful constraints on the extent and rate of baseflow input if groundwater and surface water end-members can be reliably identified.

.currently and future water diversions for agricultural or other uses should focus on the downgradient sections (i.e., beyond Furey Lane) and the distinct upgradient stretch (i.e., around McCoy Lane) of the Pahsimeroi where continuous baseflow input prevents the river from rapidly drying up. However, future development should include time series streamflow and water quality monitoring to trace the zone where the water table intercepts the river channel altitude and, more importantly, to document how this zone responds to increasing groundwater extraction and irrigation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2014.10.031.

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