Coal aquifer contribution to streams in the Powder River Basin, Montana

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SUMMARY

Groundwater contributions to streams can be reduced by groundwater withdrawal associated with coalbed methane and coal mine production. Quantifying the groundwater contribution to streams aids the assessment of potential impacts to in-stream flow and provides information necessary for energy producers to use coproduced water for beneficial purposes, rather than treating it as a waste product. Stream flow, field parameters, common ions, and isotopes of carbon and strontium were measured on Otter Creek and the Powder River in southeastern Montana. Direct streamflow measurements were ineffective because of the magnitude and nature of coalbed contribution. The coal groundwater contribution did not exceed the geochemical detection threshold on two nearby streams. Geochemical models based on isotopic data proved to be the most effective analytical method, resulting in baseflow measurements from coal aquifers of 28–275 l s^{-1}.

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1. Introduction

1.1. Project purpose and scope

Groundwater withdrawal during coalbed methane (CBM) production or coal mine development, upgradient from where a developed coalbed subcrops to streams, has the potential to reduce the coal aquifer contribution (baseflow) to those streams. This study quantified coal aquifer contributions to streams to help assess potential impacts to total flow. This information is necessary for environmental permitting of mines and for energy producers to apply for permits to put CBM coproduced water to beneficial purposes.

Measuring flowrate gain and loss along a river reach is a common method to quantify baseflow. However, this method is of limited use along short reaches where water moves in and out of bank storage and contribution from baseflow is small compared to overall streamflow. The best time to measure small gains in flow from groundwater is during low flow periods in the winter; but in winter the rivers are often too dangerous to measure or are ice covered. Additionally, gain/loss measurement does not identify the aquifer source of the baseflow. However, carbon and strontium isotopes have been shown to effectively fingerprint the contribution of coal aquifer groundwater to surface water in the Powder River

Basin of Montana and Wyoming (e.g. Brinck and Frost, 2007; Meredith and Kuzara, 2012; Sharma and Frost, 2008).

1.2. Previous investigations

Surface coal mining in the Powder River Basin drove the initial description of the regional hydrogeology and the decades long monitoring of groundwater (Van Voast and Reiten, 1988). The network of monitoring wells, established in the mid-1970s, continues to be maintained and supplemented through the on-going monitoring of CBM development. Annual reports published since 2004 document groundwater geochemistry and drawdown of water levels in coal aquifers, followed by recovery in some areas where CBM production rates have decreased (Meredith and Kuzara, 2015).

The carbon isotope ratio in coal aquifers is controlled by the native $^{13}C/^{12}C$ ratio of the coal and microbial processes, such as methanogenesis, which fractionate the carbon isotopes. Methanogens preferentially use ^{12}C in their biological processes because the ^{12}C–H bond is more easily broken than ^{13}C–H bond. This causes the ratio of $^{13}C/^{12}C$ to increase and generally results in groundwater that is isotopically distinct from surface water (Bates et al., 2011; Bottinga, 1969; Flores et al., 2008; Schoell, 1980; Sharma and Frost, 2008).

The ratio of $^{87}Sr/^{86}Sr$ in aquifer matrices is determined by radioactive decay of 87-Rubidum. Variability in the strontium isotope ratio of the aquifer is caused by the original ^{87}Rb

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concentration and age of the rock. Therefore aquifers with distinct geologic history often have unique strontium isotope ratios. Coal aquifers are often distinguishable from alluvial and sandstone aquifers and surface water (Brinck and Frost, 2007). Coal aquifers of different ages can also be distinguished (Campbell et al., 2008).

Use of isotopes to trace groundwater-surface water interaction is well established for both carbon and strontium (Brinck and Frost, 2007; Clark and Fritz, 1997; Frost and Toner, 2004; Frost et al., 2002; Meredith and Kuzara, 2012; Sharma and Frost, 2008). Carbon isotopes to identify coal aquifer groundwater in surface water have been used by Sharma and Frost (2008) and Meredith and Kuzara (2012). Strontium isotopes to identify aquifer mixing, including that of groundwater associated with CBM, have been used in several studies (Brinck and Frost, 2007; Frost and Toner, 2004; Frost et al., 2002).

Previous work on Otter Creek by Meredith and Kuzara (2012) demonstrated the potential to use carbon isotopes to trace coal aquifer contributions to this small Powder River Basin stream. Carbon isotope ratios increased as the stream crossed the Knobloch coal outcrop in response to the higher carbon isotope ratio found in coal aquifer baseflow. The study presented here builds upon this work by adding analyses of DIC concentrations, strontium isotope ratios and concentrations, and conservative anions as well as comparing these results to results from the nearby Powder River.

1.3. Study area

The semi-arid Powder River Basin typically has warm, wet summers and cool, dry winters. The Moorhead, Montana meteorological station (Fig. 1) has recorded an average 30.7 cm (12.09 in.) of precipitation per year since 1970 (National Weather Service, 2013). The surface geology is mostly flat-lying, Tertiary Fort Union Formation: interbedded sandstone, shale and coal. The landscape is notable for its red clinker beds created by naturally occurring coal fires. Clinker is highly transmissive and can be a significant conduit for recharge to regional aquifers. The geology has been described by the United States Geological Survey (USGS) and the Montana Bureau of Mines and Geology (MBMG) (Culbertson, 1987; Culbertson and Klett, 1979; Heffern et al., 2013; Lopez, 2006; Lopez and Heath, 2007; McLellan, 1991; McLellan et al., 1990; Vuke et al., 2001a, 2001b).

In the Powder River Basin, groundwater is the primary source for both domestic and stock water. Coal beds, because of their relatively high transmissivity, reasonably low salinity water, and lateral continuity, are the targets for many of the water wells in the Powder River Basin. Irrigation water comes almost exclusively from surface water sources, either pumped directly from the rivers or diverted through ditches.

The Powder River Basin economy is agricultural, primarily cattle ranching with dry-land and irrigated hay grass and alfalfa grown in support of ranching. Irrigation typically starts in May and continues through September (Art Hayes, written personal communication November 18, 2014). Much of the valley floor along Otter Creek is sub-irrigated hay (plant roots reach the water table) with few diversions or sprinklers adding water to the soil surface. Most land along the Powder River is used as pasture for cattle but several hay fields are also harvested. Irrigation along the Powder River valley floor is through a combination of ditch diversions from the river and center pivot sprinklers using surface or groundwater.
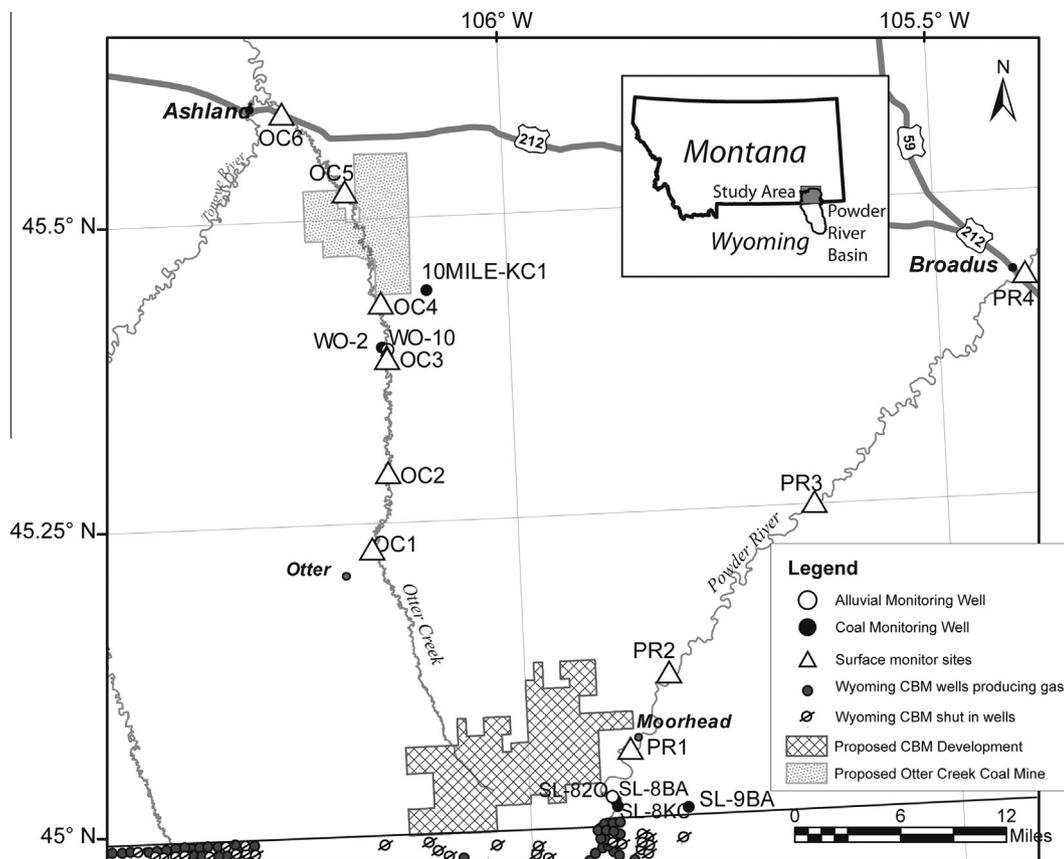

Fig. 1. The study area includes Otter Creek and the Powder River in southeastern Montana.

1.4. Sample sites

1.4.1. Otter Creek

Quantifying the groundwater contribution to Otter Creek is of particular interest because of the proposed open-pit coal mine in the valley (MT DNRC, 2010) (Fig. 1). Currently there is no CBM development in the Otter Creek watershed, but there is a plan for CBM development in its upper tributaries (MT DNRC BOGC, 2013). The Otter Creek study site spans a 70 km reach from Otter to Ashland, Montana where the creek joins the Tongue River. Otter Creek sites OC1 through OC6 were sampled in winter of 2013 (Fig. 1). Meredith and Kuzara (2012) presented a methods paper on the development of carbon isotopes for baseflow quantification using carbon isotope analyses of samples collected in 2010 at these same sample sites.

The perennial reach of Otter Creek begins just north of Otter and crosses several coals including those that make up the Knobloch coal zone. Where the coal comes together in one unit it is approximately 15 m (50 feet) thick. The thickest subunit of the coal zone crops out just south of Ashland near sample site OC5. The Otter Creek alluvium varies from 6 to 10 m thick (20–30 feet) along the sampled reach.

1.4.2. Powder River

The Powder River has its headwaters in the Bighorn Mountains of Wyoming, crosses the border from Wyoming into Montana near Moorhead, Montana and meets the Yellowstone River near Terry, Montana. All CBM development along the Powder River is in Wyoming, including areas just south of the Montana/Wyoming state line (Fig. 1). The sampled river reach crosses many thin coals; the thickest named coals are the Brewster-Arnold and Knobloch. The Powder River sampled reach was approximately 100 km, beginning near the state line. A long river reach was sampled because there were few coal aquifer wells completed near coal outcrops and few thick coals.

The Powder River valley has been the target for extensive USGS coal-resource assessment drilling that identified many thin coals; few exceed 3 m (10 feet) in thickness. The thickest coal is the Brewster-Arnold at 4.9–5.5 m (16–18 feet). Monitoring wells installed by the MBMG at sites SL8 and SL9 (Fig. 1) provide the most information on coals near the Powder River where it crosses the state line.

2. Methods

Samples for geochemical analysis were collected at surface water sites and from wells completed in coals of interest (Fig. 1). Surface water samples were collected during low flow periods in November and December after the first killing frost shut down transpiration from surrounding vegetation and when irrigation

was no longer occurring (Fig. 2). Post irrigation season sampling reduced or eliminated the influence of irrigation return flows. There were no perennial tributaries to account for along the monitored stream reaches.

To avoid issues associated with geographic variability of groundwater geochemistry in coals, wells close to where coals subcrop to the alluvium were sampled. This ensured the best representation of the groundwater end member in geochemical mixing calculations. Additional selection criteria included well completions that isolated the coal from other aquifers. Groundwater samples were collected in fall or winter. Prior to sample collection, wells were purged so that at least three casing volumes of water were removed and field parameters were stable. Field parameters of specific conductance, pH, and temperature were measured in the field using a YSI Professional Plus multiparameter meter calibrated according to factory specifications. Samples were collected, processed and stored based upon laboratory protocol. Analysis included major and minor constituents, and isotopes of carbon and strontium.

The MBMG Analytical Laboratory analyzed samples for fluoride concentrations using a Metrohm Ion Chromatograph following EPA method 300.0. The detection limit using this method is 0.01 mg/L. The University of North Carolina Geochronology and Isotope Geochemistry Laboratory did the strontium isotope and strontium concentration analyses on a thermal ionization mass spectrometer by isotope concentration and isotope dilution methods, respectively. Standardization is based on the NBS-987 standard. Carbon isotopes in dissolved inorganic carbon were measured by the University of Arizona Environmental Isotope Laboratory using a continuous-flow gas-ratio mass spectrometer. Samples are reacted for greater than one hour with phosphoric acid at room temperature. Standardization is based on NBS-19 and NBS-18 standards. Long term precision for strontium isotope analysis (2 sigma) is 0.00010 from the University of North Carolina laboratory. Analytical precision (1 sigma) for carbon isotope analysis is 0.30 per mil from the Arizona State laboratory.

Surface water flow rates were measured using a Doppler based flow meter using the 0.6 depth method described by USGS (Rantz et al., 1982). At least 20 velocity measurements across the stream, perpendicular to the flow direction, were measured. More measurements were added if more than 10 percent of the total flow was reflected in one measurement. Duplicate measurement sets were made at approximately 1 in 5 sites, the error associated with those measurements was 5 percent, which is the standard error for flow measurement. If ice was present, or otherwise dangerous conditions prevented entering a stream, flow rates were not measured.

Otter Creek samples (OC1–OC6) were collected in November 2013. Samples were depth and width integrated by slowly righting an inverted, clean sample bottle as it was raised through the water column. This process was repeated at least five times across the
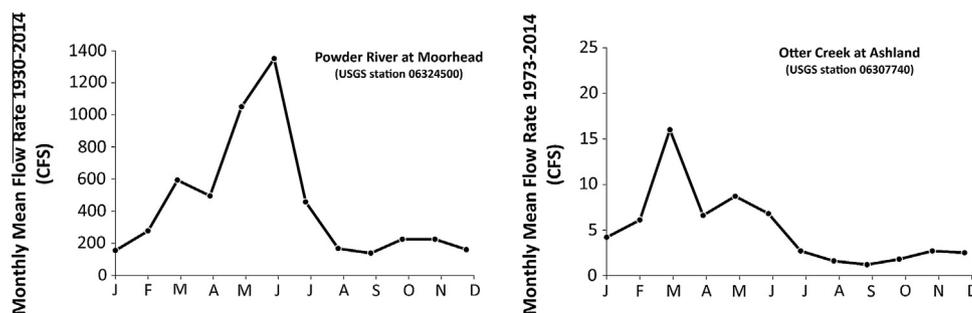

Fig. 2. The monthly mean flow rate (CFS) over the USGS period of record for Otter Creek and the Powder River. Flows in Powder River Basin streams increase in the spring from rain and snow melt, and in the fall after frost shuts down transpiration (USGS, 2015).

creek and the five vertically integrated samples were combined to create one homogenized sample. Groundwater samples were collected from Knobloch coal aquifer wells WO-2 and 10Mile-KC1.

The Powder River was sampled at four locations (PR1–PR4) in December 2013. Grab samples were collected as close to the fastest flowing section of the river as could safely be obtained. Nearby Knobloch and Brewster Arnold coal aquifers were sampled at monitoring sites SL8 and SL9.

All information collected by the MBMG on surface and groundwater is stored on the MBMG Groundwater Information Center (GWIC) database and is publically available at: http://mbmggwic.mtech.edu/. In addition to a common name, wells are identified by their GWIC ID number which links to all associated information including drillers' logs and water chemistry.

3. Theory and calculation

Contributions to a stream from two or more water sources can be quantified using conservative constituents in the water if the concentrations are sufficiently different. However, common ions, including major cations and anions, are generally not conservative. A more robust tracing tool includes using ratios of isotopes in conjunction with concentrations. Calculations of relative contributions from coal aquifers to streams using a two-end member mixing model were done under the following assumptions:

1. The collected groundwater samples accurately reflect the chemistry of groundwater discharging to the river.
2. Non-coal aquifer contributions to the stream are minimal compared to contributions from coal aquifers in the Fort Union Formation.
3. At the time of sampling, groundwater flux in the alluvial aquifer is at steady-state with the surface water.
4. At the time of sampling, surface runoff to the streams from recent precipitation is minimal.

In-stream flow for a measured stream reach is considered to be a mixture of two end-members: the up-gradient surface water and the groundwater contribution (Fig. 3). The equation used to calculate the fractional contribution of coal aquifer groundwater to a

stream using conservative-ion concentrations (e.g. chloride, fluoride) is:

$$X\left(\frac{mg}{L}\right)_{Mix} = X\left(\frac{mg}{L}\right)_{Coal} f_{Coal} + X\left(\frac{mg}{L}\right)_{Upgradient}(1 - f_{Coal}) \quad (1)$$

where X_{Mix}, X_{Coal}, and $X_{Upgradient}$ are the concentrations in mg/L of an ion in surface water downgradient from coal aquifer contributions, in coal aquifer groundwater, and in surface water upgradient from the coal aquifer contribution, respectively (Fig. 3).

If the ion concentration is known for these three water samples, and the upgradient and coal aquifer concentrations of a conservative constituent are sufficiently different, Eq. (1) can be solved for the fraction of water that originated from the coal aquifer, f_{Coal}.

Isotopic mixing equations account for both the concentration of the ion and the isotopic ratio of the ion. For example, the carbon isotope mixing equation is:

$$\delta^{13}C_{Mix} = \delta^{13}C_{Coal} f_{Coal} \frac{[DIC]_{Coal}}{[DIC]_{Mix}} + \delta^{13}C_{Upgradient}(1 - f_{Coal})$$
$$\times \frac{[DIC]_{Upgradient}}{[DIC]_{Mix}} \quad (2)$$

where $\delta^{13}C_{Mix}$, $\delta^{13}C_{Coal}$, and $\delta^{13}C_{Upgradient}$ are the delta values of the $^{13}C/^{12}C$ ratio of dissolved inorganic carbon (DIC) in the surface water downgradient from coal aquifer contributions, in the coal aquifer groundwater, and in surface water upgradient from coal aquifer contributions, respectively.

$[DIC]_{Mix}$, $[DIC]_{Coal}$, and $[DIC]_{Upgradient}$ are the concentrations, in mg/L, of dissolved inorganic carbon (DIC) in surface water downgradient from coal aquifer contributions, in the coal aquifer groundwater, and in surface water upgradient from coal aquifer contribution, respectively.

If the concentrations and isotope ratios of DIC are known for these three water samples, this equation can be solved for the fraction of water contributed by the coal aquifer, f_{coal}. The concentrations and isotope ratios of strontium in the water can be substituted into this equation.

It is important to specify that the calculated value f_{coal} is only that fraction of coal aquifer water contributed over the measured reach, not the total amount of coal aquifer water in the stream. In Powder River Basin streams, the upstream sample will likely already have a component of coal aquifer groundwater.

4. Results

4.1. Otter Creek

In downstream Otter Creek samples, strontium isotope ratios decrease and carbon isotope ratios increase, reflecting the increasing contribution from the Knobloch coal aquifer that was sampled at well WO-2 (Table 1, Fig. 4A). Changes in isotope ratio are particularly pronounced as the creek crosses the large Knobloch coal outcrop near sample site OC5 (Fig. 4B).

Isotope analysis improves understanding of other components of the hydrologic system. Samples collected at OC2, near the confluence of Otter Creek and Taylor Creek, show the influence of an additional water source (Fig 4A). Although there was no surface water flowing in Taylor Creek in November and December, isotopic evidence suggests it as a source of subsurface alluvial flow to Otter Creek.

Monitoring wells WO-2 and 10Mile-KC1, completed in the Knobloch coal, produce groundwater with very different geochemistry and isotopic fingerprints (Table 1). While the strontium isotope ratios are similar, the strontium concentration of water from 10Mile-KC1 is much greater than that from well WO-2. The carbon isotope ratio is positive in sample WO-2 and negative in
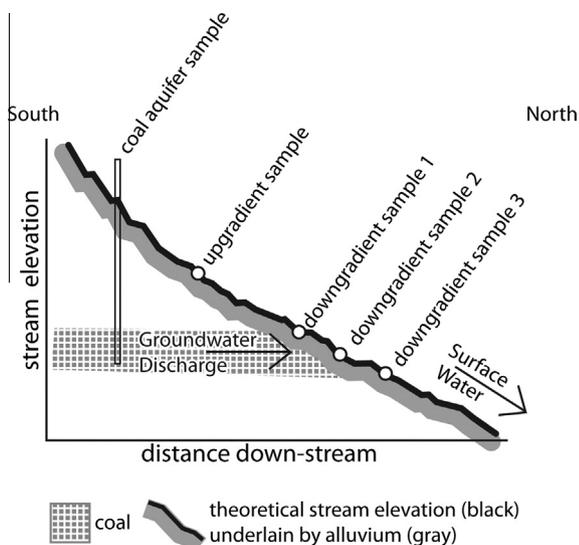

Fig. 3. Surface water samples were collected from above, adjacent, and below coal subcrop areas. Groundwater samples were collected as close to subcrop as possible. The two endmembers of the mixing calculations, outlined in Eqs. (1) and (2), are the coal aquifer sample and the upgradient sample.

Table 1
Otter Creek and associated coal aquifer isotope and field parameters.

|	Site name	GWIC ID	Sample date	d^{13}C	DIC (mg/L)	^{87}Sr/^{86}Sr	Sr (mg/L)	Flow rate l s^{-1} (CFS)	SC (µS/cm)	T (°C)	pH	F (mg/l)
Otter Creek near	OC1	259296	11/6/2013	−7.4	70.7	0.709577	2.33	–	3970	3.9	7.9	0.71
Knobloch Coal	OC2	7910	11/6/2013	−2.3	37.2	0.709616	1.83	39 (1.38)	3495	3.1	8.4	0.74
Outcrop	OC3	259300	11/6/2013	−7.1	67.7	0.709615	1.94	44 (1.55)	3701	3.8	8.5	0.78
	OC4	259302	11/6/2013	−6.8	56	0.709598	1.90	70 (2.49)	3747	3.3	8.6	0.77
	OC5	259304	11/6/2013	−6.3	65.8	0.709442	1.93	–	3730	2.7	8.6	0.74
	OC6	259306	11/6/2013	−5.8	68.4	0.709258	1.80	136 (4.8) USGS	3342	4.2	8.9	1.12
Knobloch Coal	WO-2	7781	10/16/2013	3.7	58.9	0.708402	0.111	–	993	12.2	8.6	2.58
	10Mile-KC1	276654	10/16/2013	−12.3	69.1	0.708401	5.03	–	4020	12.9	6.6	0.72
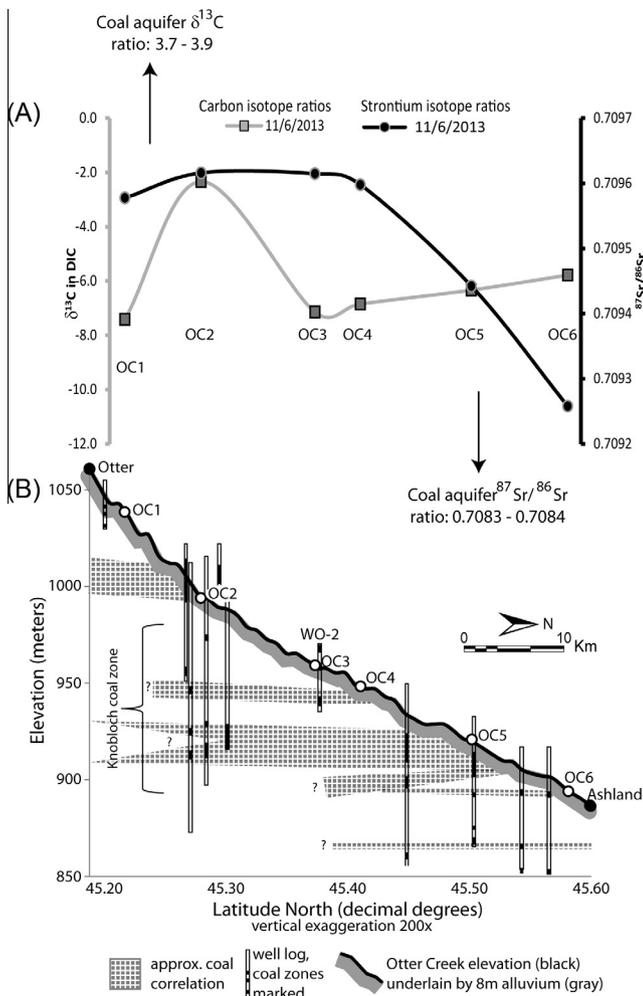
Fig. 4. The Knobloch coal is approximately 15 m thick where it subcrops to Otter Creek. Surface water samples were collected at locations OC1–OC6. Knobloch coal groundwater samples were collected from monitoring well WO-2. The cross-section is based on drillers' logs from wells with GWIC IDs (from south to north): 224416, 176321, 104244, 258141, 104238, 104230, 7781 (WO-2), 236191, 262615, 261932, and 235849. The carbon isotope ratio increases, and the strontium isotope ratio decreases, as Otter Creek crosses the Knobloch outcrop. The Knobloch coal aquifer groundwater in this area provides a higher carbon isotope ratio and lower strontium isotope ratio as compared to surface water.

10Mile-KC1. Water from well WO-2 is sodium-bicarbonate type, which is typical of coal aquifers in the Powder River Basin, but water from 10Mile-KC1 is sodium-sulfate type, similar to that of Otter Creek and alluvial aquifer (GWIC, 2015). The sulfate dominated anion chemistry at well 10Mile-KC1 is an indication of a different

flow path than that of groundwater at site WO-2, which has bicarbonate dominated anion chemistry (Brinck et al., 2008; Van Voast and Reiten, 1988; Wheaton et al., 2008).

Wells WO-2 and 10Mile-KC1 present a good example of the importance of sampling wells as close to subcrop as possible to get representative samples of groundwater contributions to streams. Because of its proximity to the streambed, samples collected from well WO-2 are taken to be the most representative of coalbed contributions to the stream.

Standard field measurements of flow, salinity, and temperature did not correlate to increasing coal aquifer baseflow with downstream distance (Table 1). Increased contribution of coal aquifer groundwater should cause the surface water to be warmer and more saline as the creek crosses the coal outcrop. However, there was no consistent change in the salinity or temperature in downgradient stream samples. While measured temperature did not show a consistent change, it was noted during field work that the frozen stream was open at two locations, potentially indicating the addition of warm groundwater at those sites. Downgradient pH did change in response to additional baseflow, eventually becoming similar to the pH of the coal aquifer measured at WO-2.

Otter Creek alluvial water levels in well WO-10 are near the elevation of the creek. Alluvial aquifer behavior is discussed in more detail in Meredith and Kuzara (2015). The elevation of Otter Creek near well WO-2 is 957.7 m above mean sea level (amsl), and the water level elevation in the Knobloch coal in well WO-2, at the time of sampling in 2013, was 958.4 m amsl. The slight upward gradient implies that the Knobloch could be contributing to the surface flow of Otter Creek (GWIC, 2015; Meredith and Kuzara, 2015).

4.2. Powder River

In downstream samples on the Powder River, the strontium isotope ratio becomes progressively lower, and the carbon isotope ratio progressively higher, reflecting additional contribution to the stream from coal aquifers (Table 2, Fig. 5A). Although the progressively lower downstream strontium isotope ratios present a clear trend toward ratios from coal aquifer water, the trend in carbon isotope ratios is less clear. The steepest gradient in strontium and carbon isotope ratio change occurs between samples sites PR1 and PR3, reflecting the effect of the numerous small coals that outcrop near the Wyoming-Montana boarder (Fig. 5B). The Brewster-Arnold and the Knobloch coals' subcrops to alluvium along the Powder River are not well mapped, but coal exploration drilling by the USGS provides an indication of where along the river the coals may be expected to outcrop (Fig. 5B; McLellan et al., 1990).

There was an initial rise in the carbon isotope ratio from sample site PR1 to PR3 as would be expected from coal aquifer baseflow; however, the ratio slightly decreased in PR4 (Fig 5A). There are few mapped coals between sample sites PR3 and PR4 and carbon isotopes in open water will equilibrate with the carbon in the

Table 2
Powder River and associated coal aquifer isotope and field parameters.

|	Site name	GWIC ID	Sample date	d13C	DIC (mg/L)	87Sr/86Sr	Sr (mg/L)	Flow rate l s⁻¹ (CFS)	SC (μS/cm)	T (°C)	pH	F (mg/l)
Powder River near	PR1	276144	12/2/2013	2.8	56.5	0.711129	1.24	7080 (250) USGS	1679	1.6	8.6	0.38
Fort Union Coal	PR2	276145	12/2/2013	3.1	55.9	0.711086	1.21	–	1637	1.4	8.5	0.37
Outcrops	PR3	276146	12/2/2013	3.4	60.9	0.711067	1.20	–	1713	1.5	8.6	0.37
	PR4	276147	12/2/2013	3.2	62.8	0.711050	1.19	–	1774	0.4	8.5	0.36
Brewster-Arnold	SL8-BA	277327	10/22/2013	15.9	138	0.709148	0.253	–	2026	11.8	7.8	1.05
Coal	SL9-BA	259683	10/23/2013	10.4	30.5	0.709483	0.117	–	1192	13.7	8.8	1.47
Knobloch Coal	SL8-KC	277326	10/22/2013	8.6	79.0	0.709280	0.116	–	1350	16.7	8.3	1.83
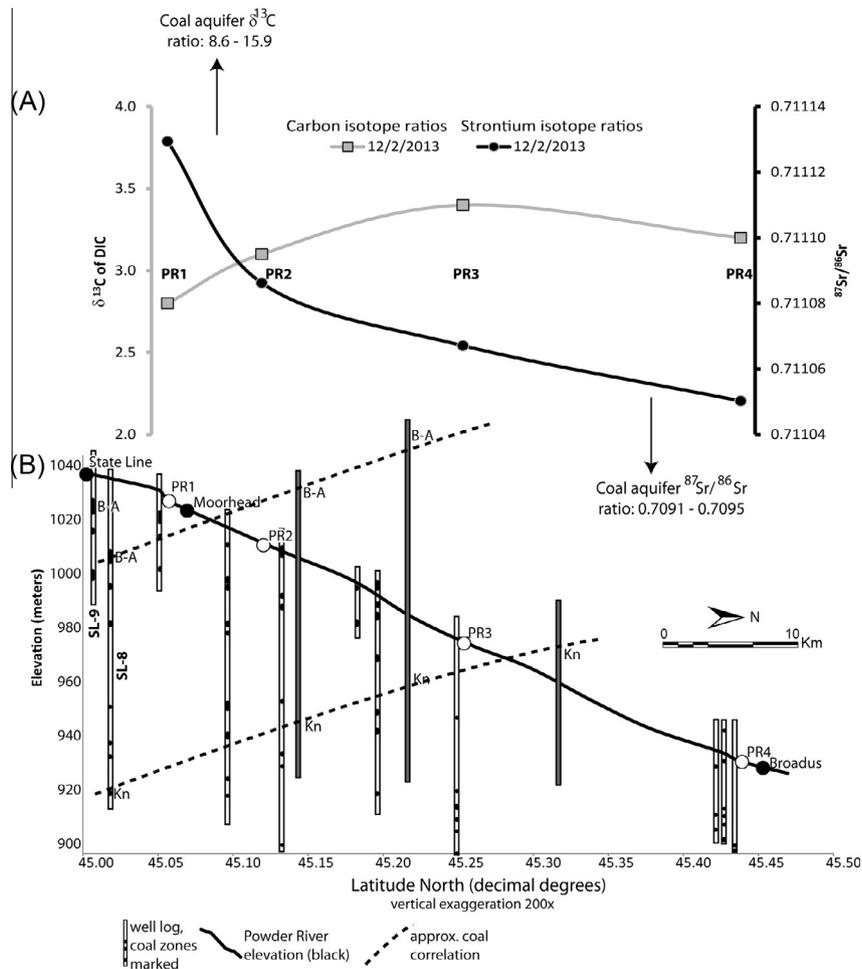
Fig. 5. Well logs indicate multiple thin coals present near the Powder River; however, no surficial coal is visible along the Powder River in Montana. Where coal names have been noted on the log, they abbreviated B-A for Brewster-Arnold and Kn for Knobloch. Wells depicted in grey are from McLellan et al. (1990) noting just the elevations of these two coals. The approximate correlation of the coals is shown by dashed lines. The cross-section is also based on drillers' logs from wells with GWIC IDs (from south to north): 259676 (SL-9), 277326 (SL-8), 257893, 258500, 258499, 257866, 257864, 258490, 167947, 254719, and 263426. Brewster-Arnold and Knobloch coal aquifer wells were sampled at monitoring sites SL-8 and SL-9. The carbon and strontium isotope ratios of the Powder River become progressively more like that of coal-aquifer groundwater as the river flows from the state line to Broadus.

atmosphere; these factors that may act to decrease the isotope ratio at PR4 down from that of PR3.

The samples from SL8 and SL9 Brewster-Arnold coal aquifer wells had measurably different strontium and carbon isotope values (Table 2). These wells are 10 km apart and the cross section (Fig. 5B) shows there is an elevation offset that could restrict hydrologic continuity. This is another example of the importance of well location in selecting sample sites for end-member mixing analyses. Because the coal aquifer samples are intended to represent the many thin coals that the river crosses, the average of the SL8 values were used in mixing calculations.

The salinity of the Powder River is generally similar to or above the salinity of the coal aquifers that subcrop to the river (Table 2). Therefore, in this watershed, salinity is a poor tracer of groundwater – surface water interaction. The temperature of the water was not significantly changed from the upgradient sample to the downgradient sample and is probably primarily controlled by the size of the river, which gets smaller downgradient as more surface flow moves into the alluvium. The field parameter of pH did not change in the river. Measuring flow rates in December is complicated by ice, which impedes accurate flow measurements and can make entering the river hazardous.

5. Discussion

Conservative tracers identified in the literature as being minimally affected by ion interactions include silica (SiO_2), chloride (Cl), and fluoride (F) (Barthold et al., 2010; O'Brien and Hendershot, 1993). In Otter Creek and the Powder River, silica and chloride concentrations in coal aquifers are similar to surface water, so were not useful tracers (GWIC, 2015). Fluoride appears to be a useful tracer in Otter Creek where concentrations increased downstream in response to contributions from the coal aquifer (Table 1). Fluoride concentrations changed very little in downstream Powder River samples, and the measured change of 0.02 mg/L is near the analytical detection limit of 0.01 mg/L (Table 2).

The percent contribution from coal aquifers was calculated for the streams using Eq. (1) for fluoride and Eq. (2) for carbon and strontium isotope tracers (Table 3). The endmember values used in Otter Creek calculations were from well WO-2 to represent the groundwater endmember, and from OC1 to represent the upgradient endmember. The values from OC6 represent the downgradient, mixed sample. The groundwater values used in Powder River calculations were the average of the two coal aquifer samples collected from monitoring site SL8, the site closest to the river. The upgradient values used were from site PR1. The downgradient, mixed samples were from PR3, to minimize the effect of atmospheric equilibration. Only the mixing results from the most downgradient sample is presented to indicate the maximum potential baseflow.

The compared methods resulted in calculated contributions that varied by 0.6–7 percentage points (Table 3). Using the average percent calculations and flow rates measured at the USGS gauging stations at Moorhead and Ashland (Tables 1–3; USGS, 2015) the contributions from coal aquifers were 275 and 28 l s^{-1} (9.7 and 1.0 CFS) for the Powder River and Otter Creek, respectively. This represents an estimate because it does not account for environmental influences on the carbon isotope ratio (e.g. atmospheric equilibration), which would make the computed contribution appear less, nor does it account for other potential groundwater sources, such as sandstones, that would cause the calculated contribution to overstate the actual amounts. As was stated in the assumptions, it is predicted that sandstone contribution will be minimal from the Fort Union Formation.

Commonly used tracers of temperature and salinity in groundwater/surface water interaction studies had limited success in Powder River Basin streams. The contribution of warm groundwater to the cold surface water is especially evident in winter, but was only measureable in Otter Creek. In both streams, the salinity difference between the groundwater and surface water was not pronounced enough to create a downgradient trend in salinity (Tables 1 and 2).

5.1. Conclusions

Groundwater withdrawal during CBM and coalmine production has the potential to reduce groundwater baseflow to streams. The volume of water contributed by coal seams to surface drainages in the Powder River Basin was, for most watersheds, completely unknown, which created discord between the many water users in both Montana and Wyoming. Depending upon focus, area stakeholders wish to preserve in-stream flows, groundwater availability, senior water rights, and/or resource development. Additional divergence in priorities stems from Montana's requirement for a water right prior to putting CBM-produced water to beneficial use, such as irrigation. However, for industry to acquire a water right, it must be shown that the development will either not adversely impact down-gradient water users, or water users who are impacted will be compensated (MCA 85-2-501 et. seq.). The presence or magnitude of impact is difficult or impossible to show without a better understanding of the relationship between coal aquifers and surface streams in the Powder River Basin.

Isotopic tracing of coal aquifer contributions to streams was successfully applied to two watersheds in the Powder River Basin: Otter Creek and the Powder River.

Otter Creek: Both carbon and strontium isotopes indicate an increased proportion of coal aquifer baseflow in Otter Creek as it crosses the Knobloch coal outcrop. Otter Creek is an ideal candidate for the baseflow measurement methods presented here because it is small, which makes the contribution of coal aquifer baseflow proportionally larger, and it crosses a large coal outcrop. The measured coal baseflow contribution to Otter Creek was 28 l s^{-1} (approximately 21%). On a small creek system such as Otter Creek, this amount of water can make a difference as to whether the stream flows along its entire length in winter.

Powder River: The Powder River crosses numerous coals less than 3 m thick. Sampling the Powder River along a 100 km reach captured the contributions of these thin coals. Additionally, there are no surface tributaries contributing to this reach of the Powder River in December, when the sampling took place. For this study site, strontium proved to be a more sensitive tracer of coal aquifer groundwater contributions than did carbon because carbon isotope values of the Powder River was already similar to coal aquifer baseflow at the upstream end of the sampled reach. The measured coal baseflow contribution to the Powder River was 275 l s^{-1} (approximately 3.9%). Though small in terms of percentage, in a semi-arid, agricultural landscape, all water is a valued commodity.

Two additional nearby streams, the Tongue River and Hanging Woman Creek, were also measured as part of this study. However the isotopic tracing method presented here was not successful because the groundwater contribution did not exceed the measurement threshold.

Tongue River: The flowrate of the Tongue River rarely falls below 2800 l s^{-1} and previous work (Woessner et al., 1981) measured baseflow along this reach, crossing two large coals, as 4–16 l s^{-1}. This does not exceed the measurement threshold of the strontium and carbon isotopic signature of the coal groundwater.

Hanging Woman Creek: This under-fit stream has very high natural salinity compared to most surface water in the Powder River Basin. The thick saturated alluvium dilutes the baseflow addition and high salinity masks its chemical signature.

Additional details about these streams can be found in Meredith et al. (2016).

This study showed that traditional methods of baseflow measurement are often ineffective in semi-arid streams with large alluvial valleys. In some settings, however, geochemical tracers can provide a powerful tool for baseflow studies that overcome the limitations of traditional methods. Additionally, this study

Table 3
The percent contribution of coal aquifer baseflow to streams by tracer.

	Powder River at PR3	Otter Creek at OC6
Strontium Isotope	3.6%	24%
Carbon Isotope	4.2%	17%
Fluoride	–	22%
Average	3.9%	21%

illustrated the importance of site selection when sampling groundwater endmembers.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2016.03.042. These data include Google maps of the most important areas described in this article.

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