ground water

Detecting Infiltration and Impacts of Introduced Water Using Strontium Isotopes

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Abstract

Water introduced to surface drainages, such as agricultural and roadway runoff, mine drainage, or coalbed natural gas (CBNG)–produced water, potentially can be of environmental concern. In order to mitigate potential environmental effects, it may be important to be able to trace water discharged to the surface as it infiltrates and interacts with near-surface aquifers. We have chosen to study water withdrawn during CBNG production for isotope tracing in the hyporheic zone because it poses a variety of economic, environmental, and policy issues in the Rocky Mountain states. Ground water quality must be protected as CBNG water is added to semiarid ecosystems. Strontium (Sr) isotopes are effective fingerprints of the aquifer from which water originates. In this study, CBNG water was found to have a higher $^{87}Sr/^{86}Sr$ ratio than the local alluvial aquifer water. This measurable difference allows the strontium isotope ratio and concentration to be used as tracers of CBNG water following its discharge to the surface. The dissolution and mobilization of salts from soil are an important contributor to ground water quality degradation. In the Powder River basin of Wyoming, the soils are calcium carbonate–buffered systems. The chemical similarity of strontium to calcium allows it to substitute into calcium minerals and enabled us to use strontium isotopes to identify calcium salts mobilized from the soil. Strontium isotopes are an effective monitor of the source of ions and the volume and direction of introduced water flow in the hyporheic zone.

Introduction

The importance of the interface between surface water and ground water, known as the hyporheic zone, is becoming increasingly recognized for its role in biologic and abiotic processes. Hyporheic zone processes influence stream water quality as well as the health of the surrounding riparian zone (Boulton 2000; Conant 2004; Harvey et al. 2003). The water retention in hyporheic zones enables water contact with periphyton biofilms and geochemical coatings (Harvey et al. 2003). Biofilms filter dissolved oxygen, increase nutrients, and participate in denitrification, potentially significantly altering water

chemistry (Boulton 2000). Additionally, in situations where ground water contaminants threaten streams, it is important to be able to measure direction and magnitude of water flux in hyporheic zones (Conant 2004).

Current methods of measuring the exchange between surface water and ground water in the hyporheic zone, including dyes, temperature, solute, and geochemical tracers, are limited by physical and chemical parameters. Temperature studies are limited to situations where there is a large difference in the temperature of the streambed, ground water, and surface water (Conant 2004) and often have to be used in conjunction with hydraulic head and geochemical measurements (Anderson 2005). Geochemical studies that consider only ion concentrations are limited by the large variation ground water often exhibits within a stream reach (Conant 2004). For example, an intermediate concentration of a particular ion such as chloride may be interpreted as either ground water with a midrange concentration or a mixture of high-concentration ground water and low-concentration surface water.

Strontium isotopes have been used in water mixing studies for many years, including lake/ground water

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interaction (Katz and Bullen 1996; Lyons et al. 1995; Ojiambo et al. 2003), river/ground water flowpaths (Johnson et al. 2000; Katz et al. 1998), and ground water/ground water mixing (Frost and Toner 2004; Lyons et al. 1995). This study introduces the use of strontium isotopes as an alternative method for studying the interaction of introduced surface water and ground water within the hyporheic zone, where "introduced water" is considered to be water with distinctive chemical and/or isotopic composition discharged onto and interacting with existing surface systems.

Many situations exist where it would be useful to monitor and track the introduction of water to a surface drainage and the associated hyporheic zone because of either potential environmental concern or water resource investigations. In several of these circumstances, the introduced water has a high probability of having a unique strontium isotope ratio as compared to the local surface and near-surface ground water due to its geologic origin or anthropogenic additives. Many studies have looked at the potential for contamination of watersheds by roadway runoff. Potential sources of pollution include heavy metals, polycyclic aromatic hydrocarbons, sediment, and, in some developing countries, sewage (Koeleman et al. 1999; Lottermoser 1998; McAlister et al. 2000; Turer et al. 2001; Watts and Smith 1994). Similarly, agricultural runoff is of high concern in many areas. The potential for contamination from fertilizer nutrients, pesticides, and herbicides is well studied (Dougherty et al. 2006; Smith et al. 1993), including several isotope studies, some of which have used strontium isotopes to identify the presence of fertilizer inputs (Bohlke and Horan 2000; Magner and Alexander 2002; Martin and McCulloch 1999).

The potential for using strontium isotopes to fingerprint springs, leaking water mains, and geothermal waters has been demonstrated but not widely explored in hyporheic zone studies (Bahati et al. 2005; Barbieri and Morotti 2003; Leung and Jiao 2006; Siegel et al. 2004). An obvious application where introduced water poses a potential environmental concern is mine drainage. Acid drainage has been characterized by hydrogen and oxygen isotopes (Hazen et al. 2002) and strontium concentration (Davidson et al. 2005) and could potentially be characterized by strontium isotopes as well. However, strontium isotopes will not always fingerprint mine waters because they can interact with the same lithologies as surface water as shown by Verplanck et al. (2001). Mine drainage in Colorado was shown to have an indistinguishable $^{87}Sr/^{86}Sr$ ratio from the local water. Of growing interest in the Rocky Mountain states is the addition of coalbed natural gas (CBNG)–produced water to surface water systems. Due to its origin in deep coal aquifers, CBNG water is likely to have a unique, traceable strontium isotope ratio. We have used CBNG-produced water discharged to the surface to study the potential for using strontium isotopes to track the fate of introduced water to surface drainages.

CBNG is extracted from coal seams, and in 2005, the Powder River basin of northeast Wyoming and southeast Montana (Figure 1) produced 335.8 billion cubic feet (9.508 billion cubic meters, ~344.9 trillion BTU) of natural gas from 17,069 wells (Wyoming Oil and Gas
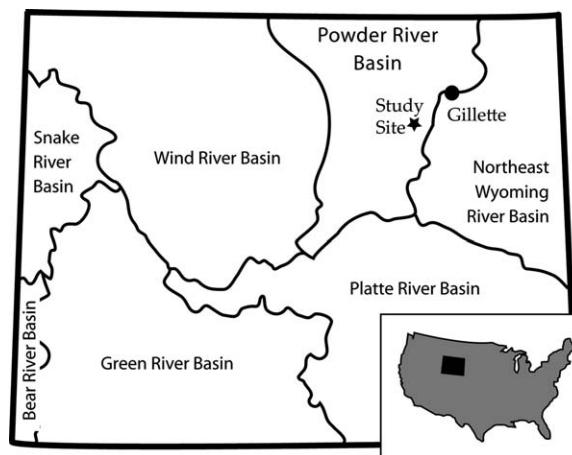

Figure 1. Wyoming river basins including the starred location of the study site (from Wyoming State Water Plan). Inset is the location of Wyoming within the continental United States.

Conservation Commission, no date). In the Powder River basin, the coal seam is depressurized by the removal of the coal aquifer water which allows the dissolved and adsorbed natural gas to come out of solution and be collected (DeBruin et al. 2004). The aquifer water is pumped to the surface through a central pipe, while the natural gas is collected in an annular pipe. Water can be reinjected, but in Wyoming's Powder River basin, most is discharged to the surface. In 2005, the Powder River basin produced 88.62 billion liters of water during CBNG production (Wyoming Oil and Gas Conservation Commission, no date). The total projected water produced over the life of CBNG production in the Powder River basin is 7 trillion liters (DeBruin et al. 2004). Water disposal is therefore an important environmental, agricultural, and legislative issue.

The Powder River basin is a semiarid basin that receives an average of 42 cm of rain annually with average daily temperatures from 1961 to 1990 ranging from −6°C in January to 21°C in July (Natural Resources Conservation Service [NRCS] 2004). Discharging CBNG-produced water to the surface in the Powder River basin introduces warm, approximately 20°C, sodium bicarbonate–dominated water, with total dissolved solid (TDS) concentrations ranging from 600 to 3000 mg/L (Rice et al. 2002), to this semiarid watershed. CBNG water is discharged to the surface in a variety of ways, including irrigation, off-channel impoundments, and on-channel impoundments (King 2006). On-channel impoundments are excavated ponds within existing drainages. Pond water is kept at a predetermined volume by allowing excess water to flow overland through the channel. Two of these ponds are the focus of this study. The addition of CBNG water is often to ephemeral drainages, as in this study. This introduced water creates a perennial stream with a corresponding perennial hyporheic zone. The ecology associated with the hyporheic zone in this situation has not been studied extensively, but it is clear that vegetation in the associated riparian areas is highly susceptible to change, both in species composition and in biomass due to increased water availability as well as changes in soil properties such as increased salinity (excess of soluble salts), sodicity (sodium ions on the

exchange complex), and pH (Essington 2004; Micale and Marrs 2006; Stearns et al. 2005; Zou et al. 2006).

In addition to the potential biological and geochemical changes one would expect with the addition of CBNG-produced water to semiarid drainage basins, other topics of concern include rate and location of recharge to aquifers and the impacts of discharged CBNG water upon drainages and soils (Rice et al. 2002). Additional considerations include Wyoming Department of Environmental Quality regulations that require the class of ground water be protected in all situations. Investigating these concerns requires a tool to identify and monitor the aquifers and hyporheic zones impacted by CBNG-produced water as well as monitor the influence of semiarid soils upon ground water quality in these zones.

The first step in addressing these concerns is to identify the specific aquifers with which the discharged water is interacting. This can be accomplished by tracking the CBNG water as it is discharged into ponds and surface drainages and infiltrates into the shallow ground water system. It has been shown that water originating from distinct geologic settings may have unique chemical characteristics that can be used to trace the source of the water (Clark et al. 2001). However, geochemical concentration measurements, even in addition to stable isotopic ratios of oxygen and hydrogen, are insufficient to distinguish ground water in coal aquifers from sandstone aquifers in the Powder River basin (Frost et al. 2002).

Strontium (Sr) isotopes, however, have been shown to be effective tracers of aquifer interactions (Frost and Toner 2004). The daughter product of radioactive decay is referred to as "radiogenic"; in the case of ^{87}Rb decay, it results in the stable, radiogenic isotope ^{87}Sr. The strontium concentration in conjunction with the ratio of the stable, radiogenic isotope ^{87}Sr to the naturally occurring stable isotope ^{86}Sr has been shown to be an effective fingerprint that distinguishes coal seam water from other ground and surface water. Strontium is an appealing candidate for isotopic tracing because it does not fractionate during evaporation or precipitation and small variations in the $^{87}Sr/^{86}Sr$ ratio can be measured precisely (± 0.00002). Ground water obtains strontium through its interaction with aquifer material and therefore has as great a range of $^{87}Sr/^{86}Sr$ ratios as does geologic material. The natural variation in the $^{87}Sr/^{86}Sr$ ratio in geologic material is caused by the beta decay of ^{87}Rb into the stable isotope ^{87}Sr. The concentration of the ^{87}Sr isotope in geologic material will be determined by its age and original concentration of ^{87}Rb (Faure 1998). Therefore, when applying this tool to the interaction of CBNG-produced water with near-surface ground water, it is likely that the deep, coal aquifer will have a measurably different ratio than that of shallow, alluvial aquifer. This situation is true in the Beaver Creek area near Gillette, Wyoming, where the CBNG-produced waters have a higher average $^{87}Sr/^{86}Sr$ ratio of 0.7142 (0.00041) than the alluvial aquifer's average ratio of 0.7127 (0.00012) (1 standard deviation is in parentheses).

While natural processes such as evaporation, precipitation, and biological uptake do not change the $^{87}Sr/^{86}Sr$ ratio in water, this ratio can be changed when water interacts with the surface environment. Dissolution of salts and cation exchange with clays can alter the $^{87}Sr/^{86}Sr$ ratio, with cation exchange often occurring very rapidly (Johnson and DePaolo 1997a, 1997b). The strontium isotope ratio associated with the salts and clays will alter the original $^{87}Sr/^{86}Sr$ ratio of the introduced water. These processes have to be accounted for when using strontium isotopes as tracers because the strontium isotope ratio is not immutable and therefore not a permanent "fingerprint" in surface environments.

It has been shown that the Powder River basin coal and sandstone aquifers have distinctive strontium isotopic compositions that successfully fingerprint these aquifers, whereas other stable isotopes and major ion chemistry have not (Frost et al. 2001, 2002). This study has applied strontium isotopes as a tracer in a situation where deep ground water is discharged to the surface. However, as this study shows, strontium isotopes can be a useful tool in hyporheic zone investigations that involve the interaction of many different types of water sources with measurably different strontium isotope ratios. This technique could potentially be used in roadway and agricultural runoff investigations, spring and geothermal water studies, and tracking acid mine drainage. While the $^{87}Sr/^{86}Sr$ ratio is subject to change due to interactions with the environment, we have shown that changes to both the strontium isotope ratio and the strontium concentration can be used to investigate geochemical processes resulting from the introduction of CBNG water to the surface.

Trace element studies of CBNG-produced water and the associated on-channel ponds and impacted creeks show that aluminum (Al), iron (Fe), arsenic (As), selenium (Se), and fluoride (F) concentrations increase in some ponds, whereas barium (Ba), manganese (Mn), chromium (Cr), and zinc (Zn) decreased in the impoundments. McBeth et al. (2003) correlated these changes to the increase in pH that occurs when the atmospherically isolated CBNG-produced water is introduced to the surface. CBNG-produced water increases in pH when introduced to surface drainages due to the degassing of CO_2 (McBeth et al. 2003; Patz et al. 2006). In general, water with alkaline pH values discharged onto alkaline soils increases the mobility of anionic species such as As, Se, and F. Mobility of these anionic species is controlled primarily through adsorption and desorption onto soil mineral phases that, in this area, primarily have a negative surface charge. Additionally, the increase in pH causes the precipitation of $BaSO_4$, $MnCO_3$, $Cr(OH)_3$, and $ZnCO_3$, resulting in lower Ba, Mn, Cr, and Zn concentrations (McBeth et al. 2003; Patz et al. 2006). The water quality of these ponds is a concern because the water is used by ranch and wild animals. In calcite-dominated soils, like those in much of the Powder River basin (NRCS 2004), strontium is a good candidate to monitor the water quality changes that are due to the dissolution of local salts. Strontium is chemically similar to calcium (Ca) and follows it closely in geological processes.

The objective of this research is to use strontium isotopic tracing to study the fate and impact of CBNG product waters on shallow aquifers and the hyporheic zone. Our study looks at two on-channel CBNG-produced water

disposal ponds in the ephemeral upper reaches of the Beaver Creek area, approximately 80 km southwest of Gillette, Wyoming. This site was chosen due to the aforementioned measurable difference in strontium isotope ratios, as well as the ability to start water sampling within 2 months after CBNG-produced water discharge began in November 2002. We use strontium isotope and concentration data to:

1. Distinguish CBNG water from surface and shallow ground water.
2. Trace the infiltration of CBNG water through the hyporheic zone and near-surface aquifers.
3. Monitor the dissolution of local salts and their mobilization into the ground water.
4. Detect geochemical changes as the atmospherically isolated CBNG water is discharged into the on-channel impoundments.

Local Geology, Site Location, and Experimental Methods

Local Geology

The coalbeds in the Powder River basin are primarily located in the Paleocene Fort Union Formation and the Eocene Wasatch Formation. The coalbeds vary in thickness from a few centimeters to more than 61 m, with the most continuous coalbeds found in the upper part of the Fort Union Formation, the Wyodak-Anderson coal zone (Flores and Bader 1999), including the Big George Coal. Much of the CBNG production in the Powder River basin occurs in this coal zone, including the CBNG production from wells included in this study.

Site Location

This study was performed in an area of increasing CBNG production in the headwaters of the Beaver Creek watershed, a tributary to the Powder River. This ephemeral drainage is approximately 80 km southwest of Gillette, Wyoming (Figure 2). Within a 2-km stretch of this ephemeral drainage, two ponds were excavated within the tributary, including the widening and deepening of an existing stock pond to create the upgradient pond (herein referred to as the upper pond). Water production from CBNG wells began to be discharged into the upper pond on November 20, 2002, while the larger, downgradient pond (the lower pond) began filling 10 d earlier on November 10, 2002. After the upper pond filled (around December 8, 2002; Payne 2004), water began flowing down the once-ephemeral, now-perennial stream channel. Water piped from several (up to five) natural gas wells are combined and discharged from a central pipe at each pond. The specific wells discharging into these ponds vary based on the gas and water production history of each well in addition to the production company's specific goals. All CBNG wells in this area are completed in the Big George Coal. The strontium isotope ratio for the CBNG water has varied with time from 0.71388 to 0.71457, perhaps due to varying combinations of wells or fluctuations in pumping rates. However, the $^{87}Sr/^{86}Sr$ ratio of the produced water
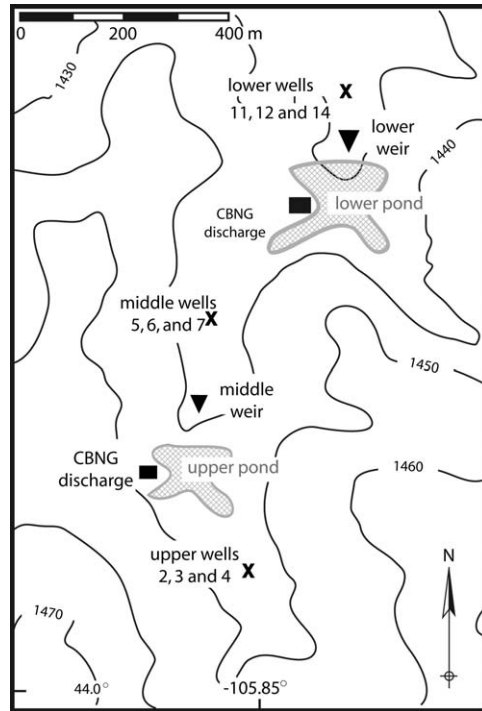

Figure 2. Topographic map of Beaver Creek study site showing the location of the nested well sites (crosses), CBNG discharge points (squares) and the weirs (triangles) from which samples were taken (from Payne and Saffer 2005). Contours are labeled in meters above sea level. Location within Wyoming is marked with a star on Figure 1.

is distinct from water from near-surface aquifers despite these temporal variations in strontium isotope ratio.

The soil in this part of the Powder River basin is classified under the Cambria-Theedle-Kishona association. These medium-textured soils are moderately deep (50 to 100 cm) and very deep (more than 150 cm over bedrock). They have formed on gently sloping to moderately steep (3% to 30%) alluvial fans, ridges, and hills. The soil overlies soft shale and interbedded sandstone and shale. Cambria soils are fine-loamy, mixed, superactive, mesic Ustic Haplargids, whereas Theedle and Kishona soils are fine-loamy, mixed, superactive, calcareous, mesic Ustic Torriorthents. All soil profiles in this area are characterized by Bk (calcareous) horizons (NRCS 2004).

Experimental Methods

Three sets of nested monitoring wells were installed by the Western Research Project Cooperative (Payne and Saffer 2005; Wheaton and Brown 2005). The first set of wells is upgradient from both the CBNG water impoundments (the upper well site), the second set is between the two impoundments (the middle well site), and the third set is downgradient from both impoundments (the lower well site). The upper well site (ambient ground water) allows seasonal sampling of ground water unaffected by the infiltrating CBNG water. The middle well site was placed within the ephemeral channel itself, allowing the investigation of CBNG water's interactions with the hyporheic zone and shallow aquifer below the streambed. The lower well site is slightly off-channel on the floodplain,

enabling the investigation of the interaction of CBNG water with the floodplain soils and off-channel ground water. Additionally, four weirs were installed within the streambed, two of which were used for sampling (Figure 2).

Water sampling of the two CBNG-produced waters, the two ponds, two of four installed weirs, and two wells from each of the three sets of wells began in January 2003, 1 month after the upper pond filled. Sampling continued approximately every 3 months for 3 years. In each of the well locations, samples were collected from two depths—the alluvial layer (~5 m below the ground surface) and the underlying Wasatch Formation (~10 m below the ground surface). The weir samples were collected from the weirs directly below each pond.

Monitoring well samples were collected after two well-casing volumes of water were removed. Water samples from CBNG discharge points, the ponds, and streams were collected using rinsed 2-L containers. Temperature and pH were measured in the field; samples were filtered through a 0.45-μm filter and kept cool and dark until laboratory analysis. Half of each sample was acidified to pH 2 for major ion analysis.

Strontium was isolated from a 3-mL aliquot of each unacidified water sample using Teflon® columns filled with Eichrom® Sr-Spec resin and the strontium isotopic composition determined by thermal ionization mass spectrometry at the University of Wyoming. The internal precision of $^{87}Sr/^{86}Sr$ isotope ratio measurements is ±0.00001. Seventy-six analyses of NBS 987 strontium standard measured during the course of this study gave an average value of $^{87}Sr/^{86}Sr = 0.71026 \pm 0.00002$ (2 standard deviations). All analyses were normalized to an $^{86}Sr/^{88}Sr$ ratio value of 0.1194. Analytical blanks were less than 0.2 ng, negligible compared to sample sizes of at least 0.1 μg strontium. An additional 1-mL aliquot of each sample was spiked with an ^{84}Sr-enriched tracer and strontium concentration determined by isotope dilution. Strontium concentrations are reproducible at the 1% level. Replicates collected in January 2003 show that $^{87}Sr/^{86}Sr$ ratios are reproducible within the error expected from the precision of the instrument, but strontium concentrations vary more than would be expected due to error associated with the analytical processes. These samples were collected while the monitoring wells were being pumped and suggest either that strontium concentration varies as a function of the amount of water pumped from the well or that strontium is not remaining in solution during transport and storage prior to analysis (Table 1).

Major ion concentrations were measured for the entire set of samples from four sampling dates (August 2003, August 2004, August 2005, and February 2005) and 12 samples from lower well 14. Major cations and trace elements were measured by inductively coupled plasma mass spectrometry, sodium (Na) was measured by flame atomic absorption, anions were measured by ion chromatography, and alkalinity was measured by potentiometric titration at the University of Wyoming. TDS was calculated by summing the major ionic constituents and converting bicarbonate into equivalent carbonate (Drever 1997).

Water quality was modeled with Visual MINTEQ (Allison and Brown 1992). This model incorporates

Table 1 Sr Reproducibility		
	January 2003	
	Sr (ppm)	$^{87}Sr/^{86}Sr$
MT BC-4	2.29	0.71262
WY BC-4	1.88	0.71260
MT BC-6	1.59	0.71343
WY BC-6	0.67	0.71344
MT BC-11	4.97	0.71269
WY BC-11	3.35	0.71271
MT BC-14	3.47	0.71282
WY BC-14	3.59	0.71282

Note: Samples labeled MT were taken to Billings, Montana, before being mailed to Laramie, Wyoming, for Sr analysis. Samples labeled WY were taken directly to Laramie, Wyoming.

complete analytical data, including major cation, major anion, and trace element concentrations, pH, and alkalinity. The calculated outputs include the charge balance, ionic strength, chemical speciation, and saturation indices (McBeth et al. 2003). The saturation index is defined as the log of the quotient of the ion activity product and solubility product (K_{sp}). A solution in equilibrium has saturation indices equal to zero. A saturation index greater than zero implies a species that is oversaturated, whereas a negative saturation index implies undersaturation (Drever 1997).

Results

Strontium Isotope Results

Water samples were collected on 13 different dates over a period of 35 months at the Beaver Creek study site (Table 2). The strontium concentration and $^{87}Sr/^{86}Sr$ ratio of the CBNG product water (black squares) and the local ground water monitored at the upper well site (open squares) remained relatively constant throughout the monitoring period (Figures 3A to 3D). The $^{87}Sr/^{86}Sr$ ratio of the CBNG water ranges from a minimum of 0.71388 to a maximum of 0.71457, whereas the local alluvial and Wasatch Formation ground water ranges from a minimum of 0.71255 to a maximum of 0.71279. These values are easily distinguished by thermal ionization mass spectrometry. This distinguishable fingerprint results from the waters' interaction with stratigraphically separated aquifer material of very different composition (coal and alluvium) and allows us to follow the infiltration of the CBNG water.

The on-channel ponds (circles in Figure 3A) in which the CBNG water is collected before it is allowed to run overland show a decrease in strontium concentration from the discharged CBNG water. The stream samples (diamonds in Figure 3B) were collected at two weirs in the stream channel below both ponds. Most of these samples have similar concentrations as the CBNG discharged water but a slightly lower $^{87}Sr/^{86}Sr$ ratio.

Ambient water collected from the upper wells had a constant strontium isotope ratio throughout the 3-year sampling period. However, from the time of the first sampling in January 2003, the middle well site water samples

Table 2
Beaver Creek Sr (ppm) and $^{87}Sr/^{86}Sr$ for CBNG Discharge, Ponds, Streams, and Wells

Stream Location	ID	Depth (m)	January 2003		April 2003		August 2003		October 2003		December 2003		February 2004		May 2004	
			Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$
Upper	Up-CBNG		1.36	0.71401	0.97	0.71411	1.40	0.71388	1.23	0.71391	1.21	0.71391	1.19	0.71402	1.09	0.71397
	Up-pond	0	0.87	0.71397	0.69	0.71402	0.75	0.71394	0.75	0.71394	0.74	0.71393			0.63	0.71397
	BC-2	5.5	1.32	0.71276	2.48	0.71255	1.54	0.71278	1.38	0.71275	1.77	0.71260			1.34	0.71276
	BC-4	9.6	1.88	0.71260	1.63	0.71271	1.90	0.71260	1.80	0.71259	1.10	0.71274			1.88	O.7125B
Middle	M-weir	0	Dry	Dry	1.28	0.71380	0.68	0.71388	0.58	0.71390	0.85	0.71374			0.60	0.71342
	BC-5	11.6	1.70	0.71312					0.85	0.71324	1.02	0.71312			0.95	0.71323
	BC-6	7.9	0.67	0.71344	0.94	0.71346					0.69	0.71329				
	BC-7	7.6					1.19	0.71311	1.09	0.71311					0.93	0.71311
Lower	L-CBNG		1.29	0.71411	0.89	0.71417	1.36	0.71422	1.20	0.71420	1.08	0.71423	1.14	0.71423	1.22	0.71436
	L-pond	0	0.99	0.71403	0.70	0.71410	0.63	0.71415	0.71	0.71416	0.78	0.71416			0.74	0.71428
	L-weir	0			1.02	0.71344	0.75	0.71392	0.65	0.71381	0.91	0.71370			0.62	0.71392
	BC-11	11.6	3.35	0.71271	1.37	0.71274	2.30	0.71278	2.01	0.71276	1.94	0.71271			193	0.71273
	BC-14	4.6	3.59	0.71282	3.57	0.71233	5.2a	0.71289	6.35	0.71287	6.58	0.71289	6.45	0.71287	7.07	0.71239

Stream Location	ID	Depth (m)	August 2004		September 2004		February 2005		May 2005		August 2005		November 2005	
			Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{87}Sr/^{86}Sr$
Upper	Up-CBNG		1.15	0.71415	1.17	0.71420	1.12	0.71415	1.21	0.71402	1.22	0.71399	1.16	0.71400
	Up-pond	0					0.79	0.71405	0.69	0.71396	0.79	0.71401	0.72	0.71398
	BC-2	5.5	1.40	0.71275			1.16	0.71277	1.37	0.71275	1.30	0.71277	1.35	0.71275
	BC-4	9.6	1.75	0.71260			1.57	0.71260	1.73	0.71260	3.74	0.71258	1.87	0.71260
Middle	M-weir	0	Dry	Dry			1.77	0.71330	3.09	0.71299	Dry	Dry	Dry	Dry
	BC-5	11.6	1.03	0.71316			1.15	0.71309	1.10	0.71312	1.06	0.71307	0.95	0.71307
	BC-7	7.6	0.98	0.71310			0.95	0.71307	0.80	0.71305	1.03	0.71305	1.14	0.71311
Lower	L-CBNG		1.26	0.71441	1.29	0.71457	1.05	0.71430	1.19	0.71432	1.21	0.71442	1.13	0.71437
	L-pond	0					0.90	0.71438	0.99	0.71434	0.90	0.71436	0.95	0.71437
	L-weir	0	0.44	0.71382			0.97	0.71372	0.80	0.713B4	0.43	0.71381	Frozen	Frozen
	BC-11	11.6	1.92	0.71272			1.71	0.71274	1.86	0.71272	1.94	0.71273	1.96	0.71272
	BC-14	4.6	7.38	0.71293	6.93	0.71293	7.00	0.71291	7.27	0.71294	7.35	0.71293	6.77	0.71294

Note: Sample identification terms beginning with BC represent monitoring wells. Wells 2 and 4 are in the upper well set, wells 5, 6, and 7 are in the middle well set, and wells 11 and 14 are in the lower well set. Prefixes Up-, M-, and L- represent the sample location within the study of upper, middle, and lower.
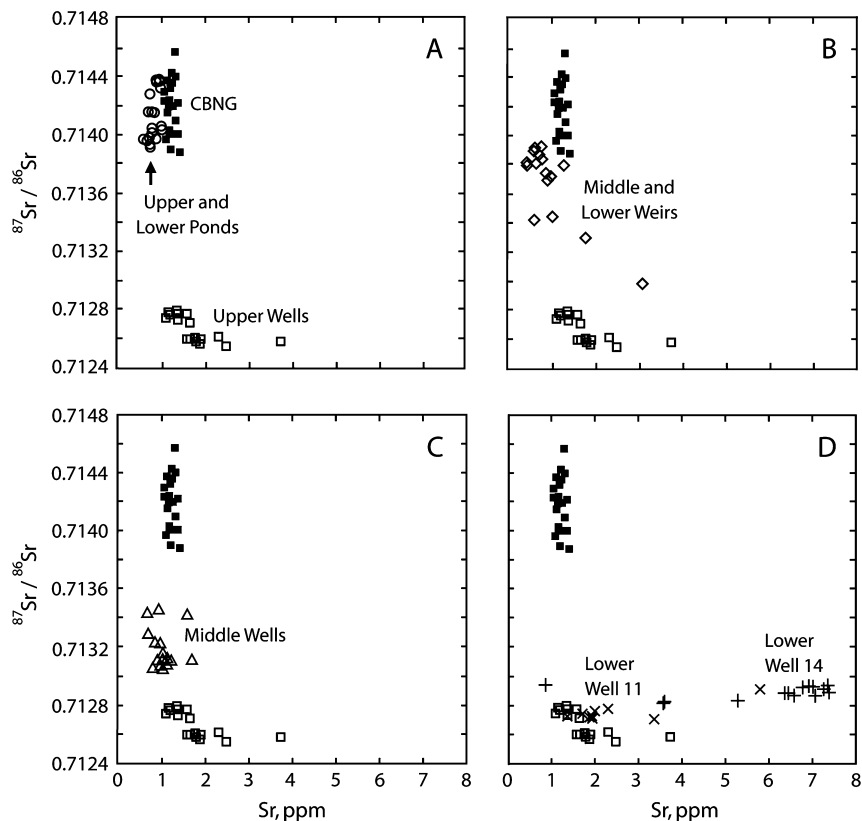
Figure 3. Summary of Sr isotopic and concentration data. The CBNG-produced water (black squares) and the upper wells that monitor the local ground water (open squares) are included in graphs A through D for reference. In addition to the upper wells and CBNG water samples, graph A shows the upper and lower CBNG collection ponds (open circles), graph B shows the stream water sampled at the middle and lower weirs (open diamonds), graph C shows the middle well site (open triangles), and graph D shows lower wells 11 (×) and 14 (+).

(open triangles) have yielded $^{87}Sr/^{86}Sr$ ratios intermediate between the ambient ground water ratio and the CBNG water ratio (Figure 3C). The increasing water levels at well 6 indicate that the aquifer at the middle site had been influenced by CBNG water prior to the January 2003 sampling date; therefore, this intermediate strontium value does not reflect baseline conditions.

The two lower wells, well 11 (×) and well 14 (+), are displayed separately due to their distinct strontium characteristics. Lower well 14 has shown a steady increase in strontium concentration away from both ambient conditions and CBNG values (Figures 3D and 4A) over time, accompanied by a slight but significant shift in $^{87}Sr/^{86}Sr$ ratio toward that of the CBNG water (Figure 4B). Well 11 does not display this trend but rather stays near ambient conditions. Possible reasons for this difference include the difference in depth of well 14 (at 4.5 m deep) and well 11 (at 11.6 m deep). Additionally, well 14 is 5.5 m off the main stream channel, whereas well 11 is 14 m off the stream channel (Payne and Saffer 2005). Strontium concentrations and $^{87}Sr/^{86}Sr$ ratios in water samples from all other monitored wells have remained consistent since sampling began (Figures 4A and 4B).

Water Quality Results

CBNG product water is characterized by high concentrations of TDS, sodium (Na), potassium (K), and alkalinity (as HCO_3) and low concentrations of calcium

(Ca) and magnesium (Mg) as compared to the local ground water in this area measured at the upper well site (Table 3). Additionally, compared to local water, CBNG water has a low concentration of the trace element manganese (Mn) and high levels of the trace elements boron (B) and barium (Ba). The usefulness of Ba as a tracer of CBNG water is limited by the precipitation of $BaSO_4$ (McBeth et al. 2003) as seen by the decrease in Ba concentration from the CBNG discharge to the pond to the middle wells. The pond water has similar levels of TDS, Na, HCO_3, Mg, K, and B as CBNG water. However, the pond water has lower concentrations of Ca, Mn, Sr, and Ba and a higher concentration of Al. The concentrations in the stream water are similar to the pond water except for higher sulfate (SO_4) and Mn and lower Ba values.

The middle well site has lower Na, K, B, and Ba and higher Mg, Ca, and SO_4 compared to the pond and stream water. However, the concentrations of Na, Mg, K, and Ca are similar to the upper wells. Ba is higher and SO_4 is lower in the middle wells than the upper wells. TDS concentrations at the middle well site are initially much higher than the ambient conditions and then decrease.

Well 11 in the lower well site is similar in composition and concentration to the upper well site but has higher Ca and SO_4 values. Well 14 in the lower well site has rising concentrations of TDS, Na, Mg, Ca, SO_4, B, and Sr with time, and all these species are higher in concentration in well 14 than in the upper wells and the CBNG
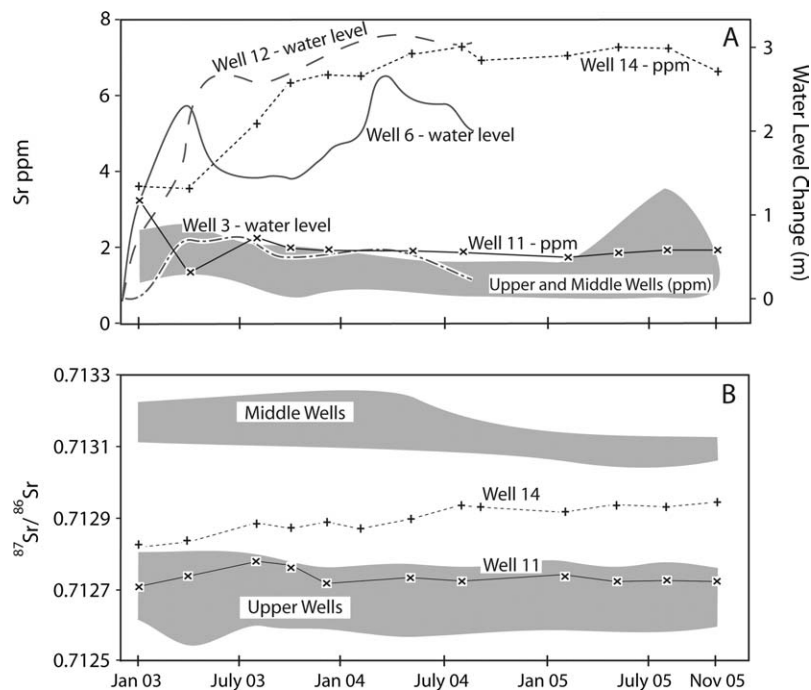
Figure 4. (A) Change in Sr (ppm) with time for lower wells 11 (×) and 14 (+). The Sr concentrations for the upper and middle wells are generalized in the shaded area. Also included on the secondary *Y* axis is water level data (from Payne and Saffer 2005) for one well at each of the three monitoring well sites (measured for the first 20 months). Well 3 is in the upper well site, well 6 is in the middle well site, and well 12 is in the lower well site. Well 12 is the same depth and distance from the streambed as well 14. (B) Strontium isotope ratios for lower monitoring wells 11 (×) and 14 (+). Strontium isotope ratios for the upper and middle well sites are generalized in the shaded areas. The average CBNG strontium isotope ratio is off axis at 0.714.

water. Manganese values, however, in well 14 are lower than those in well 11 and the upper wells. Concentrations of uranium (U) were measured for the last three samples taken from well 14. All three values are higher than both the upper well site and the CBNG water.

Variations in ion concentrations can be seen between wells at different depths within the same nested well site. Wells 2 and 4 in the upper well site are 5.5 and 9.6 m below the ground surface, respectively. Well 2 has consistently higher concentrations than well 4 in Al and U, whereas well 4 has consistently higher concentrations of Na, Ca, SO_4, Mn, and Sr. Wells 7 and 5 in the middle well site are 7.6 and 11.6 m deep, respectively. Well 7 has consistently higher alkalinity, Na, B, and U, whereas well 5 has consistently higher SO_4 and Mn.

Discussion

Geochemical Evolution

In the ephemeral tributary of Beaver Creek, the CBNG-produced water (black squares) has a higher $^{87}Sr/^{86}Sr$ ratio than the local ground water (open squares) and is easily distinguished from ambient shallow ground water and surface water by the $^{87}Sr/^{86}Sr$ ratio (Figures 3A to 3D). The $^{87}Sr/^{86}Sr$ ratio of the CBNG water ranges from 0.71388 to 0.71457 and is therefore easily distinguished from the shallow ground water $^{87}Sr/^{86}Sr$ ratios ranging from 0.71255 to 0.71279.

Strontium concentration is higher in the CBNG discharge points (black squares) than in the collection ponds (circles) to which they discharge (Figure 3A). Using the

major ion concentrations for the upper and lower CBNG discharge points and pond samples collected in December 2003 (Montana Bureau of Mines and Geology) and February 2005 and the water quality model Visual MINTEQ, the saturation indices were calculated for the upper and lower discharge points and ponds. Aragonite ($CaCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), strontianite ($SrCO_3$), and vaterite ($CaCO_3$) are all near saturation (saturation indices near zero) or oversaturated (have saturation indices greater than zero) in the CBNG discharge water. The saturation indices of all these species increase in the associated collection ponds. The introduction of the atmospherically isolated CBNG water to the holding ponds causes the pH to increase from an average of 7.28 in the CBNG discharge water to an average of 8.55 in the associated ponds (Table 3). This more alkaline pH reduces the ability of the pond water to hold calcium carbonate in solution, increasing the likelihood of precipitation. The increase in pH from CBNG to pond was also observed by Patz et al. (2006) and McBeth et al. (2003). In addition to precipitating as strontianite, the chemical similarity of strontium to calcium allows strontium to substitute into calcium carbonate minerals. The precipitation of these species causes the concentration of strontium to be lower in the collection ponds than the CBNG water (Figure 3A).

The increase in Al and decrease in Ba and Mn concentrations from CBNG discharge to the ponds were also noted by Patz et al. (2006) and McBeth et al. (2003). They proposed that these changes were due to the increase in pH, which increases the mobility of Al due to the formation of anionic Al complexes in alkaline pH and causes the precipitation of $BaSO_4$ and $MnCO_3$.

Table 3
Beaver Creek Water Quality

	Sample Date	ID	pH	TDS (mg/L)	Cation						ALK (mg/L)	Anion		B (ppb)	Al (ppb)	Mn ppb	Trace Element		U (ppb)
					Na (ppm)	Mg (ppm)	Si (ppm)	K (ppm)	Ca (ppm)	Fe (ppm)		Cl (ppm)	SO₄ (ppm)				Sr (ppb)	Ba (ppb)	
Upper wells	August 6, 2003	BC-2	7.29	791.05	74.9	41.9	5.0	1.7	132.5	4.3	415.42	4.1	321.8	27.2	443.5	132.6	1150.6	32.7	22.6
	August 6, 2003	BC-4	6.79	1038.78	121.7	41.8	5.9	4.3	173.2	12.2	318.25	3.5	519.2	23.9	18.5	361.1	1463.4	14.3	1.1
	August 21, 2004	BC-2	7.35	788.34	77.2	44.1	5.4	1.8	142.6	4.7	303.94	3.2	359.4	33.6	462.5	171.9	1240.0	27.0	22.6
	August 21, 2004	BC-4	7.20	1085.14	123.3	42.7	5.8	4.4	180.5	13.1	325.48	2.9	551.7	28.8	33.8	429.0	1524.2	35.6	1.0
	February 5, 2005	BC-2	6.69	771.07	69.9	46.7	4.2	1.5	125.2	0.6	398.37	2.9	323.6	36.0	71.3	130.3	1155.4	48.8	
	February 5, 2005	BC-4	6.85	1142.20	127.8	49.3	5.8	4.2	173.5	2.2	386.35	2.9	586.0	34.2	19.5	444.0	1572.2	31.9	
	August 9, 2005	BC-2	7.50	742.11	57.6	38.5	3.9	1.9	120.8	2.1	434.55	4.4	296.6	36.1	83.5	176.3	1053.0	23.3	20.3
	August 9, 2005	BC-4	7.00	1151.99	116.1	40.9	5.1	4.5	173.4	10.9	417.33	3.7	591.6	39.7	46.0	442.2	1461.9	22.4	1.0
CBNG water	August 5, 2003	Up-CBNG	7.20	1411.03	483.3	18.4	4.7	8.0	43.9	3.3	1705.74	8.1	<0.2	90.0	4.5	18.4	1038.6	929.6	0.0
	August 5, 2003	L-CBNG	7.65	1346.20	459.6	18.4	4.7	8.2	49.0	4.9	1608.32	8.0	0.1	87.4	22.9	43.6	1011.3	969.5	0.0
	August 21, 2004	Up-CBNG	7.41	1445.42	502.2	18.7	5.2	8.5	47.4	3.2	1726.06	8.6	0.2	98.6	15.5	26.1	1037.1	907.7	0.2
	August 21, 2004	L-CBNG	7.26	1385.09	481.6	18.3	4.8	8.3	54.1	2.3	1534.69	8.3	0.5	92.7	34.8	53.3	1089.4	937.6	0.1
	February 5, 2005	Up-CBNG	7.28	1399.38	528.0	22.2	5.8	8.6	48.9	0.5	1551.98	7.0	12.8	112.6	9.1	28.2	1115.2	950.6	
	February 5, 2005	L-CBNG	7.23	1282.56	479.9	20.3	4.8	8.3	47.3	0.5	1446.05	6.3	1.8	100.7	10.2	40.5	1053.1	982.7	
	August 9, 2005	Up-CBNG	6.90	1438.37	484.9	19.5	4.8	8.0	44.4	2.3	1742.40	13.8	1.1	116.9	6.1	19.2	980.3	871.0	0.0
	August 9, 2005	L-CBNG	7.30	1360.53	458.0	17.1	4.7	8.0	50.7	4.0	1639.26	8.9	0.5	83.7	14.3	56.2	1047.1	876.3	0.0
Pond water	August 6, 2003	Up-pond	8.63	1393.68	486.1	16.9	2.7	8.6	17.1	0.7	1716.82	8.7	6.0	88.0	130.8	4.6	559.9	283.9	0.5
	August 6, 2003	L-pond	8.97	1394.66	488.6	18.1	4.1	9.2	19.4	0.7	1704.49	9.0	4.7	92.6	126.3	4.6	631.2	376.8	0.4
	February 5, 2005	Up-pond	7.98	1225.46	483.0	20.1	3.2	8.0	17.8	0.2	1377.56	7.1	5.9	108.4	144.8	5.6	785.1	456.5	
	February 5, 2005	L-pond	8.65	1218.07	478.5	20.3	0.9	8.1	24.4	0.1	1365.17	6.3	6.1	95.5	14.4	<2.9	895.3	687.7	
	August 9, 2005	Up-pond	8.70	1769.45	629.2	19.9	1.2	10.5	10.4	1.1	2188.87	12.8	4.6	140.2	311.6	4.8	668.3	268.1	0.8
	August 9, 2005	L-pond	8.40	1535.10	548.8	20.2	4.6	10.7	15.5	0.0	1868.22	11.8	1.9	103.3	44.4	6.6	778.7	507.2	0.0
Stream water	August 6, 2003	M-weir	9.20	1433.62	502.6	17.1	2.6	9.4	17.1	0.8	1758.14	9.2	7.5	89.1	130.5	6.2	486.5	153.6	0.9
	August 6, 2003	L-weir	8.52	1304.83	447.6	20.5	3.3	8.4	25.0	0.6	1557.72	8.5	22.4	88.5	42.1	18.2	578.9	256.9	2.0
	August 21, 2004	L-weir	8.76	1406.87	496.6	22.9	1.4	7.8	15.8	0.4	1626.37	9.4	50.2	93.7	13.5	4.7	386.6	99.8	3.5
	February 5, 2005	M-weir	7.42	1936.97	441.8	70.7	3.3	6.1	181.7	0.9	1004.39	10.6	726.5	78.5	27.7	223.3	1771.7	180.0	
	February 5, 2005	L-weir	7.31	1268.46	415.3	32.6	2.2	5.7	75.6	0.4	1142.05	6.7	166.7	34.6	87	127.3	972.8	411.4	
	August 9, 2005	L-weir	8.30	1438.18	490.7	21.9	2.7	8.3	15.2	-0.3	1641.46	9.4	80.5	93.8	13.7	5.0	384.7	141.5	4.9
Middle wells	August 6, 2003	BC-7	7.49	778.78	136.7	38.6	6.7	3.8	193.8	4.2	655.97	7.9	63.5	70.3	178.7	13.1	942.4	80.9	15.3
	August 21, 2004	BC-5	7.33	760.33	88.8	38.2	5.0	2.8	151.9	6.4	393.93	7.0	265.8	24.6	74.7	128.9	911.3	35.1	9.2
	August 21, 2004	BC-7	7.20	1151.94	304.2	34.7	6.5	3.1	175.6	3.7	892.52	10.2	183.8	90.4	129.8	6.6	872.1	76.9	28.5
	February 5, 2005	BC-5	6.69	1013.52	97.2	49.3	4.9	30	172.6	1.7	392.26	8.5	487.9	25.9	136.2	152.3	1147.4	42.7	
	February 5, 2005	BC-7	6.51	932.25	155.0	38.4	6.5	2.9	171.0	0.7	855.77	7.4	128.2	51.9	65.8	8.4	947.9	80.6	
	August 9, 2005	BC-5	6.90	884.66	92.3	36.6	4.1	2.8	147.7	4.7	379.85	11.3	397.8	23.3	41.1	120.5	881.6	28.3	9.8
	August 9, 2005	BC-7	6.90	920.09	169.9	34.6	6.0	3.0	181.8	3.2	677.68	8.5	178.9	48.2	91.7	7.5	887.6	73.5	22.6
Lower well 11	August 6, 2003	BC-11	6.93	1489.56	156.6	73.1	6.5	3.5	250.4	14.1	261.18	4.8	851.7	28.1	667.2	237.3	1702.2	154	6.6
	August 21, 2004	BC-11	7.37	1486.88	157.8	69.4	4.9	3.1	239.5	10.5	311.20	4.6	843.6	28.8	23.0	236.5	1628.0	12.5	5.4
	February 5, 2005	BC-11	6.50	1556.13	154.6	77.4	5.1	3.2	229.0	2.0	411.82	4.5	877.1	32.2	54.1	231.2	1710.8	33.2	
	August 9, 2005	BC-11	7.30	1505.41	154.8	70.5	5.7	4.3	237.8	11.6	370.97	6.2	831.5	34.6	529.7	230.6	1635.5	44.7	7.9

Table 3 (Continued)
Beaver Creek Water Quality

				Cations							Anions			Trace Element					
Sample Date	ID	pH	TDS (mg/L)	Na (ppm)	Mg (ppm)	Si (ppm)	K (ppm)	Ca (ppm)	Fe (ppm)	ALK (mg/L)	Cl (ppm)	SO_4 (ppm)	B (ppb)	Al (ppb)	Mn ppb	Sr (ppb)	Ba (ppb)	U (ppb)
Lower well 14																		
January 21, 2003	BC-14	7.05	2132.89	136.1	144.1	4.8	1.3	322.1	1.7	216.62	4.4	1411.6	49.6	0.2	4.3	3593.3	17.7	
April 9, 2003	BC-14	7.40	2095.97	131.1	138.9	4.4	1.7	336.6	1.7	271.47	4.8	1343.3	40.5	10.7	<2.9	3572.3	26.9	
August 6, 2003	BC-14	6.83	2880.36	150.0	173.9	5.1	1.0	495.7	2.0	418.88	6.0	1839.5	67.2	35.2	67.2	5277.9	30.5	
October 5, 2003	BC-14	7.73	4060.87	326.4	261.0	4.9	2.4	542.7	2.2	413.17	5.8	2711.6	107.1	76.3	38.6	6347.4	24.6	
February 13, 2004	BC-14	7.23	4598.59	462.2	351.6	3.9	1.8	481.5	2.4	388.87	5.3	3098.2	95.9	42.6	7.1	6448.7	55.2	
May 15, 2004	BC-14	7.64	5135.06	556.5	397.0	3.7	1.5	473.7	2.2	403.61	6.6	3494.7	96.8	38.1	7.2	7068.3	23.3	
August 21, 2004	BC-14	7.50	5750.91	713.6	461.9	4.1	1.7	458.6	2.3	449.59	7.9	3878.9	144.1	18.5	36.4	7375.9	368	
September 18, 2004	BC-14	.796	5335.76	666.4	424.5	4.3	5.5	425.9	2.2	448.26	10.5	3575.4	142.5	21.7	36.4	6925.1	42.8	
February 5, 2005	BC-14	6.64	4786.97	483.1	398.0	4.0	0.3	447.4	2.3	508.17	6.7	3193.8	106.4	33.8	20.1	7004.0	30.1	
May 7, 2005	BC-14	8.66	4779.28	524.4	376.3	3.4	0.9	446.6	7.4	580.63	8.7	3125.3	115.2	5.6	20.4	7270.0	15.3	269.2
August 9, 2005	BC-14	7.30	4864.84	528.0	371.5	4.3	1.0	449.9	3.3	666.80	9.8	3162.6	150.7	104.1	84.2	7350.2	25.0	276.5
November 4, 2005	BC-14	7.70	4285.01	361.8	348.0	4.9	0.9	451.1	8.4	738.03	9.9	2735.9	153.6	172.8	80.5	6769.1	26.9	263.5

Additional evidence that may indicate the precipitation of strontium is found in the stream samples. The stream samples collected from weirs below both ponds were found to have, in general, a slightly lower $^{87}Sr/^{86}Sr$ ratio than the CBNG water (Figure 3B). This lower $^{87}Sr/^{86}Sr$ ratio is not expected to result from the addition of local ground water because base flow is unlikely in a loosing stream such as Payne and Saffer (2005) predict for this reach of Beaver Creek (Figure 5). However, if the lower $^{87}Sr/^{86}Sr$ ratio was from the dissolution of salts, one would predict an increase in strontium concentration—a condition not supported by the data. This downward shift in the $^{87}Sr/^{86}Sr$ ratio without a corresponding increase in strontium concentration is interpreted as evidence of either the precipitation and redissolution of strontium-bearing salts along the length of the streambed or cation exchange with clays present in the soil. Cation exchange would contribute a lower strontium isotope ratio to the water without changing the concentration.

Binary Mixing

The middle well site wells (open triangles in Figure 3C) are between the two on-channel ponds and within the stream channel. The $^{87}Sr/^{86}Sr$ ratios at this site are intermediate between the upper pond and the local ground water (upper well) values, interpreted to represent mixing of strontium from these two endmembers. The average strontium concentrations of the upper pond water, upper well site, and middle well site are 0.74, 1.69, and 1.01, respectively. The average $^{87}Sr/^{86}Sr$ ratios for the upper pond, the upper well site, and the middle well site are 0.71398, 0.71267, and 0.71316, respectively. To determine the fraction of strontium in the middle well samples contributed by the upper CBNG-produced water collection pond, we use a binary mixing equation (Equation 1a) (Faure 1998):

$$\frac{^{87}Sr}{^{86}Sr_{Middle}} = \left(\frac{^{87}Sr}{^{86}Sr_{Pond}}\right) f_{Pond} \frac{(Sr_{Pond})}{(Sr_{Middle})}$$
$$+ \left(\frac{^{87}Sr}{^{86}Sr_{Upper}}\right)(1 - f_{Pond}) \frac{(Sr_{Upper})}{(Sr_{Middle})} \quad (1a)$$

The two endmembers in this mixing equation are the pond water and the upper well water. The resulting mixture is the middle well water. The terms "$^{87}Sr/^{86}Sr$" in the equation refer to the $^{87}Sr/^{86}Sr$ ratio of water samples in the upper pond, upper wells, and middle wells as indicated by the subscripts "Pond," "Upper," and "Middle." The quotient terms in the equation (Sr) refer to the concentration of strontium in the water samples indicated by the subscripts. This equation is solved for the unknown "f," which is the fraction of water in the middle well water that is contributed by the pond. Substituting the average concentrations and $^{87}Sr/^{86}Sr$ ratios into this equation results in:

$$0.71316 = (0.71398) f \frac{0.74}{1.01}$$
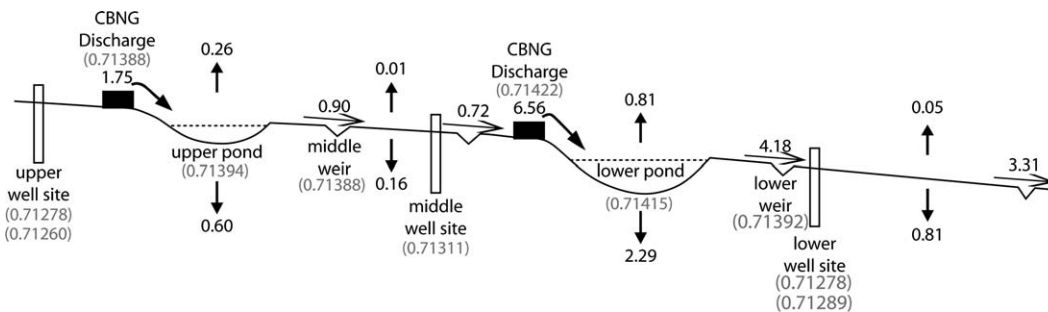$$+ (0.71267)(1 - f) \frac{1.69}{1.01} \quad (1b)$$

Figure 5. Beaver Creek water budget for the week of August 5 to 11, 2003. Values are in liters per second. Downward, upward, and horizontal arrows represent infiltration, evaporation, and surface flow, respectively (from Payne and Saffer 2005). Parenthetical values in gray are the $^{87}Sr/^{86}Sr$ ratios for the sample set collected in August 2003.

This equation is solved for the fraction of water from the pond (f):

$$f = 0.72 \tag{1c}$$

The CBNG pond water contributes roughly 70% of the water in the middle wells, and 30% is contributed by the local ground water. This calculation assumes that strontium concentrations of pond and CBNG-produced water are constant. If strontium from local sources enters the CBNG-produced water, either through dissolution of local salt or through cation exchange, the fraction of water contributed by CBNG water could actually be much higher. Observations of the stream samples as described earlier indicate that it is unlikely that the pond water infiltrated to the depth of the middle wells without interaction with the local strontium. The 70% estimate was calculated using the average values for the three sources of water samples. By adding and subtracting 1 standard deviation from the average values, we estimate the potential range in the fraction of water supplied by the pond water. Using the variation within the data, a minimum of 65% and a maximum of nearly 100% were calculated using Equation 1a. It is unlikely that all the water in the well originated from the CBNG-produced water, so this calculation is probably an artifact of averaging seasonal variation.

Because the $^{87}Sr/^{86}Sr$ ratio has remained unchanged from this intermediate value since the first collection, which was made 32 d after the upper pond began to fill, the data indicate that CBNG water has either infiltrated to 11.5-m depths within this time frame or flowed through the alluvial aquifer from the pond to the middle well site. Thirty-two days, therefore, represents a maximum time for subsurface flow and infiltration to the water table.

This estimate agrees well with the hydrological measurements made by Payne and Saffer (2005) (Figure 5). Evidence of mixing as observed in intermediate strontium isotope values is corroborated by hydrologic monitoring of middle well 6, which shows increased ground water levels due to the infiltration of CBNG water (Figure 4A) (Payne and Saffer 2005). The water level in well 6 increased by 2 m by May 2003, a rise attributed to CBNG water infiltration. This rise was followed in the

summer by a decrease of 1 m, perhaps due in part to increased transpiration rates in the spring and summer retarding CBNG infiltration and/or a change in water management by the CBNG production company that minimized overland flow. The water level increases again to 2.5 m above the baseline from January 2004 to May 2004, followed again by a decrease in water level during the growing season to the end of the monitoring period (August 2004).

There is a slight decrease in the $^{87}Sr/^{86}Sr$ ratio in the middle wells beginning July 2004 (Figure 4B). The timing of this decrease corresponds roughly to a change in water management. Minimal overland flow from the upper pond was allowed after this date, and the middle stream site was found to be dry during the August 2004, August 2005, and November 2005 sampling dates. However, the slight changes in average strontium concentration for the upper pond, upper wells, and middle wells before August 2004 (0.738, 1.669, and 1.003, respectively) and after August 2004 (0.747, 1.724, and 1.019, respectively) result in the same percentage of strontium contribution from CBNG using the binary mixing equation (Equation 1a). Although there was no surface flow in August 2004, August 2005, and November 2005, there was the same percent contribution of CBNG water to the middle wells. This implies that there is a significant CBNG contribution to the water in the middle wells through subsurface flow.

Mobilization of Salts

The addition of water to semiarid soils has the potential to mobilize the salts that accumulate over time. Salts in soil originate from a number of sources, including in situ weathering, atmospheric deposition, and the fossil salts associated with sedimentary rocks (Essington 2004). Because strontium is chemically similar to calcium, changes in strontium concentration closely follow changes due to precipitation or dissolution of calcium-bearing salts. The soil in this area is calcium carbonate buffered (NRCS 2004), so strontium should be a good indicator of mobilization of Beaver Creek salts. Additionally, some of the soils classified in this area are gypsum rich, including the Lismas series (found in T79N, R71W) partially composed of a Cy horizon with masses of

gypsum throughout. Whereas the soil classifications in the drainage studied here do not include specific gypsum horizons, this mineral is common in Powder River basin soils (NRCS 2004).

The crosses in Figures 3D, 4A, and 4B represent wells 11 ($\times$) and 14 (+) in the lower well site, a set of nested wells that are below both ponds and slightly off-channel. Over time, well 14 has shown only modest increases in strontium isotope ratio upward toward that of the CBNG input water (Figure 4B) but has shown strontium concentrations much greater than that of CBNG water (Figure 4A). We interpret the increase in strontium concentration in well 14 to indicate the dissolution of salts in the previously unsaturated alluvial material as CBNG water infiltrates. The increase in strontium concentration without a large increase in the $^{87}Sr/^{86}Sr$ ratio implies the mobilization of local salts, not the presence of salts originating in the CBNG water. The local ground water as measured in the upper wells acquires its $^{87}Sr/^{86}Sr$ ratio from the soil and alluvium with which it interacts; therefore, the local soil and alluvium must have an $^{87}Sr/^{86}Sr$ ratio of 0.7127. The high concentration of strontium derived from local sources in well 14 water keeps the overall strontium isotope ratio in well 14 from increasing to the higher $^{87}Sr/^{86}Sr$ ratio of CBNG-produced water despite the addition of CBNG water indicated by the increase in water level in lower well 12 (Figure 4A) (Payne and Saffer 2005). Cation exchange may play a role in maintaining a strontium isotope ratio in well 14 water near to that of the local ratio. However, the increase in strontium concentration implies that a larger role is played by the dissolution of salts.

The increase in strontium concentration and the slight increase in strontium isotope ratio in well 14 were not observed in well 11. We attribute this discrepancy to the greater depth of well 11 and the greater distance from the CBNG-produced water source in the streambed. These strontium data can constrain the extent of the water mounding predicted by the single soil layer SUTRA model of Payne (2004). Well 11 is out of the range of impact of the water mounding under the streambed, whereas well 14, being closer to the streambed and shallower, is within the zone impacted by the CBNG water. Using the strontium data from wells 11 and 14, we are able to verify the potential accuracy of this model and help constrain future, more detailed water-mounding models.

The twofold increase in strontium concentration in lower well 14 and the relative absence of such changes in concentration at the middle well site may be related to the locations of the wells relative to the thalweg. The middle site wells are screened in the aquifer directly below the stream channel itself. This is a location that normally experiences annual to semiannual flushing of soluble salts in the soil profile during spring runoff. These annual to semiannual saturated flow events prevent the accumulation of soluble salts within the ephemeral channel. Therefore, when CBNG water is introduced to the channel, there is no appreciable increase in strontium concentration and other water quality indicators such as TDS. In contrast, the lower site monitoring well 14 lies

5.5 m off the stream channel on a terrace over a meter above the channel and is screened 4.5 m below the surface. Annual spring flows persist only as long as the snowmelt, which most likely does not result in water mounding to the extent seen in lower well 12 (Figure 4 A). Prior to the introduction of CBNG water, this stream bank soil built up soluble salts between rare flooding events. The lower well site at well 14 is now experiencing saturated conditions due to ground water mounding related to CBNG discharge (Payne 2004; Payne and Saffer 2005). The water mounds to a greater extent at the lower site than the middle well site due to higher surface flows (Figure 5) and possibly more subsurface flow due to the larger size of the lower pond compared to the upper pond. The water mounding at the lower well site impacts a larger volume of soil that is rarely saturated in contrast to the middle well site where CBNG water infiltrates well-flushed soil. We infer that the water at the lower well site is dissolving some of these soluble salts, leading to the observed increased concentrations of strontium and other major ions seen at the lower well site and not at the middle well site.

The composition (Table 3) of water in well 14 shows that Na, Ca, Mg, and SO_4 concentrations increase and then decrease with time and the concentrations are higher compared to both the upper wells and the CBNG water. By using the water quality model MINTEQ, the saturation indices of calcite and gypsum were calculated for the 12 well 14 samples. Calcite is oversaturated, implying that it is unlikely to dissolve in this water, whereas gypsum is undersaturated, implying that it would likely dissolve if present. Dissolution of gypsum yields Ca ions, which, due to the oversaturation of calcite, may then precipitate with carbonate as calcite. This reprecipitation of cations may explain why the concentration of SO_4 increases by 2500 ppm (52 meq/L), while Ca increases by only 200 ppm (10 meq/L). Additionally, SO_4 ions may also be contributed by the dissolution of $MgSO_4$, as indicated by the increase in Mg concentration in well 14.

If we use the upper wells as an indication of what salts may be present in local soil and alluvium, we see that the concentration of calcium (in meq/L) exceeds that of alkalinity. When this water evaporates in the soil, the alkalinity in the upper well water would first be taken up as calcite, leaving the remaining Ca and Mg to form sulfate salts. These sulfate species are far more soluble than calcite (Drever 1997). The introduction of CBNG water to soils containing these salts would first mobilize these sulfate species, resulting in the increase in SO_4 we see in lower well 14. The change in concentration of Mg and Na is nearly balanced (in meq/L) by the change in SO_4. This fits the stoichiometry of bloedite ($Na_2SO_4 \times MgSO_4 \times 4H_2O$), which may be an ephemeral phase formed by evaporation in the vadose zone (Drever 2006). While the Na increase may be explained by bloedite, the high solubility of sodium species would imply an even greater concentration of Na than seen in well 14. In arid and semiarid areas, it has been shown that Na and Cl are the first to dissolve (Drever and Smith 1978). This apparent discrepancy may be the result of prior mobilization of Na species by flooding events.

It would be useful to predict how long soil and alluvium must be flushed before the pulse of high-TDS water has been removed from the system. At Beaver Creek well 14, the concentration of a number of ions peaked within 9 to 18 months: the concentration of Ca peaked in October 2003 and Na, Mg and SO_4 peaked in August 2004. Strontium also peaked in August 2004, but the concentration did not drop significantly in the year following. We suggest that it is premature to make predictions about when water quality may improve on the basis of this limited monitoring history. Accurate predictions of ground water quality will require a longer monitoring period and a detailed soil chemistry investigation.

Conclusions

We used strontium isotopes in conjunction with strontium concentration to:

1. Fingerprint water from distinct aquifers.
2. Trace the interaction of water discharged during CBNG production as it interacts with the surface, hyporheic zone, and near-surface aquifers. Strontium isotope data from the middle well site illustrate that fractions of water from different sources can be estimated at sites irrespective of the effects of evaporation or precipitation.
3. Identify the mobilization of local soil-based salts. The Sr concentration and $^{87}Sr/^{86}Sr$ ratio of lower well 14 indicate that increasing ion concentrations in the water is due to mobilization of local salts in the soil.
4. Corroborate other geochemical data in explaining water quality changes due to precipitation and dissolution of salts.

The fundamental characteristic that allows this tracer to be applied is that the $^{87}Sr/^{86}Sr$ ratio of CBNG water is markedly different than that of the surface and near-surface waters in the Powder River basin. However, the strontium isotope technique used here can be of use in other hyporheic zone investigations where amount and direction of water movement are of concern. In situations where the $^{87}Sr/^{86}Sr$ ratios are measurably different in surface and ground water, the volume of contributed water can be estimated using simple mixing calculations. Introduced water such as roadway runoff is also a good candidate for strontium isotope tracing due to its interaction with asphalt, hydrocarbons, road salt, and gravel. Additionally, agricultural inputs such as fertilizer, pesticides, and herbicides make irrigation runoff an equally appealing candidate for strontium isotope tracing. The chemical and isotopic compositions of mine drainage, springs, and geothermal water have a good possibility of being distinguishable from surface and near-surface water chemistry and may therefore also be good candidates for strontium isotope tracing.

We used this tool to trace the infiltration of product water and show a connection between changes in water quality and strontium concentration at an on-channel CBNG disposal site. We suggest that on-channel discharge shows promise for future disposal in that there are fewer salts in existing channels due to annual flushing.

However, the amount and duration of CBNG discharge may exceed the water mounding caused by annual flooding, in which case stream bank salts may be mobilized. Additionally, the change in vegetation species and biomass that occurs due to the creation of a perennial stream may be of concern to landowners if the local vegetation, adapted to semiarid conditions, is outcompeted by undesirable riparian vegetation or by a floral community that is not stable when the source of water is removed (Stearns et al. 2005). The conclusions drawn here that existing ephemeral channels have fewer soluble salts than the associated floodplain imply that ponds excavated off existing channels (off-channel) may also experience the mobilization of local salts. Further work on salt mobilization from soils and the duration of ground water degradation in CBNG situations is needed. The strontium isotope ratio may be used to fingerprint salts in off-channel situations as well. Additionally, in situations where CBNG product water is used for irrigation, strontium isotopes are a good candidate for following changes to the calcium cycle caused by the high sodium levels in the CBNG water.

Editor's Note: The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the authors, their employers, or the National Ground Water Association.

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