



Infiltration from an impoundment for coal-bed natural gas, Powder River Basin, Wyoming: Evolution of water and sediment chemistry

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[1] Development of coal-bed natural gas (CBNG) in the Powder River Basin, Wyoming, has increased substantially in recent years. Among environmental concerns associated with this development is the fate of groundwater removed with the gas. A preferred water-management option is storage in surface impoundments. As of January 2007, permits for more than 4000 impoundments had been issued within Wyoming. A study was conducted on changes in water and sediment chemistry as water from an impoundment infiltrated the subsurface. Sediment cores were collected prior to operation of the impoundment and after its closure and reclamation. Suction lysimeters were used to collect water samples from beneath the impoundment. Large amounts of chloride (12,300 kg) and nitrate (13,500 kg as N), most of which accumulated naturally in the sediments over thousands of years, were released into groundwater by infiltrating water. Nitrate was more readily flushed from the sediments than chloride. If sediments at other impoundment locations contain similar amounts of chloride and nitrate, impoundments already permitted could release over 48×10^6 kg of chloride and 52×10^6 kg of nitrate into groundwater in the basin. A solute plume with total dissolved solid (TDS) concentrations at times exceeding 100,000 mg/L was created in the subsurface. TDS concentrations in the plume were substantially greater than those in the CBNG water (about 2300 mg/L) and in the ambient shallow groundwater (about 8000 mg/L). Sulfate, sodium, and magnesium are the dominant ions in the plume. The elevated concentrations are attributed to cation-exchange-enhanced gypsum dissolution. As gypsum dissolves, calcium goes into solution and is exchanged for sodium and magnesium on clays. Removal of calcium from solution allows further gypsum dissolution.

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1. Introduction

[2] In arid and semiarid regions of the United States, salts are deposited onto the land surface from precipitation and dry atmospheric deposition. As water from precipitation infiltrates, it carries these salts into the subsurface. Most of the water that infiltrates is eventually returned to the atmosphere by evaporation from soil or plants; therefore most of the salts remain in the subsurface. As the cycle of deposition and evaporation is repeated over hundreds to thousands of years, large quantities of salts accumulate in the unsaturated zone in these regions. Phillips [1994] reported chloride storage greater than 20,000 kg/ha in some areas of the western United States. Patterns of chloride accumulation in sediments can be used to estimate rates of groundwater recharge [Allison and Hughes, 1978; Allison, 1988; Cook *et al.*, 1992; Phillips, 1994]. Typically, areas of

low chloride accumulation correspond to areas of active recharge (i.e., percolating recharge water transports chloride out of the unsaturated zone), whereas areas of high chloride accumulation are associated with low rates of recharge (i.e., chloride is being deposited on land surface at rates greater than it is being transported out of the unsaturated zone). Because streams in these regions often are a source of recharge, salts tend to be flushed out of sediments underlying stream channels [Hartsough *et al.*, 2001; Heilweil and Solomon, 2004; Heilweil *et al.*, 2006]. Nitrate also has accumulated in sediments in arid and semiarid regions [Boyce *et al.*, 1976; Hartsough *et al.*, 2001; Walvoord *et al.*, 2003; McMahon *et al.*, 2006]. There can be multiple sources for this nitrate, including atmospheric deposition, plant fixation of atmospheric nitrogen, and oxidation of geologic sources of NH_4 to nitrate.

[3] Climate or land-use changes can cause displacement of salts stored in the unsaturated zone [Boyce *et al.*, 1976; Walvoord *et al.*, 2003]. Stonestrom *et al.* [2004] showed that peaks in chloride concentration occurred at much deeper depths in unsaturated zones underlying irrigated fields in the Amargosa Desert as compared with unsaturated zones in areas of native vegetation. Presumably, percolating irri-

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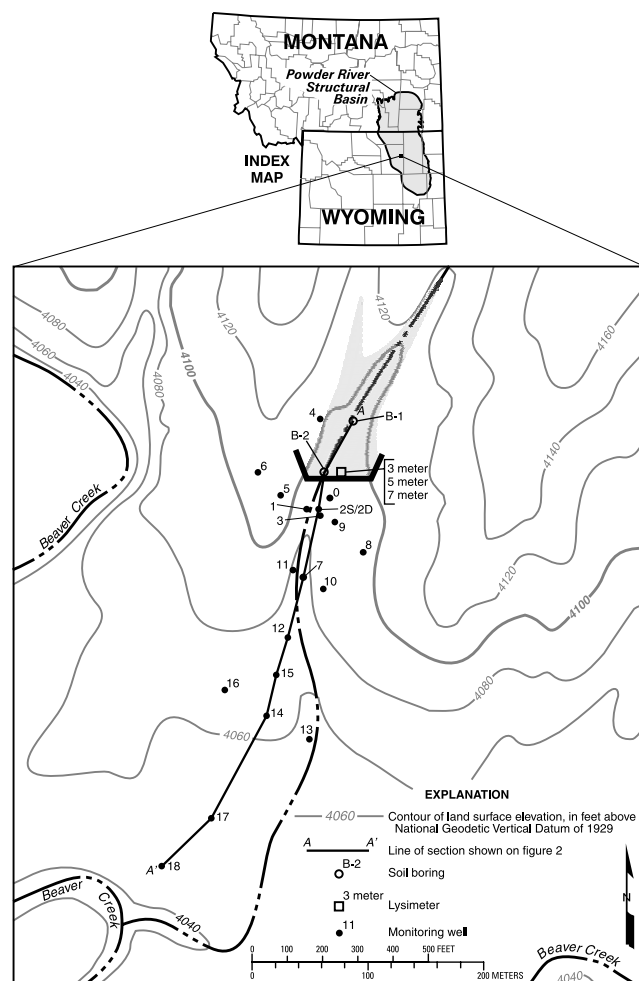


Figure 1. Location map for Skewed Reservoir study and monitoring network.

tion water transported the chloride peak downward. Replacement of native vegetation with dryland crops, such as wheat, has led to increased recharge rates, with the unintended consequence of increased salinization of local aquifers due to a flushing of accumulated salts in areas of Montana [Miller *et al.*, 1980] and Australia [Salama *et al.*, 1993]. Land surface storage of groundwater extracted during energy development in northern Wyoming raises some concerns in regard to flushing of naturally occurring salts into ground or surface waters.

[4] The Powder River Structural Basin comprises more than 61,000 km² in Wyoming and Montana (Figure 1). It has historically been an important source of energy resources, containing the largest coal resources of any coal field in the contiguous United States [Glass, 1997]. Oil and conventional natural gas resources also are abundant. Recent technological advances have allowed development of a known, but unconventional, source of natural gas, gas stored in coal beds (CBNG). Since 1997, development of CBNG has increased rapidly in the Basin. As of 2006, there were more than 19,000 active CBNG wells in the Wyoming part of the Basin; that number is projected to exceed 50,000 by 2013 [U.S. Bureau of Land Management (U.S. BLM), 2003b].

[5] CBNG wells generally tap coal beds in the Fort Union Formation at depths of 100–1000 m. Overlying the Fort Union Formation in much of the Basin is the Wasatch Formation, which consists of shales, siltstones, and sandstones. The Wasatch Formation is overlain in many areas with unconsolidated surficial sediments. The steppe climate in the Basin is typical of semiarid grassland prairies [Martner, 1986]. Average temperature in Gillette is about 7°C; average annual precipitation is 410 mm [Western Regional Climate Center, 2001].

[6] Natural gas in the Basin is extracted by withdrawing water from coal beds, thus lowering the water pressure and releasing the gas. Additional information on CBNG generation, reserves, and development within the Powder River Basin is given by De Bruin *et al.* [2000], Bartos and Ogle [2002], and Rice *et al.* [2002]. The rapid and extensive development gives rise to several environmental issues, including depletion of groundwater resources, soil erosion, changes in wildlife habitat, possible introduction of invasive plant species, and air quality and noise impacts [U.S. BLM, 2003a]. The fate of the produced CBNG water, one of the most salient of these issues, is the focus of this study.

[7] The average rate of water pumpage from new wells in the Basin is about 47 m³/d [Wheaton and Brown, 2005]. Water production declines gradually over the 7- to 10-year life of the well. In 2006, about 680 million barrels (108,000,000 m³) of water were produced (Wyoming Oil and Gas Conservation Commission; see <http://wogcc.state.wy.us>). CBNG water in the Basin is generally a sodium-bicarbonate type with total dissolved solids (TDS) and sodium adsorption ratio in the range of 200–4000 mg/L and 5.6–69, respectively [Rice *et al.*, 2002; Bartos and Ogle, 2002]. Sodium adsorption ratio (SAR) is a measure of the concentration of sodium in water or sediment relative to the concentrations of calcium and magnesium. Concern about the CBNG water cited in the Federal Environmental Impact Statement [U.S. BLM, 2003a] centers on high values of SAR. Water with SARs in excess of 13 can cause deterioration of soil structure [Soil Survey Laboratory, 1995]. Hence such waters are undesirable for irrigation. A preferred option for disposal of CBNG water is to place it in impoundments where the water can infiltrate and evaporate [U.S. BLM, 2003b]. As of January 2007, permits had been issued for more than 4000 of these impoundments in the Powder River Basin in the state of Wyoming (Wyoming State Engineer's Office, written communication, 2007). Typical surface water storage capacity of an impoundment is 12,000 m³.

[8] The impact of impoundments for CBNG water on naturally occurring salts stored in sediments and the possible transport of those salts to surface water and groundwater bodies within the Powder River Basin are critical questions. This paper presents results of a study of the fate of CBNG water placed in one such impoundment. We report on water and sediment chemistry in the subsurface immediately underlying the impoundment prior to the initial introduction of CBNG water and how that chemistry changed through the 10-month period that the impoundment was in operation and for more than a year after the impoundment was decommissioned. Results presented here are based on analyses of sediment cores obtained before and after the operational life of the reservoir and on analyses of water

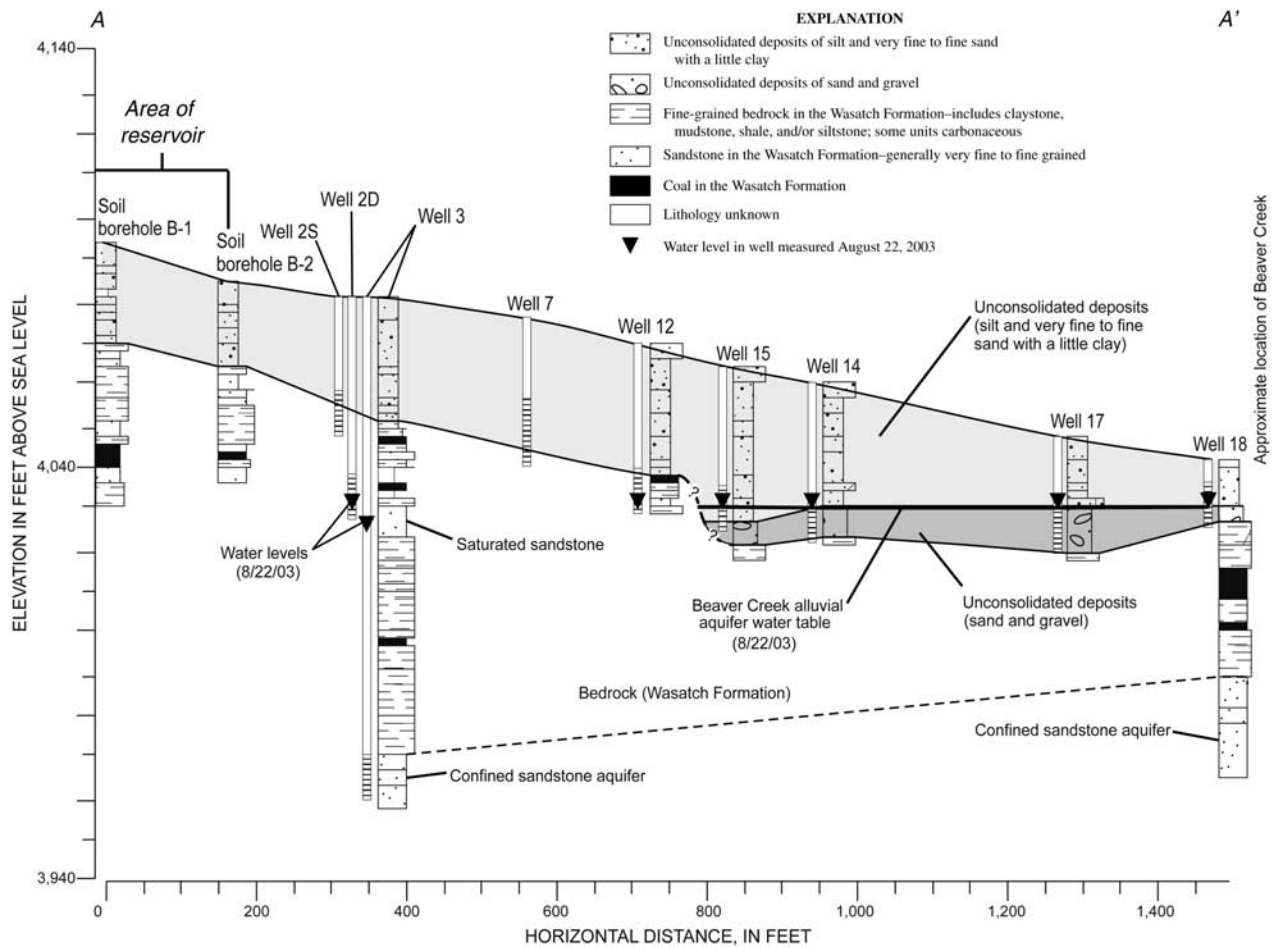


Figure 2. Skewed Reservoir north-south hydrogeologic section (prior to discharge of water into Skewed Reservoir). Line of section shown on Figure 1.

samples obtained from suction cup lysimeters installed beneath the reservoir. Groundwater transport of solutes, which is the subject of another paper, is not discussed here, with the exception that concentrations of chloride and nitrate in samples from observation wells are used to estimate the total amounts of those constituents that were flushed from sediments.

2. Methods

[9] The study was conducted at Skewed Reservoir in Johnson County, Wyoming (Figure 1). A compacted earthen dam, approximately 6 m in height and 1 ha in area, was constructed with native colluvial sediments in July 2003 to create the reservoir. The dam was built across a small ephemeral channel that drained approximately 20 ha of land. Capacity of the reservoir was about 12,000 m³. Underlying the impoundment were 8 m of unconsolidated deposits on top of bedrock. While the reservoir was under construction, and prior to the introduction of CBNG water, 50-mm-diameter suction cup lysimeters were installed into the sediments beneath the base of the reservoir at depths of 3, 4.9, and 6.7 m. (For convenience, these will be referred to as the 3-m, 5-m, and 7-m lysimeters throughout the remainder of this paper.) An additional lysimeter was installed at a

depth of 5.2 m at a control site, which is unaffected by any impoundments or CBNG discharge water, about 1.5 km north of Skewed Reservoir. Suction lysimeters allow collection of water samples when the sediments are fully or partially saturated. A hand auger was used to bore holes for the lysimeters; sediment samples were collected at intervals of about 0.3 m. Sediment samples were also obtained by means of a hollow-stem auger at two locations along the ephemeral channel across which the dam was constructed (Figure 1). Nineteen observation wells were installed near the reservoir (Figure 1) with a hollow-stem auger. The unconsolidated surficial sediments, which consist of very fine to fine sand with silt and clay, were initially unsaturated. Bedrock is part of the Wasatch Formation; its surface is variable in terms of lateral continuity, elevation, degree of weathering and fracturing, and composition (shale, siltstone, or sandstone). Along the center axis of the small valley that contained the reservoir, the bedrock surface dips toward the south-southwest, eventually intersecting the Beaver Creek alluvial aquifer at a distance of about 200 m from the dam (Figure 2). Most wells were screened at the bottom of the unconsolidated deposits (Figure 2), immediately overlying the bedrock, and thus were initially dry. In the immediate vicinity of the reservoir, groundwater was initially encountered in only four wells (2D, 3, 5, and 6). These wells all

extended into bedrock. On the basis of depth of geologic units, water levels, and water chemistry, it was determined that these saturated zones were hydraulically isolated from each other. A confined sandstone aquifer was encountered at a depth of about 33 m in well 3; no other aquifers were encountered. Wells 13–18 were completed in the Beaver Creek alluvial aquifer (Figures 1 and 2). Well 12 is completed in bedrock, but appears to be hydraulically connected to the alluvial aquifer and is the closest such well to the reservoir.

[10] The reservoir began accepting water from 6 CBNG wells on 16 August 2003 and continued to accept water until May 2004. A flowmeter measured the volume of water discharged to the reservoir. Approximately 95,000 m³ of water was pumped into the reservoir, an average of 52 m³/d per well. Anecdotal evidence suggests that initial infiltration rates from the reservoir were high; stage height in the reservoir was stable at about 2 m for the first several months of operations. Over time, the stage height increased as, presumably, the infiltration rate decreased. By May 2004, the stage height was greater than 4.5 m. Stage height in the reservoir decreased gradually after discharge to it was halted in May 2004. By mid-August 2004, there was standing water with a height less than 0.5 m in only the lowest reaches of the reservoir. Some standing water remained there until the area was reclaimed in August 2005. During reclamation, the remaining water was pumped out of the reservoir, the dam was torn down, the sediments that made up the dam were redistributed over the base of the reservoir, and the site was reseeded. Two months after reclamation, in October 2005, 50-mm-diameter continuous sediment cores were collected from land surface to bedrock using a pneumatic drill rig at three sites close to the lysimeters. These cores are referred to as postreservoir sediment samples.

[11] The prereservoir sediment samples were analyzed for moisture content, bulk density, and particle size by methods described by *Dane and Topp* [2002]. Concentrations of water-leachable ions in prereservoir and postreservoir sediment samples were determined with the method described by *McMahon et al.* [2003]. Briefly, air-dried sediment was mixed with deionized water in a 1:10 mass ratio, as recommended by *Faulkner et al.* [2001]. After mixing, samples were placed on an orbital shaker for 1 h at 170 rpm. The samples were then spun in a centrifuge for 10 min, after which water was extracted and passed through a 0.45- μ m filter. Anion concentrations were determined using standard ion chromatographic methods [*Dionex Corporation*, 2001] with an AS14 column; cation concentrations were determined by inductively coupled plasma-atomic emission spectrometry [*Briggs*, 2003; *Lamothe et al.*, 2002]. Cation exchange capacity on samples of bulk soil and sediment was determined by utilizing a modification of the unbuffered salt extraction method described by *Sumner and Miller* [1996]; 0.1M SrCl₂ and 0.1M CaCl₂ were used instead of 0.2M NH₄Cl and 0.2M KNO₃ (B. Jones, U.S. Geological Survey, oral communication, 2005). Bulk soil and sediment samples were prepared for X-ray diffraction (XRD) analysis by air-drying the sample and splitting by hand. The representative splits were then processed for either bulk XRD or clay mineral identification according to the respective methods for each. X-ray diffraction identification of bulk soil and

sediment samples was accomplished according to methods described by *Eberl* [2003] utilizing a micronized sample to which a known amount of zinc oxide was mixed as a reference intensity pattern. Identification of minerals was accomplished utilizing Jade 7 software [*Materials Data, Inc.*, 2005] (any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. government), and X-ray diffraction patterns of bulk samples were analyzed with the RockJock software [*Eberl*, 2003] to quantify the minerals. RockJock can generally quantify minerals to $\pm 5\%$ of a particular phase if a good degree of fit can be obtained for the calculated pattern versus the measured pattern. Clay minerals were prepared and analyzed by methods described by *Moore and Reynolds* [1997] using the glass-slide method and a four-step technique that notes changes in mineralogy following air-drying, ethylene glycol solvation, heating to 400°C, and heating to 550°C.

[12] Water samples were collected from lysimeters and wells on 15 dates between late August 2003 and October 2005. Lysimeter water samples were obtained by applying suction to each lysimeter, waiting about 4 h, and then applying positive air pressure to push the water sample out of the lysimeter through a sampling tube. This first sample was discarded, and the process was repeated. The second sample was saved for analysis. Water samples from wells were obtained after purging three casing volumes with either submersible pumps or bailers. Samples were analyzed for major dissolved-ion chemistry and metals using standard methods [*Rice et al.*, 2002; *Bartos and Ogle*, 2002]. Geochemical modeling was performed with the Phreeqc model [*Parkhurst and Appelo*, 1999].

3. Results

3.1. Sediment Properties

[13] The unconsolidated sediments are very fine to fine sand and silt with about 11% clay; there was little variation in texture with depth. Gravimetric soil moisture contents between the depths of 0.5 and 4.5 m were relatively uniform at about 0.07. From depths of 5 to 6.25 m, moisture contents were higher, between 0.12 and 0.14. Cation exchange capacity (CEC) varied little with depth. Samples from 36 different depths were analyzed for CEC. The average CEC was 24.5 meq per 100 g sediment (standard deviation of 4.4). Results of bulk mineralogical analyses (Figure 3) show that quartz is the predominant mineral, generally accounting for 30–50% of total mass. Gypsum, calcite, and dolomite are present throughout the profile, in abundances of about 1–2%, although at some depths abundances exceed 8%. Clay minerals account for about 30–35% of total mass. Smectites account for 10–18% of the sediment mass. To gain some understanding of possible cation-exchange mechanisms as water infiltrated from the reservoir, an effort was made to identify cations that originally occupied exchange sites on the smectites. Distinguishing calcium and sodium saturated smectites by analysis of initial X-ray diffraction patterns with the RockJock software proved problematic. A second round of X-ray patterns was run on samples from 10 depths (0.3–7 m). For this second round, samples were heated to 400°C for 24 h and then immediately X rayed, thus minimizing the possibility

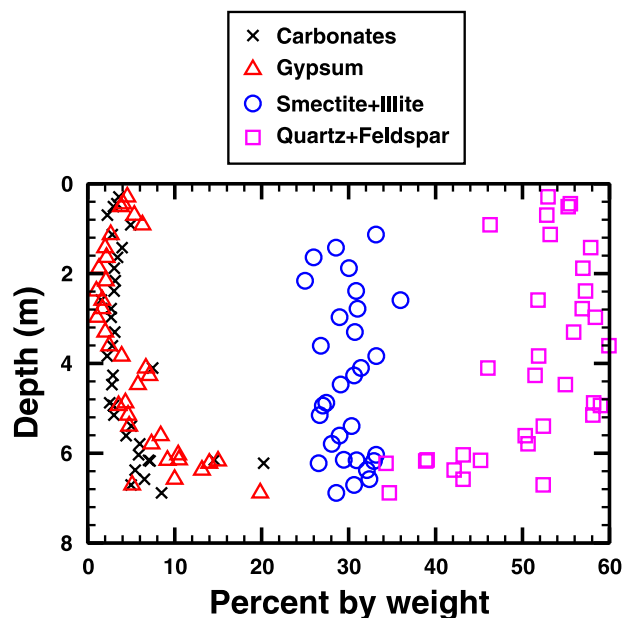


Figure 3. Mineralogy as a function of depth at lysimeter borehole.

of dried clays becoming rehydrated. Although this procedure was not able to provide actual percentages of sodium and calcium saturated exchange sites, qualitative trends were apparent. At the shallowest depths, X-ray patterns resembled patterns produced from a 15% pure calcium-saturated smectite standard (mixed with quartz). At the deepest depths, X-ray patterns were very similar to those for an analogous sodium-saturated smectite standard. There was a consistent trend in the intermediate depths: The deeper the sample, the more the X-ray pattern resembled that of the sodium-saturated smectite. Although not quantifiable, the implication is that calcium-saturated smectites, which dominated at shallow depths, grade into sodium-saturated smectites at depth. A similar trend was noted for

smectites in sediment samples obtained at well 12. Attempts were also made to directly measure the amount of sodium-occupied exchange sites, referred to as the exchangeable sodium percentage, or ESP, by the standard laboratory method of *Helmke and Sparks* [1996]. These results were inconclusive; the possible presence of naturally occurring soluble salts in these sediments made it impossible to distinguish between dissolution phenomena and exchange reactions.

3.2. Initial Water Chemistry

[14] CBNG water is a sodium-bicarbonate type with an average TDS concentration of 2275 mg/L (Table 1), typically void of available oxygen, nitrate, sulfate, and other electron acceptors due to the reducing environment of the coal beds in which natural gas is generated. Data for the CBNG water in Table 1 represent average concentrations from nine gas production wells located within 2 km of Skewed Reservoir. These wells do not discharge to the reservoir, but they produce from the same coal bed (Big George) at about the same depth (408 m) as the wells that do discharge to the reservoir. It was not possible to directly sample the wells that discharged into Skewed Reservoir.

[15] The sediments within which the lysimeters were installed were initially too dry to allow collection of water samples (lysimeters cannot collect samples if soil-water tension exceeds about 1 bar). The lysimeters were unable to produce water samples until 5 d after water began flowing into the reservoir (21 August 2003). Although there are no background data on unsaturated zone water chemistry at the site, water samples were obtained from the control site lysimeter. Sediments at the control site were similar in texture to those near Skewed Reservoir. Unsaturated zone water at the control site is a magnesium-sodium-sulfate type with TDS concentration of 13,400 mg/L (Table 1).

[16] Most observation wells were initially dry. Table 1 shows data for water from monitoring wells 2D and 6 that produced water prior to the reservoir going into operation (Figure 1). Data in Table 1 are from samples obtained before

Table 1. Total Dissolved Solids (TDS), Major Ion Concentrations, and Sodium Adsorption Ratio (SAR) for Coal-Bed Natural Gas (CBNG) Water, Shallow Groundwater, and Lysimeter Water Samples From Beneath Skewed Reservoir and From a Control Site Away From the Reservoir^a

Location and Date	TDS ^b (mg/L)	SO ₄ (mg/L)	HCO ₃ ^c (mg/L)	NO ₃ as N (mg/L)	Cl (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	pH Units	SAR
CBNG water	2,275	0.03	3,038	<0.05	28.9	50.5	37.5	1,040	47.4	8.37	27
GW monitoring well 2D, 27 Aug 2003	1,050	380	527	0.33	15	53.6	23.8	300	17.5	7.51	8.6
GW monitoring well 6, 27 Aug 2003	7,504	5,240	749	0.97	42	424	1,038	350	41	7.62	2.1
3-m lysimeter, 12 Nov 2003	5,950	2,890	1,495	0.2	206	663	251	1,033	11.4	7.30	8.6
5-m lysimeter, 12 Nov 2003	15,100	8,300	482	118	1,822	480	1,680	1,987	11.0	7.28	9.5
7-m lysimeter, 12 Nov 2003	105,000	79,000	484 ^d	736	181	443	12,300	12,700	20.3	7.12	24.3
Control lysimeter, 30 May 2002	13,400	9,720	310	23	87	435	1,710	1,260	23.1	7.45	5.7

^aCBNG water represents average values from nine natural gas production wells near Skewed Reservoir; all other data represent individual samples.

^bCalculated value [Hem, 1992].

^cTotal alkalinity, expressed as HCO₃.

^dEstimated value; alkalinity contains some noncarbonate species.

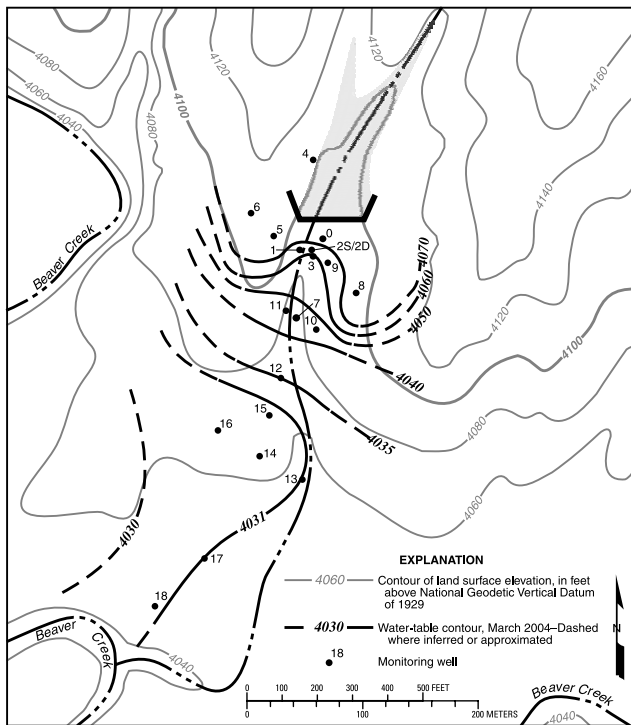


Figure 4. Water table contours, March 2004, in the vicinity of the Skewed Reservoir study area and monitoring network.

these wells were affected by reservoir water. Well 2D is screened at a depth of 16 m in sandstone; its water was originally a sodium-bicarbonate-sulfate type with TDS concentration of 1050 mg/L. Well 6 is screened at a depth of 5 m in shale and sandstone; its water was a magnesium-sulfate type with TDS concentration of about 7500 mg/L. In general, groundwater chemistry within the Wasatch Formation is highly variable depending on local geology. In sandstone aquifers within the Formation, *Bartos and Ogle* [2002] and *Rice et al.* [2002] found that TDS concentrations were in the range of from 200 to about 4000 mg/L; sulfate and bicarbonate were the dominant anions, and calcium and magnesium were the dominant cations. *Lowry et al.* [1986] reported TDS concentrations as high as 8200 mg/L in groundwater from the Formation, so the chemistries of the initial groundwater samples from wells 2D and 6 were not atypical for the Wasatch Formation.

3.3. Groundwater Mound Formation

[17] After the reservoir began accepting water, a perched groundwater mound formed above the bedrock surface and all wells yielded water. Figure 4 shows the configuration of the water table surface in March 2004; the water level contours indicate that the water is following the dip in the bedrock surface, moving to the south and west toward the Beaver Creek alluvial aquifer. Figure 5 shows water levels over time for three wells. The hydrograph for well 12, which is near the alluvial aquifer, shows an abrupt rise in January 2004. This rise and chemical data (not included here) indicate that water from the reservoir affected groundwater at this location about 4 months after water was first put into the reservoir. Hydrographs from other wells (Figure 5) show that the mound formed fairly quickly but

was slow to dissipate. The water table formed by the groundwater mound reached heights in excess of 7 m above the bedrock surface at some well locations.

3.4. Chloride and Nitrate in Sediment Samples

[18] Figure 6 shows profiles of chloride and nitrate in leachates obtained from sediment cores from beneath the reservoir before the reservoir accepted any water and after it was reclaimed. The prereservoir data represent natural conditions; data from the lysimeter site (Figures 6a and 6b) are typical for arid or semiarid regions where chloride and nitrate have accumulated for thousands of years [*Allison et al.*, 1985, 1994; *Prudic*, 1994; *Walvoord et al.*, 2003]. The “bulges” in concentrations shown in Figures 6a and 6b are generally attributed to evaporative concentration below the root zone [*Phillips*, 1994; *McMahon et al.*, 2006]. Peak concentrations were at a depth of 1.5 m for chloride and 3 m for nitrate. The prereservoir cores from the two sediment borings (B-1, B-2) in the channel (Figures 6a and 6b) show much less chloride and nitrate than sediments at the lysimeter site; these cores were collected in the poorly defined ephemeral channel that ran through the area before construction of the reservoir (Figure 1). The peaks in nitrate and chloride concentration for these channel sites are not well defined. As described earlier, it is typical for salt to be flushed out of sediments immediately underlying stream channels because streams in these regions are the primary source of recharge. Unpublished data that we have collected in the Powder River Basin indicate that this flushing occurs even for ephemeral channels that might see flow for only a few hours or days each year.

[19] Approximately 8500 kg nitrate (as N) per hectare of land surface were stored in the unconsolidated sediments at the lysimeter location prior to the onset of reservoir operations. This value lies within the range of 1000 to more than 13,000 kg/ha of nitrogen stored as nitrate in sediments at four arid sites in the western United States [*Walvoord et al.*, 2003]. *Boyce et al.* [1976] determined subsurface nitrate storage between 6200 and 12,700 kg/ha in Pleistocene loess in the Northern High Plains in Nebraska, with the peak nitrate concentrations generally occurring at depths exceeding 10 m. At three rangeland sites, also in the High Plains,

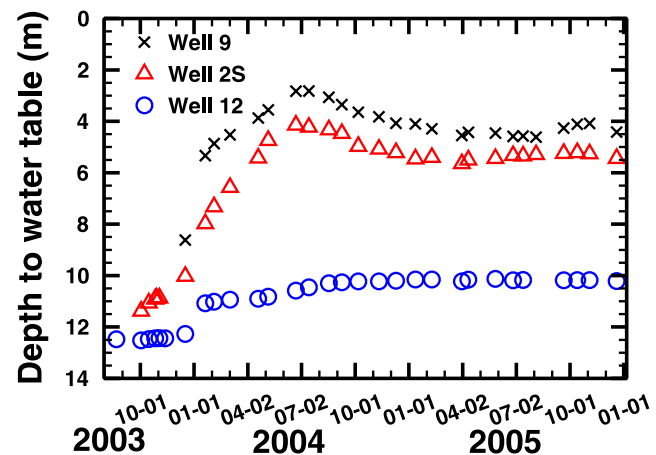


Figure 5. Groundwater levels in observation wells 2S, 9, and 12, August 2003 through December 2005.

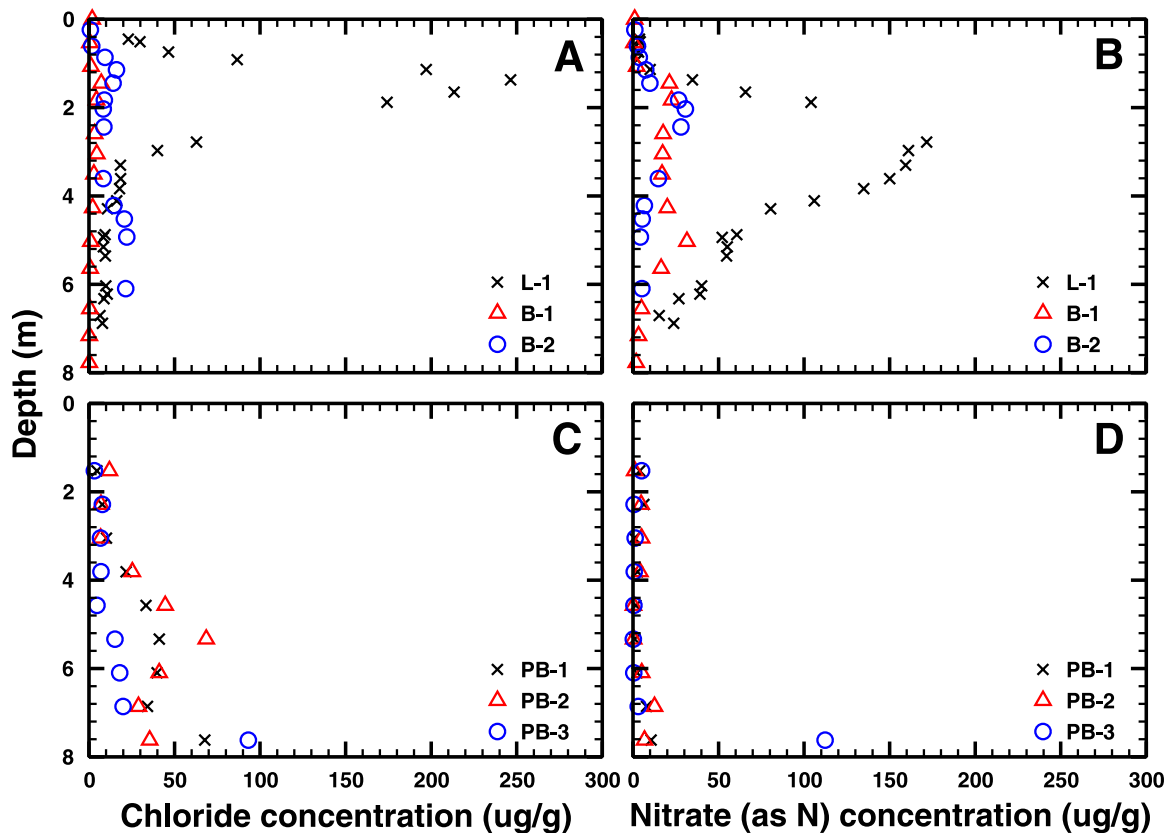


Figure 6. Concentration profiles from 10:1 water/sediment extracts on sediment cores obtained beneath Skewed Reservoir: (a) chloride from preservoir samples at lysimeter location and borings B-1 and B-2 located on ephemeral channel; (b) nitrate (as N) from preservoir samples; (c) chloride from postreservoir samples collected at borings PB-1, PB-2, and PB-3 near lysimeter location; and (d) nitrate (as N) from postreservoir samples collected at borings PB-1, PB-2, and PB-3. Concentrations are in micrograms per gram of sediment. Depths are relative to original land surface.

McMahon *et al.* [2006] estimated nitrate storage at 27, 70, and 5400 kg/ha, respectively.

[20] An estimated 6500 kg/ha of chloride initially was stored in the sediments at the lysimeter location. This value is similar to the median value of 7100 kg/ha determined from eight boreholes in low-recharge areas by Heilweil *et al.* [2005] at an arid site in southwestern Utah. McMahon *et al.* [2006] estimated storages of 360, 2000, and 12,000 kg/ha at their three High Plains sites.

[21] Chloride and nitrate concentrations were similar in the three postreservoir sediment cores (PB-1, PB-2, PB-3) that were collected near the lysimeters (Figures 6c and 6d). The data indicate that a substantial amount of chloride and nitrate remained in the sediments, even after 10 months of infiltration from the reservoir. It is likely that these anions were held in very small pores, where water was essentially immobile. Concentrations in the postreservoir sediment cores indicate that approximately 1250 kg/ha nitrate (as N) remained in storage. Chloride was less easily flushed from the sediment profile. Analyses of the postreservoir cores indicate that 3970 kg/ha of chloride were still in storage. Comparison of the preservoir and postreservoir cores (Figure 6) indicates that after 10 months of reservoir operation the bulge in chloride mass was transported downward but not completely through the sediment profile.

[22] On the basis of an average chloride wet deposition rate of 0.2 kg/ha/a measured at nearby National Atmospheric Deposition Program (NADP) stations in Wyoming and Montana (<http://nadp.sws.uiuc.edu/>) and assumptions that dry deposition was equal to wet deposition (i.e., total deposition rate of 0.4 kg/ha/a) and that current deposition rates are similar to those in the past, sediments at the lysimeter site represent about 16,000 years of chloride accumulation. The dynamics of the nitrogen cycle within the biosphere complicate efforts to estimate the rate of accumulation of nitrate in the unsaturated zone. The profile of nitrate in the unsaturated zone is consistent with atmospheric deposition as the primary source. However, all of the nitrogen deposited on land surface may not go into storage. Plants may take up some nitrogen. Other plants may actually be a source of nitrate by fixing atmospheric N_2 . Geologic sources of nitrate have been found in other locations [Boyce *et al.*, 1976; Holloway *et al.*, 1998] but are not believed to be significant in this area. If, like chloride, nitrate has been accumulating in the unsaturated zone at this site for 16,000 years, an accumulation rate of 0.53 kg/ha/a is required to account for the 8500 kg. This rate seems reasonable in light of the measured wet deposition rate of 0.68 kg/ha/a nitrate as N at nearby NADP sites.

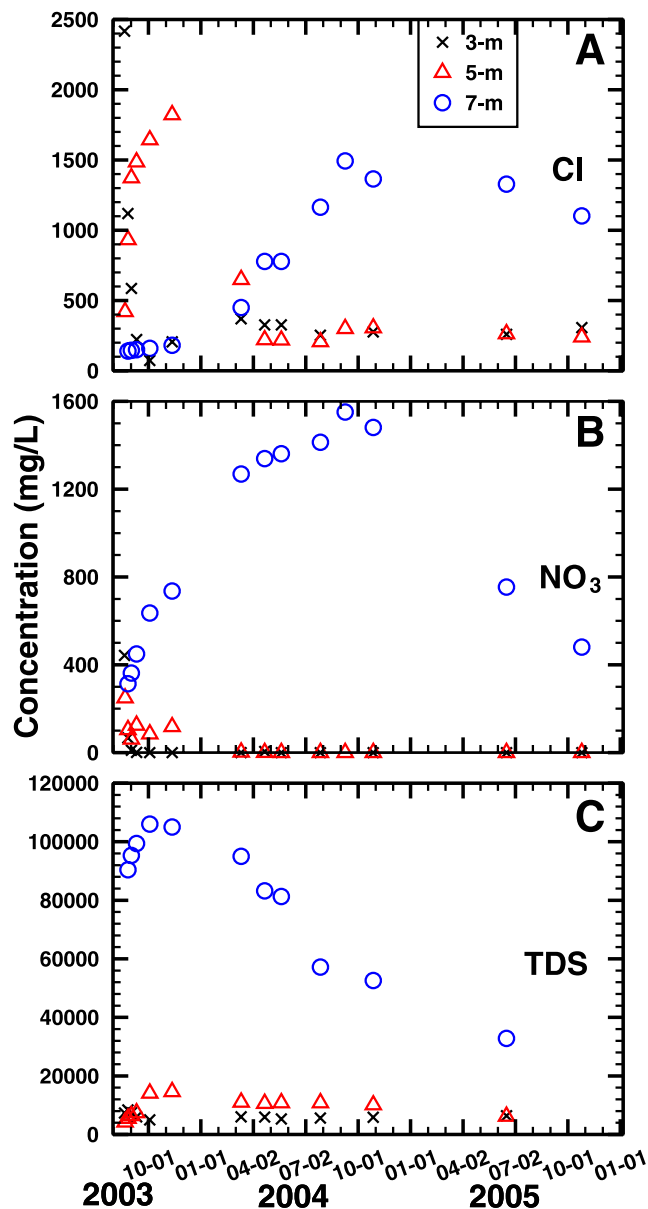


Figure 7. Trends over time in concentration of water samples from the 3-, 5-, and 7-m lysimeters: (a) chloride; (b) nitrate as N; and (c) total dissolved solids.

3.5. Chloride and Nitrate in Water Samples

[23] Chloride and nitrate concentrations for water from the lysimeters are shown in Figures 7a and 7b, respectively. At the 3-m depth, the highest concentration of chloride (about 2400 mg/L) occurred in the first sample obtained after the reservoir began accepting water (21 August 2003). Concentrations declined rapidly over time, falling to about 100 mg/L within 6 weeks. Chloride concentrations remained relatively stable, ranging between 100 and 300 mg/L, throughout the remainder of the study period. The highest concentration of nitrate at the 3-m depth (about 450 mg N/L) was also measured in the initial sample. Nitrate concentrations declined more rapidly than chloride concentrations over time. Four weeks after the reservoir went online, nitrate concentration at the 3-m depth was less than 1 mg/L.

Concentrations generally remained less than 1 mg/L throughout the duration of the study.

[24] Chloride concentrations in water at the 5-m depth initially rose over time (Figure 7a). The peak concentration of about 1800 mg/L was measured on 12 November 2003, eighty-eight days after operations at the reservoir began. After that time, concentrations decreased rapidly, falling to about 200 mg/L by April 2004. Chloride concentrations remained in the range of 200–300 mg/L throughout the remainder of the study period. The peak nitrate concentration of about 250 mg N/L was measured in the first sample obtained from the 5-m lysimeter on 21 August 2003 (Figure 7b). Concentrations fell to less than 1 mg/L by March 2004 and remained at that level through 2005.

[25] Trends in chloride and nitrate concentrations in waters at the 7-m depth show a rise and fall in concentration (Figures 7a and 7b). The peak chloride concentration of about 1500 mg/L occurred on 8 September 2004, more than a year after reservoir operations began. The peak nitrate concentration at the 7-m depth (about 1550 mg N/L) also occurred on that date. There are differences, however, between trends in concentrations of the two anions. Chloride concentrations increased gradually from 200 to 400 mg/L over the first 8 months of sampling. After April 2004, concentrations increased more rapidly. Nitrate concentrations, on the other hand, showed rapid increases over the first 6 months of sampling and more rapid decreases in concentration after the peak was reached. There is a lag of approximately 10 months between the peak concentration of TDS (Figure 7c) and that of chloride and nitrate. At the 3- and 5-m depths, the nitrate and chloride peak concentrations either preceded or coincided with the timing of the peak TDS concentration.

[26] The peak chloride concentration at the 7-m depth was less than that at the 5-m depth, which, in turn, was less than that at the 3-m depth. For nitrate, the peak concentration at the 7-m depth was substantially greater than those at the two shallower depths. The peak nitrate concentration in the prereservoir sediments occurred at a depth of about 3 m, whereas the peak chloride concentration was at a depth of about 1.5 m (Figures 6a and 6b). It is possible that higher concentrations of nitrate would have been observed at the shallower depths if samples could have been obtained more frequently during the early stages of the study. The highest chloride concentration measured in lysimeter samples, 2400 mg/L, is less than the highest pore water concentration measured in prereservoir sediment samples, about 3500 mg/L. (Pore water concentration in prereservoir sediments is calculated by dividing concentrations in micrograms per gram sediment shown in Figures 6a and 6b by measured soil moisture content.) Similarly, the peak nitrate concentration in lysimeter samples, 1550 mg/L as N, is less than that measured in prereservoir sediment samples, about 2100 mg/L as N. These results are consistent with the hypothesis that chloride and nitrate in the lysimeter samples came from storage within the sediment column.

[27] Attempts to estimate the mass of chloride and nitrate that were flushed from the sediments at Skewed Reservoir are worthwhile, both for understanding the processes that have occurred at the site and for predicting impacts at other impoundments in the Basin. These attempts are problematic, though. Natural salt concentrations in these sediments vary

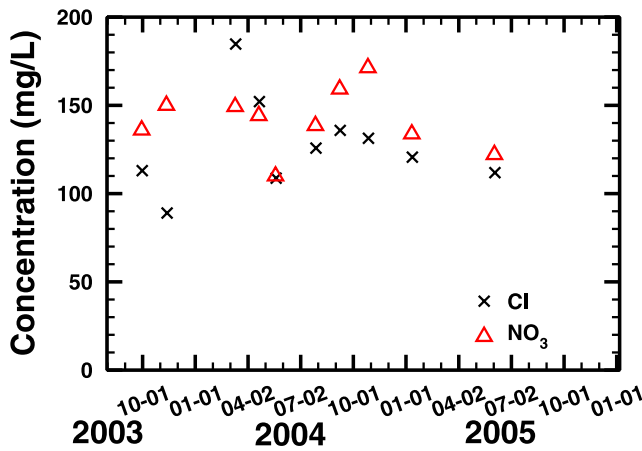


Figure 8. Average concentration over time of chloride and nitrate (as N) in observation wells affected by Skewed Reservoir.

spatially, as clearly indicated in Figure 6. To estimate these flushed masses, a simple mass balance model based on chloride and nitrate concentrations in groundwater was used. Because there was initially no perched groundwater above bedrock, the reservoir is the source of the free-moving perched water, and the chloride and nitrate in the perched groundwater derive either from the CBNG water itself (chloride concentration 28.9 mg/L, nitrate concentration less than 1 mg/L as N, Table 1) or from the sediments.

[28] The mass of chloride in the perched water is equal to the volume of water times the average concentration of that water. Generally, the volume of water in a perched zone such as this is very difficult to determine because of geologic heterogeneities. However, in this study, the volume of water put into the reservoir is known, about 95,000 m³. Assuming that all of this water ended up in the perched layer, it remains then to estimate the average chloride concentration of the perched groundwater. To do this, chloride concentrations in observation well samples were averaged by date. Figure 8 shows the average chloride concentrations in water samples from all observation wells affected by infiltration from the reservoir for sampling dates between October 2003 and May 2005 (Note that the number of wells included in the calculations shown in Figure 8 varied over time. For the first sample date shown, only two wells were affected by the reservoir. The number of affected wells rose to 15 by July 2004 and remained at 15 thereafter.) On any individual sampling date there was variability in chloride concentrations; the coefficient of variation (CV) ranged from 46 to 78%. However, the average value for each sample date did not vary substantially over this period. The average concentration over all sample dates was 129 mg/L (CV of 19%). Thus about 12,300 kg of chloride were in the groundwater mound produced from the reservoir. About 22% of this chloride, or about 2700 kg, can be attributed to the CBNG water itself. The remaining 9600 kg were flushed from the sediments. It is important to note that it is not just the sediments immediately underlying the reservoir that contribute chloride to the perched groundwater; sediments that the perched water encounters as it moves toward the alluvial aquifer may also contribute chloride. This can be shown by simply calculating the mass that

would exist in the sediment column if only the 1-ha area of the reservoir were contributing chloride. This amount, 9600 kg/ha, is much greater than that measured at the lysimeter location (6500 kg/ha) or at any other borehole location in the study area for which chloride concentration data are available.

[29] A similar approach is used to estimate the total amount of nitrate in the perched groundwater. Figure 8 shows average nitrate concentrations for water samples obtained in observation wells that were affected by the reservoir for sample dates between October 2003 and May 2005. Variability in nitrate concentration among wells on the same sampling date

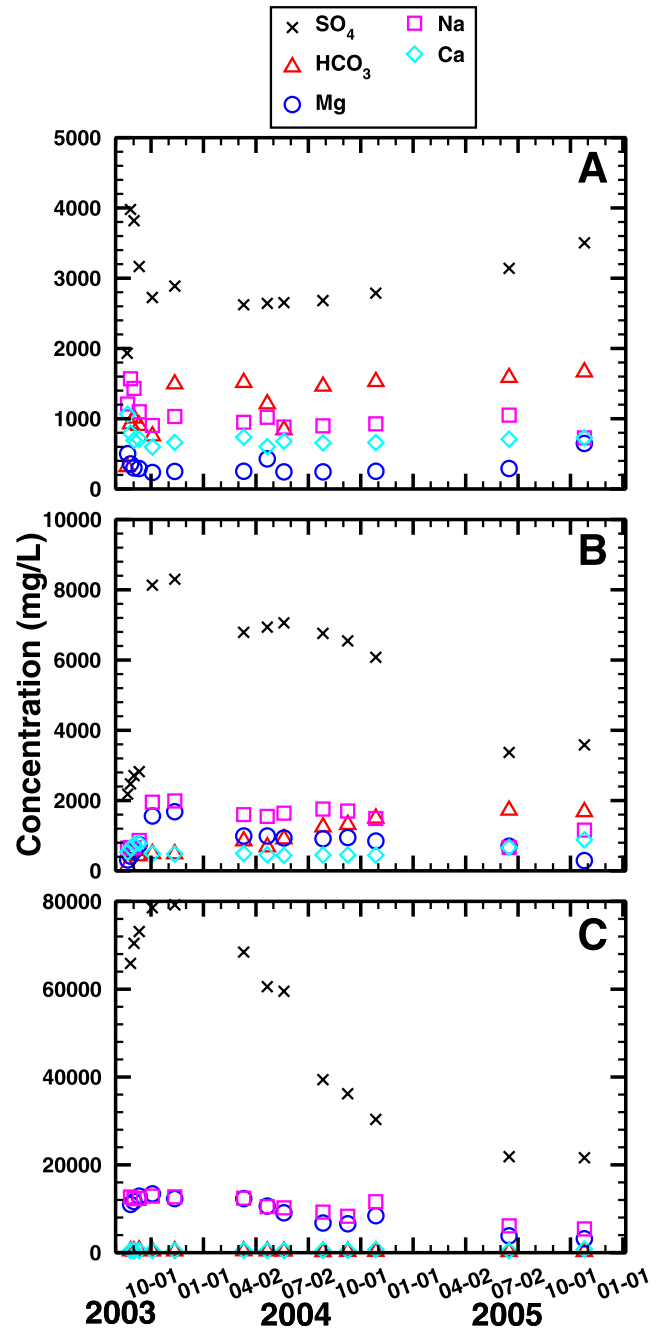


Figure 9. Trends over time of major ion concentrations for water samples from (a) 3-m lysimeter, (b) 5-m lysimeter, and (c) 7-m lysimeter.

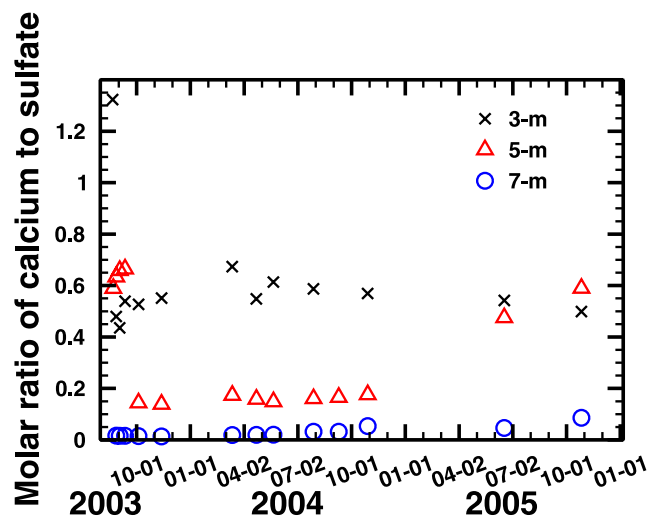


Figure 10. Molar ratio of calcium to sulfate in lysimeter water samples.

was greater (average CV of 103%) than that for chloride. As with chloride, however, the average concentration for each sample date did not vary greatly; the average for all sample dates was 142 mg/L (as N), with a CV of 13%. Multiplying this average value by the 95,000 m³ of water from the reservoir produces an estimate of 13,500 kg of nitrate (as N) within the perched groundwater. The CBNG water is essentially void of nitrate, but it does contain about 6.3 mg/L NH₄ as N. If all of this ammonium were oxidized to nitrate, it could account for about 600 kg of the nitrate in the perched groundwater. The remaining 12,900 kg must have been flushed from the sediments. The concentration of nitrate that would be required, if all of the nitrate came from the 1-ha area of the reservoir, is calculated to be 12,900 kg/ha. Again, this number is considerably greater than the 8,500 kg/ha that was measured for the lysimeter site. The ratio of these two numbers for nitrate of 1.52 is very similar to the ratio found for chloride of 1.48.

3.6. Major Ion Water Chemistry of Lysimeter Samples

[30] Water samples from the 3-m lysimeter were a sodium-calcium-sulfate-bicarbonate water type (Table 1, Figure 9a). Total dissolved solid concentration peaked at 8400 mg/L (Figure 7c) on the second sampling date, 27 August 2003. After that date, concentrations were fairly stable, ranging from 5000 to 6000 mg/L. The influence of the CBNG water on the water at the 3-m depth is apparent in the high sodium and bicarbonate concentrations. The increased sulfate and calcium concentrations, relative to CBNG water, can be attributed at least partially to dissolution of gypsum. The mole ratios of calcium to sulfate in solution ranged from 0.43 to 0.67 after the first sampling date (Figure 10), indicating that other reactions also must be involved in order to produce this water chemistry.

[31] Water samples obtained from the 5-m lysimeter were a magnesium-sodium-sulfate type (Table 1, Figure 9b). Magnesium concentrations were substantially greater than those in the 3-m water. Perhaps more surprisingly, when viewed in light of the high SAR values for the CBNG water and the 3-m lysimeter samples, sodium concentrations were approximately double those in the CBNG water. Total

dissolved solid concentration in these samples rose quickly after the reservoir came on line, reaching a peak of 14,600 mg/L on 12 November 2003 (Figure 7c). After that, there was a gradual decrease in sulfate, magnesium, and sodium concentrations and a slight rise in bicarbonate concentrations over time (Figure 9b). Molar ratios of calcium to sulfate were similar to those in water from the 3-m depth at early and late times (about 0.6), but between October 2003 and November 2004 these ratios were consistently about 0.16 (Figure 10). At early times, water chemistry at the 5-m depth was fairly similar to that at the control lysimeter (Table 1), and it was distinguished from that at the 3-m depth by higher concentrations in TDS and sodium. With decreasing sulfate and increasing bicarbonate concentrations over time, water chemistry at the 5-m depth became similar to that at the 3-m depth by late 2005.

[32] The earliest date that a water sample could be obtained from the 7-m lysimeter was 27 August 2003. Concentrations of TDS, sulfate, magnesium, and sodium of that first sample (Figures 7c and 9c) were almost an order of magnitude greater than values measured in CBNG water or in water at the 3- and 5-m depths (Table 1, Figures 7c and 9). Water at the 7-m depth was a magnesium-sodium-sulfate type. Concentrations of the three major ions rose during the first 2 months of sampling. Peak concentrations of TDS (106,000 mg/L) and sulfate (79,000 mg/L) were reached on 3 October and 12 November 2003, respectively, about the same times that peaks occurred at the 5-m depth. Following the peaks, concentrations at the 7-m depth declined steadily over time. The high solute concentrations at the 7-m depth were not expected. We are unaware of any reports of other waters in the Wasatch Formation with concentrations this high. Molar ratios of calcium to sulfate were quite low, generally less than 0.02 for the first year of sampling but increasing gradually over time to about 0.08 by late 2005 (Figure 10).

3.7. Hydrogeochemical Reactions

[33] The geochemical reaction model Phreeqc [Parkhurst and Appelo, 1999] was used to study the hydrogeochemical reactions that occurred as water moved downward from the reservoir. Specifically, reactions involving reservoir water and measured geochemical properties of the sediments were investigated with equilibrium batch models in attempts to reproduce water chemistry at the 3-, 5-, and 7-m depths in November 2003 (Table 1). In addition, one-dimensional reactive transport through a hypothetical sediment column was simulated.

[34] The water chemistry at the 3-m depth (sodium-calcium-sulfate-bicarbonate, TDS concentration of about 8400 mg/L) could be closely reproduced by the batch reaction model if the initial reservoir water (sodium-bicarbonate, with 2275 mg/L of TDS) were equilibrated to saturation with gypsum (CaSO₄·2H₂O). The magnesium-sodium-sulfate water chemistry at the 5- and 7-m depths appears to derive from gypsum dissolution accompanied by cation exchange of calcium for sodium and magnesium on clays:



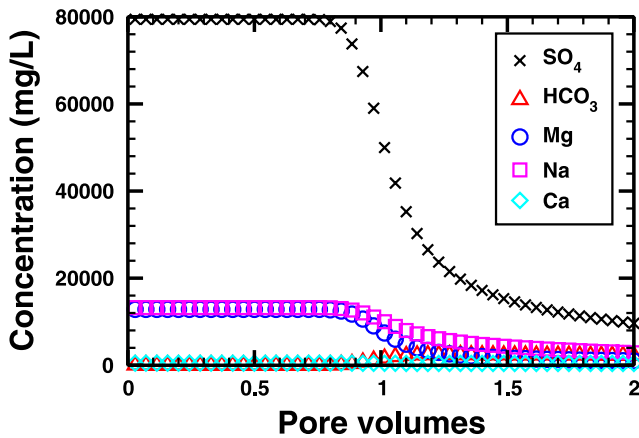
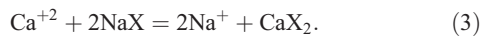
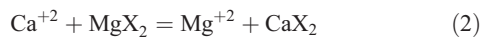


Figure 11. Major ion concentrations in outflow from a hypothetical 7-m-long column as simulated with Phreeqc. Inflow to the column is coal-bed natural gas (CBNG) water (Table 1). In the column, the water is equilibrated to saturation with gypsum, calcite, and dolomite; and there is 1 mole of exchange sites with initial composition of 66% Mg, 32% Na, and 2% Ca.



[35] As calcium is removed from solution by exchange onto clays, more dissolution of gypsum can occur. Water chemistry at the 5-m depth could be reasonably well reproduced with the batch model by equilibrating the reservoir water to saturation with gypsum, calcite, and dolomite and including 1 mole of cation-exchange sites with an initial composition that was 67% Mg, 14% Na, and 19% Ca by equivalents. The average cation exchange capacity of 24.5 meq per 100 g of sediment and moisture content of 0.28 g water per gram of dry sediment (as measured in the postreservoir sediment cores) imply that there were about 0.875 moles of exchange sites per liter of water at the lysimeter location, in good agreement with the 1 mole used in the model. Water chemistry at the 7-m depth could be created by the same model but with cation-exchange sites having an initial composition that was 66% Mg, 32% Na, and 2% Ca. As discussed previously, mineralogical and laboratory analyses were unable to quantify cation concentrations on clay exchange sites. No inferences on magnesium could be made, but the mineralogical analyses did indicate that the relative number of sodium-occupied exchange sites increased with depth and that sodium-saturated smectites dominated at the 7-m depth.

[36] To further examine water chemistry at the 7-m depth, a one-dimensional reactive solute transport simulation was constructed with Phreeqc for flow through a hypothetical 7-m-long column. As with the batch model, water in the column was equilibrated to saturation with gypsum, calcite, and dolomite, and 1 mole of exchange sites per liter was available with initial composition that was 66% Mg, 32% Na, and 2% Ca. Inflow to the column was reservoir water. This simulation should be considered qualitative in nature. Because Phreeqc assumes that all pores are water

filled, the advancement of a wetting front through a column whose sediments are initially only partially water saturated is not exactly represented. Nonetheless, the model is a useful tool for examining the above stated hypothesis.

[37] Initial column outflow (Figure 11) has high concentrations of sulfate, magnesium, and sodium, values similar to those in the 7-m lysimeter samples from late 2003 (Figure 9c). After about one pore volume has flowed through the column, simulated sulfate, sodium, and magnesium concentrations decrease, and alkalinity increases. In a qualitative sense, concentrations in the 7-m lysimeter samples (Figure 9c) show similar trends. The timescales for Figures 9c and 11 cannot be directly compared because the actual flux rates within the subsurface, as discussed below, are unknown and probably vary widely in both space and time. Nonetheless, the simulation results demonstrate the plausibility of the hypothesis that gypsum dissolution is enhanced by cation exchange. The amount of gypsum required to support results of the transport simulation is equivalent to slightly less than 2% of the solids in the column; this amount is consistent with the mineralogy shown in Figure 3. Predicted changes in calcite and dolomite amounts were negligible.

[38] The rates at which water moves through the subsurface and the pathways it follows are difficult to discern. Apparent vertical water velocity, v_A , can be calculated based on measured chloride and nitrate concentrations:

$$v_A = (D_{\text{lys}} - D_{\text{peak}}) / \Delta t, \quad (4)$$

where D_{lys} is lysimeter depth, D_{peak} is depth of the initial peak concentration in sediments (1.5 m for chloride and 3 m for nitrate), and Δt is the difference between the time of peak concentration in lysimeter samples and the time when the reservoir first received water. Apparent velocity can also be calculated from the time it took for the wetting front from the reservoir to reach each lysimeter depth ($\Delta t'$):

$$v_A = D_{\text{lys}} / \Delta t'. \quad (5)$$

[39] Wetting front movement was not directly monitored, but it can be inferred from lysimeter performance. The suction lysimeters can obtain samples only when soil matric potentials are greater than -100 kPa. The fact that the lysimeters were unable to collect samples prior to water entering the reservoir indicates that matric potentials were initially less than -100 kPa. Because the wetting front must have reached the depth of each lysimeter by the first date that each lysimeter was able to collect a sample, those first sample dates can be used to approximate $\Delta t'$: 5 d for the

Table 2. Apparent Vertical Velocities Calculated by Using Equation (4) on the Basis of Chloride and Nitrate Concentrations and Equation (5) on the Basis of Wetting-Front Movement^a

Depth, m	Chloride	Nitrate	Wetting Front
3	0.3	...	0.6
5	0.04	0.7	1
7	0.01	0.01	0.64

^aVelocities are m/d.

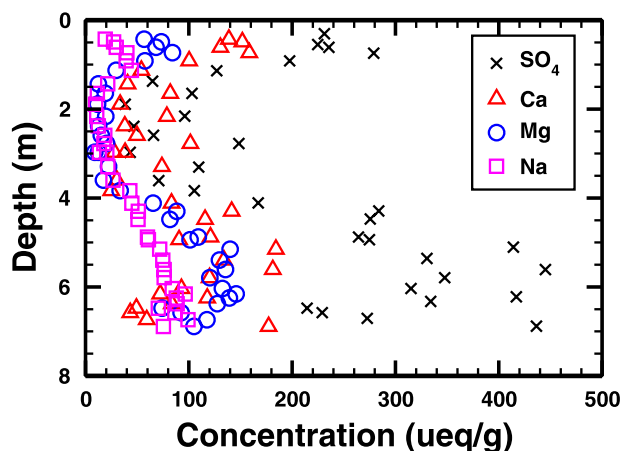


Figure 12. Major ion concentrations in water/sediment extracts of prereservoir sediment samples at the lysimeter location (microequivalents per gram of sediment).

3- and 5-m depths and 11 d for the 7-m depth. The inconsistency in the calculated apparent velocities (Table 2) demonstrates the complexity of subsurface water movement at the site and highlights the difficulty in reconciling the timescales of Figures 9c and 11. Particularly noteworthy is the discrepancy in velocities at the 7-m depth; the wetting-front-based velocity is much higher than those based on chloride and nitrate. This discrepancy and the fact that the peak TDS concentration at the 7-m depth occurred almost a year before those of nitrate and chloride (Figure 7) cast considerable doubt on the initial assumption that the three lysimeters were aligned along a single flow path (i.e., that water movement was strictly vertical). An alternative hypothesis is that the water sampled at early times from the 7-m lysimeter infiltrated at some other part of the reservoir where chloride concentrations in sediments were low (such as the ephemeral channel); that water then became perched above the bedrock surface and moved laterally to the 7-m lysimeter. The uncertainty in travel paths limits the options for more detailed solute transport modeling.

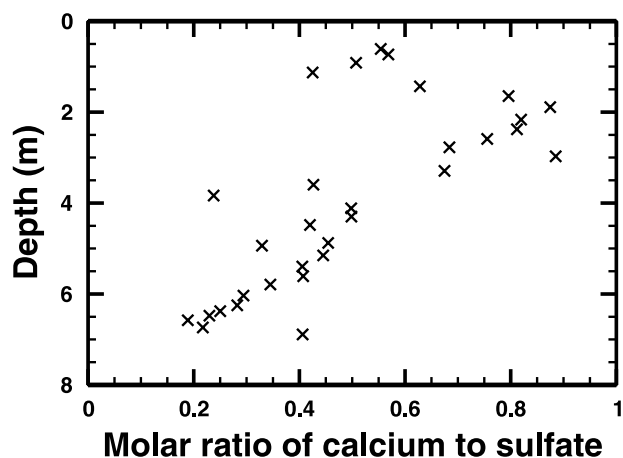


Figure 13. Molar ratio of calcium to sulfate in water/sediment extracts of prereservoir sediment samples at the lysimeter location.

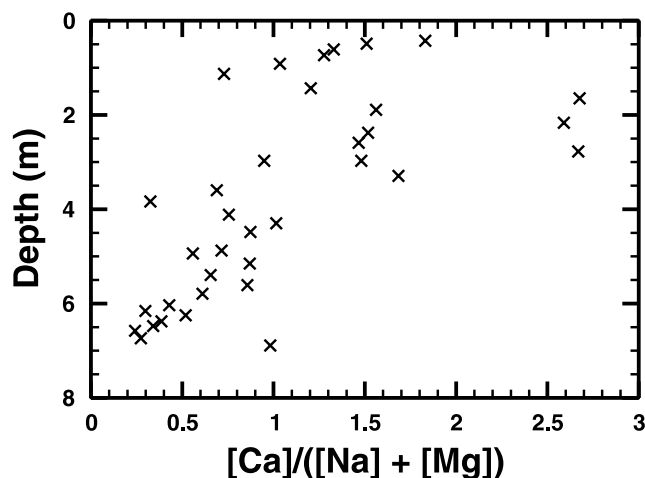


Figure 14. Molar ratio of calcium to sodium plus magnesium in water/sediment extracts of prereservoir sediment samples at the lysimeter location.

[40] The water/sediment extracts of the prereservoir sediment samples were prepared primarily to examine chloride and nitrate profiles; however, some qualitative insight can be gained from analysis of major ion chemistry of the extracts (Figure 12). Sulfate is the dominant anion in the extracts, presumably from dissolution of gypsum. Calcium is the dominant cation at shallow depths, consistent with gypsum dissolution. The largest sulfate concentrations occur at depths greater than 4 m. The ratio of moles of calcium to moles of sulfate in the extract solution generally decreases with depth below 4 m (Figure 13); the concomitant rise in magnesium and sodium concentration relative to that of calcium (Figure 14) lends credence to the hypothesis that calcium from gypsum dissolution is being exchanged for these other cations on the sediment. It appears the sediments in the 5- to 7-m depth are conducive to cation-exchange-enhanced gypsum dissolution. Comparison of Figures 10 and 13 shows that mole ratios of calcium to sulfate in water from the 3- and 5-m lysimeters are consistent with the ratios derived from the sediment extracts. That cannot be said about water from the 7-m lysimeter; ratios for that water (0.01–0.08) are substantially less than those shown in Figure 13.

[41] Cation-exchange-enhanced gypsum dissolution has been observed elsewhere. Salinity of groundwater in a region of the Great Plains in Montana is ascribed to this phenomenon [Donovan *et al.*, 1981]. It serves as the basis for reclaiming sodic soils with gypsum and other amendments [Jury *et al.*, 1979; Oster and Frenkel, 1980; Frenkel *et al.*, 1989], a practice coming into widespread use in the Basin as irrigation with CBNG water increases [Ganjegunte and Vance, 2006]. Frenkel *et al.* [1989] observed that this phenomenon can continue until all gypsum is dissolved or until all available exchange sites become occupied by calcium. Cation-exchange-enhanced dissolution of minerals has also been observed for barite [Matthews *et al.*, 2006; Eberl and Landa, 1985], celestite [Eberl and Landa, 1985], and apatite [Lai and Eberl, 1986].

[42] An alternative hypothesis on the origin of the high TDS concentration water from the 7-m lysimeter warrants consideration. It is conceivable that sulfate, magnesium, and

sodium are stored in the sediments in the form of soluble magnesium-sodium-sulfate salts. Modeling indicated that dissolution of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), mirabilite ($\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and calcite (CaCO_3) in CBNG water could produce water with a chemistry similar to that of the 7-m lysimeter samples. Mineralogical analysis of the preresevoir cores and cores from observation wells did not indicate the presence of any of these salts. It is possible that these salts are present in concentrations less than detection levels and that as water moves along the flow path that leads to the 7-m lysimeter it continually dissolves these salts so that the concentrations of sulfate, magnesium, and sodium increase along the flow path. That possibility seems remote, however, because these types of salts, which are formed as water evaporates and concentrates solutes, generally are found at or very close to land surface [Keller et al., 1986; Timpson et al., 1986; Whittig et al., 1982]. Beke and Palmer [1989] did find mirabilite crystals at a depth of 1.2 m in southern Alberta, Canada, and attributed their presence, at least in part, to the concentrating effect of an overlying zone of frozen soil. In southern Nevada, Buck et al. [2006] identified soluble magnesium-sodium-sulfate salts in a soil horizon at depths between 1.3 and 1.5 m and attributed their formation to evaporation from the capillary fringe of a shallow water table. Neither of these scenarios for subsurface formation of salts seems likely for the Skewed Reservoir site. A relict surface, long ago covered by younger sediments, could conceivably be a location of salt formation at the Skewed Reservoir site, but visual inspection and physical and chemical analyses of sediments provide no evidence of such a feature. Figure 12 shows that sodium and magnesium concentrations in preresevoir water/sediment extracts change gradually with depth; there is no indication of a horizon with high salt concentration.

4. Discussion

[43] Anecdotal observations provide some additional insight into the interaction between sediment and water at the Skewed Reservoir site. Land-surface subsidence, of the order of tens of millimeters, was observed over a 0.25-ha area immediately south of the dam. In October 2003, a slump, which was subsequently repaired, occurred on a section of the dam. By late fall of 2003, land-surface fissures appeared in some areas near the reservoir. These were about 10 mm in width and extended radially to tens of meters from the reservoir. All these phenomena are consistent with widespread dissolution and compaction of subsurface sediments.

[44] Decreased infiltration rates from the reservoir over time are attributed to a reduction in hydraulic conductivity caused by the dispersal of clay particles near land surface by the high SAR CBNG water. Sodium in the water replaces calcium in the clays, altering clay structure and leading to clogging of pores [Frenkel et al., 1978]. Hydraulic conductivity of preresevoir and postresevoir sediment cores was not measured directly, but the top 2 m of the postresevoir cores lacked structure and were quite mucky. The dispersal of clays may have also led to an increase in the amount of immobile water, thus inhibiting the complete flushing of chloride and nitrate from the sediments.

[45] Interesting anomalies illustrate the complex character of the unconsolidated sediments at the study site and

highlight the difficulties associated with studying the interactions between CBNG water and these sediments. The high SAR of the CBNG water led to dispersal of clays and reduction in hydraulic conductivity, at least in the upper 2 m of sediments. Clays deeper in the sediment profile appear to release magnesium and sodium from exchange sites in favor of calcium supplied by gypsum dissolution, leading to large increases in magnesium and sodium concentrations in lysimeter water samples, even though the SAR of samples from the 7-m lysimeter exceed 20.

[46] It is somewhat surprising to find a natural system in which sodium smectites reside in the presence of gypsum. It seems that this situation could occur only if there were very little or no water movement through the sediments over a long period of time. (The large accumulations of chloride and nitrate in the lysimeter site sediments support this idea.) With any water movement, one would expect that either all of the gypsum would dissolve or the smectites would become saturated with calcium. How such a system evolved is an interesting question for future research. Whether this phenomenon is strictly local to the immediate vicinity of Skewed Reservoir or whether these conditions are widespread throughout the Powder River Structural Basin is a question with important implications for placement of future impoundments.

[47] Data from water and preresevoir and postresevoir sediment samples indicate that nitrate is more readily transported through the subsurface than chloride. The earlier arrival of the nitrate peak (relative to the chloride peak) at the 3- and 5-m lysimeters can be attributed to the fact that the preresevoir nitrate bulge was deeper than the chloride bulge (Figure 6). Comparison of preresevoir and postresevoir samples, however, clearly shows that a much higher percentage of nitrate relative to chloride was removed from the sediments. Water samples from the 3- and 5-m lysimeters support the sediment data; from April 2004 through November 2005, nitrate concentrations were less than 1 mg/L, whereas chloride concentrations were consistently between 200 and 300 mg/L, even though chloride concentration of the CBNG water was only about 29 mg/L. Denitrification may have been occurring. The sediments in this environment usually experience oxic conditions, but the decreased permeability of the shallow sediments underlying the reservoir caused by dispersal of clays may have reduced the flow of oxygen through them. However, another line of evidence seems to argue against widespread denitrification. Comparison of peak concentrations in the 7-m lysimeters samples relative to those in the preresevoir sediment pore water show that the nitrate peaks are much higher (1550 mg/L in the lysimeter sample is equal to 74% of the maximum preresevoir pore water concentration of 2100 mg/L as N) than the lysimeter chloride peak (1500 mg/L in the lysimeter sample is equal to 43% of the peak chloride concentration of 3500 mg/L in preresevoir pore water).

[48] Few other data on groundwater chemistry near CBNG impoundments are available. Wheaton and Brown [2005] present preliminary results of groundwater quality monitoring at three CBNG impoundment sites in the Powder River Basin. They found, in general, that TDS concentrations in groundwater increased due to infiltration from the impoundments. The maximum TDS that they report is 12,400 mg/L. The Bureau of Land Management has mon-

itoring wells in the vicinity of four impoundments; their groundwater chemistry data do not show the high TDS and ion concentrations found in the 7-m lysimeter samples at Skewed Reservoir. These results could mean that sediments characteristic of the Skewed Reservoir site are not widespread throughout the Basin; they also could mean that the complex geology and groundwater flow paths that typify the Basin require very detailed monitoring well networks to accurately assess flow and transport patterns.

[49] Impoundments built over existing channels should minimize the flushing of chloride, nitrate, and other constituents into groundwater. Most CBNG impoundments in Wyoming are classified as “on-channel” by the state. Indeed, Skewed Reservoir was an “on-channel” impoundment. In the small watersheds of the Basin, stream channels are quite narrow, typically less than 1 m in width. Because of the height of the dam and the surface extent of the reservoir, streams channels may make up only a small percentage of the base of reservoirs. Even though the lysimeters were located near a channel, the sediments there contained a large store of chloride and nitrate. So if “on-channel” impoundment waters extend beyond established channels, there is potential for flushing salts from sediments.

[50] On the basis of sediment samples collected in and around the Skewed Reservoir site, the bulk of the naturally occurring chloride and nitrate resides in the top few meters of sediments. Removal of these sediments from areas to be inundated by an impoundment would remove the source of contamination. At one of the study sites reported on by *Wheaton and Brown* [2005], unconsolidated surface sediments were removed during construction. The base of the reservoir was in weathered bedrock. The maximum concentrations reported in groundwater were 26.7 mg/L chloride and 8.8 mg/L nitrate, values much less than those measured at the Skewed Reservoir site.

[51] It is difficult to predict the fate of the solute plume that formed in the perched saturated zone atop the bedrock surface beneath the reservoir. Movement of that water is to the south and west toward the Beaver Creek alluvial aquifer at a distance of about 200 m from the reservoir site. Chloride and nitrate may behave conservatively within groundwater. Water in the alluvial aquifer will dilute the plume and reduce nitrate and chloride concentrations. The fate of the high sulfate, magnesium, and sodium concentrations in the plume is not so clear. The reactions that produced the high TDS concentration water at the 7-m depth occurred in sediments that had historically witnessed very low rates of water flow. If groundwater moving along the top of the bedrock encounters sediments with similar chemical characteristics, continued gypsum dissolution and cation exchange reactions could occur, thus enhancing the TDS concentrations. It also is possible that other, different reactions would occur to reduce the TDS concentration (e.g., if clays with calcium-saturated exchange sites are present, the process could be reversed with sodium reexchanging for calcium and subsequently causing gypsum to precipitate). These reactions would not be expected to continue once the perched water flows into the alluvial aquifer.

[52] The importance of our results lies largely in how representative they are for other impoundment sites in the Powder River Basin. We have collected sediment cores from several different areas across the Basin and analyzed

them for chloride and nitrate. Preliminary results suggest that the profiles seen at the Skewed Reservoir site are typical of other areas. In addition, our data are similar to sediment profile data for arid and semiarid regions presented by *Boyce et al.* [1976], *Walvoord et al.* [2003], and *McMahon et al.* [2006]. So it is reasonable to expect similar chloride and nitrate profiles at other impoundment sites in the Basin. As of January 2007, in excess of 4000 permits had been issued for impoundments in the Basin by the state of Wyoming. On the basis of findings at Skewed Reservoir, we determined that water infiltrating from 4000 reservoirs could release more than 48 million kg of chloride and 52 million kg of nitrate (as N) into groundwater.

[53] It is not possible to estimate loads of sulfate, sodium, and magnesium to groundwater at the Skewed Reservoir site or to calculate potential loads for the Powder River Basin as a whole. In addition to the nonconservative nature of these constituents, quantification of available source material for these solutes is problematic. For chloride and nitrate, there is a limited, quantifiable source in the sediments. According to our hypothesis, gypsum dissolution is accompanied by cation exchange at our study site. There is an abundance of gypsum in sediments at the Skewed Reservoir site and, in general, in sediments across the Basin [*Bartos and Ogle*, 2002]. The limitation on these reactions is the presence of clays whose exchange sites are dominated by magnesium and sodium. Efforts to directly measure the abundance of such clays at the Skewed Reservoir site have not been fully successful. Currently (2007), there is no way to determine whether cation-exchange-enhanced gypsum dissolution is occurring at other impoundments except by detailed monitoring of groundwater chemistry. Ongoing research is aimed at developing easily measured indicators that could be used to identify areas susceptible to these reactions.

[54] The fast pace and wide extent of energy development in the Powder River Basin complicate efforts for controlled study of surface and subsurface hydrology. Our investigation was designed to study water movement from Skewed Reservoir through the subsurface and associated changes in groundwater chemistry for 3 years. However, the reservoir was shut down after only 10 months of operation. In addition, the down gradient area between the reservoir and Beaver Creek underwent extensive development over the course of the study. Several pipelines were installed in the subsurface to transport gas and water. A center pivot irrigation system was put into operation, and a large water treatment facility was constructed. All of these features affected the local hydrology. Results reported in this paper are not affected by these features, but it will be difficult in the future to distinguish impacts on the Beaver Creek alluvial aquifer due to Skewed Reservoir from those associated with other local development.

5. Summary

[55] CBNG water infiltrating from Skewed Reservoir produced a groundwater contaminant plume. Total dissolved solids concentration in CBNG water was about 2300 mg/L; concentrations in excess of 100,000 mg/L were measured in samples from the 7-m lysimeter. Magnesium, sodium, and sulfate were the dominant ions in the plume. The mechanism for the creation of the high TDS concentrations at the 7-m depth appears to be a coupling of mineral

dissolution and cation exchange, whereby calcium that becomes available from the dissolution of gypsum displaces sodium and magnesium on clays. This exchange reduces the calcium concentration in groundwater, allowing additional dissolution of gypsum.

[56] Large amounts of chloride (12,300 kg) and nitrate (13,500 kg as N) were released into groundwater by water infiltrating from the reservoir. Concentrations of nitrate (as N) in groundwater were as high as 1550 mg/L; the maximum chloride concentration was about 2400 mg/L. As of January 2007, permits for more than 4000 impoundments for CBNG water had been issued for the Wyoming portion of the Powder River Basin. If conditions at Skewed Reservoir are typical of other impoundment sites, construction and operation of the impoundments could result in over 48 million kg of chloride and 52 million kg of nitrate (as N) being released into shallow groundwater.

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