8 Geochemical Processes Governing Trace Elements in CBNG-Produced Water

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CONTENTS

ABSTRACT

and deficiency of trace elements to humans, plants, animal, and aquatic life depend on geochemical processes. These processes include adsorption–desorption and dissolution–precipitation processes. The objective of this chapter is to discuss geochemical processes controlling trace elements [e.g., arsenic (As), selenium (Se), iron (Fe), aluminum (Al), barium (Ba), and fluoride (F)] in coalbed methane natural gas (CBNG)-produced water in semiarid environments. The chapter presents

- Background information
- The CBNG extraction process and quality of produced water
- Geochemical processes of trace elements in CBNG-produced water
- Potential impacts of CBNG-produced water on rangeland and riparian zone plants, soils, and sediments

Results show that cationic trace elements in produced water precipitate as oxides and hydroxides when they interact with semiarid soils or channel sediment. However, anionic trace elements in produced water become more soluble and mobile in semiarid environments. Findings of this study will be useful in properly managing CBNG-produced water in western ecological environments.

8.1 INTRODUCTION

Trace elements in excess of small concentrations can be toxic to human, plants, animals, and aquatic life. The toxicity of trace elements in natural waters depends on various geochemical processes, including mineral dissolution; ion desorption; complexation; speciation; adsorption; precipitation; and transport [1]. As rain water infiltrates through watershed soils, trace elements are released into surface water as a result of mineral dissolution and desorption (Figure 8.1). Once trace elements are in water, they undergo rapid hydrolysis, ion complexation, and ion-pair formation. Also, trace elements in water are adsorbed by the colloidal particles and are precipitated into sediment as solid

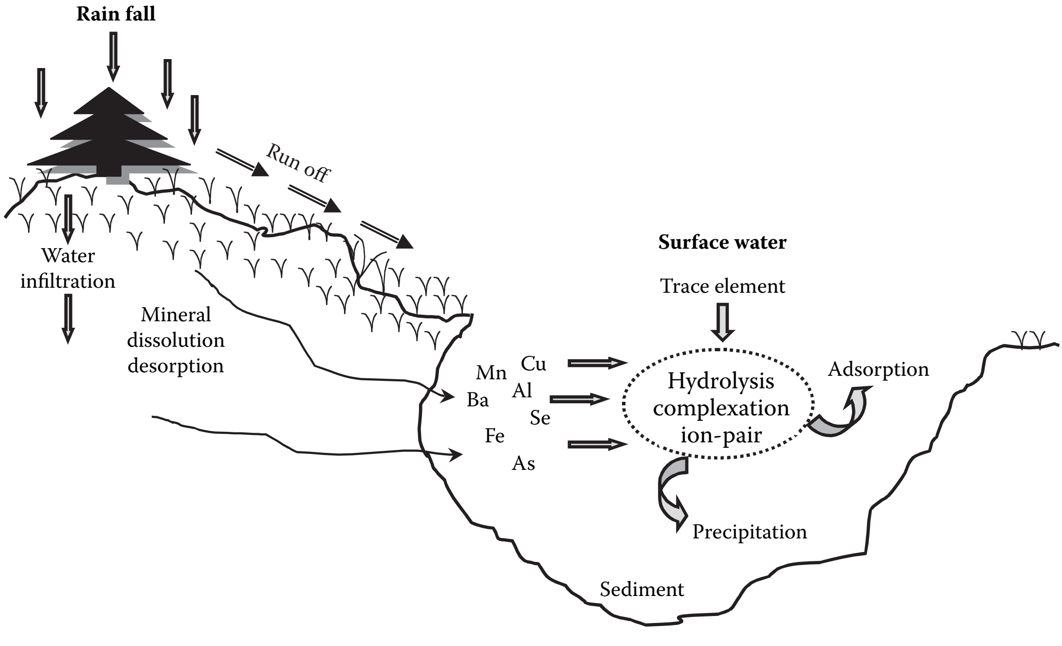

FIGURE 8.1 Hypothetical geochemical processes in surface water systems.

phases. These processes in turn control availability, toxicity, and transport of trace elements in water. Thus, understanding geochemical processes of trace elements in natural waters is key to predicting toxicity issues, which have gained interest in recent years because of human health problems.

In numerous cases, trace element contamination of drinking water supplies has led to serious human health problems. For example, arsenic contamination of drinking water supplies was linked to mass poisoning of people in Bangladesh and India [2]. Some estimates suggest that several million people are potentially at risk from drinking arsenic-contaminated water [3]. Although trace element contamination of surface water may be a natural process of weathering and erosion, anthropogenic sources exist as well. These include

- Energy production processes (e.g., coal- and natural gas-burning power plants, oil refineries)
- Mineral mining (e.g., coal, uranium)
- Oil and natural gas extraction
- Agriculture production (e.g., intensive application of irrigation, intensive application of fertilizers, pesticides, and herbicides)
- Livestock production (e.g., confined and unconfined animal feeding operations)
- Others (e.g., urbanization, solid waste disposal, deforestation)

The focus of this chapter is coalbed methane, which is a major source of natural gas. Worldwide use of different energy sources is shown in Figure 8.2 [4]. These results suggest a significant increase in use of natural gas over a period of approximately 20 years because extraction of natural gas is less expensive compared to other energy sources and is a clean-burning fossil fuel.

Coalbed methane natural gas (CBNG) extraction from coal deposits of Wyoming, Montana, Colorado, and New Mexico is occurring rapidly to meet energy needs of the U.S. For example, the natural gas industry produced 10 Bcf (billion cubic feet) of methane from 282 wells in 1984. By 1998, this had increased to 1200 Bcf from 7500 wells [5]. It is estimated that Wyoming coal deposits contain approximately 31.7 Tcf (trillion cubic feet) of recoverable natural gas. Within Wyoming, the Powder River Basin (PRB) contains the majority of natural gas and is in the forefront of development in North America [6,7]. Extraction of methane from a confined coal seam aquifer

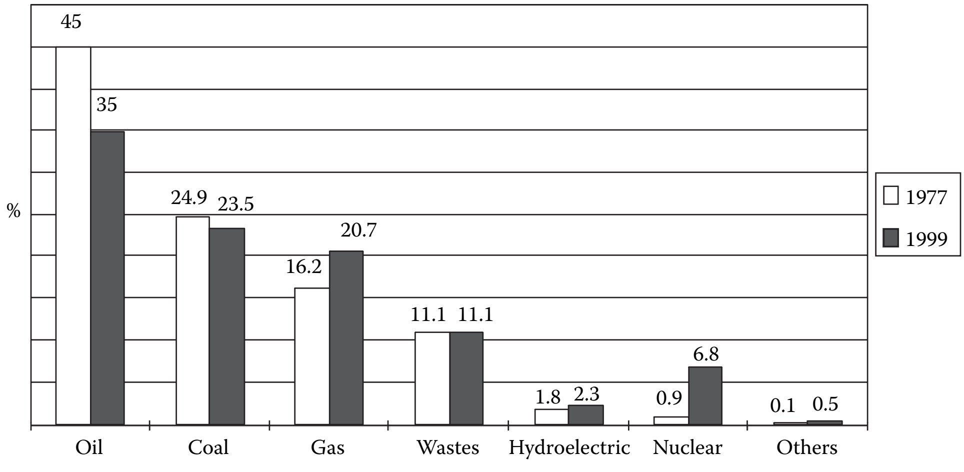

FIGURE 8.2 Worldwide use of different energy sources. (From Kluger, J. and A. Dorfman. 2002. *Time* Special Report. A6).

is facilitated by pumping large volumes of groundwater. The pumped groundwater is called "product water" or "produced water"; it is discharged into disposal ponds and stream channels, and reinjected into an aquifer. However, the chemistry of produced water (salinity, sodicity, and trace elements) varies with aquifer geology and watershed physical and chemical properties.

The objective of this chapter is to discuss geochemical processes governing trace elements in produced water. Also, salinity and sodicity of produced water are discussed because these parameters influence geochemical processes of trace elements in produced water. Information is organized as sections in a sequential order to help readers understand CBNG concepts.

8.2 BACKGROUND INFORMATION

It is important to discuss geology, groundwater, surface water, soils, and plant communities of the PRB because quality of produced water depends on the aquifer geology. Also, discharge of produced water (groundwater) from natural gas development increases overall flow of receiving tributaries, which drain through local soils and plant communities. Subsequently, these processes influence the quality of CBNG-produced water.

8.2.1 GEOLOGY AND GROUNDWATER

The Powder River Basin (Figure 8.3), which is a semiarid basin with average annual precipitation ranging from 30 to 60 cm, is located in northeastern Wyoming within Campbell County and small portions of Converse, Johnson, and Sheridan Counties. This basin (bounded by the Black Hills on the east, the Hartville Uplift to the south, the Big Horn Mountains on the west, and the Yellowstone

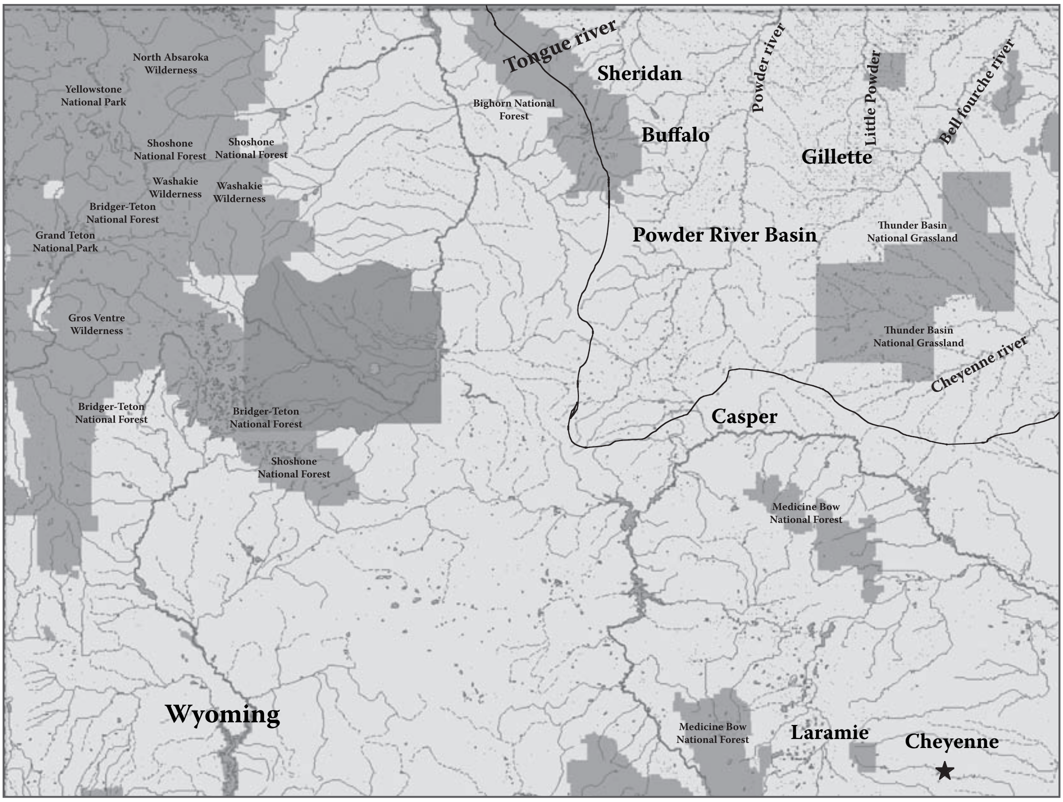

FIGURE 8.3 Study area: the Powder River Basin showing different watersheds.

River to the north) is generally high plains with elevations from 1640 to 1800 m above sea level. Eastern portions of the basin are typically high plains, but the central and western portions contain the Powder River Breaks and have a more diversified landscape setting and associated flora. More details regarding the geology and flora of the PRB are published elsewhere [8–10].

The aquifer geology of the PRB primarily comprises five distinct coalbed formations. These include: (1) Alluvium; (2) Wasatch; (3) Wyodak; (4) Upper Fort Union; and (5) Lower Fort Union. Methane is primarily extracted from confined deeper aquifers of Wasatch and Fort Union formations. Geologic studies of PRB suggest that methane is formed deep in confined coalbed aquifers through biogeophysical processes and remains trapped by water pressure.

It is not clearly understood whether methane contained in these aquifers is in a free state, adsorbed to the interior pore surfaces, or dissolved in aquifer water. Recovery of the methane is facilitated by depressurizing and pumping water from the aquifer (Figure 8.4). The quality of aquifer water varies from basin to basin. For example, aquifer water from deeper formations such as Fort Union is generally salty and dominated by sodium and bicarbonate. A shallow aquifer such as Wasatch formation contains low salt, sodium, and bicarbonate. The groundwater uses within the PRB include domestic, industrial, irrigation, municipal, and livestock watering.

8.2.2 SURFACE WATER

The PRB consists of five perennial rivers, Cheyenne River, Belle Fourche River, Little Powder River, Powder River, and Tongue River, which are all tributaries of the Missouri River. Tributaries

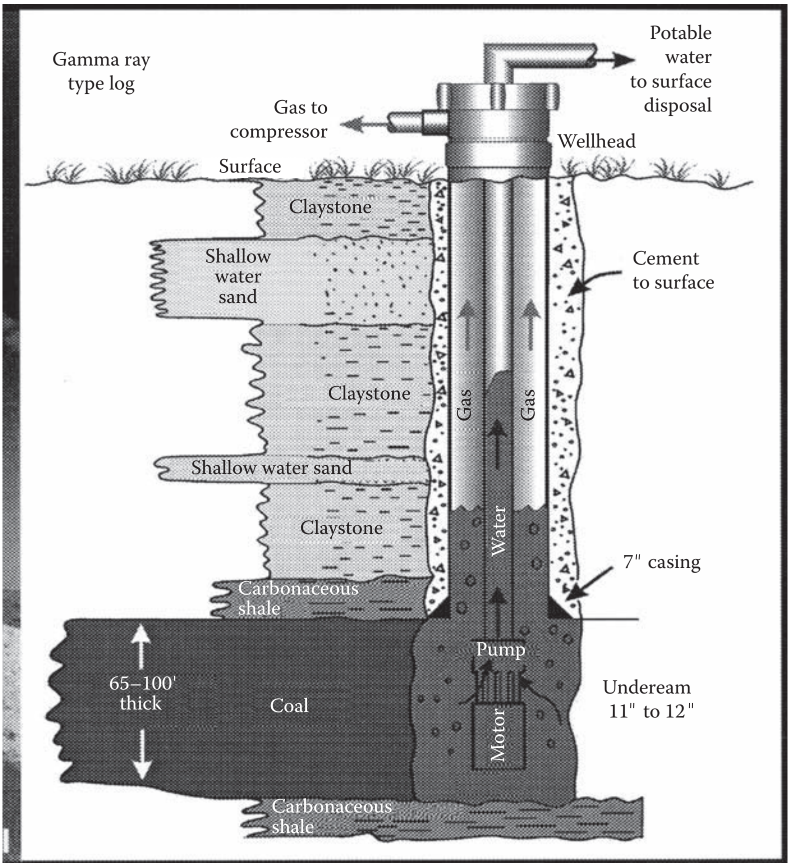

FIGURE 8.4 Coalbed methane natural gas extraction well.

of these perennial rivers are ephemeral with flow occurring in response to snowmelt and storm event. The Cheyenne River flows to the east or southeast part of the basin. The Belle Fourche River flows to the northeast of the basin and Little Powder River flows north of the basin. The Powder River flows northwest of the basin. The Tongue River flows through the northeast of the PRB. Surface water found in the PRB, except for Tongue River, is generally dominated by sodium sulfate, followed by calcium, magnesium, and alkalinity. These surface waters also contain higher total dissolved solids. The surface water uses within the basin include livestock watering, agriculture, and domestic.

8.2.3 SOILS

Powder River Basin rangeland soils are loamy, sandy clay loam and clay loams underlaid with gravels and sands. Soils of PRB vary from basin to basin; the landscape is dominated by short hills and deep erosion gullies. The soils carry a chemistry rich in natural sodium and calcium carbonate. Cheyenne River Basin watershed soils are dominated by Ustic Haplargids (clay loam). The upper 0 to 11 cm of these soils contain a neutral pH of 7.2 with 1% organic carbon. These soils are well drained with slow permeability and have low to high runoff. The BFR soils are Ustic Calciargids (fine loamy). These soils also are well drained with moderate permeability and have low or medium runoff. The upper 0 to 11 cm of these soils have a neutral pH of 7.2 with 1.2% organic carbon.

The LPR watersheds soils are Ustic Torriorthents (loamy). The upper 0 to 11 cm contain 0.85% organic carbon with a pH of 8.0. These soils are well drained with moderate permeability and have medium or high runoff depending upon slope. Soils in PR are loams, silty clays, fine sandy loams, and sandy loams, with shale and sandstone outcrops. Soils in the study area are classified as moderately to well drained [11,12].

8.2.4 PLANT COMMUNITIES

The PRB lies on the western edge of the U.S. Northern Mixed Grass Prairie [13]. Lower elevation grassland is interspersed with shrub species of sagebrush (*Artemisia* L.). Scattered ponderosa pine (*Pinus ponderosa* Laws. and Laws.) and juniper (*Juniperus* L.) forested areas may occupy higher elevation hills and rugged drainage basin ridge areas. Scattered cottonwood (*Populus* L.) trees and willows (*Salix* L.) may occupy stream channel flood plains of larger stream systems [14]. Linear meadow land parallels larger streams where water supplies have been developed for irrigation. Some dryland wheat (*Triticum avestivum* L.) and irrigated barley (*Hordeum vulgar* L.), oats (*Avena sativa* L.), and alfalfa *(Medicago* L.) are produced within this region’s rangeland.

Basin grassland is composed of cool- and warm-season grass species. Cool season grasses grow in response to soil moisture stored during fall and early spring snow melt and rain. Warm season grasses respond to late spring and summer precipitation. Stream flow that may occur because of snow melt, rain, or groundwater springs may support riparian grasses along channel flood plains. Existing grasslands are supported by soil water that is concentrated in the upper part of the soil profile and seldom percolates below the root zone. Therefore, plant nutrients and salts are generally concentrated near the soil surface and root zone. Although the near surface soils may be nutrient limited, nutrients are regenerated because precipitation is insufficient to leach them below the root zone and to underlying aquifers. Limited grass production of the PRB is therefore nutritious relative to that of higher rainfall areas. Because rangeland of the PRB is composed of cool- and warm-season grass species, the overall nutritional value of this grassland is prolonged later in dry summer months by the later warm-season grass production. Dominant grass species of the PRB by plant community are presented in Table 8.1 [15].

TABLE 8.1
Dominate grass species of the Norther Mixed Grass Prairie within the Powder River Basin, Wyoming from the Grasses of Wyoming.

Upland rangeland	Riparian Zones	Meadows
Poa secunda Presl.[a]	*Stipa viridula* Trin.[a]	*Elytrigia intermedia*
Poa cambyi Howell[a]	*Pascopyron smithii*	*Bromus inermis* Leyss.[c]
Stipa comata Trin. & Rupr.[a]	*Elymus canadensis* L.[a]	*Alopercurus pratensis* L.[a]
Oryzopsis hymenoides Ricker	*Leymus cinereus* A. Love[a]	*Alopercurus arundinaceus* Poir.[c]
Koeleria cristata Pers.[a]	*Spartina gracilis* Trin.[b]	*Alopercurus carolinius* Walt.[a]
Pascopyron smithii A. Love[a]	*Spartina pectinata* Link[b]	*Phleum pratense* L.[a]
Elymus lanceolatus Gould	*Sporobolus airoides* Torr.[b]	*Agrostis alba* L.[a]
Elymus trachycaulus Gould ex Shinners[a]	*Distichlis spicata* Green[b]	*Dactylis glomerata* L.[a]
Bouteloua gracilis Lag. Ex Steud.[b]	*Hordeum jubatum* L.[a]	*Phalaris arundinaceae* L.[a]
Pseudoroegneria spicata A. Love1	*Elymus lanceolatus*	*Pascopyron smithii*
Calamovilfa longifolia Scrib.[b]	*Sporobolus cryptandrus*	*Elymus lanceolatus*
Sporobolus cryptandrus Gray[b]	*Puccinellia nuttalliana* Hitchc.[b]	*Elytrigia intermedia*
Sporobolus heterolepis Gray[b]	*lytrigia intermedia* Nevski[a]	*Bromus tectorum*
Andropogon hallia Hack.[b]	*Bromus tectorum*	*Bromus japonicus*
Bromus tectorum L.[c]	*Bromus japonicus*	
Bromus japonicus Thunb.[c]		

[a] cool season
[b] warm season
[c] introduced

8.3 CBNG EXTRACTION PROCESS AND QUALITY OF PRODUCED WATER

The previous section reviewed background information of the PRB. This section discusses the CBNG extraction process and disposal methods for produced water and chemistry of major elements in CBNG-produced water — particularly, salinity, sodium adsorption ratio (SAR), and sodicity. Chemistry of trace elements in produced water is discussed in detail later in the section on geochemical processes.

It is estimated that a single CBNG well in the PRB may produce from 8 to 80 L of produced water per minute, but this amount varies with aquifer pumped and the density of wells (Figure 8.4). At present, more than 16,000 wells are under production in the PRB and this number is expected to increase to at least 30,000. Approximately 2 trillion L of produced water eventually will be produced over a period of 15 to 20 years from CBNG extraction in Wyoming [6]. Commonly, several CBNG extraction wells are placed together in a manifold system discharging to a single point and releasing into constructed unlined disposal ponds and/or into stream channel systems (Figure 8.5).

The chemistry of produced water (salinity, sodicity, and trace elements) in the PRB varies with geology and depth of the coal formation. Only a few studies have examined the changes in the chemistry of produced water in the PRB [11,16]. Rice et al. [16] examined the chemistry of discharge water at wellhead across the PRB, Wyoming, and reported that moving from north and west toward deeper coal seams within the PRB produces saline and alkaline water. The studies of McBeth et al. [11] examined the chemistry of produced water at wellhead and in associated disposal ponds of the PRB. The study area consisted of the Cheyenne River Watershed, Belle Fourche Watershed, and Little Powder Watershed within the PRB. Results suggested an increase in SAR, EC, TDS, and pH of discharge water in associated disposal ponds moving from the south to the north of the PRB.

Pond disposal
(a)

Channel disposal
(b)

FIGURE 8.5 Disposal of coalbed methane natural gas-produced water.

Patz et al. [17] studied the chemistry of produced water released to the upland channel systems that support ephemeral streams in the PRB. Results suggest that produced water consisted of higher concentrations of sodium and alkalinity compared to other components. The pH of produced water increased in the downstream channel water; however, the pH of sediment water interface within the top 2 cm decreased due to the precipitation of calcite. Subsequently, precipitation of calcium carbonate in the downstream channel decreased calcium concentration and increased SAR. This literature review suggested that salinity and sodicity of produced water increase within the PRB moving from south to northwest. Often, produced water is dominated by sodium and bicarbonate.

8.4 GEOCHEMICAL PROCESSES OF TRACE ELEMENTS IN CBNG-PRODUCED WATER

This section presents information about the chemistry of trace elements in produced water interacting with channel sediment of Dead Horse Creek from the PRB and geochemical processes governing trace elements in produced water under semiarid environments.

8.4.1 STUDY AREA

This study was conducted using sediments collected from the channel system of Dead Horse Creek, a tributary to the Powder River in Johnson and Campbell Counties, Wyoming [18]. Dead Horse Creek is an intermittent and fifth-order stream, map scale 7.5″ [19,20] located in the grassland and sagebrush Mixed Grass Prairie [13]. The drainage basin has a southeast to northwest orientation with headwaters just west of Gillette, Wyoming (Figure 8.3). This region receives 25 to 45 cm of annual precipitation, mostly as winter snow. High-intensity and short-duration thunder storms are common in summer. Dominant upland soils are predominantly classified as Ustic Torriorthents (loamy). Sediment samples collected from channel alluvium were approximately 40% clay. Major coal formations in this region include the Tertiary White River formation and the Tertiary Tongue River member of the Fort Union formation [11].

8.4.2 SEDIMENT SAMPLING

Three individual sediment samples were collected along Dead Horse Creek. Site 1 was located on a headwater low gradient channel reach along a third-order tributary of Dead Horse Creek. Site 2 was located on a low gradient channel reach along a fourth-order tributary of Dead Horse Creek just below the confluence of the site 1 channel; site 3 was located on a low gradient channel reach along the main stem of Dead Horse Creek just before it joined the Powder River.

Slit trenches, approximately 1ft deep and 1 ft wide, were dug, perpendicular to flow, across the creek channel bottom. Samples were loaded and transported in a plastic liner to the University of Wyoming. The sediment samples were spread out on large plastic sheets and allowed to air dry and then crushed using a 20-lb rubber-coated sledge hammer. Larger plant parts were removed by hand and samples were then passed through a no. 10 mesh screen to remove smaller plant and larger sediment materials. Each screened sample was stored in a separate plastic container for future use in column studies.

8.4.3 WATER SAMPLING

One 400-gal sample of CBNG-produced water was collected from a single extraction well located in the Dead Horse Creek watershed after the well was flushed to obtain a representative aquifer sample. The sample was pumped directly from the well head to a clean, plastic, truck-mounted tank and transferred to a clean and rinsed plastic storage tank in the Environmental Simulation Laboratory, College of Agriculture at the University of Wyoming. Distilled water was obtained, when needed, from a central distillery within the College of Agriculture. This supply was stored in a smaller clean and rinsed 300-gal storage tank located next to the produced water.

8.4.4 COLUMN FACILITY

Using 15.2 cm diameter PVC pipe, 48 1-m columns were constructed (Figure 8.6). The PVC pipe was inserted and sealed with silicone into 0.50-cm bottom plates. Five inlets or outlets evenly spaced in the column walls were inserted along one side of the column to within 5 cm of the top. One inlet or outlet was located 5 cm down and directly across from the top outlet on the opposite side. Constructed columns were then placed on three benches under lights within the column facility.

FIGURE 8.6 Design of column studies.

Feed and drain lines using tubing were then attached to appropriate inlets or outlets of each column and produced and distilled water storage tanks as planned for individual experiments. Control valves within the tubing apparatus were located at the end of each bench and between individual columns to control flow when appropriate.

8.4.5 COLUMN EXPERIMENTAL DESIGN

The 48 columns were allocated to six blocks along bench space and under the light system, where eight combinations of two water types (produced water and distilled water) and four sediment types (sediment samples one through three and a sand control) would be positioned within each block. Position of one of each of the eight possible combinations of water and sediment in each block was randomly selected within each block using random number tables. This provided one repetition for each of eight possible combinations in each of six blocks. This design provided each column combination of water and sediment equal exposure to possible variation in light quality produced by the light apparatus.

Columns were then placed on bench space and labeled according to bench positions within blocks and for each water and sediment combination. They loaded in approximately 15-cm lifts by placing each sediment in each assigned water and letting the sediment settle to within 2.54 cm of the water surface. This procedure ensured complete saturation throughout the filling process and simulated settling of sediment in surface runoff. Sediments in the column were filled to the bottom of top inlets and were allowed to settle or swell for 6 days. In columns where swelling occurred, sediment was removed to the depth of 5 cm. Each assigned column water was then added to a depth of 5 cm above sediment level for 5- and then 10-day contact experiments.

8.4.6 LIGHTS

Three light fixtures, 2.4 m long, comprised a combination of high-output fluorescent lights and 60-W incandescent bulbs attached to automatic timers for control of light intensity and duration. Each fixture provided 570 to 600 μολ σ^{-1} m^{-2} light intensity within 15 to 30 cm of the light fixture. Full light intensity was provided for 14 h each day for all column experiments. Light fixture fans plus one oscillating fan provided air circulation for cooling the atmosphere above the columns and between the lighting apparatuses.

8.4.7 ANALYSIS

Differences in water quality data of sediment and water combinations were determined using one-way analysis of variance (ANOVA) procedures using a SAS [34] package. An alpha level of 0.05 was used to determine if differences existed at a 95% confidence interval. The Levene test was used to determine homogeneity of variance. The Tukey HSD post hoc test allowed for a pairwise comparison for all designated combinations of data.

8.4.8 EXPERIMENTS

8.4.8.1 Saturated Paste Experiments

Standard saturated paste procedures were used for the first experiment to determine whether drainage net sampling site locations and respective sediment supplies would produce different sediment water quality. This procedure requires using distilled water. Once distilled water was used, this procedure was modified by substituting distilled water with the produced water and conducting a second test. The objective of these two tests was to provide data sets that could be used to determine whether it would be justifiable to combine the results of the three channel sediments into one sediment source. No or minor differences in sediment chemistry by site location and respective sediment samples meant that sample numbers could be increased for the analysis of remaining experiments. Sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), sulfate (SO_4), pH, and electrical conductivity (EC) were used to determine any differences in sediment water quality. It was determined that no significant differences existed between sample site locations.

8.4.8.2 Surface Ponding Experiments

These column experiments were designed to evaluate change in surface water chemistry after setting on the surface of the saturated column sediments for 5 and then 10 days. The columns were filled 5 cm deep above the sediment surface with produced water or distilled water and stirred twice daily to simulate turbulence similar to that caused by channel runoff or wind action for the 5-day test. All surface water was then drained, labeled, preserved, and stored while the columns were again filled to 5 cm deep above the sediment for the 10-day test. Change in chemistry for the 5-day test was analyzed during the 10-day test. Following the 10-day test, this water was collected, labeled, preserved, and analyzed for change in water chemistry.

All column water experiments were analyzed for major and trace elements. Trace elements analyzed were manganese (Mn), iron (Fe), arsenic (As), selenium (Se), fluoride (F), and barium (Ba). All samples were filtered through a 0.45-μmpore filter. Each filtered sample was divided into two subsamples. One sample was acidified to pH of 2.0 with HNO_4^- and the other remained unacidified. Acidified samples were analyzed for Mn, Fe, As, Se, and Ba using inductively coupled plasma mass spectrometry (ICP-MS). Unacidified samples were analyzed for pH, alkalinity, and major elements. All analyses were performed following standard procedures [21].

8.4.8.3 Groundwater Experiments

After the surface water experiments, 500 ml of assigned water type was added to determine change in sediment water chemistry (groundwater) of all columns. The groundwater was collected from the second outlet from the top of the columns in individually sealed plastic containers. The second outlet was used for extractions because of the high clay content of sediments used and expectations that this depth would also produce the highest root biomass when plants were established in the columns. Once a sufficient amount of groundwater was collected, samples were analyzed for changes in trace element chemistry following procedures described earlier for column experiments.

Nebraska sedge (*Carex nebraskensis* Dewey), water sedge (*Carex aquatilis* Wahl.), and Baltic rush (*Juncus balticus* Wild) nursery stock grown in individual containers in New Mexico were transplanted to columns immediately following the completion of the first groundwater experiment. Within each of the eight water and sediment combinations, 16 plants of each species were randomly assigned. This resulted in 2 plants of each species for each combination; 8 plants of each species for each water type; 4 plants of each species for sand; and 12 plants of each species for the three sediments combined before transplanting occurred. Plants were watered daily for 2 months with the original water assignment so that column sediments were always flooded.

When plant roots and new stems were established, 500 ml of prescribed water was added to the sediment surface and the groundwater experiment was replicated to determine change in sediment water chemistry (groundwater) of all columns after establishing plants. Collection of groundwater and analysis of chemistry for this experiment remained as described previously.

8.4.8.4 CBNG-Produced Water Tank

Produced water tank samples were analyzed prior to the first saturated paste experiments, following the analysis of the surface water experiments, and prior to the final ground water test. Produced water samples were analyzed for the same chemical constituents as those for surface- and groundwater.

8.5 RESULTS AND DISCUSSION

8.5.1 CBNG-Produced Water Samples

The trace element water quality for the produced-water holding tank changed for some elements. Manganese and Fe decreased by approximately 50% from 4.0 to 1.7 mg/L and 290.3 to 115.2 mg/L, respectively. All other parameters remained unchanged. The pH increased from 7.89 to 8.49 and remained at 8.49 for the third sampling.

8.5.2 Surface Ponding

The 5- and 10-day tests (Table 8.2) were designed to evaluate change in trace element ponded water quality with prolonged exposure to surface sediments. Presented data of distilled water vs. produced water over sand illustrates the influence of water type on trace element water quality. Sediment vs. sand data comparisons isolate probable influence of channel sediment on water quality.

Arsenic, Ba, and pH in ponded distilled vs. produced water over sand-filled columns were significantly different and the remaining six parameters were not. Arsenic, Ba, and Cl increased from 1.0 to 3.7 μg/L, 5.6 to 239.6 μg/L, and 4.4 to 15.9 mg/L, respectively (Table 8.2). The pH increased from 6.27 for distilled water to 9.15 for produced water. Mn, Fe, Se, and F, remained constant. Mn, Fe, Se, and Ba in ponded distilled water over sand vs. ponded distilled water over

TABLE 8.2
Trace element release from Dead Horse Creek channel sediment with and without produced water for 5 and 10-day surface water.

	pH	Mn mg/L	Fe mg/L	As ug/L	Se ug/L	Ba ug/L	F mg/L
Produced Water/Sediment							
(5-day Surface water)							
Mean	7.82c	1.01ab	1.139b	4.05a	4.49b	99.36c	1.58a
(10-day Surface water)							
Mean	7.93c	1.01ab	1.139b	4.05a	4.49b	99.36c	1.58a
Distilled Water/Sediment							
(5-day Surface water)							
Mean	7.44c	1.743b	1.06b	2.14ab	3.36b	39.6d	2.95d
(10-day Surface water)							
Mean	8.00a	0.009a	1.22a	2.72a	3.04a	46.7a	1.83a
Produced Water/Sand							
(5-day Surface water)							
Mean	9.15a	0.0003a	0.039a	3.7a	1.20a	239.6a	1.15a
(10-day Surface water)							
Mean	9.13a	0.0006a	0.025a	1.8a	0.80a	193.7a	1.05a
Distilled Water/Sand							
(5-day Surface water)							
Mean	6.27b	0.0005a	0.046a	1.0b	0.50a	5.56b	0.01a
(10-day Surface water)							
Mean	8.74b	0.0001a	0.028a	0.90a	0.30a	5.14b	0.0001a
Produced Water							
Mean	8.49	0.0017	0.115	0.50	0.70	593.1	0.93

sediment increased from 0.5 to 1753.8 µg/L, 46.3 to 1066.6 µg/L, 0.5 to 2.8 µg/L, and 5.56 to 39.6 µg/L, respectively (Table 8.2). The pH varied between 6.27 for sand water to 7.44 for sediment water. Other measured parameters were not significantly different; however, As (1.0 to 2.14 µg/L) and F (0.01 to 2.95 mg/L) followed a trend of increasing when distilled water was over sediment instead of sand.

The results of the 10-day test (Table 8.2) are similar to that of the 5-day test, with only As changing. Arsenic went from 1.0 to 3.7 µg/L and significantly different, to not different (0.9 to 1.8 µg/L) in ponded distilled vs. water over sand-filled columns. Barium increased from 5.14 to 193.8 µg/L. The pH increased from 8.74 for distilled water to 9.31 for produced water. Manganese, Fe, Se, and F were not significantly different, but trends in the data suggest that they could increase with produced water over sand.

When comparing distilled water over sand with sediment, Mn, Fe, and Se increased from 1.0 to 913.0 µg/L, 28.9 to 1225.0 µg/L, and 0.3 to 2.7 µg/L, respectively (Table 8.2). All other parameters were not significantly different. However, As, Se, Ba, and F did follow a trend in increasing from 0.9 to 2.7 µg/L, 0.3 to 2.7 µg/L, 5.1 to 46.7 µg/L, and 0.0 to 1.83 mg/L, respectively. The pH dropped from 8.74 for sand to 8.00 for sediment. Analysis of the data from sand-filled columns of both tests would suggest that application of produced water may increase the concentrations of As and Ba. The data from distilled water columns would indicate that application of rain or produced water applied to the sediment in the Dead Horse Creek drainage will likely increase the concentrations of Mn, Fe, Se, and Ba.

8.5.3 GROUNDWATER

The groundwater sampled from all columns represented over 2 months of contact with sediments and should be as close as possible to equilibrium conditions between water types and sediment. These data suggest that, given time, distilled water in the column sediments will approach the measured chemistry of those subjected to produced water and that both will be higher than observed for surface contact only.

8.5.4 SURFACE- AND GROUNDWATER

The difference in surface- and groundwater trace element chemistry with distilled water and then CBNG-produced water are shown in Table 8.3. Significant differences are present for Se and Ba between the surface 5- and 10-day and groundwater data. The Se concentration increased from surface pond water (2.1 and 2.7 μg/L) to groundwater (8.4 μg/L) and Ba decreased from surface- (39.6 and 46.7 μg/L) to groundwater (11.6 μg/L). No significant difference in concentrations was found for all other chemical parameters analyzed. However, trend in the data suggests that Mn decreased from surface- (1753 and 913 μg/L) to groundwater (236.3 μg/L) and Ba decreased from surface- (39.60 and 46.7 μg/L) to groundwater (11.6 μg/L). In contrast, As increased from surface- (2.1 and 2.7 μg/L) to groundwater (75.9) and Se increased from surface- (2.8 and 2.7 μg/L) to groundwater (8.4 μg/L). The pH increased from surface- (7.44) to groundwater (8.59). Fe and F do not appear to be different.

The difference in surface- and groundwater trace element chemistry with produced water was similar to those found for distilled water. Se concentration increased from surface pond water (2.9 and 3.6 μg/L) to groundwater (7.7 μg/L) and Ba decreased from surface- (99.36 and 57.17 μg/L) to groundwater (18.91 μg/L). These differences were significant, as was pH surface- (7.82 and 7.93) to groundwater (8.89). The trends in changes of all other chemical parameter concentrations were identical to those observed for distilled and ponded surface water.

A recent study by McBeth et al. [22] indicated that Mn and Ba concentrations will decrease with time when stored in retention ponds. This same trend was noted in the distilled- and produced-water experiments. Mn was observed to drop (1010 to 917 for produced and 1753 to 913 μg/L for distilled) for both surface water tests and in the groundwater test (134 for produced water and 236 μg/L for distilled water). The Ba concentration fell from the surface water test (99.4 to 57.2 for produced water) to the groundwater test (18.9 μg/L). Though the Ba concentration remained similar

TABLE 8.3
Comparison of Trace Element Release from Dead Horse Creek Channel Sediment for 5- and 10-Day Surface Water vs. Groundwater

	pH	Mn (mg/L)	Fe (mg/L)	As (μg/L)	Se (μg/L)	Ba (μg/L)	F (mg/L)
Produced water/sediment							
5-Day surface water (mean)	7.82c	1.01ab	1.139b	4.05a	4.49b	99.36c	1.58a
10-Day surface water (mean)	7.93c	1.01ab	1.139b	4.05a	4.49b	99.36c	1.58a
Groundwater	8.89a	0.134a	1.06a	62.2a	7.66b	18.91c	0.86a
Distilled water/sediment							
5-Day surface water (mean)	7.44c	1.743b	1.06b	2.14ab	3.36b	39.6d	2.95d
10-Day surface water (mean)	8.00a	0.009a	1.22a	2.72a	3.04a	46.7a	1.83a
Groundwater	8.59a	0.236a	1.36b	75.9a	8.38a	11.55b	0.84a
Produced water							
Mean	8.49	0.0017	0.115	0.50	0.70	593.1	0.93

for the 5- and 10-day surface water test (39.6 to 46.7 μg/L), it did drop in the groundwater test (11.6 μg/L). Overall, results observed in this study are consistent with results reported by McBeth et al. [22]. A detailed discussion regarding geochemical processes controlling trace elements in semiarid environments is presented later in this section.

In summary, trace element analyses of column studies suggest that sediments of Dead Horse Creek drainage will alter the quality of produced water and precipitation surface- and groundwater runoff. Though produced water discharges can slightly alter the water quality of runoff, the sediment appears to be a stronger contributor to the overall water quality of stream channel runoff. Precipitation events will likely alter water quality of stream runoff by dissolving and leaching chemicals and thus increasing the chemical concentrations of downstream flows. Trace element availability seems to be predominantly affected by sediment interaction, with Mn and Ba decreasing and As and Se increasing from surface water retention to groundwater retention. Iron and F appear to be less affected by this difference in interaction.

Plants did not alter the sediment trace element water chemistry but did increase the rate of infiltration. Release of produced water may increase the pH of stream channel runoff and the mobility of anions, while decreasing the solubility of cations in soils. Overall results suggest that most constituents in produced and distilled water runoff were below the established criteria required for human consumption, except for Mn and Fe. Further research to determine the potential balance of produced water discharge and precipitation events (flushes) on downstream water quality will be useful in determining potential beneficial uses for produced water in the Powder River Basin.

8.5.5 Geochemical Processes

This section reviews geochemical processes controlling trace elements in produced water. McBeth et al. [22] examined the chemistry of trace elements in produced water at discharge points and in associated holding ponds across the PRB, Wyoming. Produced water samples from discharge points and associated holding ponds were collected from three different watersheds within the PRB (CHR, BFR, and LPR) and were analyzed for pH, Al, As, B, Ba, Cr, Cu, F, Fe, Mn, Mo, Se, and Zn. The chemistry of trace element concentrations was modeled with the MINTEQA2 geochemical equilibrium model.

Results of this study show that pH of produced water for three watersheds increased in holding ponds. For example, the pH of produced water increased from 7.21 to 8.26 for LPR watershed. Among three watersheds, produced water from CHR watershed exhibited relatively less change in trace element concentrations in holding ponds. Concentration of dissolved Al, Fe, As, Se, and F in produced water increased in BFR watershed holding ponds. For example, concentration of dissolved Fe increased from 113 to 135 μg/L. Boron, Cu, and Zn concentrations of produced water did not change in BFR watershed holding ponds.

However, concentration of dissolved Ba, Mn, and Cr in produced water decreased in BFR watershed holding ponds. For instance, Ba and Cr concentrations decreased from 445 to 386 μg/L and from 43.6 to 25.1 μg/L, respectively. In the LPR watershed, Al, Fe, As, Se, and F concentrations of produced water increased substantially in holding ponds. For example, Fe concentration increased from 192 to 312 μg/L. However, concentration of dissolved Ba, Mn, Cr, and Zn decreased in holding ponds.

Geochemical modeling calculations suggested that observed increase of Al and Fe concentrations in holding ponds was due to increase in concentration of $Al(OH)_4^-$ and $Fe(OH)_4^-$ species in water, which were responsible for pH increases [23]. Decreases in Ba, Mn, Cr, and Zn concentrations were attributed to the increase in pH, resulting in precipitates of $BaSO_4$ (barite), $MnCO_3$ (rhodochrosite), $Cr(OH)_2$ (chromium hydroxide), and $ZnCO_3$ (smithsonite) in pond waters, respectively. Several studies suggested that solubility of As, Se, and F in alkaline environments is controlled by the adsorption and desorption processes and increases as pH increases. Because As, Se, and F are anionic in nature and most of the soil mineral phases contain negative surface charge, these elements become soluble and mobile in alkaline watershed soils. The results found in this study are consistent with those in previous studies [24–27]. For example, concentration of dissolved As, Se, and F concentrations increased substantially in LPR watershed pond waters, which also had the highest increase in the pH.

Patz et al. [17] examined chemistry of trace elements in produced water interacting with Burger Draw and Sue Draw stream channels in the PRB, Wyoming. Significant change occurred for Fe, Mn, and As in flow of Burger Draw. As expected, Fe precipitates at once after discharge from wells (887.90 to 738.15 μg/L) as it transforms from a reduced to an oxidized state in Burger Draw (108.00 μg/L) or Sue Draw (3006.15 μg/L to 92.60 μg/L). Further reduction in Fe concentration in downstream flow did not appear to occur. Manganese reacted like Fe and decrease in concentration was low after initial contact with the atmosphere and the channel system. Arsenic and Se appeared to increase with downstream flow, but As was significantly higher after reservoir storage in Sue Draw (2.58 μg/L above and 4.48 μg/L below storage). McBeth et al. [22] and Hulin [18] report similar results.

In general, Al and Fe become less soluble and mobile in natural waters of the western alkaline environments. However, produced water may contain higher concentrations of Al and Fe in disposal pond water and these increases may be explained by the presence of Al and Fe hydroxyl species (e.g., $Fe(OH)_4^-$) in waters with a high pH [22]. Other studies also suggest that when anionic species of Al and Fe dominate in water, the solubility increases with increasing pH. Even though Al and Fe concentrations remained relatively unchanged, they may decrease with time in alkaline environments due to the likely precipitation of aluminum and iron hydroxides [28].

The decreases in Mn and Ba concentrations are likely due to the precipitation of oxides, hydroxides, and carbonates of these metals, common in the calcite-rich, alkaline environment of the PRB. Overall, the preceding review suggested that, in alkaline environments, cationic trace elements (e.g., Al, Fe, Mn, and Ba) become less soluble and mobile due to precipitation of oxides and hydroxides. However, anionic trace elements (e.g., As, Se, and F) become more soluble and mobile as a result of mineral dissolution and desorption processes.

8.6 POTENTIAL IMPACTS OF CBNG-PRODUCED WATER TO RANGELAND PLANTS, RIPARIAN PLANTS, SOILS, AND SEDIMENTS

In this final section, potential impacts of produced water to rangeland plants, soils, and sediment are summarized. Different management alternatives are proposed for produced water within the PRB, Wyoming. These options include surface land application (e.g., irrigation), aquaculture, and livestock watering. Nonetheless, any management option for produced water within the semiarid areas requires a careful evaluation of its salinity (e.g., EC, TDS), sodicity (e.g., SAR), and trace elements.

Common and observed issues associated with plant species and community impacts while developing CBNG in the PRB may be categorized as follows:

- Produced water and toxicity to native plants
- Native plant toxicity when produced water is applied to rangeland soils and to stored sediment in stream channel systems
- Change in plant species composition after produced water is released as perennial channel flow
- Vegetation response and ability to resist accelerated channel erosion after produced water is released as perennial channel flow
- Land application of produced water and change in soil chemistry and structure

- Change in land and stream channel characteristics as land application and channel release ends
- Role of plants in accumulation and turnover of trace elements

In the PRB, toxicity to plants was addressed in a preliminary laboratory study using produced water, nutrient solution, and perlite as a plant support system. Western wheatgrass, a dominate upland and riparian zone grass, was fed 100% produced water; 50% produced water and 50% nutrient solution water; and nutrient water alone. No plants died and no differences in total biomass were observed between 100% nutrient and 50% produced water and 50% nutrient solution; however, growth was reduced when no nutrients were supplied to 100% produced water (Figure 8.7). Plant nutrients in the tested produced water appear to limit growth response, and toxicity of the water did not appear to be an important issue [29].

Application of produced water to stored sediment of stream channel systems and plant toxicity was surveyed by Hulin [18] and Jackson [30] in a laboratory study using column techniques. Of three common wetland plants — Nebraska sedge (*Carex nebraskensis* Dewey); water sedge (*Carex aquatilis* Wahl.); and Baltic rush (*Juncus balticus* Wild) — grown in columns, only Baltic rush survived. These data suggest that when a produced water like that used for their experiments is applied to stored channel sediment, plant toxicity is an issue and that some native plant species cannot tolerate produced water and sediment chemistry under saturated conditions (Figure 8.8).

Change in plant species composition after produced water was released as perennial channel flow was observed by Patz [31]. Approximately 3000 containerized plants of each of the three

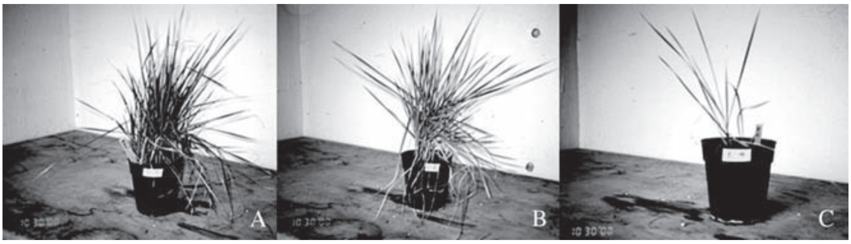

FIGURE 8.7 (A) Western wheatgrass grown in perlite and watered with nutrient solution; (B) 50% nutrient solution and product water; (C) product water only.

FIGURE 8.8 (A) All three plant species could survive in a control with soil and distilled water plus nutrients; (B) only Baltic rush was able to survive in soil plus product water; (B) Nebraska and water sedge could not survive product water and soil utilized for experiments.

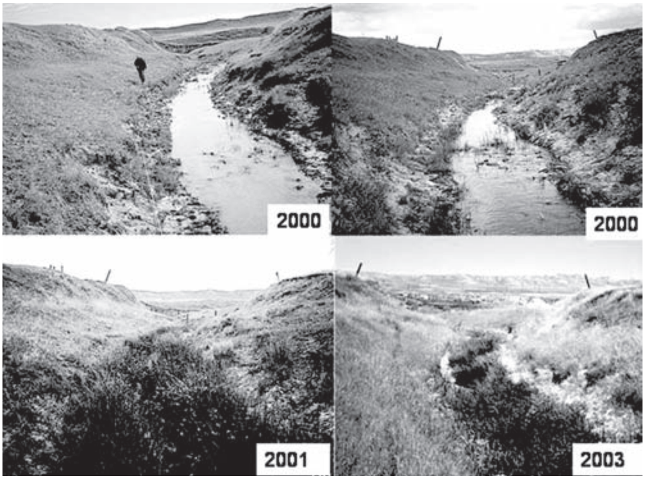

FIGURE 8.9 Wetland plants adapted to saline conditions occupied stream channel area where saturated conditions exist after perennial release of product water. These plants replaced those species occupying the ephemeral channel area.

wetland species used in Hulin and Jackson's study were transplanted in and along three study sites of a single stream discharging produced water. Only Baltic rush survived and was confined to a narrow zone next to the water edge and bank. Rangeland plant species that had occupied the ephemeral channel area before release of produced water were being replaced by the riparian grass or grasslike species: inland salt grass (*Distichlis spicata* L.); foxtail barley (*Hordium jubatum* L.); Nutall's alkali grass (*Puccinellia nuttalliana* (Schult.) Hitchc.); Western wheatgrass (*Pascopyron smithii* Rydb.); American bullrush (*Scirpus americanus* Pers.); and maritime bullrush (*Scirpus maritumus* L. var. paludosus (A. nels.) Kukenth). These replacement species are known to be salt tolerant, whereas the grasses being replaced are not. This preliminary study suggests that upland rangeland grasses may be replaced by riparian zone and more salt-tolerant species when produced water is released as perennial flow, stored in ponds, or detained behind water spreaders or debris dams for extended lengths of time (Figure 8.9).

The change in plant composition observed by Patz [31] in addition to follow-up photo monitoring confirms that the vegetation response to perennial release of channel flow creates a stable riparian zone capable of resisting accelerated channel erosion. Plant height, cover, and stem density appear equivalent to riparian zones found throughout the PRB [35]. Three extreme flood events caused by summer convective storms have not caused low flow channel conditions to change. Figure 8.10 illustrates stability of riparian vegetation near Patz's 2002 study sites.

Land application of produced water and change in plant and soil characteristics in the PRB are yet to be confirmed within the scientific literature even though potential impacts of salinity and sodicity are well established. Figure 8.11 illustrates limited observations of soil conditions in which produced water is applied through sprinkler irrigation. Application of saline and sodic water for irrigation is not a problem in humid areas compared to arid and semiarid areas because rainfall is a major source of salt-free water. However, use of salty and sodic water for irrigation in arid and semiarid areas, particularly containing clay minerals with poor drainage, accumulates salts, decreases infiltration, and increases runoff and erosion [32]. A recent study reported that water with SAR as low as 5 will have an adverse effect on the soil structure and infiltration rates [33].

Surface disposal of produced water in ponds and in stream channels is creating riparian zone and wetland habitat in addition to that which is natural and has been developed through irrigation using historic water supplies. The additional produced water supply is limited to the time that it takes to remove the coalbed gas supply. Once this supply is harvested, it must be assumed that

FIGURE 8.10 Wetland plants that occupied ephemeral stream channel area after perennial release of product water continue to create stable conditions for reducing erosion and transport of sediment.

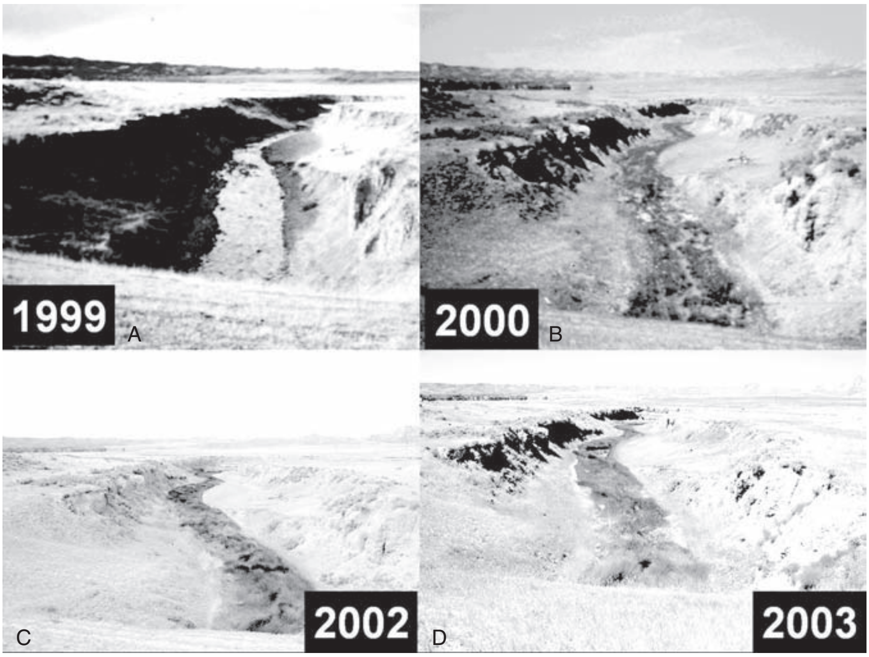

FIGURE 8.11 (A and B) sprinkler irrigation used to apply product water on (C) seeded and (D) native rangeland appears to cause crusting and cracking of some soil types.

riparian zone and forage plant resources created because of surface disposal of produced water will suffer drought conditions. The question of if and how vegetation will respond to no produced water has not been answered. It can be assumed that sodicity and salinity of soil and sediment resources should have increased through the influence of CBNG surface water supplies. However, fate and transport of trace elements by plants remain unknown. The questions associated with assimilation, accumulation, and transformation of trace elements by plants that can and cannot tolerate produced water should be answered knowing that reclamation of riparian zones, wetlands, and native range soils will be needed in the future.

Release of produced water into established watershed can have an impact on the water quality of the watershed, but this impact may be similar to that of naturally occurring precipitation events. However, precipitation is sporadic in causing runoff, and release of produced water may be perennial for some given period. From the authors' data, continual release of produced water would be expected to alter the chemistry of channel flow to assume eventually the chemical composition of the produced water discharge and naturally occurring precipitation combined. These data would further suggest that, following completion of CBNG discharge, naturally occurring precipitation would likely bring the concentrations of trace elements deposited back towards original levels.

The travel time of stream flow from the head water tributaries of Dead Horse Creek to the Powder River is not known. However, the authors' data suggest that containment behind debris dams, water spreader dikes, and even in ponds of low gradient stream channel reaches may produce local and high contributions of chemistry associated with trace elements to flow moving towards the Powder River. It did not matter if the stored water was CBNG-produced water or distilled water. When the water types were stored as ground water for approximately 2 months, both types of sediment water assumed about the same water chemistry. Although the pond water types were lower in chemistry after 5 and 10 days, they approached the water quality of the ground water supplies. Therefore, the issue of travel time to the Powder River as channel flow vs. detention storage is an important consideration for developing regulatory and management options for disposing of or using this new and potential CBNG-produced water supply.

It is important to note that stream flow of water from precipitation represents a baseline for evaluating potential water quality issues associated with managing CBNG-produced water. If CBNG water is released into Powder River tributaries, then water from precipitation represents a blending of two different supplies. The data suggest that rain water may contribute substantial amounts of chemistry to the Powder River system and this load should be considered as it varies in time and space. Then, blending and water treatment alternatives for adding produced water sources that range in quality and lie within the time and space distribution of precipitation runoff may be feasible for helping achieve acceptable water quality in a downstream direction.

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