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WATER QUALITY CHANGES AS A RESULT OF COALBED METHANE DEVELOPMENT IN A ROCKY MOUNTAIN WATERSHED[1]

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ABSTRACT: Coalbed methane (CBM) development raises serious environmental concerns. In response, concerted efforts have been made to collect chemistry, salinity, and sodicity data on CBM produced water. However, little information on changes of stream water quality resulting from directly and/or indirectly received CBM produced water is available in the literature. The objective of this study was to examine changes instream water quality, particularly sodicity and salinity, due to CBM development in the Powder River watershed, which is located in the Rocky Mountain Region and traverses the states of Wyoming and Montana. To this end, a retrospective analysis of water quality trends and patterns was conducted using data collected from as early as 1946 up to and including 2002 at four U.S. Geological Survey gauging stations along the Powder River. Trend analysis was conducted using linear regression and Seasonal Kendall tests, whereas, Tukey's test for multiple comparisons was used to detect changes in the spatial pattern. The results indicated that the CBM development adversely affected the water quality in the Powder River. First, the development elevated the stream sodicity, as indicated by a significant increase trend of the sodium adsorption ratio. Second, the development tended to shrink the water quality differences among the three downstream stations but to widen the differences between these stations and the farthest upstream station. In contrast, the development had only a minor influence on stream salinity, as indicated by that the stream electrical conductivity exhibited either no trend or a marginally significant positive trend. Hence, the CBM development is likely an important factor that can be managed to lower the stream sodicity. The management may need to take into account that the effects of the CBM development were different from one location to another along the Powder River.

(KEY TERMS: coalbed methane, produced water; Montana; natural gas; pattern analysis; salinity; sodicity; trend analysis; Wyoming.)

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INTRODUCTION

Coalbed methane (CBM) is a product of biogeophysical processes that occur within a deeply confined coalbed. It is trapped in the bed by the aquifer hydrostatic pressure, which keeps the CBM gas adsorbed to the surface of the coal. Because of its large amount of recoverable storage volume and low rate of carbon dioxide (CO_2) emission (Nelson, 2000; Nuccio, 2000), CBM now accounts for about 7.5% of the total natural gas production in the United States and is expected to supply much of the nation's increasing natural gas demand in the next few decades (Rice and Nuccio, 2000; Hightower, 2001). For example, approximately 1×10^{12} m^3 CBM are recoverable in the 55,926 km^2 Powder River basin, located in the states of Wyoming and Montana (Nelson, 2000; Nuccio, 2000). Since 1993, this basin has emerged as one of the most active new areas of CBM production in the Rocky Mountain Region (Hill *et al.*, 2000; Rice *et al.*, 2000; Reddy *et al.*, 2001). Within the basin, the 33,785 km^2 Powder River watershed has demonstrated the most potential (Veil *et al.*, 2004), and by 2002, 5,774 wells had obtained drilling permits and 2,068 wells had begun production of CBM (Figure 1 and Table 1). Its economic and environmental importance to the region is why the Powder River watershed was selected for this study.

Extraction of CBM requires the aquifer water to be pumped out to lower the hydrostatic pressure and stimulate the desorption of methane from the coal

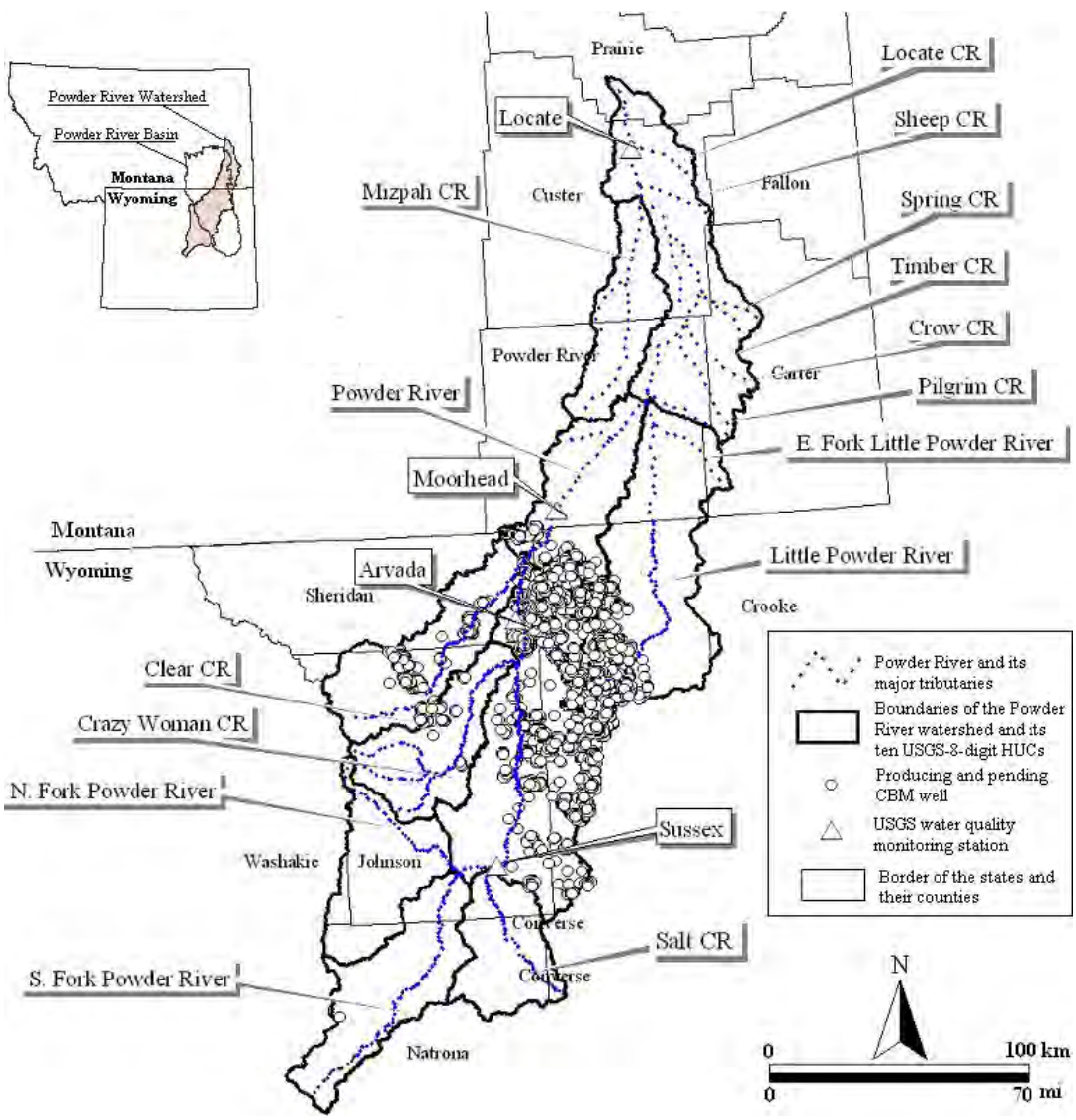

FIGURE 1. Map Showing the Powder River Watershed and Four USGS Stations Where Data Were Used.

TABLE 1. Reach Characteristics of the Powder River in Wyoming and Montana.

Reach*	Length (km)	Gradient (m/km)		Approximate 2002 CBM Wells				Water Yield, gpm†			Major Tributaries
				Total	Producing	Priority Date	Range	Mean	Standard Deviation	
Headwaters to Sussex	180	5.3		1	0	-‡	-‡	-‡	-‡	South Fork Powder River, North Fork Powder River, Salt Creek
Sussex to Arvada	145	1.6		3,882	822	25Mar98-09Mar01	0.1-200.0	35.0	35.0	Crazy Woman Creek
Arvada to	65	1.2	Wyoming	1,513	247	25Mar98-14Feb01	0.7-42.0	11.5	6.3	Clear Creek
Moorhead			Montana	38	38	28Sep01-06Oct01	-§	-§	-§	
Moorhead to Locate	290	1.0		2,408	961	28Dec89-09Apr01	1.0-252.0	29.4	23.5	Little Powder River, Mizpah Creek, Pilgrim Creek, Crow Creek, Timber Creek, Spring Creek, Sheep Creek, Locate Creek
Total	680	-		7,842	2,068	-¶	-¶	-¶	-¶	-¶

*See Figure 1 for the locations defining the reach;
†In gallons per minute (gpm) to be consistent with the unit in which it was originally reported, 1 m^3/s = 15,850.4 gpm;
‡No producing well;
§Water yield data unavailable for these producing CBM wells;
¶No sense for tabulation. CBM, coalbed methane.

(Rice and Nuccio, 2000). This extracted water is referred to as CBM produced water. The amount of water involved is substantial; for example, a typical water yield is 8-80 l/min for a single CBM well (McBeth *et al.*, 2003), and Rice and Nuccio (2000) and Veil *et al.* (2004) have estimated that nearly 7.57×10^9 m^3 water would be brought to the surface in the Powder River watershed every year. This large amount of water has raised serious concerns about its potential impact on the stream water quality in the watershed (Rice and Nuccio, 2000; Horpestad *et al.*, 2001; Veil, 2002). In response to these concerns, the Wyoming and Montana Departments of Environmental Quality implemented a concerted discharge elimination program in the Powder River watershed, which regulates the river's water quality to the same extent for the two states (D. Hengel, formally Senior Analyst at the Wyoming Department of Environment Quality, 2005, personal communication). However, it is uncertain whether the program prevented possible impacts as expected. For the watershed, the major concerns are related to the impact on water uses such as irrigating crops, riparian vegetation, and aquatic species (Horpestad *et al.*, 2001).

For crop irrigation and riparian vegetation, salinity and sodicity are the two principal constituents of concern. Salinity is usually expressed in terms of either electrical conductance (EC) at 25°C, in μS/cm, or total dissolved solids (TDS), in mg/l. This provides a comprehensive indicator of the proportions of salts in solution, including calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), chloride (Cl^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-). Sodicity indicates the relative proportions of Na^+ to Ca^{2+} and Mg^{2+} and is usually measured as the sodium adsorption ratio (SAR), which is defined as the ratio of Na^+ concentration in mEq/l to the square root of the average of the Ca^{2+} and Mg^{2+} concentrations in mEq/l, that is, $SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}}$. In practice, depending upon crops and vegetations, both SAR and EC have site-specific thresholds as determined by Hansen *et al.* (1999) and applied by Horpestad *et al.* (2001) in the Power River watershed. In addition, Hansen *et al.* (1999) found that when its EC and SAR values are lower than the corresponding thresholds, the water might be judged usable if its SAR is lower than a value computed based on a mathematical equation with EC as the independent variable. In addition, recognizing that the assumptions on which the equation is based (e.g., uniform leaching throughout a field) rarely hold in reality, Hansen *et al.* (1999) suggested that the individual salts contributing to EC and SAR also be examined.

For aquatic species (e.g., fathead minnows) in the Powder River, water temperature (T_w), pH, alkalinity,

and discharge (Q) are the most important indicators of stream habitat quality (Horpestad *et al.*, 2001). In addition, Mount *et al.* (1997) described the acute toxicity of major ions to fathead minnows, noting that potassium (K^+) and HCO_3^- are relatively toxic. For water with a pH value between 7.5 and 8.5, its alkalinity is primarily determined by the presence of HCO_3^- (Pankow, 1991), which may be a typical situation for natural streams, including the Powder River. However, because alkalinity and pH have an interrelated functional relationship (Marmorek *et al.*, 1996), both alkalinity and HCO_3^- were included in this study as water quality variables.

Because understanding the relationship and chemical associations among the constituents mentioned above was not the focus of this study, these constituents were treated as independent water quality variables. Although the authors were fully aware of the existence of these associations, they believed that treating these constituents as independent variables in this study would not bias the results, as the observed data reflected the values of the variables at an aquatic equilibrium governed by these associations. The focus of this study was to determine how these water quality variables might be altered as a result of CBM development.

Driven by environmental concerns, a great deal of effort has been made to collect chemistry, salinity, and sodicity data on water from selected CBM wells in the Powder River basin (e.g., Rice *et al.*, 2000; McBeth *et al.*, 2003). Rice *et al.* (2000) examined the chemistry of CBM produced water at wellheads across the watershed and reported that moving from north and west (Figure 1) toward deeper coal seams within the basin tends to produce more saline and alkaline water. McBeth *et al.* (2003) studied the chemistry of the water produced both at wellheads and in retention ponds and reported an increase in SAR, EC, TDS, and pH of CBM discharge water in associated retention ponds moving from the south to the north. Further, Hulin (2003) conducted a laboratory study on CBM produced water chemistry changes as influenced by the Dead Horse Creek channel sediment in the basin, and Patz *et al.* (2004) conducted a field study in the Burger Draw of the Powder River watershed. These studies agreed that both EC and SAR of the discharged CBM produced water tended to increase when the water was flowing downstream along the study channels from the wellheads. They attributed the SAR increase to precipitation of calcium carbonate in the downstream channels, which decreased calcium concentration and attributed the EC increase to the water's acquisition of additional dissolvable constituents from the channel beds. However, these data collection efforts and studies provided no information on water quality changes in the Powder River resulting either directly and/or indirectly from receiving CBM produced water.

In a study designed to address this issue, Horpestad *et al.* (2001) used a steady state mass balance model, assuming that flows from the tributaries would be instantaneously and uniformly mixed with water in the Powder River at the confluences, to determine the discharge limits of the untreated CBM produced water in accordance with a Montana irrigation water quality standard. The results indicated that to ensure this irrigation standard was met, the discharge of CBM produced water should be limited and, consequently, the number of wells that can discharge untreated produced water directly to the Powder River must also be limited.

In a separate study, Kurz *et al.* (2005) developed and used a statistical model to predict the prospective EC and SAR along the Powder River by assuming that all the water produced from the existing and proposed wells listed in Horpestad *et al.* (2001) would be directly discharged into the river with a zero conveyance loss. This study analyzed all six combinations between the number of wells (existing wells only and existing plus proposed wells) and the hydrologic conditions (dry, normal, and wet) on a monthly basis. The results were summarized for two U.S. Geological Survey (USGS) gauging stations in Wyoming, namely the Powder River at Sussex, or Sussex (USGS 06313500), and the Powder River at Arvada, Colorado, or Arvada (USGS 06317000), and another two stations in Montana, namely the Powder River at Moorhead, or Moorhead (U.S. Geological Survey (USGS) 06324500), and the Powder River at Locate, or Locate (USGS 06326500). The results indicated that compared with the river background conditions, SAR would be significantly increased but EC was likely to have a negligible change or be only slightly decreased.

These two studies conducted "what-if" analyses and did not examine any alterations of the water quality that might be caused by further CBM development in the Powder River watershed. Clark *et al.* (2001) summarized the available data and plotted SAR and EC *vs.* streamflows at eight USGS gauging stations along the Powder River. These plots indicated that both SAR and EC tended to decrease with increasing streamflows. However, they did not expand their analysis to explore changes in the water quality. Lacking this information, it may not be feasible to investigate impacts resulting from CBM development.

The objective of this study was therefore to examine changes in the stream water quality as a result of CBM development in the Powder River watershed. To this end, a retrospective analysis of water quality trends and patterns was conducted using data collected up to and including 2002 at the four USGS

gauging stations that Kurz *et al.* (2005) used for their study, namely Sussex, Arvada, Moorhead, and Locate. Although this study focused on the Powder River watershed, the analysis of water quality trends and patterns has a broader interest at a larger geographical scope because with the nation's increasing energy demand, CBM is expected to be massively explored in numerous watersheds, particularly ones located in the arid and semi-arid regions (Nuccio, 2000).

As discussed above, EC, SAR, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, and SO_4^{2-} are important constituents for both irrigated crops and riparian vegetation, whereas aquatic species are more sensitive to elevated concentrations of K^{+} and HCO_3^{-} and changes of Q, T_w, pH, and alkalinity. For the aforementioned reasons, although these constituents may have chemical associations (in particular, HCO_3^{-} can be a substantial part of alkalinity depending on pH), they were analyzed as independent water quality variables for this study. In addition, air temperature (T_A) was taken as an additional analysis parameter to differentiate changes of T_w caused by CBM development from those occurring naturally. Although the authors fully understood that Q and T_A are rarely classified as water quality variables in the literature, for description purposes, in this study the term "water quality" will refer to the combination of these 14 parameters. Note, however, that this is solely for convenience of presentation; the authors have no intention of redefining the meaning of water quality. Further, previous studies (Clark *et al.*, 2001; Tetra Tech Inc., 2003) have indicated that values for 11 of these 14 parameters (excluding T_A, Q, and pH) were affected by varying streamflow conditions at the time of sampling. Hence, when used for trend and pattern analysis in this study, the data for these 11 parameters were preprocessed to remove the confounding effect of flow using a nonparametric locally weighted regression and smoothing scatterplot (LOWESS) regression with a smoothing parameter (f) of 0.5 (Schertz *et al.*, 1991; Helsel and Hirsch, 1992; Robson and Neal, 1996). LOWESS was used because it is usually superior to the parametric ordinary least squares regression suggested by Räike *et al.* (2003) in removing the confounding effect (Bekele and McFarland, 2004).

MATERIALS AND METHODS

The Powder River Watershed

The 33,785 km^2 Powder River watershed traverses the states of Wyoming and Montana, with the upper 23,650 km^2 covering portions of seven Wyoming counties and the remaining lower 10,135 km^2 covering portions of four Montana counties (Figure 1). The watershed is drained by the Powder River, which flows generally from northeastern Wyoming into southeastern Montana, toward its confluence with the Yellowstone River in Prairie County. The Powder River is sustained by source flows from the North Fork Powder River and South Fork Powder River and by runoff from Salt Creek, Crazy Woman Creek, Clear Creek, Little Powder River, Mizpah Creek, and a number of other small tributaries. The watershed consists of ten USGS 8-digit hydrologic cataloging units, with codes of 10090201 through 10090210. The elevation within the watershed ranges from 3,900 m in the southwestern portion to 665 m in the northern portion, leading to an average gradient of 0.006-0.001 along the Powder River (Table 1).

Based on a database derived from satellite imagery taken during the early 1990s (Multi-Resolution Land Characteristics, 1992), the land use within the watershed consists of 58.9% grass, 28.8% shrub land, 6.2% evergreen forest, 1.4% small grains, 1.4% fallow land, and 1.2% pasture/hay. Other miscellaneous land use types include herbaceous wetlands (0.77%), deciduous forest (0.44%), wooded wetlands (0.31%), water (0.17%), row crops (0.12%), and residential, transportation, and commercial (0.28%). USGS used the same satellite imagery in the ongoing Gap Analysis Program (GAP) (http://www.gap.uidaho.edu) to generate more detailed land use classifications. The classifications indicated that irrigated crops in Wyoming are concentrated along the mountain foothills of the Clear Creek subwatershed and on the valley floor along the Powder River, and in Montana are typically located on the valley floors along the Powder River and its major tributaries. These irrigated crops, along with other vegetation and aquatic life identified through GAP, mainly rely on the Powder River and its tributaries for their water supply (Tetra Tech Inc., 2003).

The clay content of most of the soils in the Powder River watershed ranges from 40 to 60% but reaches as high as 70% in the farthest downstream portion of the watershed (Tetra Tech Inc., 2003). Because of this high clay content, the soils in the watershed are susceptible to the effects of high sodium concentrations that can disperse clay soils, change the soil structure, and render the soils hard and resistant to water and aeration. The soils in the South Fork Powder River subwatershed have a SAR higher than 10, whereas the soils in the remaining portion of the watershed have lower SAR values (EDE Consultants, 2005). In general, SAR in soil tends to be higher in the headwaters than in the plains of the Powder River, and higher in the floodplains than in the upland areas.

Further, most soils in the watershed have an EC of between 2,000 and 8,000 μS/cm, which makes the soils naturally limiting to plant growth. In particular, with an EC higher than 4,000 μS/cm, the soils in the floodplains of the Powder River, Little Powder River, and Mizpah Creek may be saline (Miller and Donahue, 1990; Brady and Weil, 1999).

The natural-limiting effect on plant growth may relax in the plains, where the soils have a moderately low to moderately high permeability, but deteriorate in the headwaters, where the soil permeability is very low. The majority of the soils in the Powder River watershed can be classified as hydrologic Group D, which is defined as having a very low infiltration rate but a high runoff tendency (Wischmeier and Smith, 1978). In addition, the soils have a high erosion risk, as indicated by the great Universal Soil Loss Equation k-factors ranging from 0.2 to 0.4. Because using stream water with elevated SAR and EC for irrigation may deteriorate the natural-limiting effect and further increase the erosion risk, SAR and EC were taken as two important water quality indicators for this study.

The climate in the Powder River watershed is characterized by cold and wet conditions in the mountainous areas, which are at elevations of 1,825-3,965 m above sea level, and by temperate to semiarid conditions in the valley areas, which are at elevations of 915-1,825 m. Precipitation is typically greatest from March to July. Significant snowfall begins in October and continues through May. Based on data from the National Climate Data Center (NCDC) (http://lwf.ncdc.noaa.gov/oa/ncdc.html), the mountainous areas have an annual average precipitation of 290 mm, 40% of which is in the form of snow, while the valley areas have a greater total annual average precipitation of 325 mm, 25% of which is snow. Temperatures reach a maximum in July and drop to a minimum in January. The average monthly temperature ranges from −5.5 to 20.9°C in the mountainous areas and from −9.5 to 22.5°C in the valley areas. Evaporation is a major water loss factor in the watershed and can exceed precipitation on an annual average basis. The annual average evaporation is about 510 mm in the mountainous areas and can be as high as 890 mm in the valley areas.

The USGS has been collecting flow and water quality data for the Powder River and its major tributaries at 68 gauging stations (Clark *et al.*, 2001). Among these stations, the four stations along the Powder River that are used in this study, namely Sussex, Arvada, Moorhead, and Locate (Figure 1), have relatively long records, hence their selection. Based on the available data, the flows at these four stations share a similar temporal variation pattern. In February and March flows increase as a result of the snow that has accumulated in the valley areas over the winter melts. The flows then decrease in April because of low precipitation. In May, the flows increase again as the snow that has accumulated in the mountainous areas melts, as well as the increased rainfall across the watershed. By the end of July, due to increased evaporation, withdraws, and reduced precipitation, the flows decrease to a minimum. As expected, the flows increase from upstream to downstream but the increase is not large. At a given location, the most pronounced temporal variations in the flows occur in spring, when snow starts melting and rainfall is increasing. Controlled by the intense rainstorm and snowmelt runoff, the daily flows in the Powder River have an even higher temporal variability (USGS, 1999).

Tributaries that originate in the mountainous areas, such as the North Fork Powder River, Crazy Woman Creek, and Clear Creek, are perennial and generally sustained by snowmelt runoff. In contrast, the tributaries that flow entirely through the plains, such as the Little Powder River and Mizpah Creek, are ephemeral. For the ephemeral tributaries, the flows are mainly controlled by localized snowmelt, intense rainstorms, withdraw, and return water. In the Powder River watershed, more than 86.7% of the streams (in terms of length) are intermittent. During summer, the flows are usually withdrawn to irrigate croplands that range in size from 50 to 9,400 acre (Tetra Tech Inc., 2003). The withdrawn water is mostly applied in the form of flood irrigation, although sprinkler and spreader dikes are also employed in some locations.

Data Availability and Collapsing

The data used in this study were downloaded from the National Water Information System website (NWISWeb) (http://waterdata.usgs.gov/nwis/qw) for the Sussex, Arvada, Moorhead, and Locate monitoring stations along the Powder River. The data were collected, maintained, distributed, and reviewed in accordance with relevant measurement standards by USGS. Because the focus of this study was not to examine how the data were measured, the readers who are interested in the measurement methods and standards used by USGS are recommended to surf the NWISWeb.

The number of years for which data has been recorded varies greatly from station to station, and the records for each of the stations include gaps from months to years in duration. For each of the stations, no data collection occurred in some months, while in other months data for some years were recorded for two or more different dates. Table 2 summarizes the

TABLE 2. Water Quality Parameters Analyzed in This Study, the Years and Number of Months for Each Parameter at Each USGS Station for Which Data Were Available, and Summary Statistics.*

USGS Station	Item	Q	T_w	T_A	pH	EC	SAR	Alkalinity	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	Mean	Median	Standard Deviation
Sussex (06313500)	Record Years	1966-1968 and 1976-2002														-†	-†	-†
	Missing Years	1976 1999-2001	-‡	1966-1968 1976	1984-1987 1990-1992	1984-1987	-‡	1966-1968 1976-1997 1999	-‡	-‡	-‡	-‡	-‡	-‡	1981-2002	-†	-†	-†
	No. of Years Analyzed	26	30	26	23	26	30	4	30	30	30	30	30	30	8	25	30	8.5
Arvada (06317000)	Record Years	1946, 1948-1953, 1955, and 1967-2002														-†	-†	-†
	Missing Years	-‡	1946 1948-1953 1955	1946 1948-1953 1955 1967-1977 1979	1955 1975 1983-1987 1990-1992	1983	1946 1948-1951	1946 1948-1953 1955 1967-1997 1999	-‡	-‡	1946 1948-1950	1946 1948-1952	1953 1955	1953 1955	1953 1955 1982-2002	-†	-†	-†
	No. of Years Analyzed	44	36	24	34	43	39	4	44	44	40	38	42	42	21	35	40	11.5
Moorhead (06324500)	Record Years	1969-1972 and 1974-2002														-†	-†	-†
	Missing Years	-‡	-‡	1969	1985 1990-2000	-‡	1969 1983-2002	1969-1972 1974-2000	1969 1985 1990-2000	1969 1985 1990-2000	1969 1985 1990-2000	1969-1971 1985 1990-2000	1969 1985 1990-2000	1985 1990-2000	1969-1971 1979-2002	-†	-†	-†
	No. of Years Analyzed	33	33	32	21	33	12	2	20	20	20	18	20	21	6	21	20	9.9
Locate (06326500)	Record Years	1948-1962, 1965, and 1974-2002														-†	-†	-†
	Missing Years	-‡	1948-1962	1948-1962 1965	1965 1995-1998	1965	1948-1949 1965 1995-1998	1948-1962 1965 1974-1998	1965 1995-1998	1965 1995-1998	1948-1949 1965 1995-1998	1948-1949 1952 1965 1995-1998	1965 1995-1998	1965 1995-1998	1965 1979-2002	-†	-†	-†
	No. of Years Analyzed	45	30	29	40	44	38	4	40	40	38	37	40	40	20	35	39	11.0
Sussex	Record Months	263	239	216	155	184	231	18	231	231	232	230	231	231	57	196	231	72.4
	Pre-1990 Months	156	141	118	92	92	133	0	133	133	134	133	135	135	57	114	133	41.6
	Post-1990 Months	107	98	98	63	92	98	18	98	98	98	97	96	96	0	83	98	32.9
Arvada	Record Months	527	274	151	221	313	282	24	314	314	288	281	317	317	191	272	285	111.0
	Pre-1990 Months	371	200	77	170	239	209	0	241	241	215	208	243	243	191	203	212	85.1
	Post-1990 Months	156	74	74	51	74	73	24	73	73	73	73	74	74	0	69	73	33.8
Moorhead	Record Months	384	278	247	190	270	103	17	180	181	166	158	180	189	54	186	181	93.1
	Pre-1990 Months	228	190	161	173	186	103	0	163	164	149	141	163	172	54	146	163	58.5
	Post-1990 Months	156	88	86	17	84	0	17	17	17	17	17	17	17	0	39	17	45.8
Locate	Record Months	252	258	253	360	413	271	38	289	288	341	248	306	338	205	276	280	87.3
	Pre-1990 Months	154	157	153	294	312	205	0	223	223	275	182	240	272	205	207	214	78.8
	Post-1990 Months	98	101	100	66	101	66	38	66	65	66	66	66	66	0	69	66	27.2

*Q is discharge, T_w water temperature, T_A air temperature, EC electrical conductivity, SAR sodium adsorption ratio, Ca^{2+} calcium, Mg^{2+} magnesium, Na^+ sodium, K^+ potassium, Cl^- chloride, SO_4^{2-} sulfate, and HCO_3^- biocarbonate. †The summary statistic has no sense for either Record Years or Missing Years. ‡Annual median values were available for all record years.

availability of data across the four stations for the 14 water quality parameters analyzed in this study, including Q, T_w, T_A, pH, EC, SAR, alkalinity, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and HCO_3^-.

At Sussex, data for T_w, SAR, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-} were recorded from 1966 to 1968 and from 1976 to 2002, during which from 230 to 239 months had at least one observation. However, data for Q, T_A, pH, EC, alkalinity, and HCO_3^- had 4-, 4-, 7-, 26-, and 22-year gaps during the 30 record years, respectively. The number of months when there was at least one observation varied from 18 to 263 across the parameters, with a mean of 196 and a standard deviation of 72.4. Arvada had records for the year 1946, from 1948 to 1953, 1955, and from 1967 to 2002. During the 44 record years, Q, Ca^{2+}, and Mg^{2+} had at least one observation for each year, but T_w, T_A, pH, EC, SAR, alkalinity, Na^+, K^+, Cl^-, SO_4^{2-}, and HCO_3^- all suffered from gaps ranging from 4 to 40 years in length. The number of months when there was at least one observation varied from 24 to 527 across the 14 parameters, with a mean of 272 and a standard deviation of 111.

Moorhead had records for the years from 1969 to 1972 and from 1974 to 2002. During the 33 record years, Q, T_w, and EC had at least one observation for each year, but the other 11 parameters were not observed at all for periods ranging from 1 to 31 years. The number of months when there was at least one observation varied from 17 to 384, with a mean of 181 and a standard deviation of 93.1. Locate had the longest record, covering the years from 1948 to 1962, 1965, and from 1974 to 2002. However, only Q had at least one observation for each of the 45 record years and the other 13 parameters gaps ranging from 5 to 41 years in length.

Although the number of months when there was at least one observation varied from 38 to 360, data availability for these four stations was judged to be comparable because the available data had a similar dispersion. For this study, the dispersion was measured in terms of the coefficient of variation (C_v), defined as the ratio of mean to standard deviation of the number of months. The C_v values for the stations (0.3-0.5) were almost the same, with only a small variation, although Moorhead had a slightly larger C_v of 1.17 after 1990.

The quantity and wide variation of the raw data required an effort to collapse the data into a more manageable form, and the method suggested by Passell *et al.* (2004) was used. When a parameter was measured on two or more dates in a single month, those values were combined to calculate a monthly median. When no data in a month were available, no monthly median was recorded. Monthly medians across each calendar year were then used to identify an annual median. In addition, for the parameters except for T_A, Q, and pH, both the annual and monthly medians were regressed over the corresponding discharges using LOWESS by following the procedure suggested by Bekele and McFarland (2004) to remove the confounding effect of flow.

Analysis Methods

For trend analysis purposes, categorized in terms of the 14 water quality parameters and the four stations, the collapsed/corrected data were subdivided into three datasets. The "whole dataset" composed of the data up to the end of 2002, the "pre-1990 dataset" composed of the data before 1990, and the "post-1990 dataset" composed of the data from 1990 to 2002. This subdivision formulated 336 datasets, with 42 monthly and 42 annual median datasets for each of the stations. Because of no CBM development before 1990, this year was chosen as the inflexion point.

The annual medians were plotted to visualize the overall changes of water quality spanning all the record years, before 1990, and after 1990. The visualization provided a broad picture of the water quality trends. In addition, in order to reveal the existence and strength of trends in the data, two types of statistical tests (Passell *et al.*, 2004) were performed on the monthly and annual medians using a significance level of 0.1 (i.e., $\alpha = 0.1$). Instead of 0.05, this study selected a popular larger significance level of 0.1. Other researchers (e.g., Liu *et al.*, 1997; Goodman, 1999) showed that this larger significance level is a better compromise between Type I error (i.e., failing to accept a true null hypothesis) and Type II error (i.e., failing to reject a false null hypothesis) for the analysis on coarse data, which is the case of this study. First, the annual medians over the record periods were used in least squares linear regression models. Because the datasets for the 11 parameters (excluding alkalinity and HCO_3^-), were large, consisting of at least 25 data points, it was presumed that the assumptions governing the use of linear regression (e.g., normality) could be relaxed (Neter *et al.*, 1996), and thus no data transformation was necessary. Also, the residual plots (not shown) indicated no serial correlation. Estimated slopes and p-values from the linear regression were then used to detect and quantify the trends. The second trend analysis applied a Seasonal Kendall test, in which the monthly medians were used to calculate the Seasonal Kendall statistic S' (Mann, 1945; Kendall, 1975; Hirsch *et al.*, 1982; Brauner, 1997), and a p-value was used to determine the significance of S'. The detected trends were interpreted to qualitatively determine

the impact of CBM development in the Powder River watershed.

Linear regression is a parametric method that is sensitive to deviations from normal distribution and the existence of outliers (Neter *et al.*, 1996). Consequently, when data for parameters such as alkalinity and HCO_3^- are small in size (say, less than five) and/or have a large degree of skewness, this method may be unable to detect trends that are present in the data. In contrast, the Seasonal Kendall test is a nonparametric approach (Hirsch *et al.*, 1982). Its application does not require any assumptions regarding distribution and it is insensitive to outliers. Hence, the Seasonal Kendall test is more robust than linear regression. In particular, because it considers the interaction of seasonal and annual variations, the Seasonal Kendall test may be more capable of detecting trends for parameters with an obviously seasonal variability, such as T_A, T_w, and Q. However, as a nonparametric method, the Seasonal Kendall test cannot give any information on trend gradients (i.e., the rate at which the trend changes), whereas this information is reflected by the slopes that are estimated from a linear regression. Therefore, this study used both linear regression and Seasonal Kendall test for the trend analysis.

Coalbed methane development may also cause changes of water quality spatial patterns because it primarily affects the downstream reaches of the watershed. The changes were therefore expected to be exhibited as the water quality in the downstream reaches differed from the predevelopment conditions but that in the upstream reaches remained unchanged. This study used Tukey's test for multiple comparisons, with a family significance level α of 0.1 (Neter *et al.*, 1996), to examine whether and how the pre-1990 water quality spatial patterns along the Powder River were different from the post-1990 patterns. Because the major CBM development in the Powder River watershed began operations in 1990, the post-1990 water quality patterns will be different from the pre-1990 patterns if the effects of the CBM development are significant.

Table 2 shows that the four stations had a common record period of from 1976 to 2002. For the pattern analysis, this study used annual medians that were computed from the data observed during this period. The medians were also computed using the method suggested by Passell *et al.* (2004). A close examination reveals that for any given year, not all of the four stations had annual medians for all 14 parameters. That is, during this record period, annual medians for some of the 14 parameters were available for all stations, but for the other parameters annual medians were unavailable for at least one station. To implement Tukey's test across the four stations, the unavailable medians were set to values imputed using the Estimate and Maximum (EM) algorithm (Johnson and Wichern, 1998). The EM algorithm is a widely used multivariate statistical method for imputing missing values. In this study, the EM algorithm used the available annual medians to impute the unavailable ones to create a complete dataset. Spanning the record period for each station, this dataset thus consists of both the observed and imputed annual medians. As with the trend analysis, the spatial pattern analysis was also conducted on three datasets, as a result of subdividing this complete dataset.

The raw data were manipulated in Microsoft Excel 2000 and ArcView 3.2a (ESRI, Redlands, California) to create the collapsed datasets. The least square linear regression and LOWESS were performed using WinSTAT for Excel developed by R. Fitch Software (2002). The EM algorithm was realized using a computer program written by the authors in IML language using the SAS System for Windows (version 8) (SAS, 2000). In addition, Tukey's test was performed with the SAS system, and the Seasonal Kendall test was conducted using a Microsoft Excel Add-In developed by Libiseller (2002). Further, the authors wrote a number of computer programs in Visual Basic 6.0 and ArcView Avenue computer languages to facilitate data transmission between the software packages. The computer programs written by the authors are available upon request.

RESULTS AND DISCUSSION

Temporal Trends

Across the four stations, the pre-1990 datasets exhibited more marked trends than the post-1990 datasets (Tables 3A-3D). For a given station, the Seasonal Kendall test detected more trends than linear regression, indicating that the water quality parameters might have an inherent seasonal variability or follow a distribution that is different from the normal distribution assumed by linear regression. Note, however, that the trends detected by these two methods were consistent, thus validating the existence of these trends.

At Sussex, six parameters, namely T_w, pH, SAR, Na^+, Cl^-, and HCO_3^-, had significant positive (increase) trends before 1990, but after that time, T_w exhibited a significant negative (decrease) trend and the other five parameters exhibited no trend (Table 3A). One explanation for these contrasting

TABLE 3A. *p*-Values of Tests for Trend at the Powder River at Sussex, Wyoming (USGS 06313500).

Parameter*	Whole Dataset		Pre-1990 Dataset		Post-1990 Dataset	
	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall
Q	0.300	0.280	0.200	0.200	0.300	0.037
T_W	0.230	0.420	0.900	0.009	0.150	0.010
T_A	0.780	0.496	0.989	0.263	0.255	0.073
pH	0.100	0.270	—†	0.059	—†	0.290
EC	0.008	0.005	0.800	0.180	0.600	0.400
SAR	0.000	0.006	1.000	0.007	0.230	0.200
Alkalinity	0.800	0.150	—‡	—‡	—‡	0.150
Ca^{2+}	0.070	0.046	0.010	0.012	0.500	0.100
Mg^{2+}	0.300	0.220	0.004	0.009	0.300	0.150
Na^{+}	0.000	0.005	0.400	0.015	0.300	0.215
K^{+}	0.130	0.440	0.090	0.330	0.090	0.110
Cl^{-}	0.000	0.005	0.300	0.042	0.300	0.220
SO_4^{2-}	0.600	0.490	0.060	0.100	0.380	0.230
HCO_3^{-}	0.100	0.032	0.100	0.032	0.800	—‡

*Q is discharge, T_w water temperature, T_A air temperature, EC electrical conductivity, SAR sodium adsorption ratio, Ca^{2+} calcium, Mg^{2+} magnesium, Na^+ sodium, K^+ potassium, Cl^- chloride, SO_4^{2-} sulfate, and HCO_3^- biocarbonate.; †The variance is too small to conduct the test. ‡The sample size is too small to conduct the test. ▒ Significant ($\alpha = 0.1$) negative trend, and ■ Significant ($\alpha = 0.1$) positive trend.

TABLE 3B. *p*-Values of Tests for Trend at the Powder River at Arvada, Wyoming (USGS 06317000).

Parameter*	Whole Dataset		Pre-1990 Dataset		Post-1990 Dataset	
	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall
Q	0.200	0.098	0.100	0.036	0.970	0.430
T_W	0.090	0.350	0.710	0.125	0.600	0.013
T_A	0.200	0.240	0.800	0.394	0.600	0.184
pH	0.300	0.000	0.147	0.000	—†	0.360
EC	0.700	0.150	0.000	0.000	0.900	0.118
SAR	0.220	0.490	0.000	0.000	0.340	0.085
Alkalinity	0.200	0.000	—‡	—‡	0.200	0.000
Ca^{2+}	0.003	0.000	0.001	0.000	0.600	0.360
Mg^{2+}	0.200	0.028	0.500	0.022	0.658	0.130
Na^{+}	0.400	0.490	0.000	0.000	0.600	0.088
K^{+}	0.340	0.023	0.340	0.039	0.860	0.340
Cl^{-}	0.900	0.125	0.000	0.000	0.700	0.120
SO_4^{2-}	0.060	0.031	0.300	0.180	0.530	0.150
HCO_3^{-}	0.000	0.000	0.000	0.000	—‡	—‡

*Q is discharge, T_w water temperature, T_A air temperature, EC electrical conductivity, SAR sodium adsorption ratio, Ca^{2+} calcium, Mg^{2+} magnesium, Na^+ sodium, K^+ potassium, Cl^- chloride, SO_4^{2-} sulfate, and HCO_3^- biocarbonate.; †The variance is too small to conduct the test. ‡The sample size is too small to conduct the test. ▒ Significant ($\alpha = 0.1$) negative trend, and ■ Significant ($\alpha = 0.1$) positive trend.

trend changes was that the brine and brackish water produced by an oil field located upstream of Sussex that had been discharged into the stream up until 1990, started to be reinjected back into ground from February 1990 onwards (EDE Consultants, 2005). Thus, the trend changes were an indication

TABLE 3C. *p*-values of Tests for Trend at the Powder River at Moorhead, Montana (USGS 06324500).

Parameter*	Whole Dataset		Pre-1990 Dataset		Post-1990 Dataset	
	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall
Q	0.700	0.460	0.800	0.235	0.900	0.169
T_W	0.080	0.080	0.700	0.407	0.400	0.024
T_A	0.450	0.188	0.770	0.373	0.200	0.160
pH	0.200	0.098	—†	0.023	—†	—†
EC	0.000	0.115	0.800	0.013	0.200	0.136
SAR	0.008	0.006	0.008	0.006	—‡	—‡
Alkalinity	—‡	—‡	—‡	—‡	—‡	—‡
Ca^{2+}	0.900	0.359	0.200	0.059	—‡	—‡
Mg^{2+}	0.500	0.209	0.600	0.440	—‡	—‡
Na^{+}	0.960	0.014	0.010	0.006	—‡	—‡
K^{+}	0.006	0.068	0.430	0.461	—‡	—‡
Cl^{-}	0.600	0.117	0.100	0.005	—‡	—‡
SO_4^{2-}	0.200	0.094	0.800	0.294	—‡	—‡
HCO_3^{-}	0.200	0.293	0.200	0.293	—‡	—‡

*Q is discharge, T_w water temperature, T_A air temperature, EC electrical conductivity, SAR sodium adsorption ratio, Ca^{2+} calcium, Mg^{2+} magnesium, Na^{+} sodium, K^{+} potassium, Cl^{-} chloride, SO_4^{2-} sulfate, and HCO_3^{-} biocarbonate. †The variance is too small to conduct the test. ‡The sample size is too small to conduct the test. ▒ Significant ($\alpha = 0.1$) negative trend, and ■ Significant ($\alpha = 0.1$) positive trend.

TABLE 3D. *p*-Values of Tests for Trend at the Powder River near Locate, Montana (USGS 06326500).

Parameter*	Whole Dataset		Pre-1990 Dataset		Post-1990 Dataset	
	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall	Linear Regression	Seasonal Kendall
Q	0.050	0.030	0.100	0.006	0.700	0.120
T_W	0.907	0.200	0.500	0.500	0.063	0.104
T_A	0.210	0.290	0.830	0.340	0.920	0.037
pH	0.000	0.000	0.000	0.001	0.008	0.030
EC	0.020	0.003	0.001	0.000	0.700	0.035
SAR	0.003	0.000	0.000	0.000	0.040	0.021
Alkalinity	0.690	—‡	—‡	—‡	0.690	0.023
Ca^{2+}	0.008	0.007	0.010	0.024	0.620	0.280
Mg^{2+}	0.400	0.080	0.100	0.017	0.400	0.156
Na^{+}	0.004	0.000	0.000	0.000	0.050	0.050
K^{+}	0.680	0.473	0.520	0.153	0.050	0.110
Cl^{-}	0.001	0.000	0.000	0.000	0.800	0.240
SO_4^{2-}	0.600	0.100	0.200	0.041	0.090	0.029
HCO_3^{-}	0.001	0.007	0.001	0.007	—‡	—‡

*Q is discharge, T_w water temperature, T_A air temperature, EC electrical conductivity, SAR sodium adsorption ratio, Ca^{2+} calcium, Mg^{2+} magnesium, Na^{+} sodium, K^{+} potassium, Cl^{-} chloride, SO_4^{2-} sulfate, and HCO_3^{-} biocarbonate. †The variance is too small to conduct the test. ‡The sample size is too small to conduct the test. ▒ Significant ($\alpha = 0.1$) negative trend, and ■ Significant ($\alpha = 0.1$) positive trend.

that discharges from the oil field had previously had a significant impact on water quality in the Powder River.

The pre-1990 positive trend for SAR was a result of the significant positive trend for Na^{+} and the significant negative trends for Ca^{2+} and Mg^{2+}. After

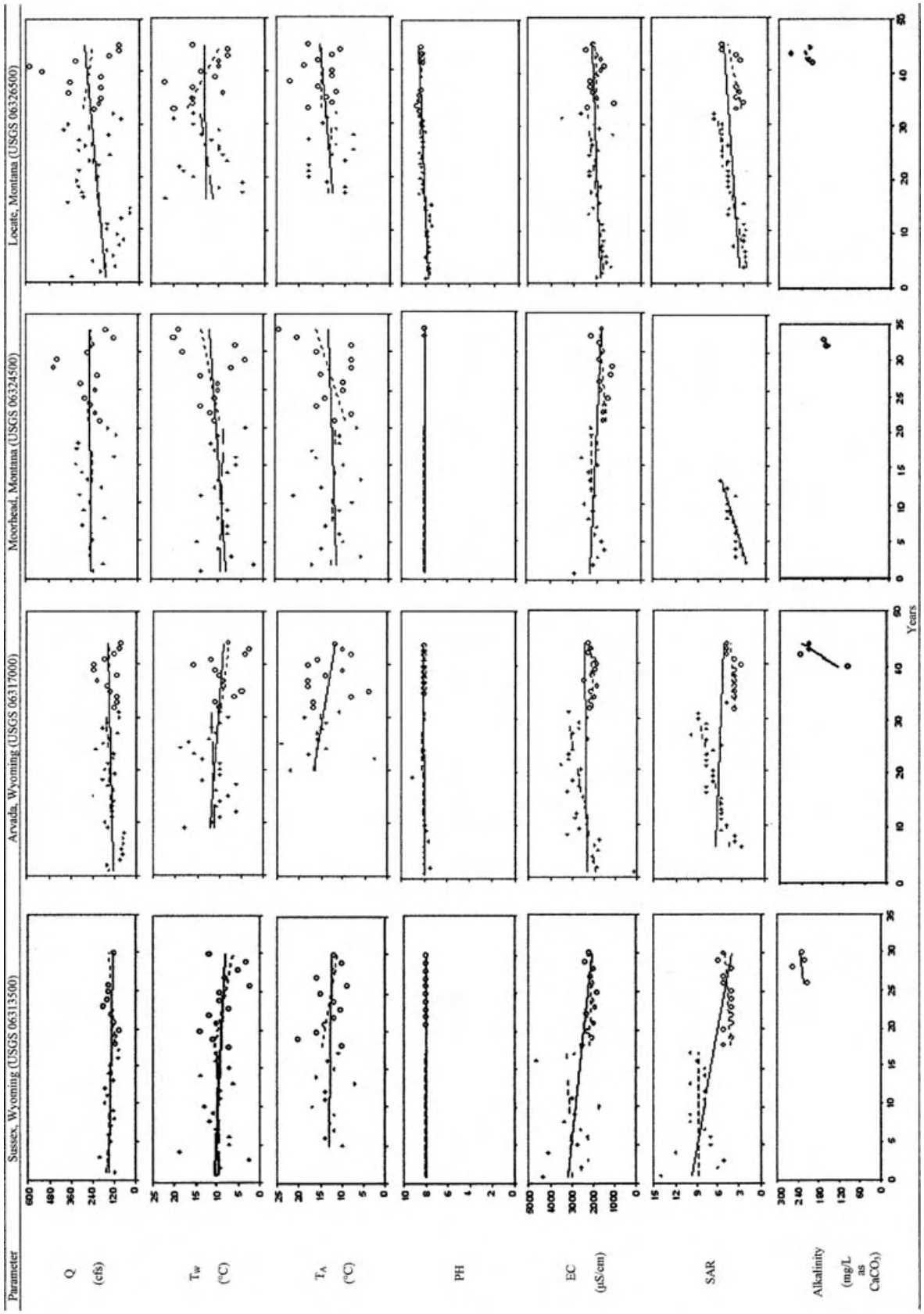

FIGURE 2. (a) Least Squares Regression Analysis for Discharge (Q), Water Temperature (T_w), Air Temperature (T_A), pH, Electrical Conductance (EC), Sodium Adsorption Ratio (SAR), and Alkalinity. Q is reported in cubic feet per second (cfs) to be consistent with the unit in which it was originally reported; 1 m^3/s = 35.3 cfs. The record years are listed in Table 2. (b) Least squares regression analysis for cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) and anions (Cl^-, SO_4^{2-}, and HCO_3^{2-}) based on the available data for the years listed in Table 2.

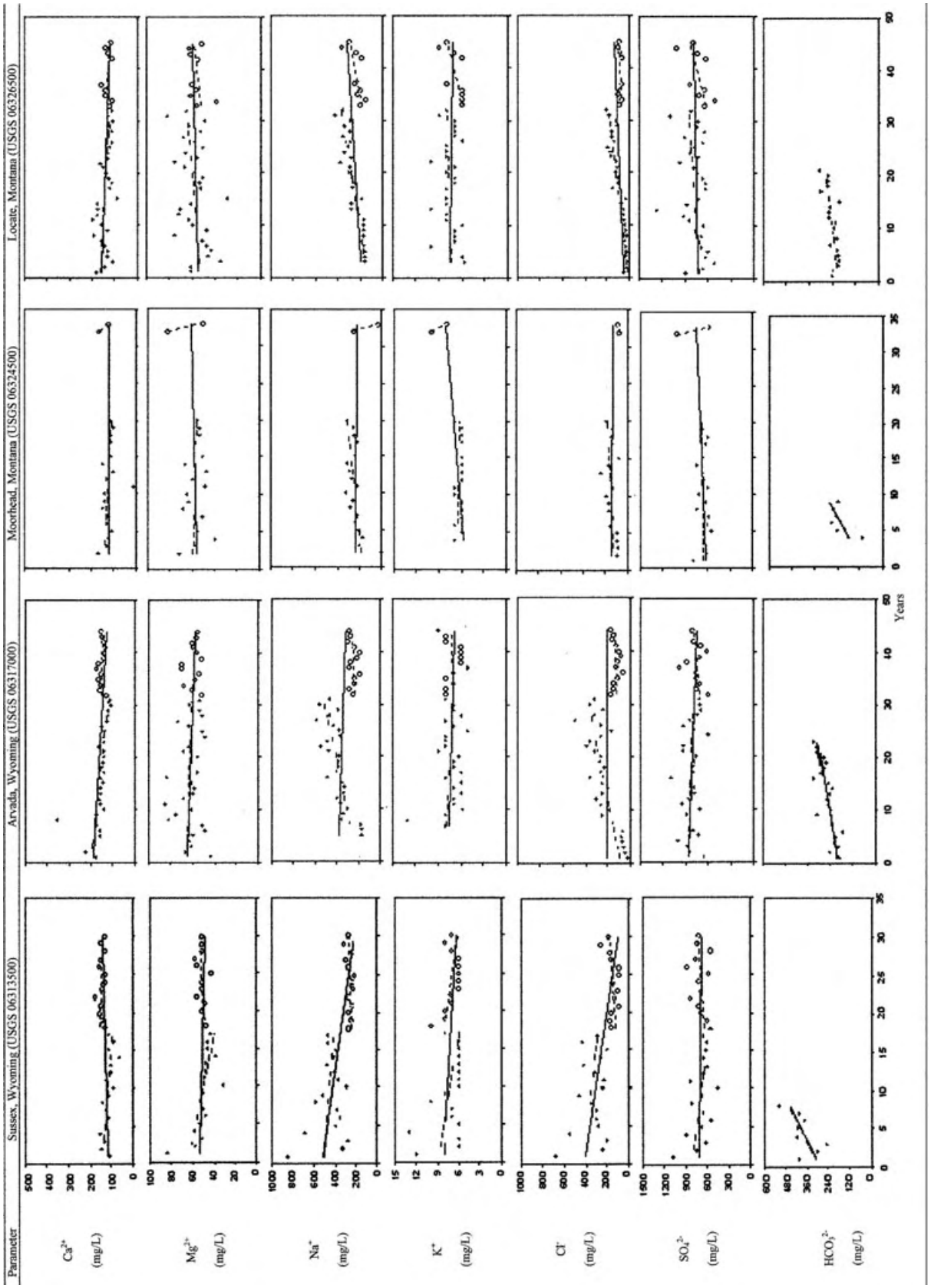

FIGURE 2. (*Continued*).

(a)

	1	2	3	4
Q				
2	0.911			
3	0.000	0.001		
4	0.000	0.000	0.983	
SAR				
2	0.080			
3	0.000	0.000		
4	0.000	0.000	0.041	
K^+				
2	1.000			
3	0.263	0.237		
4	0.811	0.841	0.041	
T_W				
2	0.399			
3	0.800	0.073		
4	0.167	0.954	0.020	
Alkalinity				
2	0.001			
3	0.000	0.087		
4	0.941	0.000	0.000	
Cl^-				
2	0.759			
3	0.000	0.000		
4	0.000	0.000	0.951	
T_A				
2	0.837			
3	0.979	0.610		
4	0.975	0.975	0.847	
Ca^{2+}				
2	0.031			
3	0.837	0.195		
4	0.218	0.807	0.679	
SO_4^{2-}				
2	0.009			
3	0.997	0.015		
4	0.006	1.000	0.011	
pH				
2	0.581			
3	1.000	0.581		
4	0.000	0.004	0.000	
Mg^{2+}				
2	0.001			
3	0.004	0.986		
4	0.000	0.929	0.776	
HCO_3^-				
2	0.000			
3	0.000	0.015		
4	0.000	0.908	0.079	
EC				
2	0.770			
3	0.000	0.009		
4	0.001	0.010	1.000	
Na^+				
2	1.000			
3	0.000	0.000		
4	0.000	0.000	0.108	

(b)

	1	2	3	4
Q				
2	0.996			
3	0.006	0.010		
4	0.002	0.004	0.983	
SAR				
2	0.782			
3	0.099	0.496		
4	0.874	0.998	0.386	
K^+				
2	1.000			
3	0.638	0.638		
4	0.941	0.941	0.926	
T_W				
2	0.995			
3	0.140	0.224		
4	0.016	0.030	0.788	
Alkalinity				
2	0.000			
3	0.000	0.922		
4	0.937	0.000	0.000	
Cl^-				
2	0.500			
3	0.001	0.053		
4	0.000	0.019	0.976	
T_A				
2	1.000			
3	1.000	1.000		
4	0.507	0.550	0.521	
Ca^{2+}				
2	0.736			
3	0.001	0.000		
4	0.228	0.024	0.181	
SO_4^{2-}				
2	0.569			
3	0.203	0.010		
4	0.984	0.784	0.100	
pH				
2	1.000			
3	1.000	1.000		
4	0.000	0.000	0.000	
Mg^{2+}				
2	0.066			
3	0.886	0.010		
4	0.419	0.752	0.119	
HCO_3^-				
2	0.000			
3	0.000	0.069		
4	0.000	0.011	0.000	
EC				
2	0.995			
3	0.000	0.001		
4	0.563	0.716	0.012	
Na^+				
2	0.960			
3	0.001	0.004		
4	0.755	0.960	0.014	

(c)

	1	2	3	4
Q				
2	0.939			
3	0.000	0.000		
4	0.000	0.000	0.953	
SAR				
2	0.549			
3	0.000	0.001		
4	0.003	0.128	0.350	
K^+				
2	1.000			
3	0.138	0.126		
4	0.993	0.996	0.075	
T_W				
2	0.639			
3	0.739	0.998		
4	0.003	0.079	0.053	
Alkalinity				
2	0.000			
3	0.000	0.134		
4	1.000	0.000	0.000	
Cl^-				
2	0.778			
3	0.000	0.001		
4	0.000	0.000	0.975	
T_A				
2	0.906			
3	0.992	0.775		
4	0.588	0.935	0.415	
Ca^{2+}				
2	0.035			
3	0.577	0.001		
4	0.930	0.145	0.240	
SO_4^{2-}				
2	0.012			
3	0.546	0.000		
4	0.063	0.927	0.001	
pH				
2	0.651			
3	1.000	0.651		
4	0.000	0.000	0.000	
Mg^{2+}				
2	0.000			
3	0.178	0.093		
4	0.000	0.996	0.148	
HCO_3^-				
2	0.000			
3	0.000	0.005		
4	0.000	0.616	0.000	
EC				
2	0.864			
3	0.000	0.001		
4	0.004	0.039	0.640	
Na^+				
2	0.999			
3	0.000	0.000		
4	0.030	0.040	0.111	

FIGURE 3. (a) *p*-VALUES for Tukey's TEST on the PRE-1990 Dataset; (b) *p*-VALUES for Tukey's TEST on the POST-1990 Dataset; (c) *p*-VALUES for Tukey's TEST on the WHOLE DATASET. 1 = Sussex (USGS 06313500), 2 = Arvada (USGS 06317000), 3 = Moorhead (USGS 06324500), 4 = Locate (USGS 06326500). ■ Significant at $\alpha = 0.1$.

1990, Na^+ and Mg^{2+} exhibited no trend, while Ca^{2+} exhibited a marginally significant negative trend. As a result, the positive trend for SAR was discontinued. The negative trend for Ca^{2+} seemed to have a loose relationship with discharges from the oil field. It was predominantly controlled by the natural precipitation of calcium carbonate. In contrast, the discharges may be the main reason for the pre-1990 negative trends of K^+ and SO_4^{2-} and the pre-1990 positive trend of HCO_3^-. Further, because the salts had opposite trends before 1990 and no trend after that time, EC failed to exhibit any significant trend (Table 3a). This implies that discharges from the oil field had no significant affect on stream salinity. In addition, the positive trend detected for Q and the negative trend for T_w were probably controlled by natural factors other than the discharges. For example, the post-1990 negative trend for T_w accompanied a negative trend for T_A.

At the other three downstream stations, before 1990 both SAR and EC exhibited significant positive trends (Table 3b-d). The reason for the positive trend of EC was that K^+ and SO_4^{2-}, which exhibited negative trends at Sussex, shifted to having positive trends, whereas, the positive trend for SAR was a result of the positive trend for Na^+ and negative trend for Ca^{2+}. After 1990, SAR and EC both continued to have significant positive trends. The positive trend for SAR was a result of the positive trend for Na^+, and the positive trends of Na^+ and Cl^- are likely to be one reason for the positive trend of EC. Further, the negative trends that Ca^{2+} and Mg^{2+} exhibited before 1990 discontinued after that time. This discontinuity of the negative trend for Ca^{2+} may be because the pre-1990 positive trend of pH reversed. The decreasing pH tended to lessen the natural precipitation of calcium carbonate.

Plotting the observed data revealed that SAR and EC at all four stations had a sharp decline in 1990 (Figure 2a). This decline reflected the effects of reinjecting the brine and brackish water into the ground upstream of Sussex. The effects were also embodied by the overall decreasing trends of SAR and EC at Sussex (Table 3a and Figure 2a). However, these decreasing trends did not propagate downstream toward the other three stations. At Arvada and Moorhead, SAR exhibited an overall positive trend, and both SAR and EC exhibited overall positive trends at Locate (Tables 3b-d and Figure 2a).

The disrupted propagation of the decreasing trend at Sussex implied that the CBM development in the areas downstream of Sussex affected water quality in the Powder River. The effects typically manifested by SAR tending to be noticeably elevated but EC tending to have only a minor change. In addition, the CBM development was likely to elevate the concentrations of Na^+, Cl^-, and SO_4^{2-} (Figure 2b) but had only a slight influence on Q and T_w. T_w was mainly controlled by air temperature, T_A.

Spatial Patterns

Before 1990, SAR was distinctly different among the four stations, but EC was differentiated at the state border (Figure 3a). That is, EC was statistically the same for Sussex and Arvada, and for Moorhead and Locate, but differed between the two Wyoming stations and the two Montana stations. However, after 1990, both EC and SAR at Arvada, Moorhead, and Locate were statistically the same, but these were significantly different from the values at Sussex (Figure 3b). The altered spatial patterns for EC and SAR implies that the CBM development tended to shrink the water quality differences among the three downstream stations, but widen the differences between these stations and Sussex.

In contrast, both Ca^{2+} and Mg^{2+} were statistically the same among the three downstream stations before 1990, but after that time they were differentiated at the state border. In addition, the spatial pattern of Na^+, which was typified by having distinct Na^+ concentrations among the four stations, remained unchanged. These inconsistent pattern changes indicated that the effects of CBM development might have a complex spatial variability in the Powder River watershed and that this variability was likely to be controlled by the geographic distribution of the CBM wells. As indicated by Rice *et al.* (2000), water pumped from wells located in different geographic locations within the watershed was distinctly different both in quantity and quality. Also, the chemistry of CBM produced water may be subject to changes that vary geographically, depending on sediment properties in the channel conveying the water (Hulin, 2003; Patz *et al.*, 2004). For the remaining parameters, Tukey's test detected no pattern change. Further, when implemented on the whole dataset, Tukey's test indicated no pattern change for any of the 14 parameters (Figures 3a and c).

The inability of the test to detect pattern changes using the whole dataset and for some parameters using the post-1990 dataset may be ascribed to the use of annual medians rather than monthly medians, which smoothed out the seasonal variations that are inherent in the data. In this regard, compared with the Seasonal Kendall test, Tukey's test indicated that fewer parameters were affected by the CBM development. Nevertheless, because of the large number of

missing values, it was almost impossible to conduct Tukey's test on the monthly medians.

SUMMARY AND CONCLUSIONS

Bringing a large amount of CBM produced water to the surface raises serious concerns regarding its potential impact on stream water quality. Although efforts were made to collect comprehensive chemistry, salinity, and sodicity data on CBM produced water, little information is available in the literature about how stream water quality is changed as a result of CBM development. To address this issue, this study analyzed temporal trends and spatial patterns of water quality in the Powder River, which drains a 33,785 km^2 watershed traversing the states of Wyoming and Montana. The observed data at the four USGS gauging stations along the Powder River, namely Sussex, Arvada, Moorhead, and Locate, was used. The trend analysis was conducted using both linear regression and the Seasonal Kendall test, while the pattern analysis was implemented using Tukey's test for multiple comparisons.

The results indicated that the CBM development did adversely affect the stream water quality. The development tended to elevate Na^+ and lower pH. While the decreased pH might lessen the natural precipitation of calcium carbonate, the increased Na^+ resulted in an elevated stream sodicity, as indicated by a significant increasing trend for SAR. The development did not lower pH to a level harmful to biological species. In addition, the water generated by the CBM development tended to offset the positive effects obtained from reinjecting the brine and brackish water produced by an oil field located upstream of Sussex that had been discharged into the stream prior to 1990. As a result, the decreasing trend for SAR at Sussex did not propagate downstream toward the three downstream stations. The development altered the positive trends for salts K^+ and Cl^-, and thus had an overall minor impact on stream salinity, as indicated by that EC exhibited no trend or a marginally significant increasing trend. This is consistent with Rice *et al.* (2000) who found that the CBM produced water has an EC value comparable with that of the Powder River. Further, the development tended to shrink the water quality differences among the three downstream stations but widen the differences between these stations and Sussex. The CBM development is likely an important factor that can be managed to lower the stream sodicity. However, the management may need to take into account that the effects of the CBM development vary from one location to another along the Powder River.

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