Geochemical and Stable Isotopic Analysis of the Tongue River and Associated Tributaries in the Powder River Basin: An Analysis of the Cause of Annual Elevated Salinity in Spring Runoff

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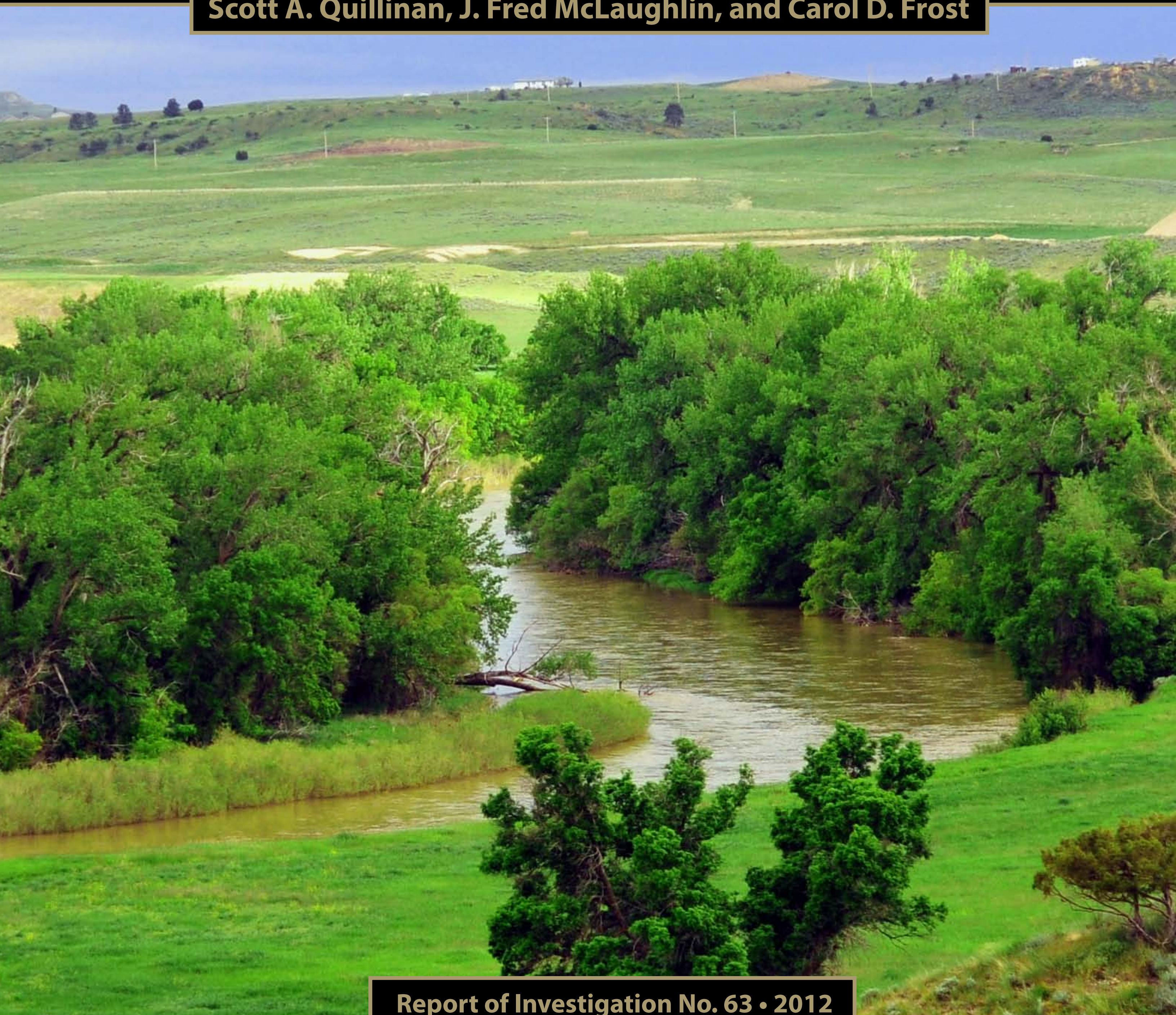

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Thomas A. Drean, State Geologist

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Chamois L. Andersen

View south to Wyoming's Tongue River, flowing north toward the Wyoming/Montana border.

44° 57' 42.09" N. 106° 55' 29.18" W. 6/16/2011, 08:47 hrs, EL: 3593', Wasatch Formation, Eocene 33.90-55.80 MA, Fort Union Formation, Paleocene 55.8-65.50 MA, Photograph #WSGS.WLU.2995 by Wallace Ulrich.

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Introduction

The suitability of surface water for agricultural irrigation depends in part on salinity. Salinity reflects soil composition and the underlying geology of the watershed, and varies seasonally with precipitation and snowmelt. In addition, there may be anthropogenic influences on salinity related to land use, including energy development. The purpose of this study is to evaluate whether an observed, annual short-term rise in salinity in the Tongue River of northeastern Wyoming is due to natural or anthropogenic causes.

The Tongue River flows north out of Wyoming's Bighorn Mountains and the Powder River geologic basin into Montana. It is a major source of water for agriculture and several residential communities in Wyoming and Montana. The Tongue River and associated tributaries pass through areas of coalbed natural gas (CBNG) production in both states. There are concerns that water discharged during CBNG production in Wyoming is impacting Tongue River water quality. Specifically, a short period of elevated total dissolved solids (TDS) concentrations have been observed in the Tongue River, north of the Wyoming state line, during a short period between late February and early April (Figures 1 and 2; Appendix A). The purpose of this study is to use water quality data and isotopic ratios of carbon to characterize the water of the Tongue River and associated tributaries, and to determine whether the source of elevated salinity in the early spring is the result of natural processes or human activities.

Surface water sample sites were chosen to include water samples collected upstream, proximal, and downstream of CBNG development. Water collected upstream of CBNG development provides information about the natural system unaffected by CBNG development. If surface waters are chemically and/or isotopically distinct from CBNG produced water, then it is possible to identify if CBNG produced water is influencing the quality of surface water.

Results of this study show that CBNG produced water can be distinguished from natural surface waters in the Powder River Basin on the basis of water quality and the carbon isotope ratio of dissolved inorganic carbon. The data suggest that natural spring runoff processes within the basin interior are responsible for elevated TDS measured at the Wyoming/Montana state line during late February and early April. Isotopic and geochemical evidence suggests that CBNG production in the area is likely not the cause of high salinities in the early spring in the Tongue River.

Study Area

The study area includes parts of the Tongue River and associated tributaries that drain the northeast portion of the Powder River geologic basin (Figure 3). The drainages sampled include two types: those with headwaters in the Bighorn Mountains (montane) and those that originate from within the basin (intra-basinal). The montane drainages sampled for this report include the Tongue River and the Goose Creek tributaries. The intra-basinal drainages include Prairie Dog Creek and the Dutch Creek tributaries (Figure 3). It is important to note that

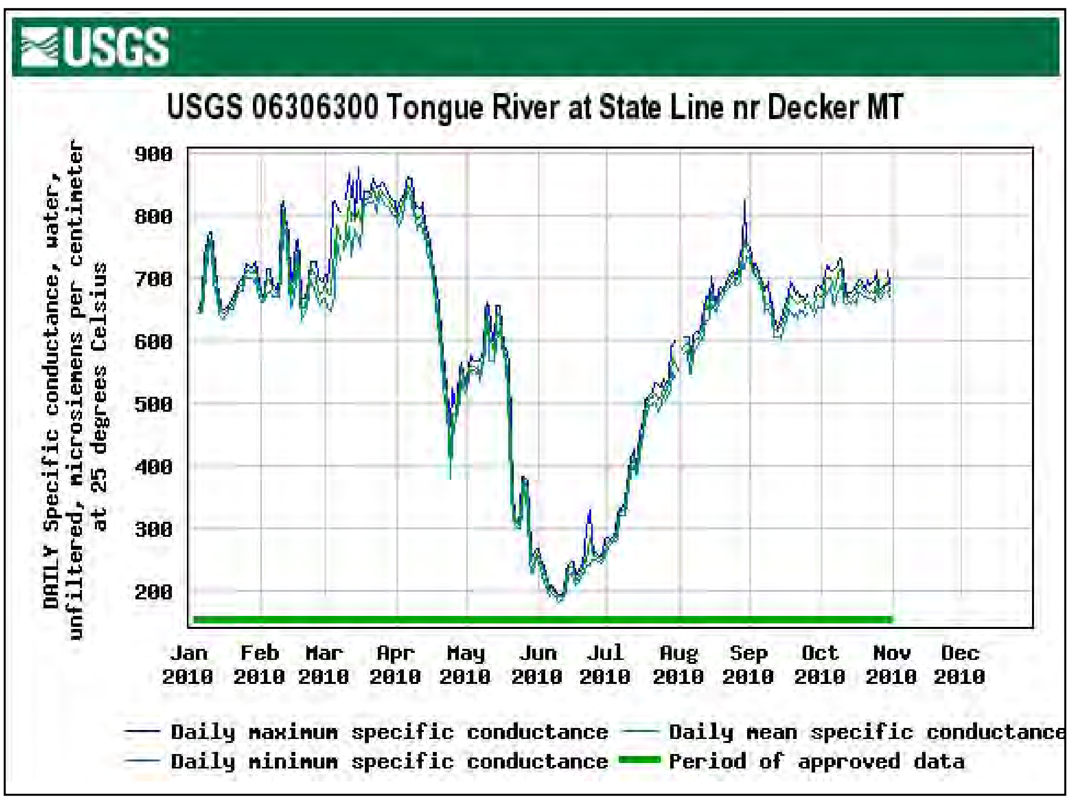

Figure 1. Daily specific conductance measured at the Wyoming/Montana state line for the year 2010 (USGS, 2011a). Note the period of high salinity from March 3 through April, 16.

Prairie Dog Creek receives a portion of water via trans-basin diversion in late summer and fall from North Piney and South Piney creeks, both of which have montane headwaters.

The geology of the montane drainages contrasts with the geology of the intra-basinal drainages. The geology of the montane drainages is comprised of Archean metamorphic gneiss and plutonic igneous rocks that form the mountain core (Frost et al., 2006). The flanks of the basin expose Paleozoic and Mesozoic rocks, including abundant Pennsylvanian and Permian carbonates. The geology of the intra-basinal drainages is comprised primarily of the Tertiary Fort Union Formation and overlying Wasatch Formation, both of which are composed of shales, sandstones, and coals (Love and Christiansen, 1985; Figure 3). The CBNG wells in the study area produce gas from coals of the Tongue River Member of the Fort Union Formation.

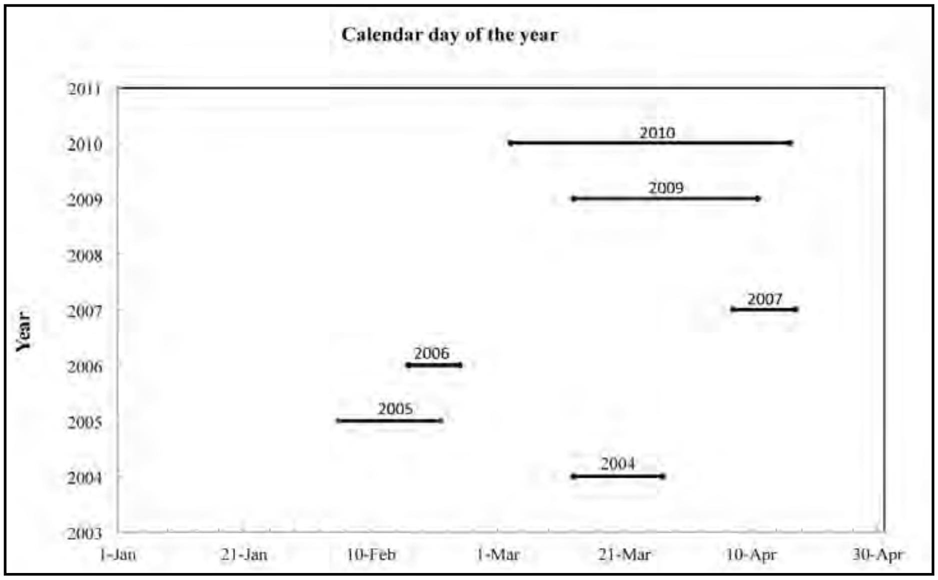

Figure 2. Period of relatively high early spring salinities measured north of the Wyoming/Montana state line sorted by year, a summary of Appendix A (USGS, 2011a). Sufficient data is not available for year 2008.

Methods

Samples were collected at two times: in the fall during low flow conditions, and in the spring when elevated TDS concentrations have been observed. Forty-two water samples were collected on September 2, 2009 (referred to as the fall sample set) and 44 samples were collected on March 15, 2010 (the spring sample set). Surface waters were sampled from the Tongue River, Goose Creek, Prairie Dog Creek, and Dutch Creek. CBNG produced waters were sampled from individual wells and from outfalls. Sample locations are shown in Figure 3.

Employees of the Wyoming Department of Environmental Quality (WDEQ) collected water samples according to WDEQ testing procedures (see WDEQ Water Quality Rules and Regulations) into 250 mL acid washed bottles and transported to the Wyoming State Geological Survey in iced coolers. From this sample, three aliquots were prepared and filtered using a Cameo 0.045 micron nylon pre-filter. All samples were filled to the point of overspill to eliminate headspace. Samples for water chemistry analysis were separated into two 30 mL Nalgene (registered) bottles, one of which was acifdified with 0.5 mL nitric acid for cation analysis. Samples for isotopic analysis were separated into 30 mL Wheaton vials. Two to three drops of benzalkonium chloride was added to halt microbial activity. The Wheaton vial was capped with Teflon® septa and sealed with an aluminum cap using a crimper.

Water chemistry analyses were completed at the Wyoming State Veterinary Laboratory. Cation concentrations were determined using inductively coupled plasma mass spectrometry (Fishman, 1993) anions by ion chromatography, and alkalinity by potentiometric titration. The TDS and determination of water type was calculated on the basis of water chemistry analyses using Geochemist's Workbench, an aqueous geochemistry-modeling software.

Carbon isotope analyses were completed at the University of Wyoming's Stable Isotope Facility. Carbon isotope compositions of dissolved inorganic carbon, expressed as $\delta^{13}C_{DIC}$ were analyzed on a GasBench-II device coupled to a Finnigan DELTA plus mass spectrometer in the Stable Isotope Facility at the University of Wyoming. Replicate analysis of the samples and internal lab standards establish precision and accuracy of ± 0.1‰. The $\delta^{13}C_{DIC}$ values are reported in per mil relative to V-PDB standard (Table 1).

Results and Discussion

Identification of water-types in the Tongue River drainage

Two types of surface waters were identified in the Tongue River drainage: calcium-magnesium-bicarbonate and calcium-magnesium-sulfate (Table 1). The calcium-magnesium-bicarbonate samples are from tributary

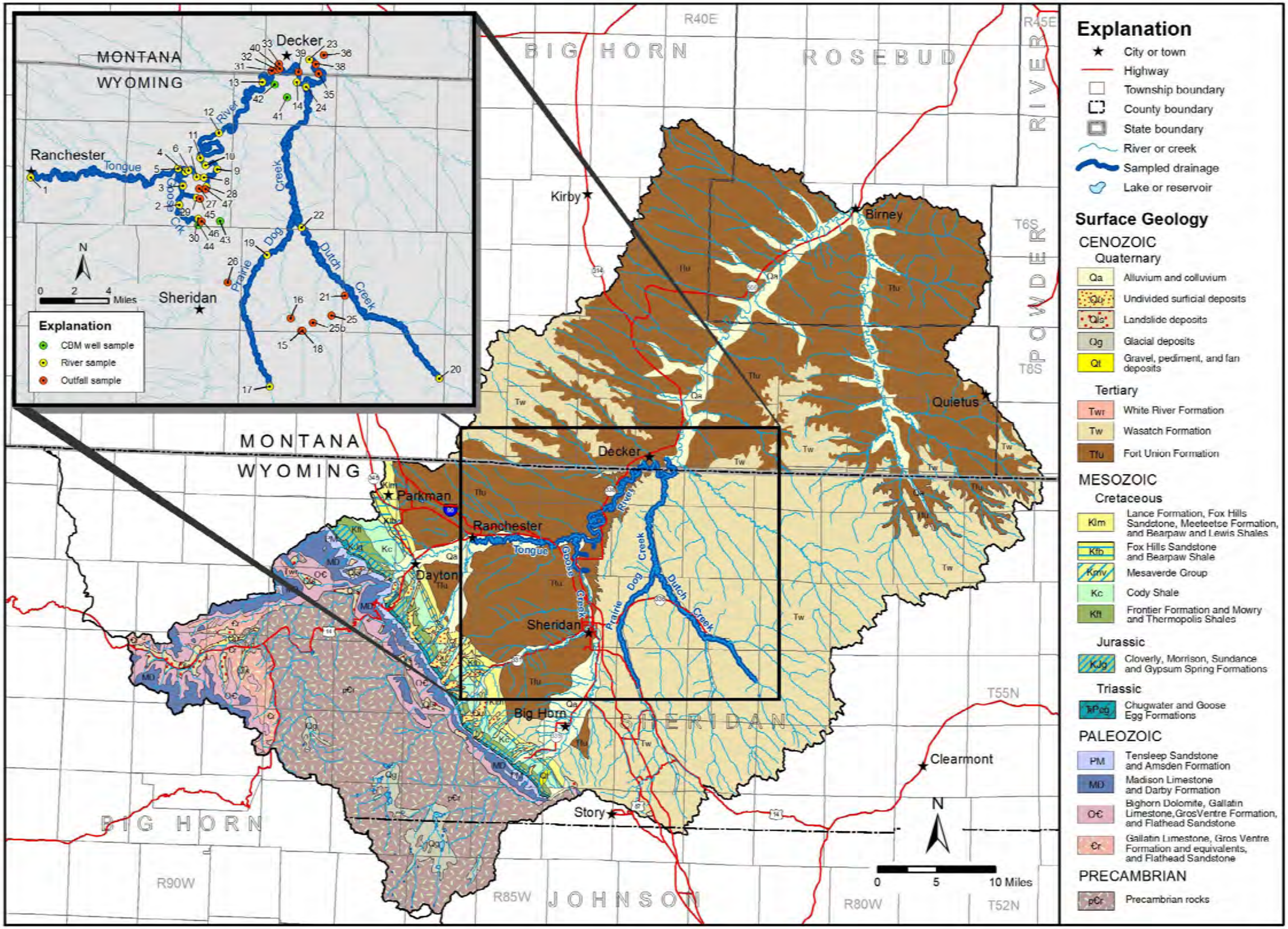

Figure 3. Geologic map of the Tongue River drainage. Inset shows sample locations, which include environmental and CBNG produced water samples collected from wellheads and outfalls.

Table 1. $\delta^{13}C_{DIC}$ values are reported in per mil relative to V-PDB standard.

Site description	Site ID	Latitude	Longitude	TDS (mg/L)	$\delta^{13}C_{DIC}$ (‰)	Water Type
Site 1. Tongue River at Ranchester City Park	Fall	44.90311	-107.16631	178.9	-9.3	Ca-HCO_3
	Spring			386.9	-8.3	Ca-HCO_3
Site 2. Goose Creek above Dietz 2 coal outcrop	Fall	44.882690	-106.987750	543.4	-12.6	Mg-HCO_3
	Spring			538.5	-11.1	Mg-HCO_3
Site 3. Goose Creek Below Dietz 2 coal outcrop	Fall	44.899120	-106.983890	581.3	-11.4	Mg-HCO_3
	Spring			530.5	-10.6	Mg-HCO_3
Site 4. Goose Creek above Tongue River confluence	Fall	44.911140	-106.981550	583.7	-11.4	Mg-HCO_3
	Spring			506.5	-10.4	Mg-HCO_3
Site 5. Tongue River above Goose Creek confluence	Fall	44.913600	-106.989990	401.3	-8.8	Ca-HCO_3
	Spring	44.90311	-107.16631	389.2	-7.6	Ca-HCO_3
Site 6. Tongue River above Dietz 3 coal outcrop	Fall	44.912320	-106.977390	562.6	-11.0	Mg-HCO_3
	Spring			440	-10.2	Mg-HCO_3
Site 7. Tongue River at Dietz 3 coal outcrop	Fall	44.907010	-106.967910	473.2	-9.9	Ca-HCO_3
	Spring			440.9	-8.9	Mg-HCO_3
Site 8. Tongue River at Dietz 2 coal outcrop	Fall	44.906660	-106.959040	484.3	-10.5	Ca-HCO_3
	Spring			451.9	-9.2	Ca-HCO_3
Site 9. Tongue River above 2nd Dietz 2 & 3 coal outcrop	Fall	44.913630	-106.943330	477.5	-11.0	Ca-HCO_3
	Spring			452.9	-9.3	Mg-HCO_3
Site 10. Tongue River at 2nd Dietz 2 outcrop	Fall	44.916950	-106.957250	478.2	-10.9	Ca-HCO_3
	Spring			451.9	-9.5	Ca-HCO_3
Site 11. Tongue River at 2nd Dietz 3 coal outcrop	Fall	44.923110	-106.963980	479	-11.0	Ca-HCO_3
	Spring			455	-9.5	Ca-HCO_3
Site 12. Tongue River below Dietz 3 coal outcrop	Fall	44.944770	-106.942200	496.9	-10.5	Ca-HCO_3
	Spring			448.9	-9.2	Ca-HCO_3
Site 13. Tongue River upstream of Montana Border	Fall	44.988832	-106.891830	550.8	-10.7	Ca-HCO_3
	Spring			444	-9.1	Ca-HCO_3
Site 14. Tongue River in Wyoming downstream of the Montana border	Fall	44.989470	-106.850640	319.5	-10.5	Ca-HCO_3
	Spring			450.3	-9.1	Mg-HCO_3
Site 15. Paul 3 Reservoir (WY0052141)	Fall	44.778150	-106.838370	1670.9	10.6	Na-HCO_3
	Spring			1626	13.1	Na-HCO_3
Site 16. Spring below Paul reservoir # 3 (WY0052141 - IMP 1)	Fall	44.788760	-106.851550	2667.8	-12.5	Mg-SO_4
	Spring			2308	-11.6	Ca-SO_4
Site 17. Prairie Dog Creek Above CBNG development at Highway 14 Crossing	Fall	44.730330	-106.874530	336	-12.1	Ca-HCO_3
	Spring			822.5	-11.6	Mg-HCO_3
Site 18. CBNG Outfall WY0052141 - 003 (Treated)	Fall	44.778340	-106.836840	1696.9	10.5	Na-HCO_3
	Spring			1746	13.0	Na-HCO_3
Site 19. Prairie Dog Creek at Wakely (USGS Gauging Station 35694)	Fall	44.842070	-106.881420	444.8	-10.7	Ca-HCO_3
	Spring			859.4	-11.4	Mg-HCO_3
Site 20. Wagner Prong of Dutch Creek above CBNG development	Fall	44.740420	-106.672550	1697.9	-14.3	Mg-HCO_3
	Spring			1632	-11.9	Mg-SO_4
Site 21. Headwater Reservoir (WY0055107 - 025)	Fall	44.808750	-106.787370	2176.2	11.1	Na-HCO_3
	Spring			326.4	8.5	Na-HCO_3
Site 22. Dutch Creek above confluence with Prairie Dog Creek	Fall	44.865980	-106.841040	3204.9	-12.9	Na-SO_4
	Spring			2227	-11.2	Mg-SO_4
Site 23. Tongue River at stateline near Decker (USGS gauging station 6306300)	Fall	45.008980	-106.836290	346.6	-11.0	Ca-HCO_3
	Spring			647.7	-9.7	Mg-HCO_3

Table 1. Continued.

Site description	Site ID	Latitude	Longitude	TDS (mg/L)	$\delta^{13}C_{DIC}$ (‰)	Water Type
Site 24. Prairie Dog Creek near Acme (USGS Gauging Station 6306250)	Fall	44.985430	-106.839130	536.1	-12.8	$Ca-SO_4$
	Spring			1617	-11.2	$Mg-SO_4$
Site 25a. CBNG Outfall WY0052671 - 005	Fall	44.791970	-106.803020	2321.1	12.1	$Na-HCO_3$
Site 25b. Outfall WY0052671-009 (Substituted for outfall 005)	Spring	44.7852	-106.82498	1860	13.9	$Na-HCO_3$
Site 26. CBNG Outfall (WY0051080-001)	Fall	44.817950	-106.927510	1255.7	6.3	$Na-HCO_3$
	Spring			1415	8.6	$Na-HCO_3$
Site 27. CBNG Outfall (WY0051471-001)	Fall	44.896930	-106.964480	2228.1	-17.8	$Na-HCO_3$
	Spring			2070	-16.6	$Na-HCO_3$
Site 28. Unnamed Drainage Downstream of CBNG outfall WY0038636	Fall	44.898770	-106.955830	1933.2	-8.8	$Na-HCO_3$
	Spring			486.7	-9.3	$Na-HCO_3$
Site 29. Unnamed Drainage Downstream of CBNG outfall WY0038628	Fall	44.889470	-106.967180	2667.9	-7.2	$Na-SO_4$
	Spring			2482	-7.7	$Na-SO_4$
Site 30. Unnamed drainage downstream from CBNG outfall WY0038628	Fall	44.871380	-106.964810	4688.2	-11.5	$Na-SO_4$
	Spring			3594	-9.7	$Na-SO_4$
Site 31. CBNG Outfall MT-0030457-008	Fall	44.998620	-106.880670	2249.7	1.9	$Na-HCO_3$
	Spring			1825	-16.3	$Na-HCO_3$
Site 32. CBNG Outfall MT-0030457-004	Fall	44.999740	-106.874780	1506.2	-9.6	$Na-HCO_3$
	Spring			1340	-8.7	$Na-HCO_3$
Site 33. CBNG outfall MT-0030457-001	Fall	45.004720	-106.872340	1691.4	1.0	$Na-HCO_3$
	Spring			1080	2.3	$Na-HCO_3$
Site 35. CBNG outfall MT-0030457-012	Fall	44.997070	-106.824650	2136.9	10.0	$Na-HCO_3$
	Spring			1903	10.7	$Na-HCO_3$
Site 36. CBNG outfall MT-0030457-016	Fall	45.012890	-106.819120	2745.9	11.1	$Na-HCO_3$
	Spring			2600	12.1	$Na-HCO_3$
Site 38. Treated CBNG outfall (MT-0030724-001)	Fall	45.005070	-106.828540	595.6	12.0	$Ca-SO_4$
	Spring			672.3	13.8	$Na-SO_4$
Site 39. CBNG outfall MT-0030457-014	Fall	44.998040	-106.848880	1742	-1.1	$Na-HCO_3$
	Spring			1753	7.2	$Na-HCO_3$
Site 40. CBNG outfall MT-0030457-010	Fall	45.000390	-106.871060	2022.8	4.8	$Na-HCO_3$
	Spring			1850	5.7	$Na-HCO_3$
Site 41. CBNG well (12D2-2783)	Fall	44.976310	-106.861600	2584.1	15.0	$Na-HCO_3$
	Spring			2298	16.2	$Na-HCO_3$
Site 42. CBNG well (23D2-2183)	Fall	44.986950	-106.877060	1757.2	5.6	$Na-HCO_3$
	Spring			1611	6.4	$Na-HCO_3$
Site 43. CBNG well (WY-3322214)	Fall	44.869960	-106.938600	1420.8	-4.8	$Na-HCO_3$
	Spring			1252	-5.8	$Na-HCO_3$
Site 44. CBNG well 14D3-3574	Fall only	44.866170	-106.964430	1428.1	-11.1	$Na-HCO_3$
Site 45. Fidelity outfall WY0038628-002 (Outfall above site 29)	Spring only	44.8884	-106.96343	1738	-9.6	$Na-HCO_3$
Site 46. CBNG Well 23C-3574	Spring only	44.86926	-106.96051	1364	3.0	$Na-HCO_3$
Site 47. CBNG outfall WY0038636 – 001 (Outfall above Site 28)	Spring only	44.89667	-106.95665	1854	-14.8	$Na-HCO_3$

headwaters that lie in the Bighorn Mountains to the west. The calcium-magnesium-sulfate type samples are from intra-basinal tributaries. This contrast in water type reflects the differences in the geology of the watersheds: The montane drainages consist of erosion-resistant Precambrian igneous and metamorphic silicate rocks and more soluble carbonate rocks. The latter is likely the dominant source of ions in the calcium-magnesium-bicarbonate-type water. The intra-basinal tributaries traverse the Eocene Wasatch Formation and overlying arid soils that provide readily dissolved evaporate minerals and salts that likely impart the calcium-magnesium-sulfate chemistry to the waters (Figure 3).

The calcium-magnesium-bicarbonate type waters of the montane drainages are relatively dilute: TDS concentrations range from 387 to 553 mg/L in the spring and from 179 to 563 mg/L in the fall (Table 1). In addition to varying seasonally, TDS concentrations increase downstream within each tributary (Figure 4). In Goose Creek, samples collected both in spring and fall record slightly higher TDS than the Tongue River. This results in a step to higher TDS in the Tongue River below the confluence of the two waters. Nevertheless, the TDS measured in the fall along the Tongue River remains under 500 mg/L for most of the measured section of the river (Figure 4a). The TDS concentration measured at the Wyoming/Montana state line in the fall sample set is 347 mg/L (Figure 4a). On the other hand, the spring sample set records a significant increase in TDS of the Tongue River beyond the confluence with Prairie Dog Creek. The higher TDS waters of Prairie Dog Creek increase the TDS concentrations of the Tongue River from 450 mg/L to 648 mg/L.

During the irrigation season, trans-basinal diversion waters effectively dilute TDS concentrations of Prairie Dog Creek, which receives a larger percentage of water via trans-basinal diversion in the fall as compared to the spring. In both the fall and spring, Prairie Dog Creek has magnesium-calcium-bicarbonate water (Figure 5). However, TDS concentrations for Prairie Dog Creek are much higher in the spring (823 to 860 mg/L) than in the fall (336 to 445 mg/L), due to these seasonal variations in the proportion of water provided by trans-basinal diversion from the montane drainages of North and South Piney creeks.

Intra-basinal Dutch Creek carries magnesium-sodium-sulfate type waters. TDS concentrations for Dutch Creek are the highest observed in this study; they range from 1,699 to 3,206 mg/L (upstream to downstream) in the fall sample set, and from 1,632 to 2,227 mg/L in the spring sample set.

TDS concentrations of Prairie Dog Creek increase beyond the confluence with Dutch Creek in both the spring sample set and fall sample set (Figure 4). The increase is more significant in the spring. In the fall, TDS concentrations increase in the Prairie Dog Creek drainage from 445 to 536 mg/L, but in the spring the TDS concentrations nearly doubles from 860 to 1,617 mg/L (Figure 4).

CBNG produced water in the Powder River geologic basin is strongly sodium-bicarbonate (Rice et al., 2000; Brinck et al., 2008; Campbell et al., 2008; Frost and Mailloux, 2011). The sodium-bicarbonate water type residing in a coal seam is the result of a series of geochemical and biochemical reactions that occur in the coal seam during the generation of methane (Brinck et al., 2008; Quillinan and Frost, 2011; Quillinan, 2011). TDS of CBNG produced waters range from 326 mg/L to 2,746 mg/L, and all CBNG samples are sodium-bicarbonate-type water (Table 1).

In addition to being distinguished by their water-type, CBNG produced waters can be isotopically distinct. CBNG produced waters within the Powder River Basin are enriched in 13-carbon relative to other natural waters (Sharma and Frost, 2008; Campbell et al., 2008; Mailloux et al., 2011; Quillinan and Frost, 2011). Most natural waters typically have $\delta^{13}C$ that range from -12 to -7‰ (Mook and Tan, 1991), whereas CBNG produced water have $\delta^{13}C$ that range from 10 to 30‰ (Sharma and Frost, 2008; McLaughlin et al., in press; Quillinan and Frost, 2011; Quillinan, 2011). This characteristic has been used to identify and quantify the presence of CBNG produced water in the main stem and tributaries of the Powder River (Sharma and Frost, 2008; Mailloux et al., in press).

All surface water samples measured for this study have negative $\delta^{13}C_{DIC,}$ ranging from -14.3‰ to -7.6‰. The carbon isotope ratios for CBNG produced waters analyzed in this study are mostly positive (Table 1). All produced water samples from within the Prairie Dog Creek (intra-basinal) drainage have positive carbon isotope ratios. However, some produced water samples (seven sites) collected along Goose Creek and the Tongue River exhibit negative carbon isotope ratios. This may suggest that the water is not produced solely from coal beds (McLaughlin et al., 2011). Pearson (2002) noted that the coals in this area are highly faulted and may not be hydraulically confined. Furthermore, strongly negative carbon isotope ratios (less than -15‰) like those

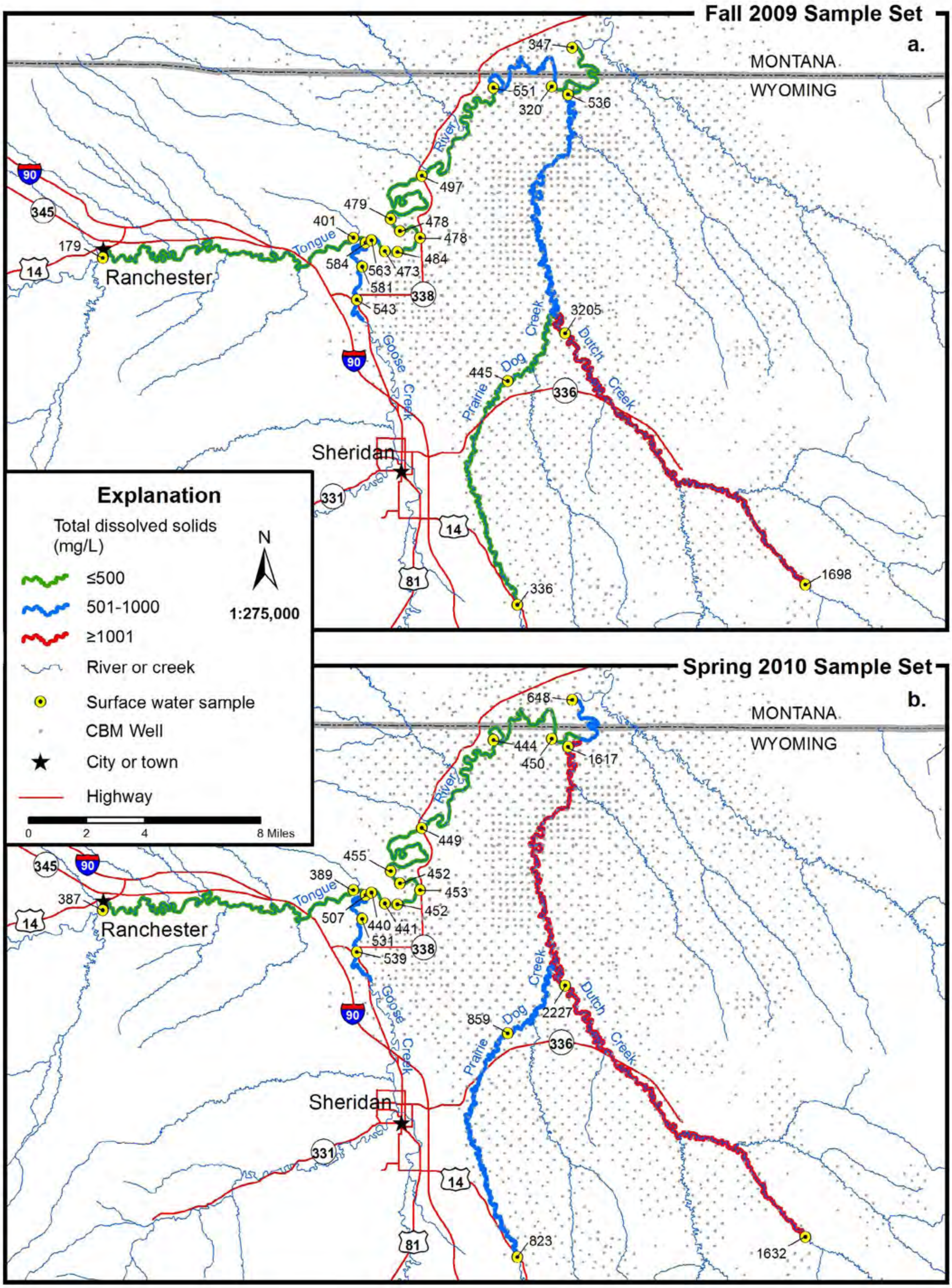

Figure 4. Total dissolved solid concentrations for the fall and spring measured within the Tongue River drainage.

measured at sites 27 and 31 (spring sample set) indicate coal beds that are subject to oxidizing conditions, which are more likely in shallow or unconfined coals (Quillinan and Frost, 2011).

The analyses of this study confirm that water quality and carbon isotopic data can be used to distinguish the surface waters of the Tongue River drainage from the CBNG produced water from this area. We will use this observation for the basis of further discussion.

Origin of the early spring, high TDS river water

This section describes why the annual elevated TDS measured at the Wyoming/Montana state line during the spring sampling event could originate primarily from the Dutch Creek tributary of Prairie Dog Creek, which has TDS in excess of 1,000 mg/L (Figure 4).

The geochemical composition of the water in the Tongue River at the Wyoming/Montana state line varies seasonally. The star symbol in Figure 5, which is open for the fall analysis and closed for the spring, illustrates the geochemical composition of the Tongue River measured at the Wyoming/Montana state line. Circles (open for the fall and closed for the spring) in Figure 5 illustrate the geochemical composition of the montane waters of the Tongue River drainage. Open squares for the fall and closed squares for the spring show the geochemical composition of the intra-basinal waters of the Prairie Dog Creek drainage.

Inspection of Figure 5 indicates that during the spring

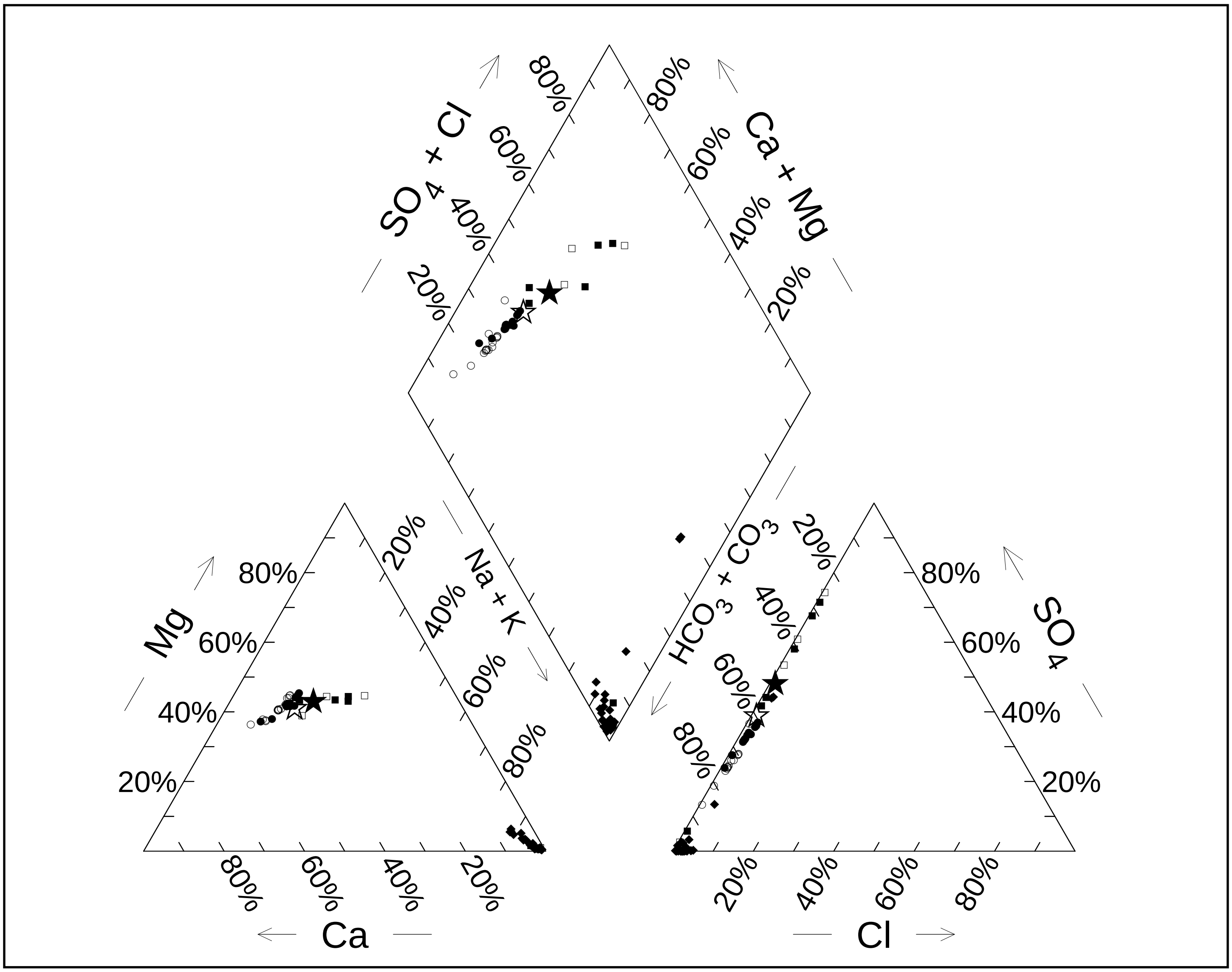

Figure 5. Geochemical composition of the Tongue River (circles), Prairie Dog Creek (squares), coalbed natural gas produced waters (diamonds), and the Tongue River north of Wyoming/Montana state line (stars). Open symbols represent the fall, and closed symbols represent the spring sample set. Note the shift in geochemical composition of the Tongue River at the state line toward the composition of the Prairie Dog Creek drainage.

sampling event, the geochemical composition of the Tongue River shifts toward the geochemical composition of the Prairie Dog Creek drainage (Figure 5). An increase of distinctively saline, sulfate-type water from the Prairie Dog Creek drainage would both increase the salinity and in turn affect the geochemical composition of the Tongue River.

Possible impact of CBNG development

As discussed above, the source of the elevated TDS concentrations observed in the Tongue River in the early spring could originate from the Prairie Dog Creek drainage. In this section we discuss the possibility that surface discharge of CBNG produced water increases TDS concentrations of the Prairie Dog Creek drainage. To address this possibility we examine the geochemistry and isotopic composition of both surface waters and CBNG produced waters from within the Prairie Dog Creek drainage.

CBNG produced water is geochemically distinct from surface water in the Powder River Basin: on the trilinear diagram produced water is strongly sodium-bicarbonate type, and is distinct from the composition of the surface waters (Figure 5). If CBNG produced water was added to the Prairie Dog Creek drainage, it should shift the geochemical composition of the surface water to more sodium-bicarbonate-rich compositions. There are increases in both sodium and bicarbonate concentrations along with concentrations of many other constituents between the fall to spring sampling events in the Prairie Dog Creek drainage (Figure 3, site 24). However, the most noticeable increase is in sulfate concentrations. For this reason, the geochemical composition plots farther from the geochemical composition of the CBNG produced water, indicating that waters from Prairie Dog Creek are influencing the TDS.

Multiple samples were collected and analyzed in the direction of flow where they pass through areas of CBNG development for Prairie Dog Creek (sites 17, 19 and 24) and Dutch Creek (20 and 22) (Figure 3). Along the main stem of Prairie Dog Creek salinity is relatively constant until the confluence with Dutch Creek (Figure 4). Between sites 17 and 19 sodium decreases from 40 mg/L to 34 mg/L, bicarbonate increases slightly from 400 mg/L to 410 mg/L. There is a slight increase in sulfate 230 mg/L to 260 mg/L. Very little change is measured in the concentrations of calcium, magnesium, or chloride. At site 24 there is a noticeable increase in many constituents; this increase is likely in response to the addition of high TDS waters from Dutch Creek.

In the Dutch Creek tributary, there are concentration increases in many constituents as the water flows through an area of CBNG development. These include an increase in sodium (140 to 210 mg/L), sulfate (650 to 1,100 mg/L), calcium (120 to 180 mg/L), and magnesium (120 to 170 mg/L). Bicarbonate concentrations decrease from 580 to 540 mg/L. The increase in sodium concentration, which is more conservative than bicarbonate, could indicate the addition of CBNG produced water. However, CBNG produced water is essentially devoid of calcium, magnesium, and sulfate. Therefore, the

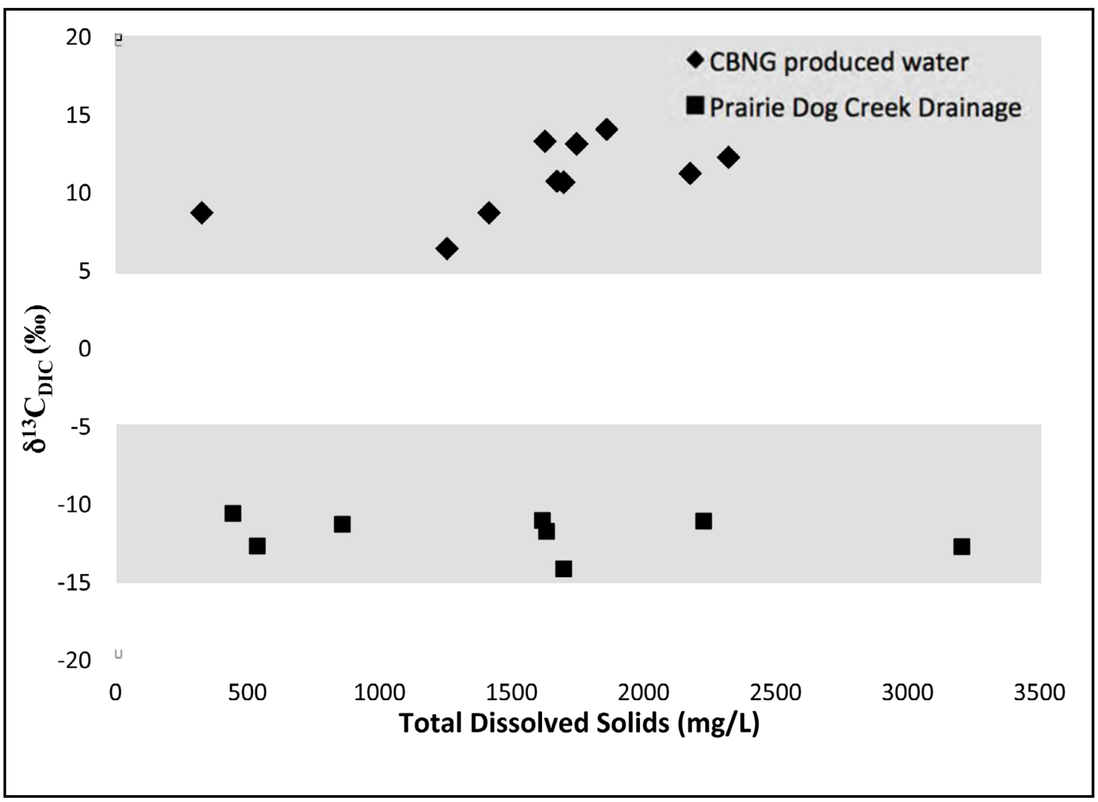

Figure 6. Carbon isotope ratios plotted as a function of total dissolved solids concentrations. Note that the positive carbon isotope ratios of the produced waters are isotopically distinct from the negative carbon isotope ratios of the surface waters.

addition of sodium-bicarbonate CBNG produced water would not result in increasing calcium, magnesium, and sulfate concentrations or the decreasing bicarbonate concentrations. Thus, there is little major-ion evidence that CBNG produced waters affect the geochemistry of the Prairie Dog Creek drainage as it flows through areas of CBNG development.

Carbon isotope compositions provide a more robust approach to evaluating the possibility that CBNG produced waters have contributed to the salinity in the Prairie Dog Creek drainage. Carbon isotope compositions have been used to quantify proportional inputs of CBNG produced water to surface waters in the Powder River drainage, a drainage adjacent to the Tongue River study area (Frost and Mailloux, 2011; Mailloux et al., in press). In the Prairie Dog Creek drainage, all of the surface water samples for both fall and spring have $\delta^{13}C$ less than -10‰, while all of the CBNG produced waters are greater than 5‰ (Figure 6). If CBNG waters were mixing with surface waters, we would expect to see intermediate carbon isotope ratios (Mailloux et al., in press). However, the carbon isotope ratios for both surface waters and produced waters remain constant and distinct in both fall and spring (Figure 6).

Spring samples were specifically taken in areas of CBNG development to investigate the possibility of enrichment from CBNG produced water (Figure 3). Frost et al. (2010) reported higher carbon isotope ratios in the Powder River resulting from the addition of CBNG produced water with $\delta^{13}C_{DIC}$ up to 25‰, showing that discharge of CBNG produced waters directly affects the carbon isotope ratio of surface waters.

Along the main stem of Prairie Dog Creek, $\delta^{13}C_{DIC}$ ranges between -11.6‰ and -11.2‰. Along Dutch Creek drainage, $\delta^{13}C_{DIC}$ ranges between -11.9‰ and -11.2‰. Carbon isotope ratios from the spring set in areas of CBNG production varied by less than 1‰, which is within the expected variance due to CO_2 outgassing (2.4 ± 0.1 ‰; Doctor et al., 2008). All surface water samples in this study recorded negative carbon isotopes that are within the range of typical Wyoming surface waters (Sharma and Frost, 2008; Table 2).

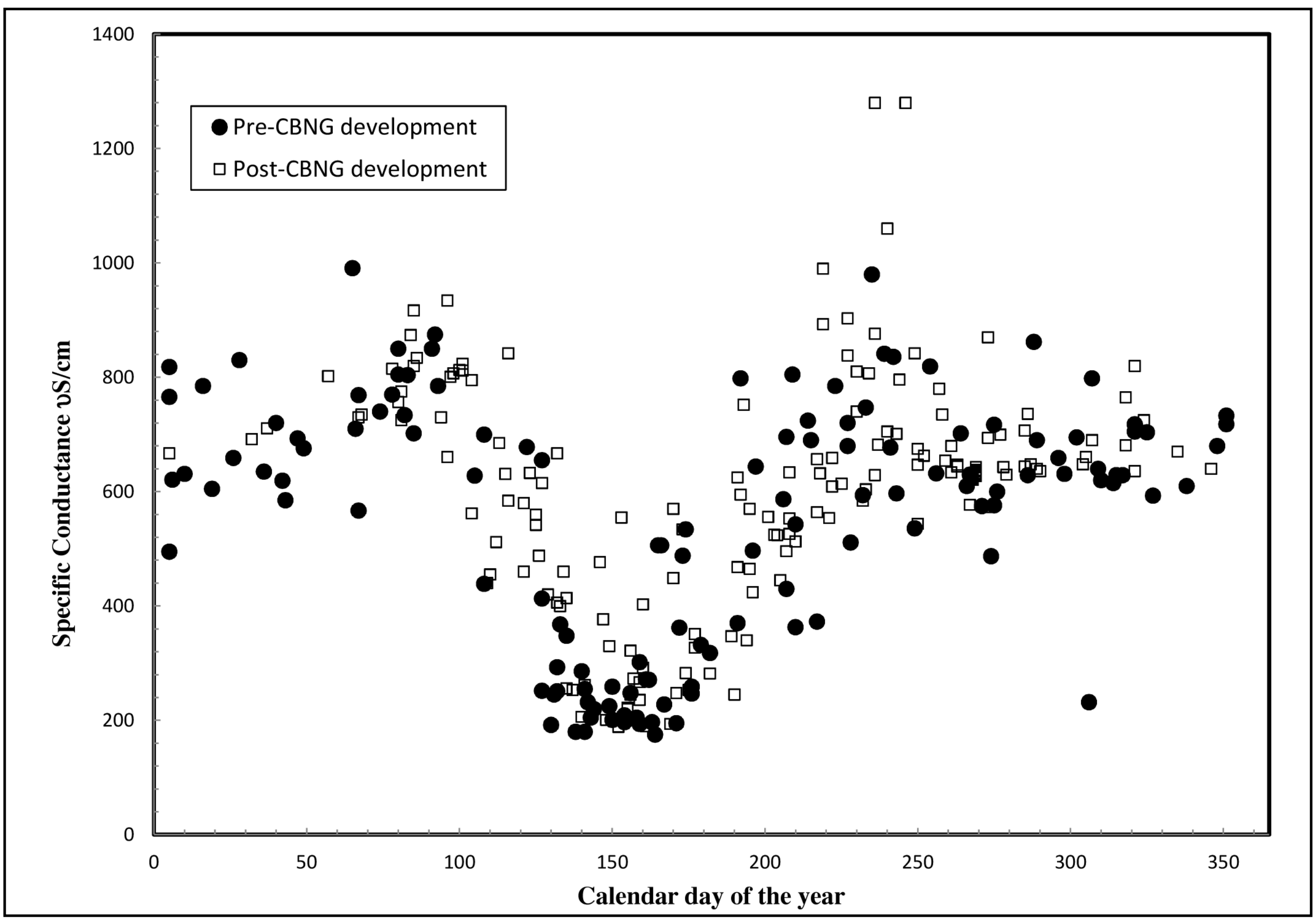

Figure 7. Specific conductance measurements for pre (1985-1999) and post (2000-2011) CBNG development at the Wyoming/Montana state line, as the result of USGS monitoring efforts from 1985 to 2011 (USGS, 2011a).

We also compared water quality data for the Tongue River collected prior to CBNG development with more recent water quality data. As an example, Figure 7 shows the specific conductance field measurements by the U.S. Geological Survey (USGS) at the Wyoming/Montana state line for the years 1985 to 2011 (USGS, 2011a). There is no observable difference in data collected from the period 1985-1999 and 2000-2011 that might be attributable to discharge of CBNG produced water.

Timing of the elevated TDS in the Tongue River drainage

This study establishes that the origin of the TDS spike measured in early spring on the Wyoming/Montana state line primarily originates from the addition of water from the Prairie Dog Creek drainage and not from CBNG produced water. We next consider the timing of the TDS spike, which occurs during the early spring months.

The Tongue River flow generally peaks during late spring to early summer (Clark and Mason, 2007). Figure 7 shows peak runoff for the Tongue River occurs between 140 and 205 days into the calendar year (mid May to late-June). By contrast, peak flow in Prairie Dog Creek occurs earlier in the spring, between 50 and 100 days into the calendar year (February to March; Figure 8). This earlier peak in flow reflects the earlier spring snowmelt and runoff within the intra-basinal tributaries of the Powder River Basin compared to the late spring snowmelt in the mountains that supply the montane tributaries of the Tongue River.

Furthermore, similar TDS trends are recorded in water quality data from adjacent drainages. For example, the Bighorn River drainage has montane and intra-basinal streams. It also records a decrease in salinity beginning in June and lasting through July (Figure 9), a trend that parallels observations from Figure 7. In contrast, the Cheyenne River in eastern Wyoming mostly drains the basin interior. As seen in Figure 10, the Cheyenne River water quality data is scattered and specific conductance values are far higher than drainages with montane headwaters. Salinity levels in the Cheyenne River correlate to measured discharge, and the large variances are most likely associated with specific precipitation events (Figure 11). These data suggest that seasonal salinity fluctuations in Laramide drainages are a natural phenomenon that are related to the timing of snowmelt in mixed headwater

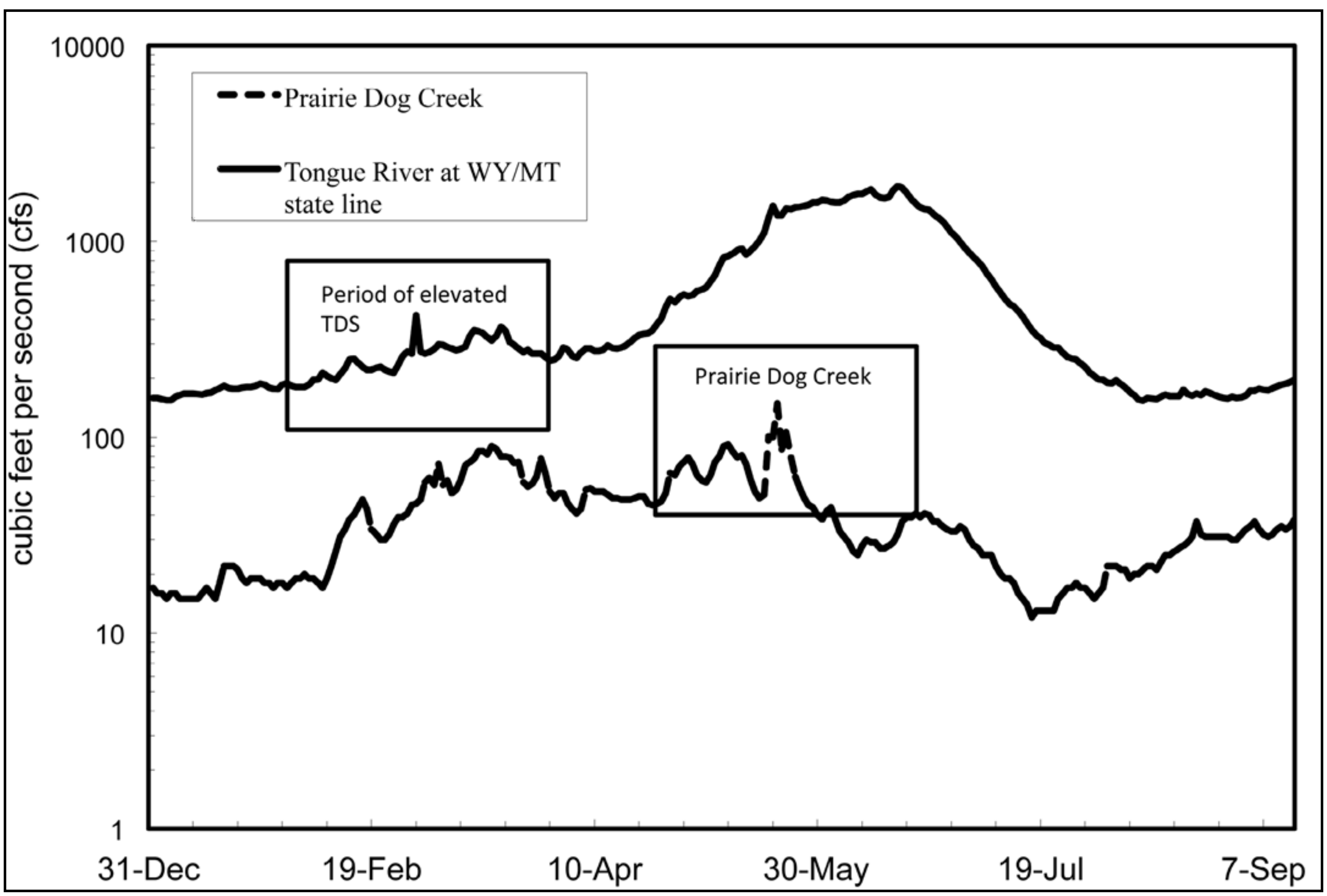

Figure 8. Mean daily stream flow for the Tongue River and Prairie Dog Creek (1985-2011; USGS, 2011a). The black box indicates the window in which the TDS spike may occur depending on specific weather patterns in a given year.

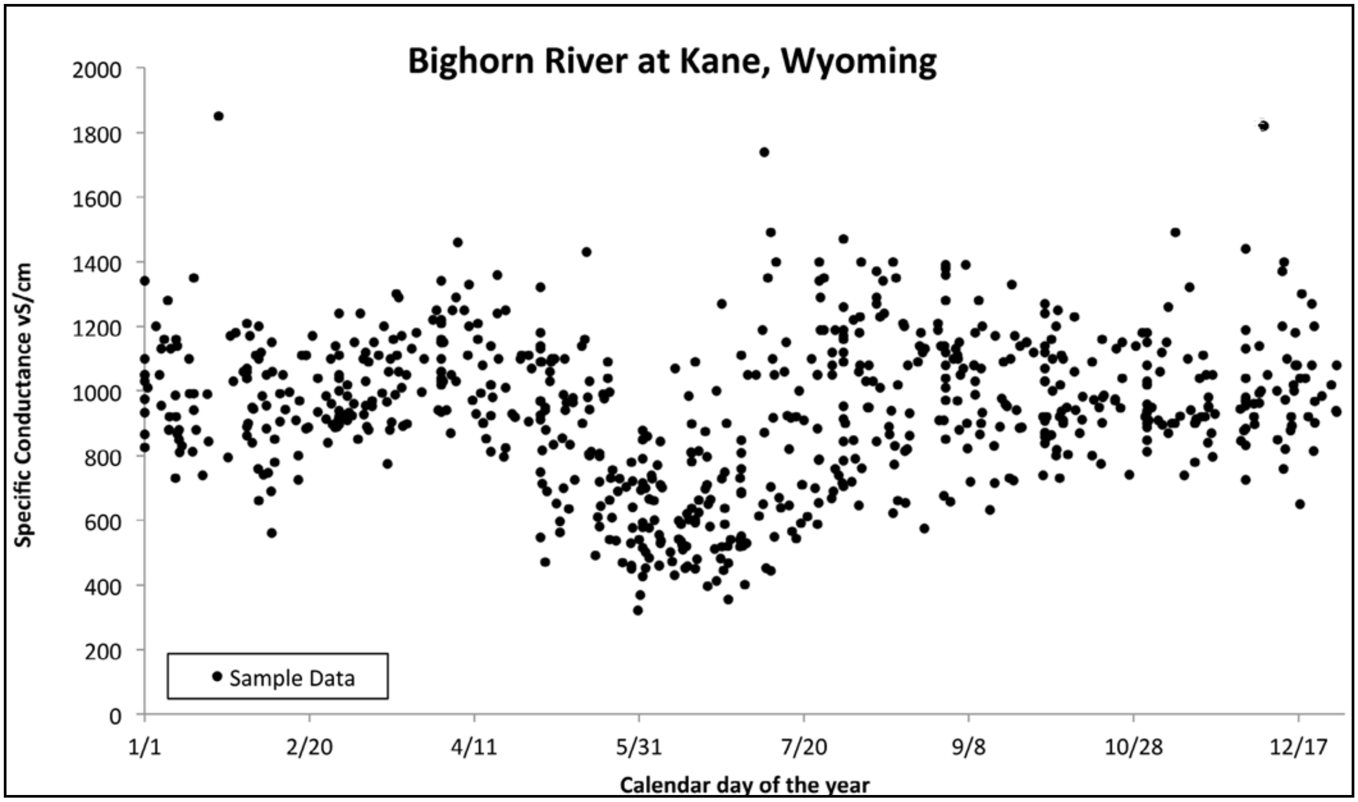

Figure 9. Specific conductance measurements from the Bighorn River near Kane, Wyoming, as a result of USGS monitoring efforts from 1947 to 2011 (USGS, 2011b).

drainages, and specific melting and precipitation events in intra-basinal drainages.

The arid soils of the Powder River geologic basin have significant accumulations of salts that are remobilized in the presence of water (see for example, Brinck and Frost, 2007). The TDS spike observed in the Tongue River in early spring is likely the result of the natural peak flow within the basin interior that dissolves and mobilizes soluble salts from the soil profile. The timing of peak flow and the geochemical and isotopic evidence presented above suggest that the TDS spike during early spring on the Tongue River is a result of natural, annual processes rather than discharge of CBNG produced water.

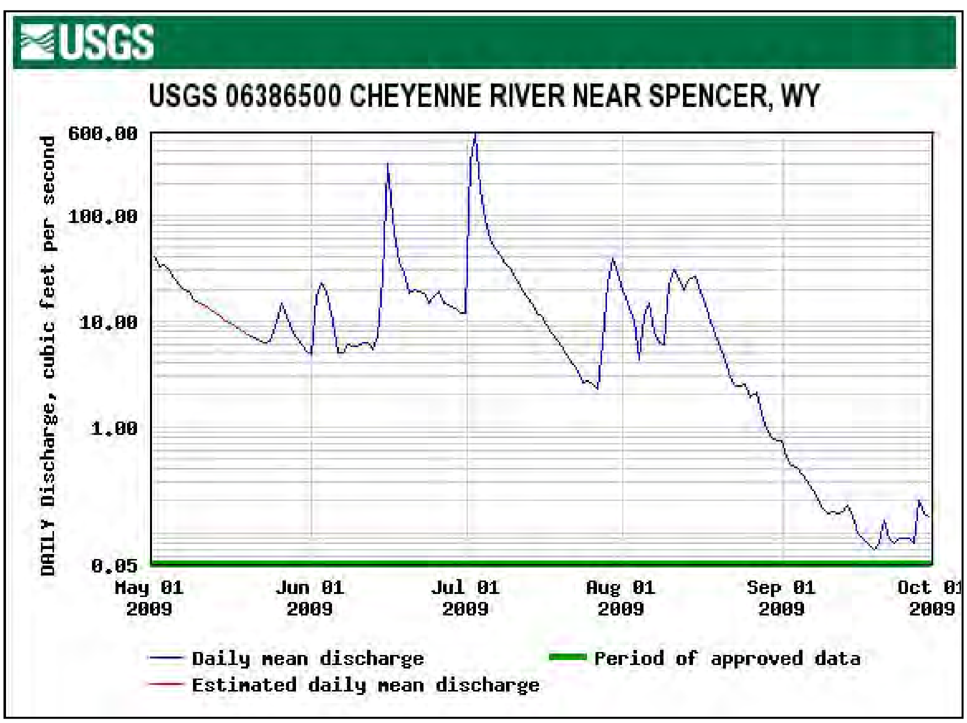

Figure 10. Daily discharge measured on the Cheyenne River near Spencer, Wyoming from May 1 through September 30, 2009 (USGS, 2011c).

Conclusion

The results of this study show that waters draining from the interior of the Powder River geologic basin during early spring runoff are associated with high TDS. Spring runoff occurs earlier in the year in the basin interior than it does in the mountains. As a result, during the times of peak spring runoff in the basin interior there is relatively low flow from mountain drainages. All evidence presented in this study is consistent with elevated TDS measured during late February and

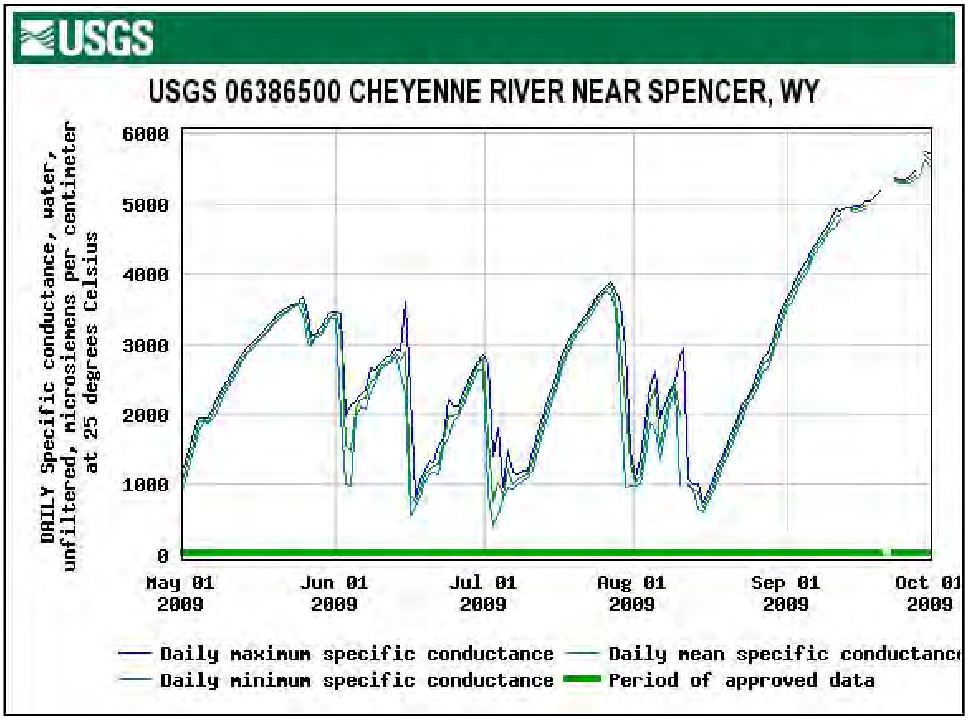

Figure 11. Daily specific conductance measured on the Cheyenne River near Spencer, Wyoming from May 1 through September 30, 2009 (USGS, 2011c). Note that lower salinity correlates with higher discharge events illustrated in Figure 10.

early March on the Tongue River being the result of runoff from the intra-basinal drainages. There is no geochemical or isotopic evidence that suggests that CBNG produced waters are directly mixing with surface waters in the study area during this time period. Therefore, it is unlikely that the direct discharge of CBNG produced water is contributing to the elevated salinity in the Tongue River.

In this paper we show how conventional approaches, including TDS and major ion measurements may be augmented by stable carbon isotope measurements to evaluate the possibility of anthropogenic sources contributing to the salinity of surface water. This approach could serve useful in identifying many other potential anthropogenic activities to surface and groundwater-quality degradation in which the anthropogenic contribution has a distinct carbon isotope signature (i.e. landfills, concentrated animal feeding operations, and septic systems and other waste facilities).

The Wyoming Department of Environmental Quality funded this work. In addition to collecting the samples for this study Jim Eisenhower and other WDEQ staff at the Sheridan field office organized the sampling strategy and protocol. Fidelity Exploration and Production Company granted access to the sampled coalbed natural gas wells and outfalls. Tomas Gracias, GIS Specialist at the WSGS, created the maps and geospatial data presented in this report. This project received thoughtful guidance from former State Geologist Ronald Surdam. This document also received many helpful comments from two anonymous reviewers from the U.S. Geological Survey. The authors wish to thank all these, and others who have helped during the preparation of this report.

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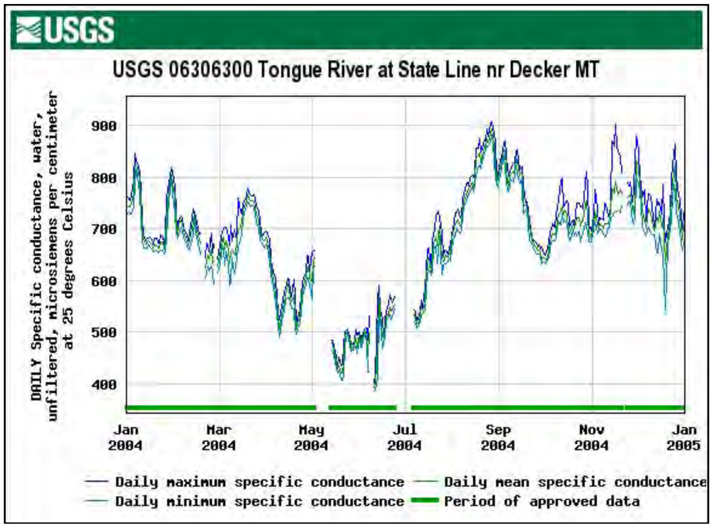
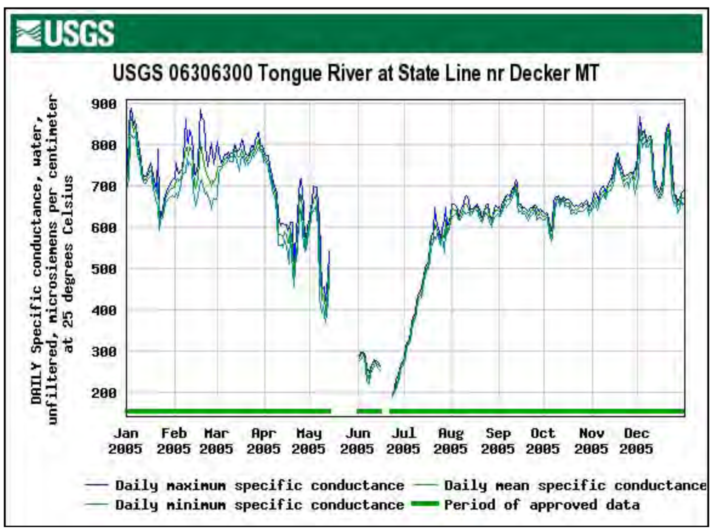
Appendix A: USGS Graphs

This appendix includes graphs describing the seasonal variations in salinity measured on the Tongue River, north of the Wyoming/Montana state line. These graphs were generated by the USGS National Water Information System: Web Interface, available at http://waterdata.usgs.gov/nwis.

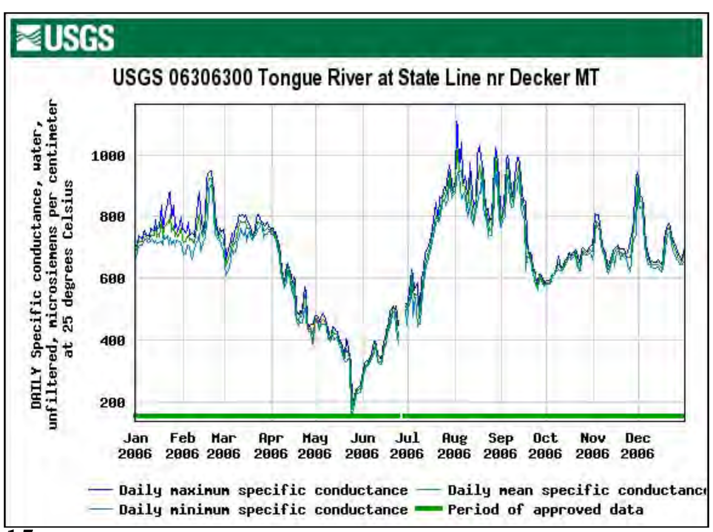
2004



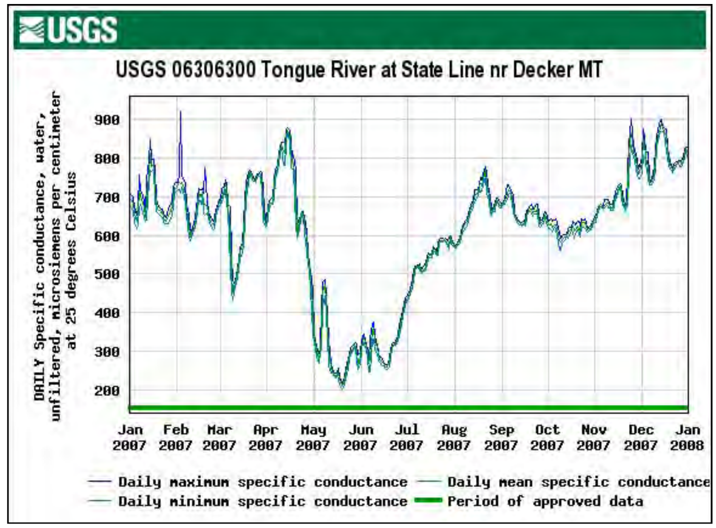
2005



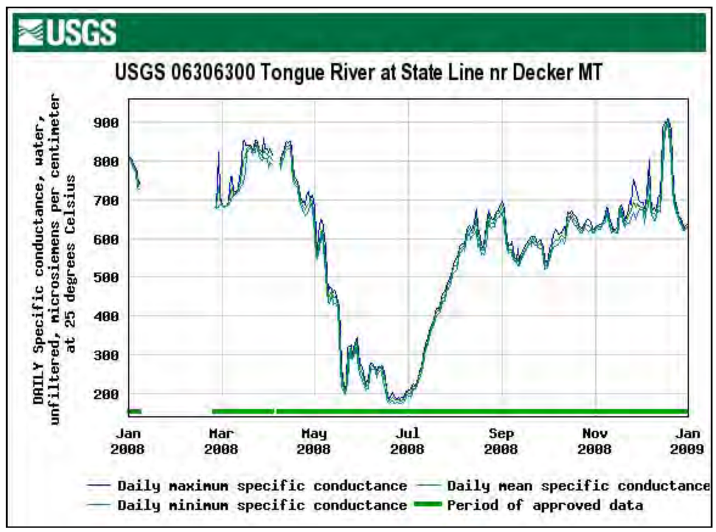
2006



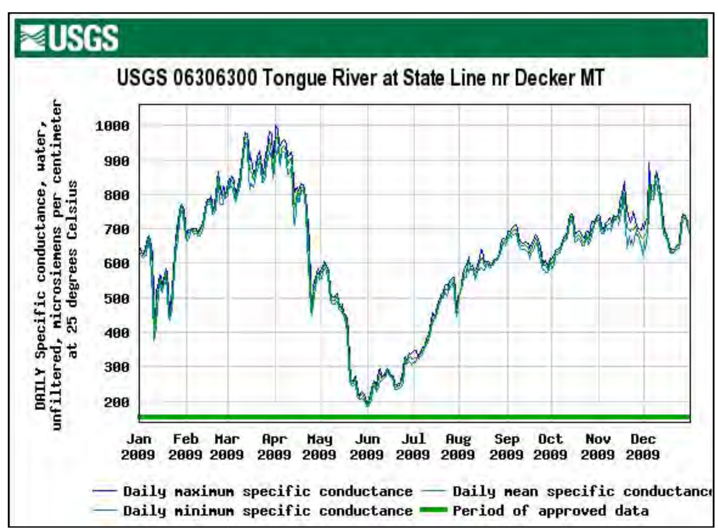
2007



2008



2009



Notes

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