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Evaluating and remediating metals and arsenic in surface waters of the Northern Cheyenne Reservation, Montana

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Evaluating and remediating metals and arsenic in surface waters of the Northern Cheyenne Reservation, Montana.

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Abstract

Located in southeastern Montana, the Northern Cheyenne Reservation sits within the Powder River Basin energy development boundary. The Northern Cheyenne Tribe (Tribe) has had a long history of resisting energy development on the reservation. The Tribe has also opposed off-reservation development that impacts reservation water, air, and cultural resources. Current coal bed methane and coal mine developments near the reservation threaten the quality of life for the Northern Cheyenne people.

Trace metal content of the surface waters on the reservation have not been adequately studied. Providing baseline data for future reference for the Tribe will be beneficial for their future studies of impacts to Tribal natural resources. This paper analyzes arsenic and heavy metals levels in surface waters on the Northern Cheyenne Reservation. The Crazy Head Springs site located in the central portion of the reservation exceeded the U. S. drinking water standard for arsenic. This spring is important to the Tribe culturally and is used as a water source for Tribal members as well as for livestock watering and agriculture irrigation.

Zr-BPAP Silica Polyamine Composite, a selective arsenate adsorbent developed at the University of Montana, was used to treat the Crazy Head Spring in the laboratory. Zr-BPAP was used to extract arsenic using a breakthrough filtering system. Zr-BPAP was shown to reduce arsenic below U. S. drinking water standards to render the spring water safe for human consumption.

Recommendations are made for a water quality monitoring plan and for revisions to tribal water quality standards.

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Chapter 1

Background

1.1 Introduction

The fight of The Northern Cheyenne Tribe (Tribe) against energy development in southeastern Montana has been well documented. In 1973 the Bureau of Indian Affairs (BIA) signed coal leases with six different t coal companies to mine leases on 56% of the Northern Cheyenne Reservation. The Tribe petitioned the United States Department of the Interior (DOI) in 1974 and was successful in getting the leases canceled, citing 36 violations of DOI rules and regulations. The Tribe's desire to cancel the leases was due to the low royalty rate that was afforded to the Tribes as reimbursement (Champagne, 2007; Studer, 1977). In the Northern Cheyenne Tribe v. Hollowbreast case 425 U.S. 649 (1976), the United States Supreme Court ruled in favor of the Tribe, preventing individual allottees from owning mineral rights on the Northern Cheyenne Reservation (NCR). The owner of the mineral rights is the Tribe thus preventing allottees from developing minerals, particularly coal (FindLaw, 1976; Studer, 1977).

In 2002, the Tribe sued the state of Montana over the transfer of the Otter Creek Tracts from Federal to the state of Montana ownership. The transfer was an exchange that preempted a gold mine from being developed near Yellowstone National Park. Instead of developing the gold mine, the state was given the option of mining for coal in southeastern Montana. The Otter Creek tracts are, at the nearest, four miles from the eastern boundary of the reservation. The Tribe's concern for this plan was that the Tribe would be stripped of legal protections that were previously afforded under Federal ownership. Since the state of Montana now claimed ownership over these tracts, those protections could have been lost. The Otter Creek Settlement was agreed upon in 2002, and stipulations required that the Tribe be consulted on the State Operating Plans. This gave the Tribe involvement in the development of the Otter Creek tracts (McGrath, 2002; Spang, 2009).

On May 21, 2010, the Montana Supreme Court ruled in favor of the Tribe, voiding 900 CBM well permits in the state of Montana. The Supreme Court sided with the Tribe, saying that the Montana Department of Environmental Quality (DEQ) failed to do its job when it permitted CBM energy companies to discharge salty well water into streams and rivers without treating it first. The Court stated that the DEQ violated the United States Clean Water Act (Dennison, 2010).

1.2 Energy Development Bordering the Northern Cheyenne Reservation

The Northern Cheyenne Reservation (NCR) is bordered by multiple energy development companies. To the west the Crow Tribe leases land for coal mining, recently signed an agreement with an Australian company to build a coal to liquid power plant, and has started producing CBM on their Reservation (Keen, 2009; Brown(c), 2009). The town of Colstrip is 20 miles north of the reservation and is the home of the Western Energy Coal Mining Company and the PP&L Power Plant. To the south of the reservation lies the coal mines Decker and Spring Creek as well as the CBM development that stems from Wyoming. To the east lies the Otter Creek Coal Tracts which are estimated to be 731 million tons that are being developed by the state of Montana and Arch Coal of St. Louis (Brown, 2009(a))

1.3 Coal Resources on the Northern Cheyenne Reservation

On the NCR, coal is the primary mineral resource, with an estimated 23 billion tons of coal under the surface. Five to six billion tons is estimated to be mineable using surface mining methods. Surface mining involves draining the aquifers over the coal beds. The overburden is drilled and broken by explosives, then removed by draglines and deposited in adjacent cuts where previous coal beds have been removed. The remaining coal beds are blasted, then loaded by power shovels or front end loaders and hauled away. (Mapel, et al. 1975). To date, the Tribe has yet to mine any coal on the reservation.

1.4Coal Bed Methane

The Northern Cheyenne Tribe has proposed to tighten the restrictions of how much by-product water produced by Coal Bed Methane (CBM) can be disposed of in surface waters that border the reservation. The Tribe intends to raise restrictions on the Tongue River to decrease the amount of CBM water disposed during irrigation season. The proposed restriction would be more than twice as stringent as the state of Montana restrictions. The EPA has commented on the proposal saying they would evaluate it, but would not say whether it would be approved. (Brown, 2009b)

The reservation lies within the Powder River Basin (PRB) (see Appendix 1) which encompasses 14 million acres in southeastern Montana and northeastern Wyoming (EWG 2009). The PRB is an energy development hotspot due to the billions of tons of coal, oil and gas which lie beneath the surface. According to the U.S. Geological Survey there is an estimated 16.6 trillion cubic feet of undiscovered natural gas, 639 million barrels of undiscovered oil, and 131 million barrels of natural gas liquids in the Powder River Basin Province (Anna et al., 2006).

CBM is a naturally occurring methane gas contained in coal seams as a result of chemical and physical processes. It currently supplies 8 % of the nation’s natural gas (ALL 2004). New development is expected to occur as new seams are discovered and as extraction technology advances (Van Voast, 2003). The natural gas is suited for a variety of purposes that range from domestic, commercial, industrial, and electrical power generation (Surdam, R.C., 2007). An area of apprehension for CBM extraction is quality of the discharge water that is sealed in the coal seam along with the gas. The concerns include quality of the water from the extraction, and what effect that water may have on stream-water quality (Clark et al., 2001). Along with the water directly discharged into local surface water, product water is used for irrigation and stock water, either directly or from the surface water into which it has been discharged. The effects of discharge water on plants and soils are an area that needs further investigation.

Extraction of CBM involves pumping large volumes of water from the saturated coal seam to release the water pressure holding the gas in the seam. What to do with this volume of often marginal-quality CBM product water is a source of much debate. Each well produces 5 to 20 gallons of water per minute. At 12 gallons per minute, one well produces a total of 17,280 gallons of water per day. It is common to have one well every 80 acres, and in the Powder River Basin, there are up to three methane-bearing coal seams. Therefore, there may be up to three wells per 80 acres. (Keith, K. et al., 2003) Most water produced during CBM extraction in the PRB is discharged either into constructed reservoirs or into surface drainages, where it may become part of the stream flow or infiltrate into the groundwater (Clark et al., 2001).

Streams receiving the CBM produced water are used for irrigation by Montana farmers and ranchers. The boom of the energy business in Wyoming and southeast Montana has been far ahead of studies on effects that CBM well water can have on streams and soils.

Scientific understanding and production experience with coal-bed methane extraction are both in the early learning stages. Understanding and predicting the effect of CBM-produced water on stream-water quality is complicated by many factors including local hydrology and geology, stream chemistry, land use, and climate (Clark et al., 2001). Research being developed to better understand the parameters that control the occurrence and recoverability of coal-bed methane. These are: geologic, geochemical, engineering, technological, and economic factors; as well as the environmental implications of developing the resource (Nuccio, V., 2000).

The CBM water discharged into streams tends to be high in salinity and sodium. This poses a problem for irrigators whose irrigated land has clay rich soils. The clay soils may have a reaction with high levels of sodium, thus forming an impermeable layer that plants cannot penetrate with their roots. One of the main waterways being used as a discharging channel is the Tongue River, the eastern border of the NCR. The Tongue River's headwaters originate in Wyoming and flow into Montana and onto the Northern Cheyenne Reservation.

In 2003 The Bureau of Land Management (BLM) in Wyoming issued a final Environmental Impact Statement (EIS) on energy development in Wyoming. The EIS research anticipated combined activity of more than 60,000 new wells, with accompanying roads, pipelines and electrical utilities (ALL 2004). These additional wells will supplement the existing 14,000 - 24,000 producing wells in the basin, mainly in Wyoming. The Montana BLM office released their supplemental EIS in 2008 and the preferred alternative called for a multiple screen phased development approach. The number of cumulative CBM wells projected in Montana's EIS preferred alternative is 26,425 wells (BLM, 2008).

Wyoming has developed its energy program at an accelerated rate compared to Montana. CBM well fields in Wyoming are discharging water into tributaries of streams that flow into Montana, such as the Tongue River. Currently, WY BLM issues permits for companies to drill wells for coal bed methane extraction, and Wyoming's Department of Environmental Quality (DEQ) issues permits to discharge CBM waste water into streams.

1.5 Tribal Self-Regulation

The Tribe is currently in the approval process with the Environmental Protection Agency (EPA) for establishing tribal water quality standards on the reservation. The Tribe has a water rights compact with the state of Montana and owns a considerable amount of surface water in the Tongue River Basin and Tongue River Reservoir (BLM, 2008). The EPA facilitates tribal jurisdiction over environmental protection through self-regulation. Most tribes have their own environmental regulation due to the EPA's limited budget resources for funding such programs. "The EPA policy includes working with tribal governments in a government-to-government relationship and recognizing tribal governments as the primary parties for setting standards, making environmental policy decisions and managing programs for reservations, consistent with agency standards and regulations" (Allen, 1989).

The Tribe has recently been granted Treatment as a State (TAS) according to Clean Water Act (CWA) 518 (e) to administer CWA 303 (c) and CWA 401. CWA 518 (e) requires the EPA to treat Native American Tribes as states for purposes of implementing and administering CWA programs. These CWA programs include 303 (c) water quality standards and the section 401 water quality certification program. CWA 303 (c) requires a state to develop, review and revise water quality standards for surface waters of the United States. These standards must, at minimum, include:

- Designated uses
- In-stream criteria to protect such uses
- An anti-degradation policy

CWA section 401 provides states the ability to grant or deny "certification" for federally-permitted or licensed activities that may result in discharge to water of the United States. Whether the state will allow certification will depend on if the proposed activity will comply with the water quality standards adopted under CWA 303 (c). If denied state certification, federally-permitted or licensed activities may not be issued permits or licenses (EPA, 2009).

The approval of the TAS is contingent on meeting the requirements of the TAS. These requirements are:

> The Indian Tribe is recognized by the Secretary of the Interior and meets the definitions in 40 C.F.R. $5 13 1.3(k) and (1) which establishes if the Northern Cheyenne tribe is "any Indian tribe, band, group, or community recognized by the Secretary of the Interior and exercising governmental authority over a Federal Indian reservation" (U.S. EPA, 2009).
>
> 1. The Indian Tribe has a governing body carrying out substantial governmental duties and powers; The water quality standards program to be administered by the Indian Tribe pertains to the management and protection of water resources that are held by the Indian Tribe, held by the United States in trust for Indians, held by a member of the Indian tribe if such property interest is subject to a trust restriction on alienation, or otherwise within the borders of the Indian reservation; and
> 2. The Indian tribe is reasonably expected to be capable, in the Regional Administrator's judgment, of carrying out the functions of an effective water quality standards program in a manner consistent with the terms and purposes of the Act and applicable regulations (U.S. EPA, 2009).

The approval of these requirements only means that the application to develop and administer the water quality standards is approved. The actual water quality standards and priority pollutants (Appendix 9.1-9.5) are to be reviewed and treated as a separate EPA action. The TAS also only applies to the waters within the borders of the Northern Cheyenne Reservation (U.S. EPA, 2009). The NCT wants to continue to have tribal land free from coal mining activity and to avoid problems from the discharge waters from coal bed methane extraction. There are positive economic advantages to these energy development opportunities; however, there exist numerous negative ecological and cultural impacts that are associated with mining activities, some of which are not currently understood.

1.6 Need and Purpose of Project

Surface waters on the NCR have not been adequately sampled for heavy metal content and possible contamination. A thorough examination of heavy metals is needed due to the extensive energy development completely surrounding the Reservation borders, as well as abandoned historical mines that lie within the Reservation. Currently there is no coal extraction or coal bed methane development occurring within the internal boundaries of the NCR. The tribal membership and government decided not to explore mining potential due to long standing cultural concerns that link the tribe's religion, language, culture and health to the integrity of its land and water.

Native people use the reservation surface waters for subsistence including recreation, fishing, irrigation, livestock purposes, consumption, and cultural ceremonies. Though there is no current mining on the Reservation, the potential for heavy metal contamination of surface waters on the reservation exists from historic mining and from energy development bordering the reservation. Heavy metal content of Reservation surface waters will be compared to water quality standards set by the Northern Cheyenne Tribe, as well as Montana water quality standards, and US drinking water standards.

This report will present an accurate profile of the heavy metal content of streams and rivers within the NCR. This is needed to assess the water quality of the NCR. Identification of heavy metals, their concentrations, and possible water quality violations of Tribal, State, or Federal water quality standards will be addressed and reported to the Northern Cheyenne Tribe. It is important to establish baseline data of heavy metal concentrations or potential contaminations on the reservation surface waters before further energy development in this area of Montana. Such a baseline will help the Tribe establish what constitutes degradation of water quality in Reservation streams.

Possible remediation measures will also be explored here for reduction of any heavy metal contamination. If these measures are successful, possible protocols will be considered and suggested for this type of contamination. The possibility of extracting metals for monetary benefit will also be discussed.

The target audiences for this project are the Northern Cheyenne Tribe, including policy makers, individual tribal members, the Tribal Water Quality Department; as well as other concerned citizens who are following the rapid energy development in the state of Montana. Results of this project will be beneficial to NCR as it will provide a complete heavy metal content profile of the reservation waters, as well as a possible means for remediation and recovery if any contamination is present. Currently, 20 water quality monitoring stations, including two United States Geological Survey (USGS) station, are located on the reservation or on the boundary. These stations test 16-27 different water parameters that include pH, alkalinity, salinity, and sodium adsorption ratio. Heavy metal content has not been extensively sampled or studied by these monitoring stations. Energy development companies may be interested in these results to offset their own costly water remediation processes associated with extraction activities. They may also be interested in possible benefits from salvage of previously lost elements.

Chapter 2

Study Area

The Northern Cheyenne Reservation (NCR) is one of seven Indian Reservations in the state of Montana. The NCR lies within the southeastern portion of the state (Figure 1). Occupying approximately 445,000 acres, the NCR is also located in eastern Bighorn and southern Rosebud counties. The reservation covers nearly 695 square miles and is bordered on the east by the Tongue River and on the west by the Crow Reservation. The Tribe also owns 160 acres of off reservation trust lands near the Tongue River Reservoir, located 37 miles south and upstream of the reservation (BLM, 2008; Rundle, 1990). The total population of the reservation is 4,470 with 91.9 percent being American Indian (Factfinder, 2009). The principal settlements within the reservation are Lame Deer and Busby located in the northern section of the reservation along U.S. Highway 212. The largest nearby towns are Ashland at the east edge of the reservation, Hardin, about 30 miles west, and Forsyth, about 40 miles north (Mapel et al., 1975).

2.1 Ecoregion

The NCR study area is located within the Northwestern Great Plains eco-region. The Northwestern Great Plains eco-region is a region with unglaciated, semiarid, and rolling plains that is underlain by shale, sandstone and siltstone. The area contains land formations such as buttes, badlands, ephemeral-intermittent streams and a few perennial rivers. Low precipitation and high summer evapo-transpiration rates restrict groundwater recharge rates. Sub-divisions of the reservation are Pine Scoria Hills located in the western portion and Mesic Dissected Plains located in the eastern portion of the reservation (Woods, A; et al., 2002). Much of the landscape is dry open rangeland, with smaller areas of irrigated farmland along river bottoms. The area also contains some forestland, primarily in the hills. Elevations range from approximately 3,000 to 5,000 feet above sea level (Beck Consulting, 2007)

Figure 1.1 Indian reservation in the state of Montana, with Northern Cheyenne Indian Reservation highlighted

2.2 Geologic Setting

The Bedrock transected by the streams in the study area is the Hell Creek Formation of the Late Cretaceous age and the Fort Union Formation of Paleocene age. Alluvium of Holocene age underlies the channels of the streams. The Hell Creek Formation consists of siltstone and silty, sandy, carbonaceous, and bentonitic shale. Yellow-gray to tan, fine to medium grained silty sandstone with thin coal bed predominates. The formation is as much as 850 feet thick within the study area. The Fort Union Formation is composed of basal Tullock Member, the intervening Lebo Shale Member, and the overlying Tongue River Member. The lower part of the Tullock Member in the study area is composed of interbedded medium to light-gray shale, light-gray fine grained sandstone, siltstone, and persistent thin coal beds. The member grades upward to light-gray carbonaceous shale. The Tullock Member is as much as 800 feet thick in the study area. The Lebo Shale Member consists of as much as 600 feet of predominately dark shale interbedded with light-gray and brown to black carbonaceous shale, siltstone, and local thin coal beds. The member contains coarse grained channel sandstone. Included in the Tongue River Member is as much as 2,500 feet of fine to medium grained, massive to locally cross bedded and lenticular sandstone and siltstone. The member commonly contains shale and multiple coal beds as much as 80 feet thick. Burning of coal beds alongside the outcrops has burned the overlying and underlying rocks to form red and lavender clinker. Alluvium along the streams contains sand, silt, clay and local lenses of gravel. Gravel consists of clinker fragments on many smaller streams. Deposits are as much as 75 feet thick along the Tongue River and as much as 40 feet thick along smaller streams. This unit includes many low lying terraces adjacent to streams (Lee et al., 1977; USGSa, 1981.). (See Appendix 2)

2.3 Climate

The climate of the Northern Cheyenne Reservation was estimated by taking the average annual data from three stations on the reservation. The stations are: Lame Deer 3 W (244839), Busby (241297), and Birney (240819). Each station had a different period of record and none of the records were for the time and day of water sampling occurrences.   Station Lame Deer 3 W has a period of record from July 1, 1948 to May 31, 1998. The Busby station period of record was July 24, 1944 to December 31, 2005. The Birney station period of record was November

13, 1954 to February 7, 2001. Annual mean data was collected and averaged to get an approximation of the average maximum and minimum temperatures, average total precipitation and total snowfall as well as average snow depth. The average maximum temperature for the period of record was 61 degrees Fahrenheit, while the minimum temperature was 29 Fahrenheit. The total precipitation was 14.1 inches, the total annual snowfall was 42.4 inches, and the average snow depth was 1.3 inches for the study area (WRCC, 2010).

2.4 Northern Cheyenne Reservation Watersheds

Two watersheds exist on the reservation, the Tongue River watershed and Rosebud Creek watershed. The Tongue River watershed drains an area of 2,100 square miles and is one of the largest perennial streams in the Powder River Basin (Lee et al. 1977). The Tongue River headwaters originate in Wyoming's Bighorn Mountains. The Northern Cheyenne Reservation lies in Montana 60 miles downstream from the base of the Bighorn Mountains. The Tongue River forms the entire 47-mile eastern border of the reservation (Rundle, 1990). The Tongue River empties into the Yellowstone River at the town of Miles City. The annual mean flow of the Tongue River as it enters the NCR at the Birney Day School Bridge monitoring station is 374 cubic feet per second (USGSc, 2008). See Appendix 3 for the daily mean flow of this USGS monitoring station for 2009-2010.

The Rosebud Creek headwaters originate in the Wolf Mountains, a sedimentary upland with a maximum elevation of 5,400 feet. The creek flows through the reservation for about 73 miles and then through another 132 miles of private land before it empties into the Yellowstone River. Two principal streams, Lame Deer and Muddy Creek, flow into the Rosebud creek on the reservation (Rundle, 1990). The annual mean flow of the Rosebud Creek at the Reservation Boundary monitoring station near Kirby, MT is 6.09 cubic feet per second (USGSd, 2008). See

Appendix 4 for the daily mean flow of this USGS monitoring station for 2009-2010.

The Powder River Basin (PRB) is the fastest growing basin for CBM development (ALL 2004). The basin extends from central Wyoming, 25,800 square miles into south central Montana. The PRB drainage includes the Powder River and other tributaries, such as the Tongue River that flow into Montana (Bartos, T.T. and Ogle, K.M. 2002).

Waterways on the Northern Cheyenne Reservation were chosen for sampling based on committee advice and related to abandoned mine site data gathered from the Montana Natural Resource Information System Digital Atlas of the NCR (NRIS, 2009). Water samples were taken from waterways including: Rosebud Creek, Lame Deer Creek, Alderson Creek, Tongue River, which makes up the eastern border of the NCR, as well as two drilled well springs located at Crazy Head and Birney Road. The springs were also sampled because they are heavily used by the public as water sources, and they directly contribute to the Rosebud Creek and Tongue River watersheds.

Chapter 3

Methodology

Fourteen separate sites were sampled (Figure 2.1 and Table 1.1, 1.2). Nine sites were sampled twice, August 2009 and January 2010; while five sites were sampled once in August 2009. The five sites that were not sampled in January could not be accessed due to ice cover.

Samples were collected using the “grab” method (EPA, 1996; USGS, 2006). A two person team sampled at each site, one member designated “dirty hands” and the “other clean hands”. The dirty hands member drove to the site, collected field data, removed all caps from sampling equipment, acidified and capped all samples. Clean hands member collected samples from the waterway and made sure to touch nothing else, except items the dirty hands member passed to them. Clean hands member submerged each sample container into water making sure container mouth was facing upstream to reduce contamination. After 500 mL container was full, clean hands member passed the sample to dirty hands member to quickly cap off container to minimize contamination from airborne particulate matter. All sampling was taken from land or while clean hands member was in the waterway downstream from sampling site. All members wore disposable gloves to reduce contamination.

Samples were sent to Montana Bureau of Mines and Geology (MBMG) at Butte Montana for testing at their analytical laboratory. All water samples were taken with Nalgene bottles (500-ml) that had been cleaned with weak acid and triple rinsed in deionized water. These bottles were supplied by MBMG with data sheets and 5 mL vials of nitric acid for preservation of the samples.

Two sets of samples were taken at each site. The first set of water samples was taken straight from the waterway and labeled RAW sample meaning there was no alteration of the water sample besides acid preservation. Analysis of the RAW sample produced total recoverable metal levels. A second set of water samples was taken from the waterway and labeled dissolved metals sample. The dissolved sample was filtered using a .45 micron filter attached to a plastic 60 mL syringe. The syringe was filled with the sampled water and pushed through the filter to remove particles within the water column. The syringe was rinsed using water from the waterway before filtering the samples. Syringes were used 8 or 9 times at each site until a 500 mL bottle was filled with filtered sample water. Syringes were re-used at the next sampling site. Syringes were rinsed out after use using de-ionized water and before use at next sampling site using water from site to be sampled.

To preserve the samples for metal testing, nitric acid was added to each sample in 5 mL increments. Specific conductance measurements were also taken using an YSI 556 MPS Multi-Probe Field Meter courtesy of the Northern Cheyenne Tribe Environmental Protection Department. The YSI field meter is a multi use probe that allows the user to collect specific conductance, pH, temperature, dissolved oxygen and other parameters (Geotech, 2009). The YSI field meter was calibrated using 1 micro-Siemens/cm solution each day before sampling was conducted. These measurements were sent to the Montana Bureau of Mines and Geology in Butte, Montana to assist in analyzing the heavy metals in surface waters of the NCR.

The Montana Bureau of Mines and Geology laboratory (MBMG), Butte, Montana, an EPA certified laboratory, analyzed the field samples. MBMG analyzed samples from 14 sampling sites for 15 potential metal contaminants in August 2009 and from 9 sampling sites for 39 potential metal contaminants in January 2010 The field samples were analyzed using an Inductively Coupled Plasma Mass Spectrometer using EPA method 200.8 (Creed et al, 1994).

Samples run through the breakthrough column in the Rosenberg Laboratory were analyzed at the University of Montana Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) using EPA method 200.7 (Martin et al, 1994)

The Specific conductance measurements taken in the field were analyzed in the MBMG laboratory. Specific conductance measures the amount of dissolved solids in the sample. The more dissolved solids there are, the higher the viscosity of the solution. The viscosity determined the method that the sample is sprayed into the analyzer. If the viscosity of the sample is greater than that of the calibration standards, then the concentration that is reported may not be correct. This can be corrected by using internal standards. Internal standards are elements that are not usually in a sample itself. When internal standards are put in the calibration solutions and in the sample at the same concentration, the same response should be seen for the internal standard elements in both solutions. If the sample internal standard response is lower, the reported concentrations are adjusted by the same amount that the internal standard response is lowered. Concentrated solutions are diluted to about the same viscosity as the standards so as to make only small corrections. Specific Conductance measurements are used as a simple indicator of the amount of dissolved solids and as a guide to how much dilution is needed (Mcgrath, 2010)

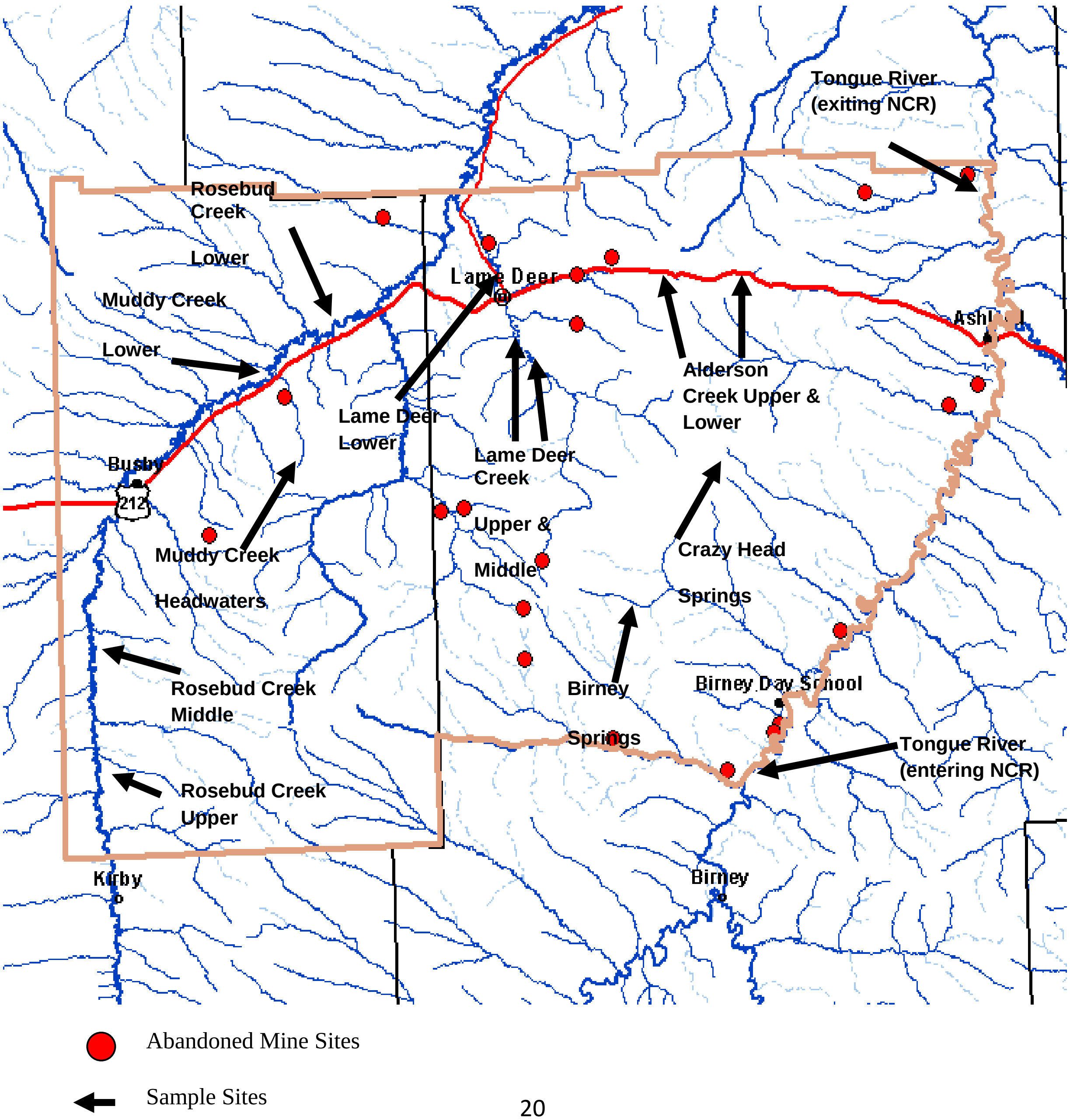
Metal levels were compared to U.S. drinking water standards (Appendix 5.1-6.2). At one sampling site where metal concentrations exceeded standards, a remediation objective was employed. Metal levels were also compared to Montana water quality standards to protect aquatic life (Appendix 7.1,7.2)

Based on the MBMG data, sites were chosen to undergo further testing of remediation efforts to clean up trace metal contamination. Silica Polyamine Composites (SPC) was used in the laboratory at University of Montana (UM) Environmental Chemistry Laboratory to filter, isolate, and remove unwanted metals. SPC's are an engineered materials developed by the Rosenberg Research Group at the University of Montana that are designed to bond with a specified metal and extract said metal from aqueous solutions (Kailasam, 2009; Hughes, 2007). SPCs act as a chelating agent for a range of metal ions (Hughes, 2007). Chelating is the process of binding with a metal ion through more than one ligand atom (Harris, 1999). With the use of SPC it is possible to recover the heavy metals and reuse them if they are valuable. This could be a source of revenue used to fund metal extraction and decontamination of water bodies (Wood, 2008). SPCs can also be useful for toxic metal immobilization and disposal. Acid stripping is the primary method of extracting immobilized metals from SPCs. Without the acid strip, metals can remain on the SPC and can be used as a medium for long term disposal (Rosenberg et al., 2003).

Zr-BPAP was used as the primary SPC to extract metals from surface water on the NCR because of its affinity for arsenic. Zr-BPAP was supplied by the UM Chemistry Department Laboratory by Dr. Ed Rosenberg. The Zr-BPAP SPCs are the size of sand grains and are inserted into a 5cc column which is a glass or plastic tube filled to the 5cc mark. Columns were packed dry. Frits were attached to both ends and water was pushed through the column at a specific rate set by adjusting the variable flow FMI Lab Pump model QG150 (Fluid Metering Inc., Syosset, NY) (Kailasam, 2009). The variable flow of the pump used in this column run was 1 mL per minute.

After a specified time the column was taken out of the instrument and "stripped" of metals using a wash of 10% sulfuric acid. The stripped aqueous material was collected and analyzed using the ICP-AES to determine the metal content of the solutions. The data were graphed, and standard errors were factored into the final data set. Based on the speed of the water being pushed through the column, the time allowed to run, and amount of metal extracted from the SPC, percentages of heavy metals extracted from the water were calculated and compared to initial concentrations. This information was used to evaluate whether the NCR contaminated waters can be remediated using this approach.

Figure 2.1 Water sampling sites on the Northern Cheyenne Reservation in relationship to abandoned mine sites (courtesy of Natural Resource Information System-Montana State Library).



Chapter 4

Results

4.1 Metal Levels in Northern Cheyenne Reservation Surface Waters

The August 2009 sample set was sent to the Montana Bureau of Mines and Geology in Butte Montana where samples from 14 sites were analyzed for 15 separate metals. The dissolved metals in these samples are listed in Table 1.1. The Crazy Head Spring sampling site showed an arsenic level of 12. 6 ug/L. The EPA drinking water quality standard for arsenic is 10 ug/L (Appendix 5). Uranium levels in the Upper Muddy Creek site were 8.5 ug/L but that is well below the EPA Maximum Contaminant Level (MCL) of 30 ug/L.

Total recoverable metals are listed in Table 1.2. Total recoverable arsenic in Crazy Head Spring also violates EPA water quality standards with a concentration of 12.2 ug/L. Uranium levels in the Upper Muddy Creek site were 9.2 ug/L but also below drinking water standards. The Lower Rosebud Creek had a Mercury concentration of 2.38 ug/L, violating the EPA drinking water standard of 2 ug/L. Each table has the Montana Numeric Water Quality Standards included (DEQ, 2008).

Table 1.1 Dissolved metals (15) of surface waters on the Northern Cheyenne Reservation, August 2009.

Site	Date	Fe	As	B	Cr	Cu	Pb	Ni	Se	Sn	U	Zn	Hg	Mg	Ca	Sb
		mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L
Montana Standards*		n/a	10	n/a	20	1300	15	100	50	n/a	20	2100	2	n/a	n/a	6
Tongue River Entering	Aug-09	0.0	1.2	38.3	<0.04	0.7	<0.15	0.7	0.3	<0.04	1.6	<0.90	<0.10	19.8	57.5	0.3
Tongue River Exiting	Aug-09	0.0	1.0	44.1	<0.04	0.7	<0.15	0.7	0.3	<0.04	1.7	<0.90	<0.10	21.8	60.1	<0.24
Muddy Creek Upper	Aug-09	0.0	0.7	152.4	<0.20	<2.00	<0.76	0.5	2.0	<0.21	8.5	<4.50	<0.50	133.2	138.8	<0.48
Muddy Creek Lower	Aug-09	0.0	1.9	454.1	<0.20	2.5	<0.76	1.0	<0.50	<0.21	4.6	<4.50	<0.50	255.5	117.1	<0.24
Crazy Head Springs	Aug-09	<0.002	**12.6**	59.3	2.4	0.4	<0.15	<0.10	2.3	<0.04	3.1	<0.90	<0.10	20.7	49.3	0.5
Birney Springs	Aug-09	0.6	0.4	74.3	<0.04	0.8	<0.15	<0.10	0.3	<0.04	1.1	3.0	<0.10	52.1	109.7	<0.05
Alderson Upper	Aug-09	0.1	6.8	45.3	0.2	<0.40	<0.15	<0.10	1.0	<0.04	2.1	<0.90	<0.10	22.0	62.8	0.2
Alderson Lower	Aug-09	0.0	2.1	82.0	<0.04	<0.40	<0.15	<0.10	0.5	<0.04	3.0	<0.90	<0.10	47.9	96.2	0.1
Lame Deer Upper	Aug-09	0.0	1.2	113.1	<0.04	<0.40	<0.15	0.4	0.4	<0.04	2.3	<0.90	<0.10	74.9	87.0	<0.24
Lame Deer Middle	Aug-09	0.0	1.8	122.7	<0.04	0.5	<0.15	0.5	0.4	<0.04	2.3	<0.90	<0.10	88.5	97.8	<0.05
Lame Deer Lower	Aug-09	0.0	1.7	173.1	<0.04	0.4	<0.15	0.6	1.4	<0.04	4.9	<0.90	<0.10	109.1	116.7	0.1
Rosebud Creek Upper	Aug-09	0.0	1.4	82.3	<0.04	0.6	<0.15	0.7	0.3	<0.04	2.6	<0.90	<0.10	63.2	71.8	0.1
Rosebud Creek Middle	Aug-09	0.0	1.3	104.5	<0.04	0.6	<0.15	0.8	0.2	<0.04	2.2	<0.90	<0.10	73.0	65.1	0.1
Rosebud Creek Lower	Aug-09	0.0	1.2	142.2	<0.04	0.8	<0.15	1.2	0.3	<0.04	2.6	<0.90	<0.10	86.7	64.6	0.3

n/a = not applicable

*Montana water quality standards based on protecting human health

**In all results tables, detection limits achieved on a particular analytical run appear as numbers preceded by the symbol <

Table 1.2 Total Recoverable metals (15) of surface waters on the Northern Cheyenne Reservation, August 2009.

Site	Date	Fe mg/L	As µg/L	B µg/L	Cr µg/L	Cu µg/L	Pb µg/L	Ni µg/L	Se µg/L	Sn µg/L	U µg/L	Zn µg/L	Hg µg/L	Mg mg/L	Ca mg/L	Sb µg/L
Montana Standards*		n/a	10	n/a	20	1300	15	100	50	n/a	20	2100	2	n/a	n/a	6
Tongue River Entering	Aug-09	0.4	1.1	58.0	0.5	4.5	0.6	1.2	0.3	93.0	1.7	101.5	<0.10	20.2	58.0	<0.24
Tongue River Exiting	Aug-09	0.4	1.0	57.2	0.6	4.3	0.7	1.3	0.3	94.4	1.8	92.0	<0.10	21.8	60.2	<0.24
Muddy Creek Upper	Aug-09	0.2	0.8	179.8	0.5	4.0	<0.76	0.8	1.9	100.0	9.2	108.8	<0.50	140.3	141.7	<0.48
Muddy Creek Lower	Aug-09	0.2	2.1	494.2	0.9	2.4	<1.52	1.2	<1.00	100.5	4.6	111.4	<1.00	257.0	127.6	<0.48
Crazy Head Springs	Aug-09	0.0	**12.2**	70.0	2.7	2.5	0.3	0.1	1.5	100.8	3.3	88.9	<0.10	24.9	55.8	0.2
Birney Springs	Aug-09	0.7	0.4	99.0	0.3	6.3	0.6	0.2	0.4	101.8	1.2	116.6	0.7	60.6	110.9	<0.05
Alderson Upper	Aug-09	0.4	6.7	60.9	0.7	1.2	0.3	0.3	0.8	100.0	2.3	86.5	<0.10	22.2	66.3	0.2
Alderson Lower	Aug-09	0.1	1.9	93.0	0.3	1.3	0.4	0.4	0.5	97.0	3.2	90.4	<0.10	47.8	98.7	0.1
Lame Deer Upper	Aug-09	0.1	1.0	114.9	0.3	1.1	0.3	0.4	0.3	99.4	2.4	62.7	<0.10	75.2	91.8	0.1
Lame Deer Middle	Aug-09	0.1	1.6	127.2	0.2	1.2	0.3	0.7	0.4	104.1	2.5	78.7	<0.10	91.5	110.1	0.1
Lame Deer Lower	Aug-09	0.3	1.9	259.0	0.4	1.1	<0.76	1.2	1.5	99.1	4.7	85.2	<0.50	113.7	131.8	<0.24
Rosebud Creek Upper	Aug-09	0.2	1.2	90.3	0.3	2.7	0.6	1.0	0.3	98.3	2.6	93.5	<0.10	70.9	82.9	0.1
Rosebud Creek Middle	Aug-09	0.2	1.3	121.3	0.3	1.7	0.5	1.1	0.2	98.0	2.2	76.9	**2.4**	62.2	67.7	0.2
Rosebud Creek Lower	Aug-09	0.6	1.2	154.3	0.6	2.5	0.9	1.8	0.3	103.1	2.7	76.2	<0.10	88.0	72.3	0.3

n/a = not applicable

* Montana water quality standards based on protecting human health

In January 2010, 39 metals were analyzed from samples taken from 9 sampling sites on the NCR. Arsenic was found again to be above drinking water standards at the Crazy Head Spring sampling site. The dissolved metals table (Table 2.1-2.4) shows arsenic levels at 13.4 ug/L. The total recoverable metals table (Table 3.1-3.4) show arsenic levels to be 13.5 ug/L. Upper Alderson Creek also showed arsenic levels above drinking water standards with dissolved levels of 10.7 ug/L and total recoverable levels of 12.5 ug/L. Uranium levels in Upper and Lower Muddy Creek sites had higher levels than most sites, ranging 9.84-10.8 ug/L for both dissolved and total recoverable levels but did not violate the EPA standard of 30 ug/L. Total recoverable Aluminum concentrations on the Upper Rosebud Creek and Upper Muddy Creek sites were 97 ug/L and 106 ug/L respectively. These concentrations were within the EPA Secondary Drinking Water Regulations which are non-enforceable Federal guidelines regarding cosmetic effects or aesthetic effects of 50 to 200 ug/L (EPA, 2006).

All metal levels were also compared to Montana water quality standards to protect aquatic life, but no levels violated these standards, see Appendices 7.1 and 7.2. Standards could not be calculated for January 2010 samples because of lack of Magnesium results from MBMG.

Table 2.1 Dissolved metals (12) of surface waters on the Northern Cheyenne Reservation, January 2010.**

Site	Date	Fe	As	B	Cr	Cu	Pb	Ni	Se	U	Zn	Ca	Sb
		mg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**mg/L**	**µg/L**
Montana Standards*		n/a	10	n/a	100	1300	15	100	50	20	2100	n/a	6
Tongue River Exiting	Jan-10	0.0	0.6	75.5	0.2	0.7	<0.15	0.5	0.3	4.4	<0.91	26.4	0.1
Muddy Creek Upper	Jan-10	0.0	0.4	108.0	0.2	0.5	<0.15	<0.10	1.7	10.5	<0.91	79.3	0.1
Muddy Creek Lower	Jan-10	0.0	<0.51	313.0	<0.20	<2.02	<0.77	1.6	<0.51	10.5	<4.55	98.6	<0.24
Crazy Head Springs	Jan-10	<0.002	**13.4**	62.3	2.8	<0.40	<0.15	<0.10	2.2	3.4	<0.91	34.3	0.2
Birney Springs	Jan-10	0.7	0.4	78.8	0.1	<0.40	<0.15	<0.10	0.2	1.2	1.7	60.1	<0.05
Alderson Lower	Jan-10	0.0	1.7	51.0	0.1	<0.40	<0.15	<0.10	<0.10	1.8	<0.91	20.6	0.1
Alderson Upper	Jan-10	0.0	10.7	43.1	1.4	<0.40	<0.15	<0.10	1.6	2.8	<0.91	27.5	0.1
Lame Deer Middle	Jan-10	0.0	0.7	157.0	0.2	0.6	<0.15	0.6	2.0	6.9	<0.91	60.1	0.1
Rosebud Upper	Jan-10	0.0	0.6	82.0	0.1	0.4	<0.15	0.3	0.3	2.8	3.1	43.7	0.1

* Montana water quality standards based on protecting human health
** Sn, Hg, and Mg could not be analyzed.
n/a = not applicable

Table 2.2 Dissolved metals (9) of surface waters on the Northern Cheyenne Reservation, January 2010; Continued.

Site	Date	K mg/L	Mn mg/L	Al µg/L	Ba µg/L	Be µg/L	Cd µg/L	Ce µg/L	Cs µg/L	Co µg/L
Montana Standards*		n/a	n/a	n/a	2000	4	5	n/a	n/a	n/a
Tongue River Exiting	Jan-10	4	0	<7.68	65	<0.20	<0.05	<0.02	<0.04	0
Muddy Creek Upper	Jan-10	11	0	<7.68	43	<0.20	<0.05	<0.02	<0.04	0
Muddy Creek Lower	Jan-10	17	0	<38.38	31	<1.01	<0.25	<0.10	<0.21	<0.51
Crazy Head Springs	Jan-10	3	<0.0001	<7.68	206	<0.20	<0.05	<0.02	0	<0.10
Birney Springs	Jan-10	6	0	<7.68	51	<0.20	<0.05	0	<0.04	<0.10
Alderson Lower	Jan-10	5	0	<7.68	204	<0.20	<0.05	<0.02	<0.04	<0.10
Alderson Upper	Jan-10	3	0	<7.68	193	<0.20	<0.05	<0.02	<0.04	<0.10
Lame Deer Middle	Jan-10	10	0	<7.68	63	<0.20	<0.05	<0.02	<0.04	0
Rosebud Upper	Jan-10	7	0	<7.68	90	<0.20	<0.05	<0.02	<0.04	0

n/a = not applicable

* Montana water quality standards based on protecting human health

Table 2.3 Dissolved metals (9) of surface waters on the Northern Cheyenne Reservation, January 2010; Continued.

Site	Date	Ga µg/L	La µg/L	Li µg/L	Mo µg/L	Nb µg/L	Pd µg/L	Pr µg/L	Rb µg/L	Ag µg/L
Montana Standards*		n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	35
Tongue River Exiting	Jan-10	<0.05	<0.02	23.6	1.1	0.1	0.2	<0.02	2.4	<0.04
Muddy Creek Upper	Jan-10	<0.05	<0.02	66.6	2.5	<0.04	0.6	<0.02	13.9	<0.04
Muddy Creek Lower	Jan-10	<0.25	<0.11	96.2	5.2	0.3	0.9	<0.11	8.7	<0.20
Crazy Head Springs	Jan-10	<0.05	<0.02	29.1	3.1	<0.04	0.3	<0.02	6.3	<0.04
Birney Springs	Jan-10	<0.05	<0.02	52.3	0.7	0.1	0.5	<0.02	5.4	<0.04
Alderson Lower	Jan-10	<0.05	<0.02	17.3	1.3	<0.04	0.3	<0.02	3.7	<0.04
Alderson Upper	Jan-10	<0.05	<0.02	23.6	2.1	<0.04	0.2	<0.02	4.5	<0.04
Lame Deer Middle	Jan-10	<0.05	<0.02	50.9	3.0	0.0	0.6	<0.02	9.0	<0.04
Rosebud Upper	Jan-10	<0.05	<0.02	36.6	1.7	<0.04	0.4	<0.02	8.1	0.1

n/a = not applicable
* Montana water quality standards based on protecting human health

Table 2.4 Dissolved metals (9) of surface waters on the Northern Cheyenne Reservation, January 2010; Continued.

Site	Date	Sr	Tl	Th	Ti	W	V	Zr	P	Nd
		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L
Montana Standards*		4200	1.7	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Tongue River Exiting	Jan-10	673.0	<0.03	<0.02	2.3	<0.05	0.8	0.1	0.0	<0.05
Muddy Creek Upper	Jan-10	1932.0	<0.03	<0.02	5.4	<0.05	0.8	<0.05	0.0	<0.05
Muddy Creek Lower	Jan-10	2630.0	<0.17	<0.12	11.1	<0.25	0.6	<0.25	0.0	<0.26
Crazy Head Springs	Jan-10	1081.0	<0.03	<0.02	0.6	0.5	65.6	<0.05	0.0	<0.05
Birney Springs	Jan-10	1464.0	<0.03	<0.02	1.3	<0.05	<0.10	<0.05	0.0	<0.05
Alderson Lower	Jan-10	927.0	<0.03	<0.02	0.2	0.1	3.2	<0.05	0.0	<0.05
Alderson Upper	Jan-10	747.0	<0.03	<0.02	<0.20	0.5	48.0	<0.05	0.0	<0.05
Lame Deer Middle	Jan-10	1984.0	<0.03	<0.02	3.4	<0.05	0.9	0.1	0.0	<0.05
Rosebud Upper	Jan-10	1163.0	<0.03	<0.02	1.2	<0.05	1.0	0.1	0.0	<0.05

n/a = not applicable
* Montana water quality standards based on protecting human health

Table 3.1 Total Recoverable metals (12) of surface waters on the Northern Cheyenne Reservation, January 2010.**

Site	Date	Fe	As	B	Cr	Cu	Pb	Ni	Se	U	Zn	Ca	Sb
		mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L
Montana Standards*		n/a	10	n/a	100	1300	15	100	50	30	2100	n/a	6
Tongue River Exiting	Jan-10	0.1	1.0	85.9	0.3	<2.02	<0.77	0.9	1.5	4.4	<4.55	26.7	<0.24
Muddy Creek Upper	Jan-10	0.5	1.0	147.0	0.6	<2.02	<0.77	0.9	3.0	9.8	<4.55	82.7	<0.24
Muddy Creek Lower	Jan-10	0.2	0.6	307.0	0.3	<2.02	<0.77	2.0	<0.51	10.8	<4.55	99.3	<0.24
Crazy Head Springs	Jan-10	0.1	**13.5**	74.9	3.4	<2.02	<0.77	<0.51	2.9	3.2	<4.55	34.4	<0.24
Birney Springs	Jan-10	0.8	0.6	95.6	0.2	<2.02	<0.77	<0.51	0.9	1.2	<4.55	61.1	<0.24
Alderson Lower	Jan-10	0.2	2.5	63.2	0.2	<2.02	<0.77	<0.51	2.0	1.8	<4.55	20.8	<0.24
Alderson Upper	Jan-10	0.2	12.6	51.9	1.9	<2.02	<0.77	<0.51	3.1	2.8	<4.55	28.0	<0.24
Lame Deer Middle	Jan-10	0.2	1.2	208.0	1.0	<2.02	3.5	1.2	3.2	6.7	<4.55	63.1	<0.24
Rosebud Upper	Jan-10	0.4	<1.01	99.1	0.5	<4.04	<1.54	<1.01	<1.01	2.7	<9.09	47.2	<0.48

* Montana water quality standards based on protecting human health
**Sn, Hg, and Mg could not be analyzed.
n/a = not applicable

Table 3.2 Total Recoverable metals (9) of surface waters on the Northern Cheyenne Reservation, January 2010; Continued.

SAMPLE	Date	K mg/L	Mn mg/L	Al µg/L	Ba µg/L	Be µg/L	Cd µg/L	Ce µg/L	Cs µg/L	Co µg/L
Montana Standards*		n/a	n/a	n/a	2000	4	5	n/a	n/a	n/a
Tongue River Exiting	Jan-10	4.1	0.0	<38.38	67.7	<1.01	<0.25	<0.10	<0.21	<0.51
Muddy Creek Upper	Jan-10	11.5	0.1	**106.0**	46.6	<1.01	<0.25	0.4	<0.21	<0.51
Muddy Creek Lower	Jan-10	17.6	0.2	<38.38	32.9	<1.01	<0.25	0.1	<0.21	0.5
Crazy Head Springs	Jan-10	3.6	<0.0003	<38.38	202.0	<1.01	<0.25	<0.10	<0.21	<0.51
Birney Springs	Jan-10	6.0	0.0	<38.38	50.2	<1.01	<0.25	<0.10	<0.21	<0.51
Alderson Lower	Jan-10	4.8	0.1	<38.38	205.0	<1.01	<0.25	<0.10	<0.21	<0.51
Alderson Upper	Jan-10	3.8	0.1	<38.38	197.0	<1.01	<0.25	<0.10	<0.21	<0.51
Lame Deer Middle	Jan-10	10.8	0.1	<38.38	67.4	<0.20	<0.25	<0.10	<0.21	<0.51
Rosebud Upper	Jan-10	8.0	0.1	**96.9**	96.9	<2.02	<0.51	0.4	<0.42	<1.01

n/a = not applicable

* Montana water quality standards based on protecting human health

Table 3.3 Total Recoverable metals (9) of surface waters on the Northern Cheyenne Reservation, January 2010; Continued.

SAMPLE	Date	Ga µg/L	La µg/L	Li µg/L	Mo µg/L	Nb µg/L	Pd µg/L	Pr µg/L	Rb µg/L	Ag µg/L
Montana Standards*		n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	35
Tongue River Exiting	Jan-10	<0.25	<0.11	26.9	1.1	<0.20	<0.51	<0.11	2.4	<0.20
Muddy Creek Upper	Jan-10	<0.25	0.2	80.3	2.5	<0.20	0.6	<0.11	13.9	<0.20
Muddy Creek Lower	Jan-10	<0.25	<0.11	97.8	5.4	<0.20	0.8	<0.11	9.0	<0.20
Crazy Head Springs	Jan-10	<0.25	<0.11	34.0	3.1	<0.20	<0.51	<0.11	6.3	<0.20
Birney Springs	Jan-10	<0.25	<0.11	58.9	0.9	1.3	0.6	<0.11	5.2	<0.20
Alderson Lower	Jan-10	<0.25	<0.11	20.7	1.3	<0.20	<0.51	<0.11	3.8	<0.20
Alderson Upper	Jan-10	<0.25	<0.11	27.9	2.2	<0.20	<0.51	<0.11	4.7	<0.20
Lame Deer Middle	Jan-10	<0.25	<0.11	62.5	3.1	<0.20	0.7	<0.11	8.9	<0.20
Rosebud Upper	Jan-10	<0.51	<0.22	47.2	1.6	<0.40	<1.01	<0.21	8.6	<0.40

n/a = not applicable
* Montana water quality standards based on protecting human health

Table 3.4 Total Recoverable metals (9) of surface waters on the Northern Cheyenne Reservation, January 2010; Continued**.**

SAMPLE	Date	Sr µg/L	Tl µg/L	Th µg/L	Ti µg/L	W µg/L	V µg/L	Zr µg/L	P mg/L	Nd µg/L
Montana Standards*		4200	2	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Tongue River Exiting	Jan-10	717	<0.17	<0.12	2.8	<0.25	0.9	<0.25	0.1	<0.26
Muddy Creek Upper	Jan-10	1978	<0.17	<0.12	9.8	<0.25	1.2	<0.25	0.0	<0.26
Muddy Creek Lower	Jan-10	2819	<0.17	<0.12	12.0	<0.25	0.7	0.3	0.2	<0.26
Crazy Head Springs	Jan-10	1107	<0.17	<0.12	<1.01	0.4	72.4	<0.25	0.2	<0.26
Birney Springs	Jan-10	1509	<0.17	<0.12	1.6	0.4	<0.51	<0.25	0.1	<0.26
Alderson Lower	Jan-10	973	<0.17	<0.12	<1.01	<0.25	4.1	<0.25	0.2	<0.26
Alderson Upper	Jan-10	796	<0.17	<0.12	<1.01	0.4	58.1	<0.25	0.2	<0.26
Lame Deer Middle	Jan-10	2070	<0.17	<0.12	4.8	<0.25	1.1	<0.25	0.2	<0.26
Rosebud Upper	Jan-10	1252	<0.33	<0.23	4.4	<0.51	1.4	<0.51	0.2	<0.52

n/a = not applicable

* Montana water quality standards based on protecting human health

4.2 Reducing Arsenic Levels with a Silica Polyamine Composite

The breakthrough column run results show that arsenic was reduced in the Crazy Head Spring site water using the Zirconium-BPAP (Zr-BPAP) Silica Polyamine Composites to a level below the Maximum Contaminant Level put forth by the Environmental Protection Agency (Figure 4.1). Arsenic levels in the Zr-BPAP column run that fell below the detection limit of 5 ug/L were automatically set at 5 ug/L. The feed solution for this column run was 300 mL of un-filtered, non-preserved, Crazy Head Spring site water with an arsenic concentration of 20 ug/L. This concentration of arsenic was above levels found in the August 2009 analysis and January 2010 analysis levels. This sample was taken in April 2010 and gave a higher concentration than the previous analyzed samples partly due to the time of year it was collected. The graph also shows that the Zr-BPAP composite was not saturated with arsenic and could have continued to be used to extract additional arsenic. The Zr-BPAP composite was also stripped of arsenic using 60 mL of 10% sulfuric acid. Three successive strip samples were analyzed for Arsenate. 6 ug of arsenate was loaded on the column assuming that all the arsenate was removed. 3ug was stripped in the 20 mL samples of 50% of that were loaded (see Figure 5.1). Based on prior work, the remaining Arsenate could have been removed. Raw Data from the column run can be seen in Figure 6.1.

Figure 3.1 Graph of Zr-BPAP breakthrough showing initial feed concentration of As in Crazy Head Spring Water, EPA MCL, and concentration of As after run through 5mL Zr-BPAP column. **Note: ICP level of detection 5ppb.**

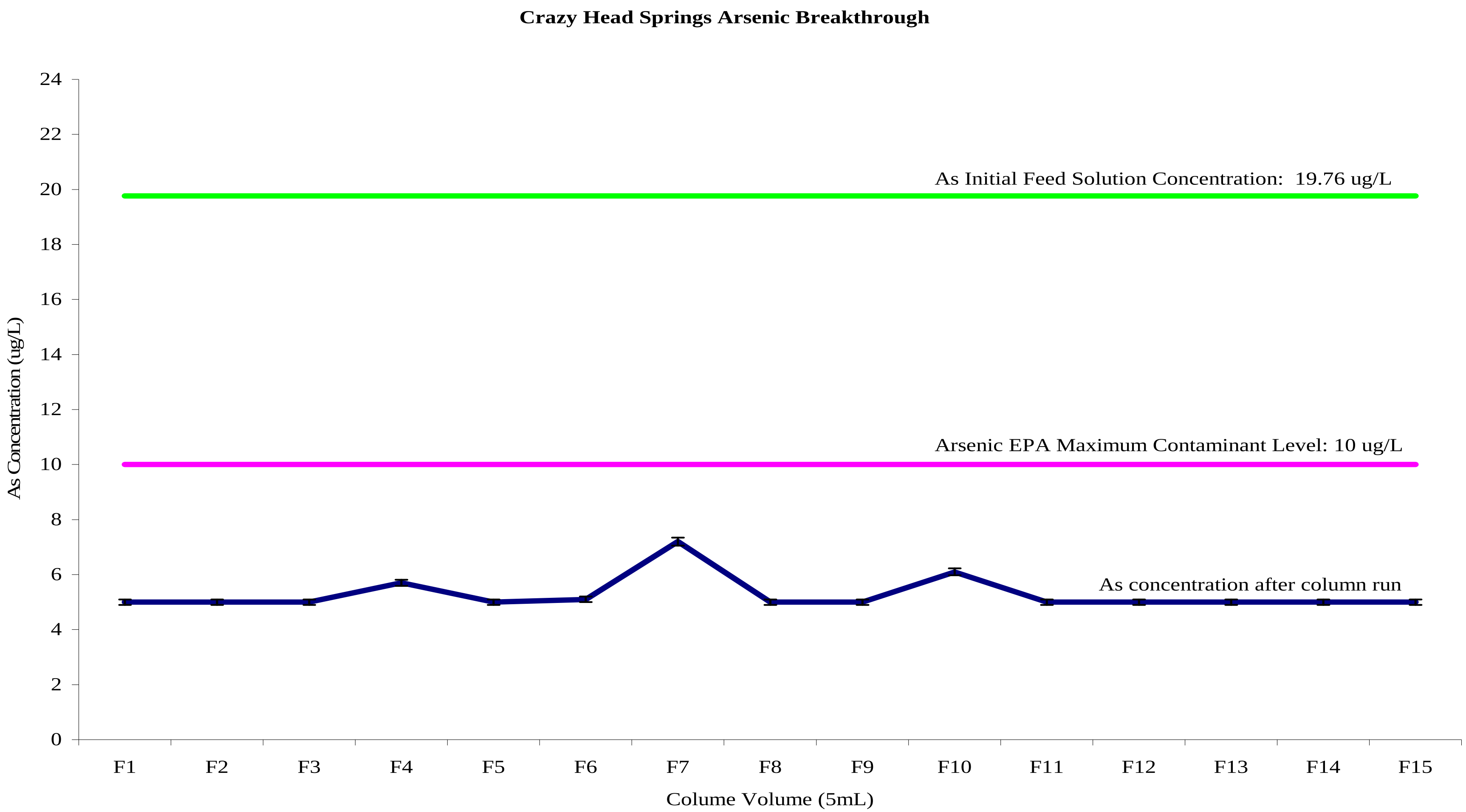


Figure 4.1 As strip results of Zr-BPAP column using 10% H_2SO_4 acid.

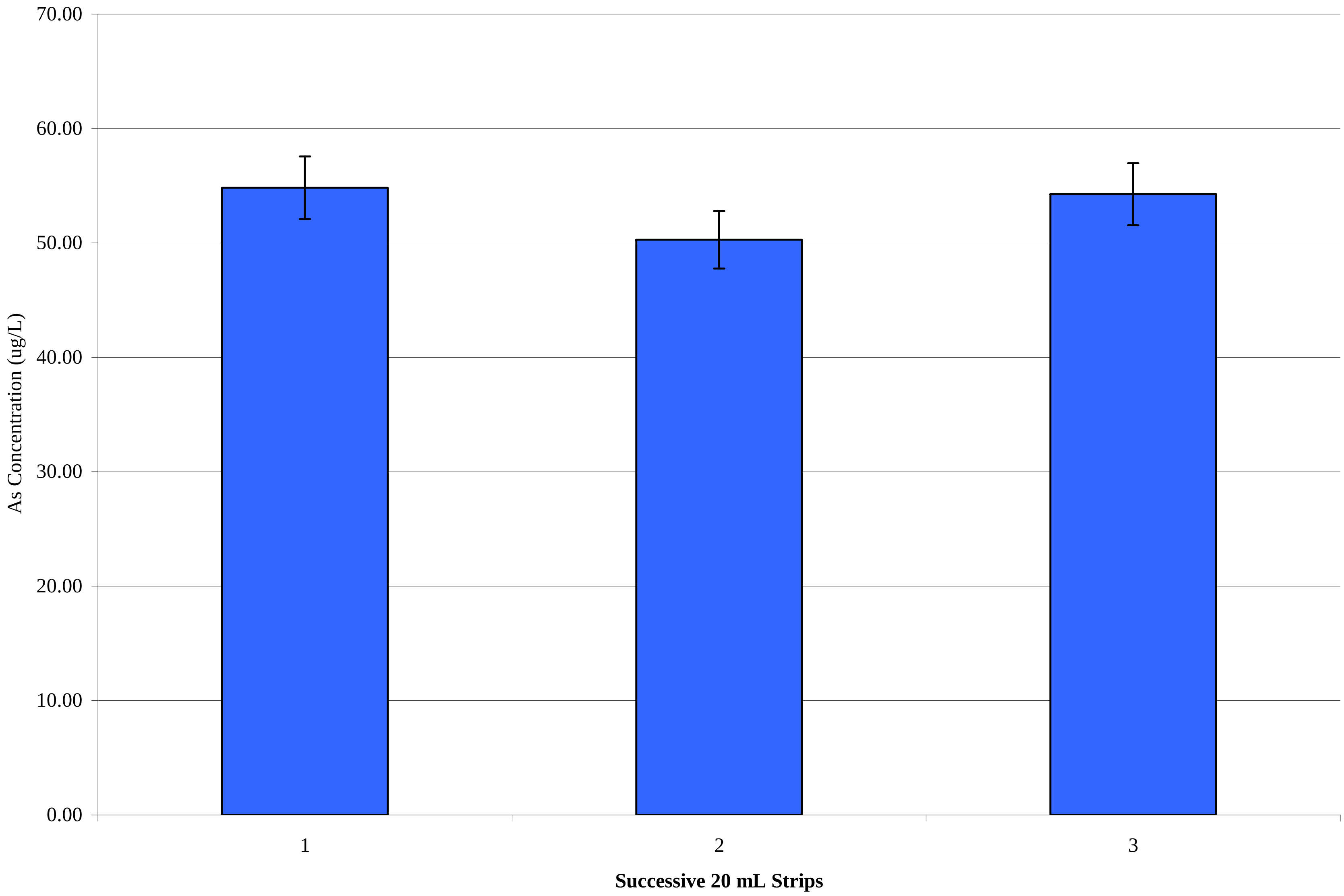


Figure 5.1 Raw data from Zr-BPAP column run.

Composite	**Zr-BPAP**	
Notebook Ref.		
Load/Strip Cycle	**#1**	
Column Volume	**0.020**	**L**
Composite Mass	**3.2287**	**g**
Regeneration pH	**6.0**	**DI H_2O**
Regeneration Flow Rate	**0.20**	**CV/min.**
Load pH	**7.0**	**As**
Load Flow Rate	**0.20**	**CV/min.**
Rinse pH	**~6**	**DI H_2O**
Rinse Flow Rate	**0.20**	**CV/min.**
Strip Solution	**4N-H_2SO_4 (60 mL)**	**pH<1**
Strip Flow Rate	**0.20**	**CV/min.**
Post-Regeneration pH	**~6**	**DI H_2O**
Post-Regeneration Flow Rate	**0.20**	**CV/min.**
As in	**5.9**	**mg**
As out	**5.6**	**mg**
Flow Through Capacity		**mg/g**
Strip Capacity		**mg/g**
% Stripped		**%**
As Unstripped (final)	**0**	**mg**

Sample	**As ug/L**	**As ug**	**C/C_0**	**Feed**	**As MCL**
Feed	20	6			
F1	5	0.10	0.2530364	20	10
F2	5	0.10	0.2530364	20	10
F3	5	0.10	0.2530364	20	10
F4	5.7	0.11	0.2884615	20	10
F5	5	0.10	0.2530364	20	10
F6	5.1	0.10	0.2580972	20	10
F7	7.2	0.14	0.3643725	20	10
F8	5	0.10	0.2530364	20	10
F9	5	0.10	0.2530364	20	10
F10	6.1	0.12	0.3087045	20	10
F11	5	0.10	0.2530364	20	10
F12	5	0.10	0.2530364	20	10
F13	5	0.10	0.2530364	20	10
F14	5	0.10	0.2530364	20	10
F15	5	0.10	0.2530364	20	10
FR	5.08	0.10	0.257085		
S1	54.81	1.10			
S2	50.28	1.01			
S3	54.25	1.09			
SR	35	0.71			

Chapter 5

Discussion

5.1 Compliance with Water Standards on the NCR

NCR stream samples collected in August 2009 and January 2010 met all state water quality standards, federal drinking water standards, and Tribal water quality standards (Appendix 9.1-9.5) for metals with a few exceptions. One exception involved arsenic levels which exceeded federal drinking water standards in both August 2009 and January 2010 samples at the Crazy Head Spring site and in January 2010 at the Upper Alderson Creek site. However, the levels fell below the Tribe's proposed standards to protect human health (14 ug/L for water where fish are consumed and 18 ug/L for water where both water and fish are consumed) (Appendix 9.1) (NCT, 2007). Both samplings occurred during low flow times of the year. Total recoverable metal levels almost certainly would be much higher under high flow conditions.

There has been very little analysis of metal levels of surface waters on the NCR. In June of 2001, the Northern Cheyenne Environmental Protection Department analyzed for 6 metals and arsenic in surface waters on the reservation (see Appendix 8.1). The metals analyzed were Al, B, Cd, Cu, Fe & Pb, and the form analyzed was total recoverable. The 2001 sampling and this study had the following sites in common: Tongue River Entering and Leaving, upper and lower Rosebud Creek, Muddy Creek, Lame Deer Creek, and two ponds below Crazy Head spring. The 2001 findings showed no violations of any standards.

In June 2001 Cd, Cu and Pb were below detection at all sites, however, the detection limits of the 2001 study were much higher than those of the current study. Al ranged from less than 0.1 mg/l to 0.9 mg/l; B ranged from 0.05 to 0. 53 mg/l and Fe from less than 0.08 to 1.78 mg/l. In 2009 & 2010, ranges for total recoverable metals were: 0.04 to 0.1 mg/L for Al; 0.05 to 0.5 mg/L for B; less than 0.002 to 0.8 mg/L for Fe. So the two studies had similar results for Al and B, but Fe had some higher levels in 2001. Given that 2001 sampling took place in June, it is surprising there were not much higher levels of total recoverable metals for all metals.

Arsenic was analyzed at the first pond of the Crazy Head Spring Recreational Area but not at the source sampled in this study. The content of the first pond was 9 ug/L (Appendix 8.1), which is near the EPA drinking water standard of 10 ug/L but is not in violation of that standard. The first pond's use is primarily for recreational purposes and livestock watering. The distance between the first pond and the Crazy Head Spring site reported in this study is 200-300 yards downstream through a wetland area. In comparison, arsenic levels in the August 2009 and January 2010 samples taken at the spring ranged from 12.2-13.5 ppb.

5.2 Why are Arsenic Levels in One Spring a Concern?

Crazy Head Springs is a culturally significant location for the Northern Cheyenne Tribe. The springs are used as a drinking water source by members of the Northern Cheyenne Tribe (Beck Consulting, 2007) and are the headwaters for the Crazy Head Ponds which are used for recreational purposes such as fishing and swimming. Downstream of the Crazy Head Ponds are ranches and farms that also use the water source for livestock watering and irrigation.

Arsenic occurs naturally in the environment and can be a by-product of agricultural and industrial uses of water. Some human health effects of many years of drinking water with arsenic levels above drinking water standards are:

- Thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhea, and liver effects;

- Cardiovascular, pulmonary, immunological, neurological (e.g., numbness and partial paralysis, reproductive, and endocrine (e.g., diabetes) effects; and
- Increasing risk of Cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate (EPA, 2007).

5.3 Feasibility and Cost of Removing Arsenic from Drinking Water

Zr-BPAP can be used to remove arsenic from Crazy Head Spring water to a safe level for human consumption. Zr-BPAP can be re-used after it is stripped with acid, allowing the composite to be used again and again to extract arsenic from polluted waters. This tool would allow the Crazy Head Springs site to continue to be a cultural, recreational, and agricultural benefit to the public.

The cost of treating Crazy Head Spring water depends on multiple variables specific to each treatment site. One pound of material needed for the treatment process would cost about twenty dollars. Other costs include: piping needed to attach to the spring, a water pump, the cost of getting electricity out to the site and the annual cost of using electricity, storage tanks for storing the material and maintenance of the tanks, labor and overhead. After factoring all these costs, a rough estimate would be <u>less than two cents per gallon</u> (Kailasam, 2010). And it would not be necessary to treat all the spring's flow – just that portion used for drinking water.

5.4 Possible Future Impacts of Nearby Energy Development on Reservation Surface Waters

The impacts of CBM development on the Northern Cheyenne Reservation surface waters continue to be studied. CBM discharge water has negative effects on soil, preventing landowners from using it directly for irrigation of farmland. However, the increase of CBM wells in the Tongue River Basin, where the Tribe has water rights, coupled with an arid landscape and drought conditions, means stream water used for summer irrigation may be predominantly CBM well water. Irrigating with contaminated stream water may reduce livestock forage and eliminate some crops. Increasing flow on ephemeral streams during times of the year when the stream beds would normally be dry could increase sedimentation downstream. The dewatering of aquifers to access the CBM will also impact rural communities that depend on water from these aquifers as their only water source. See Appendix 10.1 for irrigation season standards for electrical conductivity (EC) and sodium adsorption ratio (SAR) for the NCR.

Coal strip mining impacts on surface waters are similar to CBM development impacts but are more severe. In order to get to the coal, the aquifers above the coal seams must be dewatered. This is not done at a slow pace as is CBM aquifer dewatering. Dewatering for coal mining is done quickly because the main purpose is to mine coal not CBM. This increases the outgoing flow to holding ponds or streams which could lead to increases in sedimentation. The exposure of mine tailings in the overburden piles to natural weathering can also lead to increases in erosion and mine waste in surface waters.

CBM leases and the Otter Creek Tracts coal development threaten the Rosebud Creek and Tongue River watersheds on the NCR. These two watersheds are very important to the Tribe because they are the main waterways that flow through the reservation. It is important to monitor high priority parameters in these two watersheds such as hardness, EC, SAR, pH, arsenic, mercury, strontium, and any other trace metals and document any increase because of nearby energy development.

Recall that the hardness of water affects the toxicity of metals; hence the water quality standards for aquatic life are adjusted for hardness. In August 2009, surface water hardness on the Northern Cheyenne Reservation ranged from about 80 mg/L to 385 mg/L (see Appendix 7.2). As a result, copper standards, for example, exhibited a 4 to 5 fold range from the lowest to highest values.

The issue has been raised that CBM waters discharged to streams may alter their chemistry in a way that affects the toxicity of metals. There are some scenarios in which this may be the case. If the CBM water is softer and higher in toxic metals than the receiving water, then it could dilute stream hardness while adding metals. In addition, if a receiving water is hard mainly due to calcium sulfate and if the CBM discharge water is high in sodium carbonate, then it is likely that calcium carbonate and sodium sulfate will form in the receiving water. Much of the calcium carbonate will precipitate, lowering stream hardness (sodium sulfate does not affect hardness). So now the stream water is softer, and the toxic metals in the stream will be more toxic.

The Tribe should look at the water quality data they collected in 2001 (which includes analyses of cations and anions) and at analyses of CBM waters likely to reach the Tongue River and Rosebud Creek to determine if these waterbodies are at risk of such chemical alteration.

Chapter 6

Conclusions and Recommendations

Trace heavy metals concentrations in surface waters of the Northern Cheyenne Reservation are for the most part, at levels safe for human consumption and other uses. With rapid energy development encroaching on reservation land, it is important to have baseline information as a reference point, before sites such as the Otter Creek Tracts Coal Mine are developed. This will give the Northern Cheyenne Tribe a baseline to compare to future conditions, when coal mines and coal bed methane fields are developed near or on the reservation. These baseline levels will also be useful in determining what constitutes degradation of water quality on the NCR.

One site where water quality was a concern was Crazy Head Springs which violated drinking water standards one two samplings. Drinking water taken from this spring can be made safe by passing it through Zr-BPAP Silica Polyamine Composites for as little as two cents a gallon.

Tribal members should be notified of the arsenic levels in the Crazy Head Spring site until such a water purification system is put in place.

The Tribe should continue to monitor arsenic levels quarterly in the spring and the pond below the spring.

The Tribe should monitor Rosebud Creek and the Tongue River for high priority parameters such as hardness, EC, pH, SAR, arsenic, mercury, strontium and all other trace metals outlined in this report for increases due to nearby energy development. Quarterly sampling is recommended, but at a minimum, a base flow assessment and a rising spring hydrograph assessment are needed. Over time the Tribe should establish variability in parameters to refine the trigger values for degradation of surface waters on the NCR.

This paper only addressed surface water heavy metals and arsenic. An analysis of aquifers for heavy metals and arsenic needs to be done to establish baseline water quality. Water table levels should also be documented to establish a baseline and compared to if CBM extraction drawdown lowers local aquifers on the NCR.

Some specialized studies that may be useful include a spring sampling of reservation surface waters that catches the first snowmelt runoff to document if there is an acidic release of metals.

In addition a summer time diurnal assessment of water quality may reveal increases in metal levels due to bioturbation. This diurnal assessment can be done by students from local high schools or students and faculty from Chief Dull Knife College in Lame Deer.

The Tribe should amend their water quality standards for arsenic to be in compliance with the EPA's water quality standards. Currently the NCR's maximum contaminant level is at 14 ppb and the EPA's level is at 10 ppb. This would ensure that the Tribe is consistent with Federal standards and ensures the health and safety of the members on the reservation. The Tribe should also consider adopting the state of Montana's non-degradation trigger values of 2 ppb for arsenic and 0.01 ppb for mercury.

The lead detection level observed in the 2001 NCT data (Appendix 8.1) was at 20 ppb which is above the EPA drinking water action level of 15 ppb (Appendix 5.1). The NCT should use a method for analyzing lead that has an analytical detection limit below the EPA action level.

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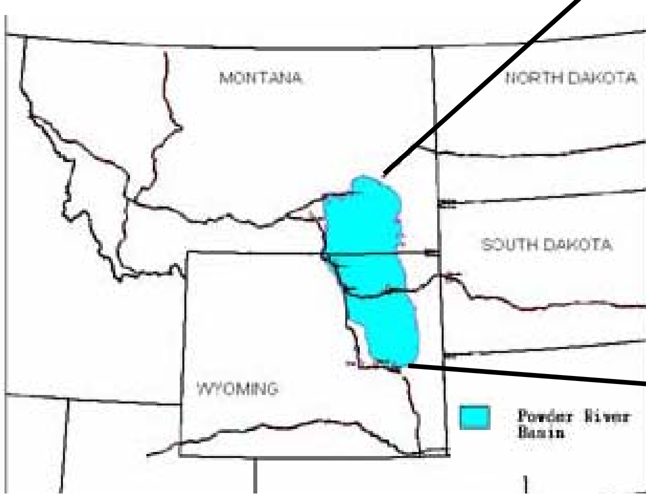
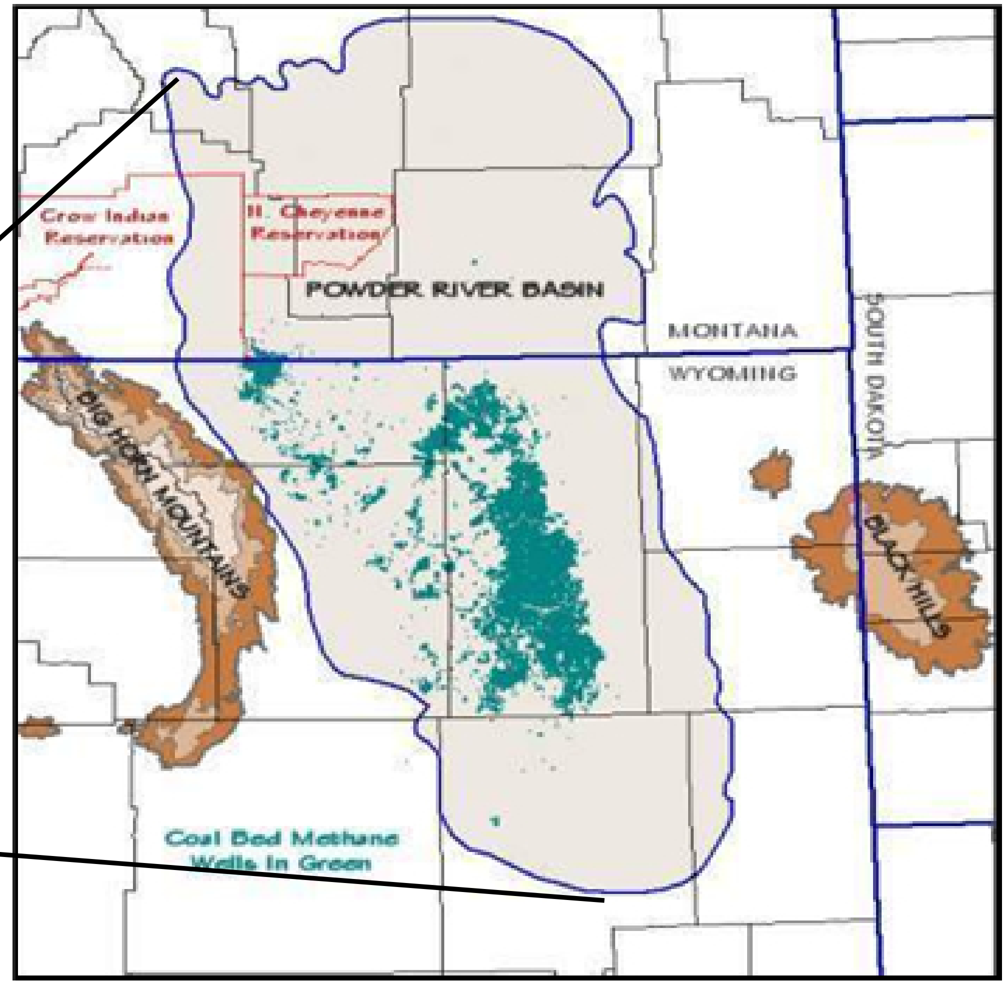
Appendices

Appendix 1.1 CBM Development in the Powder River Basin





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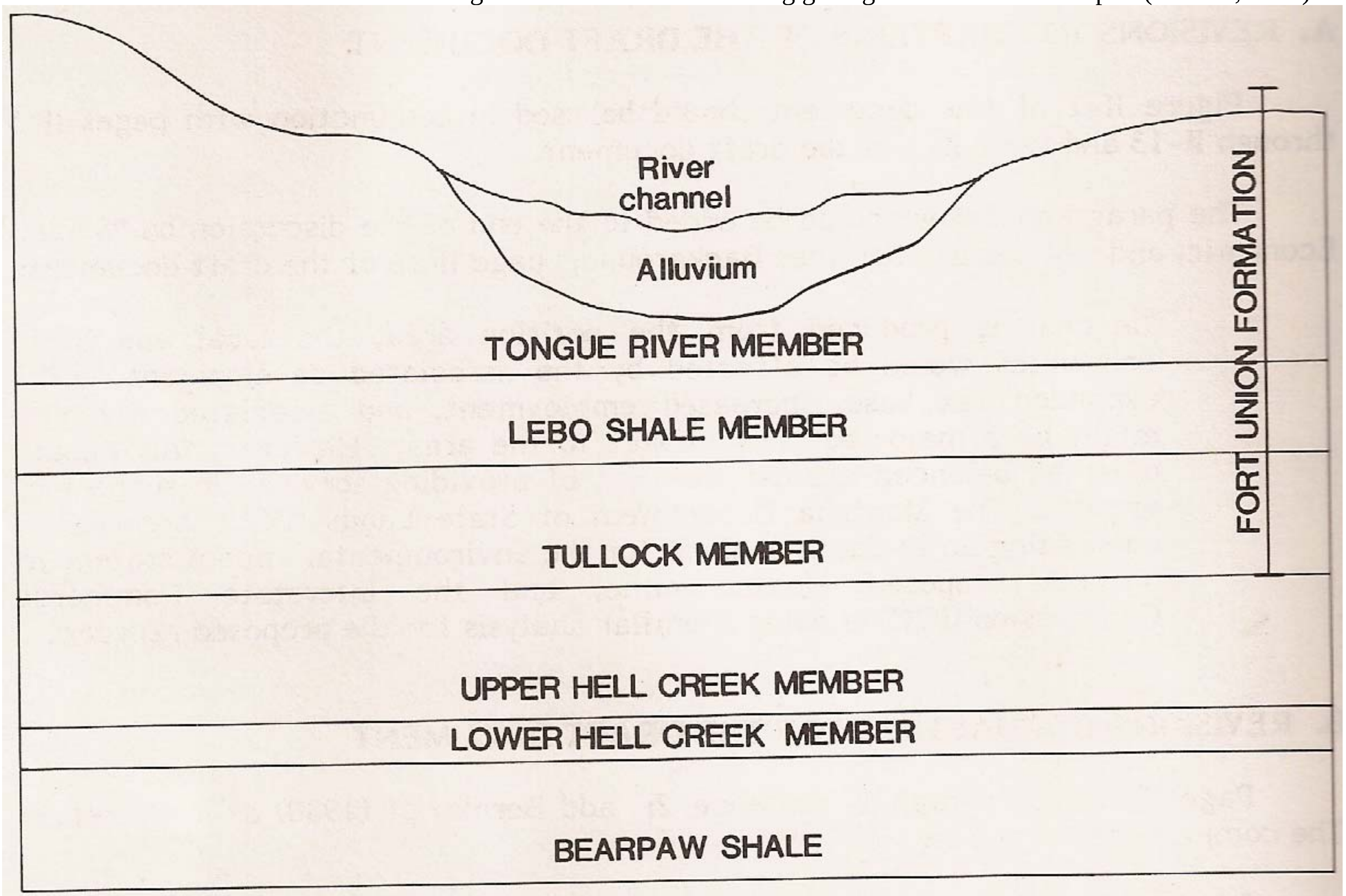
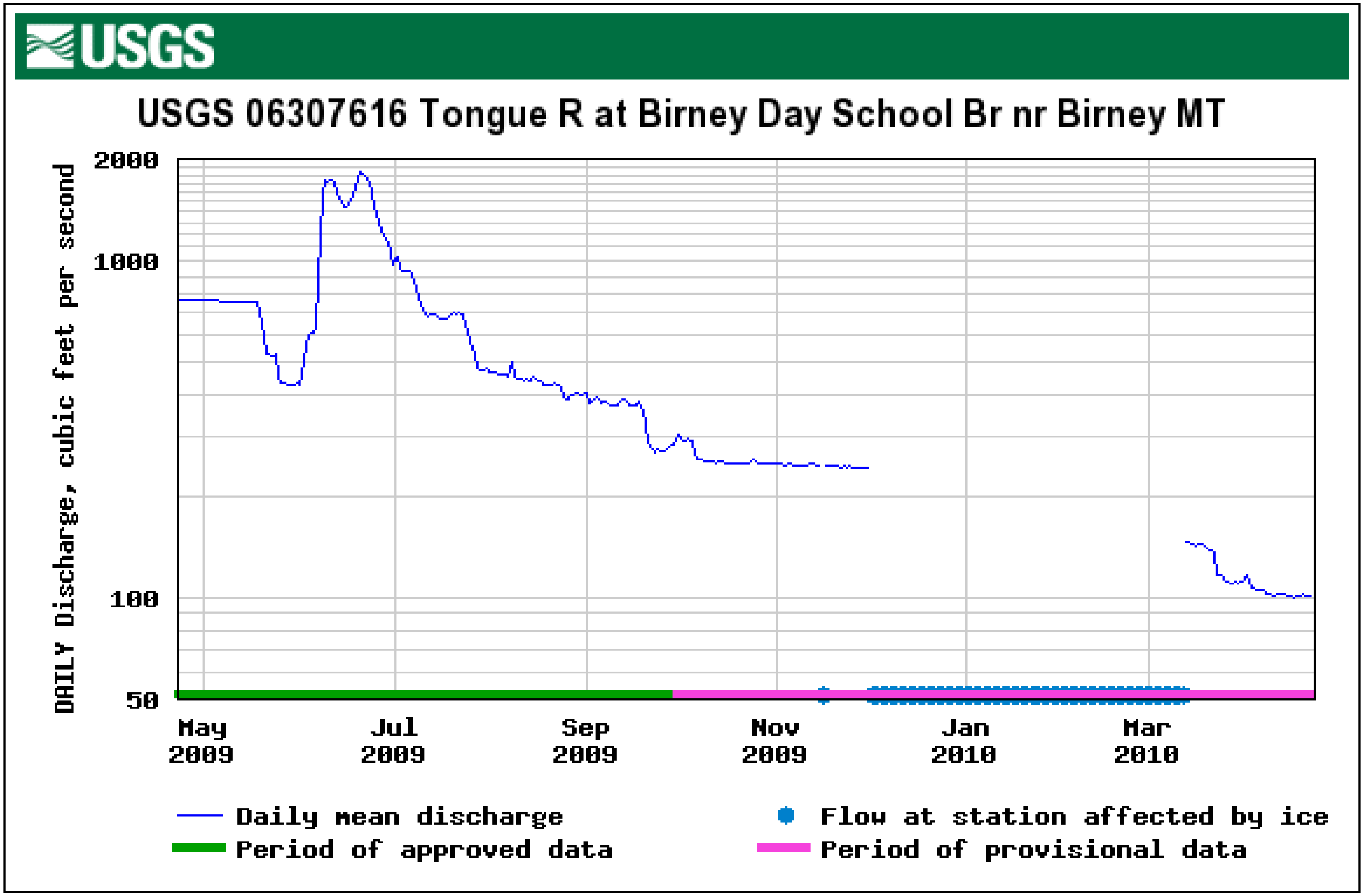
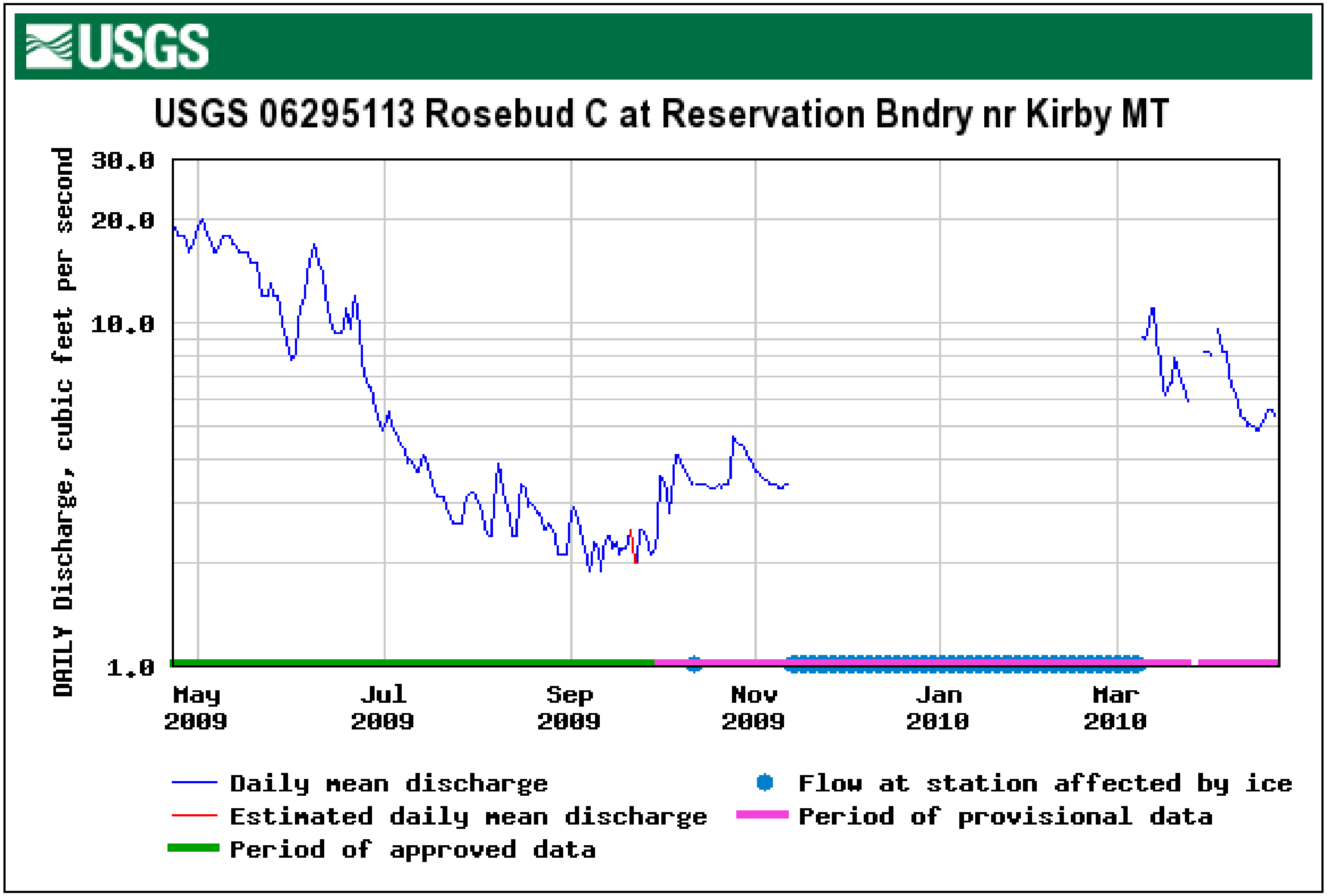
Appendix 2.1 Idealized cross-section of the Tongue River Watershed showing geological formations at depth. (USGSb, 1981)



Appendix 3.1 Daily mean flow of Birney Day School Rosebud County, Montana USGS monitoring station for 2009-2010. Latitude 45°24'42", Longitude 106°27'26". (USGSc)



Appendix 4.1 Daily mean flow of the Rosebud Creek at Reservation Boundary Bighorn County, Montana USGS monitoring station for 2009-2010. Latitude 45°21'40", Longitude 106°59'23". (USGSd)



Appendix 5.1 EPA 2006 Drinking Water Standards and Health Advisories, Inorganics (EPA, 2006)

Chemicals	CASRN Number	Standards			Status HA Document	Health Advisories						Cancer Descriptor
						10-kg Child						
		Status Reg.	MCLG (mg/L)	MCL (mg/L)		One-day (mg/L)	Ten-day (mg/L)	RfD (mg/kg/day)	DWEL (mg/L)	Life-time (mg/L)	mg/L at 10^{-4} Cancer Risk	
INORGANICS												
Ammonia	7664-41-7	-	-	-	D '92	-	-	-	-	30	-	D
Antimony	7440-36-0	F	0.006	0.006	F '92	0.01	0.01	0.0004	0.01	0.006	-	D
Arsenic	7440-38-2	F	zero	0.01	D '95	-	-	**0.0003**	0.01	-	**0.002**	A
Asbestos (fibers/l >10µm length)	1332-21-4	F	7 MFL[1]	7 MFL	-	-	-	-	-	-	700-MFL	A[2]
Barium	7440-39-3	F	2	2	D '93	0.7	0.7	**0.2**	7	-	-	**N**
Beryllium	7440-41-7	F	0.004	0.004	F '92	30	30	**0.002**	0.07	-	-	-
Boron	7440-42-8	-	-	-	D '92	4	0.9	**0.2**	7	1	-	**I**
Bromate	7789-38-0	F	zero	0.01	D '98	0.2	-	**0.004**	0.14	-	0.005	B2
Cadmium	7440-43-9	F	0.005	0.005	F '87	0.04	0.04	0.0005	0.02	0.005	-	D
Chloramine[3]	10599-90-3	F	4[4]	4[4]	D '95	-	-	0.1	3.5	3.0	-	
Chlorine	7782-50-5	F	4[4]	4[4]	D '95	3	3	0.1	5	4	-	D
Chlorine dioxide	10049-04-4	F	0.8[4]	0.8[4]	D '98	0.84	0.84	0.03	1	0.8	-	D
Chlorite	7758-19-2	F	0.8	1	D '98	0.84	0.84	0.03	1	0.8	-	D
Chromium (total)	7440-47-3	F	0.1	0.1	F '87	1	1	**0.003**[5]	0.1	-	-	D
Copper (at tap)	7440-50-8	F	1.3	TT[6]	D '98	-	-	-	-	-	-	D
Cyanide	143-33-9	F	0.2	0.2	F '87	0.2	0.2	0.02[7]	0.8	0.2	-	D
Fluoride	7681-49-4	F	4	4	-	-	-	**0.06**[8]	-	-	-	-
Lead (at tap)	7439-92-1	F	zero	TT[6]	-	-	-	-	-	-	-	B2
Manganese	7439-96-5	-	-	-	F'04	1	1	0.14[9]	1.6	0.3	-	D
Mercury (inorganic)	7487-94-7	F	0.002	0.002	F '87	0.002	0.002	**0.0003**	0.01	0.002	-	D
Molybdenum	7439-98-7	-	-	-	D '93	0.08	0.08	0.005	0.2	0.04	-	D
Nickel	7440-02-0	F	-	-	F '95	1	1	0.02	0.7	0.1	-	-

[1] MFL = million fibers per liter.
[2] Carcinogenicity based on inhalation exposure.
[3] Monochloramine; measured as free chlorine.
[4] 1998 Final Rule for Disinfectants and Disinfection By-products: MRDLG=Maximum Residual Disinfection Level Goal; and MRDL=Maximum Residual Disinfection Level.
[5] IRIS value for chromium VI.
[6] Copper action level 1.3 mg/L; lead action level 0.015 mg/L.
[7] This RfD is for hydrogen cyanide.
[8] Based on dental fluorosis in children, a cosmetic effect. MCLG based on skeletal fluorosis.
[9] Dietary manganese. The lifetime health advisory includes a 3 fold modifying factor to account for increased bioavailability from drinking water.

Appendix 5.2 EPA 2006 Drinking Water Standards and Health Advisories, Inorganics, Continued (EPA, 2006)

Chemicals	CASRN Number	Standards			Status HA Document	Health Advisories						Cancer Descriptor
						10-kg Child						
		Status Reg.	MCLG (mg/L)	MCL (mg/L)		One-day (mg/L)	Ten-day (mg/L)	RfD (mg/kg/day)	DWEL (mg/L)	Life-time (mg/L)	mg/L at 10^{-4} Cancer Risk	
Nitrate (as N)	14797-55-8	F	10	10	D '93	10[1]	10[1]	1.6	-	-	-	-
Nitrite (as N)	14797-65-0	F	1	1	D '93	1[1]	1[1]	0.16	-	-	-	-
Nitrate + Nitrite (both as N)		F	10	10	D '93	-	-	-	-	-	-	-
Selenium	7782-49-2	F	0.05	0.05	-	-	-	0.005	0.2	0.05	-	D
Silver	7440-22-4	-	-	-	F '92	0.2	0.2	0.005[2]	0.2	0.1	-	D
Strontium	7440-24-6	-	-	-	D '93	25	25	**0.6**	20	4	-	D
Thallium	7440-28-0	F	0.0005	0.002	F '92	0.007	0.007	0.00007	0.002	0.0005	-	-
White phosphorous	7723-14-0	-	-	-	F '90	-	-	0.00002	0.0005	0.0001		D
Zinc	7440-66-6	-	-	-	D '93	6	6	0.3	10	2	-	I
RADIONUCLIDES												
Beta particle and photon activity (formerly man-made radionuclides)		F	zero	4 mrem/yr	-	-	-	-	-	-	4 mrem/yr	A
Gross alpha particle activity		F	zero	15 pCi/L	-	-	-	-	-	-	15 pCi/L	A
Combined Radium 226 & 228	7440-14-4	F	zero	5 pCi/L	-	-	-	-	-	-	-	A
Radon	10043-92-2	P	zero	300 pCi/L AMCL[3] 4000 pCi/L	-	-	-	-	-	-	150 pCi/L	A
Uranium	7440-61-1	F	zero	30 µg/L	-	-	-	0.0006[4]	0.02	-	-	A

[1] These values are calculated for a 4-kg infant and are protective for all age groups.
[2] Based on a cosmetic effect.
[3] AMCL = Alternative Maximum Contaminant Level
[4] Soluble uranium salts. Radionuclide Rule.

Appendix 6.1 EPA 2006 Drinking Water Standards and Health Advisories, Secondary Drinking Water Regulations (EPA, 2006)

Chemicals	CAS Number	Status	SDWR
Aluminum	7429-90-5	F	0.05 to 0.2 mg/L
Chloride	7647-14-5	F	250 mg/L
Color	NA	F	15 color units
Copper	7440-50-8	F	1.0 mg/L
Corrosivity	NA	F	non-corrosive
Fluoride	7681-49-4	F	2.0 mg/L
Foaming agents	NA	F	0.5 mg/L
Iron	7439-89-6	F	0.3 mg/L
Manganese	7439-96-5	F	0.05 mg/L
Odor	NA	F	3 threshold odor numbers
pH	NA	F	6.5 – 8.5
Silver	7440-22-4	F	0.1 mg/L
Sulfate	7757-82-6	F	250 mg/L
Total dissolved solids (TDS)	NA	F	500 mg/L
Zinc	7440-66-6	F	5 mg/L

Appendix 7.1. MT Water Quality Standards for aquatic life, total recoverable metals for samples collected in summer 2009 on Northern Cheyenne Reservation.

site	hardness as CaCO3 **mg/L**	Cu acute **µg/L**	Cu chronic **µg/L**	**obs Cu µg/L**	Cr **µg/L**	Cr **µg/L**	**obs Cr µg/L**	Pb **µg/L**	Pb **µg/L**	**obs Pb µg/L**	Ni **µg/L**	Ni **µg/L**	**obs Ni µg/L**
Birney Springs	171.5	23.3	14.8	**6.3**	2804.7	134.1	**0.3**	162.2	6.3	**0.6**	740.5	82.3	**0.2**
Tongue River Entering	78.2	11.1	7.6	**4.5**	1473.8	70.4	**0.5**	59.7	2.3	**0.6**	381.0	42.4	**1.2**
Tongue River Exiting	82.0	11.6	7.9	**4.3**	1532.7	73.3	**0.6**	63.4	2.5	**0.7**	396.7	44.1	**1.3**
Upper Muddy Cr	281.9	37.2	22.6	**4.0**	4214.0	201.4	**0.5**	305.5	11.9	**<0.76**	1127.7	125.4	**0.8**
Crazy Head Springs	80.6	11.4	7.8	**2.5**	1511.5	72.2	**2.7**	62.1	2.4	**0.2**	391.0	43.5	**0.1**
Upper Alderson Cr	88.5	12.5	8.4	**1.2**	1630.9	77.9	**0.7**	69.9	2.7	**0.3**	423.0	47.0	**0.3**
Lower Alderson Cr	146.5	20.1	12.9	**1.3**	2464.5	117.8	**0.3**	132.7	5.2	**0.4**	647.9	72.0	**0.4**
Upper Lame Deer Cr	167.0	22.7	14.5	**1.1**	2743.8	131.1	**0.3**	156.8	6.1	**0.3**	723.9	80.5	**0.4**
Middle Lame Deer Cr	201.6	27.1	17.0	**1.2**	3201.5	153.0	**0.2**	199.3	7.8	**0.3**	849.0	94.4	**0.7**
Lower Lame Deer Cr	245.5	32.6	20.1	**1.1**	3762.5	179.8	**0.3**	256.1	10.0	**<0.76**	1003.1	111.5	**1.2**
Lower Muddy Cr	384.6	49.8	29.5	**2.4**	5434.4	259.7	**0.9**	453.6	17.7	**<1.52**	1466.5	163.0	**1.2**
Lower Rosebud	160.3	21.8	14.0	**2.5**	2653.4	126.8	**0.6**	148.8	5.8	**0.9**	699.3	77.7	**1.8**
Upper Rosebud	153.8	21.0	13.5	**2.7**	2564.6	122.6	**0.3**	141.2	5.5	**0.6**	675.1	75.1	**1.0**
Middle Rosebud	129.9	17.9	11.7	**1.7**	2233.9	106.8	**0.3**	113.9	4.4	**0.4**	585.4	65.1	**1.1**

Appendix 7.2. MT Water Quality Standards for aquatic life, dissolved metals for samples collected in summer 2009 on Northern Cheyenne Reservation.

site	hardness as CaCO3 **mg/L**	Cu acute **µg/L**	Cu chronic **µg/L**	**obs Cu µg/L**	Cr **µg/L**	Cr **µg/L**	**obs Cr µg/L**	Pb **µg/L**	Pb **µg/L**	**obs Pb µg/L**	Ni **µg/L**	Ni **µg/L**	**obs Ni µg/L**
Birney Springs	171.5	23.3	14.8	**0.8**	2804.7	134.1	**<0.04**	162.2	6.3	**<0.15**	740.5	82.3	**<0.10**
Tongue River Entering	78.2	11.1	7.6	**0.7**	1473.8	70.4	**<0.04**	59.7	2.3	**<0.15**	381.0	42.4	**0.7**
Tongue River Exiting	82.0	11.6	7.9	**0.7**	1532.7	73.3	**<0.04**	63.4	2.5	**<0.15**	396.7	44.1	**0.7**
Upper Muddy Cr	281.9	37.2	22.6	**<2.00**	4214.0	201.4	**<0.20**	305.5	11.9	**<0.76**	1127.7	125.4	**0.5**
Crazy Head Springs	80.6	11.4	7.8	**0.4**	1511.5	72.2	**2.4**	62.1	2.4	**<0.15**	391.0	43.5	**<0.10**
Upper Alderson Cr	88.5	12.5	8.4	**<0.40**	1630.9	77.9	**0.2**	69.9	2.7	**<0.15**	423.0	47.0	**<0.10**
Lower Alderson Cr	146.5	20.1	12.9	**<0.40**	2464.5	117.8	**<0.04**	132.7	5.2	**<0.15**	647.9	72.0	**<0.10**
Upper Lame Deer Cr	167.0	22.7	14.5	**<0.40**	2743.8	131.1	**<0.04**	156.8	6.1	**<0.15**	723.9	80.5	**0.3**
Middle Lame Deer Cr	201.6	27.1	17.0	**0.5**	3201.5	153.0	**<0.04**	199.3	7.8	**<0.15**	849.0	94.4	**0.5**
Lower Lame Deer Cr	245.5	32.6	20.1	**0.4**	3762.5	179.8	**<0.04**	256.1	10.0	**<0.15**	1003.1	111.5	**0.6**
Lower Muddy Cr	384.6	49.8	29.5	**2.5**	5434.4	259.7	**<0.20**	453.6	17.7	**<0.76**	1466.5	163.0	**1.0**
Lower Rosebud	160.3	21.8	14.0	**0.8**	2653.4	126.8	**<0.04**	148.8	5.8	**<0.15**	699.3	77.7	**1.2**
Upper Rosebud	153.8	21.0	13.5	**0.6**	2564.6	122.6	**<0.04**	141.2	5.5	**<0.15**	675.1	75.1	**0.7**
Middle Rosebud	129.9	17.9	11.7	**0.6**	2233.9	106.8	**<0.04**	113.9	4.4	**<0.15**	585.4	65.1	**0.8**

Appendix 8.1. Northern Cheyenne Metal Analysis Results conducted in 2003. (Courtesy of the Northern Cheyenne Environmental Protection Department)

Station Name	**StationType1**	**County**	**Al**	**As**	**B**	**Cd**	**Cu**	**Fe**	**Pb**
Detection Limit			**0.1**	**0.005**	**0.01**	**0.002**	**0.01**	**0.05**	**0.02**
			mg/L	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Rosebud Creek South Boundary	River/Stream	Bighorn	ND	ND	0.08	ND	ND	0.16	ND
Muddy Creek	River/Stream	Bighorn	0.5	ND	0.16	ND	ND	1.78	ND
Muddy Creek	River/Stream	Bighorn	ND	ND	0.53	ND	ND	0.35	ND
Rosebud Creek North Boundary	River/Stream	Rosebud	ND	ND	0.18	ND	ND	0.14	ND
Lame Deer	River/Stream	Rosebud	ND	ND	0.11	ND	ND	ND	ND
Lame Deer	River/Stream	Rosebud	0.3	ND	0.2	ND	ND	0.51	ND
Lame Deer	River/Stream	Rosebud	0.1	ND	0.22	ND	ND	0.4	ND
Lame Deer	River/Stream	Rosebud	ND	ND	0.26	ND	ND	0.14	ND
Stebbins Creek Downstream	River/Stream	Rosebud	0.9	ND	0.09	ND	ND	1.35	ND
Stebbins Creek	River/Stream	Rosebud	0.3	ND	0.05	ND	ND	0.27	ND
Club Foot Creek	River/Stream	Rosebud	0.2	ND	0.09	ND	ND	0.28	ND
Pawnee Creek	River/Stream	Rosebud	ND	ND	0.05	ND	ND	ND	ND
1st Pond	Lake	Rosebud	ND	0.009	0.09	ND	ND	0.08	ND
4th Pond	Lake	Rosebud	ND	ND	0.07	ND	ND	ND	ND
Tongue River at Birney Bridge	River/Stream	Rosebud	0.5	ND	0.07	ND	ND	1.04	ND
Tongue River North Boundary	River/Stream	Rosebud	0.8	ND	0.09	ND	ND	1.59	ND

*ND = Not Detected

Appendix 9.1. Northern Cheyenne Numeric Water Quality Standards Chart for Priority Pollutants.

NORTHERN CHEYENNE TRIBE

Numeric Water Quality Standards Chart for Priority Pollutants

(Footnotes A-O)

Priority Pollutants	CASRN	Freshwater-Aquatic Life:		Human Health for Consumption of:	
		ACUTE (CMC) (µg/L)	CHRONIC (CCC) (µg/L)	Water + Organism (µg/L)	Organism only (µg/L)
1. Antimony	74403060			5.6	640
2. Arsenic	7440382	340 [A]	150 [A]	0.018 [B,L]	0.14 [B,L]
3. Beryllium	7440417			[F]	[F]
4. Cadmium	7440439	2.0	0.27 [C,P]	[F]	[F]
5a. Chromium III	16065831	1804 [C,P]	74 [C,P]	[F]	[F]
5b. Chromium VI	18540299	16 [P]	11 [P]	[F]	[F]
6. Copper	7440508	13 [C,N,P]	9.0 [C,N,P]	1,300	
7. Lead	7439921	82 [C,P]	3.2 [C,P]	[F]	[F]
8. Mercury	7439976	1.7 [O,P]	0.012 [O,P]	0.050	0.051
9. Nickel	7440020	470 [C,P]	52 [C,P]	610	4,600
10. Selenium	7782492	[G]	5.0	170	4,200
11. Silver	7440224	4.1 [C,E,P]	0.12 [P]		
12. Thallium	7440280			0.24	0.47
13. Zinc	7440666	120 [C,P]	120 [C,P]	7,400	26,000
14. Cyanide	57125	22 [K,P]	5.2 [K,P]	140	140
15. Asbestos	1332214			7 million fibers/L	
16. 2,3,7,8-TCDD Dioxin	1746016			5.0 E^{-9} [B]	5.1 E^{-9} [B]
17. Acrolein	107028			190	290
18. Acrylonitrile	107131			.051 [B]	.25 [B]
19. Benzene	71432			2.2 [B]	51 [B]
20. Bromoform	75252			4.3 [B]	140 [B]
21. Carbon Tetrachloride	56235			0.23 [B]	1.6 [B]
22. Chlorobenzene	108907			130	1,600
23. Chlorodibromomethane	124481			0.40 [B]	13 [B]
24. Chloroethane	75003				
25. 2-Chloroethylvinyl Ether	110758				
26. Chloroform	67663			5.7 [B]	470 [B]
27. Dichlorobromomethane	75274			0.55 [B]	17 [B]
28. 1,1-Dichloroethane	75343				
29. 1,2-Dichloroethane	107062			.38 [B]	37 [B]
30. 1,1-Dichloroethylene	75354			330 [B]	7,100 [B]
31. 1,2-Dichloropropane	78875			0.50 [B]	15 [B]

A1

Appendix 9.2. Northern Cheyenne Numeric Water Quality Standards Chart for Priority Pollutants,
Continued

Priority Pollutants	CASRN	Freshwater-Aquatic Life:		Human Health for Consumption of:	
		ACUTE (CMC) (µg/L)	CHRONIC (CCC) (µg/L)	Water + Organism (µg/L)	Organism only (µg/L)
32. 1,3-Dichloropropene	542756			0.34	21
33. Ethylbenzene	100414			530	2,100
34. Methyl Bromide	74839			47	1,500
35. Methyl Chloride	74873			F	F
36. Methylene Chloride	75092			4.6 B	590 B
37. 1,1,2,2-Tetrachloroethane	79345			0.17 B	4.0 B
38. Tetrachloroethylene	127184			0.69 B	3.3 B
39. Toluene	108883			1,300	15,000
40. 1,2-Trans-Dichloroethylene	156605			140	10,000
41. 1,1,1-Trichloroethane	71556			F	F
42. 1,1,2-Trichloroethane	79005			0.59 B	16 B
43. Trichloroethylene	79016			2.5 B	30 B
44. Vinyl Chloride	75014			0.025 B	2.4 B
45. 2-Chlorophenol	95578			81	150
46. 2,4-Dichlorophenol	120832			77	290
47. 2,4-Dimethylphenol	105679			380	850
48. 2-Methyl-4,6-Dinitrophenol	534521			13	280
49. 2,4-Dinitrophenol	51285			69	5,300
50. 2-Nitrophenol	88755				
51. 4-Nitrophenol	100027				
52. 3-Methyl-4-Chlorophenol	59507				
53. Pentachlorophenol	87865	19 D	15 D	0.27 B	3.0 B
54. Phenol	108952			21,000	1,700,000
55. 2,4,6-Trichlorophenol	88062			1.4 B	2.4 B
56. Acenaphthene	83329			670	990
57. Acenaphthylene	208968				
58. Anthracene	120127			8,300	40,000
59. Benzidine	92875			0.000086 B	0.00020B
60. BenzoaAnthracene	56553			0.0038 B	0.018 B
61. BenzoaPyrene	50328			0.0038 B	0.018 B
62. BenzobFluoranthene	205992			0.0038 B	0.018 B
63. BenzoghiPerylene	191242				
64. BenzokFluoranthene	207089			0.0038 B	0.018 B
65. Bis2-ChloroethoxyMethane	111911				
66. Bis2-ChloroethylEther	111444			0.030 B	0.53 B
67. Bis2-ChloroisopropylEther	108601			1,400	65,000
68. Bis2-EthylhexylPhthalate x	117817			1.2 B	2.2 B
69. 4-Bromophenyl Phenyl Ether	101553				
70. Butylbenzyl Phthalate w	85687			1,500	1,900

Appendix 9.3. Northern Cheyenne Numeric Water Quality Standards Chart for Priority Pollutants,
Continued

Priority Pollutants	CASRN	Freshwater-Aquatic Life:		Human Health for Consumption of:	
		ACUTE (CMC) (µg/L)	CHRONIC (CCC) (µg/L)	Water + Organism (µg/L)	Organism only (µg/L)
71. 2-Chloronaphthalene	91587			1,000	1,600
72. 4-Chlorophenyl Phenyl Ether	7005723				
73. Chrysene	218019			0.0038 [B]	0.018 [B]
74. Dibenzoa,hAnthracene	53703			0.0038 [B]	0.018 [B]
75. 1,2-Dichlorobenzene	95501			420	1,300
76. 1,3-Dichlorobenzene	541731			320	960
77. 1,4-Dichlorobenzene	106467			63	190
78. 3,3-Dichlorobenzidine	91941			0.021 [B]	0.028 [B]
79. Diethyl Phthalate w	84662			17,000	44,000
80. Dimethyl Phthalate w	131113			270,000	1,100,000
81. Di-n-Butyl Phthalate w	84742			2,000	4,500
82. 2,4-Dinitrotoluene	121142			0.11 [B]	3.4 [B]
83. 2,6-Dinitrotoluene	606202				
84. Di-n-Octyl Phthalate	117840				
85. 1,2-Diphenylhydrazine	122667			0.036 [B]	0.20 [B]
86. Flouranthene	206440			130	140
87. Flourene	86737			1,100	5,300
88. Hexachlorobenzene	118741			0.00028 [B]	0.00029 [B]
89. Hexachlorobutadiene	87683			0.44 [B]	18 [B]
90. Hexachlorocyclopentadiene	77474			40	1,100
91. Hexachloroethane	67721			1.4 [B]	3.3 [B]
92. Ideno 1,2,3-cdPyrene	193395			0.0038 [B]	0.018 [B]
93. Isophorone	78591			35 [B]	960 [B]
94. Naphthalene	91203				
95. Nitrobenzene	98953			17	690
96. N-Nitrosodimethylamine	62759			0.00069 [B]	3.0 [B]
97. N-Nitrosodi-n-Propylamine	621647			0.005 [B]	0.51 [B]
98. N-Nitrosodiphenylamine	86306			3.3 [B]	6.0 [B]
99. Phenanthrene	85018				
100. Pyrene	129000			830	4,000
101. 1,2,4-Trichlorobenzene	120821			35	70
102. Aldrin	309002	3.0 [E]		0.000049 [B]	0.000050[B]
103. alpha-BHC	319846			0.0026 [B]	0.0049 [B]
104. beta-BHC	319857			0.0091 [B]	0.017 [B]
105. gamma-BHC (Lindane)	58899	0.95		0.98 [B]	1.8 [B]
106. delta-BHC	319868				
107. Chlordane	57749	2.4 [E]	0.0043 [E]	0.00080	0.00081

Appendix 9.4. Northern Cheyenne Numeric Water Quality Standards Chart for Priority Pollutants, Continued.

Priority Pollutants	CASRN	Freshwater-Aquatic Life:		Human Health for Consumption of:	
		ACUTE (CMC) (µg/L)	CHRONIC (CCC) (µg/L)	Water + Organism (µg/L)	Organism only (µg/L)
108. 4,4-DDT	50293	1.1 [E]	0.001 [E]	0.00022 [B]	0.00022 [B]
109. 4,4-DDE	72559			0.00022 [B]	0.00022 [B]
110. 4,4-DDD	72548			0.00031 [B]	0.00031 [B]
111. Dieldrin	60571	0.24	0.056 [I]	0.000052 [B]	0.000054[B]
112. alpha-Endosulfan	959988	0.22 [E,M]	0.056 [E,M]	62	89
113. beta-Endosulfan	33213659	0.22 [E,M]	0.056 [E,M]	62	89
114. Endosulfan Sulfate	1031078			62	89
115. Endrin	72208	0.086	0.036 [I]	0.059	0.060
116. Endrin Aldehyde	7421934			0.29	0.30
117. Heptachlor	76448	0.52 [E]	0.0038 [E]	0.000079 [B]	0.000079[B]
118. Heptachlor Epoxide	1024573	0.52 [E]	0.0038 [E]	0.000039 [B]	0.000039[B]
119. Polychlorinated Biphenyls PCB's			0.014 [H]	0.000064 [B,J]	0.000064 [B,J]
120. Toxaphene	8001352	0.73	0.0002	0.00028 [B]	0.00028 [B]

Priority Footnotes:

A. Applies to total arsenic.

B. Based on carcinogenicity of 10^{-6} risk.

C. Freshwater Aquatic life Standards for these metals are expressed as a function of total hardness (mg/L, $CaCO_3$). The values displayed in the chart correspond to a total hardness of 100 mg/L. The hardness relationship is as follows:

	Acute = exp {ma [ln (hardness)] + ba}		Chronic = exp {mc [ln (hardness)] + bc}	
	ma	ba	mc	bc
Cadmium	1.0166	-3.924	0.7409	-4.719
Copper	0.9422	-1.700	0.8545	-1.702
Chromium III	0.8190	3.7256	0.8190	.6848
Lead	1.273	-1.460	1.273	-4.705
Nickel	0.8460	2.255	0.8460	.0584
Silver	1.72	-6.59	--------	--------
Zinc	0.8473	0.884	0.8473	0.884

Note: If the hardness is greater than or equal to 400 mg/L of $CaCO_3$, 400 mg/L will be used in the calculation.

Appendix 9.5. Northern Cheyenne Numeric Water Quality Standards Chart for Priority Pollutants, Continued.

D. Freshwater Aquatic Life values for pentachlorophenol are expressed as a function pH, and are calculated as follows: Acute CMC = exp [1.005 (pH) – 4.869]; Chronic CCC=exp [1.005 (pH) – 5.134]. Values displayed in table correspond to a pH of 7.8.

E. If assessment is to be done using an averaging period; the values should be divided by 2.

F. EPA has not calculated a human health criterion for this contaminant. However, permit authorities should address this contaminant in NPDES permit actions using the Tribe's existing narrative criteria for toxics. (see MCLs)

G. The CMC=1/[(f1/CMC)+(f2/CMC2)] where f1 and f2 are the fractions of total selenium that are treated as selenite and selenate, respectively, and CMC1 and CMC2 are 186 µg/l and 13 µg/l, respectively.

H. PCB's are a class of chemicals which include all aroclors.

I. The derivation of the chronic (CCC) standard for this pollutant did not consider exposure through the diet, which is probably important for aquatic life occupying upper tropic levels.

J. This standard applies to total PCBs.

K. This water quality standard is expressed as µg free cyanide (as CN)/L.

L. This water quality standard refers to the inorganic form only.

M. This standard was derived from data for endosulfan and is most appropriately applied to the sum of alpha-endosulfan and beta-endosulfan.

N. Under conditions of high dissolved organic carbon, copper is substantially less toxic and the Tribe will consider use of the Water Effect-Ratio.

O. EPA Region 8 recommends adopting this CCC value for Mercury while maintaining the existing Human Health values, as an interim step until EPA completes Guidance for implementation of the fish tissue value (0.3 mg/kg) for the protection of human health. This CCC value should be protective of Human Health for fish consumption.

P. The numeric water quality standards for metals are expressed as the total recoverable form of the metal.

Appendix 10.1. Northern Cheyenne Tribe Irrigation Standards (WyBLM, 2002).

WQS for Electrical Conductivity (EC) and Sodium Adsorption Ratio (SAR) Adopted by the Northern Cheyenne Tribe

The Northern Cheyenne Tribe's EC and SAR numerical standards were adopted by the Tribal Council on May 28, 2002. The numerical standards apply to the Tongue River and tributaries within the boundaries of the Reservation.

Tongue River (within the Reservation Boundaries)	Irrigation Season (4/1 – 11/15)	Criteria Applicable All Year		Notes
	EC (30-day ave.)	EC (inst. max.)	SAR (inst. max.)	The Tribe has also adopted indicator values for total dissolved solids (TDS) that will be used to monitor conditions and trends of these waters.
Southern Boundary	1,000	2,000	2.0	
Northern Boundary	1,500	2,000	3.0	
Tributaries	1,500	2,000	3.0	