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Shallow Groundwater Quality and Geochemistry in the Shields River Basin, South-Central Montana

by

Daniel D. Blythe

A non-thesis project report submitted in partial fulfillment of the requirements for the degree of

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2015

Abstract

Water samples were collected from 33 domestic wells, 2 springs, and 3 streams in the Shields River Basin (Basin) in southwest Montana. Samples were collected in 2013 to describe the chemical quality of groundwater in the Basin. Sampling was done to assess potential impacts to water quality from recent exploratory oil and gas drilling and to establish baseline water quality conditions. Wells were selected in areas near and away from oil and gas drilling and in areas susceptible to contamination. Water samples from surface water sites were collected in October to characterize base flow conditions. Physical characteristics of the land surface, soils, and shallow aquifers were used to assess groundwater susceptibility to contamination from the land surface. This analysis was completed using GIS.

Samples were analyzed for major ions, trace metals, water isotopes of oxygen and hydrogen. A subset (24) of samples were analyzed for tritium and organic constituents (GRO, DRO, BTEX, methane, ethylene, and ethane). One sample exceeded the human health drinking water standard for selenium. Dissolved methane and ethylene gas were detected in six samples at concentrations less than 0.184 milligrams per liter. Three locations were resampled in 2014, and no methane or ethylene was detected.

Shallow groundwater and streams are generally calcium- or sodium-bicarbonate type water with total dissolved solids concentration less than 300 milligrams per liter. Some wells produce either sodium-chloride or sodium-sulfate type water suggesting slower flow paths and more rock-water interaction. Tritium concentrations suggest that older water (TU< 0.8), recharged prior to the mid-1950’s, is generally sodium type, whereas younger water (TU > 4) is generally a calcium type.

Water-quality data from this study were compared to available historic data in the Basin. Additionally, the USGS Produced Waters Geochemical database was queried for chemical data of produced waters from reservoir rocks throughout Montana and the surrounding states. Comparisons to historic and produced water chemical data suggest no impact to shallow groundwater quality from exploratory oil and gas drilling.

Keywords: Shields Valley, Oil and Gas Drilling, Shields Valley Watershed Group, Shields River Basin, Park County Conservation District

Acknowledgements

The author appreciates assistance from many individuals and organizations enabling completion of this project. This work was conducted as part of the MBMG Ground Water Characterization Program in cooperation with the Park County Conservation District and the Shields Valley Watershed Group. The Watershed Group and Conservation District provided invaluable landowner contact information in areas targeted for sampling. In addition, landowners who allowed access to their wells or springs are gratefully appreciated. Don Mason from the MBMG assisted with fieldwork; his 20 years of experience conducting well inventories undoubtedly improved the consistency and quality of data used in this report. Reviews by Dr. Glenn Shaw (Montana Tech), John LaFave (MBMG), Dr. Beverly Hartline (Montana Tech) and Dr. Elizabeth Meredith (MBMG – Billings) added to the clarity and readability of this report.

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Glossary of Terms

Term	Definition
API number	American Petroleum Institute's unique, permanent identifier assigned to each oil and gas well in the US
CBMPP	Coalbed Methane Protection Program
DEQ	Montana Department of Environmental Quality
DNRC	Montana Department of Natural Resources and Conservation
DOI	U.S. Department of the Interior
EIA	Energy Information Administration
EPA	Environmental Protection Agency
ESRI	Environmental Systems Research Institute (provider of GIS and GIS management software and applications)
Flowback	Water produced by oil and gas wells usually a mix of formation water and fracturing fluids, also referred to as "produced water"
Formation waters	Water occurring naturally within the pores of rock
Fracturing fluids	A mixture of water and additives used to hydraulically induce cracks in the target formation
GIS	Geographic Information System
GPS	Global Positioning System
GWAP	Ground Water Assessment Program (MBMG research program)
GWCP	Ground Water Characterization Program (MBMG research program)
GWIC	Ground Water Information System (maintained by the MBMG)
Hydraulic fracturing	Injecting fracturing fluids into the target formation at a force exceeding the parting pressure of the rock thus inducing a network of fractures through which oil or gas can flow into the well
IAEA	International Atomic Energy Agency
MBMG	Montana Bureau of Mines and Geology
MBOG	Montana Board of Oil and Gas
mg/L	Milligrams per liter – roughly equal to parts-per-million (ppm)
µg/L	Micrograms per liter - roughly equal to parts-per-billion (ppb)
Produced water	Excess water produced during oil and gas production, usually a mixture of fracturing fluids and formation waters
Stray gas	Gases occurring in an unexpected environment.
SOP	Standard operating procedures
SVWG	Shields Valley Watershed Group

Introduction

The Shields River Basin (Basin) covers nearly 855 square miles in south-central Montana. Most land is open range with some irrigated fields adjacent to the Shields River; uplands are National Forest lands. Between 2007 and 2009, seven oil and gas wells were drilled. The drilling raised concerns with residents about potential degradation of shallow groundwater quality. To assess potential impacts from the drilling and establish baseline water quality, 33 domestic wells, two springs, and three surface water sites were sampled in 2013. Some resampling occurred in 2014. All samples were analyzed for major ions, trace metals, and water isotopes; with a subset analyzed for tritium and organic compounds. This project was completed as part of the Montana Bureau of Mines and Geology (MBMG) Ground Water Assessment Program (GWAP). The Shields Valley Watershed Group (SVWG) and the Park County Conservation District provided financial assistance for the analysis of tritium and the organic compounds.

Note: the term "shallow groundwater" used in this report indicates usable water within 1,000 ft of land surface with a total dissolved solids (TDS) content of 1,000 mg/L or less.

1. Purpose and Scope

This report provides general hydrogeologic and groundwater quality information for the Shields River Basin. Data collected from existing wells, springs, and streams were used to characterize groundwater conditions and assess the impact from exploratory oil and gas drilling. Water-quality sampling sites were selected to assess areas of potentially impacted by oil and gas drilling and to characterize 'background' water quality in areas away from the drilling.

The sample results were compared to: (1) historic water quality data, (2) drinking-water health standards, and (3) produced waters from the extraction of oil and gas in regions of

Montana and the surrounding states, to assess potential impacts to shallow groundwater from the recent drilling and to characterize the shallow groundwater. Data generated from this project are available through MBMG's Ground Water Information Center (GWIC) at http://mbmggwic.mtech.edu/ .

2. Shields River Basin Overview

The Shields River Basin is located mostly in northern Park County in south-central Montana; lesser parts exist in Gallatin and Meagher counties. The Shields River flows west, then south about 45 miles from its headwaters in the Crazy Mountains to its confluence with the Yellowstone River near Livingston, Montana. The Basin covers nearly 855 square miles (547,048 acres) and is bounded by the Bridger Range to the west and the Crazy Mountains to the east; a divide of rolling hills marks the northern boundary (fig. 1).

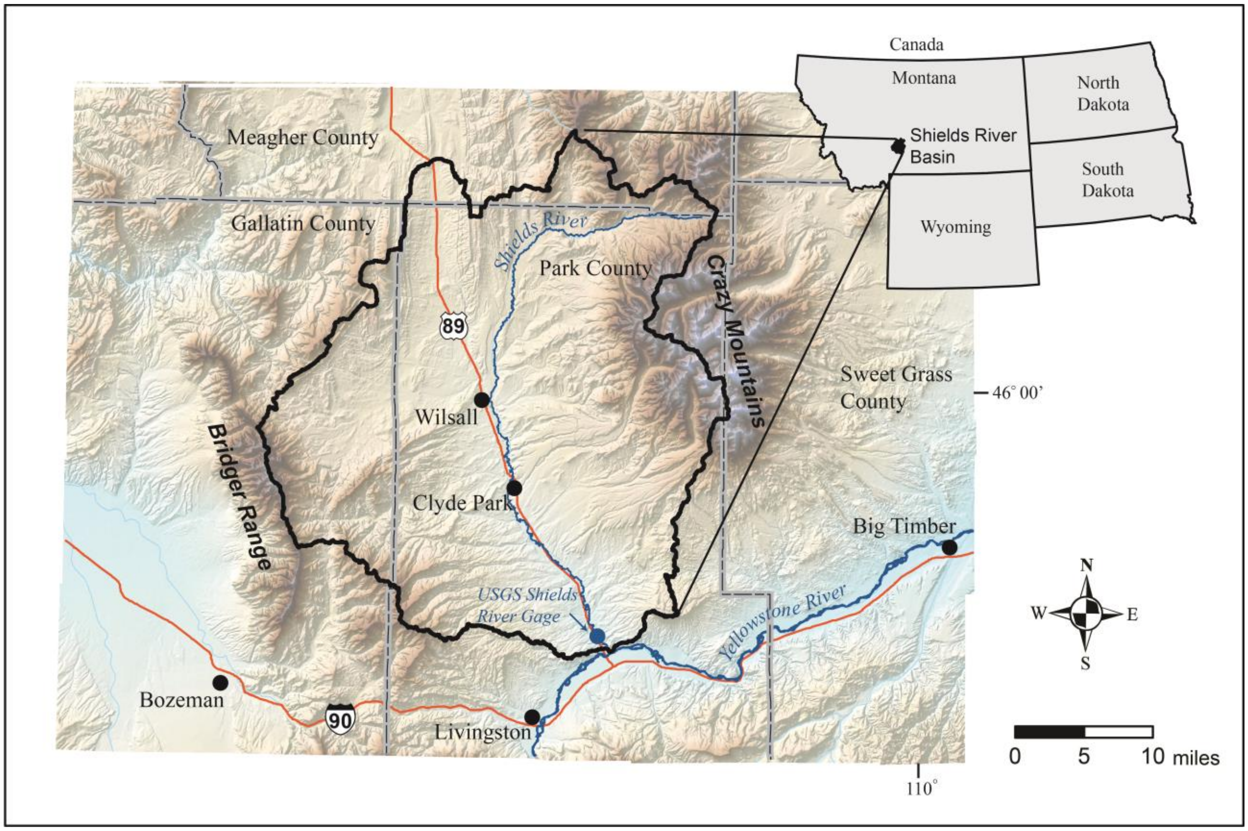


Figure 1. The Shields River Basin is located north of Livingston, in south-central Montana.

The land surface is characterized by alpine peaks of the Bridger Range and Crazy Mountains. Upland forests and grasslands flank the alpine peaks and slope towards the Shields River. Elevations range from over 10,000 ft in the Crazy Mountains to 4,375 ft where the Shields River empties to the Yellowstone River (fig 1).

Alpine areas of the Bridger Range and Crazy Mountains are part of the Gallatin National Forest. Private land adjacent to the National Forest consists mainly of open grassland used for

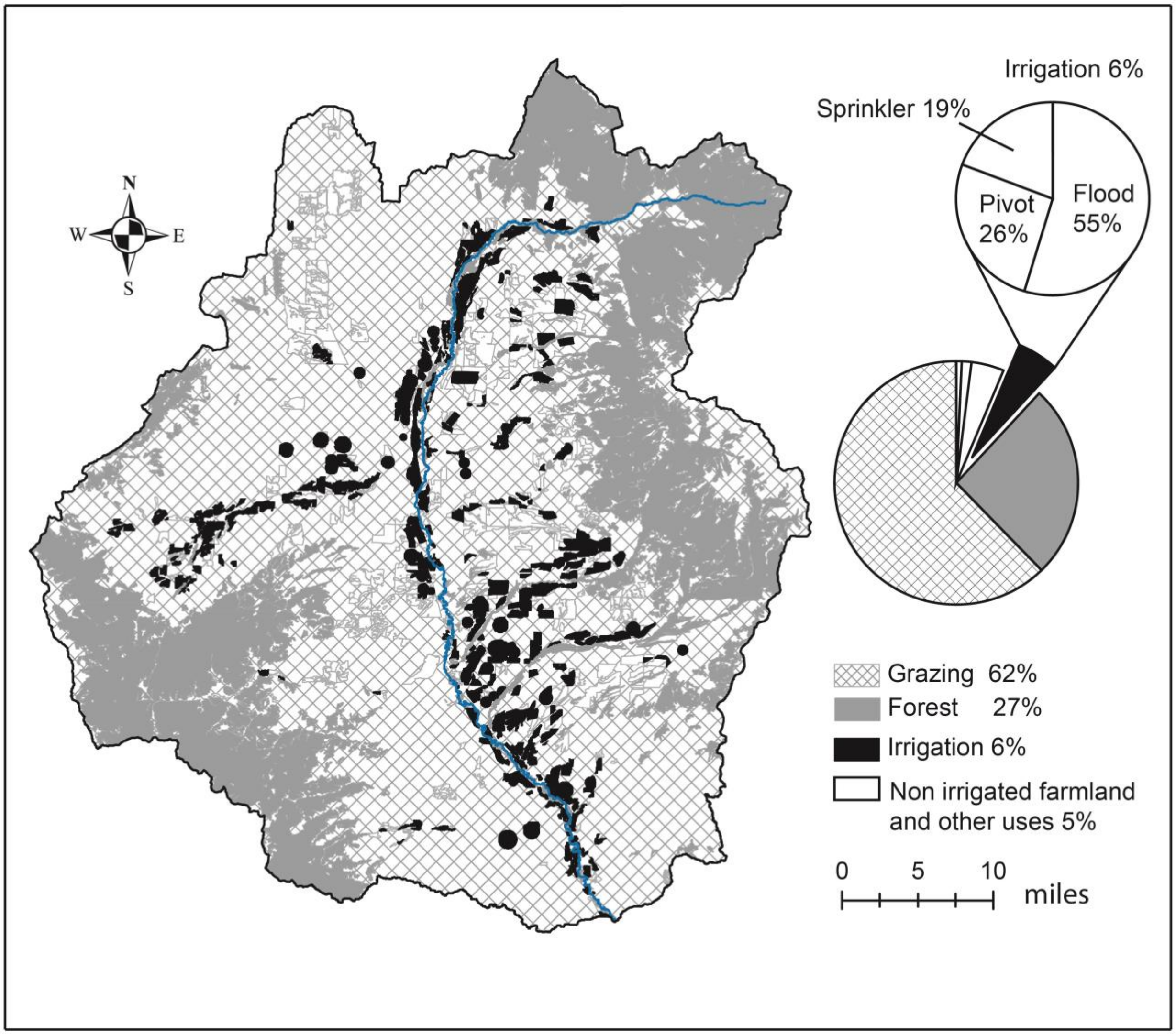


Figure 2. Montana Department of Revenue (2014) land use and detailed irrigation types.

cattle grazing. Irrigated lands occur adjacent to the Shields River and along some upland tributary areas (fig. 2). Most fields are flood irrigated; however, 26 percent are irrigated with pivot-style sprinkler systems, and 19 percent use traditional-type sprinkler methods (Montana Department of Revenue, 2014).

The main towns, Clyde Park and Wilsall, each report population totals less than 300 (U.S. Census Bureau, 2010). Farming and ranching are the main industries. Basin residents rely heavily on groundwater for municipal, domestic, and stock use. Access to shallow groundwater is primarily with wells, however many developed springs exist.

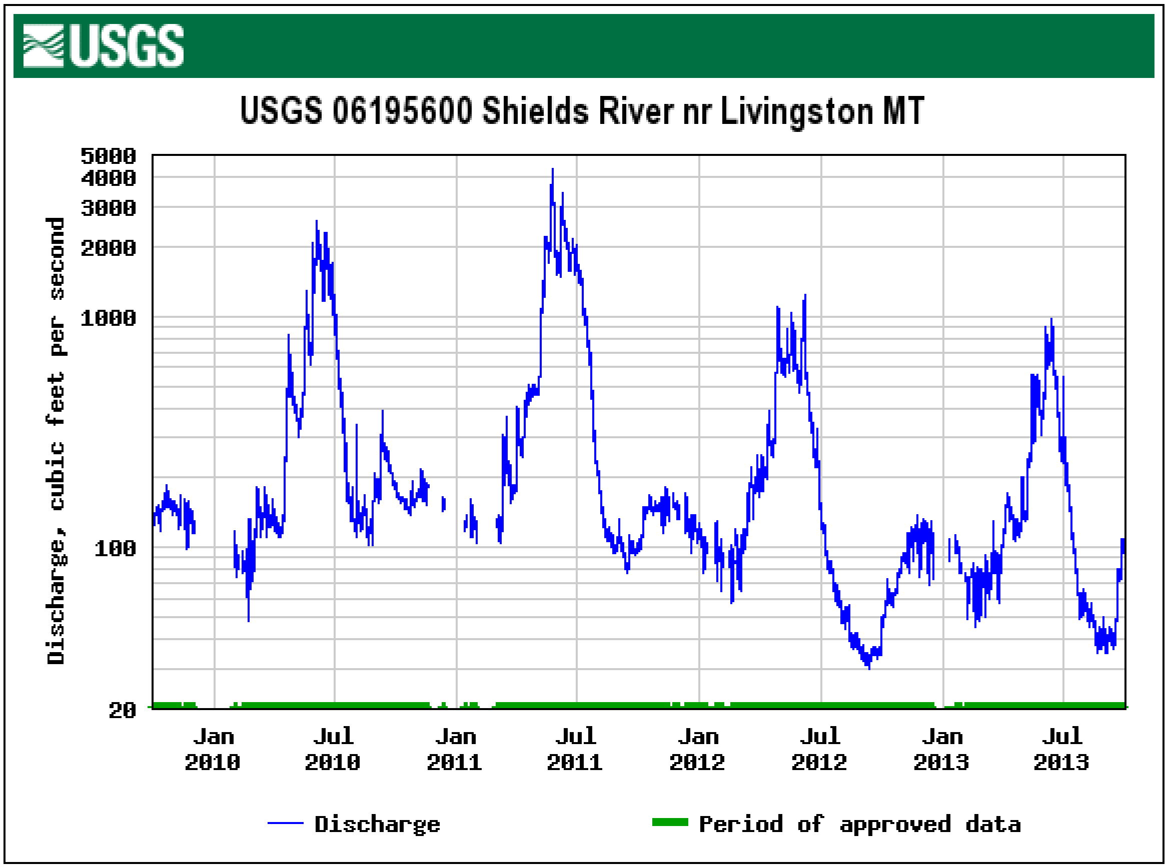


Figure 3. The USGS hydrograph from the Shields River near its confluence with the Yellowstone River shows increased flow in spring and early summer followed by a decrease in flow the remainder of the year.

The climate is semiarid and characterized by cold winters and hot summers. Average annual precipitation ranges from 14 inches in the valley to 60 inches on the alpine peaks

(Western Regional Climate Center, 2014). During the winter, precipitation is stored as snowpack in the alpine peaks and released as spring runoff. Precipitation falls as rain in the valleys during late spring or early summer (1-3 in. per month), but the remaining months are relatively dry (less than 1 in. per month).

The Shields River is a snow-melt dominated stream as shown by the hydrograph from a US Geological Survey gauge located near its confluence with the Yellowstone River (http://waterdata.usgs.gov/mt/nwis/ (fig. 3)). Shields River flows increase in response to snow melt, and they decrease in late summer as snow melt runoff wanes and irrigation withdrawals begin.

3. Previous Hydrogeological Investigations

Previous hydrogeologic studies have been concentrated near the Shields River and around the towns of Clyde Park and Wilsall. Well and spring inventory information from these studies provide some historical water quality; however, there are large parts of the Basin where no groundwater quality data exist.

Three studies focused on surface waters or irrigation ditches and provide limited information about groundwater. (1) The State Engineers Office along with the State Water Conservation Board and Montana State Agricultural Experiment Station completed a water resources survey of Park County (Montana State Engineers Office, 1951). (2) From 1999 to 2005, the Montana Department of Natural Resources and Conservation (DNRC) and the Upper Shields Watershed Association produced a report of water supply and irrigation efficiencies for reaches of the upper Shields River north of Wilsall (Dolan, 2005). (3) In 2006, the upper and lower Shields River and two of its tributaries were listed for sediment impairment by DEQ. In

2009, DEQ and others published a water quality planning document to assess the primary sources of sediment and develop best-management-practices in the watershed (DEQ, 2009).

Groundwater studies either focus on the part of Park County south of the Yellowstone River, the part of the Basin located in Gallatin County, or on selected springs. Groff (1962) completed the first study. The MBMG conducted a study funded by a Montana Department of Environmental Quality 319 program in 2004 to characterize aquifers in the Livingston, Clyde Park and Wilsall areas (Kuzara and others *in review* GWIC, 2014). Between 2010 and 2012, MBMG conducted well and spring inventories in the Gallatin County part of the Shields River Basin for a regional aquifer characterization study of Gallatin and Madison counties and for a spring inventory program in cooperation with the USDA Forest Service.

4. Oil and Gas Drilling Overview

Since 2000, natural gas production from organic rich shale formations (shale-gas) has increased in North Dakota and Montana. This increase is largely due to advances in directional drilling and hydraulic fracturing that have made shale-gas production economically viable. Drilling and production is occurring in areas that have seen little to no activity in the past (King, 2012). The Cody Shale has been identified as a potential shale-gas target (or play) in the Shields River Basin (fig. 4). Between 2007 and 2009, seven oil and gas wells were drilled (fig. 5). Oil and gas well locations, lithology data, and completion information are available from the Montana Board of Oil and Gas (MBOG, 2015) database. Prior to 2007, 16 other oil and gas wells were drilled in the Basin. The dates of these historic wells range from 1921 to 2000. These wells are located in the northern part of the Basin (fig. 5). All 16 historic wells are designated as “dry holes” indicating the absence of economically recoverable oil and gas (MBOG, 2015).

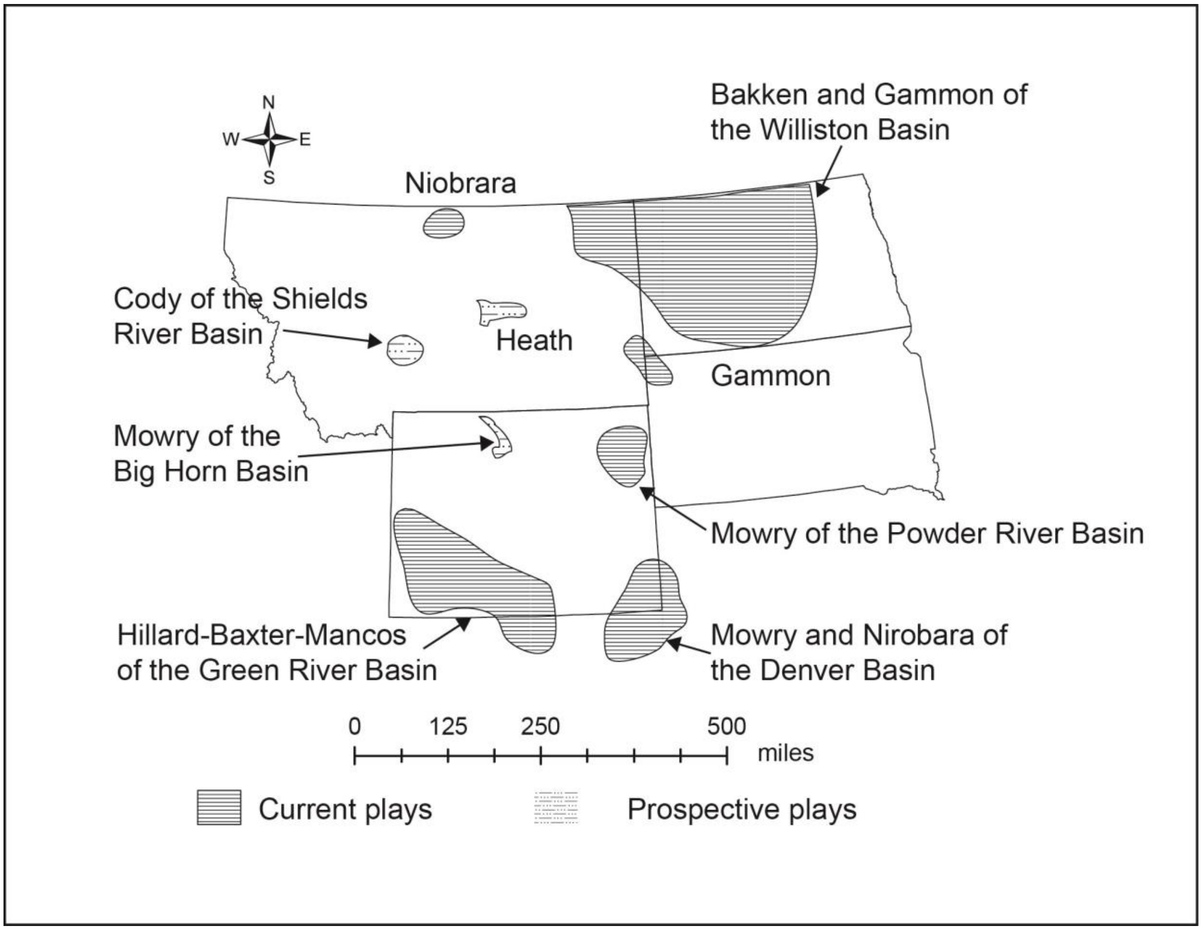
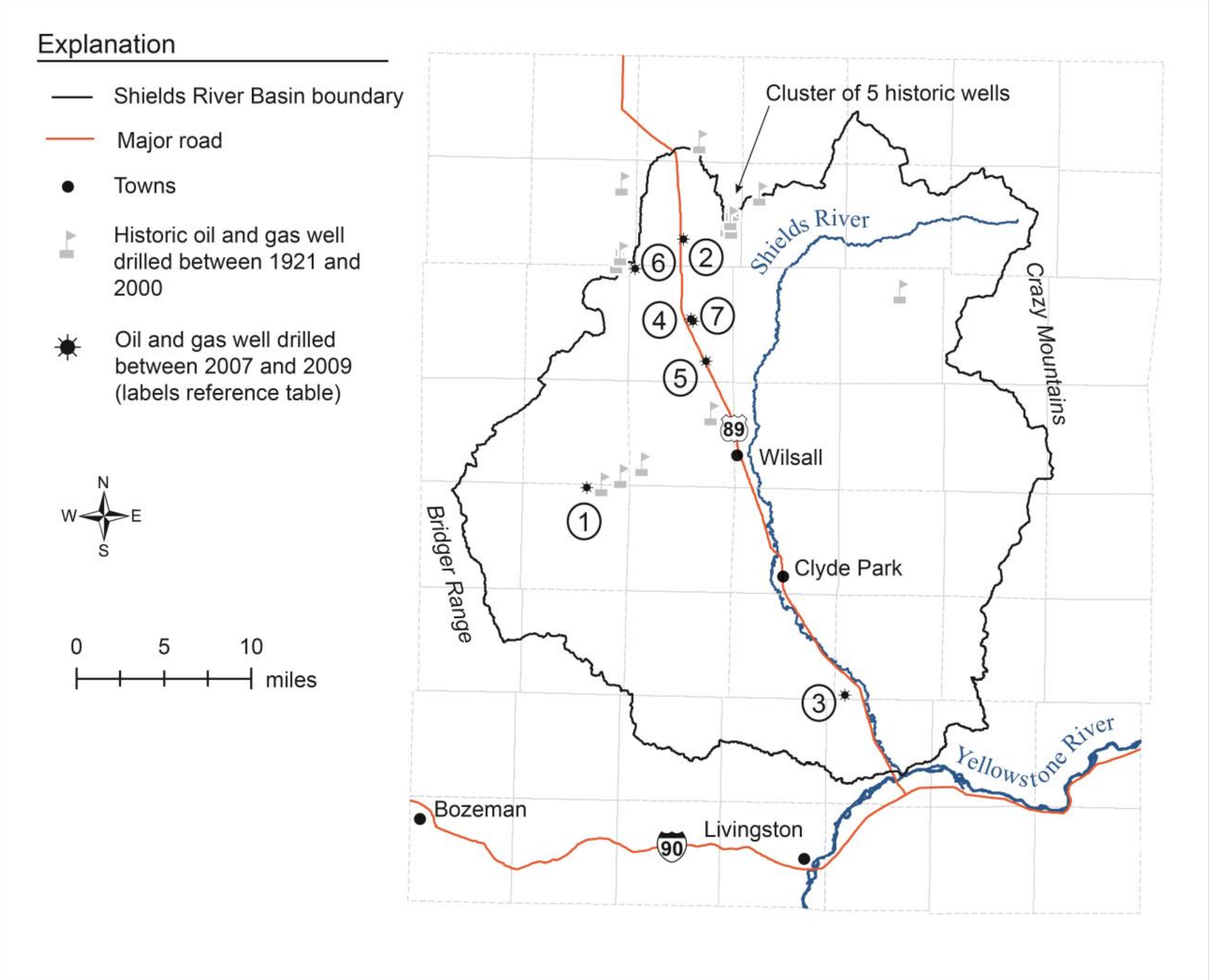


Figure 4. Shale-gas plays in Montana and the surrounding states (modified from the Energy Information Administration, 2011). The Cody Shale is a prospective shale-gas play in the Shields River Basin.

Reported depths from wells drilled between 2007 and 2009 range from nearly 5,450 ft to 12,450 ft below land surface (fig. 5). Three wells are indicated as gas wells, three as oil wells and one well reported as a dry hole (MBOG, 2015). Two wells report some production; Well 2 (fig. 5) produced 773 barrels of oil from the Cody Shale in 2009 and Well 7 reportedly produced 14 barrels of oil from the Cody Shale in 2008 (fig. 5). A 4-month production period for Well 3 was reported, but no volume of oil or gas was indicated. Well 6, drilled to nearly 10,000 ft into older Cambrian rocks, was the only well that ‘directionally drilled’ (MBOG, 2015). All the wells are reported as abandoned in the MBOG database with the exception of Well 3 that is ‘shut in’.



Label	API Well Number	Status	Completed	Total Depth	Slant	Cody Shale Top
1	25031210070000	Abandoned - Unapproved	08/08/2009	6,245	Vertical	5,170
2	25067210170000	Abandoned - Unapproved	06/24/2009	6,800	Vertical	5,170
3	25067210180000	Shut In	01/22/2009	11,456	Vertical	9,738
4	25067210140000	Abandoned - Unapproved	09/29/2008	5,439	Vertical	4,250
5	25067210160000	Abandoned - Unapproved	08/28/2008	7,239	Vertical	5,786
6	25067210100000	Abandoned - Unapproved	01/24/2008	11,005	Directional	3,096
7	25067210110000	Abandoned - Unapproved	11/24/2007	12,441	Vertical	4,200

Figure 5. Oil and gas wells drilled in the Shields River Basin. Sixteen historic wells were drilled between 1921 and 2000 and seven wells were drilled between 2007 and 2009 (MBOG, 2015).

Inspections of some of the sites in 2013 revealed that the abandoned-well sites are reclaimed and marked with a post indicating township, range, section, and the well identification number. The shut-in well had a valve at the surface and signage with similar location and well identification as the abandoned wells (Appendix A, photographs 2, 3).

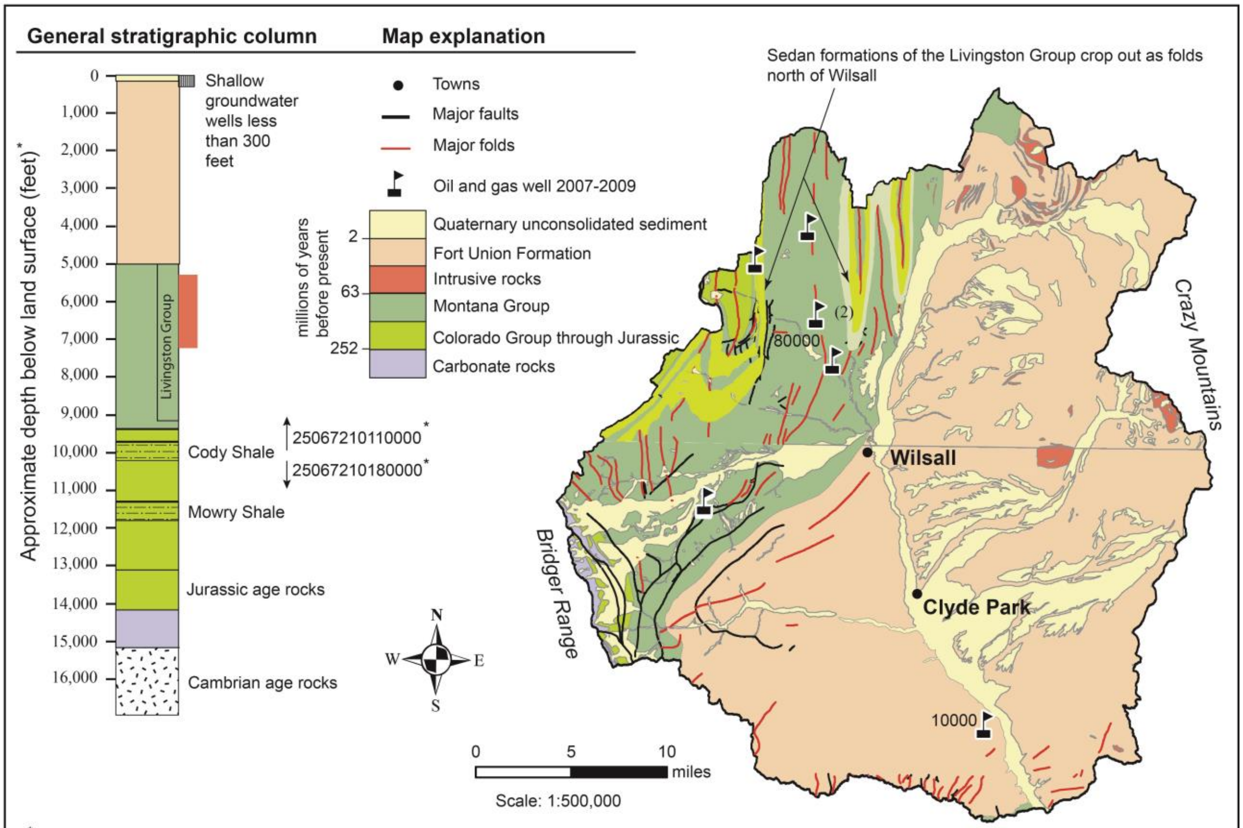
5. Geology Overview

The Shields River drainage basin lies within the western part of the Crazy Mountains structural basin. The Crazy Mountain Basin is a northwest-trending structural and sedimentary basin of about 7,800 square miles. The Crazy Mountains structural basin and Shields River drainage basin share a western boundary of the Bridger Range; however, the Crazy Mountains structural basin extends south and eastward well beyond the Shields River drainage basin boundaries (Johnson and others, 2005). Skipp and others (1999) provide detailed structural and tectonic description of the Crazy Mountains Basin. Additionally, the western boundary of both basins is the physiographic boundary between the Northern Rocky Mountain and Great Plains physiographic provinces (Fenneman, 1946).

The exposed bedrock in the Shields River Basin consists of Mississippian through Tertiary age sedimentary rocks with some Tertiary intrusive rocks in the Crazy Mountains. Younger Quaternary age unconsolidated alluvium occurs in the drainage bottoms, and terrace gravels are present at levels above the stream bottoms. Quaternary terrace gravels are most notable between the Shields River and the Crazy Mountains. In some locations along the Shields River, bedrock outcrops form the rivers bank, and at others alluvium has been removed by erosion and the riverbed is composed of scoured bedrock (Appendix A, photographs 4, 5). Geology of the area was mapped by Berg and Lopez (2000), and McDonald and others (2005) at a scale of 1:100,000. For the purposes of this report, bedrock formations were combined based on age and the degree to which they are exposed.

The bedrock formations were combined into five main groups; from youngest to oldest they are: (1) Fort Union Formation, (2) intrusive rocks, (3) Montana Group, (4) Colorado Group through Jurassic age rocks, and (5) carbonate rocks (fig. 6).

In the Livingston area and southern Shields River Basin, Roberts (1972) mapped and described the Livingston Group. The Upper Cretaceous Livingston Group contains formations that exist locally and are not regionally extensive. Skipp and others (1999), mapped similar formations as Roberts (1972) in the upper Livingston Group, but describe an additional formation (Sedan Formation) in the lower Livingston Group. All Livingston Group formations are included here as Montana Group shown (fig. 6). Where the Livingston Group formations are mapped; these formations are equivalent to the Montana Group formations mapped elsewhere



*Formation thicknesses modified from Berg and others (2000), formation top data from MBOG oil and gas wells 25067210110000 and 25067210180000 (labeled 10000 and 80000 on the map). Formation top altitudes from 25067210110000 were used to complete the stratigraphic column from Fort Union Formation to the Cody Shale and formation top data from 25067210180000 were used from the Cody Shale to Cambrian age rocks.

Figure 6. Geology of the Shields River Basin modified from Berg and others (2000) and, McDonald and others (2005). Formation top data from the Montana Board of Oil and Gas database.

(stratigraphic column, fig. 6). The Montana Group is underlain by the prospective shale-gas plays of the Cody and Mowry Shale (EIA, 2011), (fig 4). Johnson and others (2005) completed a detailed subsurface investigation and their cross sections and structural descriptions along with surface mapping by Roberts (1972), Berg and Lopez (2000), McDonald and others (2005), and oil and gas data (MBOG, 2015) were used to characterize the Cody and Mowry shales in the subsurface.

The Shields Basin straddles two different geologic settings: (1) the eastern part where the Fort Union Formation is exposed at the surface, and (2) the western part where older Cretaceous age formations are exposed. Where the Fort Union outcrops, the setting is characterized as *flat lying*, whereas the western part is structurally complex and characterized as *faulted and folded* (fig. 6). These areas are hereinafter referred to as *flat lying* and *faulted and folded*. At least 60 percent of the Basin contains the flat lying setting; although the faulted and folded setting contains six of the seven oil and gas wells drilled from 2007-2009 (fig. 6). Groundwater is produced from both geologic settings, however the flat-lying setting contains most of the water wells (GWIC, 2014).

6. Hydrogeology Overview

Residents rely heavily on shallow groundwater. There are records of about 1,040 domestic wells and 24 public water supply (PWS) wells in the Basin (GWIC, 2014). Typically, water wells are completed in bedrock aquifers within 300 ft of the land surface. The flat lying setting contains nearly 80 percent of the wells; this setting also contains the deepest wells. Total depths range from 5 to 860 ft below land surface. The average well depth in this setting is 136 ft and average depth water enters (top of perforated interval) is 83 ft. The deepest wells are west of Clyde Park. Five wells are completed at depths ranging from 600 to 725 ft. Lithology data from these wells indicate an absence of water bearing zones within 300 ft of the land surface. The wells have multiple screened intervals across several low yield zones. One well east of Clyde

Park is 820 ft deep with a reported yield of 0.25 gallons per minute (gpm). This well is unused (GWIC, 2014). Sandstones of the Fort Union Formation form the main aquifers in the flat lying setting. The saturated sandstones are interbedded with clay and silt. Water bearing zones are laterally discontinuous across large distances, and depth to these zones can vary within short distances. Even though the depth to water-bearing zones is variable, the Fort Union Formation is a widely used aquifer.

In the faulted and folded setting, most water wells are completed in the Livingston Group. Livingston Group formations are not consistently named throughout the Basin and these formations are not regional aquifers but they do contain saturated zones. Due to the complex structural setting one particular formation does not emerge as a primary aquifer in this setting. Rather, wells generally penetrate water bearing zones within 300 feet of land surface. Records of wells in the faulted and folded area range from 5 ft (dug with a backhoe) to 523 ft below land surface with an average depth of 124 ft. The average depth groundwater enters is 103 ft. Deep wells in this setting are not clustered in any particular area.

Where alluvium exists along the Shields River it is thin, narrow, and typically does not provide reliable groundwater to wells. Some well logs with locations in Quaternary terrace gravels east and south of Clyde Park report gravel thicknesses up to 40 feet thick (GWIC, 2014). Most of these wells fully penetrate the gravel and obtain water from underlying bedrock formations. Wells completed in the shallow alluvium and the terrace gravel are susceptible to contamination, changes in irrigation practices, and climatic variations.

6.1. Conceptual Understanding of Shallow Groundwater Flow

Runoff and increased precipitation in the spring cause stream flows to increase and provide water for groundwater recharge. Recharge occurs from direct infiltration of precipitation and from losing streams. Typically, losses are the greatest where streams exit the alpine peaks and flow into the Basin. Stream gradients lessen at these locations, and infiltration of stream water recharging groundwater systems can be significant. Additionally, starting in the early

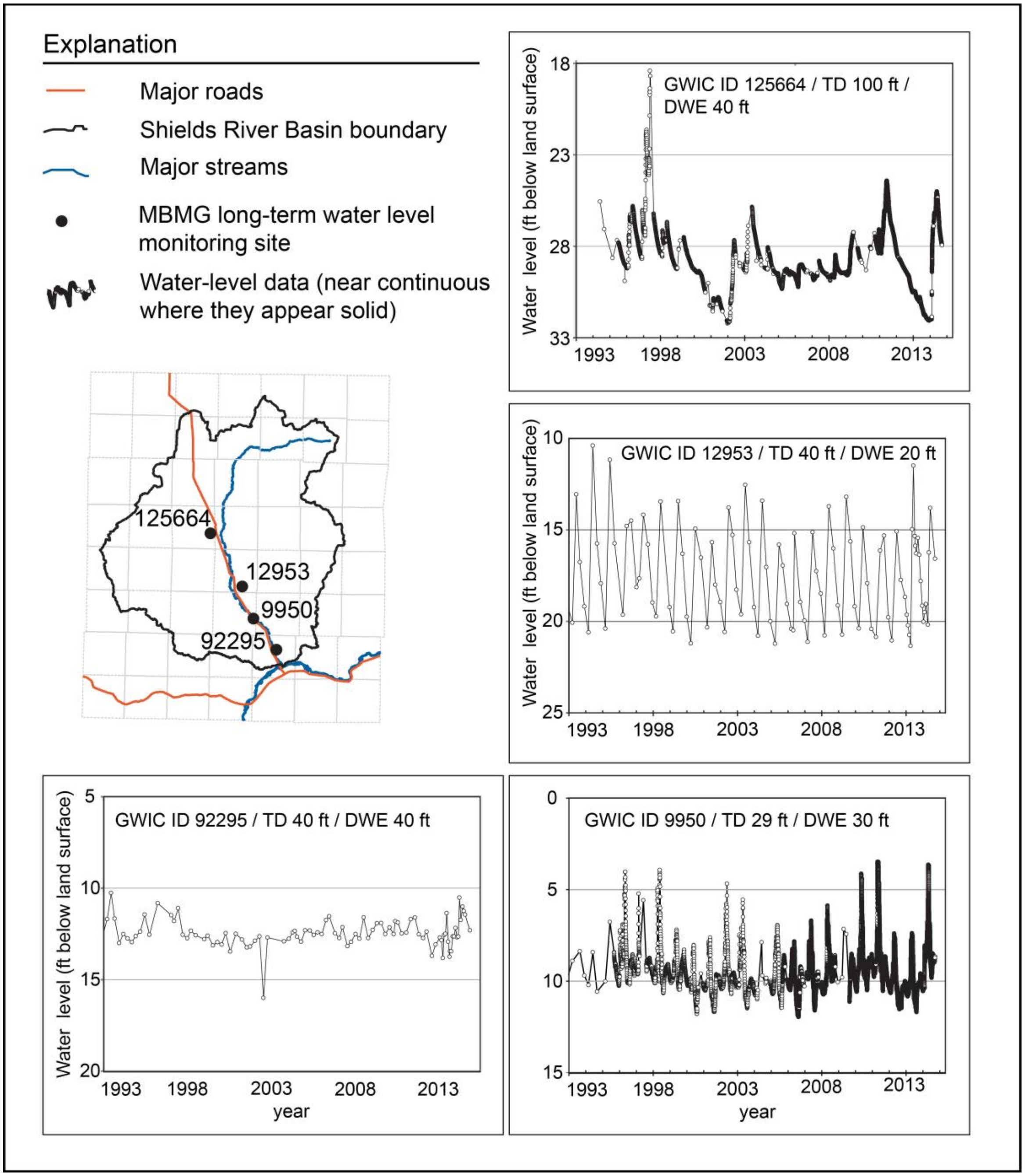


Figure 7. Hydrographs from monitoring sites in the Shields River Basin from 1993 to 2013 show water-level fluctuations or reflect the influence of the Shields River.

spring and through the summer surface waters are diverted from the Shields River and its tributary streams for irrigation use. The conveyance of water through unlined canals and excess application of water on the surface provides recharge to shallow groundwater. Groundwater discharges as base flow to streams, evapotranspiration, and to wells.

The MBMG measures groundwater levels in four wells near the center of the Basin as part of a statewide long-term groundwater-monitoring program. Three of these wells are completed in the flat lying setting, and one well is completed near the boundary between the flat-lying and faulted and folded settings east of Wilsall. The wells are adjacent to the Shields River (fig. 7). The hydrographs show water-levels rise each spring in response to recharge from snowmelt runoff and spring precipitation. Variations do exist among the hydrographs reflecting different recharge sources and hydrogeologic settings. Wells 9950 and 12953 (GWIC ID numbers) show groundwater levels fluctuating at a similar magnitude each year; these fluctuations indicate a reliable source of recharge and consistent discharge from the aquifer throughout the year. Wells 92295 and 125664 also show the seasonal water level fluctuations, but have more erratic response (fig. 7). The two periods of groundwater level decline (1998-2002 and 2011-2014) in well 125664 are related to periods of below average annual precipitation. Well 92295 is near the surface water outlet of the Basin, water levels show some seasonal variations, but the overall trend is stable/steady.

7. Potential Contamination Sources

Shallow groundwater and streams can become impacted from oil and gas extraction in many ways. Contaminant pathways to shallow groundwater are described extensively by King, 2012 and elsewhere. For the purposes of this study, three general contamination sources were considered: (1) upward migration of stray gasses from reservoir rocks, (2) upward migration of formation waters or produced waters along an improperly sealed well casing, and (3) spilling and subsequent infiltration of formation waters, produced waters, or chemicals at the land surface. The high pressures used to hydraulically fracture shale formations stresses the well casing. The well casing (or multiple casings) of the gas well is what separates it from shallow groundwater. A loss of well casing integrity may result in direct contamination to shallow groundwater. This contamination can consist of drilling fluids, fracturing fluids, deep formation brines released with the gas, or a range of organic constituents associated with the natural gas. Once a gas well is hydraulically fractured, and becomes a production well, the hydraulic fracturing fluids and deep formation waters are mixed with the natural gas. These waters are collectively termed produced waters. Produced waters are separated from the natural gas at the surface and are disposed of onsite or transported offsite for disposal. In areas of historic oil and gas drilling the poorly abandoned historic wells can provide conduits to the surface for newly mobilized hydrocarbon gases or formation waters. Geologic units that extend from depth to the surface or fractures and bedding orientations intrinsic to the geologic formations can also provide conduits for stray gases to migrate upward (Warner and others, 2012).

Stray gases discussed in this report are loosely defined as any gas found in an unexpected environment. Natural gas composition can vary widely, but typically is a mixture of mostly methane (70-90 percent) with lesser amounts of ethane, propane, and butane (collectively 0-20 percent, (http://naturalgas.org)).

Methane found in groundwater can have different sources. The two primary sources of methane in groundwater are: (1) biogenic and (2) thermocatalytic or thermogenic (Clark and Fritz, 1997). Biogenic methane is most common in shallow groundwater systems; it is derived from bacterial reduction of organic material and unrelated to oil and gas drilling. Thermogenic methane is created by thermal cracking of higher mass hydrocarbons at elevated temperatures usually in deep formations. Thermogenic methane is the traditional target of energy companies but biogenic methane has been economically produced more recently as coalbed methane (Clark and Fritz, 1997). Kappel and Nystrom (2012) found methane in 53 percent of wells and springs (239 total sites) sampled prior to oil and gas development in New York State.

Just as potential pathways exist for contaminants to migrate upward to shallow groundwater, pathways also exist from the land surface to impact surface and shallow groundwater. These pathways include leakage from earthen pits and ponds, leakage from pipes, pond overflows and spills during transport (King, 2012).

Produced oil and gas often needs to be transported for refining. There are a number of ways oil and gas can be transported from the Basin. Tanks onsite can provide storage until the product is transported or it may be loaded onto rail cars, trucked or moved through a pipeline to the refining facility. The movement of product from well pads to refinement facilities further represents potential contamination of shallow groundwater and surface water. Improperly constructed access roads to the oil and gas well drilling site (or “well pad”) can increase sedimentation to streams of small tributaries, increasing the total dissolved solids and degrading surface water quality.

In a well-development activity risk matrix involving oil and gas wells that are hydraulically fractured (p.60), King (2012) identifies and assigns frequencies to types of spills. These spills include, but are not limited to a transport load of saline water, diesel (refueling activities), concentrated liquid biocides or inhibitors, and stored or flowback and formation waters.

7.1. Surface Spills and Infiltration of Contaminants - Analysis using GIS

The intrinsic susceptibility describes the potential for an aquifer to be contaminated. Focazio and others (2002) define aquifer susceptibility as the physical factors affecting the flow of water to and through an aquifer. Vulnerability of an aquifer to contamination depends on the susceptibility in addition to naturally occurring and anthropogenic sources of contamination (Focazio and others, 2002). In this study, we conducted a Geographic Information System (GIS) analysis to evaluate shallow groundwater susceptibility throughout the Basin. The results from this analysis were used as an additional tool to help select sampling sites.

Aquifer susceptibility analysis has been completed in Wyoming and parts of Montana using the methodology described in Wyoming's *Groundwater Vulnerability Assessment Handbook* (Hamerlinck and Arneson, 1998), (TriHydro, 2008). Our susceptibility analysis follows Wyoming's methodology by ranking intrinsic properties related to the rate at which contamination migrates from the land surface to shallow groundwater. The properties ranked for this study are: (1) depth-to-water, (2) land surface slope, (3) soil permeability, and (4) aquifer hydraulic conductivity. Conceptually areas with gentle slope, well-drained soils, and a shallow water table would be more susceptible than areas where soils are relatively impermeable and groundwater is deep. Once groundwater in an aquifer has been contaminated the rate at which any contaminant moves through an aquifer is related to the permeability of the aquifer materials.

Wyoming's methodology follows the established EPA model for determining aquifer sensitivities (Aller and others, 1987). The EPA aquifer sensitivity model has been modified extensively since its introduction. However these models generally cover a large area and are not suited to make site-specific decisions (Focazio and others, 2002). The susceptibility analysis results were combined with natural and anthropogenic sources of contamination (e.g. geologic structures or oil and gas well locations) to provide an overall picture of shallow groundwater vulnerability.

The susceptibility analysis was performed using a GIS and publicly available data. Depth to water was derived from reported water-levels on existing well logs (GWIC, 2014). Land surface slopes were computed from digital elevation models (DEM) available from the Montana State Library (http://nris.mt.gov/), and soil permeability was obtained from the USDA (http://datagateway.nrcs.usda.gov/). Aquifer characteristics were derived from the MBMG 100K - scale geologic mapping. ESRI's ModelBuilder® application was used to complete the

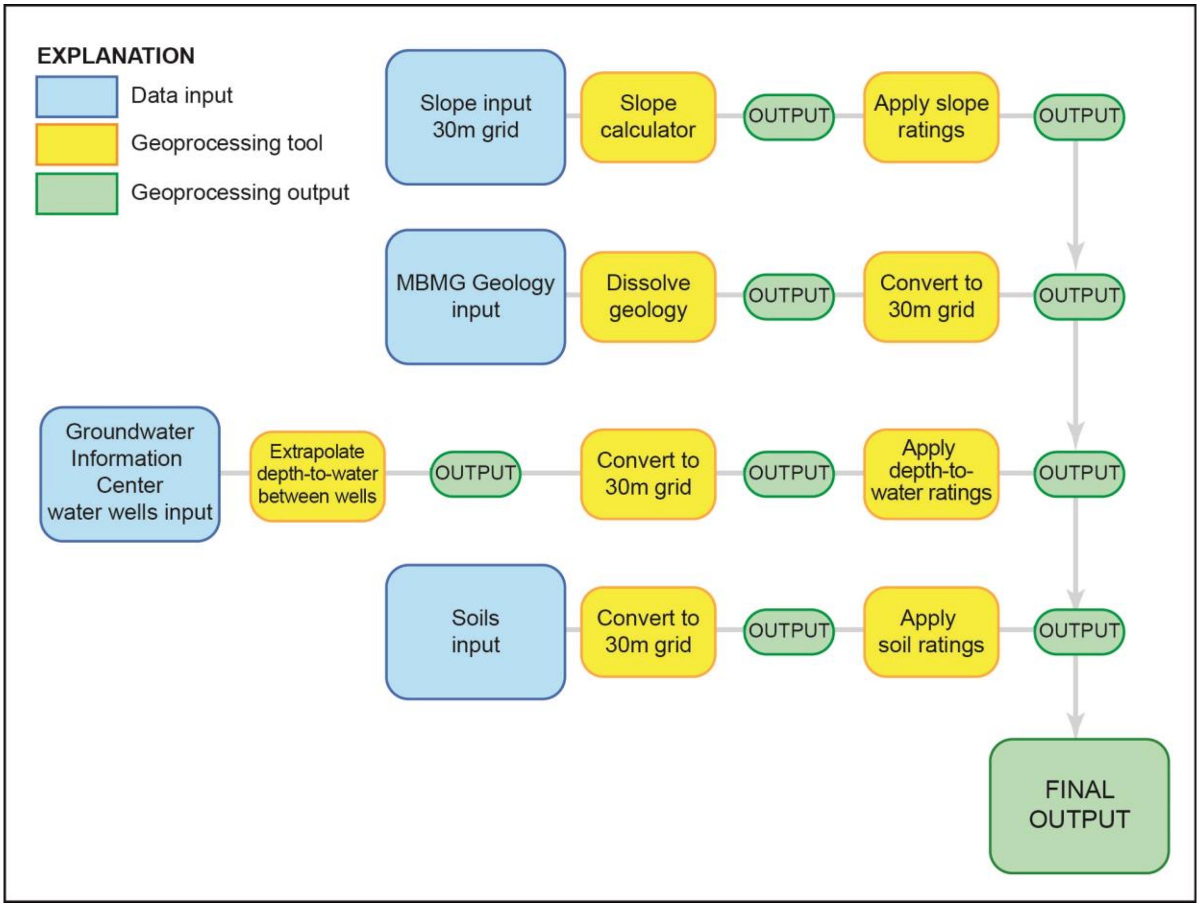


Figure 8. Flowchart showing GIS analysis of potential contaminant migration from the land surface to shallow groundwater (ModelBuilder®). Analysis parameters (yellow boxes) are easily modified, allowing multiple analysis runs.

susceptibility analysis; this application allows for the management of complex sequences of geoprocessing commands (fig. 8).

Each of the four intrinsic properties were input into ModelBuilder® and the Basin was discretized into a 30 m grid. Next ratings were applied to the 30 m grid based on published conversion tables and equations by Hamerlinck and Arneson (1998). Each grid received a rating from 1-10 for each of the four properties. The higher the rating, the higher the groundwater susceptibility at the 30m x 30m cell. The sum of ratings in each cell has a potential range from 4 to 40. Figure 9 shows a representative output from the GIS analysis. White and light gray colors show cells that have higher combined ratings, so groundwater in these areas is more susceptible to contamination than black or dark gray areas.

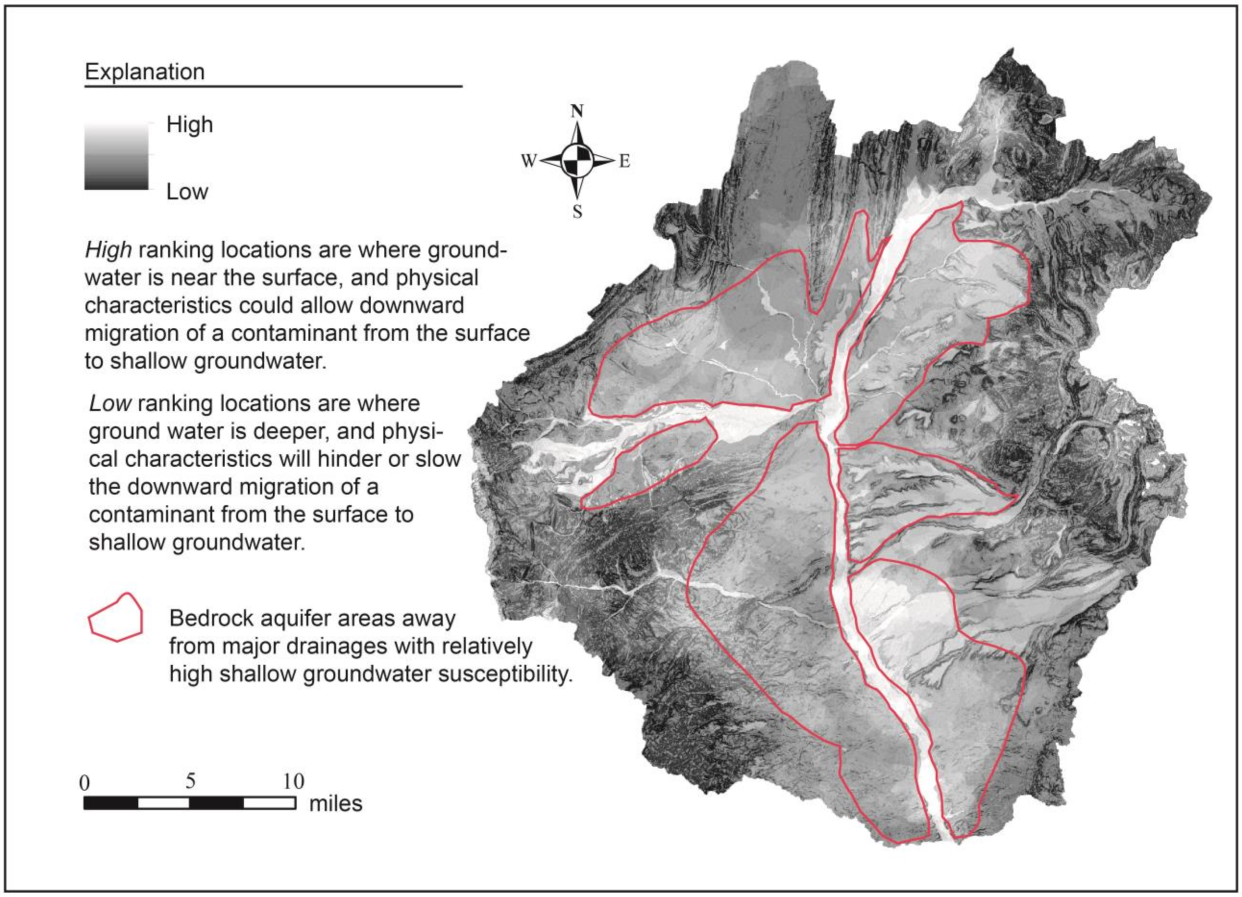


Figure 9. An example output from GIS analysis of contaminant migration pathways from the land surface to shallow groundwater (ModelBuilder®).

Many limitations exist with this type of analysis. Most notable are the wide variations in hydraulic conductivities and the uncertainties associated with driller-reported locations. Even though hydraulic conductivity in aquifers ranges across least sixteen orders of magnitude and the exact location of wells in the GWIC database are uncertain, this analysis provided another tool to help develop the sampling program.

8. Final Target Locations of the Baseline Sampling

Groundwater sample locations were identified based on aquifer susceptibility and potential contaminant pathways from oil and gas formations to shallow groundwater. For comparative purposes, locations were selected near the recent (2007-2009) oil and gas drilling and areas without recent drilling. The results from the susceptibility analysis were used to identify (and prioritize) areas where contamination could migrate downward. The locations of geologic structures and historic oil and gas wells were considered because they represent potential conduits for contaminate migration from depth. In an effort to sample groundwater representative of the bedrock aquifers, sites near main irrigation ditches and alluvial flood plains were avoided. During spring runoff or during the irrigation season these sites may represent irrigation water conveyed from elsewhere or spring runoff waters.

Within the targeted areas, preference was given to wells that: (1) had been completed within the last five years, and (2) had a well log. Well logs provide construction details and describe the well construction, total depth, and screened interval.

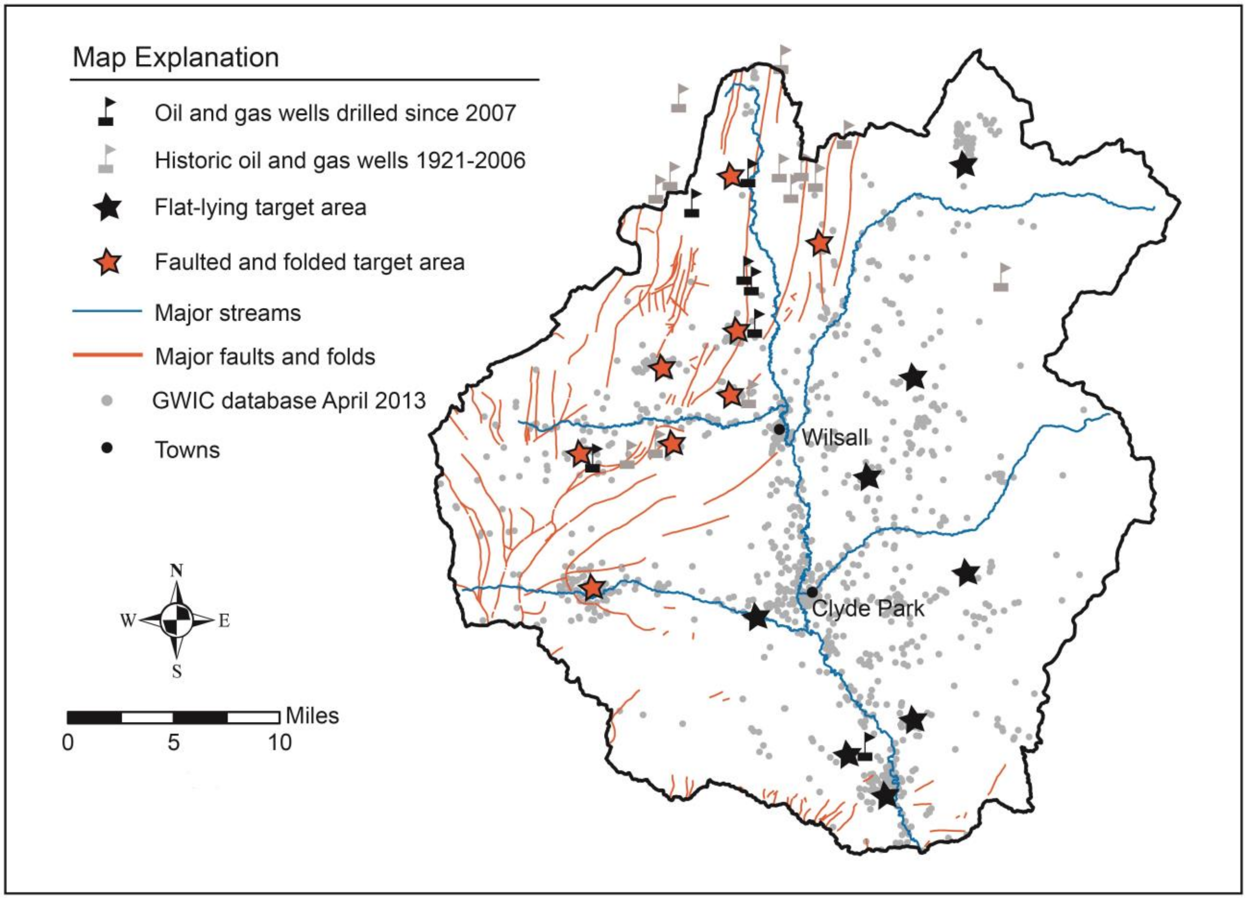


Figure 10. Initial target sites developed and presented to the Shields Valley Watershed Group and Park County Conservation District.

Methods

9. Water Sample Collection and Analysis Methods

The National Groundwater Association (NGWA) recommends testing water wells for: (1) major ions (alkalinity, calcium, chloride, magnesium, potassium, sodium, and sulfate), (2) minor and trace elements (arsenic, barium, boron, bromide, chromium, iron, manganese, selenium, and uranium), (3) water quality parameters (pH, specific conductance, total dissolved solids, and turbidity), and (4) organic chemicals benzene toluene ethylbenzene, and xylene (BTEX), diesel range organics (DRO), gasoline range organics (GRO), dissolved methane, total petroleum hydrocarbons or oil and grease) (NGWA, 2015).

We analyzed samples for major ions, trace metals, and water isotopes. A subset of samples were analyzed for analyzed for organic compounds: BTEX, GRO, DRO methane, ethane, and ethylene. Additionally, a subset of samples collected in 2013 were sent to the University of Waterloo for groundwater tritium analysis to assess relative groundwater age. Accessible water-wells with detections of organics in 2013 were resampled in 2014. A list of inventoried sites is included in Appendix E.

To obtain water representative of the aquifer, samples were collected from as close as possible to the wellhead and before any water-treatment system. Samples were collected in accordance with MBMG SOP's; three casing volumes were purged and field measurements including pH, temperature, and specific conductance and, were stable prior to sample collection. Additionally, alkalinity titrations and field measurements of nitrate, oxidation reduction potential, and dissolved oxygen were collected. Care was taken to decontaminate all equipment coming in contact with the water sample. Major structures and potential sources of organics (e.g. fueling tanks or oil barrels) were noted on field data sheets. Water samples for organic analysis were kept on ice and shipped overnight or immediately transported to Pace Laboratories in Billings, MT. Quality assurance/quality control (QA/QC) samples were collected at a frequency of 1 per 20 samples. These QA/QC samples included duplicates, equipment blanks, and trip blanks. The MBMG maintains a set of internal Standard Operating Procedures (SOP) for the collection of groundwater samples. These SOP's were modified for the collection of groundwater samples for organic analysis (Appendix B).

All samples were analyzed for major ions, trace metals, and water isotopes by the MBMG analytical lab in Butte, MT. Water samples for analysis at the MBMG were collected in two 500ml, two 250ml, and one 20ml polyethylene bottles. All 250ml and 500ml samples were filled to minimize headspace. The 20ml bottle was filled and capped with no headspace present. Cations, alkalinity, pH, and conductivity were analyzed from unpreserved unfiltered water sample collected in a 500ml bottle. Metals were analyzed from a filtered sample preserved with nitric acid collected in a 250ml bottle. Anions were analyzed from a filtered sample unpreserved collected in a 250ml bottle. Nutrients were analyzed from a filtered sample preserved with sulfuric acid in a 250ml bottle. Water isotopes were collected in a 20ml bottle with a conical lid.

At each site two 500ml unpreserved unfiltered samples were collected for tritium analysis. These samples were taken to MBMG's secure storage lockers away from large variations in temperature. These samples are reserved for tritium analysis by the University of Waterloo's Environmental Isotopes Laboratory, in Ontario Canada. Samples for tritium analysis were selected after the analytical results were available and was dependent on project funds.

Cations were determined using Thermo iCAP 6300 inductively coupled plasma optical emission spectrometer (ICP-OES). Anions were determined using Metrohm 882 Compact Ion Chromatograph Plus, trace metals with a Thermo X-Series® inductively coupled plasma/mass spectrometer (ICP/MS), and water isotopes using a Picarro Isotopic Water Analyzer, L2130-i. Total dissolved concentrations were computed as the sum of major and minor constituents: bicarbonate (divided by 2.03), calcium, magnesium, sodium, potassium, iron, manganese, silica dioxide, carbonate, chloride, sulfate, nitrogen, phosphate, fluoride, aluminum, copper and zinc.

Pace labs performed the analysis of gasoline-range-organics (EPA 8015), diesel-range-organics (EPA 8015), BTEX (benzene, toluene, ethylbenzene and xylene (EPA 8260)), and methane, ethane, and ethylene (8015M RSK175). All samples were collected using Pace Laboratories protocol and submitted in accordance with Pace's Sample Acceptance Policy. Methane, ethane and ethylene headspace equilibration and concentration calculations were performed by modification of the method of Kambell and Vandergrift (1988). A complete list of major ions, trace metals, and organic constituents is included in Appendix C.

Samples collected for BTEX and GRO analysis were collected in three 40ml volatile organic analysis (VOA) vials preserved (hydrochloric acid) with no headspace. Samples collected for DRO analysis were collected in three 1-liter amber containers preserved with hydrochloric acid with headspace. Samples collected for methane, ethane, and ethylene were collected in 25-30ml headspace vials filled halfway.

10. Data Validation

Sample collection procedures were validated to ensure the samples were collected in a consistent manner such that they are considered representative of the aquifer. Additional validation was conducted to ensure proper laboratory methods and procedures were used. The results of the data validation are included in Appendix D.

Shallow Groundwater Quality and Geochemistry

A charge balance error (CBE) is one test to verify the reliability of water quality data. The CBE is a ratio of the difference in cations and anions to the sum of cations and anions multiplied by 100 (reported in percent). Freeze and Cherry (1979) recommend an acceptable CBE for natural groundwater of +/- 5 percent. All groundwater data from 2013 have an acceptable CBE. Groundwater sample results from 32 wells and one spring collected in 2013, were compared to the historic samples. The samples from 2013 were collected from wells completed in bedrock aquifers within the faulted and folded and flat lying settings, and near to and distant from the recent oil and gas drilling.

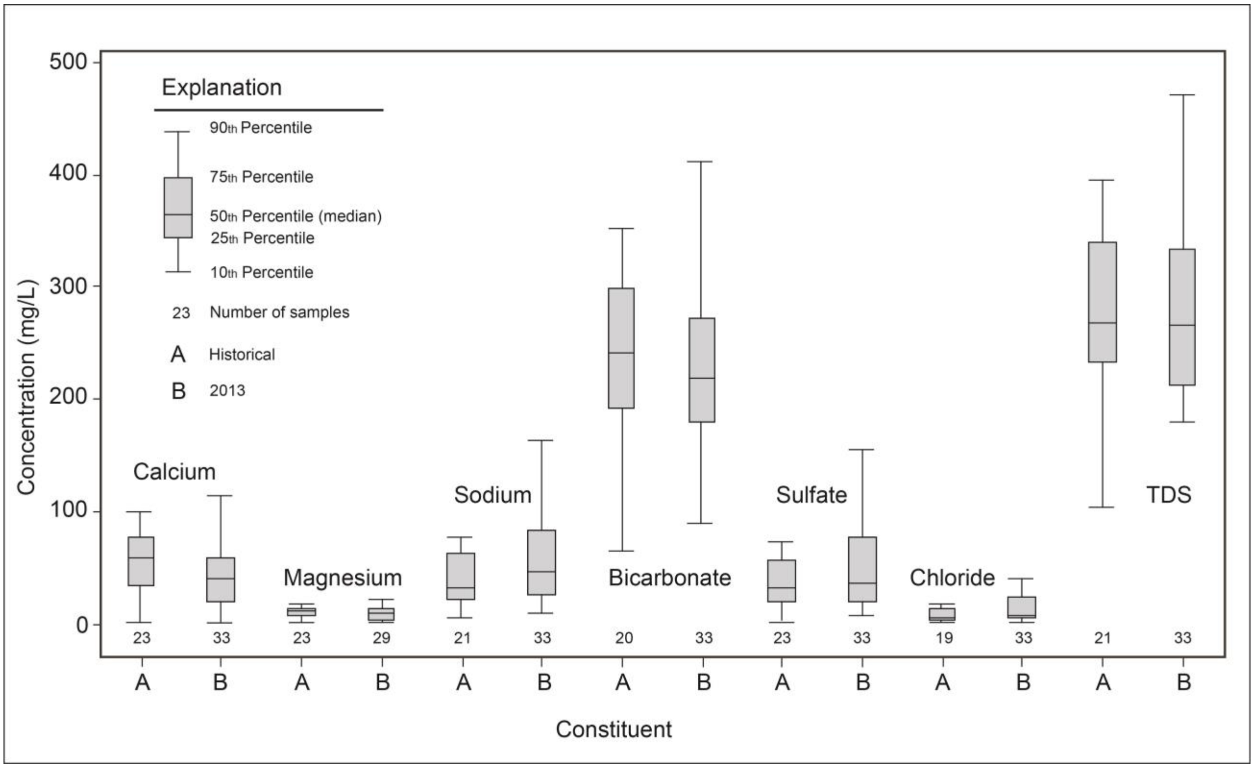


Figure 11. Selected constituents for A, historic data, and B, 2013 chemical data.

Historical groundwater-quality data were obtained from the GWIC and DEQ PWS databases (MDEQ, 2013) (GWIC, 2014). The GWIC database yielded 25 groundwater samples collected between 1992 and 2010 and the DEQ PWS database yielded 68 groundwater samples collected from 4 public water supply wells serving the towns of Clyde Park and Wilsall. For sites with multiple analyses, a median concentration of reported constituents was used for summary statistics. Additionally, groundwater-resources study yielded eight spring locations with groundwater-quality data (Groff, 1962).

Comparisons of the major ions from the historical data to the 2013 data are shown in Figure 11. Bicarbonate is the dominant anion, while calcium and sodium are the dominant cations. Chloride concentrations range from a minimum of 2.1 to a maximum of 47.1 (historic) and 0.9 to 112.4 (2013) mg/L respectively. Median chloride values are 6.0 and 7.3 mg/L. Sodium concentrations have a wider range but are still low, with historical data ranging from 6.0 to 156.0 mg/L and 2013 data from 10.1 to 163.7 mg/L. Median sodium concentrations are 30.8 and 45.8 mg/L respectively. TDS values are typical of high-quality waters. TDS concentrations range from a minimum of 102.6 to a maximum of 394.3 mg/L (historical) and 180.4 to 803.0 mg/L (2013). Median TDS concentrations are 268.4 to 266.1 mg/L respectively. The maximum TDS concentration (803.0 mg/L) was from a well completed in the upper Cretaceous Sedan Formation within the faulted and folded setting. This well is located away from the recent exploratory drilling and has a reported total depth of 195 ft.

Stiff water-quality diagrams graphically display groundwater composition. They are shown as milliequivalents per liter (meq/L) of cations (sodium, calcium, and magnesium) on the left side, and anions (chloride, bicarbonate, and sulfate) on the right side. The sizes of Stiff diagrams are correlated with TDS; larger diagrams represent samples with greater TDS concentrations.

Figure 12 shows the location of the historical samples and displays Stiff diagrams for historical samples where the full suite of major ions was available (25 of 29). Additionally, Stiff diagrams are shown for historical chemical data from streams draining the Bridger Range. These surface water data are not included in the historical groundwater summary statistics (fig. 11). Most historical sites are located in the southern part of the Basin. Historic water-quality data were not available around the five recently drilled oil and gas wells north of Wilsall (fig. 12).

The Stiff diagrams show the streams draining the Bridger Range are calcium-bicarbonate type waters with TDS values less than 221.6 mg/L (blue diagrams, fig 12). Most historic groundwater Stiff diagrams show either calcium- or sodium-bicarbonate waters, but with greater TDS concentrations (less than 363.8 mg/L) compared to the streams draining the Bridger Range.

Stiff diagrams from historical samples east of Wilsall and Clyde Park show sodium-bicarbonate type waters. Stiff water-quality diagrams from the 2013 data are shown in Figure 13. These data include three stream sites not included in the 2013 groundwater summary statistics (fig. 11). Concentrations of the major ions in 2013 were comparable with historical concentrations. Chloride concentrations are highest in wells north of Wilsall in the faulted and folded setting, where wells are completed in the Billman Creek Formation of the upper Cretaceous Livingston Group (Berg and others, 2000). The Billman Creek Formation is a valley-forming claystone interbedded with sandstone and siltstone. Reported well depths range from 45 to 305 ft deep (GWIC, 2014). Based on the 2013 data, chloride concentrations increase with depth. In contrast, the wells completed in the Fort Union Formation do not show increasing chloride concentrations with depth. The Fort Union wells range from 40 to 415 ft deep (GWIC, 2014).

Most of the water sampled in 2013 is a calcium-bicarbonate type, however 9 wells completed in the flat-lying setting have sodium type water and 5 wells completed in the faulted and folded setting are either sodium-sulfate or sodium-chloride type water. All three surface water samples collected in 2013 were calcium bicarbonate waters (fig 13).

The concentration of dissolved constituents in ground water is a result of the initial chemistry of the recharge water and the subsequent interactions with soils and aquifer materials. Typically, when water moves through an aquifer from areas of recharge to areas of discharge, the concentration of dissolved constituents increases. The type of constituents (cations and anions) dissolved in the ground water will be controlled by the length of time that the water has been in the subsurface, the composition of the aquifer materials, and the controlling geochemical reactions (primarily dissolution, precipitation, oxidation-reduction, and ion-exchange, and sorption – desorption reactions). Trilinear Piper diagrams graphically compare the relative

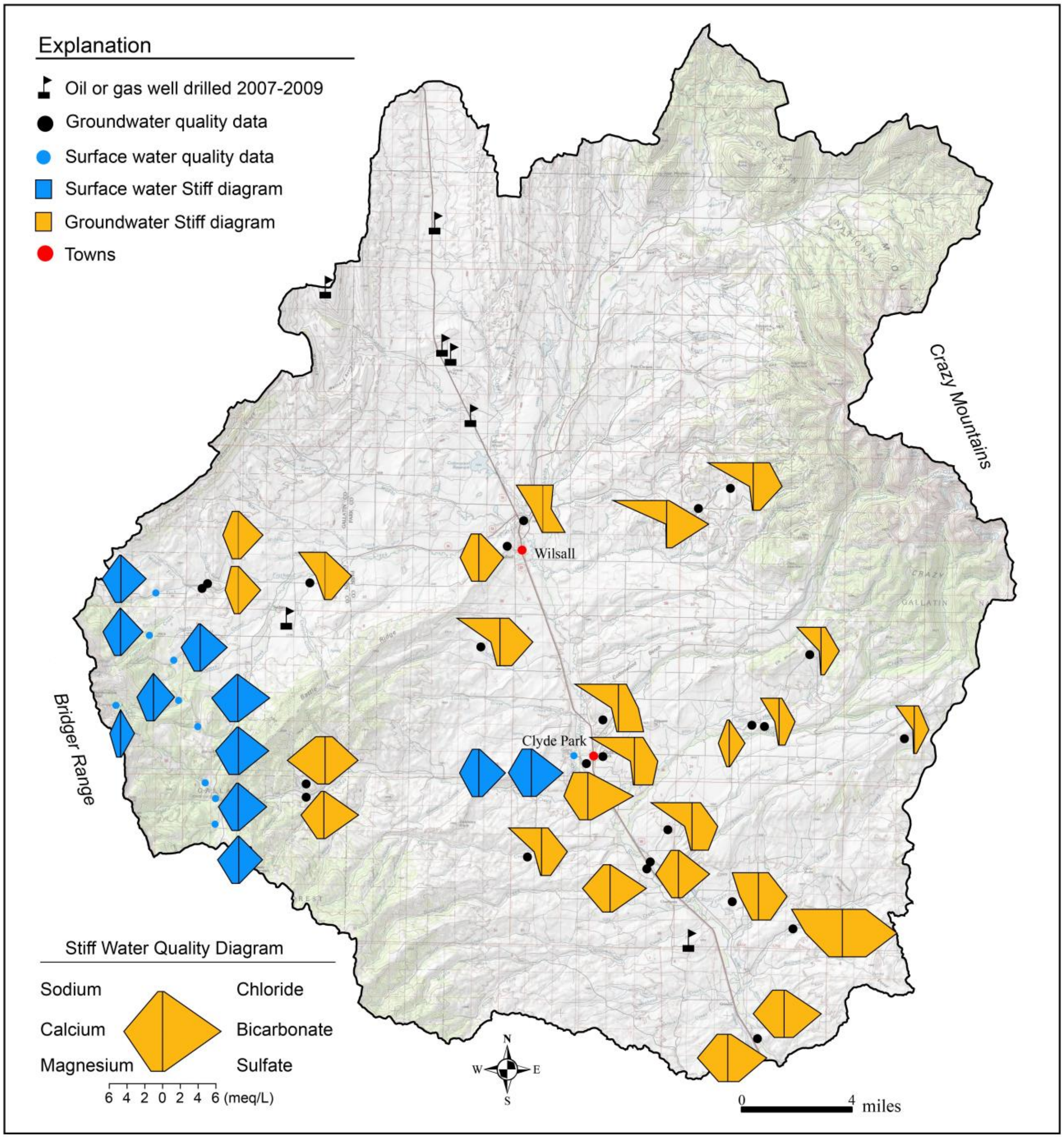


Figure 12. Historical surface water and groundwater-quality data (1961-2010) shown as Stiff water-quality diagrams.

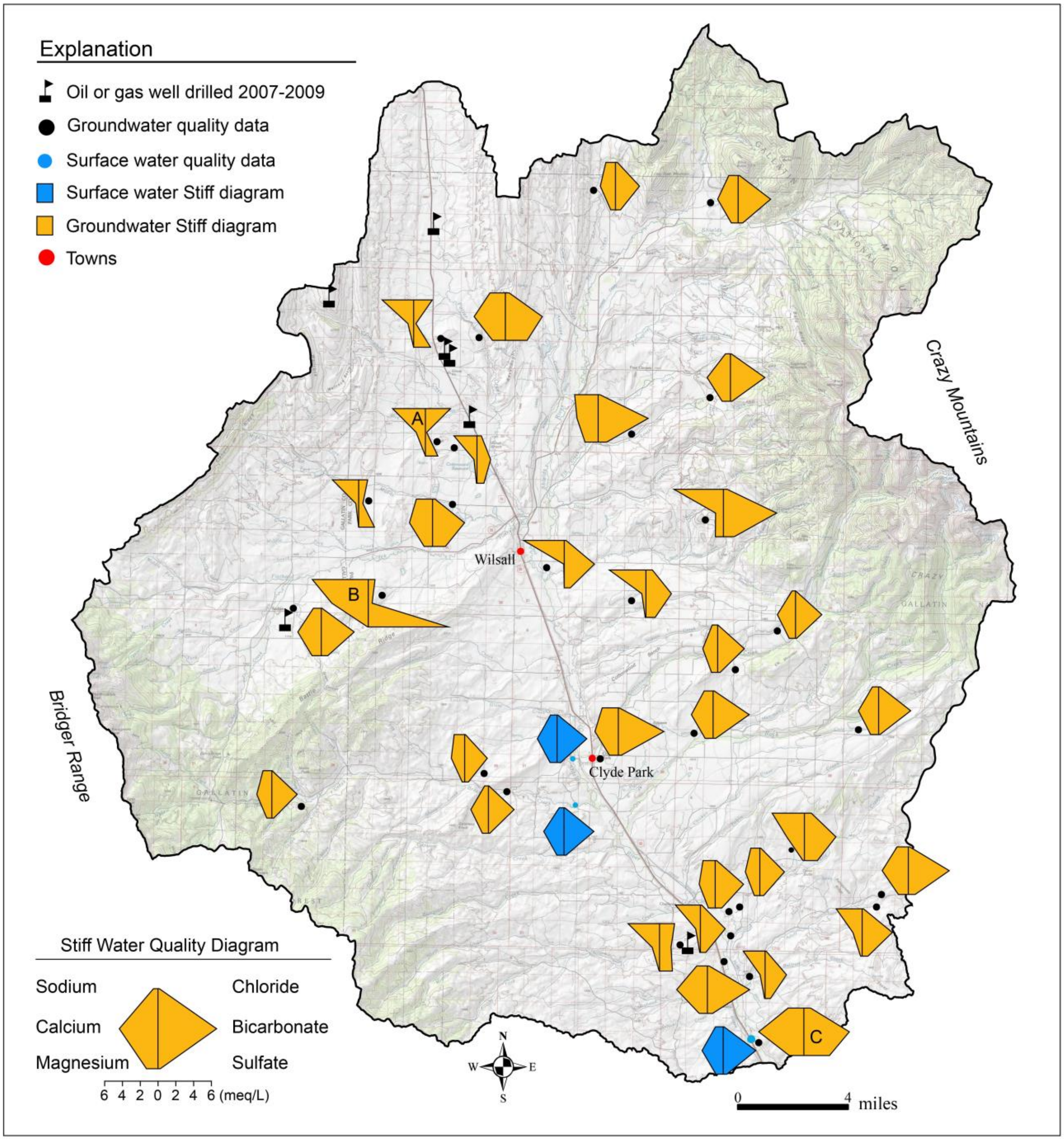


Figure 13. Current study surface water and groundwater-quality data shown as Stiff water-quality diagrams. One well exceeded human health standards for selenium and two for TDS. These wells are labeled A, B, and C respectively.

percentages of major-ion concentrations for numerous samples. The relative percentage of cations and anions are plotted in the triangles at the base of the diagram, then projected onto the central diamond. Different water types are differentiated by where they plot in the central diamond.

Major ions dissolved in the groundwater may change due to rock-water interactions. Results from the 2013 samples are shown in the Piper diagram in figure 14. Most samples plot in the calcium- or sodium-bicarbonate parts of the central diamond.

Calcium-bicarbonate type waters are typical of fresh recharge with little rock-water interaction. Wells with calcium-bicarbonate waters are likely near recharge areas. Calcite ($CaCO_3$), abundant in soils and rocks, dissolves to form calcium and bicarbonate in groundwater. Equation 1 is a simplified equation describes the dissolution of calcite. This is the primary reaction that produces calcium-bicarbonate type water.

Equation 1. Calcium bicarbonate water type

$$CaCO_3 + H^+ \Leftrightarrow HCO_3^- + Ca^{2+} \qquad (1)$$

Sodium-bicarbonate or sodium-chloride waters that are likely to be found farther away from the recharge source. These sodium type waters suggest a longer residence time that has allowed for the evolution from calcium- to sodium- type. Water enriched in sodium and bicarbonate is due primarily to ion-exchange reactions in which calcium and magnesium are removed from solution and exchanged for sodium. The removal of calcium from solution keeps the water under-saturated with respect calcite allowing it to continue to dissolve and bring more HCO_3 into solution. Equation 2 describes this reaction. Therefore, if the right mineralogy is present in the aquifer, as fresh recharge water moves though the subsurface it can evolve to sodium-bicarbonate type water (Brink and others, 2008).

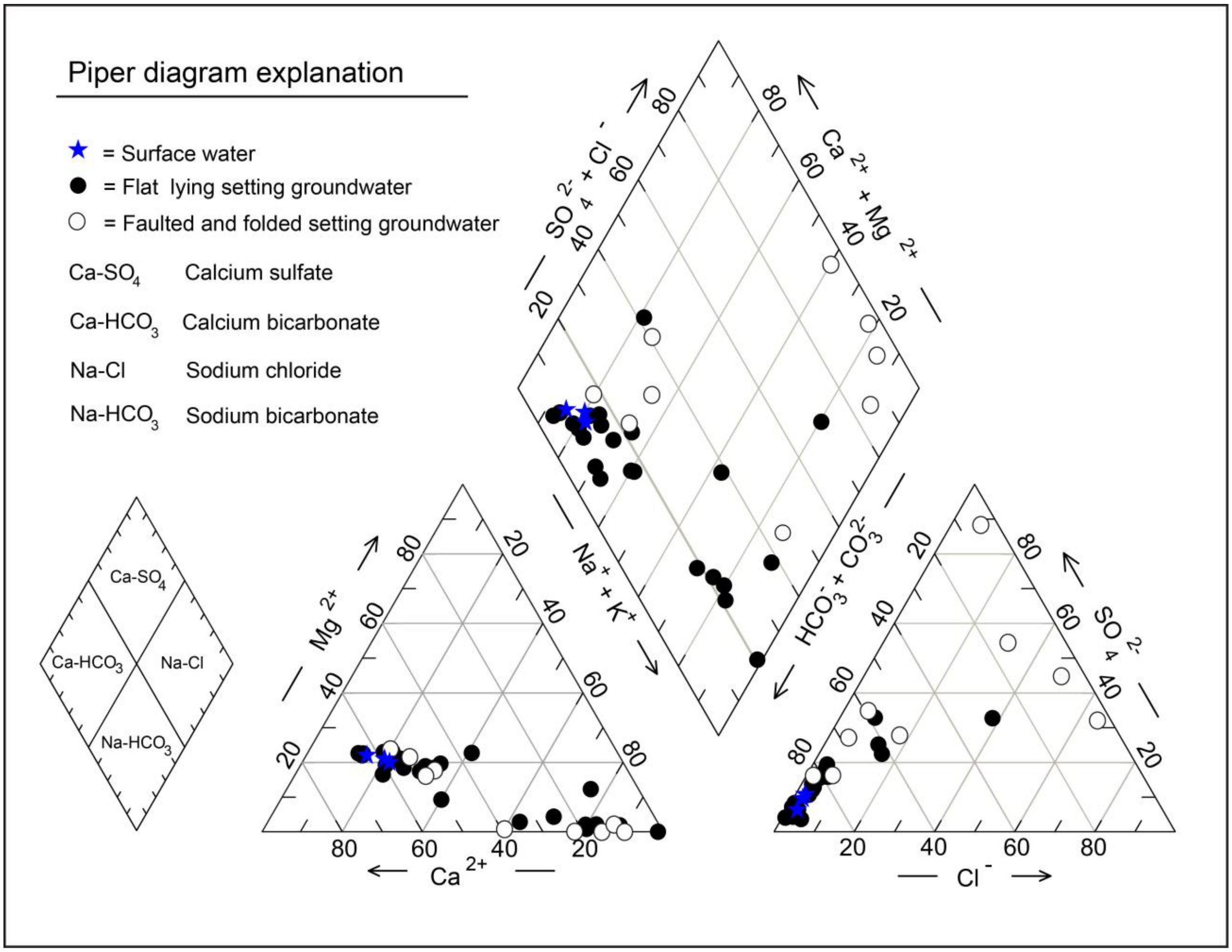


Figure 14. Piper water quality diagram showing surface water and groundwater-quality data from the current (2013) study.

Equation 2. General ion exchange or sorption / desorption reaction

$$Na_2X + Ca^{2+} \Leftrightarrow CaX + 2Na^{+} \quad (2)$$

A comparison of TDS values from the Bridger Range streams with calcium- and sodium-type waters is shown on figure 15. Additionally we compare TDS values from the faulted and folded setting to the flat lying setting (fig. 15). The Bridger Range streams have the lowest TDS concentrations with a median concentration of 186.0 mg/L. Calcium type groundwater has a lower TDS median compared with the sodium type waters (250.6 and 310.9 mg/L respectively) and median TDS values are lower in the flat lying setting compared to the faulted and folded setting (264.1 and 312.8 mg/L respectively). These comparisons of TDS values suggests that while calcium-bicarbonate type waters are found throughout the Basin, waters obtained from faulted and folded setting have longer residence time allowing for rock-water interactions.

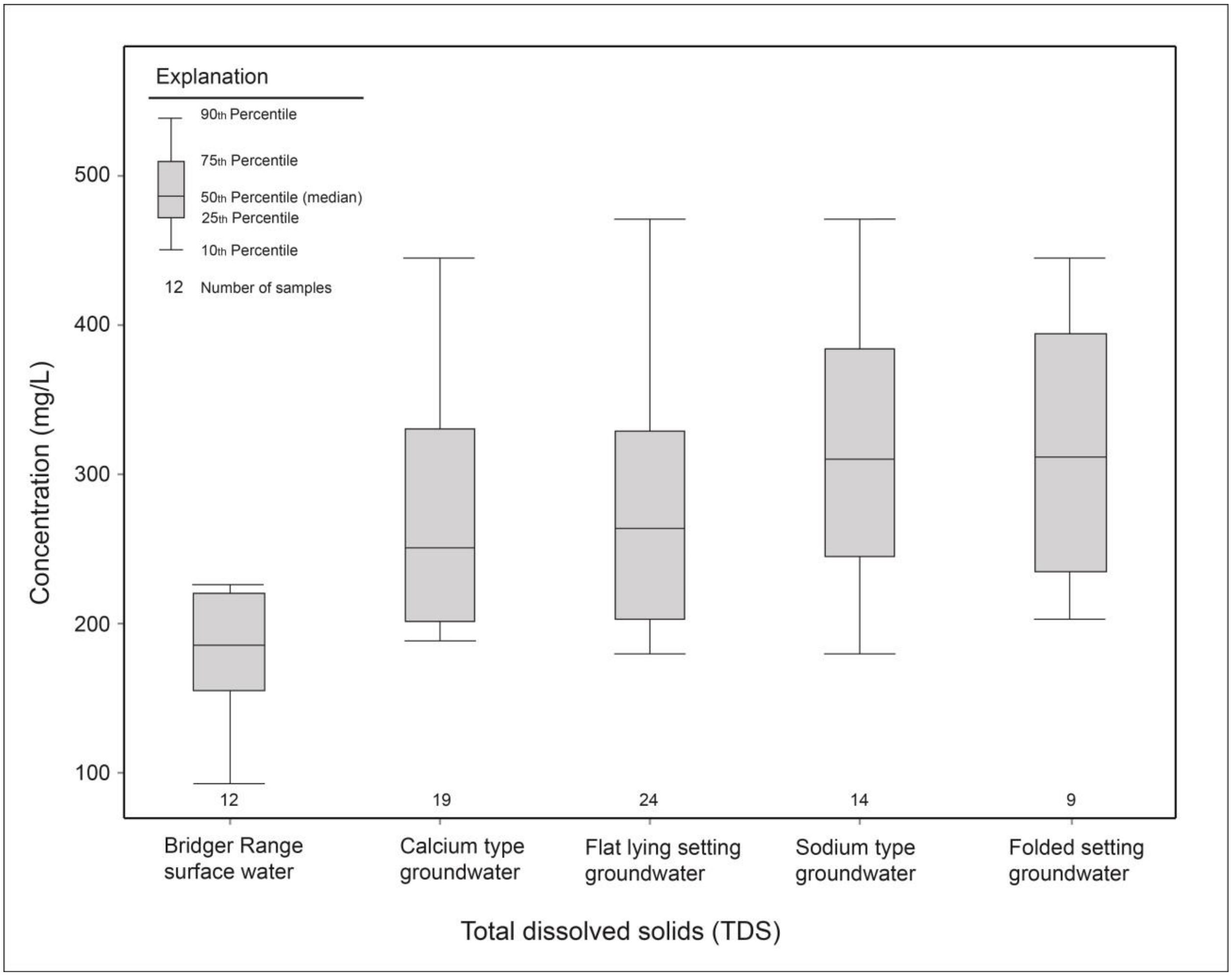


Figure 15. Current study surface water and groundwater-quality TDS shown on a box and whisker plot.

10.1. Human Health Standards

Groundwater in the Basin is of excellent quality and suitable for domestic and stock uses. The U.S. Environmental Protection Agency gives a health standard of 50 µg/L for selenium and an aesthetic quality standard of 500 mg/L for TDS; these two standards were exceeded in three samples collected in 2013. One well sample had a selenium concentration of 86.97 micrograms per liter (µg/L) (labeled A in figure 13) and two other samples had a TDS values of 803.1, and 556.6 milligrams per liter (mg/L) (labeled B and C in figure 13). Completion records for these wells indicate total depths of 40 ft (TDS, 556.6 mg/L), 295 ft (TDS, 803.1 mg/L) and 305 ft (Se, 86.97 µg/L). The deeper wells are completed in the upper Cretaceous Sedan and Billman Creek formations. The 40 ft well is completed in the Fort Union Formation near the Shields River Basin's outlet and confluence of the Shields River and Yellowstone River.

10.2. Water Isotopes

Isotopes are elements with different number of neutrons compared to protons; they are useful environmental tracers in hydrogeology. Isotopes of hydrogen and oxygen are used extensively in hydrogeological studies to fingerprint and date groundwater and surface water (Clark and Fritz, 1997). Oxygen has three stable isotopes, ^{16}O, ^{17}O, and ^{18}O. Oxygen-18 (^{18}O) is heavier than the other two, and preferentially condenses in precipitation. During evaporation the opposite occurs, ^{18}O is left behind in the evaporated water as the lighter isotopes evaporate first. The same is true for ^{2}H (deuterium), the stable heavier isotope of hydrogen. The most common form of hydrogen is ^{1}H.

Ratios of the heavy to light isotope of oxygen and hydrogen in water are reported as delta (δ) values in per mil (parts per thousand) relative to a standard known as Vienna Standard Mean Ocean Water (VSMOW). Samples with positive delta values contain more of the heavier isotope (^{18}O and ^{2}H) relative to the standard whereas samples with negative delta values contain less of the isotope relative to the standard.

Delta values of oxygen and hydrogen isotopes in global precipitation vary in their relationship to each other in a predictable linear fashion known as the Global Meteoric Water Line (GMWL) (Craig, 1961). This line serves as a reference for discussing oxygen and hydrogen isotopes in hydrological studies. Groundwater systems with isotopic compositions plotting near the GMWL are recharged from precipitation with little influence from evaporation. Evaporated sample isotope ratios plot below the GMWL. The isotopic composition of groundwater generally reflects the average isotopic composition of precipitation in a recharge area. Spatial and temporal variations in the isotope ratio of precipitation can be useful in identifying groundwater recharge sources (Clark and Fritz, 1997).

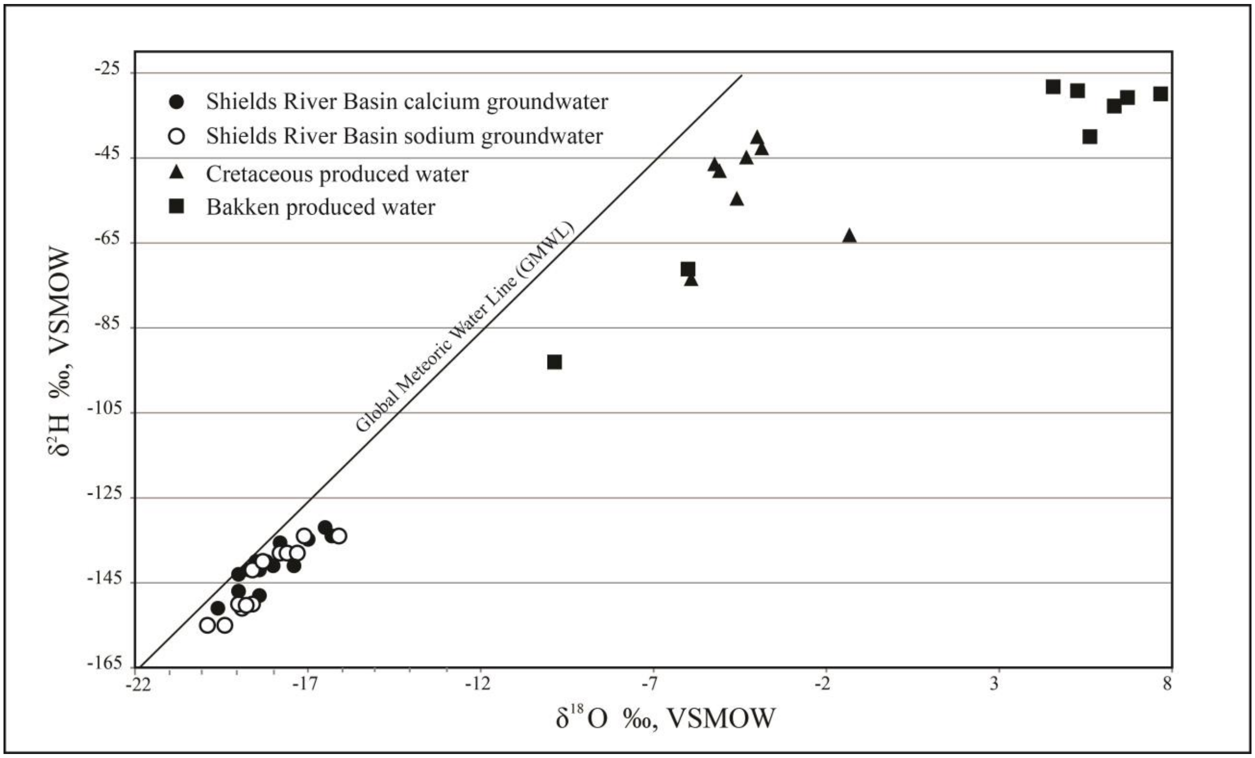


Figure 16. Oxygen and hydrogen isotope analyses from the Shields River Basin compared to production water from the Bakken and Cretaceous formations. Bakken analyses obtained from Rod Caldwell USGS, Helena, MT and Cretaceous analyses from the USGS Produced Waters Geochemical Database (USGS, 2014).

Samples from 33 wells, a spring, a holding reservoir, a lake, and 8 streams were analyzed for ratios of oxygen and hydrogen (Appendix E). Groundwater samples were collected throughout the 2013 field season (June to November). The lake, holding reservoir, and surface water samples were collected in October during base flow conditions. Additionally, one snow sample was collected from the crest of the Bridger Range on January 2, 2014.

Shields River Basin water isotopes plot near and slightly below the GMWL. Sodium-type groundwater tend to be isotopically lighter (more negative delta values), plotting in a group below the local evaporation line which indicates they may have been recharged under colder higher elevation different conditions compared to calcium type groundwater. Tritium concentrations indicate the sodium type groundwater is older than the calcium-type groundwater (see following section).

Shields River Basin groundwater isotope ratios range from δ^2H values of -155 to -128 and δ^{18}O values of -19.9 to -14.6 per mil. In order to help identify the presence of produced water in the Shields River Basin groundwater, these values are compared to the isotope ratios from produced water from Cretaceous age formations (USGS, 2014) (fig. 16). Produced water data were obtained from a recent characterization of shallow groundwater in the Williston Basin from Bakken reservoir rocks (McMahon and others, 2014). These data show produced waters from Cretaceous age and Bakken reservoir rocks are very distinctive compared to the shallow groundwater in the Basin (fig. 16). Bakken and Cretaceous reservoir produced waters have median δ^{18}O values of 5.0‰ and -4.5‰, respectively, compared to the δ^{18}O median value -18.2‰ of groundwater in the Basin. Median deuterium values are -32.0‰ and -47.2‰ from Bakken and Cretaceous reservoir produced waters, respectively, compared to the median value of -141.0‰ for groundwater in the Basin. A groundwater sample that was a mixture of produced water and shallow groundwater would fall between these two populations on fig. 16. Because the Basin groundwater is fairly tightly grouped, there does not appear to be evidence of produced water in the shallow groundwater system.

10.3. Tritium

Tritium is a radioactive isotope of hydrogen (^{3}H) with a half-life of 12.3 years (NIST, 2015) that occurs both naturally and is artificially created in nuclear reactors and weapons (Clark and Fritz, 1997). Natural tritium forms in the upper atmosphere from bombardment of cosmic radiation. Atmospheric tritium combines with oxygen to form water, in the late 50’s and early 60’s above-ground weapons testing produced a large increase in atmospheric tritium. The atmospheric tritium has been a useful hydrologic tracer.

Tritium from vintage wines in the Naples NY, and the Bordeaux and Rhone regions in France indicates weapons testing (pre-bomb) concentrations were between 3.4 and 6.6 tritium units (TU) (Clark and Fritz, 1997). Nearly six decades after the weapons testing, atmospheric tritium is approaching pre-bomb levels and quantifying mean groundwater residence times or absolute ages is more of a challenge. A parcel of precipitation or snowmelt recharged to a deep aquifer in 1980 will today have tritium concentrations of natural atmospheric production.

However, tritium can be used to qualitatively date groundwater. For this report tritium concentrations were classified: (1) sub-modern: no detectable tritium, (2) a mixture between natural atmospheric and sub-modern tritium (0.8-4 TU), (3) natural atmospheric range tritium modern (5-15 TU), and (4) tritium elevated above the atmospheric range (15-30 TU) (Clark and Fritz, 1997)

For the current study, 24 groundwater samples were submitted to Waterloo Environmental Isotope Laboratory for enriched tritium analysis (detection limit = 0.8 TU). The results indicate 5 samples without detectable tritium (<0.8 TU), 2 samples with tritium levels below natural atmospheric production (< 4 TU), and 17 samples in the natural atmospheric range (6.1- 8.2 TU). None of the samples had tritium levels above the natural atmospheric range (fig. 17).

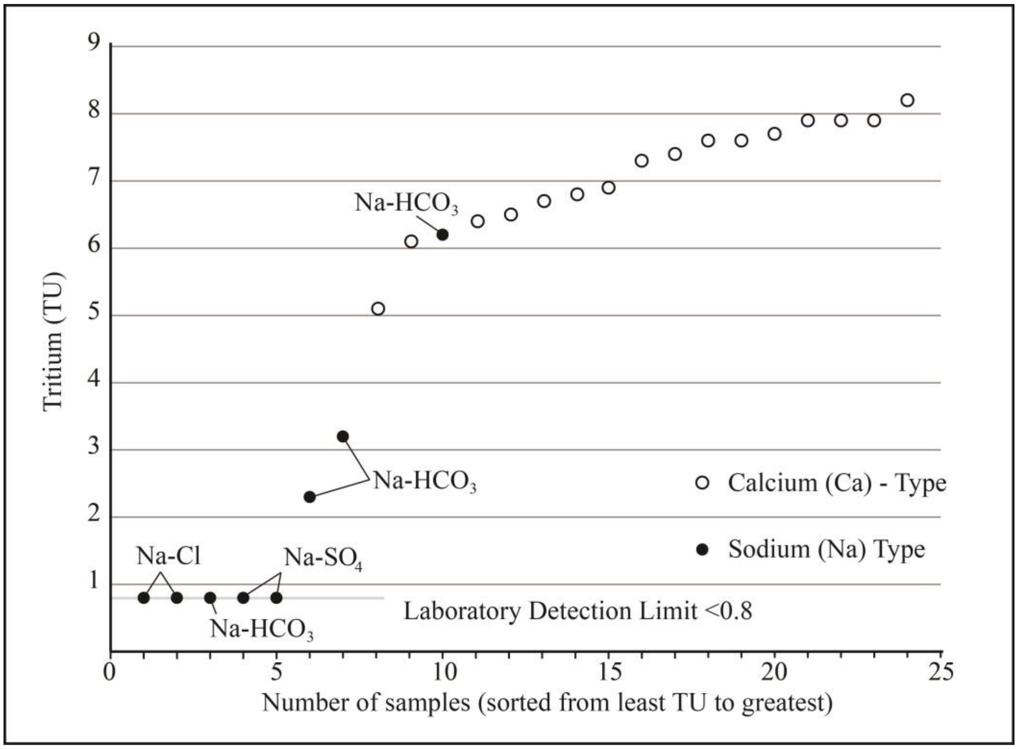


Figure 17. Tritium vs. water type

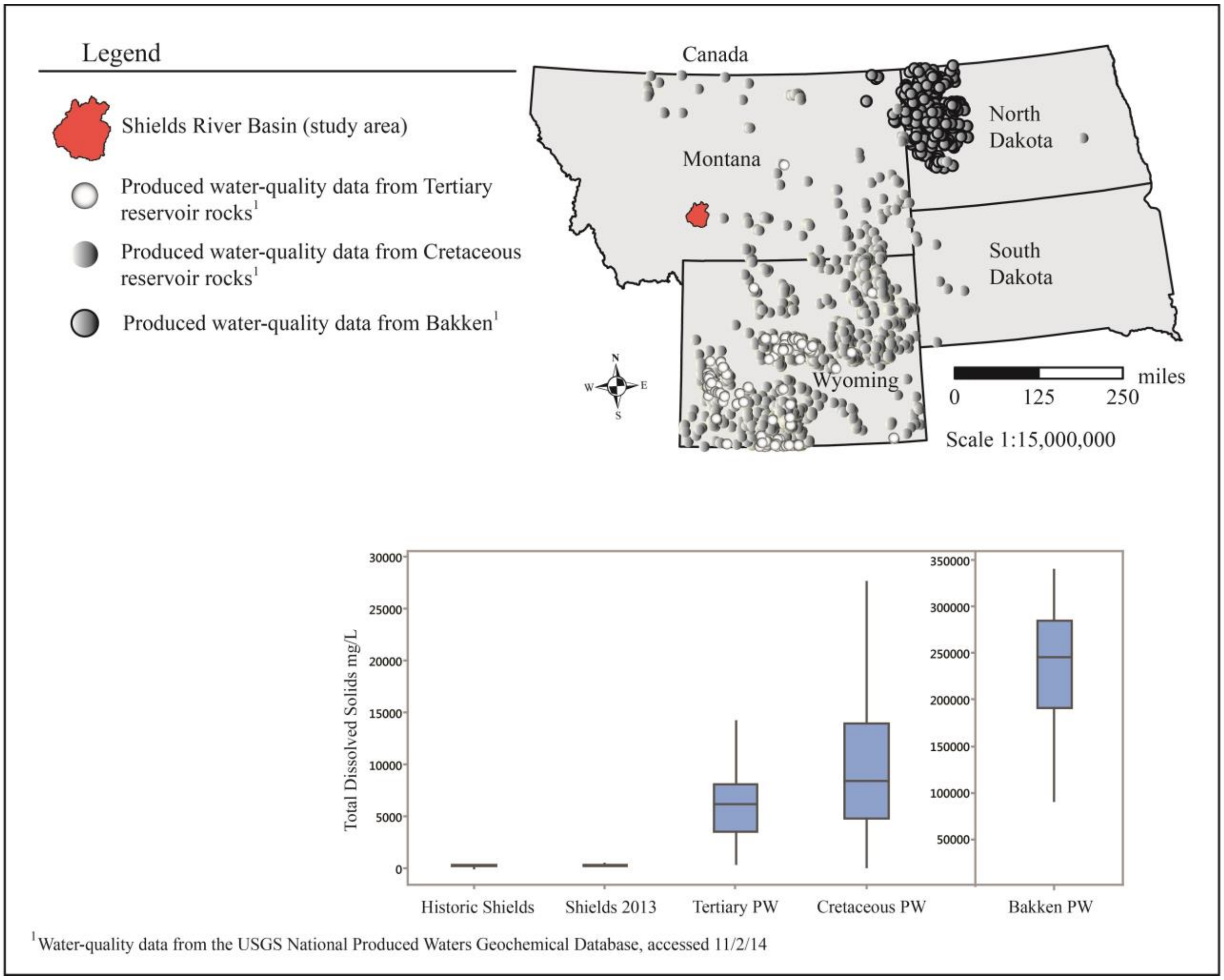
There were notable differences in the tritium concentration between different water types. Groundwater samples with tritium levels below atmospheric or non-detectable (<0.8) tritium are sodium water types (Na-Cl, Na-HCO$_3$, or Na-SO$_4$). Conversely, samples with tritium in the natural atmospheric range are calcium type waters (Ca-CO$_3$). The tritium results suggest that calcium type waters are younger and less evolved compared to the sodium waters that are older and more evolved.

10.4. Organic Water-quality Data

Samples from 24 wells, 2 springs, and 3 surface water locations were analyzed for the organic suite methane, ethylene, ethane, BTEX, DRO and GRO. No organics were detected in the 2013 samples except low concentrations of methane and ethylene. Methane concentrations were detected in 6 wells and ethylene in 3 wells. Methane concentrations range from 0.0139 to 0.184 milligrams per liter (mg/L) and ethylene from 0.0075 to 0.0138 mg/L. There is no human health standard for dissolved methane and ethylene in drinking water. The U.S. DOE Office of Surface Mining and Reclamation recommends a threshold value 10 mg/L for methane (Eltschlager, 2001). Water with methane concentrations 10 mg/L or higher, may degas and potentially create an explosive environment. Three wells with methane detections in 2013 were resampled in 2014, but methane, ethylene, and ethane were not detected. The reported laboratory detection limit from Pace laboratories is 0.0066 mg/L for methane and 0.0062 mg/L for ethylene and ethane.

11. Produced Water Quality and Geochemistry

The USGS Produced Waters Geochemical database contains chemical data on major ion, trace elements, and isotopes for waters produced in oil and gas fields nation-wide. Basin groundwater-quality data was compared to produced water-quality data from reservoir rocks in Montana and surrounding states to provide an indication of how contamination from energy development activities would affect inorganic constituents in shallow groundwater. Chemical data from Tertiary, Cretaceous, and Bakken Formation reservoir rocks in Montana, North Dakota, South Dakota, and Wyoming from sites associated with an API number and acceptable CBE were compiled (fig. 18). Tertiary reservoir rocks are equivalent in age to the Fort Union Formation (flat-lying setting), whereas the produced water from Cretaceous reservoir rocks are equivalent in age to the Cody and Mowry shales (faulted and folded setting). The Bakken Formation is older (Late Devonian and early Mississippian age), but included because of its recent development in Montana.



[1] Water-quality data from the USGS National Produced Waters Geochemical Database, accessed 11/2/14

Figure 18. Shields River Basin groundwater-quality data compared with produced waters from Montana, South Dakota, North Dakota, and Wyoming.

Figure 18 shows the locations of produced-water samples and presents a comparison to Shields River Basin (2013) groundwater. Note the scale was changed to include the higher TDS waters produced from the Bakken. Median TDS concentrations are 245,818 mg/L from the Bakken. Median values from Cretaceous- and Tertiary-age produced waters are 8,413 mg/L and 6,206 mg/L, whereas values from the Basin are less than 300 mg/L. The produced waters from areas surrounding the Basin have a sodium-chloride water type; this water type is common in deep formation waters. Samples collected in 2013 were generally calcium- or sodium-bicarbonate water type and have sodium and chloride concentrations two or more orders of magnitude lower than the produced waters.

Median sodium concentrations are 75,600 mg/L from the Bakken production. Median values from Cretaceous- and Tertiary-age produced waters are 2,946 mg/L and 2,312 mg/L, whereas values from the Basin are less than 50 mg/L. Median sodium concentrations are 149,073 mg/L from the Bakken production. Median values from Cretaceous- and Tertiary-age produced waters are 3,699 mg/L and 2,500 mg/L, whereas values from the Basin are less than 10 mg/L.

Oil and gas drilling in the Shields River Basin will likely produce water with major ion and TDS values similar to the Cretaceous age produced water shown on figure 18. This large difference in TDS concentrations and major ion values between the Basin samples and the produced water suggests that if produced water were introduced into the shallow groundwater system it would be apparent in the basic water chemistry.

12. Limitations Associated with Data Interpretation

Shields River Basin 2013 chemical data show an inherent bias toward areas where land-owners provided access and granted permission to collect groundwater samples. Existing water-wells are completed in zones that satisfy the landowner desire for use and not necessarily for the purpose of aquifer characterization.

Some limitations exist with the use of chemical data collected from domestic and stock wells with permanently installed pumps. The well and the open or screened interval may not fully penetrate or isolate aquifer zones of interest. Conversely, well screens may be installed across multiple water bearing zones; integrating the water quality of each zone. Materials of well and pump construction may affect the chemical data. Aeration and degassing in the water column when the well is pumped can affect water chemistry (USGS, 2006). This degassing can cause dissolved gas concentrations to decrease during pumping. The water chemistry presented here represents the shallow groundwater system utilized by the residents in the Basin. Dissolved organics may exist in the aquifers, but based on the samples collected in 2013 they are either non-detectable or present at low concentrations when pumped to the land surface.

Chemical data used in this 1-year study represent a snapshot of water-quality from June to November 2013. Water chemistry may vary seasonally or over larger time scales, that sampling for this study will not capture. Additionally, the extrapolation of chemical data across large distances necessary for this study may not completely represent the local variations. Water types presented here are for all the samples in the Basin containing a full suite of major ions. These classifications are meant only to portray general information and are not meant to be precise classifications. Samples where no one cation or anion represents 50 percent of the total ions present are considered mixed samples. These water types should technically be named with all major contributing ions (Hem, 1985). This precision in the naming of water-types was not incorporated in this study.

Lastly, the results of this study should be considered in the context of groundwater age. A recent study from the Williston Basin (McMahon and others, 2014) indicates some groundwater velocities in the Fort Union Formation were slow enough such that near surface contamination may not have reached their sample locations. Like this study, McMahon and others (2014) found some groundwater was recharged prior to the mid-1950’s and some was recharged since the mid-1950’s. Their more extensive groundwater age dating implies that contaminants from energy development would still be less than 0.5 km (1,640 ft) from the source. Wells that obtain younger water are likely completed in flow systems with faster velocities, but these rates are uncertain. McMahon and others (2014) conclude domestic wells obtaining water, recharged prior to the mid-1950’s may not be as well suited to detect near surface contamination as wells screened in faster flow systems. With the exception of one location water-wells tested for this study are greater than a mile away from the exploratory oil and gas drilling.

Conclusions

This study uses chemical data from surface water, springs, and existing water wells to describe the shallow groundwater resource utilized by residents of the Shields River Basin. Samples collected in 2013 show no indication that the exploratory drilling has affected shallow groundwater quality.

Based on groundwater quality, water types, and tritium, residents obtain water of varying residence times. Longer residence times are characterized by sodium-type waters. Sodium type waters exist in both the Fort Union and Cretaceous aquifers; these waters are more chemically evolved compared to younger water (shorter residence times). Typically, calcium-bicarbonate waters are associated with younger water where rock-water interactions are limited. Tritium concentrations imply sodium-type waters were recharged prior to 1950 whereas calcium-type waters are recharged more recently. A recent study in the Williston Basin indicates groundwater flow rates in the Fort Union Formation between 10 and 25 meters per year in flow paths recharged prior to 1950 (McMahon and others, 2014). Groundwater in local flow paths likely moves at a faster rate, but that rate is uncertain. Most residents in the Shields River Basin use groundwater that has been recharged since 1950 and is likely a mixture of snowmelt recharge and waters of many different ages.

A GIS model was developed to rank the shallow groundwater resource susceptibility to downward migration of surface spills. This GIS model served as another tool to select sampling locations where groundwater is susceptible to contamination from the surface.

Historical and 2013 groundwater quality data from the Basin show TDS concentrations 1-2 orders of magnitude less than produced waters. Produced waters are predominately sodium-chloride. Water isotopes in the Basin plot near and slightly below the GMWL and differ from produced water that plots below the GMWL. Produced waters from Cretaceous age reservoir rocks have median values that are enriched by 13.7 (^{18}O) and 109 (^{2}H) per mil. Low levels of dissolved methane and ethylene were detected in some samples from 2013, but were not detected in samples from 2014. No other organics were detected as part of this study.

Generally groundwater in the Basin is calcium- or sodium-bicarbonate type water. Some sodium-chloride or sodium-sulfate waters do exist. Sodium type waters typically have greater TDS values compared to the calcium waters. However, low TDS sodium waters northwest of Wilsall also have low TDS concentrations. These sodium type waters with low TDS have tritium concentrations indicating recharge prior to 1950. The geochemistry of the recharge water and groundwater evolution forming these low-TDS waters pose an intriguing problem for further study.

Recommendations

This study characterizes shallow groundwater in the Shields River Basin using existing domestic wells and springs. Chemical data from this study show water types, relative groundwater ages, concentration ranges of major ions and trace metals, and water isotopes throughout the Basin. These data do not show seasonal fluctuations in water quality.

Our first recommendation is to resample wells and springs quarterly for a year. Quarterly sampling will provide an indication of the seasonal fluctuations in water quality. Of particular interest are 2013 sample sites located in the faulted and folded setting near the exploratory drilling. Samples should be analyzed for major ions, trace metals, and the organic suite tested in this study (Appendix D). We recognize water-quality sampling is expensive and for most residents the costs may be an issue. NGWA recommends having a qualified professional conduct the sampling and this further increases the cost (NGWA, 2015). Additional samples should be collected by purging 3 casing volumes prior to sample collection. If the cost of sample analysis is a limiting factor, analyses should contain at least the major ions and methane.

Our second recommendation (should drilling occur again in the Basin) is that residents consider requiring energy development companies to install a properly constructed monitoring well near the energy production well. A monitoring well should fully penetrate the aquifer used by residents in close proximity and produce yields typical of those in the area. The well should be located immediately down gradient from energy development. A qualified third party should oversee the monitor well construction and groundwater sample collection.

In 2013, the Colorado Oil and Gas Conservation Commission approved statewide mandatory groundwater sampling and monitoring rules requiring pre- and post-drilling sampling (COGA, 2015). Colorado’s rules are rigorous and provide guidance for most oil and gas drilling scenarios; they require one initial and two subsequent samples from up to four sites located within one-half mile of a new oil and gas well or injection well. Initial samples are collected within 12 months of setting the conductor pipe. Two subsequent samples are collected after completion between 6 and 12 months, then again between 60 and 72 months (COGA, 2015)

If oil and gas drilling occurs in the Basin, the National Ground Water Association (NGWA) recommends water be retested and compared to baseline results and against any fracturing chemicals that may have been voluntarily disclosed (NGWA, 2015). The Groundwater Protection Council maintains “FracFocus”, a chemical disclosure registry website (http://fracfocus.org/). NGWA recommends testing should occur within 6 months of completion of drilling and continue at least annually as long as practical.

A less expensive way to see if changes have occurred is to screen using a pH and specific conductance (SC, related to TDS) probes. Qualitative chloride test strips can give inexpensive chloride results. An increase in SC, pH or chloride indicates the more extensive water-quality testing should be done (NGWA, 2015).

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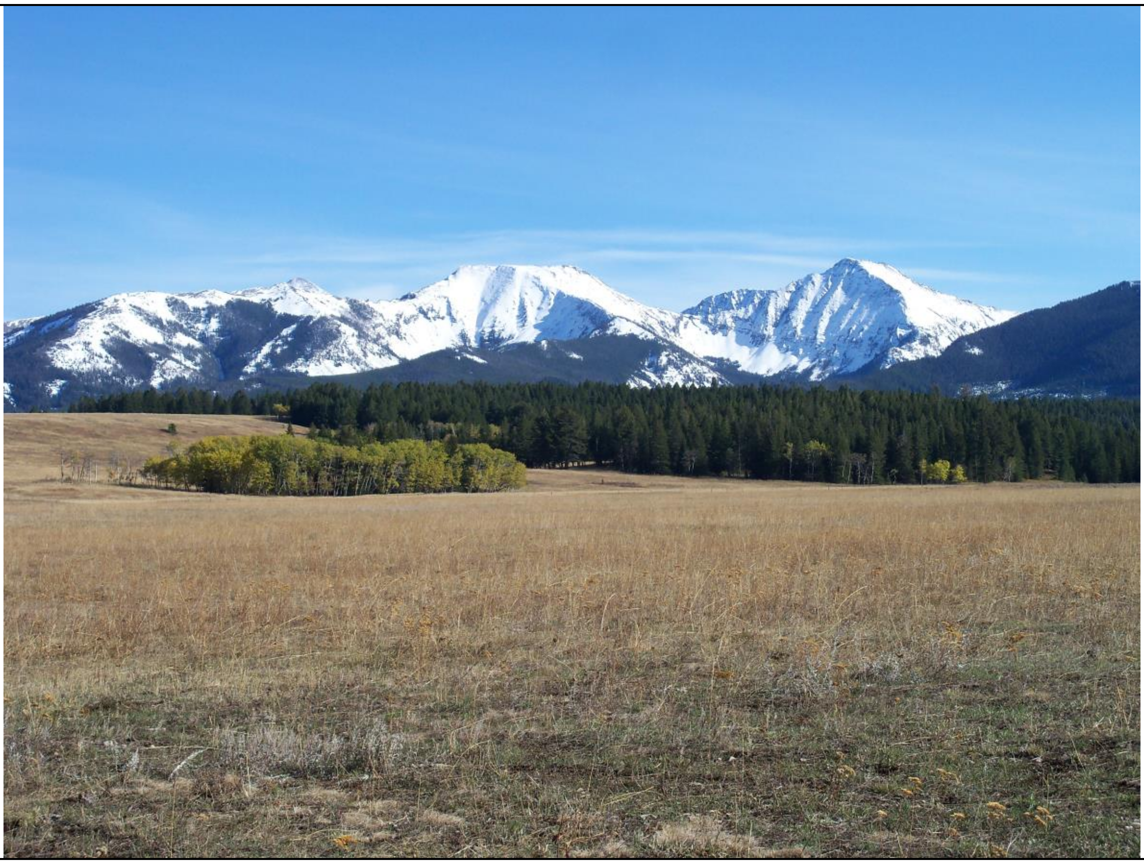
Appendix A: Photographs

Shields River Basin 2013-2014 sampling Photographs
South-Central, Montana



PHOTOGRAPH 1 Dense forests flank the Crazy Mountains with dry upland areas flanking the dense forests. Photograph taken October 2013 by D.Blythe.

Shields River Basin 2013-2014 sampling Photographs
South-Central, Montana

PHOTOGRAPH 2 Typical abandoned oil and gas well site during 2013-2014 Baseline sampling in the Shields River Basin, south central Montana. Left-Center in photograph is a steel post with location information. Site has been reclaimed. Photograph taken July 2013 by D.Blythe.

Shields River Basin 2013-2014 sampling Photographs
South-Central, Montana

PHOTOGRAPH 3 Shut in Devon Energy well 2013-2014 Baseline sampling in the Shields River Basin, south-central Montana. Photograph taken July 2013 by D.Blythe.

Shields River Basin 2013-2014 sampling Photographs
South-Central, Montana

PHOTOGRAPH 4 A Fort Union Formation outcrop forms the east bank of the Shields River near Wilsall. The photo is taken looking north. Photograph taken July 2014 by D.Blythe.

Shields River Basin 2013-2014 baseline sampling photographs
South-Central, Montana

PHOTOGRAPH 5 Alluvium has been removed by erosion near the confluence of the Shields River and Yellowstone River. Photograph taken July 2014 by D.Blythe.

Appendix B: Montana Bureau of Mines and Geology Organic Sampling SOP

Sampling Procedures at Sites for Organic Analysis Excerpt from:

"*Shields River Basin Baseline Groundwater Sampling and Analysis Plan, Park County Montana*

Montana Bureau of Mines and Geology
Park County Conservation District
Shields Valley Watershed Group"

by

Dan Blythe

Montana Bureau of Mines and Geology

Draft Version Updated May 6, 2014

Objective

The primary objective of this sampling and analysis plan (SAP) is to explicitly state the field data collection methods and data management procedures used in the Shields River Basin (Basin) baseline sampling. The goal is to provide consistency in data collection, allow uniform and efficient data handling and transfer, and provide clear documentation of sample locations, field procedures, and analytical methods. The MBMG Ground Water Characterization Program has been collecting water well samples for inorgaincs since the program was established in 1991. Modifications to the MBMG routine sample collection procedures due to the organic sampling in the Basin are provided in this document.

Well Inventory and Sampling Procedures

Well inventories and groundwater sampling will occur in the 2013 – 2014 field seasons. Groundwater samples collected in the Basin as part of the Bureau's Park-Sweet Grass study will be analyzed for major ions, trace metals, and water isotopes at the MBMG analytical lab in Butte. In cooperation with the Shields Valley Watershed Group (SVWG) and the Park County Conservation District, a subset of wells in the Basin will be sampled for organics. Tables of inventory data, standard Bureau analytes and additional organic analysis are included respectively in appendices A, B, and C,

Ground-Water Characterization Program data collection methods will follow Bureau Standard Operating Procedures (SOPs), which are continually updated to reflect changes in practices or new field equipment. At the time of this SAP Bureau SOPs had been updated in 2010. Program SOPs are summarized below as applicable to baseline groundwater sampling in the Basin. Complete SOPs are available from the Montana Bureau of Mines and Geology's main office in Butte, MT.

Several changes to the Bureau SOP's are noteworthy. First, is a ***change in decontamination fluids*** from a Clorox®-water solution to Liquinox® (an environmental detergent) and methanol for all down-hole and sampling equipment (Wilde, 2004). Second, ***the Bureau will not measure total depth (td)*** with water-level probes in the Basin wells sampled for organics. This measurement is typically done by submerging a water-level probe or steel tape to the bottom of the well. By eliminating this measurement, the need to decontaminate several tens or hundreds of feet of probe or steel tape is eliminated, reducing potential contamination. Instead, casing volumes will be determined using driller reported td and casing diameters. Where reported total depth information is unavailable, the well may be sounded after collecting samples. Third, the ***water level indicator and sampling equipment will be transported in sealed dust-free containers***. Lastly, at the wellhead ***any potential source of organics (e.g. fueling tanks or oil barrels will be noted*** either on the inventory field sheet or field book. Generators or gasoline tanks will not be transported in the same vehicle as the water-quality sampling equipment. Following is an overview of well inventory and sample procedures for the Ground-water Characterization Program and SVWG data collection in the Basin.

Accessible Wells with Pumps are Targeted for Baseline Sampling

The Bureau will target wells that are accessible, have an existing pump, and have a sample point prior to water-treatment devices such as a water softener, carbon filter, or other treatment systems. Newer wells with a well log in GWIC and a frost-free hydrant at the wellhead are preferred. If a well does not have a pump installed, but has been selected for inventory and sampling, researchers will document the physical well setup, decontamination of down-hole equipment, and well sampling in a separate field book or on Bureau well inventory sheets. Appendix D contains a completed standard site inventory sheet.

If the well column is accessible, a water-level measurement will be taken with a decontaminated water-level probe. With landowner permission, the well may be sampled at the time of inventory, however a researcher may return to sample the well later (also with landowner permission).

Sampling Procedure and Set-up

Wells with frost-free hydrants will be targeted for sampling and the following procedures describe sample collection from a frost-free hydrant. Deviations to this procedure will be documented in a dedicated field book or on MBMG well inventory sheets.

Well sampling consists of water-level and purge-rate measurement, parameter stabilization, sample collection, sample preservation, and transporting the samples to the lab for analysis. Where the water column in the well is accessible, a static water level measurement will be taken with an electronic tape and compared to a sonic water-level measurement. Where there is good agreement between the sonic and electronic tape, pumping water levels will measured throughout the well purge with the sonic water level meter (GWCP 2010, 2010a, 2010b). Where there is not agreement between the sonic and electronic tape, no pumping water-level will be measured. Prior to sample collection the tap on the frost-free hydrant will be decontaminated and a decontaminated gardener-style brass splitter valve “Y valve” with rubber of plastic gaskets removed will be attached to the hydrant (fig. 1). The hydrant is fully opened allowing unrestricted flow through one side of the Y valve. Restricting flow can cause turbulence in the standpipe between the pump and surface producing air bubbles in the water column and potentially allow organics to volatilize prior to sample collection. Restricting flow should be avoided. Flow rate is measured using a five-gallon bucket and stopwatch and recorded on the field sheet.

Figure 1. Gardeners "Y" diverter will be connected directly to hydrant.

Once the purge rate is measured, the second valve is opened on the Y valve allowing a small amount of flow through. This is the sampling point. Downstream on the other side of the diverter a flow-through cell is set up with meters to measure pH, SC, temp., ORP, and DO. Meters will be calibrated daily and checked or recalibrated if questionable readings or drift is noticed. Using the measured unrestricted flow rate and calculated casing volume, a reading interval is selected to allow for parameter stabilization (e.g. 3 casing volumes = 60gpm, and purge rate = 3gpm, then purge time = 20 minutes, parameter readings of 4 minutes will allow for 5 readings during the purge).

Well Purging and Water-Quality Monitoring

To ensure collection of a representative groundwater sample, three casing volumes will be purged and water-quality parameters will be monitored until they meet stabilization criteria. Measured water-quality parameters will include pH, temperature, oxidation-reduction potential (ORP), dissolved oxygen (DO), and specific conductivity (SC) monitored using a flow-through cell. Once three casing volumes have been removed from the well and water quality parameters are stabilized, sampling will occur (USGS, 2006). If water-quality parameters have not stabilized, the well will continue to be pumped. If one or more field measurement drifts, then researchers must make a decision based on their understanding of the study objectives whether or not to extend the purge time or accept the drift and collect the sample. Decisions of this type will be documented in field notes or on the well inventory form. Any modifications to the standard well-purging procedure will also be documented.

Water-quality parameters are considered stable when three consecutive temperature readings are within 0.5 degrees Celsius, pH readings are within 0.1 units, specific electrical conductance is considered stable if three consecutive readings are within +/- 5 percent for <100 µS/cm waters or +/- 3 percent for >100 µS/cm waters (USGS, 2006). Dissolved oxygen and oxidation-reduction potential parameters will also be monitored throughout the well purge. Operation, maintenance, and calibration of the pH, specific conductance, and any other instruments should follow procedures outlined by the manufacturer that are appropriate for the particular make and model of meter being used.

Table I Parameter Stabilization Criteria (modified from USGS, 2006)

Field Measurement	**Stability Criteria**
pH	0.1 standard units
Temperature (Celsius)	+/- 0.5 degrees Celsius
Specific electrical	+/- 5 percent for SC ≤

conductance (SC)	100µS/cm
	=/- 3 percent for SC > 100µS/cm

Any modification to the standard well purge must be documented. For wells that are flowing purging the well is not necessary, but temperature, pH and specific conductance must be measured and recorded if the well is to be sampled. If the sampling point is downstream from an aerator, remove the aerator (with landowner consent) prior to purging and water-quality parameter monitoring. Should a well be pumped dry the pump will be turned off and the well allowed to recover to eighty percent of the original volume, at that point a sample may be collected. In general wells that do not recover to ninety percent of the original casing volume within 24 hours should not be sampled (USGS, 2006)

To determine one casing volume multiply the total feet of water in the well by the “gallons per foot” conversion factor next to the diameter well in question. Hence, one casing volume for a 6 inch diameter well with 30 feet of water is 44.1 gallons, three casing volumes is 132.3 gallons (Table 2.).

Table II Volume of Water in Well Casings (modified from Driscoll, 1986)

Casing dia. (in)	Gallons per ft	Casing dia. (in)	Gallons per ft
1.0	0.41	5.5	1.23
1.5	0.09	6.0	1.47
2.0	0.16	7.0	2.00
2.5	0.26	8.0	2.61
3.0	0.37	9.0	3.31
3.5	0.50	10.0	4.08
4.0	0.65	11.0	4.94
4.5	0.83	12.0	5.88
5.0	1.02		

Sample Collection

Samples for laboratory analysis may be collected after the purging parameters have stabilized and three casing volumes have been removed from the well. Researchers will don disposable powder free nitrile gloves and collect a sample for organic analysis. Samples will be collected into pre-cleaned and preserved sample containers provided by the laboratory. All nearby vehicle engines or generator engines should be turned off at the time of organic sample collection. If a generator is needed to run the pump, is should be located downwind from the sample collection site. After the organic samples are collected, the inorganic samples will be collected. Inorganic sample containers and caps should be rinsed three times prior to collecting the sample. Some samples require filtering and in this case, an inline filter is installed to the tubing. Purge water is run through the filter for 3-5 minutes prior to sample collection downstream of the filter. MBMG Analytical lab bottles include (2) 250-ml, (2) 500-ml, and (1) 60-ml bottle without headspace (GWCP 2010c). Additional SVWG organic sampling bottles, preservatives, hold times and collection methods are shown in table 3. With any sample that is preserved, special care to not overfill the sample bottle prior to adding the preservative should be taken. Once organic samples are collected they will be packed in ice and cooled to below 6 degrees Celsius. Hold times for the organic sampling cannot exceed 7 days.

Table III Organic analysis, bottle list, preservatives, and hold times.

Analysis	Bottles (provided by Pace)	Preservative	Hold Time (days)	Sample Collection
TPH-DRO	(2) 1-L Ambers	Hcl	7	Fill completely
TPH-GRO	(3) 40-ml VOAs	Hcl	14	No headspace
BTEX	(3) 40-ml VOAs	Hcl	14	No headspace
Methane, ethane, ethylene	(3) 25-30 ml	none	7	Fill halfway

Decontamination

In order to prevent cross contamination of samples, disposable sampling equipment should be used whenever possible. The water-level probe, sample tap (frost-free tap), all non-disposable equipment, and instruments that contact the samples must be decontaminated prior to use and between samples using the following procedure from Wilde, 2004.

- Remove gross contamination by dry brushing followed by a tap water rinse.
- Wash with a laboratory grade detergent solution, such as Alconox®, Liquinox®, or equivalent mixed with DI water.
- Rinse with dilute nitric acid wash.
- Rinse with DI water.
- Methanol rinse and air dry.

Initial decontamination should be performed prior to arriving at the sampling location. Decontaminated equipment should be stored in sealed containers such as zipper-lock plastic bags or boxes with tight lids to protect from airborne dust contamination prior to use.

Appendix C: Major Ions, Trace Metals, Field Parameters and Organic Suite

Table IV MBMG Major Ions, Trace Metals Field Parameters and Analytical Results, Pace Laboratory Organic Suite

Major Ions - Cations		**Major Ions - Anions**	
Calcium (Ca)		Bicarbonate (HCO_3)	
Magnesium (Mg)		Carbonate (CO_3)	
Sodium (Na)		Chloride (Cl)	
Potassium (K)		Sulfate (SO_4)	
Iron (Fe)		Nitrate (as N)	
Manganese (Mn)		Fluoride (F)	
Silica (SiO_2)		Orthophosphate (as P)	
Trace Metals / Elements			
Aluminum (Al)	Cesium (Cs)	Molybdenum (Mo)	Strontium (Sr)
Antimony (Sb)	Chromium (Cr)	Nickel (Ni)	Thallium (Tl)
Arsenic (As)	Cobalt (Co)	Niobium (Nb)	Thorium (Th
Barium (Ba)	Copper (Cu)	Neodymium (Nd)	Tin (Sn)
Beryllium (Be)	Gallium (Ga)	Palladium (Pd)	Titanium (Ti)
Boron (B)	Lanthanum (La)	Praseodymium (Pr)	Tungsten (W)
Bromide (Br)	Lead (Pb)	Rubidium (Rb)	Uranium (U)
Cadmium (Cd)	Lithium (Li)	Silver (Ag)	Vanadium (V)
Cerium (Ce)	Mercury (Hg)	Selenium (Se)	Zinc (Zn)
			Zirconium (Zr)
Field Chemistry and Other Analytical Results			
Total Dissolved Solids		Total Kjeldahl Nitrogen	
Sum of Dissolved Constituents		Total Nitrogen	
*Field Conductivity		As(III)	
Lab Conductivity		Hardness as CaCO3	
*Field pH		*Field Alkalinity as CaCO3	
Lab pH		Alkalinity as CaCO3	
Nitrate + Nitrite			
Pace Laboratory Organic Suite			
Methane		Gasoline Range Organics (GRO)	
Ethane		Diesel Range Organics (DRO)	
Ethylene		BTEX	

Appendix D: Organic Data Validation

Table V Organic Data Validation

GWIC ID	Sample Date	A	B	C	D	E	F	G	Comments
12953	8/6/2013	Y	Y	Y	Y	Y	Y	Y	
92247	10/23/2013	Y	Y	Y	Y	Y	Y	Y	
92247	6/19/2014	Y	Y	Y	Y	Y	Y	Y	
92247	6/19/2014	DUPLICATE				Y	Y	Y	
92247	6/19/2014	TRIP BLANK				Y	Y	Y	
92247	7/16/2014	Y	Y	Y	Y	Y	Y	Y	
92295	8/6/2013	Y	Y	Y	Y	Y	Y	Y	
147224	8/6/2013	**N**	Y	Y	Y	Y	Y	Y	
148073	9/16/2013	Y	Y	Y	Y	Y	Y	Y	
148074	9/16/2013	Y	Y	**N**	Y	Y	Y	Y	**pH +/- 0.2 standard units, 4.3 casing volumes evacuated
171602	6/24/2013	Y	Y	Y	Y	Y	Y	Y	
176949	7/31/2013	Y	Y	Y	Y	Y	Y	Y	
176949	7/16/2014	Y	Y	Y	Y	Y	Y	Y	
182047	8/7/2013	Y	Y	Y	Y	Y	Y	Y	
191777	6/20/2013	Y	Y	Y	Y	Y	Y	**N**	**delay during shipping results in samples arriving over temp at lab
194587	6/25/2013	Y	Y	Y	Y	Y	Y	Y	
194589	7/1/2013	**N**	Y	Y	**N**	Y	Y	Y	**pump set up with coyote protector, pump cycling on, then off. Called landowner 1.5 hr prior to turn on pump. Pump powered by gasoline generator at well head, used oil containers on ground around well head.
195186	7/30/2013	Y	Y	Y	Y	Y	Y	Y	
205556	6/25/2013	Y	Y	Y	Y	Y	Y	Y	
207302	6/26/2013	Y	Y	Y	Y	Y	Y	Y	
214961	10/10/2013	STREAM SAMPLE				Y	Y	Y	
215800	7/30/2013	**N**	**N**	**N**	Y	Y	Y	Y	**well pumping on arrival, purged dry, let recover and sample
236348	6/27/2013	Y	Y	Y	Y	Y	Y	Y	
236901	6/25/2013	Y	Y	Y	Y	Y	Y	Y	
238560	6/24/2013	Y	Y	Y	Y	Y	Y	Y	
248622	10/24/2013	Y	Y	**N**	**N**	Y	Y	Y	**well pumped using gasoline generator (downwind from sampling collection), pH +/- 0.2, evacuated 6.2 casing volumes
248622	10/24/2013	DUPLICATE				Y	Y	Y	
273725	6/20/2013	Y	Y	Y	Y	Y	Y	**N**	**no well log depth based on water right, delay during shipping results in samples arriving over temp at lab
273891	6/26/2013	SPRING SAMPLE				Y	Y	Y	
273892	7/2/2013	Y	Y	**N**	**N**	Y	Y	Y	**no log, well sounded at 80 feet td, pH +/- 0.2 standard units, well pumped with gasoline generator
274403	8/1/2013	Y	Y	Y	Y	Y	Y	Y	
274403	7/17/2014	Y	Y	Y	Y	Y	Y	Y	
274404	8/5/2013	Y	Y	Y	Y	Y	Y	Y	**owner reported total depth of 45 feet
274487	7/31/2013	SPRING SAMPLE				Y	Y	Y	

GWIC ID	**Sample Date**	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**Comments**
275280	10/10/2013	STREAM SAMPLE				Y	Y	Y	
275281	10/10/2013	STREAM SAMPLE				Y	Y	Y	
Equip.	6/24/2013	EQUIPMENT BLANK				Y	Y	Y	

A - was well properly purged?

B - was sample collected at purge rate? (i.e. waterflow rate reduced to collect the sample?)

C - had pH, SC and temperature stabilized prior to sampling?

D - do site conditions suggest sample is representative? (i.e. is well near fueling tanks, french drain, stained ground surface etc.)

E - was proper chain of custody maintained from sample time until receipt by the laboratory?

F - was sample analyzed for the requested analyses and were proper laboratory methods used?

G - were sample hold times meet?

Appendix E: Inventoried Sites

GWIC = Ground Water Information Center

GRO = Gasoline Range Organics

DRO = Diesel Range Organics

BTEX = Benzene, Toluene, Ethylbenzene, Xylene

Table VI List of Inventoried Sites 2013-2014

GWIC Id	Site type	Date	Major ions and trace metals	Methane, ethylene, ethane	GRO	DRO	BTEX	Water isotopes	Tritium	Comments
9915	WELL	6/12/2013	x					x	x	Water isotopes duplicate
12953	WELL	8/6/2013	x	x	x	x	x	x	x	
92247	WELL	10/23/2013	x	x	x	x	x	x	x	
92247	WELL	6/19/2014		x	x	x	x			
92247	WELL	6/19/2014		x	x	x	x			Duplicate sample
92247	WELL	6/19/2014					x			Trip blank
92247	WELL	7/16/2014		x				x		
92295	WELL	8/6/2013	x	x	x	x	x	x	x	Water isotopes duplicate
147224	WELL	8/6/2013	x	x	x	x	x	x		
148073	WELL	9/16/2013	x	x	x	x	x	x	x	
148074	WELL	9/16/2013	x	x	x	x	x	x	x	
171602	WELL	6/24/2013	x	x	x	x	x	x	x	
176949	WELL	7/31/2013	x	x	x	x	x	x	x	Water isotopes duplicate
182047	WELL	8/7/2013	x	x	x	x	x	x	x	
185593	WELL	11/14/2013	x					x		
191777	WELL	6/20/2013	x	x	x	x	x	x		
194587	WELL	6/25/2013	x	x	x	x	x	x	x	
194589	WELL	7/1/2013	x	x	x	x	x	x	x	
195186	WELL	7/30/2013	x	x	x	x	x	x	x	Water isotopes duplicate
204364	WELL	8/19/2013	x					x	x	
205556	WELL	6/25/2013	x	x	x	x	x	x	x	
207302	WELL	6/26/2013	x	x	x	x	x	x	x	
208520	WELL	8/22/2013	x					x	x	
214961	STREAM	10/10/2013	x	x	x	x	x	x		
215800	WELL	7/30/2013	x	x	x	x	x	x		
236243	WELL	8/21/2013	x					x	x	
236348	WELL	6/27/2013	x	x	x	x	x	x	x	
236901	WELL	6/25/2013	x	x	x	x	x	x	x	
238560	WELL	6/24/2013	x	x	x	x	x	x		

GWIC Id	Site type	Date	Major ions and trace metals	Methane, ethylene, ethane	GRO	DRO	BTEX	Water isotopes	Tritium	Comments
247683	WELL	6/12/2013	x					x		
248622	WELL	10/24/2013	x	x	x	x	x	x		
248622	WELL	10/24/2013	x	x	x	x	x	x		Duplicate sample
250779	WELL	11/7/2013	x					x	x	
259640	STREAM	10/9/2013						x		Water isotopes only
269150	WELL	11/14/2013	x					x		
273725	WELL	6/20/2013	x	x	x	x	x	x	x	
273891	SPRING	6/26/2013	x	x	x	x	x	x		
273892	WELL	7/2/2013	x	x	x	x	x	x	x	Water isotopes duplicate
274403	WELL	8/1/2013	x	x	x	x	x	x	x	
274403	WELL	7/17/2014	x	x	x	x				
274404	WELL	8/5/2013	x	x	x	x	x	x	x	
274487	SPRING	8/5/2013		x	x	x	x			Organic suite only
275280	STREAM	10/10/2013	x	x	x	x	x	x		
275281	STREAM	10/10/2013	x	x	x	x	x	x		
275284	STREAM	10/9/2013						x		Water isotopes only
275285	LAKE	10/9/2013						x		Water isotopes only
275286	RES.	10/9/2013						x		Water isotopes only
275288	STREAM	10/9/2013						x		Water isotopes only
275289	STREAM	10/9/2013						x		Water isotopes only
275312	STREAM	10/9/2013						x		Water isotopes only
276408	SNOW	1/2/2014						x		Water isotopes only
Equip.	na	6/24/2013		x	x	x	x			Equipment blank