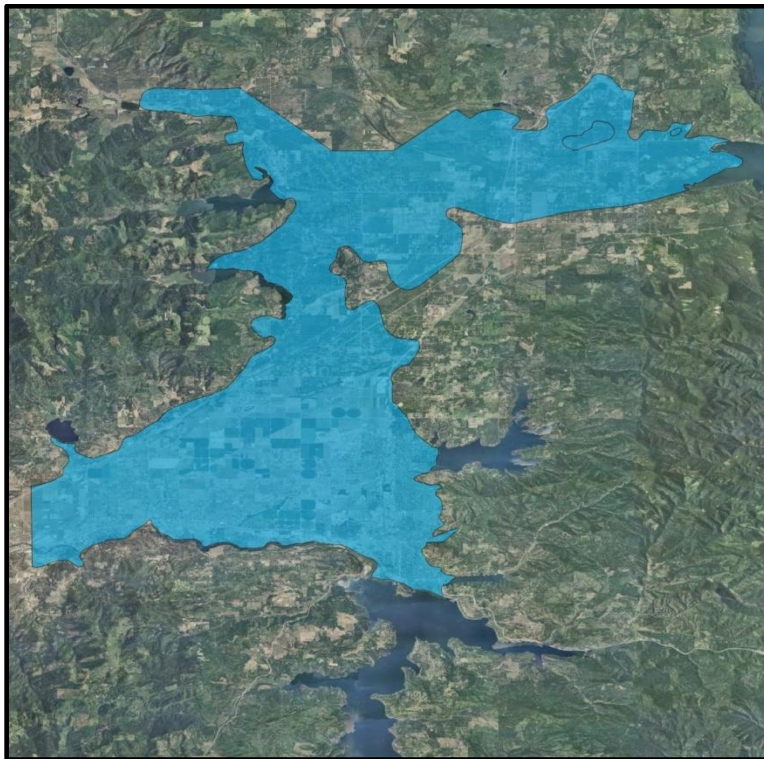


A Hydrogeochemical Investigation of the Rathdrum Prairie Aquifer, Kootenai County, Idaho

Ground Water Investigation Report DEQ-CRO-03-13



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Abbreviations, Acronyms, Symbols, and Formulas

δ	delta
μg	microgram
μS	microsiemen
As	arsenic
As(III)	arsenite
As(V)	arsenate
Br	bromide
Ca	calcium
CaCO_3	limestone
CaMgCO_3	dolomite
CFC	chlorofluorocarbon
Cl	chloride
DEQ	Idaho Department of Environmental Quality
GMWL	global meteoric water line
H_2O	water
HCO_3	bicarbonate
IDAPA	refers to citations of Idaho's administrative rules
K	potassium
kg	kilogram
L	liter
meq	milliequivalents
Mg	magnesium
mg	milligram
Na	sodium
NO_3^-	nitrate

NO ₃ -N	nitrate as nitrogen
NS	not sampled
pCi	picocurie
PHD	Panhandle Health District
pmoles	picomoles
ppt	parts per trillion
pptv	parts per trillion volume
Ra	radium
RPA	Rathdrum Prairie aquifer
SF ₆	sulfur hexafluoride
SI	Saturation indices
SO ₄	sulfate
SOC	synthetic organic compound
SS	supersaturated
U	uranium
VOC	volatile organic compound
VSMOW	Vienna Standard Mean Ocean Water

1 Introduction

The population in the area over the Rathdrum Prairie aquifer (RPA) is projected to grow from the current 142,000 to potentially 400,000 by the year 2060 (SPF Water Engineering et al. 2010). The population increase could result in potential water quality impacts from changing land use and urbanization. In addition there has been an improved awareness of the interconnection of surface water and ground water along with water quality and quantity issues. This results in increasingly complicated regulatory, political, and legal issues that not only involves municipal, county, and state entities in Idaho but the equivalent involvement in Washington state.

To aid in making informed decisions now and in the future, additional data and analysis is needed to compliment the Panhandle Health District's (PHD's) current water quality monitoring program. PHD currently samples 25 to 30 wells completed in the RPA three times a year. The emphasis on safe drinking water should continue, but due to changing potential water quality concerns, sampling could be expanded to include additional data and analysis. The purpose of this study is to address three general categories of additional data and analysis: (1) improve the geographic distribution of water quality data, (2) identify potential water quality impacts from anthropogenic activities and natural occurring constituents, and (3) determine residence times and define recharge sources. The analytical data derived from this project may also identify additional areas for further research and provide base data for other projects. Funding for this study was provided by the Kootenai County Aquifer Protection District Board to the Idaho Department of Environmental Quality (DEQ).

2 Rathdrum Prairie Aquifer

The RPA covers an area of approximately 211 square miles in Idaho and extends from Lake Pend Oreille south to Coeur d'Alene and Post Falls and then west to the Idaho-Washington border (Figure 1). The RPA is part of the larger Spokane Valley-Rathdrum Prairie aquifer that extends into Washington State. The water that recharges the RPA is mainly due to seepage from the Spokane River and adjacent lakes, contributions from adjacent watersheds, along with precipitation that falls on the Rathdrum Prairie. Ground water from the northern areas of the aquifer starts at a water elevation of about 2,100 feet and at the state line is about 1,970 feet. Depths to water from land surface range from approximately 150 feet to 550 feet.

The alluvium that forms the RPA was deposited 8,000–18,000 years ago by southerly drainage from the continental Cordilleran Ice Sheet along with enormous catastrophic floods from Lake Missoula (Alt 2005). The flood water was caused by the failure of an ice dam blocking the flow of the Clark Fork River and creating Lake Missoula (Smith 2006). The ice dam formed when the continental Cordilleran Ice Sheet flowed far enough south to intercept the river. As the volume of water stored in Lake Missoula increased, there was a corresponding increase in stress on the ice dam. When the stress of the water exceeded the mechanical strength of the ice dam there would be a catastrophic failure releasing billions of gallons of water that flowed across the Rathdrum Prairie, through Washington State, down the Columbia River, and eventually to the Pacific Ocean. The process of ice dam building and subsequent failure and flooding is believed to have been repeated approximately 40 times.

The large volume and flow rate of the floods deposited large gravel, cobbles, and boulders into the Rathdrum Prairie and carried away most of the smaller silt and sand, leaving behind the very permeable aquifer that is the source of drinking water today. The composition of the flood deposits reflects the bedrock lithology upgradient between Lake Missoula and the Rathdrum Prairie. The deposition of significant volumes of gravel onto the Rathdrum Prairie blocked the tributary valleys forming Pend Oreille, Spirit, Twin, Hauser, Hayden, and Coeur d'Alene Lakes (Alt 2005). The lakes recharge the aquifer through seepage into the coarse alluvium.

The Cordilleran Ice Sheet also formed an ice dam in central Washington blocking the Columbia River. The impounded water formed Glacial Lake Columbia that flooded an extensive area that included the Spokane Valley and most of the Rathdrum Prairie. It is thought that the flooded area extended to within a few miles of the Lake Missoula ice dam (Alt 2005). When flood events occurred from Lake Missoula they would flow directly into Glacial Lake Columbia displacing the water to the west into central Washington.

A geologic map of the area with descriptions of the unconsolidated deposits of the Rathdrum Prairie and surrounding bedrock can be seen in Figure 2. The bedrock basement of the Rathdrum Prairie is described as the Gneiss of the Priest River Complex on the west side and Wallace Formation on the east side, separated by the Purcell Coeur d'Alene Fault (Lewis et al. 2002). The very permeable aquifer allows water to flow with velocities of 20–50 feet per day. Because of the permeable nature of the unsaturated material between the aquifer and the land surface, the aquifer can be susceptible to impacts from land uses and contaminant releases. In 1978, the aquifer in Idaho and Washington was given a Sole Source Aquifer designation by the US Environmental Protection Agency (Federal Register, Vol. 43, No. 28), and in 1996, the RPA was designated a Sensitive Resource Aquifer by the State of Idaho (IDAPA 58.01.11). These designations provide additional protections to prevent water quality impacts.

3 Historic Water Quality

The PHD has been collecting water quality information from a number of wells completed in the RPA since 1975. The water quality data consist of a variety of inorganic and organic constituents that represent general aquifer ground water quality, along with some that may indicate contamination from the surface. The emphasis of the PHD sampling program has been to detect potential water quality impacts from septic systems located over the RPA. The PHD water quality database includes 33 wells distributed across the RPA. Water samples are taken from selected wells three times a year to evaluate general trends in water quality.

The DEQ requires water quality testing and analysis from all public drinking water systems with wells completed in the RPA. The required constituents are for compliance with drinking water standards and are sampled with a schedule that varies by constituent and over time for each water system. The US Geological Survey National Water Quality Assessment Program has performed some limited sampling on the RPA (Caldwell et al. 2004). The constituents primarily reflect those that may be introduced through human activities.

4 Sample Location

There are various sources that contribute water to the RPA that will affect the water quality. Depending on the location over the aquifer the water quality potentially can vary depending on the proximity and contributions from the different sources. To understand the hydrogeochemistry of the aquifer, samples were taken from wells, surface water, and precipitation samplers to help evaluate potential geographical differences.

4.1 Water Wells

Water wells used in this study were selected based on geographic location, appropriate sampling port and placement, and available well driller's reports. A relatively equally spaced distribution of wells across the aquifer is desired to evaluate any geographic differences in water quality. The majority of water wells sampled by the PHD are located in the southern portion of the RPA. Emphasis was placed in this study on locating additional wells in the central and northern areas. All the selected wells are municipal wells with required sampling ports at the wellhead that allow water samples to be obtained before any treatment. Idaho well driller's reports are available for most of the wells sampled and include a description of lithology and well construction. Additional historic well construction information for wells with no driller's logs was obtained from Nace and Fader (1951). The water wells sampled as part of this study can be seen in Figure 3. A description of well construction, location, and general lithology can be seen in Table 1. The available well driller's reports are in Appendix A.

4.2 Surface Water

A significant volume of water recharging the RPA is derived from both lakes peripheral to the aquifer and the Spokane River. The lakes include Coeur d'Alene Lake, Hayden Lake, Lake Pend Oreille, Spirit Lake, Twin Lakes, and Hauser Lake. In the northern half of the RPA (above latitude 47.850°), the surface water bodies account for approximately 53% of the total recharge and in the southern half approximately 86% (Hsieh et al. 2007). The largest recharge source in the southern RPA is the Spokane River, which supplies 54% of the recharge from surface water. Because the Spokane River initiates at Coeur d'Alene Lake, the chemistry of the Spokane River was assumed to be similar to Coeur d'Alene Lake for the purposes of this study.

Because of the large recharge volume, understanding the chemical composition of the peripheral lakes was necessary to understand the chemistry of the RPA. Coeur d'Alene Lake, Lake Pend Oreille, and Hayden Lake were sampled during June 2012. After reviewing the analytical results, DEQ decided to obtain additional samples from Spirit Lake, Twin Lakes, and Hauser Lake in the two subsequent sampling events of September 2012 and January/February 2013. The lakes sampled as part of this study can be seen in Figure 3.

4.3 Precipitation

Recharge from precipitation incident onto the ground surface of the RPA makes up a relatively small percentage of the total RPA recharge volume. Precipitation comprises 26% of recharge in the northern RPA and 11% in the south (Hsieh et al. 2007). Recharge from precipitation has a considerable travel time to the aquifer relative to other recharge sources. Precipitation samples were relevant to some of the chemical analysis in the study. Two precipitation sampler locations

were used in the study: one was located on the RPA (which had to later be relocated) and the other was placed in the upland areas to the west of the aquifer (Figure 3). The construction and sampling technique of the precipitation samplers is described in Appendix B.

5 Water Quality Parameters

Water quality constituents were chosen to help identify impacts from human activities, potentially determine sources, and determine residence time and recharge sources. A number of chemical constituents and physical parameters were chosen to accomplish the various goals of the sampling project.

5.1 Chemical Parameters

This study included sampling and analysis for major cations and anions, inorganic constituents, organic constituents, radionuclides, stable isotopes, and chemicals used for age-dating of ground water.

5.1.1 Major Cations and Anions

The chemical composition of ground water is predominantly composed of four cations—calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na)—and three anions: sulfate (SO_4), bicarbonate (HCO_3), and chloride (Cl). Cations have a positive charge and anions have a negative charge. As ground water travels through an aquifer, the composition of these cations and anions change as the water interacts with the aquifer material and potentially incorporates other inputs from anthropogenic activities. Ground water typically evolves from a Ca-Mg- HCO_3 type to a Na-Cl type.

The major ion chemical composition and/or concentration of ground water differs from surface water. Contaminants introduced from surface sources such as septic effluent or fertilizer can be reflected in the ratios of these cations and anions of the water sample. Determining the composition of the cations and anions in water samples across a region can be helpful in evaluating residence time, source of recharge, mixing of different waters, and presence and identification of contaminant sources.

5.1.2 Inorganic Constituents

Other inorganic constituents measured in this study include nitrate as nitrogen ($\text{NO}_3\text{-N}$), arsenic (As), chloride and bromide (Br). These constituents may be naturally occurring or have anthropogenic sources or causes for elevated concentrations.

5.1.2.1 Nitrate

Elevated nitrate concentrations in drinking water are a human health concern. The most significant potential sources of nitrate in ground water are inorganic fertilizer, on-site septic disposal, and animal manure (Warner and Arnold 2010). Nitrate is considered conservative in oxic environments and will not readily degrade or adsorb onto the sediments. Nitrate introduced at or near the land surface can be transported downward to the aquifer with little attenuation. Unconfined, coarse-grained aquifers are more susceptible to these types of water quality impacts than confined aquifers (Burow et al. 2010; Nolan et al. 2002). Nitrate concentrations in this

report are expressed as nitrate as nitrogen ($\text{NO}_3\text{-N}$) and reflect the nitrogen weight by volume content in the water sample.

5.1.2.2 Chloride and Bromide

Elevated concentrations of sodium and chloride may be indicators of water quality impacts from different anthropogenic activities such as septic disposal or application of road deicers. Determining the presence and concentration of bromide can help with the source identification (Panno et al. 2006).

5.1.2.3 Arsenic

Arsenic can be a naturally occurring constituent in soils and alluvium or have anthropogenic sources such as pesticides and wood preservatives (Welch et al. 1998). Elevated concentrations of arsenic in drinking water are a risk to human health. Arsenic usually occurs in ground water with two oxidation states as arsenite—As(III)—and arsenate, As(V). The presence of either As(III) or As(V) is dependent on the oxidation state of the water (Welch et al. 2000). As(V) is the dominant stable form in oxic waters, and As(III) is the dominant stable form in anoxic waters.

Arsenic can be incorporated into a solid phase in one of two ways: (1) coprecipitation with iron oxides or sulfides or (2) adsorption. Arsenic itself may not be present in sufficient concentrations to combine with other ions and precipitate, but it may be coprecipitated with others that do. Coprecipitated arsenic is incorporated into the solid structure of the precipitated mineral. The arsenic can be released by various mechanisms that break the chemical bonds through dissolution of the precipitant. Alternatively, arsenic may not be incorporated into the solid structure but will bind or adsorb onto the surface of a solid phase—such as iron oxides or sulfides—through either chemical or physical processes. There may be circumstances when the arsenic is both coprecipitated into the solid phase and adsorbed onto the surface.

The mobility of arsenic is dependent on the pH and oxidation state (redox) of the water. If the redox conditions change from oxic to anoxic or the reverse, the solid phase along with the coprecipitated arsenic may then form a dissolved state and become mobile and be transported with the ground water. If arsenic is adsorbed onto the surface of the solid phase, it will also become more mobile with dissolution of the solid phase. Once the arsenic is mobile, it has a significantly greater potential to contaminate drinking water wells. The mechanisms for changing the redox state of the water are many and may be physical, such as pumping of water wells in unconfined aquifers (Gosselin et al. 2006), or chemical through the introduction of organic carbon (Welch et al. 2000). The pH can also have an effect on adsorbed arsenic mobility by changing the surface charge of the solid phase from positive to negative with an increase in pH. The surface charge of the solid phase under certain pH ranges will have a sufficient negative charge so that it will repel the negatively charged arsenic ions.

Arsenic may also be replaced by other ions through a process of ion exchange. Introduction of phosphorus to an aquifer with arsenic-bearing alluvium—such as through subsurface septic disposal or fertilizer use—may result in an increase in the concentration of dissolved arsenic. The phosphorus replaces adsorbed arsenic, releasing the arsenic into a dissolved state with an increased potential to contaminate drinking water wells.

5.1.3 Organic Constituents

An increase in population will also result in more businesses and activities that use organic constituents. These constituents are typically petroleum based and usually consist of gasoline and diesel fuels along with organic solvents. A significant increase in the number of these types of businesses or activities can result in an increasing risk of releases to the subsurface and eventually to the aquifer. In addition, herbicides and pesticides used in either residential areas or outlying agricultural areas may also leach into the underlying aquifer and impact aquifer water quality. The particular concern for this class of contaminants is the potential carcinogenic health effects.

5.1.4 Radioactive Constituents

The RPA consist of alluvium that is derived from metasedimentary and igneous rocks. These rock types commonly contain radioactive elements that include uranium-238 (^{238}U), radium-226 (^{226}Ra), and radium-228 (^{228}Ra). Igneous rocks and metasediments commonly have elevated concentrations of uranium (Ayotte et al. 2007) and radium (Grundl and Cape 2006), respectively. Uranium is most mobile in bicarbonate-rich oxidizing ground water with low dissolved solids content, while radium is most mobile in chloride-rich, low-oxygen environments with high dissolved solids content (Zapeczka and Szabo 1986). The radioactive elements emit radioactive particles and are considered a health risk at elevated concentrations. The drinking water standard is 30 micrograms per liter ($\mu\text{g/L}$) for uranium and 5 picocuries per liter (pCi/L) combined for ^{226}Ra and ^{228}Ra .

In addition, radioactive decay of uranium-238 can form radon gas. Radon is soluble in water and if present in high concentrations has been linked to a slight increase in stomach cancer (Caldwell et al. 2004). Limited sampling of the water wells completed in the RPA was completed by Caldwell et al. (2004) and indicated elevated concentrations in all the wells sampled. There currently is no federal or state defined drinking water standard for radon, but the EPA has suggested a drinking water standard of 300 pCi/L if no corresponding air mitigation is implemented at the residence to reduce indoor air concentrations. All of the radon concentrations obtained during the Caldwell et al. 2004 sampling from water wells completed in the RPA were in excess of 300 pCi/L. Identification of areas with elevated uranium in the water may help define areas that may have elevated radon.

5.1.5 Stable Isotopes

Stable isotopic composition of water and nitrate can provide useful information in a hydrogeological investigation. Stable isotopes of hydrogen and oxygen of water can be helpful in determining the source of aquifer recharge water. The stable isotopes of nitrogen and oxygen of nitrate can indicate the potential source or sources that may be impacting water quality.

5.1.5.1 ^2H and ^{18}O of Water

Water has the chemical composition of H_2O with the hydrogen component primarily composed of ^1H (one proton) and the oxygen component primarily composed of ^{16}O (8 protons and 8 neutrons). A small fraction of water molecules will have either hydrogen composed of the ^2H isotope (one proton and one neutron) or oxygen composed of the ^{18}O isotope (8 protons and 10 neutrons). These isotopes do not decay and are considered stable. The concentration of ^2H and ^{18}O isotopes in a water sample is measured as the difference between the isotope concentration

from a known standard and is expressed as the delta (δ). The common international standard used for comparison of ^2H and ^{18}O isotopes is the Vienna Standard Mean Ocean Water (VSMOW) created by mixing distilled ocean waters from several locations around the world.

The ratio of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in a water sample depends on a number of conditions relating to the history and source of the water (Clark and Fritz 1997). The ratio is shown as a plot with $\delta^2\text{H}$ on one axis and $\delta^{18}\text{O}$ on the other. Generally, precipitation and ground water has $\delta^2\text{H}/\delta^{18}\text{O}$ concentration ratios that will plot on a single line called the global meteoric water line (GMWL). The plotted location of the ratios will change position on the line depending on various factors such as the season and distance from the ocean (Figure 4).

Water subjected to significant evaporation, such as lakes, ponds and lagoons, shows depletion in the ^2H isotope and enrichment in the ^{18}O isotope relative to the GMWL due to their different molecular weights. As water evaporates, the lighter ^2H isotope migrates at a greater rate from the surface water body to the atmosphere than the heavier ^{18}O isotope. The more the water evaporates, the greater the increase in ^{18}O isotope and decrease of ^2H isotope. Waters derived from surface water bodies plot on a line that deviates from the GMWL, reflecting the ratios caused by evaporation. Surface water bodies such as lakes, ponds, and lagoons will have ratios of these isotopes that are characteristic and may be seen in ground water that receives significant recharge from these sources. The ^2H and ^{18}O isotopes can be used to determine recharge sources, water budgets, and infiltration rates, particularly with surface water bodies (Clark and Fritz 1997; Ehlmann et al. 2005; Jonsson et al. 2009; Maloszewski et al. 1990).

5.1.5.2 ^{15}N and ^{18}O of Nitrate

Nitrate has the chemical composition of NO_3^- with the nitrogen component primarily composed of ^{14}N (7 protons and 7 neutrons) and the oxygen component primarily composed of ^{16}O (8 protons and 8 neutrons). A small portion of the nitrate molecules will have either nitrogen or oxygen composed of the isotopes ^{15}N (7 protons and 8 neutrons) and ^{18}O (8 protons and 10 neutrons).

The concentration of the ^{15}N isotope is measured relative to the standard concentration in air. The concentration of the ^{18}O isotope is measured relative to the standard concentration in sea water (VSMOW). The concentration unit for the isotopes is $\delta\text{‰}$, which is the part per thousand deviation from the standard. A negative $\delta\text{‰}$ number indicates the sample has a concentration less than the standard and a positive $\delta\text{‰}$ number indicates the sample has a concentration greater than the standard.

Studies based on empirical observations have shown that the ratio of $\delta^{15}\text{N} \text{‰}$ to $\delta^{18}\text{O} \text{‰}$ (shown as a plot with $\delta^{15}\text{N} \text{‰}$ on one axis and $\delta^{18}\text{O} \text{‰}$ on the other) of the nitrate found in ground or surface water can be dependent on the source (Aravena et al. 1993). Different $\delta^{15}\text{N} \text{‰}$ to $\delta^{18}\text{O} \text{‰}$ ratios of the nitrate found in water are associated with the different potential sources such as soil processes, fertilizers or septic drainfields.

5.1.6 Age Dating

During the past 50 to 60 years, different chemicals related to manufacturing processes and products have been released to the atmosphere, such as isotopes of chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) (Figure 5). Each has specific time periods in which they were used

in industrial applications and subsequently introduced into the atmosphere. CFCs are stable compounds developed in the 1930s that have been widely used in industrial applications such as refrigerants, blowing agents, and solvents. The three relevant isotopes of CFCs used in this study are CCl_3F (CFC-11), CCl_2F_2 (CFC-12), and $\text{C}_2\text{Cl}_3\text{F}_3$ (CFC-113). SF_6 production became significant in the early 1950s and was used predominantly in electrical switchgear.

Water in contact with the atmosphere—such as precipitation or surface water bodies—will absorb these chemicals in amounts dependent on the recharge temperature and pressure. The concentrations of these chemicals in the atmosphere have generally increased over time and are reflected in the water concentration. When water from precipitation or seepage from lakes and rivers recharges the aquifer and is no longer in contact with the atmosphere, the concentrations of CFCs and SF_6 in ground water will no longer change. To get an age date the CFC or SF_6 concentration in the ground water sample is converted back to an atmospheric concentration (equivalent atmospheric concentration) by estimating or measuring the recharge temperature and using standard atmospheric pressure. The converted atmospheric CFC or SF_6 concentration is compared to known historical values and will reflect the time of recharge. Both CFCs and SF_6 can be used for dating relatively young recharge water, generally less than 50 years old (Busenberg and Plummer 2000; Darling et al. 2012; Oster et al. 1996; Plummer et al. 2000).

Some factors complicate age dating using CFCs and SF_6 , including processes in the unsaturated zone, degradation, and mixing of water from multiple sources. CFCs are considered stable in oxic environments but can undergo degradation in anoxic environments. Degradation will result in decreased concentrations that will result in artificially older age dates. The time it takes for water to flow from different recharge sources to the aquifer varies and may result in a mixed average age depending on the number and recharge rates of the different sources.

Thick unsaturated zones can also create age complexities because the atmospheric CFCs and SF_6 concentrations at the surface will not be the same as the concentrations in the unconsolidated sediments immediately above the water table. The gasses are transported downward through the unsaturated zone over time, predominantly through diffusion. The gas concentrations at the water table will reflect an earlier time period. Water infiltrating downward and recharging the aquifer equilibrates with the gas concentrations near the water table resulting in age dates that are older. Sorption in the unsaturated zone can also reduce CFC concentrations. CFCs can also be introduced through other sources such as sewage, landfills and proximity to urban areas. These external sources of CFCs can elevate the concentrations in the ground water making the age dates significantly younger or unusable as a dating tool. However, these elevated concentrations may be useful as an indicator of anthropogenic water quality impacts.

5.2 Physical Parameters

The water quality of the aquifer reflects the chemical interaction of all the different sources and aquifer material. The physical parameters of pH, temperature, conductivity, and dissolved oxygen can govern the type and rate of chemical interactions that occur. Measuring these parameters may provide additional information to aid in interpreting analytical data.

6 Sampling Procedure and Analytical Methods

The study consisted of submitting samples from water wells, lakes, and precipitation samplers for analysis of a number of different constituents. Water wells were sampled during June and September 2012 and January/February 2013. Three lakes were sampled during the June 2012 sampling event and six were sampled during the September 2012 and January/February 2013 sampling events. Two precipitation sampler locations were used to sample precipitation: one on the Rathdrum Prairie and the other on an upland area (Ragged Mountain) to the west. The precipitation sampler on the Rathdrum Prairie was sampled during March 2012 and both the Rathdrum Prairie and Ragged Mountain samplers were sampled in December 2012.

Water systems with multiple wells often will use select wells only in the summer months when water demand is high. Some wells were not available for all three sampling events. The sampling procedures for the sampling events are described in Appendix B. The specific analytes that were sampled and method reference and minimum reporting limits, when applicable, can be seen in Table 2 through Table 6. Blind duplicate samples were obtained during all three sampling events. The results and analysis of the duplicate sampling can be seen in Appendix B (Tables B1 through B3).

7 Analytical Results

7.1 Major Anions and Cations

Water samples were obtained during June and September 2012 and January/February 2013 from all wells and submitted for analysis of calcium, magnesium, potassium, and sodium cations and sulfate, bicarbonate, and chloride anions. Surface water samples were obtained for analysis of cations and anions from Lakes Coeur d'Alene Lake, Hayden Lake, and Lake Pend Oreille during June 2012. These lakes, along with Spirit Lake, Twin Lakes, and Hauser Lake, were also sampled during September 2012 and January/February 2013.

All the water samples were submitted to SVL Analytical, Inc., in Coeur d'Alene, Idaho, for analysis. The analytical results can be seen in Table 7 through Table 9. The analytical results were also compiled in AquaChem (Waterloo Hydrogeologic, Inc. 2005) and are displayed graphically in Piper and Stiff plots (Figure 6–8 and Figures 9–11, respectively). All the Stiff plots are shown relative to each well in Appendix C. The analytical laboratory reports can be seen in Appendix D.

The Piper plot consists of two tri-linear plots with cations represented in the lower left triangle and anions represented in the lower right triangle. The third plot in the center represents both the cations and anions. In the two tri-linear plots, each axis represents the relative percent of each cation or anion for each sample. The sum of cations and anions for each sample will equal 100%. The percentages of each will determine the location of each water sample within the Piper plot. The Stiff plot shows the concentrations of cations on the left-hand side and anions on the right-hand side. The Stiff plot allows a visual comparison of the chemical composition and concentration of each cation and anion for each sample obtained from different wells during the same sampling event or for samples obtained from the same well over time.

The concentration unit used in both plots is milliequivalents per liter (meq/L), which expresses the number of ions available for exchange (concentration) as part of a chemical reaction. The meq/l is calculated by determining the weight of a cation or anion in a unit of solution (1 L) and multiplying the weight by the ionic charge of the cation or anion. The greater the weight in solution and greater the ionic charge of the cation or anion, the greater the meq/l concentration. If the meq/l concentration of cations (positive charge) is the same as the meq/l concentration of the anions (negative charge), the solution is in chemical equilibrium. If there is an imbalance in the meq/l concentrations between the cations and anion, then chemical reactions will likely occur until the solution reaches equilibrium.

7.2 Inorganic Constituents

Other inorganic constituents were sampled in the wells to demonstrate potential water quality impacts from various activities at the surface.

7.2.1 Nitrate as Nitrogen and Nitrate Isotopes

Nitrate as nitrogen is a common constituent that is associated with fertilizer application and septic effluent. Nitrate as nitrogen was sampled in all wells during the June 2012 sampling event. All those samples were submitted to the University of Arizona for analysis of nitrate as nitrogen and the stable isotopes nitrogen-15 (^{15}N) and oxygen-18 (^{18}O) of nitrate. Nitrate as nitrogen analytical results are presented in Table 7 and Figure 12. The analytical results for ^{15}N and ^{18}O are presented in Table 10. The analytical laboratory reports can be seen in Appendix D.

7.2.2 Chloride and Bromide

Although chloride is included in the cation and anion section, it will also be used in a separate analysis because chloride is commonly associated with the application of road salt and septic effluent. A recent study (Barry 2013) has indicated a number of wells completed in the RPA have increasing trends of chloride and sodium concentrations. Water quality impacts associated with this septic effluent may result in elevated concentrations of chloride. Water quality impacts from the use of road salt may have elevated concentrations of both chloride and bromide. The analytical results for chloride can be seen in Figures 13–15 and for chloride and bromide in Tables 7–9. The analytical laboratory reports can be seen in Appendix D.

7.2.3 Arsenic

Water samples were obtained by either DEQ or PHD from the wells and submitted for analysis of total arsenic. All the water samples obtained by DEQ during all three sampling events were submitted to SVL Analytical, Inc., for analysis of total arsenic with a minimum detection limit of 3.0 micrograms per liter ($\mu\text{g/l}$). All the water samples obtained by PHD during the three sampling events were submitted to Anatek Labs for analysis of total arsenic with a minimum detection limit of 1.0 $\mu\text{g/l}$. The June 2012 sampling event had all the samples submitted to SVL analytical Inc. for analysis of total arsenic with a minimum detection limit of 3.0 $\mu\text{g/l}$. The September 2012 and January/February 2013 sampling events had analytical results from both laboratories with mixed minimum detection limits. The total arsenic analytical results for all three sampling events are presented in Tables 7–9 with notations as to which samples were obtained and submitted by PHD. The analytical results for total arsenic are presented in Figures 16–18. The scale used in Figures 16 -18 shows the lowest value as concentrations less

than 3.0 µg/l. The less than 3.0 µg/l value was used so comparisons could be made between the different figures. The analytical laboratory reports can be seen in Appendix D.

7.3 Organic Constituents

A number of volatile organic compounds (VOCs) and synthetic organic compounds (SOCs) were analyzed in all the June 2012 samples. The list of constituents is comprehensive and consists of commonly found contaminants. All the analytical results for both VOCs and SOCs from all the wells sampled were below detection limits. The list of VOCs and SOCs analyzed can be seen in Table 3 and the analytical results can be seen in Tables 11–13. The analytical laboratory reports can be seen in Appendix D.

7.4 Radioactive Constituents

Uranium and radium isotopes were sampled in all wells during the June 2012 sampling event and submitted to SVL Analytical, Inc., for analysis of uranium and radionuclides. SVL performed the analysis for uranium and subcontracted the radium isotopes analysis to Energy Laboratories of Casper, Wyoming. The analytical results can be seen in Table 7, Figure 19, and Figure 20. The analytical laboratory reports can be seen in Appendix D.

7.5 Stable Isotopes (^2H and ^{18}O)

The stable isotopes of ^2H and ^{18}O were sampled in all available wells during all three sampling events. Coeur d'Alene Lake, Hayden Lake, and Lake Pend Oreille were sampled during all sampling events. In addition, Spirit, Twin, and Hauser Lakes were also sampled during September 2012 and January/February 2013.

The samples from the June and September 2012 sampling events were submitted to the University of Idaho Stable Isotopes Laboratory in Moscow, Idaho. The samples from the January/February 2013 sampling event were submitted to Boise State University, Department of Geosciences, Boise, Idaho.

Stable isotopes were also analyzed in precipitation samples. Precipitation samplers were located on the Rathdrum Prairie (PATLS(1) and PATLS(2)) and an upland area to the west (PRGMTN). The upland precipitation sampler was at an elevation of approximately 4,215 feet, and the samplers on the Rathdrum Prairie were at approximately 2,320 feet. The placement of both precipitation stations were based on the proximity of weather stations. PATLS(1) was at the same location as the Bureau of Reclamation Rathdrum Prairie weather station (RTHI), and the PRGMTN sampler was placed in the general vicinity of the Natural Resources Conservation Service Ragged Mountain SNOTEL site (RAG11).

The Rathdrum Prairie precipitation sampler (PATLS(1)) was placed in March 2012 and sampled during May 2012. The sampler was damaged shortly afterwards and was relocated to a site approximately 0.25 miles to the southeast (PATLS(2)). Station PATLS(2) was sampled in December 2012. The PRGMTN sampler was placed during June 2012 and sampled during December 2012. The samples obtained during the May 2012 PATLS(1) sampling were submitted to the University of Idaho Stable Isotopes Laboratory. The samples obtained from PATLS(2) and PRGMTN during December 2012 were submitted to the Boise State University,

Department of Geosciences. The analytical results for all the ^2H and ^{18}O isotope samples can be seen in Figures 21–23 and Tables 14–16. The analytical laboratory reports can be seen in Appendix D.

7.6 Age Dating

Sixteen wells were selected for age dating analysis during the September 2012 sampling event, and samples were submitted to the University of Utah Dissolved and Noble Gas Laboratory in Salt Lake City Utah for analysis of CFCs. The age dates calculated are average dates or apparent dates as the water sample represents all the different recharge sources and travel times in the aquifer. Samples were also obtained from the same sixteen wells and submitted to the US Geological Survey Chlorofluorocarbon Laboratory in Reston, Virginia, for analysis of SF_6 .

The solubility of the CFCs and SF_6 gases are dependent on recharge temperature. It is necessary to estimate the temperature of the recharge water at the water table to obtain accurate estimates and apply corrections. Two wells were selected (ATH2 and PF#9) and three samples from each were submitted to the US Geological Survey Chlorofluorocarbon Laboratory for analysis of dissolved gas concentrations of nitrogen and argon. The solubility of each gas varies differently as a function of temperature. Obtaining the concentrations of both of these gases allows the computation of the recharge temperature and is used for corrections applied to both CFCs and SF_6 .

In addition the dissolved gas concentrations in ground water can exceed what would be seen through equilibrium solubility with the atmosphere. The elevated gas concentrations are attributed to transient rises in the water table or in rock fractures or through purging. The trapped gas will then partition into the ground water. The “excess air” can cause elevated concentrations that result in inaccurate age dates. The quantity of excess air in a sample can also be determined through the dissolved gas concentrations of nitrogen and argon. Generally excess air corrections are most applicable to SF_6 only, due to the low solubility. The sensitivity of CFC age dates to excess air is considered to be generally very small, less than 1 year per cubic centimeter per kilogram (cm^3/kg) (IAEA 2006).

The recharge temperature was determined from the three samples submitted for each well to be an average of 6.5°C at ATH2 and an average of 12.1°C at PF#9. The other wells used a temperature of 9.3°C for calculations representing an average of the two measured values. Excess air was used for SF_6 calculations and was determined from the three samples submitted to be an average of $1.6 \text{ cm}^3/\text{kg}$ for ATH2 and an average of $2.2 \text{ cm}^3/\text{kg}$ for PF#9. The other wells used an excess air value of $1.9 \text{ cm}^3/\text{kg}$ representing an average of the two measured values.

The calculated age dates assume piston-type flow, which means that the water flowed from the point of recharge to the sampled well with no degradation or mixing of ground water with different recharge ages. Additional discussion can be found in section 8.6. The results from the age dating for both CFCs and SF_6 can be seen in Table 17 and Table 18 and Figure 24–27. The analytical laboratory reports are included in Appendix D.

7.7 Ground Water Temperature

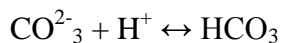
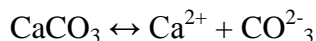
Ground water temperature was obtained during the purging of each well to determine when water quality would be stabilized. The final temperature just prior to obtaining a sample was considered representative of the ground water temperature. The ground water temperature for each well is presented in Tables 7–9 and Figures 28–30.

8 Discussion

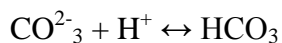
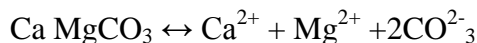
8.1 Major Cations and Anions

The cation/anion composition of the ground water appears to be in three groupings: (1) areas along the periphery of the aquifer, (2) areas within the central portion of the aquifer, and (3) bedrock. The areas along the periphery appear to be influenced by recharge from the lakes, and the stiff diagrams have a diamond shape, with the significant chemical composition of calcium and bicarbonate. The chemical composition of the samples obtained in the interior portion of the RPA appears to have greater concentrations of magnesium and bicarbonate. This composition may be the result of dissolution of carbonate rocks such as limestone (CaCO_3) and dolomite (CaMgCO_3) with increasing downgradient travel distance of the ground water in the RPA. Limestone and dolomite are common in the Helena and Empire Formations of the Belt Supergroup rocks. The carbonate rocks are found in northwest Montana in the vicinity of the historic Lake Missoula and the flood pathway to the Rathdrum Prairie. The carbonate rocks most likely were carried to the Rathdrum Prairie and deposited as flood deposits, eventually forming the aquifer material. In addition, the basement of the Rathdrum Prairie on the east side is mapped as Wallace Formation that can have significant carbonate composition. The chemical dissolution of limestone and dolomite would proceed as follows:

Dissolution of Limestone (CaCO_3)



Dissolution of Dolomite (CaMgCO_3)



The dissolution would result in greater quantities of these constituents. If the concentration became great enough, saturation would result and re-precipitation could occur. In general dolomite is more soluble than calcite. If dissolution occurred, the calcite would be more likely to re-precipitate than the dolomite. Magnesium concentrations in the water would remain at significant levels and calcium would remain relatively stable as any excess would be removed through precipitation. The ratio of Mg to Ca in meq/L for each sample for all three sampling events was calculated and can be seen in (Figures 31–33). The Mg/Ca ratios are very stable for the ground water samples obtained throughout the three sampling events. In general, the interior wells have the largest Mg/Ca ratio and the wells along the periphery have the lowest.

The results of the cation and anion analysis indicate slight differences in the cation/anion composition of the peripheral lakes. The average calcium to sodium ratios for the Lake Pend Oreille, Hayden Lake, and Coeur d'Alene Lake range from 3.0 to 8.6. The average calcium to sodium ratios for Spirit, Twin, and Hauser Lakes range from 0.8 to 1.2. The cation and anion concentrations of the lakes most likely represent differences in the chemical and physical processes along with the lithology that contains the lakes and the local geologic regimes.

The morphometric data vary significantly between the peripheral lakes (Falter and Hallock 1987; Falter 2004; Morency et al. 1990; Soltero and Hall 1985; Soltero et al. 1986; Woods 2004) and have been summarized in Table 19. The water from Twin, Spirit, and Hauser lakes are all from the Proterozoic gneisses of the Priest River Complex and Eocene age granite that predominates the west side of the Rathdrum Prairie. Coeur d'Alene Lake, Hayden Lake, and Lake Pend Oreille are from the east side of the Rathdrum Prairie where the lakes are bounded by both Precambrian Belt Supergroup rocks and Cretaceous gneiss and granodiorite. The cation and anion concentrations for Lake Pend Oreille are significantly elevated relative to the other peripheral lakes. Based on the calcium to sodium ratios, the lakes on the east side of the RPA are significantly different than the lakes on the west side.

The residence time of the peripheral lakes varies significantly (Table 19). The residence times range from 0.5 years for Coeur d'Alene Lake to 11 years for Hayden Lake (Falter and Hallock 1987; Falter 2004; Morency et al. 1990; Soltero and Hall 1985; Soltero et al. 1986; Woods 2004). There does not appear to be a correlation between residence time and lake chemistry.

The saturation indices (SI) for calcite and dolomite were calculated for each sample obtained for all three sampling events and can be seen in Table 20 through Table 22. A negative SI number indicates the mineral is under-saturated, and a positive number indicates the mineral is supersaturated. Most of the SI of the water samples for calcite are slightly negative, indicating the water is close to super-saturation. A few of the calculated SI indicate supersaturated conditions for calcite. The SI calculated for dolomite are generally more negative than the calcite, indicating under-saturated conditions.

8.2 Inorganic Constituents

Other inorganic constituents were sampled to demonstrate potential water quality impacts from various activities at the surface. These include nitrate as nitrogen, nitrate isotopes, chloride, bromide, and arsenic.

8.2.1 Nitrate as Nitrogen and Nitrate Isotopes

Twenty nine wells were sampled for nitrate as nitrogen during the June 2012 sampling event. All concentrations were low and ranged from 0.12 to 1.92 milligrams per liter (mg/L) (Table 7).

The isotopic composition in ground water of ^{15}N and ^{18}O of nitrate is useful in identifying and tracing the nitrate source. Empirical relationships have been developed through comparison of $\delta^{15}\text{N}$ (‰) and $\delta^{18}\text{O}$ (‰) concentrations from known sources. When the analytical results are plotted on a graph with $\delta^{15}\text{N}$ (‰) on one axis and $\delta^{18}\text{O}$ (‰) on the other, the data will populate specific areas or fields on the plot depending on the source. The $\delta^{15}\text{N}$ (‰) and $\delta^{18}\text{O}$ (‰) isotope results for the June 2012 sampling event can be seen in Figures 34 and 35.

The results largely plot in an area with three overlapping fields representing sources derived from ammonia-based fertilizer, soil processes, and septic waste. The soil processes involve biomass decay and the subsequent release of organic nitrogen that oxidizes to nitrate. The nitrification of organic nitrogen in soil results in $\delta^{15}\text{N}$ values between +2.5‰ to +9‰. Ammonia-based fertilizer will have $\delta^{15}\text{N}$ concentrations that generally range from -4‰ to +5‰, and septic waste can have $\delta^{15}\text{N}$ values between +1‰ and +22‰. The negative $\delta^{18}\text{O}$ values may represent the oxidation of ammonia to nitrate (Singleton et al. 2005). The ranges are approximate and may vary depending on the specific conditions of nitrification and ammonification. Given the plot location of the isotope results it would appear most wells do not have a specifically defined source. Wells BTRE, EGA1, EGA2, and HVWS have low concentrations of nitrate as nitrogen with $\delta^{15}\text{N}$ concentrations that indicate possible contributions from both ammonia based fertilizer or septic waste as they plot in the overlapping fields attributed to these sources.

8.2.2 Chloride

Chloride was sampled in all wells during the three sampling events. The analytical results ranged from 0.45 mg/L to 25 mg/L (Table 7 through Table 9). The most elevated concentrations were consistently found in the OHMA well, averaging 25 mg/L and most likely associated with the completion of the well in bedrock and increased residence times. The most elevated concentration from wells completed in the RPA was the CLAW well, averaging 9.08 mg/L. The most likely sources of chlorides in the RPA are through the introduction of septic effluent or road salt.

The application of road salt over the RPA is predominantly in the form of sodium chloride with minor amounts of magnesium chloride. A plot of sodium versus chloride for wells completed in the RPA (excluding OHMA and CHSA) and the peripheral lakes for each sampling event can be seen in Figures 36–38. There does appear to be a general trend of increasing chloride concentrations with increasing sodium concentration for all three sampling events.

In the June and September 2012 sampling events there appears to be three groupings in the figures: Group 1 includes the peripheral lakes and ground water wells with an upward trend to a chloride concentration of approximately 4.25 mg/L and a sodium concentration of 3.6 mg/L. Group 2 includes wells C4SW and USFS Nur with chloride concentrations in excess of Group 1. Group 3 includes wells CLAW, HLWA#1 and RATHG with both elevated sodium and chloride concentrations. The first group most likely has sodium and chloride concentrations that are largely associated with recharge from the peripheral lakes and then increase as the water moves through the aquifer. The peripheral lakes generally plot toward the lower left indicating sodium to chloride ratios less than ground water. The elevated sodium and/or chloride concentrations of the Groups 2 and 3 may indicate impacts from anthropogenic activities. The January 2013 sampling events indicates that wells ATH2 and PF6 have elevated chloride concentrations relative to June and September sampling events. Well C4SW has a lower chloride concentration relative to the June and September sampling events. If the elevated concentrations are from septic effluent or landfills, an indicator might be a corresponding elevation in nitrate-nitrogen concentrations.

A plot of nitrate-nitrogen versus chloride for the June sampling event can be seen in Figure 39. The plot of nitrate-nitrogen versus chloride indicates a number of wells with an upward trend of increasing nitrate-nitrogen with increasing chloride (Group 1). The Group 1 wells in the lower

left hand corner are located downgradient from the peripheral lakes and have low nitrate-nitrogen/chloride ratios most likely from significant recharge received from these lakes. The other wells in Group 1 most likely reflect increasing concentrations of nitrate-nitrogen and chloride as the water travels downgradient. A number of these wells are included in Group 1 of the sodium versus chloride plots (Figures 36 – 39).

The wells C4SW, HLWA#1 and USFS Nur are defined as Group 2 and appear to have anomalously elevated chloride concentrations relative to the nitrate-nitrogen trend of the other wells. The nitrate-nitrogen concentrations are comparable to Group 1. The wells EGA#1, EGA#2 and HVWS are defined as Group 3 and have elevated nitrate-nitrogen concentrations relative to Groups 1 and 2 with chloride concentrations comparable to Group 1. Group 4 is defined by the CLAW and RATHG wells and appears to have both elevated nitrate-nitrogen and chloride concentrations.

Wells C4SW and USFS Nur of Group 2 have elevated chlorides and do not have elevated sodium or nitrate-nitrogen. The source of the elevated chlorides would most likely exclude septic effluent or road salt. The HLWA#1 well of Group 2 appears to have elevated sodium and chloride and does not have elevated nitrate-nitrogen and could be from the application of road salt. The nitrate-nitrogen versus chloride plot does appear to indicate that wells EGA#1, EGA#2, and HVWS have elevated nitrate-nitrogen and lower chloride concentrations relative to the other wells. These three wells do have the most elevated nitrate as nitrogen concentrations relative to the other wells sampled (although still less than 2.0 mg/l). The nitrate-nitrogen/chloride ratio for these three wells may be indicative of impacts from ammonia based fertilizer and would be consistent with the nitrate isotope results. The Group 4 wells of CLAW and RATHG appear to have elevated chloride, sodium and nitrate-nitrogen and could be characteristic of impacts from septic effluent.

8.2.3 Arsenic

Analytical results for total arsenic were above detection limits for 8 of the wells in the June sampling event (bold values in Table 7). The total arsenic concentrations in the samples above the detection limit ranged between 3.2 to 7.0 µg/L. The September sampling event showed 16 wells with total arsenic concentrations above detection limits (bold values in Table 8). The arsenic concentrations in the samples ranged from 1.3 to 6.9 µg/L. The January/February sampling event showed 19 wells with total arsenic concentrations above detection limits, ranging from 1.2 to 8.0 µg/L (bold values in Table 9). The lower arsenic concentrations in the September 2012 and January/February 2013 sampling events reflect the lower detection limits from Anatek Labs, Inc. The wells CHSA, CLAW, EASA, MVT#1, PF#9, and TLWS had arsenic detected in all three sampling events. The Idaho driller's logs for the wells with consistent occurrences of arsenic do not describe a consistent lithology. Wells EASA and TLWS are completed in gravel and cobbles, while wells CHSA, CLAW, and PF#9 indicate the presence of finer-grained material. The driller's log for the MVT#1 well does not have a lithologic description (Nace and Fader 1951), but other wells in the vicinity indicate completion in sand and gravel. There does not appear to be a correlation with the dissolved oxygen measured at the time of sampling nor the general chemistry.

A RPA ground water study conducted by Stevens (2013) investigated the phosphorus content of ground water in 2011 and 2012. Three of the wells sampled (CLAW, MVT#1, and PF#9) during

the phosphorus investigation coincide with the wells that had consistent arsenic during the RPA hydrogeochemical investigation. None of these wells had elevated phosphorus concentrations relative to the other wells sampled during the phosphorus investigation. A statistically significant increase in phosphorus concentrations occurred in September of both years of the investigation and may be related to an increase in total dissolved solids content of the aquifer water, possibly derived from spring runoff. A slight increase in arsenic concentrations was detected during the September 2012 sampling event in select wells, which could be related to either arsenic attached to solids (colloids) moving through the aquifer and/or an increase in phosphorus through ionic exchange that creates increased dissolved arsenic concentrations from arsenic bound in the aquifer material.

Wells CLAW, EASA, MVT#1, PF#9, and TLWS all have the potential to be influenced by surface water bodies. Well CHSA is not near a surface water body but the Chilco Channel area receives significant recharge from the upland watershed located immediately to the east (Stevens 2005). In addition to the TLWS and EASA wells, the Upper Twin Lakes Water System Well #3 (UTL#3) located approximately 3 miles northwest and southwest of the TLWS and EASA wells, respectively, has also had historic elevated arsenic concentrations (Stevens 2004). Stevens (2004) indicates the arsenic from water sampled in UTL#3 may be controlled by redox conditions and pumping levels.

8.3 Organic Constituents

The analytical results for all the sampled VOC's and SOC's were below detection limits. Water quality impacts from activities or land uses associated with these constituents appears to be negligible.

8.4 Radioactive Constituents

Uranium concentrations were above detection limits in 18 of the 29 wells sampled in June 2012 and ranged from 0.0005 to 0.0044 mg/L (bold values in Table 7). The drinking water standard is 0.030 mg/L. The wells were also sampled for Radium-226 and Radium-228 during the June 2012 sampling event. Both were above detection limits in 2 of the 29 wells sampled. The two samples above detection limits had concentrations of 2.7 and 5.7 pCi/L. A duplicate was taken of the second sample and the analytical results indicated the concentration was below detection limits (less than 1.3 pCi/L). The results from the first sample and the average of the two results of the second sample were well below the drinking water standard of 5.0 pCi/L.

8.5 Deuterium and Oxygen-18 Isotopes

8.5.1 Surface water Bodies

The $\delta^2\text{H}/\delta^{18}\text{O}$ ratios can be very specific to the surface water body (Jonsson et al. 2009), indicating the different physical processes occurring within the peripheral lakes of the RPA. ^2H and ^{18}O have been used in various lake investigations to determine water balances, mixing, turnover rates, residence times, and contributions to ground water (Gibson et al. 2002; IAEA 1997; Katz et al. 1997).

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analytical results indicate significant differences between all the peripheral lakes (Figure 40). Coeur d'Alene Lake, Hayden Lake, and Lake Pend Oreille all plot in different locations indicative of different physical processes. The three lakes also show relatively stable $\delta^2\text{H}/\delta^{18}\text{O}$ ratios throughout the year. Spirit, Twin, and Hauser Lakes also have distinctive $\delta^2\text{H}/\delta^{18}\text{O}$ ratios and appear to demonstrate a significant seasonal shift between the September 2012 and January/February 2013 sampling events. The seasonal shift may be due to one of the following reasons: (1) a relatively large portion of recharge from precipitation with less fractionalization, typical of inland winter conditions; (2) larger temperature variations due to the smaller volume; or (3) shorter residence times. Coeur d'Alene Lake, Lake Pend Oreille, and Hayden Lake appear to have less seasonal deviation, most likely related to their larger volumes (Table 19). Spirit, Twin, and Hauser Lakes were iced over during the January/February 2013 sampling event most likely due to the smaller volume and shallow depth; Coeur d'Alene, Hayden, and Pend Oreille Lakes were ice free. Smaller volume would also result in greater through flow and shorter residence times resulting in greater seasonal variations. The three samples obtained from Lake Coeur d'Alene exhibit relatively stable $\delta^2\text{H}/\delta^{18}\text{O}$ ratios that would not correspond with a very short residence time. It would appear there are other processes that are occurring that cannot be determined from the limited sampling of this study.

The lakes with $\delta^2\text{H}/\delta^{18}\text{O}$ ratios that are depleted (lower left portion of Figure 39) are most likely indicative of higher recharge elevations, and the lakes with $\delta^2\text{H}/\delta^{18}\text{O}$ ratios that are enriched (upper right portion of Figure 39) are most likely indicative of recharge from lower elevations. A good correlation exists between average watershed elevation for Lake Pend Oreille, Coeur d'Alene Lake and Hayden Lake and the location along the GMWL. Hauser Lake, Twin Lakes and Spirit Lake all have similar average watershed elevations (Table 19) and plot between the recharge elevations of Coeur d'Alene Lake and Hayden Lake. Based on the recharge elevation it would be expected that the $\delta^2\text{H}/\delta^{18}\text{O}$ ratios of Hauser Lake and Twin Lake would plot to the right and above Hayden Lake. It would appear that there are other processes occurring for these two lakes that are affecting the $\delta^2\text{H}/\delta^{18}\text{O}$ concentrations or the recharge elevation is greater than the average.

8.5.2 Ground Water Wells

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analytical results from many of the ground water wells reflect ratios of the two isotopes that are very similar to the upgradient surface water bodies, indicating significant recharge from the lakes (Figures 41– 43). The ground water wells have been grouped according to the surface water body providing recharge to the wells (Figure 44).

There also appears to be a significant shift in the January sampling event, with most of the ground water wells plotting on or near the GMWL (Figures 21– 23). The shift is most likely caused by cooler temperatures and less evaporation. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ results from the January/February 2013 precipitation samples plot on or slightly above the GMWL. The June and September 2012 sampling events indicate significant evaporation, most likely a reflection the warmer spring and summer temperatures and greater evaporation. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ results from the June 2012 precipitation sample plots well below the GMWL.

8.6 Age Dating

8.6.1 Chlorofluorocarbons

The age date was determined by comparing known historic atmospheric CFC concentrations and the equivalent atmospheric CFC concentrations in the ground water samples obtained from the wells. A number of different sources recharge the RPA, such as the six peripheral lakes, Spokane River, watershed runoff, and infiltrated precipitation. Each of these has different recharge rates and duration. The time it takes for water to travel from the land surface to the water table ranges from a few months to multiple years.

Figures 45 and 46 show plots with CFC-11 versus CFC-12 and CFC-12 versus CFC-113 of the CFC data from the sampled wells. The figures are labeled with fields that indicate either contributions from external sources, degradation or sorption. The figures also have a line plotted (inset) of historic atmospheric CFC concentrations that would result from no external sources, degradation or sorption and simple piston flow (advective transport only). Any sample that has concentrations coincident with this line would not have been subject to an external source of CFC's, degradation or sorption. None of the samples obtained occur on this line and indicate a more complex fate and transport history. A number of wells have CFC concentrations that indicate an external source and others indicate degradation or sorption.

The equivalent atmospheric concentrations (ground water concentrations converted back to the corresponding atmospheric concentrations) in the wells sampled can be seen in Figures 47 – 49. The equivalent atmospheric CFC-11 concentrations for 10 of the 16 wells sampled were above any historic atmospheric concentrations. The equivalent atmospheric CFC-12 concentrations for 7 of the 16 wells sampled were above any historic atmospheric concentrations. The equivalent atmospheric CFC-113 concentrations for 6 of the 16 wells sampled were above any historic atmospheric concentrations. These wells are supersaturated with CFCs and are considered to have an external source. Supersaturated concentrations of CFCs are usually attributed to proximity to large municipalities, landfills, or sewage disposal (Clark et al. 1995; Ho et al. 1998; IAEA 2006).

Elevated CFC concentrations have been reported in the air of urban environments such as Las Vegas, New York City, and Beijing (Carlson et al. 2011). The increase in CFC concentrations near these urban areas was generally not greater than 50 parts per trillion by volume (pptv) for CFC-11, 30 pptv for CFC-12, and 10 pptv for CFC-113 (Barletta 2006; Ho et al. 1998; Qin 2007). The CFC concentrations in the wells on the RPA that are supersaturated are greater than the historic high CFC concentrations in the northern hemisphere with the addition of CFC concentrations that could be attributed to being in proximity to urban areas described above. Given the large geographic area that the supersaturated wells cover and the rural nature of most of this area, urban air is not considered to be an external source causing the elevated CFC concentrations. Three other sources of external CFCs that can contribute to elevated concentrations are subsurface septic disposal, landfills and urban runoff.

The number of septic permits issued per Public Land Survey System section, known landfill/dump locations and municipal sewer boundaries with corresponding CFC-11, CFC-12 and CFC-113 concentrations can be seen in Figures 50 – 52 (PHD 2013, PHD 1988, Kootenai County 2013). The very elevated CFC concentrations associated with the USFS Nur well

maybe be caused by the location downgradient from three historical landfill/dump sites. The elevated chloride concentrations as discussed in Section 8.2.2 would also be indicative of landfill leachate. The elevated concentrations of CFC's in the CLAW well may reflect the location downgradient from an area with significant subsurface septic system densities. The elevated CFC concentrations would correlate with elevated sodium, chloride and nitrate-nitrogen (Section 8.2.2) as an indication of potential water quality impacts from subsurface sewage disposal. Although to a lesser degree, the RATHG also has elevated CFC concentrations and similar sodium, chloride and nitrate-nitrogen concentrations relative to the other wells. The RATHG well might also be impacted by septic effluent and may reflect the location downgradient from areas with relatively significant subsurface densities. The RATHG well is also located downgradient from a historic landfill/dump that may also contribute to the water quality composition. Other wells with elevated CFC concentrations maybe caused by a combination of septic and/or landfill sources.

Previous studies (Carlson et al. 2011, Morris et al, 2005) have suggested that urban runoff could be a source of elevated CFC's in ground water. These previous studies have focused on large cities that included industrial areas. It is not known what the potential for the smaller predominantly residential municipalities in the study area have for contributing CFC's in storm water to the underlying aquifer.

Other processes may affect the CFC concentrations in the unsaturated zone. The wells that did not have excess CFC concentrations from external sources had age dates that were older than expected (i.e., relatively low concentrations of CFCs). The recharge to the RPA is predominantly from the peripheral lakes, the Spokane River, and watershed runoff. The travel time for water to infiltrate from these sources once entering the unsaturated sediments is most likely on the order of months. The travel time for precipitation would most likely be on the order of several years. The contribution of precipitation to the other sources would create older age dates, caused by the significant time necessary for the precipitation to infiltrate to the water table along with processes in the unsaturated zone (gas diffusion, air-water exchange, and sorption). Precipitation's contribution of recharge is relatively small and would most likely not independently create the older water calculated.

The fate of CFCs in lacustrine environments has been investigated and found to have significant impacts on concentrations. CFCs are very stable in oxic environments but can undergo significant degradation in anoxic environments. Walker et al. (2007) found that CFC concentrations can be significantly reduced in the deeper, anoxic water and sediments of northern temperate lakes. Studies conducted in the peripheral lakes (Falter and Hallock 1987; Falter 2004; Morency et al. 1990; Soltero and Hall 1985; Soltero et al. 1986; Woods 2004) indicate a significant decrease in dissolved oxygen concentrations with depth.

Most of the wells with the older dates in this study occur in areas recharged by the peripheral lakes. CFC-11 and CFC-113 have greater degradation rates in anoxic environments than CFC-12 (Balsiger et al. 2005). In general, the CFC concentrations for wells with older age dates had a greater concentration of CFC-12 than of CFC-11 and CFC-113, and would be consistent with anaerobic degradation. Once the water entered the aquifer, the ratios would be stable in the oxygenated water of the RPA. Because of the apparent degradation or supersaturation, age dating based on CFC concentrations was not possible.

8.6.2 Sulfur Hexafluoride (SF₆)

The ages determined through SF₆ age dating were younger than calculated with CFCs. SF₆ is considered to be relatively conservative and does not readily undergo degradation (Busenberg and Plummer 2000). The age dates assume piston flow but actual water most likely reflects mixing of water from different sources and age dates. The contribution of recharge from precipitation in particular would have older age dates because of the significant unsaturated thickness and resulting time of travel. Based on the SF₆ analytical results, the average ground water age is young (less than 15 years old).

8.7 Ground Water Temperature

The ground water temperatures for the three sampling events appear to have slight seasonal changes. The ground water temperatures adjacent to the peripheral lakes appear elevated relative to the central portions of the RPA and are most likely influenced by lake temperatures. The ground water temperatures adjacent to the Spokane River appear elevated, with the greatest values at the wells PF#6 and PFSP.

Avista Corporation operates the Post Falls Dam to maintain the water elevation in Lake Coeur d'Alene at 2,128 feet during the summer months (Avista Corporation 2005). The dam releases little water during this time, and the portion of the Spokane River between Coeur d'Alene Lake and the Post Falls Dam experiences minimal flow, allowing the water temperature to reach a maximum during August/September (Seitz and Jones 1982). The PF#6 and PFSP wells may be influenced by the storage and increased temperatures of water during the summer months. In addition, north-south oriented bedrock exposures immediately north of the dam site (Figure 2) may cause water seeping from this stretch of the river to flow in a northerly direction toward PF#6. PFSP also appears to be hydraulically connected to the Spokane River as evidenced by the inorganic chemistry and stable isotope data (section 8.5). The ground water temperature of the DIBE well during the June and September 2012 sampling events appears elevated relative to the surrounding wells that were sampled. The cause for the elevated temperature is not apparent.

9 Conclusions

The geochemical data acquired for this study from drinking water wells distributed over the RPA indicates that the drinking water quality is very good. All inorganic constituents were well below any drinking water standard. Concentrations of sodium, chloride and nitrate-nitrogen indicate there maybe some anthropogenic surface activities that are potentially related to minor water quality impacts. The anthropogenic sources could include, subsurface sewage disposal, road salt and historic landfill/dump sites. The nitrate-nitrogen concentrations were all below 2.0 mg/L, less than the drinking water standard of 10 mg/L and most likely represent background concentrations with potentially minor contributions from surface activities. The ¹⁵N and ¹⁸O isotope ratios did not clearly indicate a source of nitrate for most wells and could be attributed to either natural soil processes, fertilizer application or sewage disposal. The ¹⁵N and ¹⁸O isotope ratio of four wells indicate fertilizer application or septic waste as a source. Three of these wells had elevated nitrate-nitrogen concentrations with no corresponding elevated chlorides or sodium concentrations that would support fertilizer as the source.

Naturally occurring constituents were found in some wells that can affect drinking water quality. The September 2012 sampling event results for uranium and radium-226/radium-228 indicate occurrence in some wells but below the drinking water standards of 30 μ g/L and 5 pCi/L respectively. Arsenic sampling from the three sampling events also indicate occurrence in some wells but below the drinking water standard of 10 μ g/L. The multiple sampling also indicates that arsenic is consistently present in most of the wells that had arsenic concentrations above detection limits.

The use of deuterium and oxygen-18 helped identify significant recharge sources and areas of the aquifer with water predominantly derived from these recharge sources. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analytical results indicate distinct signatures from the peripheral lakes, reflecting different physical and chemical processes. The specific $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios from the peripheral lakes are apparent in downgradient wells completed in the RPA, indicating significant recharge with little mixing.

CFC analytical results from the majority of wells sampled show supersaturated concentrations most likely indicating anthropogenic impacts. The USFS Nur well is located downgradient from three historic landfill/dump sites. The CLAW well and RATHG well are located downgradient from areas with high subsurface septic density. The elevated CFC concentrations in conjunction with the inorganic constituent results of these wells would be consistent with these types of sources. Other wells with elevated (supersaturated) concentrations are most likely caused by some combination of sources. The rural environment most likely precludes elevated CFC concentrations from urban atmospheric sources/activities or runoff. Additional sampling and analysis would be necessary to determine any potential contributions from the municipalities located over the RPA. Because of the elevated CFC concentrations, age dates could not be obtained from these samples.

The CFC analytical results from the wells that did not have supersaturated conditions had age dates much older than anticipated. The older CFC age dates are most likely a result of recharge water migrating through a thick unsaturated zone (150 to 550 feet) and anaerobic degradation occurring in the peripheral lakes and are most likely not accurate. The age dates from the SF₆ analytical results are considered more representative because of the relatively conservative nature and few anthropogenic sources. The exception would be the SF₆ analytical results that are elevated to supersaturated in the USFS Nur well. Again the elevated concentrations maybe caused by the downgradient location from three historical landfills/dump sites. Dating based on SF₆ indicate young water, less than 15 years old.

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