THE UNIVERSITY OF CALGARY

Using the Chemical and Isotopic Characteristics of Drinking Water to Determine Sources of Potable Water and Subsurface Geologic Controls on Water Chemistry, Stoney Indian Reserve, Morley, AB.

by

Lynn Margaret McFarland

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF GEOLOGY AND GEOPHYSICS

CALGARY, ALBERTA

APRIL, 1997

© Lynn Margaret McFarland 1997

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced with the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-20840-0

Canada

Abstract

Subalpine regions are defined as cool upland slopes below the timber line, characterised by the dominance of evergreen trees. This thesis considers the following questions for a subalpine watershed on the Stoney Indian Reservation, using water chemistry and isotopes: 1. Can the chemistry and isotope analysis of the water be used to characterise the nature of the subsurface geology? 2. Does the aquifer geology control the quality of drinking water on the reserve? 3. Is it possible to separate the different aquifers the water comes from on the basis of their chemical and isotopic characteristics? The deeper shale and sandstones have higher total dissolved solids concentrations and greater ion variability than the waters from gravels, which closely resemble surface waters. Isotopes indicate that evaporative processes dominate the waters, water-rock interactions are occurring and that there is little bacterial sulfate reduction occurring. All reserve waters met government drinking water guidelines.

Acknowledgements

I would like to thank all the people who have contributed to this thesis. First a great deal of thanks to my supervisor, Ian Hutcheon, who always pushed me to get that little bit more out of my data. Larry Bentley and Dr. H. Roy Krouse provided many useful suggestions. I appreciate the people of the Nakoda Nation (Stoney Indian Reservation) for permitting me onto their land and for their assistance.

Maurice Shevalier and Brian Fong helped keep my computer running and healthy. Pat Michael did all the cation analyses. Thanks to the technicians of the Stable Isotope Lab, Maria, Jesusa, and Nenita for their isotope analyses.

Thanks go to my friends and family who helped me get over the challenging times. Special thanks to Anne Duguay, Christy de Mille, Jennifer Leslie, Matt Caddel, Caroline Williams and Ian Kay for making me take myself a little less seriously when things got rough. I appreciate the discussions with the other 'Dudes' regarding all matters scientific. Thanks to my parents, Kathleen and John, who were there whenever I needed them, even long-distance, and to my sister Janet.

Financial support for this thesis was provided by Health Canada under the Safe Drinking Water Programme, by the University of Calgary in the form of GAT, GRS and research grant support and by NSERC operating grants to Dr. I. Hutcheon and Dr. H. R. Krouse. I received the John. O. Galloway Memorial Scholarship for 1996, which provided much appreciated financial support. The Groundwater Information Centre, Government of Alberta provided access to the water well records. Surface water flow information was provided free of charge by the Surface Water Monitoring Brach of Environment Canada, Calgary.

Table of Contents

Chapter One: The Study and Background

Chapter Two: Study Area and Site Description

Chapter 3: Methods and Data

Chapter 4: Government of Canada Health Guidelines and Stoney Reserve Water Quality

Chapter 5: Interpretation of Data

Chapter 6: Interaction Between Groundwaters, Surface Waters and Minerals in the Study Area

Chapter 7: Discussion and Conclusion

List of Tables

List of Figures

Chapter 1

The Study and Background

1.1. Introduction

The quality of drinking water varies greatly on the Stoney Indian Reservation located west of Calgary, Alberta (Figure 1.1). Many residents of the reserve experience poor quality drinking water in terms of both taste and appearance, as well as bacterial counts. These variations in water quality can occur over very short distances. Factors contributing to this problem may include the residence time of the waters in the groundwater system, which aquifer unit or units a well is completed in, the amount of water required from the well and the presence of potential contamination sources, such as ranching operations, leaking septic tanks and fertilizer from field run-off in the area.

This study is part of the Safe Drinking Water study on the Stoney Indian Reservation and includes a programme of water sampling and water quality work being carried out under the direction of Health Canada. First Nation groups are provided with funds and assistance to examine drinking water quality and identify problem areas. This study is a joint effort of the Stoney Nation, Health Canada, and The University of Calgary, Departments of Geology and Geophysics, and Physics and Astronomy.

This thesis considers the following questions: 1. Can the chemistry and isotope analyses of the water be used to characterise the nature of the subsurface geology? 2. Does the aquifer geology control the quality of drinking water on the reserve? 3. Is it

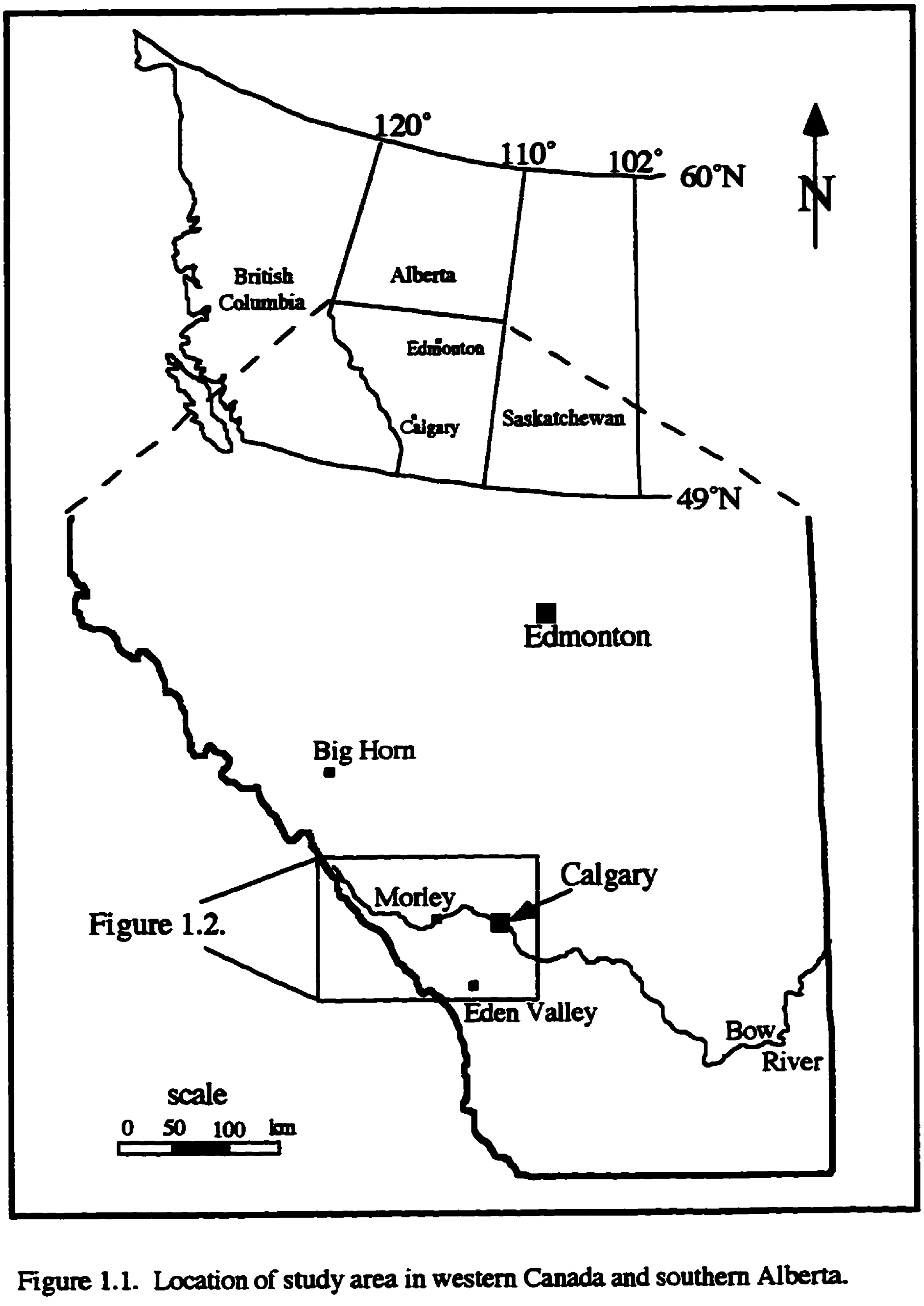


Figure 1.1. Location of study area in western Canada and southern Alberta.

possible to separate the different aquifers the water comes from on the basis of their chemical and isotopic characteristics? The identification of aquifers providing quality drinking water may be possible by understanding which factors control the characteristics of the waters.

It is often difficult to determine the detailed hydrology of an alpine or subalpine area. The exact nature of water flow and the contributions to that flow from groundwater, rainfall, snowmelt etc. are often defined poorly or, at best, estimated (Silar, 1990; Klemes, 1990). A subalpine area is defined as the "cool upland slopes below the timber line, characterised by the dominance of evergreen trees" (Bates and Jackson, 1987). The majority of the land on the Morley reserve meets this criterion, being forested on the mountainsides and hill slopes around the reserve. The area receives seasonal precipitation in the form of winter snowfall and spring and summer rains. With well-defined watershed boundaries, this study provides a good opportunity to determine chemical and isotopic characteristics of waters in a subalpine watershed.

A suite of domestic well, surface and spring waters have been collected from sites on and around the reserve. These 104 samples were analysed for alkalinity, cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Li^{+}, Sr^{2+}, Fe^{2+}, Mn^{2+}, Si and SiO_2), anions (SO_4^{2-}, NO_3^{-}, PO_4^{3}, Cl^{-} and Br^{-}), and the stable isotopes of sulfur, carbon, oxygen and hydrogen. These parameters were chosen because they are relatively straight-forward to measure and include ions and isotopes that are potentially involved in chemical and isotope fractionation reactions. The analysed values for the chemical parameters are compared to the Health Canada Drinking Water Guidelines (Health and Welfare Canada, 1993) to determine which sites have poor drinking water quality.

Additional information on subsurface lithology was determined from drillers' records provided by the Government of Alberta, Environmental Protection. Determining the direction of groundwater flow and any seasonal patterns that exist may provide additional information on what controls groundwater quality. Other aspects, such as water - rock interactions, evaporation effects and residence times for waters will also be examined in order to more completely characterise the waters on the reserve and examine the links between surface and groundwater chemistry and the subsurface geology.

This study incorporates information from well water analyses, drillers' records and Health Canada chemical records to better explain the water quality characteristics and water movement on the reserve. A more focused study area was selected to examine the details of the local groundwater recharge, discharge and surface and groundwater flow patterns. This focus area is a smaller drainage basin in the southwest portion of the reserve, centered around Chiniki Lake and Chiniki Creek. It represents a subalpine watershed that is entirely contained in the reserve boundaries. The information gleaned from the waters in this area was then extended to the rest of the reserve.

1.2. Background and previous studies in the area

Tokarsky (1973) examined groundwater availability on the Morley reserve. He reported the Upper Cretaceous strata to be the important drinking water bearing units. General conclusions indicated wells completed in well-connected gravels were most likely to have high yields when water bearing. As no chemistry data were obtained, with all interpretations based on pump tests and drilling records, no assessment of water quality is possible from this study.

A study of the groundwater in the Chiniki Village area was undertaken by Nowak Geological Services Ltd. in 1984. They reported that favourable aquifer conditions existed in buried meltwater channels trending northwest across Highway 1 from the test site. Post-glacial spillway gravels beneath Chiniki Creek turned out to be dry or too dirty to be considered as possible aquifers. Pump tests indicated a fairly uniform gravel aquifer with good hydraulic conductivity, with different water chemistry present at two depths in this aquifer. At a depth of 15.9 m below ground level the waters were of the calcium bicarbonate type, while the water from a depth of 35.1m was dominated by sodium bicarbonate. No other groundwater quality or availability studies specific to the Morley reserve were available. The regional hydrology of the Calgary to Golden area was examined by Barnes and Ozoray (1977), providing information of the large - scale flow paths in the region.

Other researchers have looked at the springs in Alberta and British Columbia. van Everdingen (1972) looked at the thermal springs, springs with water temperatures greater than 9°C. These springs are located west and primarily south of the study area. These springs tend to have higher concentrations of sulfate, H_2S and higher total dissolved solids (TDS) than waters sampled on the reserve. Borneuf (1982) examined springs all across Alberta and comiled data collected by others. There are a few springs located near the reserve boundaries. The springs tend to have low flow rates, temperatures less than 10°C and are dominated by Na^+, K^+ and HCO_3^- ions. Calcareous tufa deposits are found in the area northeast of the reserve (e.g. Big Hill Springs Prov. Park north of Cochrane). Many Springs is located in Bow Valley Provincial Park and is thought to be a deep-sourced spring. This spring is not directly comprable to those waters on the reserve, however, as the Kananaski River separates Many Springs from the study area.

1.3. Aqueous Geochemistry Applications

Geochemical studies of waters have been utilised to help define the hydrology of an area. For example, the Amazon River waters were examined geochemically and the controlling factor on the water chemistry was determined to be substrate lithology and soil geochemistry in the erosional regime (Konhauser et al., 1994). Linking discharge events such as rainfall and snowmelt to changes in concentrations of a variety of chemical parameters has been examined in several catchments in North America (Stottlemyer and Troendle, 1992; Stednick, 1987; Dethier, 1988; Davis and Keller, 1983). The amount of groundwater contribution to the chemical character of stream and river waters has been studied using water chemistry (Ferguson et al., 1994; Williams et al., 1990; Dethier, 1988). Water rock interactions have been considered as a source of dissolved solids in springs of the Sierra Nevada (Garrels and MacKenzie, 1967). Surface water, soils and rock interactions have been examined using the chemistry of stream waters in Wyoming (Miller and Drever, 1977).

Solute input - output studies have been undertaken using geochemical characteristics of water in subalpine and alpine areas of Colorado (Cleaves et al., 1970). In a long term weathering model they determined that roughly fifty percent of the erosion occurring in the catchment could be accounted for by the solute content of the waters. The erosion was predicted to be due to chemical solution of kaolinite, vermiculite, biotite and oligoclase. Mast et al. (1990) looked at stream water solute levels and solute levels in precipitation, in a high alpine setting, to determine the weathering processes affecting the area. They concluded that the solute increase in the surface waters could be linked to the bedrock weathering in the area through water-rock interactions. Attempts to determine the chemical changes that occur in an alpine - subalpine stream during spring snowmelt and runoff illustrated the irregular nature of the solute inputs to the streams

(Denning et al., 1991). High dissolved organic carbon in soil lysimeters near the streams showed that the soil waters get flushed into the streams by the initial snowmelt, carrying with it an initial pulse of higher total dissolved solids (TDS) waters into the stream. Soil pore water chemistry has been used to trace groundwater movement and to determine that the acidification of waters and soils are linked to particular temporal inputs from snowmelts and runoff (Arthur and Fahey, 1993).

Cerling et al. (1989) used cation exchange of Ca^{2+} ions with Na^{+} ions to explain the aqueous chemistry of waters draining shale bedrock regions. Clay mineral cation exchange properties also were studied in an effort to understand soil development in a montane area in New Zealand (Harrison et al., 1990)

1.4. Isotope Studies and Applications

The chemistry of isotopes can be used for a variety of environmental and hydrological studies. Isotopes are defined as atoms of the same element whose nuclei contain the same number of protons but a different number of neutrons. Stable isotopes are naturally occurring isotopes that do not undergo radioactive decay. The different isotopes of the same element have slightly different masses. Isotope fractionation can occur in a variety of chemical and physical processes, resulting from the slight differences in the properties (heat capacity, vapour pressure, density, free energy, etc.) of the various isotopic forms of the elements involved. For these reasons the stable isotopes of hydrogen, oxygen, sulfur and carbon can be used in hydrologic studies.

1.4.1. Hydrogen and oxygen isotopes

Isotopes of hydrogen and oxygen are used to determine processes related to water flow and sources. Researchers have determined the relative amount that groundwater contributes to streamflow in various environments and at different seasons (Sklash et al., 1976; Sklash and Farvolden, 1982). Maule et al. (1994) examined soil waters near Edmonton, Alberta, determining that waters from snow-melt contributed about 27% to the soil waters wheras the groundwaters contributed 44% of the soil water. Lateral flow of waters from nearby depressions may cause the snow-melt waters to pool befoire entering the soil, leading to the 27% snow-water portion. McCarthy et al. (1992) used δD and $\delta^{18}O$ values to show that the isotopically lighter Columbia River waters contribute 50% of the water pumped from municipal wells about 1 km away, near Portland, Oregon.

Wenner et al. (1991) argued that the simplistic model of two waters, old water and new water, with the old water being forced out by the new water, is too limited. They claimed that it is a difficult task to recognise different waters because the distinctive isotope values become muted very shortly after entering the soils of an area.

Limitations on these methods include defining rainfall events with significantly different δD and/or $\delta^{18}O$ values from that of the groundwaters. A limited discussion of this application will appear in this thesis, as the isotope character of the precipitation events on the reserve are unknown.

Water evaporation trends have long been established on the basis of δD and $\delta^{18}O$ relationships (e.g. Dansgaard, 1964). Changes in the oxygen and hydrogen isotope composition of water from the Aswan High Dam Lake in Egypt were examined to determine the extent of evaporation (Aly et al., 1993) and in the Gaula river catchment lake waters were found to have enriched δD and $\delta^{18}O$ values relative to the surrounding streams and rivers due to evaporation (Bartarya et al., 1995).

Dansgaard (1964) discussed altitude and latitude effects on the isotopic composition of precipitation over continents. Abundances of ^{18}O and D decrease with increasing altitude on the windward side of mountains. Typical gradients for $\delta^{18}O$ vary from -0.15‰ to -0.5‰ per 100m and for δD, -1.5 to -4‰ per 100m (Yurtserver and Gat, 1981). This is not likely to be a controlling factor for the δD and $\delta^{18}O$ values on the reserves because the reserve lies on the lee side of the mountains. The D and ^{18}O content decreases with increasing length of storm path due to Rayleigh isotopic fractionation. The D and ^{18}O contents usually decrease with increasing latitude because of larger temperature gradients with distance. This process could affect isotope composition of waters on the reserve as the land lies far inland from any major body of water.

1.4.2. Sulfur isotopes

Sulfur isotopes have been used to determine pathways and processes affecting waters. The sulfur isotope composition of dissolved sulfur species can reflect the sulfur source in the sedimentary rocks of an area (Cameron et al., 1995; Hitchon and Krouse, 1972) as sedimentary sulfate minerals generally have positive $\delta^{34}S$ values whereas sedimentary sulfide rocks have negative $\delta^{34}S$. Differentiation of sulfur from a number of sources was undertaken by Van Donkelaar et al. (1995) to determine the relative amounts of sulfur coming from a localised source of sulfur, a sour gas processing plant. Bacterial reduction of sulfate was examined in their studies and this process has long been known by researchers (e.g. Kemp and Thode, 1968; Rees, 1973).

1.4.3. Carbon isotopes

Carbon and oxygen isotopes are useful in determining the organic carbon sources and utilization in groundwater systems (Gilvear et al., 1993) and to trace deforestation practices in watersheds (Desjardins et al., 1994). Contamination of groundwater has been traced using isotopes of nitrogen and carbon (Davisson and Criss, 1993). Carbon isotopes can also be used to determine the source of carbon in water - whether it is from plant material or from rocks and minerals or from the atmosphere. C_3 and C_4 plants utilise carbon isotopes differently, leading to drastically different isotopic signatures for these plant types (O'Leary, 1981).

1.4.4. Summary

Both chemical and isotope studies have limitations to the extent that processes affecting the hydrology of an area can be predicted. Chemical characteristics of the waters are useful only if there has been sufficient time for changes to the water chemistry to have occurred. Isotope studies rely on differences in isotope abundance ratios and require that the ratio differences in the different waters examined be detectable before process or mixing of waters is traceable.

Combining water chemical analyses with isotope studies helps to resolve some of these limitations. Isotopic and chemical studies were combined for the Fraser River (Cameron et al., 1995), with the sulfur isotope ratio providing a clearer picture of how the differing bedrock geology of the river path contributes to the chemical composition of the river waters. Krothe (1982) used sulfur isotopes and water chemistry to define water flow systems in two localities in the southwestern US. The different groundwaters at each site represented waters sourced in two different aquifers and were characterised by differences in their chemistries. However, the waters had much greater differences in the sulfur isotope compositions, thus the sulfur isotope values confirmed the existence of separated aquifer systems.

1.5. Bacterial Studies

Bacteria can be found in waters in a wide variety of environments. Lithoautotrophic bacteria were detected in wells over 1400m deep (Stevens and McKinley, 1995). Studies have been done on the transport and viability of different bacteria populations in a variety of situations. Research shows that many factors contribute to the continued presence of the bacteria in water supply systems (Isaac-Renton et al., 1996; Boivin et al., 1996) such as variable chlorination levels in the water and settling times in reservoirs. Detection of bacteria in waters can be problematic due to the detailed steps necessary to successfully culture the bacteria, requiring strict adherence to accepted collection techniques (Handfield et al., 1996; Brenner et al., 1996).

1.6. Location of study

The main study area was the Stoney Indian Reservation, located approximately 65 km west of Calgary (Figure 1.2) in southwestern Alberta. The town of Morley lies in the west-central part of the reserve, in the Bow River valley, at the west end of the Ghost Reservoir. The main reserve is divided into two separate areas, north and south of the Bow River and comprises a northeastern oriented semi-rectangular area with additional land in the northwest corner. There is a small additional area of land lying to the north

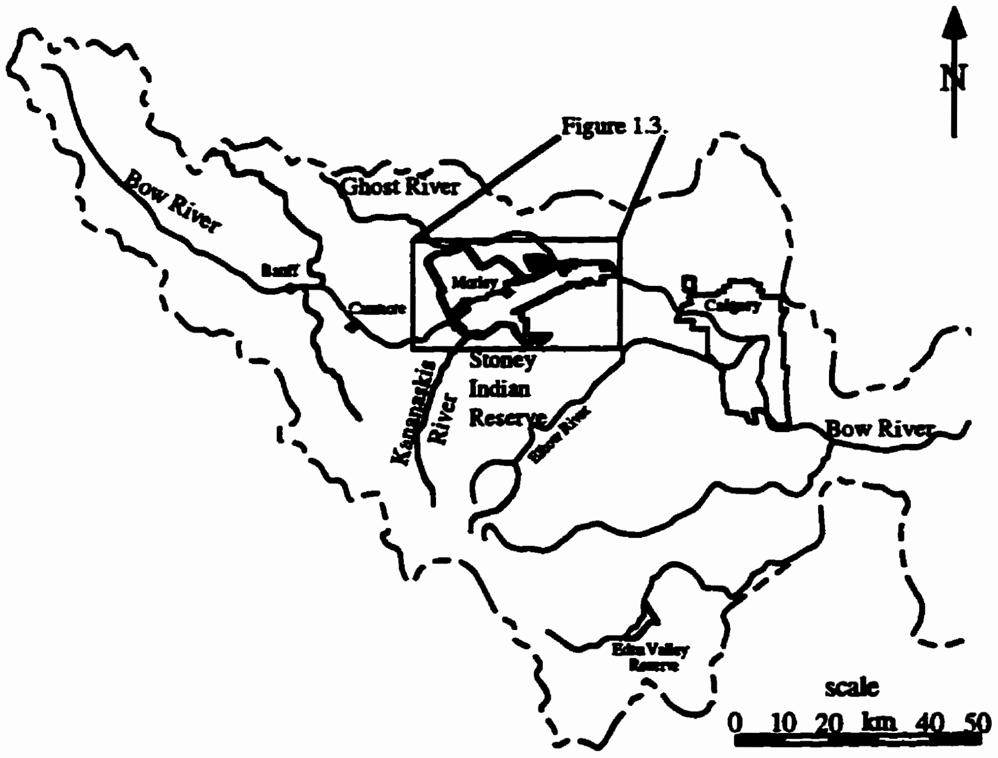


Figure 1.2. Map illustrating location of Stoney Indian Reservation and major rivers in the area. The dashed outline indicates the limit of the Bow River drainage basin (modified from Bow River Water Quality Council, 1994).

and east of the main reserve. However, the waters in this area were not tested as part of the Safe Drinking Water study.

The reserve has an area of approximately 425 km^2 and covers the area from the front ranges to the plains, with most of the land falling in the foothills terrain of the disturbed belt of the Rocky Mountain Front Ranges. The northwestern boundary of the reserve is the surface trace of the McConnell Fault, a thrust fault in the front ranges of the Rocky Mountains, with the Ghost River bounding the reserve to the north.

The majority of the land on the reserve lies at elevations of between 1200m (3750ft) and 1600 m (5000 ft) (Figure 1.3). The land gradually increases in elevation in the northwestern corner of the reserve, as it approaches the Ghost River, reaching a maximum elevation in this area of about 1824 m (5700 ft). The eastern part of the reserve is relatively uninhabited and consists of rolling grasslands.

The topography of the reserve is related to the Rocky Mountains to the west, with other features of glacial origin in evidence. The reserve is dominated by southeast-northwest trending drumlins indicative of first and second generation glacial activity in the area (Fisher and Spooner, 1994) deposited 16,000 years ago. Quaternary aged materials have been deposited along the Bow River valley. The underlying bedrock is primarily of Upper Cretaceous age and trends roughly north - south, paralleling the strike of the Rock Mountain Front Ranges.

The Bow River runs through the reserve land. In the northern half of the reserve, several smaller streams run south, ultimately draining into the Bow River. On the south side of the Bow River, Chiniki Creek runs northeast from Chiniki Lake, eventually draining into the Ghost Reservoir. Chiniki Lake is a major surface water feature in the southwest portion of the reserve. Many of the streams draining the southern hills run

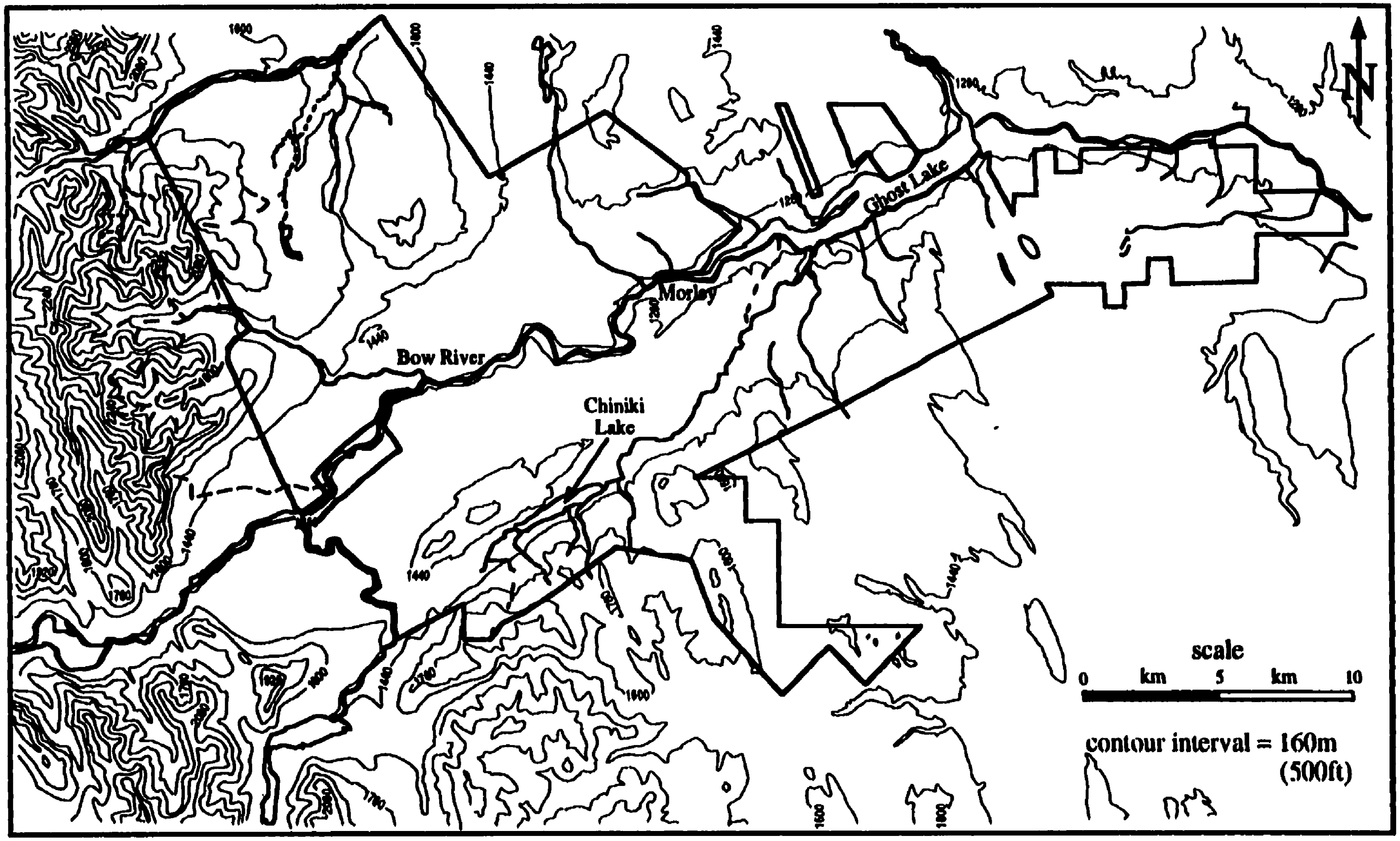


Figure 1.3. Topography of the Stoney Indian Reservation. Elevations are in feet and taken from NTS map sheets 82-O/2 and 82-O/3. Elevation in metres a.m.s.l.

north to the lake. Most of the homes in the southern part of the reserve lie along the path of Chiniki Creek or along Chiniki Lake. The Kananaskis River forms the southwestern boundary of the reserve.

As some precipitation passes through soil, a brief description of soil types in the region is presented. The reserve lands are covered for the most part with either regosolic soils (minimal profile development over unstable terrain) or gleysolic soils (poorly drained depressions with high water tables) (McGregor, 1979). On the forested south and east slopes of the reserve, the soils may have acquired enough additional organic matter to classify the soils as brunisolic order (lack of soil horizon with calcareous based materials producing soils with pH values greater than 5.5). No soil mineral data was given in the above study, nor found elsewhere for this area.

1.7. Regional climate

The regional climate is considered temperate and is characterised by long, cold winters and short cool summers with a precipitation maximum occurring during the growing season (May to September). The area usually experiences snowfall in the winter months, with snow present on the ground from October or November through March. Winter weather is variable however, as chinooks from the west often push out the arctic air, warming the area and causing melting of any snow cover. The winter of 1995 - 1996 was unusual in that it was extremely cold (less than -20°C) for extended periods during December, 1995 and during the first three months of 1996. Extensive snow cover was present throughout much of the winter, as few periods of warming occurred. The spring was fairly cool, with additional snowfalls in early May.

Precipitation in 1995 totalled 414.8 mm for the region (Environment Canada, Atmospheric Environment Services, 1996), with snow reported as H_2O equivalent in mm of precipitation (Figure 1.4). July, 1995 saw 133.4 mm of rain fall in the area, almost double the 30-year average for July of 66.9 mm, leading to flooding in southern Alberta. The first six months of 1996 had precipitation of 191.7 mm, with most of that occurring as rainfall in late May and early June.

The Bow River flow hydrograph shows high water inputs for the spring of 1995 (Figure 1.5), corresponding to the higher rainfalls and increased snowmelt. The hydrograph illustrates the regularity of the beginning of the spring melt. In mid-May each year, a large increase in the flow rate can be seen. Something of interest is the fact that the low flow rate for January, February and March of 1996 were higher than the respective months in the previous year. This may be due to higher than average precipitation in January, 1996 and much lower than normal precipitation for January, February and March, 1995 (12.2 mm total vs. 36.8 mm normally). The same three months in 1996 had 66.2 mm of precipitation.

The vegetation on the reserve is predominantly coniferous with sparse cover and little undergrowth, especially on the slopes of the hills and mountains around the reserve. Large tracts of land, both on the reserve and just outside the reserve boundaries on the southwest have been severely affected by forestry. Clear-cutting, a process by which all the trees in a given plot of land are completely removed, is the usual method for timber harvesting. This process may affect the chemistry of stream waters due to increased run-off and sediment loads, lower levels of organic matter in the waters and lower plant retention of precipitation over the affected areas. However, as access was denied to the affected areas and no chemical data were available from before the clear-cutting occurred, no comparisons can be made on the basis of the chemistry of the stream waters.

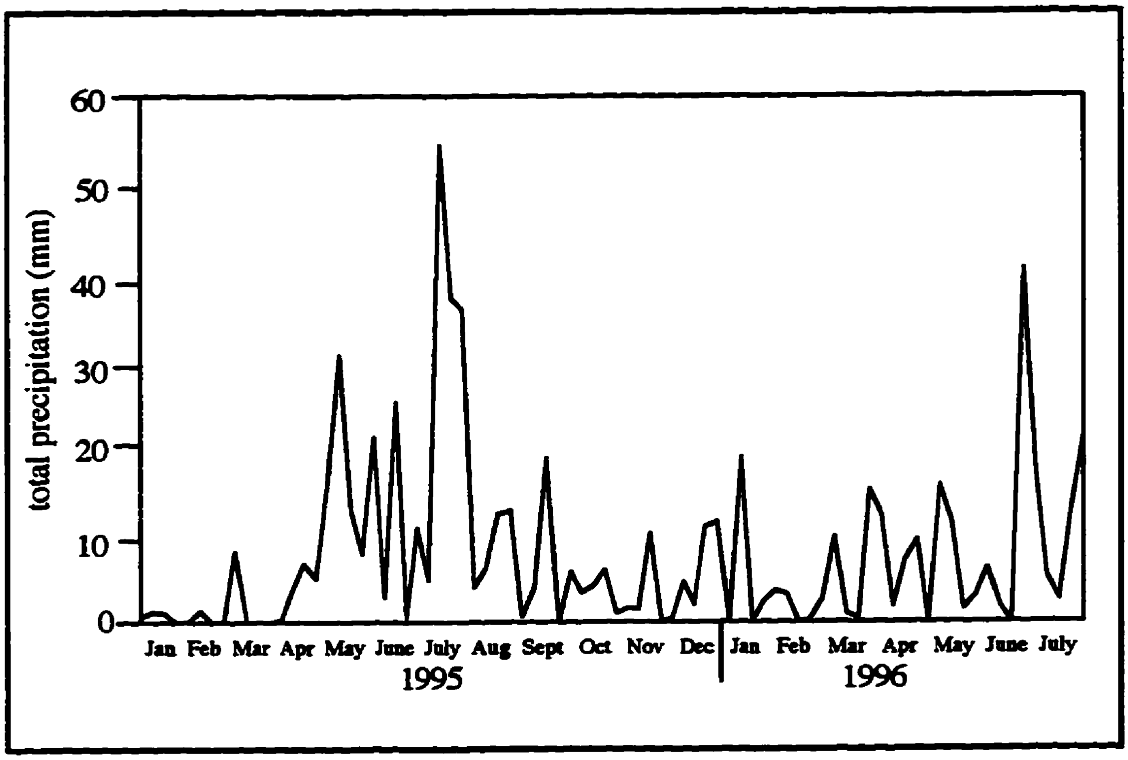


Figure 1.4. Precipitation (mm) for region for January, 1995 to July, 1996.
(Data from Environment Canada Weather Services, 1996)

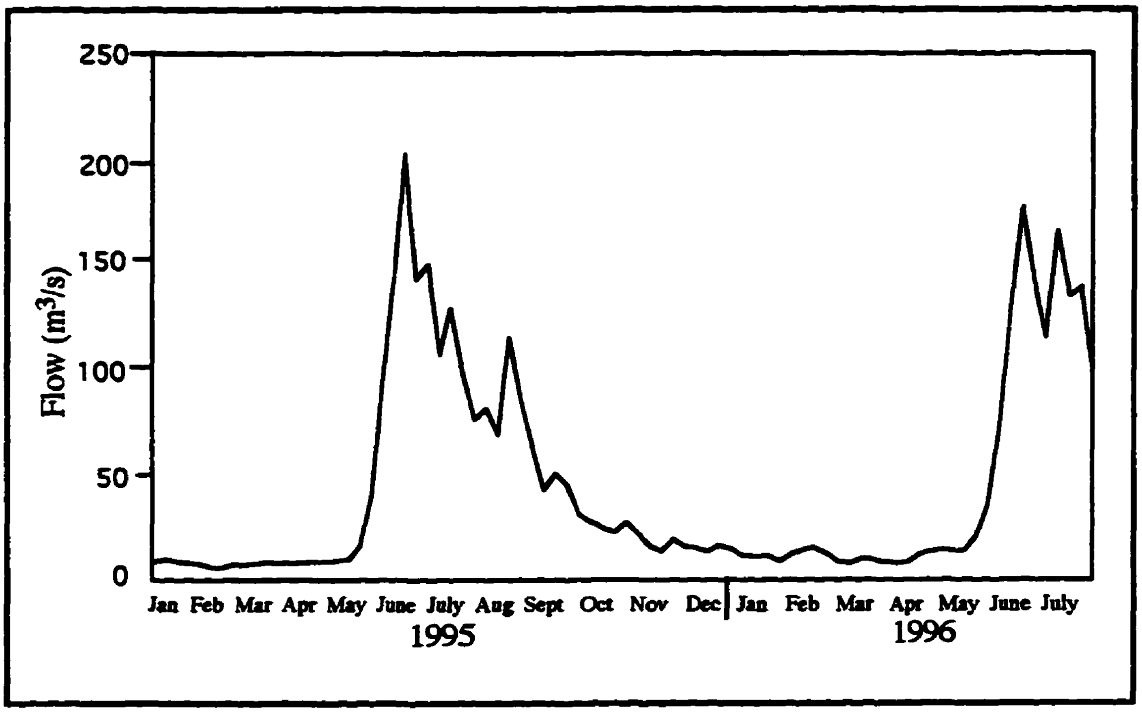


Figure 1.5. Flow rates for the Bow River from January, 1995 to July,1996. (Data from Environment Canada, Surface Water Survey)

1.8. Secondary sites at Big Horn and Eden Valley Reserves

The Stoney Nation has two smaller outlying reserves at Bighorn and Eden Valley. Bighorn is located west of Nordegg and houses approximately 30 families. The Eden Valley reserve lies west of Longview (75 kilometres southwest of Calgary), along highway 541. There are 100 houses on the reserve, most of which use well water as their drinking water source. Six sites were sampled from each reserve. The data are presented in this thesis, however this information is not included in any discussions herein as the remote locations of these reserves precludes the geology and groundwater systematics to be included under the Morley discussion. A brief discussion about whether the chemical parameters of these waters meet Health Canada guidelines is included in Chapter 4.

Chapter 2

Study Area and Site Description

2.1. Introduction

The study area is located in the foothills of the Rocky Mountains. The entire Stoney Indian Reservation was part of the sampling programme, however, a more focused study was undertaken to better examine the detailed relationship between the surface and groundwaters in this region. The study site for the more focused study was the Chiniki Lake region, in the southwest corner of the reserve. Many of the residents of the reserve live near Chiniki Lake or Chiniki Creek, which drains to the northeast.

2.1.1. Focus on Chiniki Lake

Chiniki Lake is a 1.5 km long lake located in the southwestern corner of the Stoney Reserve (see Figure 1.3). This site was chosen because it represents a definable subalpine watershed located within the larger study area of the main reserve. Chiniki Lake receives the surface runoff from the east-west trending hills on the south boundary of the reserve and precipitation percolating through the overlying gravels in the area of the lake. No direct surface water input is apparent from the major rivers in the region, the Kananaskis River to the west or the Bow River to the north. The hills to the south provide a divide between Chiniki Lake and the Elbow River drainage area.

The topography of this area is similar to that of the entire reserve, consisting of the east-west trending bedrock ridges along the southern boundary with the "flats" above the Bow River to the Ghost Reservoir to the north and east. A large gravel, drumlin-type hill separates the lake from the Bow River. There is no appreciable surface drainage from the hill. Chiniki Creek drains Chiniki Lake, flowing to the northeast and entering the Ghost Reservoir. In the Chiniki area, the elevation varies from about 1440m (4500 ft) at Chiniki Lake to 1760m (5500 ft) in the hills to the south of Chiniki Lake (Figure 1.3).

A total of 58 samples were taken from this focus area during the sampling period. Eighteen sites were sampled repeatedly, with water samples taken at least twice over the sampling year.

2.1.2. Limited amount of previous work in the area.

As mentioned earlier, very little work has been done in this area. This is due in part to the limited exploitation potential of any sort of resource as the residents of the reserve limit outside exploitation of their land. Many parts of the reserve are difficult to access as they are undeveloped and located away from the roads and tracks in the area. Other difficulties included the reluctance of some residents to allow people to sample at their houses, the refusal of people to aid in guiding samplers around parts of the reserve and the reluctance of the assistants from the reserve to travel to parts of the reserve that they did not live on. As there are three bands on reserve land, sampling had to be balanced between households of all three bands.

2.2 Geology

Both surficial and bedrock geology of the reserve are important factors controlling the chemistry of the surface waters and groundwaters. The dominant mineralogy of the different units present controls the potential water-rock interactions that might occur in the area. The mineral assemblages of the various units may provide chemical tracers to use in following water flow patterns. The surfical material is primarily recent fluvial deposits and glacio-fluvial gravels of Quaternary aged material. The rocks to the west of the reserve are Devonian, Mississipian and Jurassic in age. The bedrock underlying the reserve is highly disturbed Cretaceous and Tertiary aged units.

2.2.1. Surficial Geology

The primary surface material is glacio-alluvial deposits and reworked fluvial material consisting mainly of gravels and sands. These can be quite thick, up to 160 m (500 ft) in parts of the reserve near the river (Fisher and Spooner, 1994). The present-day Bow River has cut into these gravels, with the river as much as 160 m (500 ft) below the level of the ground surface in places. These gravels are composed of materials derived from the Rocky Mountains and consist of silisiclastic and carbonate material (Moran, 1986).

2.2.2. Bedrock Geology

If the bedrock geology is considered from west to east, the region encompasses an area from the mountains out into the foothills and plains regions. The Rocky Mountains to the west of the reserve are composed primarily of marine carbonates, both limestone and dolostone, mainly of Devonian and Mississippian age. Immediately west of the reserve is the McConnell Thrust fault which brings Cambrian aged rocks over the Cretaceous units. The rocks of the reserve are affected by the extensive folding and west dipping thrust faults in the disturbed belt immediately east of the Rocky Mountains and they are Jurassic and Cretaceous in age. The rocks are flat lying in the most easterly part of the reserve and Tertiary in age.

The Cambrian units lying west of the reserve are marine limestone, dolomite and shale while the Mississippian rocks are marine limestone and dolostone with some sandstone and shales. Marine limestone and dolomite dominate the Devonian aged bedrock near the reserve. The Jurassic units are non-marine with minor marine sandstone, shale, siltstone and minor amounts of coal.

The Upper Cretaceous rocks on the reserve are a mixture of Brazeau group non-marine sandstone, mudstone, siltstone, and conglomerates, and the Alberta Group, (Wapiabi, Cardium and Blackstone Formations), consisting of marine shale, siltstone and minor conglomerate. Lower Cretaceous units (Blairmore Group; Beaver Mines and Mill Creek Formation) are non-marine sandstone, mudstone, siltstone and conglomerate as are the Cadomin Formation and Lower Blairmore rocks. The most easterly lying rocks on the reserve are Tertiary in age, of the Paskapoo Formation, a non-marine sandstone, mudstone, siltstone and conglomerate.

2.2.3. Effects of geology and mineralogy

It is possible that waters draining these marine limestones and dolomites would have higher concentrations of Ca^{2+} and Mg^{2+} in the waters due to water-rock interaction in the subsurface of the Rocky Mountains than waters draining other bedrock.

Groundwaters tend to have higher concentrations of solutes in the water due to the longer groundwater residence time (Ferguson et al., 1994). This could be a useful tracer of waters originating in the mountains and recharging the groundwater regime. Possible cation exchange reactions may take place or dissolution of dolomite and calcite could account for the presence of these ions in the waters.

2.3. Hydrology of reserve

2.3.1. Surface Water

As the main river draining this part of the Rocky Mountains, the Bow River is the dominant surface water feature in this area and all the land of the reserve is contained in the Bow River drainage basin (Figure 1.2; Bow River Water Quality Council, 1994). The Bow River flows east through the reserve, following an approximately southwest to northeast course through the centre of the reserve. After passing the Kananaskis and Horseshoe power dams near Seebe, the river winds along until it enters Ghost Lake, just east of Morley. Ghost Lake is the reservoir for another power generating dam on the river, the Ghost Dam. The Ghost River forms the northeastern boundary of the reserve, turning south and entering the Bow River just upstream of the Ghost Dam.

The Kananaskis River forms the western boundary of the reserve, south of the Bow River, while the Ghost River delineates the northwestern boundary of the reserve. The Kananaskis River is dammed, south of the reserve, creating Barrier Lake. The two large lakes in the reserve are Chiniki Lake and the Ghost Lake (a man made reservoir). These lakes are also used for recreational purposes too, possibly affecting the water quality. Many of the residents on the reserve live in areas centered around the Bow River, Chiniki Lake and Ghost Lake. Chiniki Lake represents the southern drainage area that is being used as the focused study area, with Chiniki Creek running north-east to Ghost Lake (Figure 2.1).

Data records for flow rates on the Bow River, both historically and recently are provided by Environment Canada, Surface Water Survey. Historical data shows thirty-year trends in the streamflow and precipitation patterns. Unofficial Bow River flow data for 1995 - 1996 illustrate mid-May is the time of increased river flow. This coincides with the seasonal increase in temperature for this area, and is likely a combination of water from snowmelt and the spring rainfall. Precipitation events appear to occur before increased streamflow (see Figures 1.4 and 1.5). The purpose of examining precipitation and streamflow records is to determine if there are any water quality problems associated with the changing flow rates of the Bow River, differences associated with either the periods of increased runoff or times of low or base flow.

2.3.2. Groundwaters

The producing zone lithology of the wells was determined primarily based on the geology recorded by the drillers of the wells. In cases where these records were vague or lithology was not recorded for the sampled well, adjacent wells were examined, and the lithology was determined based on these other wells' lithologies that were completed at the same depth. The sampled wells were assigned aquifer lithologies only when records provided a reasonable confidence level for aquifer identification and these lithologies are shown on the reserve map (Figure 2.2). The sampled sites that have no aquifer lithology associated with them did not have information available from those wells or nearby ones and spring sites do not have lithology information available.

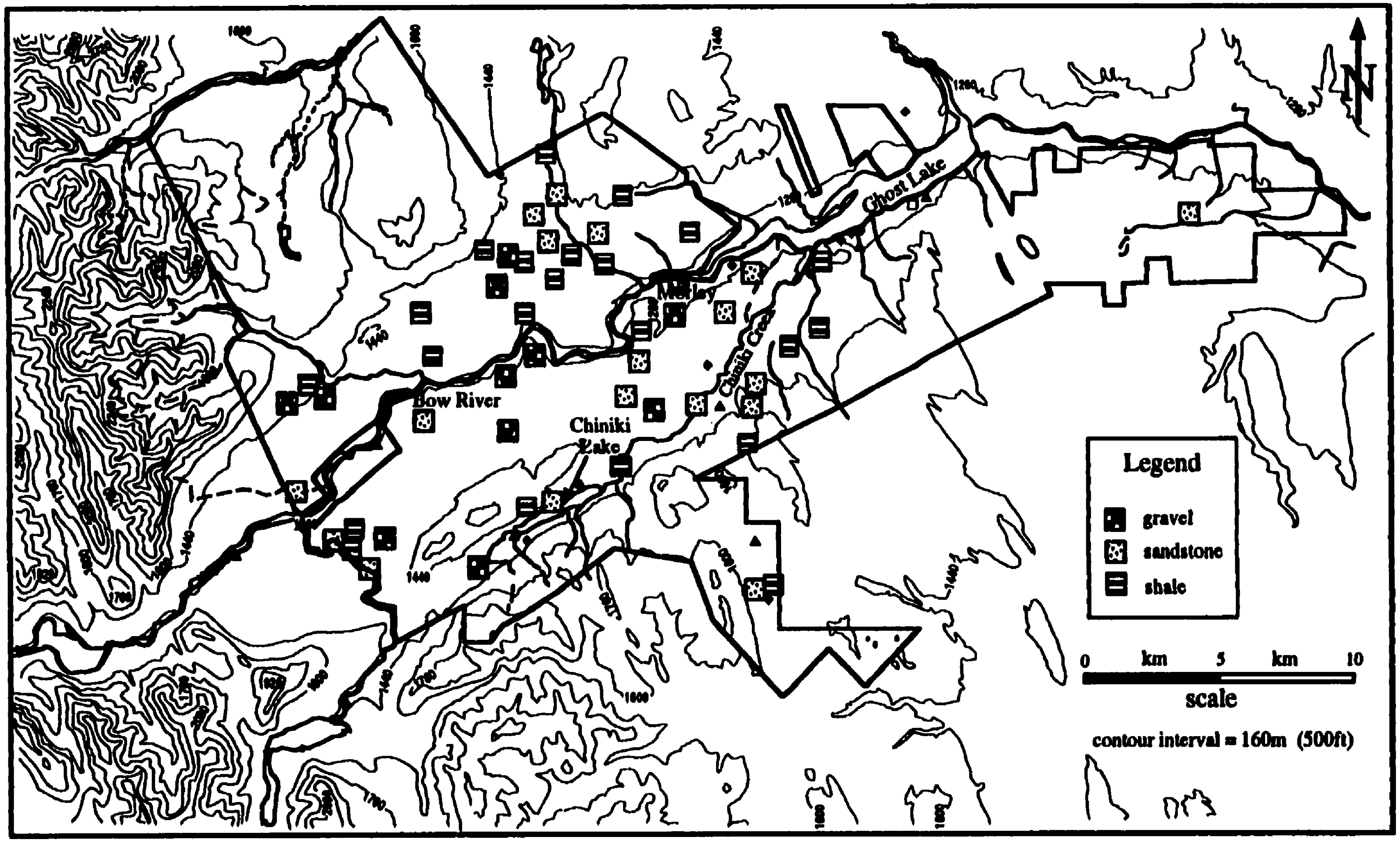


Figure 2.2. Map of the Stoney reserve showing aquifer lithology and topography.

Subsurface information was determined from records submitted by water-well drillers to the Province of Alberta Environmental Protection. The Groundwater Information Centre provided access to these records. The drillers' records were used to determine depth to the aquifer unit and the nature of the aquifer unit. Based on these records, three main aquifers were determined for the reserve. They are: 1.) gravels, usually shallow lying Quaternary aged deposits; 2.) sandstones, likely Upper Cretaceous; of the Brazeau Formation or Alberta Group and usually located in between the other two aquifers and 3.) fractured shales, sometimes with sandstone lenses interbedded, usually the deepest producing unit in the region as most of the wells completed in shales are deeper than the other wells in the study area. These shales are likely the Upper Cretaceous marine Wapiabi Formation.

2.3.3. Springs and Wells

Most of the sites sampled for the study are domestic wells of residents living on the Stoney Indian Reservation (Figure 2.1). The depths of these wells vary from under 16 m (50 ft) for wells completed in gravels near the Bow River, to depths greater than 130 m (400 ft) for the wells in these sandstone and shale aquifers. A few sites were found to be spring-fed. These were sampled with the hope of linking known geology to the regional flow and discharge patterns. These springs were viewed as alternative sources of drinking water for some residents of the reserve, saving them the expense of drilling a new well, remediating a problem well, or installing a water storage cistern.

One spring flowed year round and appeared little affected by the changes in air temperature and precipitation. This spring was located immediately north of Highway 1A, just west of the Morley turnoff. Other locations of springs were to the south of

Chiniki Lake, on the area known as the Morley Flats (near the confluence of the Kananaskis and Bow Rivers), on the south side of the Ghost Reservoir, and two in the western part of the reserve, north of the Bow River. Of these, only the spring north of the highway and the spring on the "flats" were sampled more than once.

Another spring sample, Chin5, was taken from a pool of water in a swampy area south of the Ghost Reservoir and was only active in June, 1995. The water sample taken had high levels of visible organic matter and smelled like rotting vegetation and sulfur. However, no detectable sulfide was found, as no precipitate was formed when Cd-acetate was added (see Chapter Three for method). Repeated visits to this site during the following year of sampling on the reserve failed to find evidence of an active spring.

As the early summer of 1995 was wet, with much flooding in the southern half of Alberta, it is hypothesised that this spring was an unusual occurrence associated with the extremely high water conditions in the region. The area in question does appear to be a discharge region, as it was muddy and swampy underfoot when the site was revisited in the fall of 1995 and the spring of 1996. However, no repeat water sample could be obtained as insufficient water for sampling was found.

Chapter 3

Methods and Data

3.1. Introduction

Sampling was completed over an eleven-month period from July, 1995, through June, 1996. The primary sampling sites were domestic wells belonging to residents of the Stoney Indian Reservation. Other sites selected for sampling included surface waters on and near the reservation, and springs located in the area (Figure 2.1). Twelve samples were collected from the two remote Stoney reserves located at Bighorn and Eden Valley (six samples were taken at each reserve).

Each water sample was analysed for anion and cation concentrations, dissolved SiO_2, alkalinity and the stable isotopes of sulfur ($^{34}S/^{32}S$), carbon ($^{13}C/^{12}C$) deuterium (D/H) and oxygen ($^{18}O/^{16}O$). All samples were processed as quickly as possible to prevent any chemical concentration or isotopic changes due to oxidation or atmospheric exchange processes, using the procedures outlined below.

3.2. Chemical and Isotope Sample Collection

A four litre water sample was taken at each site and immediate measurements of temperature and pH were made in the field. The pH was measured using an Orion® combination electrode standardised with pH 4, pH 7 and pH 10 buffer solutions and a portable pH meter, while the temperature was measured using the Orion® meter and a thermometer. The water was filtered through a 0.45 μm Millipore cellulose filter using a Nalgene® 15 psi hand pump with a 500ml reservoir. Two 125ml Nalgene® bottles were filled to overflowing with filtered water; one was immediately sealed and the second was acidified to pH 2 using concentrated HCl and sealed. A sample of water was taken for silica measurements, with 10ml of sampled water being diluted by 10 ml of distilled water and placed in a 60ml sample bottle.

Two 10ml vacutainers were filled with water for isotope work using a needle completely submerged in the water sample. A separate needle was used for each sample, both for the pure water sample and the $SrCl_2$- treated water. The deuterium and oxygen isotope compositions were measured directly from the waters while the carbon and oxygen isotope compositions from the carbonate were measured from $SrCO_3$ precipitated out from a $SrCl_2$-ammonium hydroxide mixture (Lico et al., 1982). The oxygen isotope composition of the carbonates are measured in order to correct the carbon isotope composition data. The $SrCl_2$ mixture was prepared just before going to the field in a nitrogen environment to prevent exchange with atmospheric CO_2 before sampling.

To analyse for sulfur isotopes, SO_4^{2-} and S^- were collected. Sulfate (SO_4) was collected in the form of $BaSO_4$ precipitated from a one-litre filtered water sample after adding barium chloride ($BaCl_2$) crystals to excess (Lico et al., 1982). This mixture was then acidified by adding concentrated HCl to attain a pH of approximately 2, preventing $BaCO_3$ from forming and contaminating the precipitate. The $BaSO_4$ precipitate was filtered through a 0.45 μm filter and washed thoroughly with distilled deionized water.

When H_2S was detected in the field, usually by its odour (a rotten egg smell), a 60 ml water sample was collected and filtered through a 0.45 μm syringe filter and then placed in an amber glass bottle. Cadmium acetate crystals were added in excess to the water to precipitate CdS (Lico et al., 1982). This CdS precipitate was filtered under a nitrogen atmosphere and while filtering $AgNO_{3\ (aq)}$ was added to convert the CdS to Ag_2S for ease of isotope analysis (Simpson, 1996).

3.2.1. Difficulties with field sampling

Some factors which might have affected the quality of the water samples taken include samples with high levels of dissolved or micro solids that clogged the filters. When this happened the sample processing time was very long, often in excess of 20 minutes, providing more opportunity for the exchange of the atmosphere with the water samples, possibly affecting the isotope composition. The effects of clogged filters were minimized by frequently changing the filter paper and filtering smaller amounts of water.

The cold weather that prevailed for most of January through March, 1996 caused water and water vapour to freeze in the vacuum line of the hand pump. Once the air temperature dropped below 4°C, the Nalgene filter and hand pump tended to clog due to the build up of ice on the equipment. To alleviate this situation the sample was processed in the cab of a vehicle, however, this proved awkward and lead to the heating of the water while processing occurred. Another method attempted was wrapping the vacuum line in pipe insulation but the flexibility needed in the line was lost and the insulation was not sufficient to prevent freezing of the plastic. The final solution was to cease sampling until the air temperature was warmer.

3.3. Bacterial Sampling

The water samples for bacterial analysis were procured by members of the Stoney Nation under the guidance of Health Canada. The samples were first analysed for presence or absence of bacteria. If bacteria were present, a second sample was taken and a more comprehensive analysis completed. From these data, 95 samples were made available by Health Canada.

3.4. Analytical methods and techniques

3.4.1. Chemical analyses

The acidified 125 ml water sample was used for cation analyses using atomic absorption and the analyses were performed in the Department of Geology and Geophysics. The unacidified 125 ml sample was used for anion analysis and alkalinity measurements in the laboratory. These analyses were done as soon as the samples were brought into the laboratory in order to prevent deterioration of the waters. The anions were run on a HPLC after filtering out the polar organic compounds using a Waters® Sep Pak® cartridge. Care was taken to ensure that the analyses were conducted as quickly as possible and that the samples were preserved properly. All samples were stored at a temperature of 4°C.

The alkalinity was determined by titration of the waters with sulfuric acid, with strengths of approximately 0.01M and 0.001M. This inflection point gives the alkalinity of the water and is reported as HCO_3^- alkalinity in units of mg/L (Lico et al., 1982), although all weak acids were titrated.

3.4.2. Isotope Techniques

The isotope analyses were carried out in the Stable Isotope Laboratory in the Department of Physics and Astronomy at the University of Calgary. Water samples were used directly to determine both δD and $\delta^{18}O$. Precipitates of carbonate from the water samples were used to determine carbon isotope values and sulfate and sulfide precipitates from the waters were analysed for sulfur isotope abundances.

3.4.2.a. Sulfur (^{34}S) Isotopes

For $\delta^{34}S$ analyses of sulfate, the $BaSO_4$ precipitate from the one-litre water sample was filtered, washed and dried in the laboratory (Lico et al., 1982). When present, the sulfide used for $\delta^{34}S$ analysis was precipitated as $CdS_{(s)}$. This precipitate was filtered and converted to Ag_2S using a 0.1M $AgNO_3$ solution. The Ag_2S precipitate is more easily and more completely combusted than the CdS and more accurate analytical results are possible. Only three samples collected produced any sulfide precipitate and were available for analysis.

The $\delta^{34}S$ values were obtained using a combination of the procedures of Yanagisawa and Sakai (1983) and Udea and Krouse (1986) where the sulfur-compound was mixed with vanadium pentaoxide and silica and heated beneath copper filings in a glass tube. The resulting SO_2 gas was analysed for the $^{34}S/^{32}S$ ratios.

3.4.2.b. Hydrogen and Oxygen Isotopes

The δD values were determined using H_2 generated by reduction of water with zinc (Coleman et al., 1982). The $\delta^{18}O$ values were measured using a variation of the CO_2 - H_2O equilibration method of Epstein and Mayeda (1953).

3.4.2.c. Carbon Isotopes

Carbon isotope analyses were performed on carbonate precipitated out of the water sample using a strontium chloride-ammonia hydroxide mixture. The precipitated $SrCO_3$ was washed with boiling distilled-water in a nitrogen environment to avoid any atmospheric oxygen exchange (Lico et al., 1982). The cleaned carbonate was reacted in phosphoric acid, the resulting CO_2 gas cryogenically collected in sealed glass tubing and then analysed for the C isotope composition, following the method of McCrea (1950).

3.5. Results

3.5.1. Chemical Data.

Results of the chemical analyses for the Morley Reserve samples are presented in Table 3.1, with all samples numbered in order of sampling. All concentrations are in mg/L except for Li^+, Mn^{2+} and Fe^{2+} which are in μg/L. The errors for the measurements are ± 2% for the cation concentrations and ± 0.5 to 1 mg/L for the anion measurements based on differences between two runs of the same sample (Shevalier, 1996). Results for BigHorn (BH38 - BH43) and Eden Valley (EV53 - EV58) are presented separately in Table 3.2.

Table 3.1. Chemical analysis and location of water samples from the Morley reserve. pH and temperature were measured in the field. b.d.l. = below detection limit. Samples 38 - 43 from BigHorn, samples 53 - 58 from Eden Valley (Table 3.2.).

Sample Name	Sample Location	Type sample	pH	Temp (°C)	Alk mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Sr mg/L	Li µg/L	Mn µg/L	Fe µg/L	Si mg/L	SiO_2 mg/L	Cl mg/L	Br mg/L	NO3 mg/L	PO4 mg/L	SO4 mg/L
Chin 1	SW-32-24-6	surface	7.29	3.0	275	5.6	17.5	0.82	64.2	0.65	7	14	49	3.44	7.33	85.6	0.0	1.3	0.0	15.2
Chin 2	15-03-24-7	surface	7.94	7.0	218	4.2	17.7	1.35	60.4	0.27	4	6	70	3.55	7.59	108.6	0.0	0.0	0.0	15.3
Chin 3	SW-13-25-7	surface	7.96	8.0	253	9.8	19.5	1.58	68.3	0.39	6	43	75	3.65	7.81	10.1	0.2	0.0	0.0	6.2
Chin 4	SW-12-26-6	surface	8.18	8.0	251	8.8	26.1	2.08	67.1	0.29	12	b.d.l.	66	4.15	8.88	4.6	0.0	0.9	1.7	42.6
Chin 5	SE-11-26-6	spring	8.08	6.0	478	24.0	51.5	3.83	123.0	0.54	36	33	63	8.60	18.40	2.6	0.7	1.0	1.5	84.3
Kan 6	14-10-24-8	surface	8.00	6.0	133	1.4	11.6	0.38	45.0	0.14	2	3	13	1.25	2.67	41.0	0.1	6.7	2.0	43.3
Kan 7	03-15-24-8	surface	6.50	7.0	134	1.4	11.4	0.38	44.4	0.14	3	4	10	1.60	3.42	46.2	0.2	10.0	2.8	42.3
Kan 8	02-31-24-8	surface	6.50	6.5	99	1.3	11.2	0.38	34.7	0.16	2	6	18	1.90	4.06	22.4	0.4	6.0	1.4	41.4
Kan 9	NE-10-25-8	surface	6.50	7.0	130	1.4	11.3	0.39	36.5	0.16	3	6	20	1.15	2.46	25.5	0.3	7.0	1.5	40.3
Chin 10	NE-30-24-7	well	7.79	10.5	433	87.0	20.5	0.93	36.4	1.10	57	19	83	4.65	9.95	17.3	0.0	1.2	0.0	1.9
Chin 11	SE-05-25-7	well	7.28	7.5	312	16.1	40.8	2.04	99.3	1.14	30	82	154	4.70	10.05	0.0	0.0	0.0	0.0	63.9
Chin 12	SW-28-25-6	well	7.86	12.0	341	30.1	27.1	1.00	73.5	1.09	36	40	1237	3.36	7.19	95.3	0.0	0.0	0.0	77.6
Chin 13	NW-20-25-6	well	7.73	12.0	567	143.0	31.4	1.12	54.8	1.65	144	31	902	1.44	3.07	0.0	0.0	0.0	0.0	88.8
Chin 14	NE-32-24-7	well	7.59	12.5	256	5.2	15.4	0.78	62.0	0.45	3	5	21	3.04	6.50	0.0	0.0	1.3	0.0	16.2
Chin 15	SW-31-25-6	well	7.70	11.7	312	9.5	21.3	1.64	68.2	0.44	4	6	23	4.54	9.71	0.0	0.0	1.9	0.0	16.3
Chin 16	SW-34-24-8	well	7.26	12.0	389	82.3	29.4	2.85	97.6	0.21	5	6	17	3.90	8.34	40.7	0.2	24.5	0.0	38.6
Chin 17	NW-07-25-7	well	8.23	10.5	704	267.0	2.0	0.99	2.3	0.18	423	7	53	2.94	6.29	78.8	0.0	0.0	0.0	1.4
Chin 18	SW-14-25-8	well	7.21	13.0	445	52.1	40.7	1.76	67.5	1.27	79	20	50	4.50	9.63	18.8	3.6	0.0	0.0	42.1
Chin 19	SE-19-25-7	well	7.80	12.0	282	72.5	15.9	0.99	15.8	0.70	96	9	144	3.52	7.53	48.9	0.0	0.0	0.0	0.8
Chin 20	SE-20-25-7	well	8.09	12.5	232	73.8	6.06	0.66	6.6	0.19	38	12	206	3.14	6.72	32.6	0.0	0.0	0.0	1.9
Chin 21	SE-31-25-6	well	7.29	12.0	351	41.3	20.5	1.36	58.9	0.47	43	14	46	3.58	7.66	0.0	0.0	1.0	0.0	17.2
Chin 22	SW-30-25-6	well	7.59	10.0	391	13.3	34.1	1.18	60.6	0.53	17	22	1071	5.64	12.07	104.6	0.0	1.0	0.0	1.2
Chin 23	SE-23-25-8	well	7.49	10.0	135	13.1	29.4	1.46	60.1	0.59	8	16	390	5.42	11.59	128.2	0.0	0.0	0.0	15.2
Chin 24	SE-27-25-7	well	7.52	10.0	240	12.5	20.9	0.93	47.6	0.31	7	0	19	4.62	9.88	76.2	0.0	8.3	0.0	25.6
Nak 25	SW-35-25-7	spring	7.77	6.5	343	27.1	30.3	2.83	77.5	1.24	8	4	16	4.40	9.41	5.5	0.0	2.2	0.0	40.0
Nak 26	SW-24-25-8	pump	8.42	6.0	606	200.0	9.2	0.93	12.8	0.51	193	13	219	2.66	5.69	4.1	0.0	0.0	0.0	0.8
Nak 27	NE-16-25-8	well	8.35	10.0	184	3.2	11.3	0.61	44.3	0.22	2	4	21	1.98	4.24	33.5	0.3	7.7	1.5	19.5
Nak 28	SE-26-25-8	well	7.90	11.0	368	13.8	20.9	1.46	82.6	0.59	5	26	102	6.50	13.91	37.6	0.0	0.9	0.3	1.9
Nak 29	SW-29-25-7	well	8.56	10.0	1113	440.0	0.8	0.83	2.3	0.23	519	6	91	2.64	5.65	101.6	0.0	0.0	0.0	5.5
Nak 30	SE-02-26-5	well	7.36	4.0	295	38.0	36.5	3.14	67.2	1.69	14	b.d.l.	30	4.76	10.18	191.7	0.5	5.6	0.0	25.2
Nak 31	SE-04-26-6	well	7.48	8.0	594	68.7	27.6	1.95	76.0	1.82	32	613	4967	8.20	17.54	0.0	0.3	0.0	0.0	1.1
Nak 32	SE-04-26-6	well	8.58	7.0	575	239.0	0.4	0.52	2.5	0.14	47	28	110	4.84	10.35	67.6	0.0	0.0	0.0	9.1
Nak 33	SW-03-26-6	well	7.46	7.0	432	84.0	27.9	1.65	61.0	1.46	48	58	2763	4.58	9.80	10.3	0.0	0.0	0.0	95.8
Nak 34	SE-36-25-7	well	8.22	8.0	340	24.2	33.0	2.67	81.2	0.41	12	4	22	3.96	8.47	33.8	0.0	5.7	24.9	62.3
Nak 35	SW-36-25-7	well	7.81	8.0	339	12.1	30.2	2.04	76.7	0.30	9	3	24	4.34	9.28	40.7	0.0	8.5	0.0	27.8
Nak 36	SE-33-25-7	well	7.62	10.0	400	119.0	10.2	0.89	27.2	0.63	12	b.d.l.	21	3.00	6.42	46.7	0.0	1.7	0.0	30.5
Nak 37	SE-05-26-7	well	7.50	11.0	363	5.1	30.6	1.78	97.1	0.39	9	47	38	3.24	6.93	0.0	1.0	46.8	0.0	44.0

Sample Name	Sample Location	Type sample	pH	Temp (°C)	Alk mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Sr mg/L	Li µg/L	Mn µg/L	Fe µg/L	Si mg/L	SiO_2 mg/L	Cl mg/L	Br mg/L	NO3 mg/L	PO4 mg/L	SO4 mg/L
Nak 44	SW-04-25-8	well	6.98	7.0	382	8.0	28.6	1.94	15.3	0.51	7	6	38	3.84	8.21	0.0	0.0	5.3	0.0	36.1
Nak 45	SE-17-25-8	well	7.51	7.0	432	136.0	10.4	0.76	10.6	0.31	186	5	34	2.80	5.99	50.5	0.0	0.0	0.0	7.6
Nak 46	NW-04-26-7	well	7.73	8.0	421	176.0	1.9	0.50	8.5	0.30	16	173	99	2.72	5.82	53.8	0.0	0.0	0.0	30.7
Nak 47	NE-32-25-7	well	7.72	6.0	406	86.0	19.4	1.19	44.1	0.98	14	4	26	3.46	7.40	65.6	0.0	4.6	0.0	26.6
Nak 48	NW-31-25-7	spring	6.65	4.0	373	6.1	19.4	1.37	87.7	0.41	5	5	24	5.40	11.55	10.6	0.0	0.0	0.0	11.7
Nak 49	NE-30-25-7	well	7.09	10.0	442	20.1	31.5	1.96	83.5	0.54	20	66	5990	4.54	9.71	177.2	0.0	0.0	0.0	18.0
Nak 50	SW-16-26-7	well	7.91	7.0	348	67.4	13.3	0.93	45.4	1.86	5	4	30	2.90	6.20	0.9	0.0	0.0	0.0	23.4
Nak 51	NE-03-26-7	well	8.25	7.0	511	205.0	0.1	0.30	1.9	0.18	18	7	74	3.38	7.23	59.0	0.0	1.2	1.7	12.3
Nak 52	SE-01-26-7	well	7.05	7.0	508	19.6	47.0	1.82	135.0	0.53	30	7	28	5.88	12.58	8.8	0.0	0.9	0.2	131.8
Chin 59	NE-30-24-7	well	7.69	7.0	459	86.7	21.0	0.92	37.5	1.10	55	32	471	4.60	9.84	8.6	0.0	0.0	0.0	0.1
Chin 60	SE-05-25-7	well	7.18	7.5	469	14.6	39.8	1.94	98.5	1.10	31	84	261	4.50	9.63	163.8	0.4	0.0	0.0	56.0
Chin 61	SW-28-25-6	well	7.23	10.0	355	30.8	27.2	0.97	72.3	1.02	40	27	184	3.72	7.96	192.8	0.0	0.9	0.0	67.0
Chin 62	NW-20-25-6	well	7.48	7.0	583	151.0	31.1	1.06	54.0	1.64	142	26	837	3.56	7.62	17.7	5.7	0.0	0.0	69.5
Chin 63	SE-23-25-7	well	7.48	10.0	335	12.4	29.2	1.44	62.0	0.54	11	20	866	5.48	11.70	11.8	0.3	0.0	0.0	13.7
Chin 64	NW-07-25-7	well	8.86	8.0	717	281.0	1.7	0.81	2.1	0.15	445	b.d.l.	39	3.26	6.97	76.1	0.0	0.0	1.6	8.1
Chin 65	SW-14-25-8	well	7.51	11.0	458	56.8	40.4	1.67	60.6	1.30	85	12	432	4.90	10.50	26.4	0.0	0.0	0.1	32.4
Chin 66	SE-19-25-7	well	7.54	8.5	271	70.9	15.5	0.92	15.4	0.64	92	b.d.l.	185	3.62	7.74	21.5	1.8	2.2	2.6	1.0
Chin 67	SE-27-25-7	well	7.43	11.0	217	11.5	22.1	0.90	49.8	0.31	7	b.d.l.	15	3.44	7.36	156.2	0.0	8.3	2.0	26.8
Kan 68	14-10-24-8	surface	6.96	2.0	141	1.1	10.5	0.32	43.7	0.15	3	b.d.l.	7	1.24	2.65	5.0	0.0	0.0	0.0	26.8
Kan 69	03-15-24-8	surface	7.14	3.0	138	1.2	10.6	0.31	45.1	0.15	3	b.d.l.	13	1.22	2.61	28.2	0.1	0.0	0.0	28.0
Nak 70	SW-35-25-7	spring	7.15	6.0	376	28.8	31.2	2.75	79.8	1.23	9	b.d.l.	17	4.72	10.10	25.6	0.0	3.6	0.0	41.7
Chin 71	SW-30-25-6	well	7.20	6.0	419	13.2	33.2	1.11	62.3	0.44	19	27	1700	5.42	11.60	177.7	0.0	0.0	0.0	1.1
Chin 72	SE-31-25-6	well	7.70	4.5	528	152.0	14.0	1.06	36.3	0.39	171	4	11	3.62	7.74	55.3	1.8	0.0	0.0	9.2
Chin 73	SW-31-25-6	well	7.18	5.0	340	10.4	23.6	1.68	75.8	0.44	8	7	8	4.62	9.88	13.3	0.0	2.5	0.0	17.6
Chin 74	SE-04-26-6	well	8.31	6.0	564	240.0	0.4	0.50	2.3	0.15	50	30	109	5.18	11.10	79.5	0.3	1.1	0.2	5.9
Chin 75	NW-34-25-6	surface	7.47	1.5	406	33.1	34.7	1.99	116.0	0.46	18	9	20	4.94	10.60	107.0	0.0	1.7	2.2	43.5
Nak 76	SW-36-25-6	tap	7.24	9.0	345	12.0	30.0	1.96	80.0	0.30	8	b.d.l.	6	4.50	9.63	36.6	0.0	7.7	0.0	22.9
Chin 77	SW-13-25-7	surface	7.33	2.5	339	9.6	23.4	1.51	75.7	0.37	6	63	35	4.58	9.80	16.9	0.0	1.3	0.2	11.4
Chin 78	SW-05-25-7	well	7.18	7.0	474	91.2	23.1	1.25	52.0	1.34	74	79	10550	3.46	7.40	8.8	0.0	0.0	0.0	28.2
Chin 79	SW-34-24-8	spring	7.51	7.0	345	52.0	30.2	2.69	99.7	0.17	5	b.d.l.	12	4.02	8.60	113.3	0.0	34.5	0.0	35.7
Nak 80	SW-24-25-8	pump	8.79	5.0	384	273.0	5.0	0.76	7.9	0.27	285	7	26	2.56	5.48	73.1	0.0	0.0	0.0	0.0
Nak 81	NE-14-26-6	well	7.11	7.0	215	7.1	29.4	1.13	85.8	0.34	13	6	13	3.48	7.44	0.0	0.2	7.4	0.0	0.0
Chin 82	NW-07-25-6	well	6.84	5.0	424	20.6	27.6	1.92	88.7	1.68	8	6	21	4.28	9.16	3.8	0.0	6.5	0.0	14.8
Chin 83	NW-18-25-6	well	7.98	9.0	64	145.0	6.2	0.90	19.5	0.52	16	24	270	3.46	7.40	1.2	0.3	0.0	0.0	17.4
Chin 84	NW-18-25-6	well	7.72	8.0	345	120.0	12.6	1.24	32.0	0.58	23	83	41	4.32	9.24	2.1	0.0	0.0	0.2	88.5
Chin 85	SE-24-25-7	well	7.36	8.0	400	35.7	33.2	1.28	82.8	1.34	13	26	8	4.48	9.58	108.0	0.2	1.3	0.2	17.5
Nak 86	NE-16-25-8	spring?	7.31	7.0	382	56.7	28.4	1.08	36.7	0.52	70	15	1500	4.14	8.86	26.3	0.0	0.0	0.3	0.0
Nak 87	NW-33-25-7	well	7.06	7.0	317	67.6	37.0	1.65	70.1	1.41	50	339	1900	5.68	12.10	25.1	0.0	0.0	0.0	94.2
Nak 88	NE-33-25-7	well	7.40	5.5	346	8.0	22.6	1.75	77.9	0.34	5	b.d.l.	37	6.08	13.00	3.5	0.0	1.9	0.0	5.7
Nak 89	SW-34-25-7	well	7.09	7.5	461	15.8	38.7	1.84	104.0	1.10	10	b.d.l.	34	5.10	10.90	202.6	0.2	21.0	0.0	39.5

Sample Name	Sample Location	Type sample	pH	Temp (°C)	HCO_3 mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Sr mg/L	Li µg/L	Mn µg/L	Fe µg/L	Si mg/L	SiO_2 mg/L	Cl mg/L	Br mg/L	NO_3 mg/L	PO_4 mg/L	SO_4 mg/L
Nak 90	SW-35-25-7	spring	7.16	6.0	411	28.3	31.2	2.69	77.9	1.21	7	5	18	4.36	9.33	17.7	0.0	4.5	0.0	38.8
Chin 91	SW-14-25-7	well	7.75	5.5	332	199.0	10.1	1.51	41.5	1.69	55	68	149	3.84	8.21	2.5	0.0	1.3	0.0	0.0
Chin 92	SE-10-25-7	well	7.64	6.0	461	94.6	16.6	1.01	46.4	0.38	92	61	395	3.66	7.83	3.2	0.0	1.5	0.3	11.5
Kan 93		surface	7.79	3.5	141	0.5	15.3	0.32	52.5	0.18	b.d.l.	4	22	1.36	2.91	0.1	0.2	1.5	8.7	65.3
Chin 94	SW-33-25-6	well	8.14	5.5	624	231.0	14.6	1.03	12.3	0.46	232	7	72	5.18	11.08	65.9	1.1	0.0	0.0	10.4
Nak 95	SE-31-25-7	well	7.42	9	417	13.0	26.5	1.20	83.1	0.37	11	27	466	4.30	9.20	0.0	0.2	1.3	0.0	9.6
Nak 96	SW-32-25-7	well	7.36	10	526	41.0	59.7	2.03	115.0	2.15	41	67	943	3.94	8.43	185.0	0.0	0.0	0.0	103.0
Chin 97	SE-34-24-8	well	7.7	9	259	17.4	25.5	1.02	32.6	0.85	17	10	15	3.58	7.66	2.3	0.0	0.0	0.0	3.8
Chin 98	SW-34-24-8	well	9.02	10	474	199.0	0.6	0.32	1.3	0.10	209	b.d.l.	10	3.08	6.59	3.9	0.0	0.0	0.0	13.2
Chin 99	SW-34-24-8	well	8.52	7	253	82.1	6.6	0.48	5.0	0.50	103	3	24	2.94	6.29	1.8	1.3	1.4	0.4	1.1
Chin 100	NW-34-24-8	well	9.41	6.5	405	167.0	0.4	0.22	0.7	0.15	251	b.d.l.	12	3.70	7.92	14.9	0.3	1.3	0.3	0.9
Chin 101	SW-13-25-7	surface	7.59	2	254	7.7	17.5	2.16	57.3	0.30	4	87	87	3.72	7.96	9.5	0.4	1.9	0.2	8.6
Chin 102	NE-30-24-7	well	7.51	8	407	72.5	24.0	1.01	41.8	1.12	47	29	13	4.58	9.80	18.6	0.0	1.4	0.0	5.1
Chin 103	SW-05-25-7	well	7.32	8	480	93.8	22.1	1.28	52.9	1.24	73	47	417	2.58	7.66	84.6	0.0	0.0	0.0	29.7
Chin 104	SW-14-25-7	well	7.62	9	405	87.7	17.2	2.46	52.1	2.02	27	122	26	4.64	9.93	8.4	0.0	0.0	0.0	62.8
Chin 105	NW-14-25-7	well	8.74	8	405	177.0	1.6	0.67	4.2	0.10	56	b.d.l.	26	3.18	6.80	12.8	0.7	1.3	0.4	37.6
Chin 106	NW-25-25-7	well	7.99	9	331	105.0	5.7	0.94	7.9	0.39	34	10	16	3.58	7.66	1.53	0.3	1.3	0.5	0.1
Chin 107	NW-29-24-6	well	7.01	7	460	17.4	27.5	2.50	111.2	0.95	12	34	28	5.38	11.51	242.0	0.3	31.9	0.0	12.5
Chin 108	NW-29-24-6	well	7.32	10	482	66.0	21.8	2.38	84.2	1.91	18	4	28	4.26	9.11	143.5	0.2	34.5	0.0	19.3
Chin 109	NW-29-24-6	well	7.09	9	608	112.0	16.2	1.77	109.0	0.43	11	3780	6891	6.70	14.33	147.5	0.2	1.2	0.0	46.9
Chin 110	SW-32-24-6	surface	7.18	1.8	278	9.8	16.1	4.63	62.4	0.42	3	102	160	5.08	10.87	5.5	0.3	1.2	0.4	9.0
Nak 111	SE-36-25-7	well	6.49	8	332	19.1	32.9	0.80	7.3	0.28	9	b.d.l.	27	4.00	8.56	26.2	0.2	4.1	0.0	56.3
Nak 112	SW-36-25-7	well	6.89	6	330	13.0	28.8	1.87	73.8	0.29	3	b.d.l.	10	4.00	8.56	23.2	0.0	7.8	0.0	24.7
Kan 113	03-15-24-8	surface	6.84	9	141	1.5	11.3	0.41	44.9	0.14	3	b.d.l.	11	1.88	4.02	3.7	0.0	0.6	0.0	26.1
BR 114	02-31-24-8	surface	7.13	7	68	1.3	10.1	0.40	30.7	0.12	2	3	15	1.70	3.64	2.0	0.0	0.5	0.0	22.1
Nak 115	SW-35-25-7	spring	7.09	7	367	25.9	27.6	2.48	69.4	1.02	7	b.d.l.	11	4.34	9.28	3.9	0.5	4.6	0.0	28.7
Nak 116	SW-24-25-8	pump	8.44	6	674	252.0	5.02	0.80	7.3	0.28	247	8	40	2.94	6.29	72.3	0.0	0.0	0.0	0.0

Table 3.2. Chemical data for Bighorn (BH) and Eden Valley (EV) reserves. pH and temperature were measured in the field. All values are in mg/L except for Li, Mn and Fe, which are in μg/L. b.d.l. = below detection limit.

Sample	location	type	pH	HCO_3	Mg	K	Ca	Sr	Li	Mn	Fe	Si	SiO_2	Cl	NO_3	PO_3	SO_4
BH 38	7-19-39-16	well	6.88	298	24.2	1.22	68.7	0.40	17	15	98	2.80	5.99	137.3	1.2	0.0	44.5
BH 39	9-32-39-16	well	7.29	324	38.9	1.35	91.0	1.80	11	3	28	4.32	9.24	0.5	0.7	0.0	124.8
BH 40	6-33-39-16	well	6.99	341	29.0	1.82	95.4	0.53	17	7	32	4.86	10.4	234.0	0.8	0.1	75.5
BH 41	9-33-39-16	well	7.11	343	29.0	1.54	67.4	0.35	12	77	3387	4.42	9.46	174.4	0.0	0.0	24.5
BH 42	6-19-39-16	surface	7.62	183	18.0	0.78	53.8	0.31	5	3	25	2.18	4.66	21.3	0.0	0.0	65.6
BH 43	3-20-39-16	well	7.27	223	20.6	0.91	61.0	0.32	8	3	28	2.16	4.62	144.1	2.7	0.0	64.7
EV 53	SE-25-17-4	well	6.93	373	20.9	1.64	92.6	0.39	8	b.d.l.	21	4.00	8.56	184.4	4.9	1.5	35.1
EV 54	NE-13-17-4	well	6.98	308	12.1	1.10	38.3	0.79	8	117	73	3.74	8.00	50.9	0.0	0.0	10.3
EV 55	SW-13-17-4	well	7.11	308	17.1	1.58	71.8	0.73	5	b.d.l.	33	3.54	7.57	95.3	4.5	0.0	20.3
EV 56	07-14-17-4	well	7.61	435	4.4	1.16	8.34	0.54	27	110	30	3.42	7.32	50.4	0.0	3.6	2.6
EV 57	11-11-17-4	well	7.27	386	24.7	1.46	83.5	1.23	13	6	15	3.62	7.74	7.7	8.9	0.0	38.6
EV 58	14-24-17-4	surface	7.76	196	14.1	0.57	58.2	0.37	4	b.d.l.	20	2.14	4.58	6.7	0.1	0.1	46.9

3.5.2. Isotope Results

Isotopic analyses are reported using the delta (δ) notation. This is defined as:

$$\delta = (R_{sample}/ R_{standard} - 1) \times 1000 \qquad (1)$$

where R is the abundance ratio of the heavy isotope to the light isotope of the measured parameter (i.e. $^{2}H/^{1}H$ or D/H) and the value is expressed as per mil, and written ‰ (Craig, 1957).

The comparison of the abundance ratio in the sample to that in the standard permits the analysis of the small abundance differences between the stable isotopes analysed. The standards used to determine these values are given below, along with the associated laboratory errors for the procedures as described above.

Table 3.3. Error for isotopic analyses. V-SMOW is Vienna-Standard Mean Ocean Water, V-PDB is the Vienna PeeDee Belemnite standard and V-CDT is the Vienna Cañon Diablo Troilite (FeS) meteorite standard.

element	standard	error
δD(water)	V-SMOW	± 1.0 ‰
$\delta^{18}O$ (water)	V-SMOW	± 0.5 ‰
$\delta^{34}S$ (sulfate)	V-CDT	± 1.0 ‰
$\delta^{13}C$ (carbonate)	V-PDB	± 0.5 ‰

The isotopic results for Morley and area, excluding sulfide $\delta^{34}S$, are given in Table 3.4. The three sulfide $\delta^{34}S$ values are given in Table 3.5. (Morley Reserve and area). Samples with very small gas yields are indicated with an asterisk. Small yields

indicate poor sample resolution and these values cannot be considered accurate. Any sample with an asterisk is not considered in the discussions.

Table 3.5. δ ^{34}S values for sulfide samples.

Sample	$\delta^{34}S$ (sulfide)
Chin 13	10.6
Nak 45	19.9
Chin 98	-7.0

Table 3.6. below gives δ - values for the water samples from the Bighorn and Eden Valley Reserves. No Bighorn or Eden Valley sample yielded sufficient sulfide for sulfur isotope analysis.

Table 3.6. δ - values for waters from Bighorn and Eden Valley.

Sample	$\delta^{34}S$ (SO_4)	$\delta^{13}C$ (CO_3)	δD (H_2O)	$\delta^{18}O$ (H_2O)
BH 38	6.5	-8.3	-146.5	-16.8
BH 39	16.5	-10.4	-148.7	-17.4
BH 40	-17.0	-9.9	-141.6	-17.2
BH 41	10.1	-10.6	-149.2	-19.4
BH 42	5.4	-5.9	-149.8	-18.9
BH 43	12.1	-4.5	-148.7	-19.7
EV 53	-2.1	-12.7	-135.8	-17.9
EV 54	n.d.	-12.3	-145.1	-19.2
EV 55	n.d.	-12.0	-136.6	-18.4
EV 56	n.d.	-6.1	-138.5	-18.2
EV 57	-4.0	-12.1	-138.2	-16.8
EV 58	13.8	-7.7	-140.1	-18.8

3.5.3. Bacteria Results

Waters were sampled for bacteria from all households on the reserve. Only samples taken from wells sampled for chemical parameters were of interest for this study as cistern samples do not provide information about the subsurface geology. The results of the bacteria tests are presented in Table 3.7. The households are identified using the same sample number as was used for the chemical and isotope samples.

These results are the 15 wells out of 95 samples that have chemical samples. There were 18 positive results in the remaining 80 wells, however, they were not studied in any detail as part of this thesis. No indication is given as to whether the samples came from wells or cisterns.

Table 3.7. Bacterial results for selected wells on the Morley Reserve. Wells were also sampled for chemistry.

Sample number	Fecal coliform	Sample number	Fecal coliform
Chin 22	nil	Chin 97	nil
Nak 36	nil	Chin 98	nil
Nak 37	nil	Chin 99	nil
Nak 44	nil	Chin 100	nil
Nak 47	nil	Chin 104	nil
Nak 89	nil	Chin 107	nil
Chin 91	nil	Chin 108	nil
Nak 95	nil		

3.5.4. Repeat Sampling

Repeat samples were taken over a number of seasons at a variety of locations around the reserve during the sampling year. The purpose of these samples was to determine if seasonal variation of the chemical concentrations can be detected in the waters of the reserve. Domestic wells, springs and surface waters were sampled more than once. The variety of water types will permit differences that exist, if any, between the three main waters on the reserve to be determined. Several sites were sampled only twice, as winter road and ice conditions prevented access to the sampling sites. Care was taken to maintain similar sampling conditions each time and to resample at the same location for the surface water samples. The sites resampled along with the concentrations are given in Table 3.8 and the isotope values in Table 3.9.

Table 3.8. Repeat sampling sites and analyses. All parameters are the same as previous data tables. b.d. indicates sample below detection limit.

Site	Sample	Season	pH	Temp	HCO_3	Na	Mg	K	Ca	Sr	Li	Mn	Fe	Si	SiO_2	Cl	Br	NO_3	PO_4	SO_4
1	Kan 6	summer	8.00	6.0	133	1.4	11.6	0.38	45.0	0.14	2	3	13	1.25	2.67	41.0	0.1	6.7	2.0	43.9
	Kan 68	fall	6.96	2.0	141	1.1	10.5	0.32	43.7	0.15	3	b.d.	7	1.24	2.65	5.0	0.0	0.0	0.0	25.5
2	Kan 7	summer	6.50	7.0	134	1.4	11.4	0.38	44.4	0.14	3	4	10	1.60	3.42	46.2	0.2	10.0	2.8	42.3
	Kan 69	fall	7.14	3.0	138	1.2	10.6	0.31	45.1	0.15	3	b.d.	13	1.22	2.61	28.2	0.1	0.0	0.0	28.0
	Kan 113	spring	6.84	9.0	141	1.5	11.3	0.41	44.9	0.14	3	b.d.	11	1.88	4.02	3.7	0.0	0.6	0.0	26.1
3	Kan 8	summer	6.50	6.5	99	1.3	11.2	0.37	34.7	0.16	2	6	18	1.90	4.06	22.4	0.4	6.0	1.4	41.4
	BR 114	spring	7.13	7.0	68	1.3	10.1	0.40	30.7	0.12	2	3	15	1.70	3.64	2.0	0.0	0.5	0.0	22.1
4	Chin 3	summer	7.96	8.0	253	9.8	19.5	1.58	68.3	0.39	6	43	75	3.65	7.81	10.1	0.2	0.0	0.0	6.2
	Chin 77	fall	7.33	2.5	339	9.6	23.4	1.51	75.7	0.37	6	63	35	4.58	9.80	16.9	0.0	1.3	0.2	11.4
	Chin 101	winter	7.59	2.0	254	7.7	17.5	2.16	57.3	0.30	4	87	87	3.72	7.96	9.5	0.4	1.9	0.2	8.5
5	Nak 34	fall	8.22	8.0	340	24.2	33	2.67	81.2	0.41	12	4	22	3.96	8.47	33.8	0.0	5.7	0.0	62.3
	Nak 111	spring	6.49	8.0	332	19.1	32.9	0.80	7.34	0.28	9	b.d.	27	4.,00	8.56	26.2	0.2	4.1	0.0	56.3
6	Nak 35	fall	7.81	8.0	339	12.1	30.2	2.04	76.7	0.30	9	3	24	4.34	9.28	40.7	0.0	8.5	0.0	27.8
	Nak 112	spring	6.89	6.0	330	13.0	28.8	1.87	73.8	0.29	3	b.d.	10	4.00	8.56	23.2	0.0	7.8	0.0	24.7
7	Chin 10	summer	7.79	10.5	433	87.0	20.5	0.93	36.4	1.10	57	19	83	4.65	9.95	17.3	0.0	1.2	0.0	1.9
	Chin 59	fall	7.69	7.0	459	86.7	21	0.92	37.5	1.10	55	32	471	4.60	9.84	8.6	0.0	0.0	0.0	0.1
	Chin 102	winter	7.51	8.0	407	72.5	24	1.01	41.8	1.12	47	29	13	4.58	9.80	18.5	0.0	1.4	0.0	5.1
8	Nak 25	summer	7.77	6.5	343	27.1	30.3	2.84	77.5	1.24	8	4	16	4.40	9.41	5.5	0.0	2.2	0.0	40.0
	Nak 70	fall	7.15	6.0	376	28.8	31.2	2.75	79.8	1.23	9	b.d.	17	4.72	10.10	25.6	0.0	3.6	0.0	41.7
	Nak 90	winter	7.16	6.0	411	28.3	31.2	2.69	77.9	1.21	7	5	18	4.36	9.33	17.7	0.0	4.5	0.0	38.8
	Nak 115	spring	7.09	7.0	367	25.9	27.6	2.48	69.4	1.02	7	b.d.	11	4.34	9.28	3.9	0.5	4.6	0.0	28.7
9	Nak 26	summer	8.42	6.0	606	200.0	9.17	0.93	12.8	0.51	193	13	219	2.66	5.69	4.1	0.0	0.0	0.0	0.8
	Nak 80	fall	8.79	5.0	384	273.0	5.02	0.76	7.89	0.27	285	7	26	2.56	5.48	73.1	0.0	0.0	0.0	0.0
	Nak 116	spring	8.44	6.0	674	252.0	5.02	0.80	7.34	0.28	247	8	40	2.94	6.29	72.3	0.0	0.0	0.0	0.0
10	Chin 11	summer	7.28	7.5	312	16.1	40.8	2.04	99.3	1.14	30	82	154	4.70	10.05	0.0	0.0	0.0	0.0	63.9
	Chin 60	fall	7.18	7.5	469	14.6	39.8	1.94	98.5	1.10	31	84	261	4.50	9.63	163.8	0.4	0.0	0.0	56.0
11	Chin 12	summer	7.86	12.0	341	30.0	27.1	1.00	73.5	1.09	36	40	1237	3.36	7.19	95.3	0.0	0.0	0.0	77.6
	Chin 61	fall	7.23	10.0	355	31.0	27.2	0.97	72.3	1.02	40	27	184	3.72	7.96	192.8	0.0	0.9	0.0	67.0

Site	Sample	Season	pH	temp	HCO_3	Na	Mg	K	Ca	Sr	Li	Mn	Fe	Si	SiO_2	Cl	Br	NO3	PO4	SO4
12	Chin 13	summer	7.73	12.0	567	143.0	31.4	1.12	54.8	1.65	144	31	902	1.44	3.07	0.0	0.0	0.0	0.0	88.8
	Chin 62	fall	7.48	7.0	583	151.0	31.1	1.06	54.0	1.64	142	26	837	3.56	7.62	17.7	5.7	0.0	0.0	69.5
13	Chin 23	summer	7.49	10.0	135	13.1	29.4	1.46	60.1	0.59	8	16	390	5.42	11.59	128.2	0.0	0.0	0.0	15.2
	Chin 63	fall	7.48	10.0	335	12.4	29.2	1.44	62.0	0.54	11	20	866	5.48	11.70	11.8	0.3	0.0	0.0	13.7
14	Chin 17	summer	8.23	10.5	704	267.0	2.0	0.99	2.3	0.18	423	7	53	2.94	6.29	78.8	0.0	0.0	0.0	1.4
	Chin 64	fall	8.86	8.0	717	281.0	1.7	0.81	2.1	0.15	445	b.d.	39	3.26	6.97	76.1	0.0	0.0	1.6	8.1
15	Chin 78	fall	7.18	7.0	474	91.2	23.1	1.25	52.0	1.34	74	79	10550	3.46	7.40	8.8	0.0	0.0	0.0	28.2
	Chin 103	spring	7.32	8.0	480	93.8	22.1	1.28	52.9	1.24	73	47	417	2.58	7.66	84.6	0.0	0.0	0.0	29.7
16	Chin 18	summer	7.21	13.0	445	52.1	40.7	1.76	67.5	1.27	79	20	50	4.50	9.63	18.8	0.0	3.6	0.0	1.4
	Chin 65	fall	7.51	11.0	458	56.8	40.4	1.67	60.6	1.30	85	12	432	4.90	10.5	26.4	0.0	0.0	0.1	32.4
17	Chin 19	summer	7.80	12.0	282	72.5	15.9	0.99	15.8	0.70	96	9	144	3.52	7.53	48.9	0.0	0.0	0.0	0.8
	Chin 66	fall	7.54	8.5	271	70.9	15.5	0.92	15.4	0.64	92	b.d.	185	3.62	7.74	21.5	1.8	2.2	2.6	1.0
18	Chin 24	summer	7.52	10.0	240	12.5	20.9	0.93	47.6	0.38	7	b.d.	19	4.62	9.88	76.1	0.0	8.2	0.0	25.6
	Chin 67	fall	7.43	11.0	217	11.5	22.1	0.9	49.8	0.31	7	b.d.	15	3.44	7.36	156.2	0.0	8.3	2.0	26.8
19	Chin 22	summer	7.59	10.0	391	13.3	34.1	1.18	60.6	0.50	17	22	1071	5.64	12.07	104.6	0.0	1.0	0.0	1.2
	Chin 71	fall	7.20	6.0	418	13.2	33.2	1.11	62.3	0.44	19	27	1700	5.42	11.60	177.7	0.0	0.0	0.0	1.1
20	Chin 21	summer	7.29	12.0	351	41.3	20.5	1.36	58.9	0.47	43	14	46	3.58	7.66	0.0	0.0	1.0	0.0	17.2
	Chin 72	fall	7.70	4.5	528	152	14.0	1.06	36.3	0.39	171	4	11	3.62	7.74	55.3	1.8	0.0	0.0	9.2
21	Chin 15	summer	7.70	11.7	312	9.47	21.3	1.64	68.2	0.44	4	6	23	4.54	9.71	0.0	0.0	1.9	0.0	16.3
	Chin 73	fall	7.18	5.0	340	10.4	23.6	1.68	75.8	0.44	8	7	8	4.62	9.88	13.3	0.0	2.5	0.0	17.6
22	Nak 32	summer	8.58	7.0	575	239	0.4	0.52	2.49	0.14	47	28	110	4.84	10.35	67.6	0.0	0.0	0.0	9.1
	Chin 74	fall	8.31	6.0	564	240	0.4	0.50	2.32	0.15	50	30	109	5.18	11.10	79.5	0.3	1.1	0.2	5.9

Table 3.9. Isotope values for repeat samples. Standards as before. n.d. indicates no data available for the sample.

Site	Sample	Season	$\delta^{34}S$ (SO_4)	$\delta^{13}C$ (CO_3)	δD (H_2O)	$\delta^{18}O$ (H_2O))
1	Kan 6	summer	19.7	n.d.	-150.9	-17.5
	Kan 68	fall	10.4	-8.9	-144.7	-19.0
2	Kan 7	summer	19.9	-7.3	-151.5	-17.7
	Kan 69	fall	11.1	-7.9	-145.6	-19.3
	Kan 113	spring	5.0	-11.9	-145.0	-20.7
3	Kan 8	summer	18.8	-11.4	-152.6	-17.1
	BR 114	spring	14.0	-8.5	-151.0	-19.5
4	Chin 3	summer	16.9	-5.9	-132.7	-14.7
	Chin 77	fall	10.8	-10.6	-126.3	-15.4
	Chin 101	winter	5.9	-5.7	-133.3	-16.7
5	Nak 34	fall	-4.8	-5.1	-137.1	-15.0
	Nak 111	spring	-8.0	-13.9	-133.1	-17.2
6	Nak 35	fall	11.5	-4.7	-133.1	-14.9
	Nak 112	spring	5.27	-13.6	-128.6	-17.2
7	Chin 10	summer	30.1	-2.1	-151.7	-19.6
	Chin 59	fall	n.d.	-9.2	-147.7	-20.7
	Chin 102	winter	18.4	-6.8	-151.7	-19.6
8	Nak 25	summer	6.9	-2.8	-133.5	-15.4
	Nak 70	fall	-1.2	-11.9	-138.6	-17.2
	Nak 90	winter	14.2	-11.8	-137.8	-17.4
	Nak 115	spring	1.3	-12.5	-135.7	-18.5
9	Nak 26	summer	67.6	-4.5	-155.3	-17.5
	Nak 80	fall	15.5	5.6	-150.8	-19.3
	Nak 116	spring	n.d.	3.28	-147.2	-19.6
10	Chin 11	summer	11.9	-0.9	-148.5	-18.8
	Chin 60	fall	-7.1	-12.3	-138.3	-18.2
11	Chin 12	summer	-15.8	n.d.	-140.5	-18.2
	Chin 61	fall	-15.1	-12.6	-136.8	-17.8
12	Chin 13	summer	-10.0	-0.4	-139.4	-18.4
	Chin 62	fall	-12.6	-12.1	-137.4	-18.0
13	Chin 23	summer	12.6	0.0	-137.3	-15.5
	Chin 63	fall	-3.9	-11.8	-141.1	-17.3
14	Chin 17	summer	9.4	1.9	-147.2	-19.5
	Chin 64	fall	22.5	-6.2	-152.9	-19.6
15	Chin 78	fall	-9.6	-12.9	-135.2	-17.1
	Chin 103	spring	-9.5	-12.2	-144.8	-18.0
16	Chin 18	summer	7.5	-1.9	-141.5	-17.7
	Chin 65	fall	0.1	-12.6	-143.2	-17.6
17	Chin 19	summer	18.3	-2.7	-140	-17.7
	Chin 66	fall	20.7	-5.2	-142.4	-17.6
18	Chin 24	summer	15.2	-3.0	-124.5	-13.7
	Chin 67	fall	7.3	-6.7	-131.2	-16.0
19	Chin 22	summer	20.7	-0.8	-138.4	-16.2
	Chin 71	fall	n.d.	-10.9	-142.4	-17.8
20	Chin 21	summer	27.7	-10.4	-132	-14.2
	Chin 72	fall	5.8	-1.9	-136.6	-17.4
21	Chin 15	summer	15.6	-5.8	-124.5	-15.6
	Chin 73	fall	5.3	-11.0	-128.8	-15.5
22	Nak 32	summer	29.2	-3.4	-150.6	-17.6
	Chin 74	fall	24.9	-12.6	-147.8	-19.0

Chapter 4

Government of Canada Health Guidelines
and Stoney Reserve Water Quality

4.1. Introduction

Water quality standards published by the Government of Canada are used as a comparison to determine if the concentrations of various ions in the Morley water samples exceed the levels recommended for chemical and bacterial drinking water quality. These standards are used to determine if the waters are safe to drink. There are two main categories of water quality determinations of concern for this study: firstly, chemical parameters that examine the dissolved components of the water and secondly, water bacteria levels. The specific guidelines are given below.

4.2. Chemical Parameters

4.2.1. Morley Reserve

The Government of Canada has standards for chemical and bacterial levels in drinking waters (Health and Welfare Canada, 1993). For the chemical parameters there are three categories: 1. compounds that are considered hazardous to human health and have levels set that are considered the maximum acceptable concentrations (MAC), 2. hazardous compounds where the standards are under review and exist as interim maximum acceptable concentrations (IMAC) and 3. aesthetic objectives (AO), parameters that make the water look, taste or smell bad (i.e.. odour, colour, turbidity) but are not considered on their own to affect the quality of the drinking water. These aesthetic parameters may make the waters unpleasant to consume or may cause problems in treating the waters to sufficiently safe levels for consumers.

Of the chemical parameters determined for the waters from the Stoney Indian Reserve only chloride, iron, manganese, nitrate, pH, sodium, sulfate and temperature have government standards. Of these, only nitrate has a MAC level (45 mg/L). The other parameters are considered aesthetic properties only. The acceptable levels for the measured parameters are given in Table 4.1. below.

Table 4.1. Parameters and their accepted level in drinking waters. Based on Government of Canada Guidelines (1993)

parameter	level	rating
chloride	≤ 250 mg/L	AO
iron	≤ 0.3 mg/L	AO
manganese	≤ 0.05 mg/L	AO
nitrate	45.0 mg/L	MAC
pH	6.5 - 8.5	AO
sodium	≤ 200 mg/L	AO
sulfate	≤ 500 mg/L	AO
temperature	≤ 15° C	AO

The samples taken on the reserve met the official guidelines (Health and Welfare Canada, 1993) with a few exceptions. The exceptions were for iron, manganese, nitrate, pH and sodium (Figure 4.1). All sampled waters meet drinking water health guidelines. One sample exceeded the recommended level of nitrate with a measured concentration of 46.83 mg/L, however, the error on the analysis (± 1.5 mg/L) would put this value close to the acceptable health range.

4.2.2. Eden Valley and Bighorn Reserves

As there are only twelve samples from the Eden Valley and Bighorn reserves, a detailed discussion of the data is not possible. For the same parameters as outlined above, only two are exceeded. One sample from the Bighorn reserve has an Fe^{2+} level considerably above the accepted standard of 300 µg/L, with a value of 3387 µg/L (Figure 4.2.a). Three samples, two from Eden Valley and one from Bighorn, exceed the 50 mg/L government accepted standard for manganese, with values of 117, 110 and 77 µg/L (Figure 4.2.b).

4.3. Bacterial Parameters

The government has set levels for bacteria in drinking waters (Health and Welfare Canada, 1993). These guidelines are given as:

1. No sample should contain more than 10 total coliform organisms per 100 ml, none of which should be fecal coliforms:

2. No consecutive sample from the same site should show the presence of total coliform organisms; and

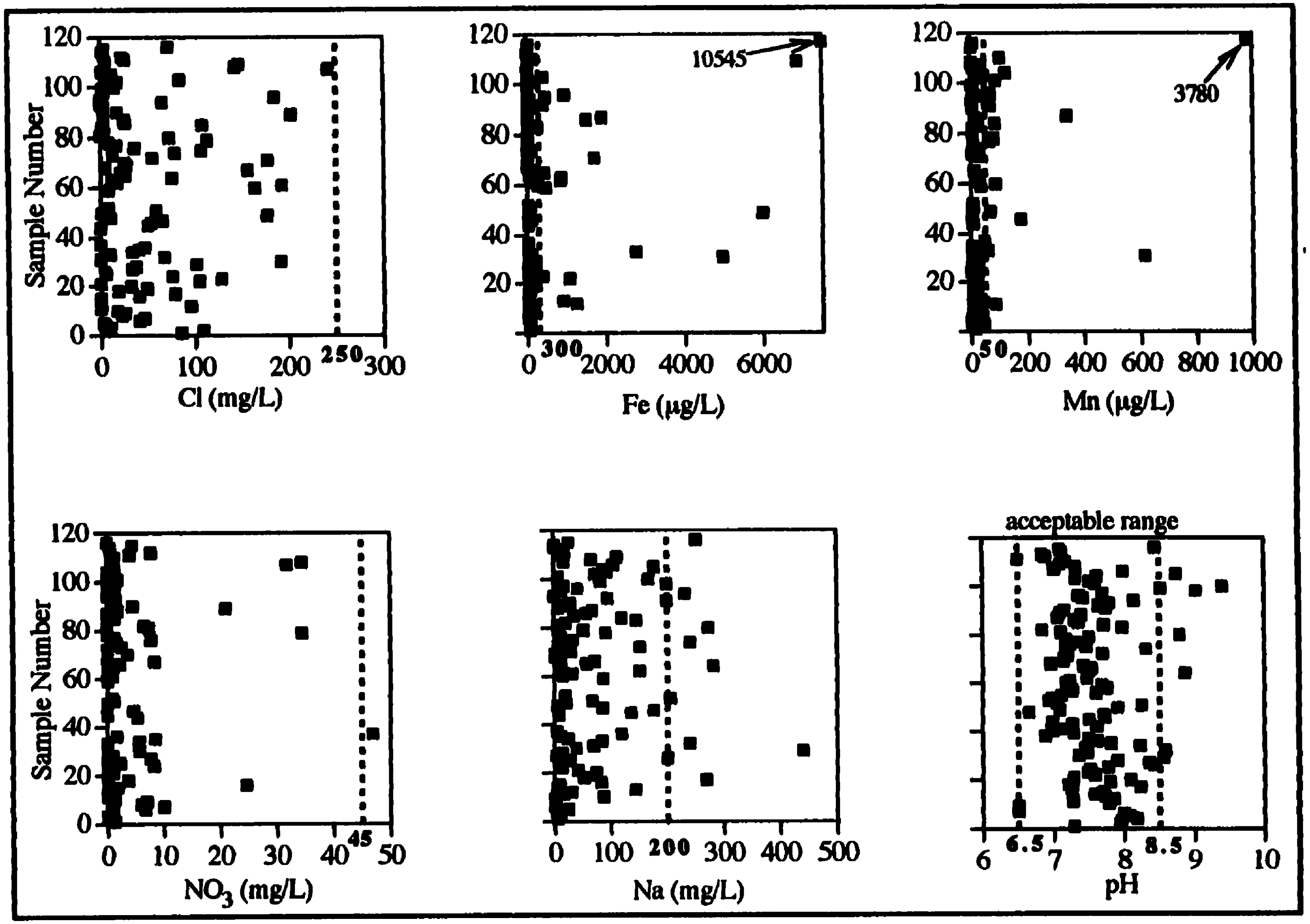
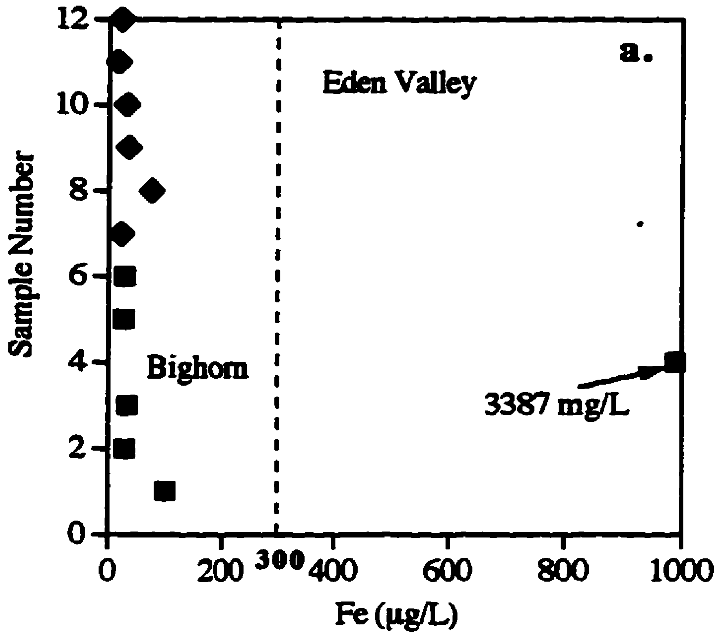


Figure 4.1. Graphs showing the parameters that exceed government levels on the reserve. Dotted line(s) indicates the level as set by Health Canada Safe Drinking Water Guidelines (1993).



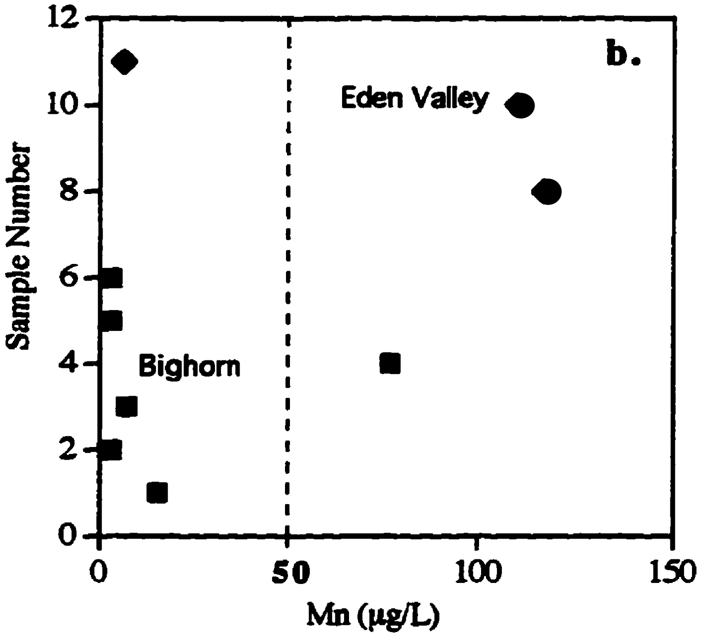


Figure 4.2. Graphs of Fe (a.) and Mn (b.) concentrations in the waters from Eden Valley (diamonds) and Bighorn (squares) showing samples that exceed the government reccomended levels, which is represented by the dashed line.

3. For community drinking water supplies:

a) not more than one sample from a set of samples taken from the community on a given day should show the presence of total coliform organisms; and

b) not more than 10% of the samples based on a minimum of 10 samples should show the presence of coliform organisms.

The Stoney Nation and Health Canada sampled the drinking waters on the reserve for bacteriological data. The samples were first analysed on a positive - negative test basis. If the initial test produced a positive result and the bacteria levels exceeding the set guidelines, a second water sample was collected and a full bacteriological test was run. Of the 15 sampled sites in the study, no sample showed fecal coliform or total coliform present, thus none of the samples exceeded the allowable level. As only 95 records were made available by Health Canada, a comparison of bacterial levels to other chemical parameters could not be undertaken. The eighteen positive tests (of the 95 samples examined) indicate that there is a bacterial problem in the reserve drinking waters. Health Canada is discussing steps to mitigate the problem with the Stoney Nation.

Chapter 5

Interpretation of Data

5.1. Introduction

There are several aspects to the data interpretation. Chemical trends are presented along with frequency plots to illustrate the range of chemical and isotopic values in the waters. The chemical and isotopic compositions are used to determine if there are significant chemical differences between the surface waters and groundwaters present in the three aquifer units on the reserve. The samples have been plotted as surface waters and groundwaters for ease of examining the data. If there are sufficient differences, the groundwaters have been further subdivided into the three aquifer types for the reserve.

Graphical representation of the data using Stiff plots has permitted the identification of end-member water compositions for the groundwater samples and illustrates a typical surface water composition. Triangular Piper diagrams show grouping of the chemistry of the surface waters and the compositional spread in groundwater data. This presentation of the data aids in clarifying the dominant water types and dominant ions in the waters on the reserve and the relationship(s) of the surface waters to the groundwater end members may be determined.

Isotope data trends may indicate the processes that affect the hydrologic cycle on the reserve. Seasonal temperature and precipitation changes, evaporation of water, water-rock interactions, sources of the solutes in waters, bacterial processes and possible altitude or latitude effects may be defined using the changes in the δD and $\delta^{18}O$ values for the reserve waters.

5.2. Discussion of Chemical and Isotopic Data

5.2.1. General chemistry

Surface waters were collected from the major rivers of the area, the Bow River and the Kananaskis River, and from smaller creeks and bodies of standing-water on the reserve. These have been examined to determine if there are apparent differences in the geochemistry of quickly moving, large-scale bodies of water as compared to the smaller scale water bodies. The larger rivers show no significant differences in their chemical constituents from the other surface waters, except during the late spring / early summer 1995 snowmelt period. The TDS concentrations were very low for the samples from the Bow and Kananaskis Rivers as compared to the other surface waters.

The groundwater samples came from domestic drinking water wells and springs located over the reserve (see Figure 2.1). All wells were shallow, with no sampled well deeper than 130 m. The sampled springs are being used as sources of drinking water, either as a permanent domestic supply or as an occasional supplemental source of water.

5.2.2. Frequency distribution of chemical data

The purpose of this discussion is to show the overall range of the data and to illustrate differences between surface and groundwaters, if differences exist. When the data illustrate a high degree of variation they will be examined and possible reasons for ion and isotope variability will be presented.

5.2.2.a. Alkalinity and TDS

Samples examined as part of this study all have, with a few exceptions, low total dissolved solids (TDS), the highest TDS concentration being 1671 mg/L for sample Nak29. There is relatively little variation in alkalinity as 65% of the samples have HCO_3^- alkalinity between 400 and 600 mg/L (Figure 5.1). The groundwaters have alkalinity values ranging from 135 to 1113 mg/L and TDS values from 262 to 1671 mg/L. Surface waters have HCO_3^- concentrations from 68 to 407 mg/L and TDS values from 139 to 757 mg/L, much lower than the groundwater samples.

The samples from the groundwaters with the highest TDS and alkalinity values are associated with the shale and sandstone mixed with shale units. The TDS of the samples have a similar trend due to the fact that the bicarbonate ion (HCO_3^-) is the dominant ion in all the groundwaters on the reserve.

Some of the surface water samples also appear to be affected by the high flow episodes during the flooding. These samples came from the Bow River and Kananaskis River at a time of high flow and have different chemical and isotopic characteristics. These differences, where appropriate, will be highlighted in the following discussion.

5.2.2.b. Cations

Groundwater Ca^{2+}, Na^+ and Mg^{2+} concentrations have been measured and have concentrations from 0.7 to 135 mg/L, 3.3 to 441 mg/L and 0.6 to 60 mg/L, respectively.

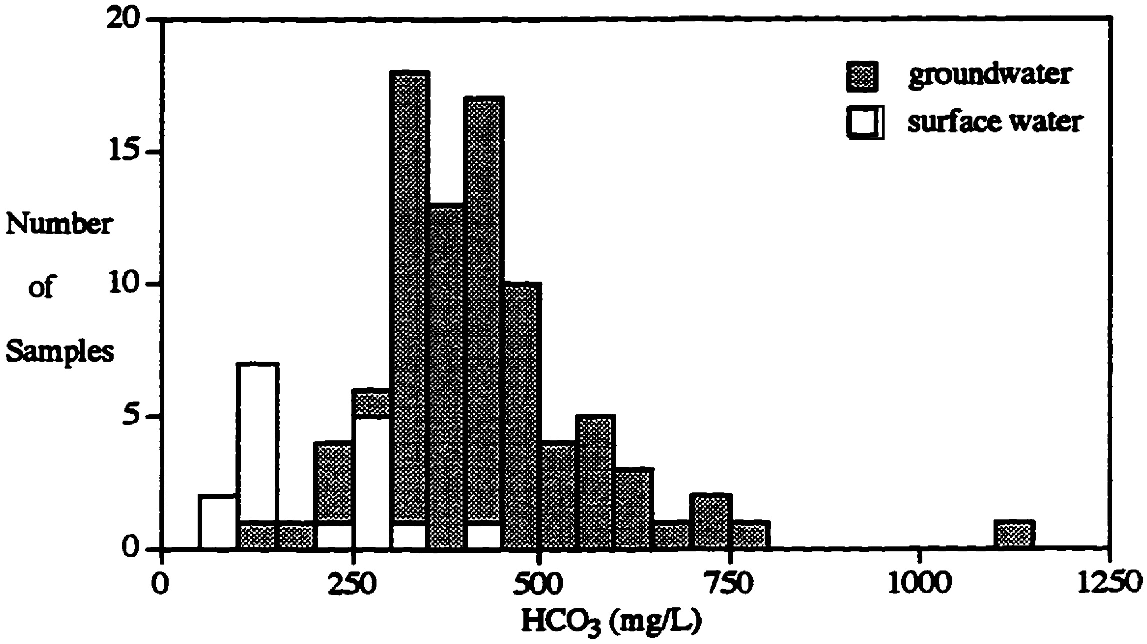


Figure 5.1. Frequency plot of bicarbonate alkalinity illustrating the different distribution for surface and groundwaters of the Morley reserve.

Surface water Ca^{2+} ranges from 31 to 116 mg/L, Na^{+} concentrations from 0.5 to 73 mg/L and levels for Mg^{2+} from 10 to 35 mg/L. K^{+} and Sr^{2+} concentrations in the waters are much lower, with concentrations of K^{+} from 0.2 to 3.1 mg/L and Sr^{2+} values of 0.1 to 2.2 mg/L in the groundwaters and 0.3 to 4.6 mg/L for K^{+} and 0.1 to 1.1 mg/L for Sr^{2+} in surface water samples.

Three cations are present at µg/L levels, namely, Li^{+}, Mn^{2+} and Fe^{2+}. All three ions have large ranges in concentrations, which range from 2 to 519 µg/L for Li^{+} in groundwaters and 0 to 47 µg/L in surface waters. The Mn^{2+} levels measured in groundwaters have a range of 3 to 3780 µg/L and 0 to 102 µg/L for surface waters. Groundwater Fe^{2+} concentrations range from 8 to 10545 µg/L and surface waters have Fe^{2+} levels of 6 to 160 µg/L. These differences between the lowest and the highest concentrations are orders of magnitude different, especially for Fe^{2+}, however, the majority of the samples have less than 200 µg/L Fe^{2+}. In the case of Li^{+} and Mn^{2+} the majority of the samples fall below 50 µg/L; 70% of the samples for Li^{+} and 82% of the samples for Mn^{2+}. SiO_2 values were also higher in groundwaters than surface waters, with SiO_2 levels in the groundwaters of 3.1 to 14.3 mg/L and 2.5 to 10.9 mg/L in the surface waters.

Six cations, Na^{+}, Sr^{2+}, Li^{+}, Mn^{2+}, Fe^{2+} and SiO_2 have groundwater concentrations greater than surface water values. Potassium values were higher in the surface waters than the groundwaters. Ca^{2+} and Mg^{2+} concentrations in groundwaters range from the lowest value to the highest value, while the surface water concentrations fall in the middle of the range.

5.2.2.c. Anions

All anions are measured to within approximately 1 to 1.5 mg/L (Shevalier, 1996). Cl^-, SO_4^{2-}, PO_4^{3-} and NO_3^- are the dominant. anions analysed. Only one sample, Chin62, has a Br^- concentration above 2 mg/L with a concentration of 5.3 mg/L.

Cl^- concentrations in groundwaters range from 0 mg/L to 203 mg/L, while the surface water ranges from 0.1 to 109 mg/L. 75 % of all the samples have concentrations of Cl^- less than 50 mg/L. NO_3^- concentrations are greater than 20 mg/L in 6 samples, with the highest value being 47 mg/L. Surface water sample concentrations range from 0 to 10 mg/L.

SO_4^{2-} levels in the groundwaters also have a wide concentration range, from a low of 0 mg/L to a high of 132 mg/L. Surface waters range in values from 5.1 to 65 mg/L. Approximately 90% of all samples lie below 50 mg/L SO_4^{2-} and 20 samples have less than 2 mg/L. The only groundwaters with any detectable PO_4^{3-} (up to 2.6 mg/L) were from the gravel aquifer and surface water samples and have concentrations from 0 to 8.7 mg/L.

Both Cl^- and NO_3^- have higher concentrations in the groundwaters than the surface waters. PO_4^{3-} has higher levels in the surface waters, with very low values in the groundwaters sampled. This suggests contamination by detergents or fertilizers or very low biological activity in surface waters. SO_4^{2-} concentrations follow the same pattern as Ca^{2+} and Mg^{2+}, with the surface water values lying intermediate to the high and low values measured in the groundwater samples.

5.2.3. Effect of pH on ionic concentration

Measurements of pH were made on all water samples in this study. This data was plotted against the various anion and cation analyses to determine if pH contributes to the ionic conentrations in the waters. The ions K^+, Sr^{2+}, Fe^{2+}, Mg^{2+},Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-} all have peaks in concentrations at a pH of 7 (e.g. Sr^{2+}; Figure 5.2.a). Mn has a peak of concentrations at pH $\approx$ 7, with most samples very close to 0 µg/L; PO_4^{3-} and Br- have low concentrations, with the higher values peaking at a pH $\approx$ 7.5. Na^+ and Li^+ have concentrations gradually rising from lows around 6.5 to 7 pH units to a peak at approximately 8.8 pH units. There is no apparent link to pH for alkalinity (HCO_3^-), Si, and SiO_2 in the waters (Figure 5.2.b) and overall there is no distinct trend between the pH values and the ion concentration. Samples with anomalously high concentrations are found in the same pH range as low concentrations of the same ions.

5.3. Graphical presentation of chemical data

Techniques used to display the chemical character of the waters in a useful way include STIFF diagrams (Stiff, 1951) and Piper plots (Piper, 1944). As there are three separate aquifer units, it is possible that the waters of each aquifer might have different chemical characteristics. This visual presentation of the data will enable a determination of the difference or similarity of the three aquifer waters to one another.

5.3.1. STIFF diagrams

A Stiff diagram is a multivariable graphical representation of concentration data for waters (Stiff, 1951). The graph consists of selected anion and cation concentrations

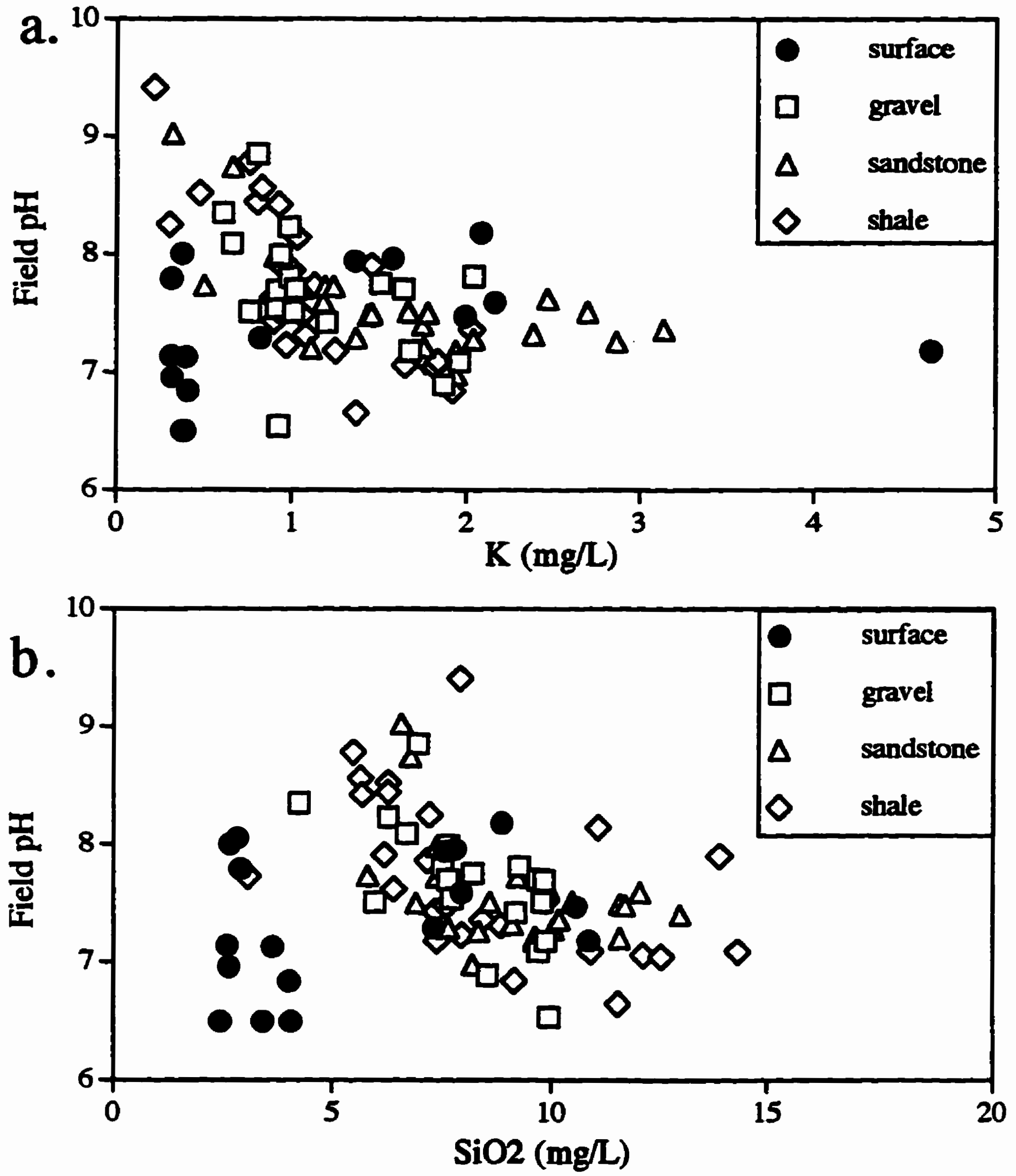


Figure 5.2. Graphs of pH vs. a.) concentration of K^+ and b.) SiO_2 concentration in water samples.

(in milliequivalents per litre; ion concentration (mg/L) x absolute ion valence charge divided by ion mass) plotted on opposite sides of a zero line. This permits initial visual recognition of differences in the concentrations of various ions in the water. For this study the cations plotted were ($Na^+ + K^+$), Ca^{2+} and Mg^{2+} and the anions plotted were ($HCO_3^- + CO_3^{2-}$), Cl^- and SO_4^{2-}. All waters sampled were dominated by the HCO_3^- anion with either Ca^{2+} or ($Na^+ + K^+$) as the dominant cations. This is consistent with the two water types sampled by Nowak (1984) in their Chiniki Village study. They found Ca^{2+} - HCO_3^- waters and Na^+ - HCO_3^- as did Barnes and Ozoray (1977) for the region.

5.3.1.a. Surface waters

STIFF plots of the surface water samples show relatively low concentrations of ions as most of the samples have extremely low TDS. Surface waters tend to be dominated by HCO_3^- with low levels of most other plotted ions (e.g. sample Kan6; Figure 5.3.a).

5.3.1.b. Groundwaters

The STIFF plots for groundwaters illustrate that there are two end members, waters that appeared most dissimilar based on the STIFF diagrams (Figure 5.3.b and c). These end-member waters represent a water dominated by sodium-potassium and bicarbonate-carbonate (Nak29) and a water with low TDS (Chin 23). Chin23 closely resembles the character of the surface waters, whereas Nak29 represents the sample with the greatest TDS in this study. The STIFF plots for the remaining samples appear to fall somewhere between these two end members and may represent a mixing of the two waters. Forty-five water samples resemble Chin23, while 30 samples have

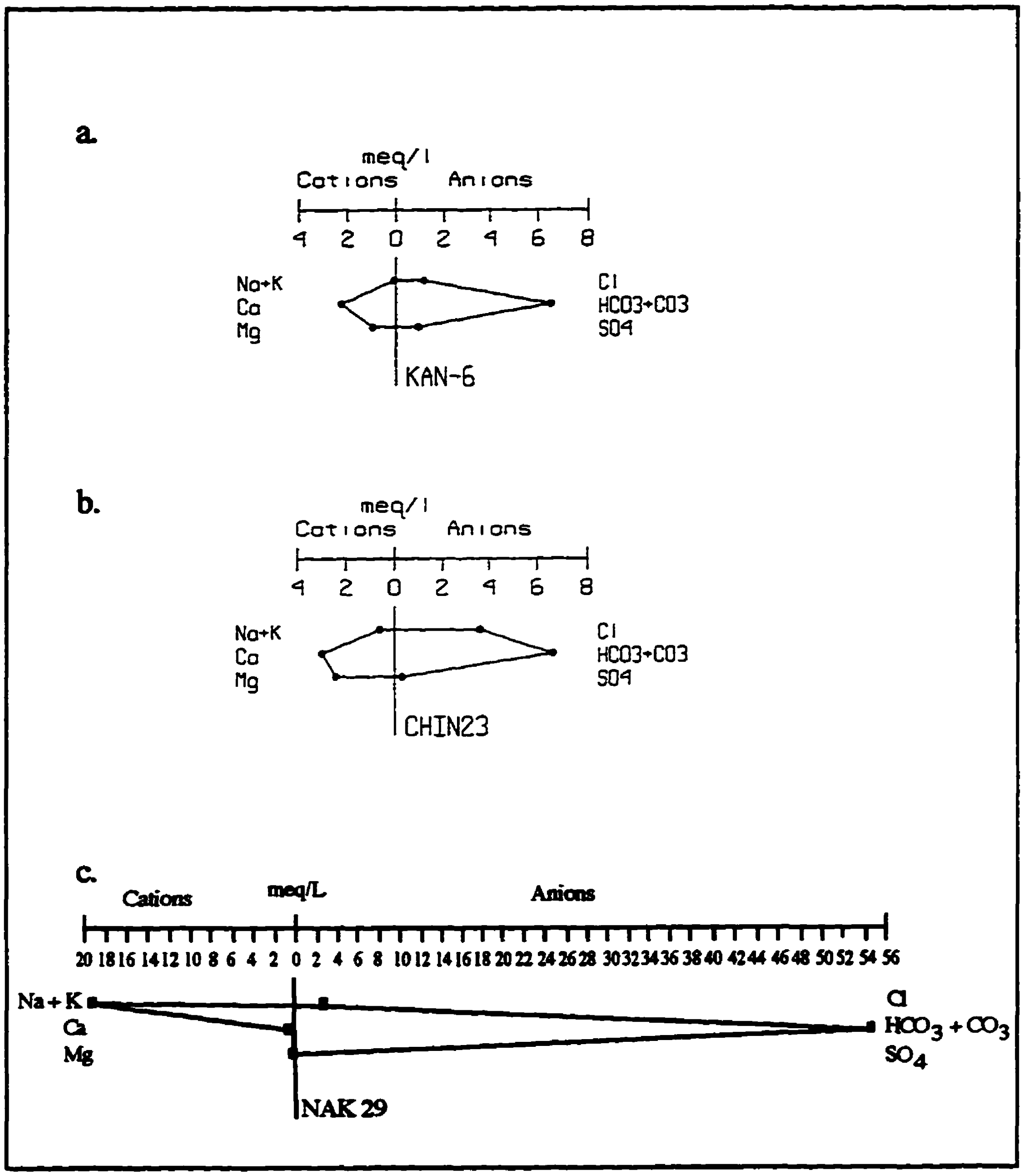


Figure 5.3. STIFF diagrams for : a.) representative surface water; b.) low TDS, Ca - HCO_3 groundwater end member; and c.) high TDS, Na-K - HCO_3 groundwater end member.

characteristics similar to Nak29. There are thirteen groundwater samples that are intermediate between these end members, with features of both present.

Sample Nak29 is obtained from a deeper well within a shale aquifer while the end member Chin23 represents a well completed in the shallower sandstone. There is no apparent correlation with depth or aquifer to water character, however, as the samples plotting in the region between these two waters represent a range of depths and all the defined aquifer units on the reserve. Although many of the deeper wells appear to be completed in shale and plot nearer to the Nak29 end member, there are samples representing deeper waters plotting near Chin23.

5.3.2. Piper plots

The chemical data (in meq/L) is plotted on several triangular Piper diagrams (Piper, 1944), with Cl^-, HCO_3^- and SO_4^{2-} as the selected anions and Ca^{2+}, Na^+ + K^+ and Mg^{2+} the cations plotted. Surface waters all group closely, with low TDS values (Figure 5.4). The groundwater plot (Figure 5.5) illustrates the groundwater is derived ultimately from meteoric waters, as there are clusters of data in the same regions as the surface water plot, but that some additional ions have been added to the waters, causing the waters to plot along lines away from the surface water composition. In particular, Na^+ and K^+ have higher relative amounts in the groundwaters. These groundwaters with high Na^+ and K^+ concentrations resemble plots of bank-storage springs and tufa-depositing springs in the Calgary - Golden area reported by Barnes and Ozoray (1977) and are attributed to springs discharging from gravels, limestone-fragment-drift or from drift-veneered sandstone. They state that the low sodium and high magnesium percentages show that the springs are discharge points of small, local flow systems, while the

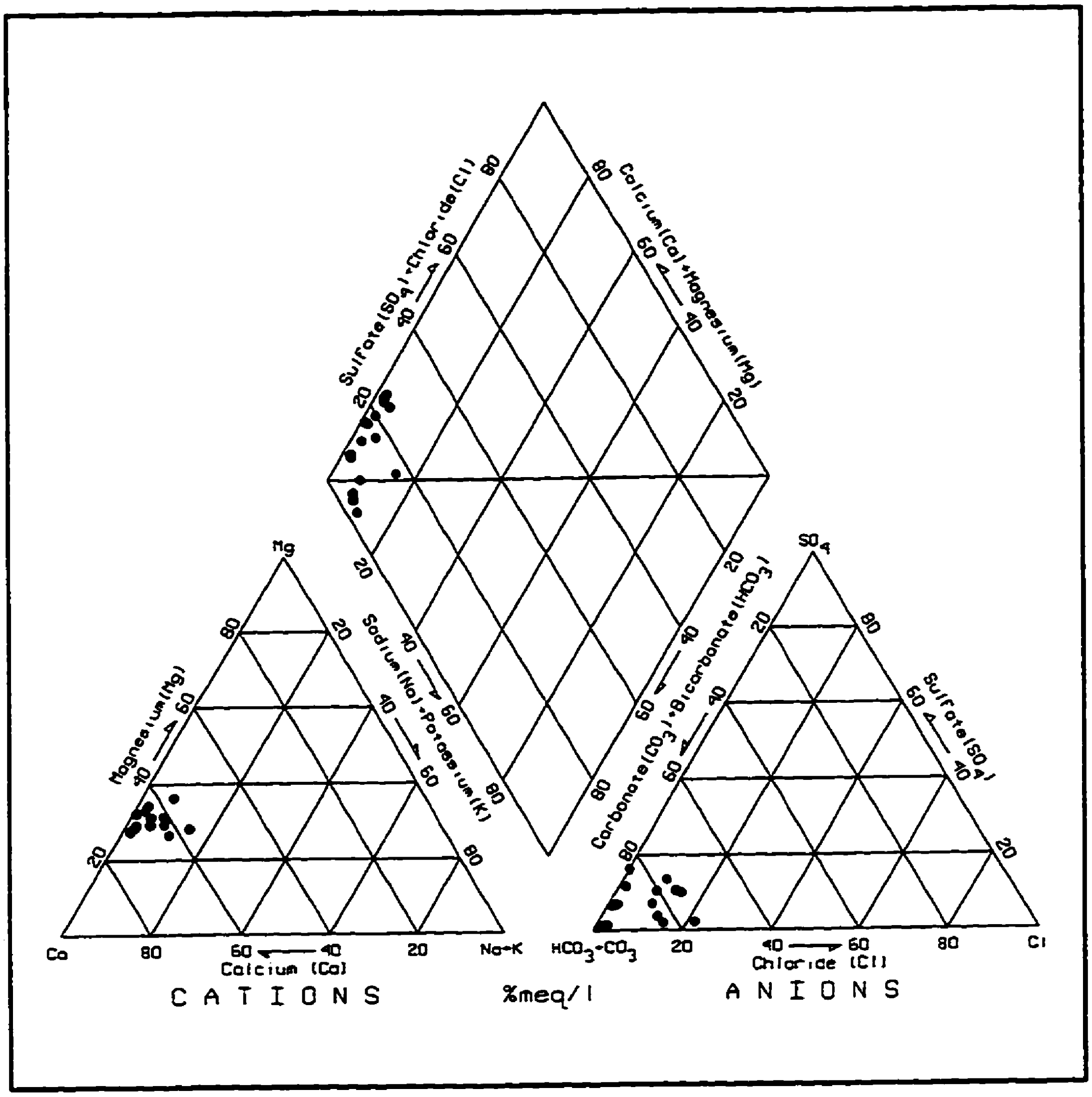


Figure 5.4. Piper diagram for surface waters in and around the Morley reserve.

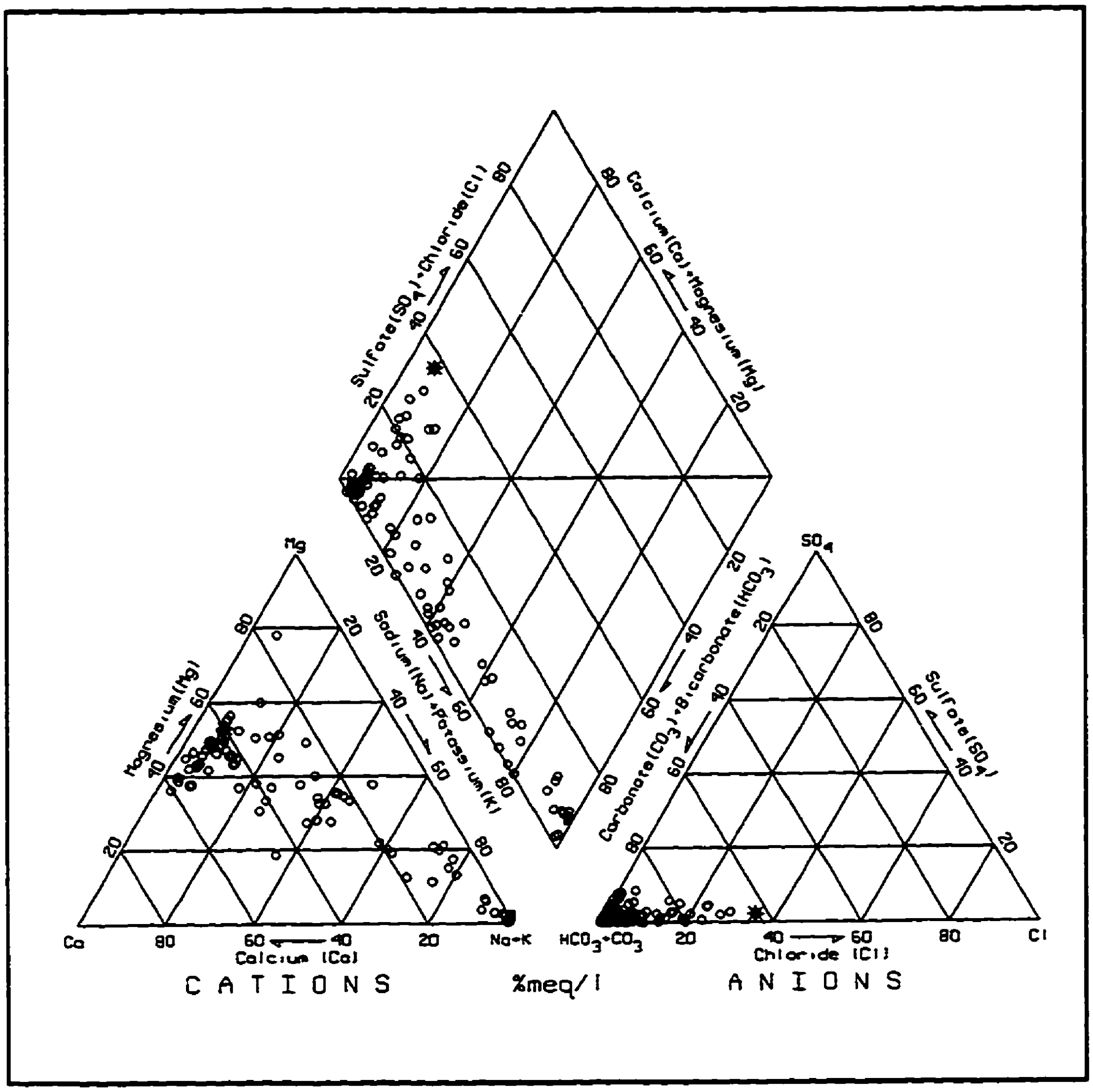


Figure 5.5. Piper diagram for groundwaters. Groundwater end-members shown; Nak29 by rectangle and Chin23 shown by 'star'.

groundwater plots are more enriched in Na^+ and K^+ and may represent water from bedrock or non-gravely drift.

The end members identified from the STIFF plots are shown on the groundwater plot. They illustrate the range of concentrations of the ions in the water. These two waters plot as distinctly different waters, particularly sample Nak29 which has much higher percentages of $Na^+ + K^+$ and HCO_3^- than the other waters.

5.3.3. Summary of Chemical Concentration Data

The groundwaters have higher concentrations of SiO_2, Na^+, Sr^{2+}, Li^+, Mn^{2+}, Fe^{2+}, Cl^- and NO_3^- than the surface waters. The surface waters have higher concentrations of K^+ and PO_4^{3-}. Examining both the STIFF and Piper plots, it appears that all the reserve waters are ultimately derived from recent meteoric waters as the low TDS end-member water plots in the same region as the surface waters on the Piper diagram. A general linear trend of increasing ionic concentration, and the increasing relative amounts of Na^+ and K^+ illustrate the progressive change in ion concentration between the two groundwater end-members.

5.4. Isotopic interpretations

The isotopic plots are used to determine trends in the waters. The physical processes that affect the waters cause differential fractionation of the stable isotopes. Thus differences in physical processes may be detectable by examining the isotopes. The groundwaters tend to be subject to more water-rock interactions than the surface waters as well as having different fractionation processes, so differences in the isotopic values should be meaningful. If frequency distributions for the isotope values are examined, interpretations regarding the source of the isotopes in the region and the hydrologic processes acting in the area may be possible.

5.4.1. Sulfur Isotopes

Sulfur has a wide range of isotopic composition in nature due to the fact that it has oxidation states from S^{2-} to S^{6+}. The $\delta^{34}S$ values measured in the sulfates from the waters on the reserve fall within the natural range of -60‰ to +40‰. Sources of sulfur in nature include sulfate in the tills and rocks on the reserve, mineral dissolution, bacterial reduction of sulfate, which changes the availability of sulfur, the mineralisation of organic matter and precipitation of sulfates or sulfides (Nriagu et al., 1991; Krouse, 1989). At the low temperatures present in the shallow groundwaters of the reserve, only biologic activity is likely to effect reduction of SO_4^{2-} as the high activation energy of the sulfate must first be overcome. The different sources of sulfur lead to differing $\delta^{34}S$ values.

5.4.1.a. $\delta^{34}S$ of sulfates

The range in isotope values for $\delta^{34}S$ from dissolved sulfate is -1.5‰ to +27.8‰ for surface waters and from -20.4‰ to +30.4‰ in the groundwaters. These range in value span most of the naturally occurring sulfur isotope values.

Figure 5.6 shows the frequency plots for surface waters and groundwaters, separated by aquifer type. These plots illustrate the range of $\delta^{34}S$ values that are present for the Morley data set. The waters identified as coming from the shales appear to have a

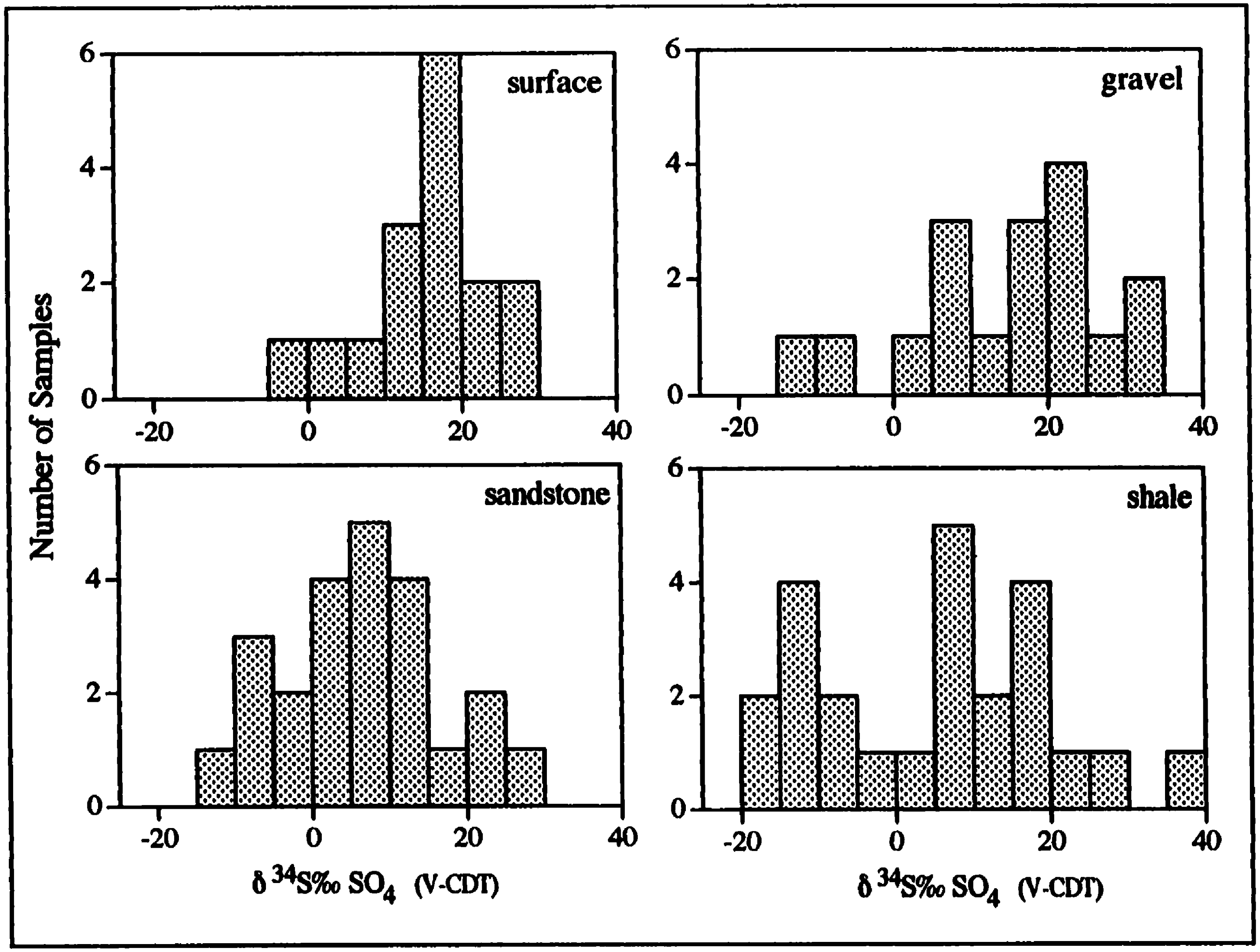


Figure 5.6. Frequency plots for $\delta^{34}S$ values separated into surface waters and the three groundwater aquifer units.

different distribution of $\delta^{34}S$, with both the largest range of values and the greatest number of samples falling below 0‰ $\delta^{34}S$.

A $\delta^{34}S$ frequency graph for the combined surface and groundwater samples has been overlain by the value range for various sources of the sulfur in nature (Figure 5.7). The sulfur in sulfate appears to be coming from several sources. There is a peak at +7.5‰, close to the range of evaporitic sulfate (10‰ to 27‰). A slight peak is also seen at -10‰, suggesting that some of the sulfur may be derived from pyrite in the rocks of the area. The more negative $\delta^{34}S$ values, to below -20‰, may be due to some amount of bacterial reduction, or due to mixing of waters having more negative values with waters having more positive $\delta^{34}S$ values. As there are no extremely negative $\delta^{34}S$ values, it is unlikely that bacterial reduction has a major impact on waters in the area. However, van Donkelaar et al. (1995) reported $\delta^{34}S$ values ranging from -12‰ to approximately +19‰ and found two samples that indicated presence of sulfate reducing bacteria being present, so less extreme negative values for $\delta^{34}S$ may be consistent with bacterial sulfate reduction (BSR).

The values above +15‰ are possibly due to water-rock interactions that have occurred within geologic units, containing marine carbonates and sulfates, that lie to the west of the study area and probably are present in the soils and till of the study area. As these rocks are predominantly Mississippian and Devonian in age, these higher $\delta^{34}S$ values for the dissolved sulfate are reasonable.

If the $\delta^{34}S$ values of sulfate are plotted against $\delta^{18}O$ values of water (Figure 5.8) samples from the shales show a somewhat different trend than those of the surface waters or waters from the sandstone and gravels. Samples showing an enrichment in the heavier isotope of sulfur may indicate bacterial reduction. The bacteria preferentially use the

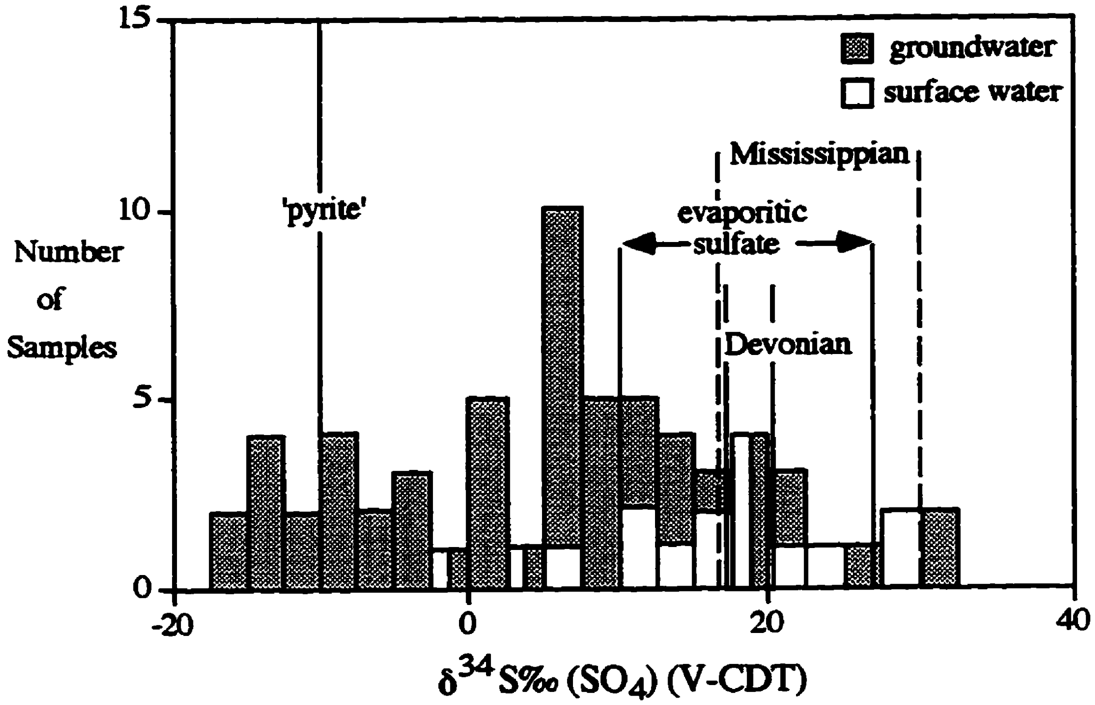


Figure 5.7. Sources of sulfur in nature and their $\delta^{34}S‰$ values.

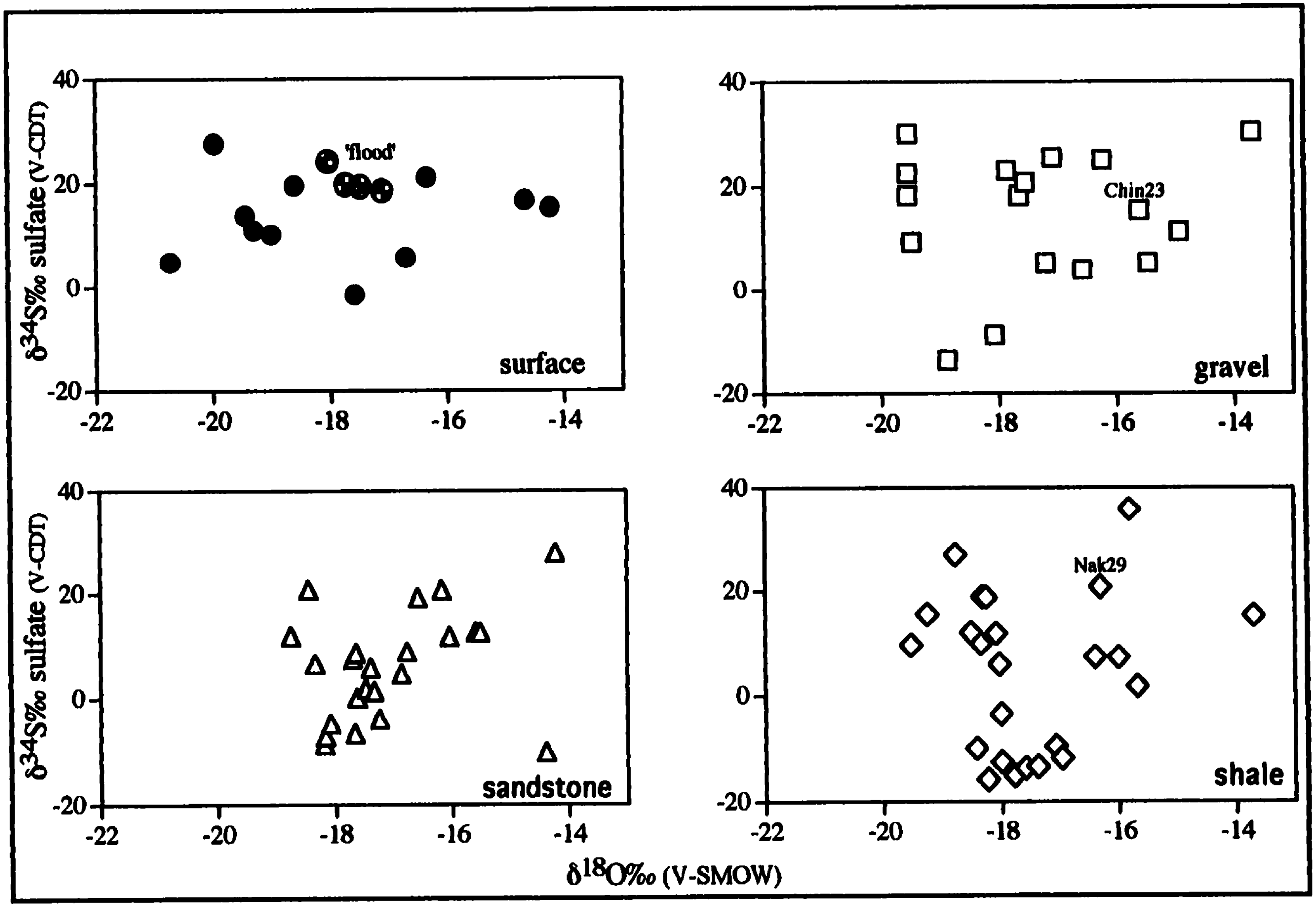


Figure 5.8. Graph of $\delta^{34}S$ vs. $\delta^{18}O$, separated into surface waters and the three aquifer units.

lighter sulfur isotopes and the remaining sulfate becomes enriched in the heavier isotope and the ratio becomes more positive.

5.4.1.b. $\delta\ ^{34}S$ (‰) in sulfate vs. concentration of SO_4^{2-}

The relationship between the amount of dissolved sulfate in the waters and the $\delta^{34}S$ values is plotted in Figure 5.9. The surface waters have the smallest range in values for $\delta^{34}S$‰, with values from +15‰ to +25‰. The three aquifers show a much larger range of $\delta^{34}S$‰ values of sulfate The gravels have the largest $\delta^{34}S$ change from +31‰ to -15‰, although none of the gravels have sulfate concentrations greater than 20 mg/L.

Although the shales have $\delta^{34}S$ values of a similar range to those seen in the gravels, the shale data appear to have a trend of decreasing $\delta^{34}S$ values with increasing concentrations of dissolved sulfate. This shale trend may represent the oxidation and dissolution of pyrite in the shale as there are a number of samples with $\delta^{34}S$ values around the -10‰ value, typical of pyrite in this area or it may indicate the presence of sulfate reducing bacteria in the waters, as the remaining sulfate becomes enriched in the heavier isotope as the bacteria preferentially takes up the lighter sulfur isotope first, thus lower sulfate concentrations would have more positive $\delta^{34}S$ ratios. These values may be modifed by mixing of greater proportions of surface water with an isotopic signature inherited from dissolution of sulfate in Mississippian and Devonian rocks. This agrees with the $\delta^{34}S$ vs. $\delta^{18}O$ graphs (Fig. 5.8).

If the $\delta^{34}S$ values of marine sulfate from the Devonian and Mississippian units and pyrite are plotted on Figure 5.9, it is possible that the sulfate is coming from several sources, some from the Mississippian and Devonian rocks to the west of the

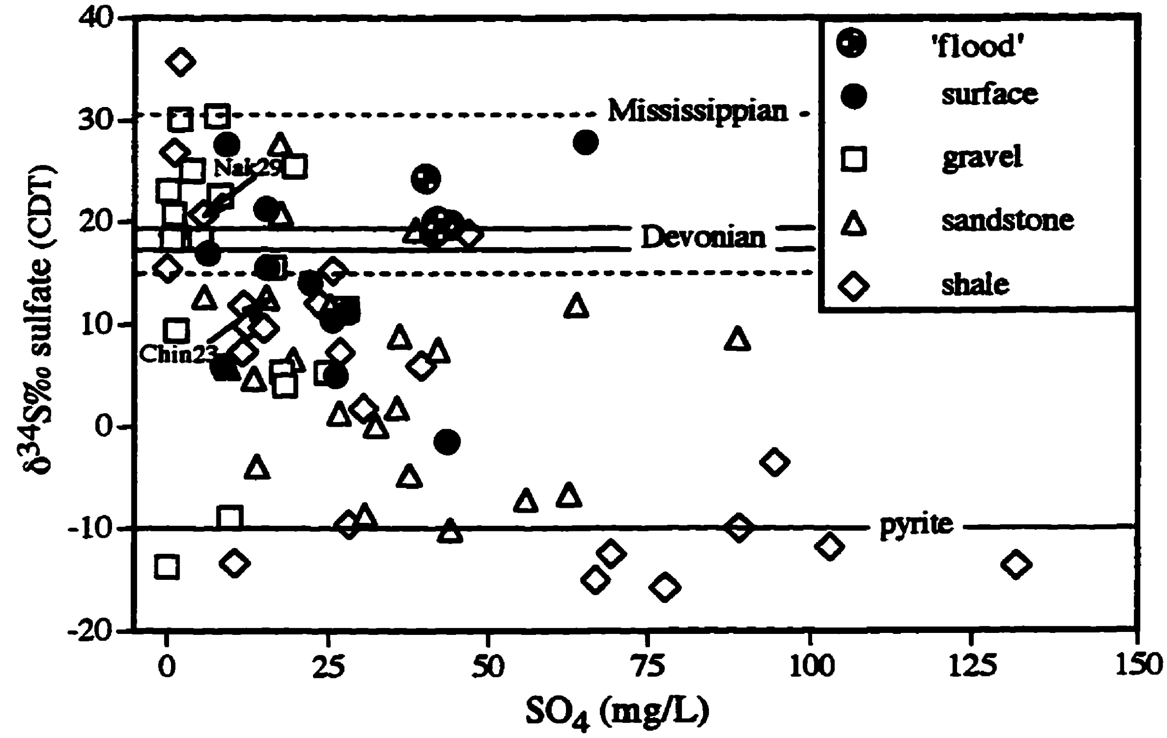


Figure 5.9. Graph of $\delta^{34}S$‰ (sulfate) vs. concentration of sulfate in the water. Lines show $\delta^{34}S$‰ for the carbonate rocks and pyrite in the study area.

reserve and some possibly from the dissolution and oxidation of pyrite in the shales of the area.

5.4.1.c. $\delta^{34}S$ (‰) vs. concentration of phosphate

The purpose of this plot (Figure 5.10) is to determine if there is a relationship between a "nutrient" in the waters with the $\delta^{34}S$ values. If the $\delta^{34}S$ values were linked to bacterial activity, the sulfate that remains gets heavier and the more negative $\delta^{34}S$‰ values would be linked to higher concentrations of PO_4^{3-} in the water. There is little evidence of this trend in the data from the study area. Phosphate data (Fig. 5.10) show a poor correlation between increased levels of phosphate and the more negative $\delta^{34}S$ values. As this "nutrient" concentration decreases there is no corresponding depletion in the $\delta^{34}S$ values that would be due to bacterial reduction of sulfate, thus the evidence tends to rule out bacterial sulfate reduction as a mechanism that contributes significantly to the water chemistry.

5.4.2. Carbon Isotopes

There are many processes affecting carbon in nature. The different types of plants, C3 and C4, have different pathways of fixing carbon and thus have different $\delta^{13}C$ values. C3 plants have $\delta^{13}C$ values of -28.1 ± 2.5‰ while C4 plants have $\delta^{13}C$ of -13.5 ± 1.5‰. Although the range is typically illustrated as being larger, there is no apparent overlap of values (O'Leary, 1981; Veizer and Hoefs, 1976). Aquatic plants tend to have more positive $\delta^{13}C$ values due to the slower diffusion of CO_2 in water. Some members

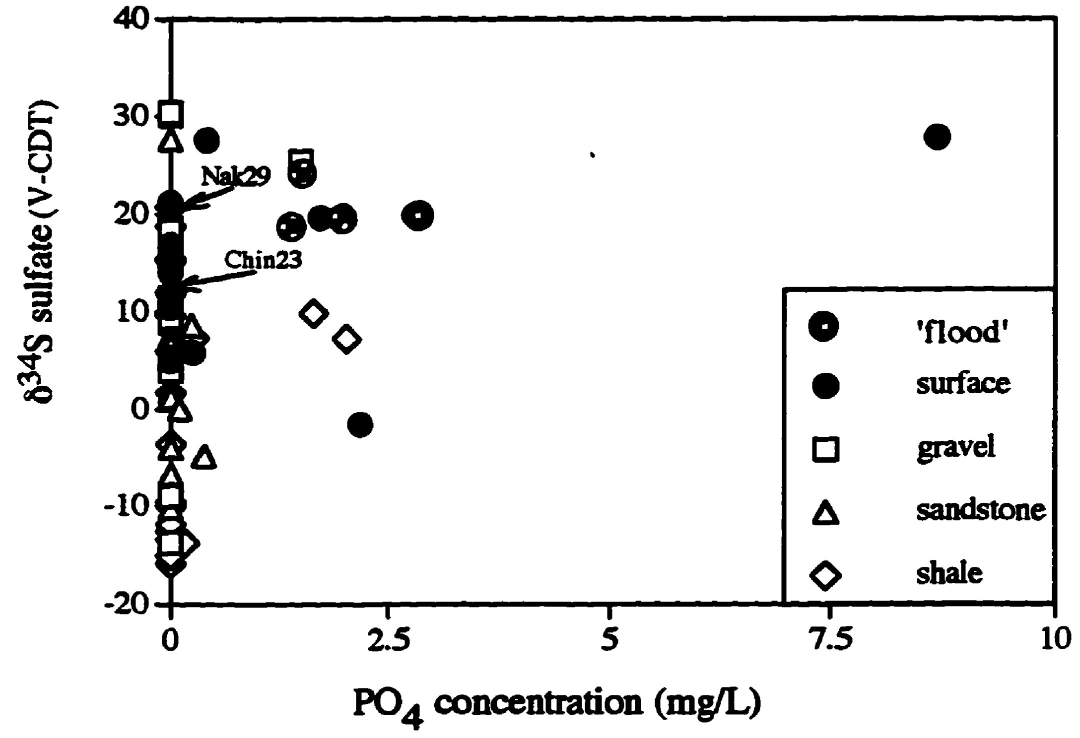


Figure 5.10. Separated water plots of $\delta^{34}S$ vs. phosphate concentrations.

of the grass family and "cane" plants are representative of the C4 plants, while most land plants would fall in the C3 category.

Bacterial respiration may contribute to lighter $\delta^{13}C$ values (Yang et al., 1996) while a longer residence time for the waters may allow for equilibrium to occur with atmospheric CO_2, which would yield $\delta^{13}C$ values of approximately -5‰. Other researchers have noticed positive $\delta^{13}C$ values in dissolved inorganic carbon with significant bacterial reduction (Drimmie et al., 1991), however, these may be linked to methanogenesis processes. Other sources of dissolved carbon in nature may include the decay of organic material.

5.4.2.a. $\delta^{13}C$ (dissolved carbonate)

The range in the $\delta^{13}C$ values is -14.0‰ to -2.9‰ for surface waters and -16.3‰ to +5.6‰ for the groundwater (Figure 5.11). It is possible that more than one process is affecting the carbon in the system because of the wide range in the values. The frequency graph shows a left skewed frequency, with a peak at -12.5‰ to -10.0‰. Only 7 samples had positive $\delta^{13}C$ values. The lines on the graph show the range of values for $\delta^{13}C$ in various plants and minerals in nature (Veizer and Hoefs, 1976).

For the range of values found in this study, the dissolution of carbonates in the rocks would appear to be a reasonable explanation of the more positive $\delta^{13}C$ values determined. Plant $\delta^{13}C$ values are also plotted on the graph, and the soil carbon may be derived from C4 plants and subsequently picked up by the waters. The waters with more negative $\delta^{13}C$ values, less than -20‰, may be due to the mixing of waters influenced by biogenic carbon with the more positive $\delta^{13}C$ waters from carbonate dissolution or may be

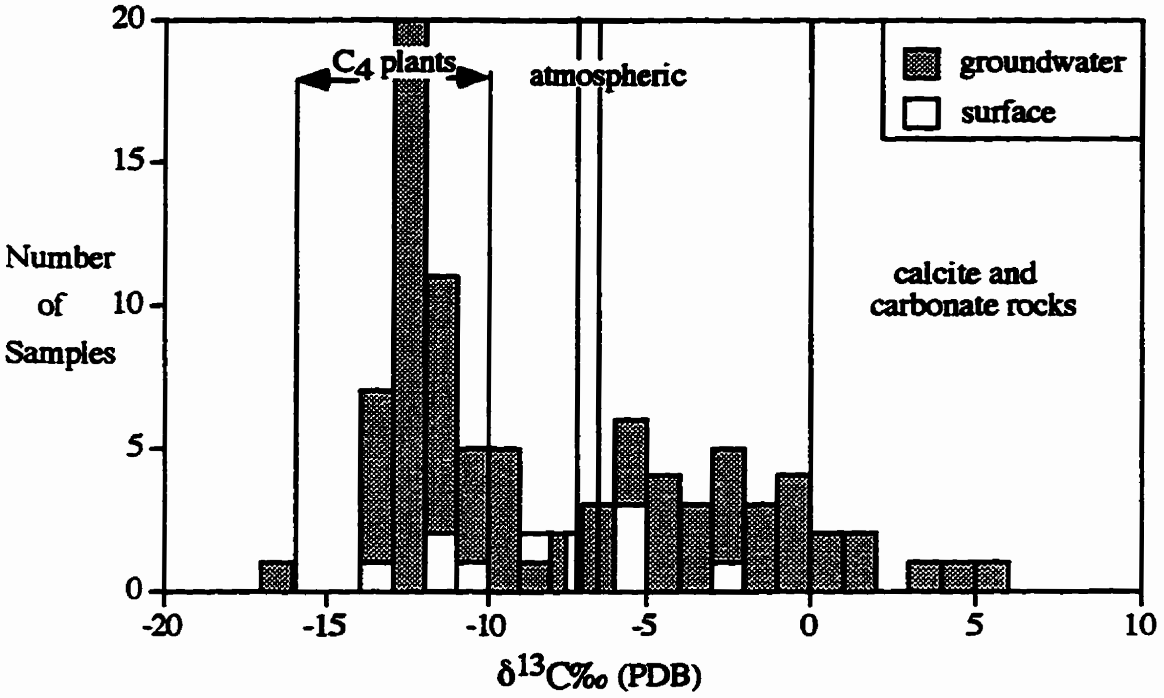


Figure 5.11. Frequency graph for surface and groundwater $\delta^{13}C$ in study area. Overlay lines illustrate range of $\delta^{13}C$ values in nature.

linked to soil CO_2 generated by C3 plants which have been found to have a $\delta^{13}C$ value from -18‰ to -22‰ (Aravena and Suzuki, 1990).

5.4.2.b. Mixing of waters

The spread of $\delta^{13}C$ data indicate possible mixing of the waters influenced by carbonate dissolution, having positive $\delta^{13}C$ values, and groundwater possibly enriched in organic matter from the soils and subsurface with the -15‰ $\delta^{13}C$ values. The surface waters tend to have low concentrations of HCO_3, but a wider range of $\delta^{13}C$. This suggests that the surface waters easily pick up the carbon produced, or that the stream waters may have significant contributions to their baseflow from groundwater. It seems likely that there is mixing of waters, as the $\delta^{13}C$ values that would reflect the presence of C3 plants would have more depleted $\delta^{13}C$ values than those found in the waters.

To determine the extent to which the carbon in waters may originate as plant matter, some of the possible nutrient material was examined. $\delta^{13}C$ were plotted against phosphate concentrations to see if there is any evidence to support a plant source for carbon (Figure 5.12). Higher concentrations of PO_4^{3-} appear to occur in the range of -5‰ to -10‰. This range is consistent with the carbon originating from plant matter, provided some fractionation or contrbution from other sources has also occurred. The dominant plants in the study area are C_3 plants. These plants would typically have $\delta^{13}C$ values fron -18‰ to -22‰. As the $\delta^{13}C$ values in the samples do not have any values this negative, if the waters have a biogenic derived portion there must be mixing with more isotopically positive waters to produce the $\delta^{13}C$ values observed. Mixing of waters with more negative $\delta^{13}C$ values with waters from carbonate rocks could produce these less negative $\delta^{13}C$ values.

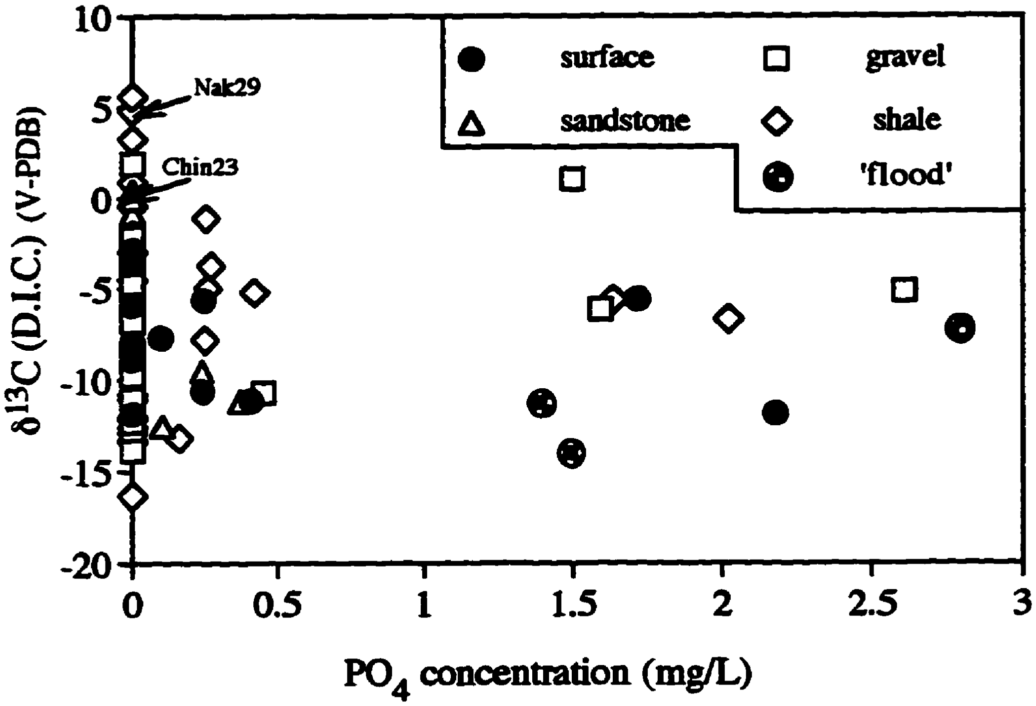


Figure 5.12. Graph of $\delta^{13}C$ of dissolved inorganic carbon vs. concentration of phosphate.

5.4.2.c. Possible bacterial control of isotope abundances in waters

Figure 5.13 shows the carbon and sulfur isotope data cross plotted. If there was bacterial sulfate reduction occurring, the trend would have $\delta^{13}C$‰ values and $\delta^{34}S$‰ values decreasing oppositely as the $\delta^{34}S$ of unreacted SO_4^{2-} increases, more organic matter is oxidised to give more negative $\delta^{34}S$ values. This is not very evident in this data set. The majority of the samples have values between -10‰ and -15‰ for $\delta^{13}C$, but all aquifer units have randomly distributed values. The sandstone-aquifer derived waters show a weak BSR-trend, although the scatter in the data is still great. There may be a weak trend toward BSR effects in the shales.

5.4.3. Hydrogen and Oxygen Isotopes

5.4.3.a. δD vs. $\delta^{18}O$

The range of values for δD are - 152.8‰ to - 125.0‰ for surface waters and from -155.5‰ to -122.1‰ for groundwaters. $\delta^{18}O$ values are -20.7 ‰ to -14.2‰ for surface waters and -20.7‰ to -13.7‰ for groundwater samples. This wide range of values is reasonable given the fact that sampling occurred over a full year, the elevations in and near the study area differ by only 100's of metres and the δD and $\delta^{18}O$ relationships are very sensitive to changes in temperature.

Plots of δD vs. $\delta^{18}O$ have been used to determine potential factors that are controlling the hydrology on the reserve. Craig (1961) determined a global meteoric water line (GMWL) defined as:

$$\delta D = 8\,\delta^{18}O + 10 \qquad (5.1)$$

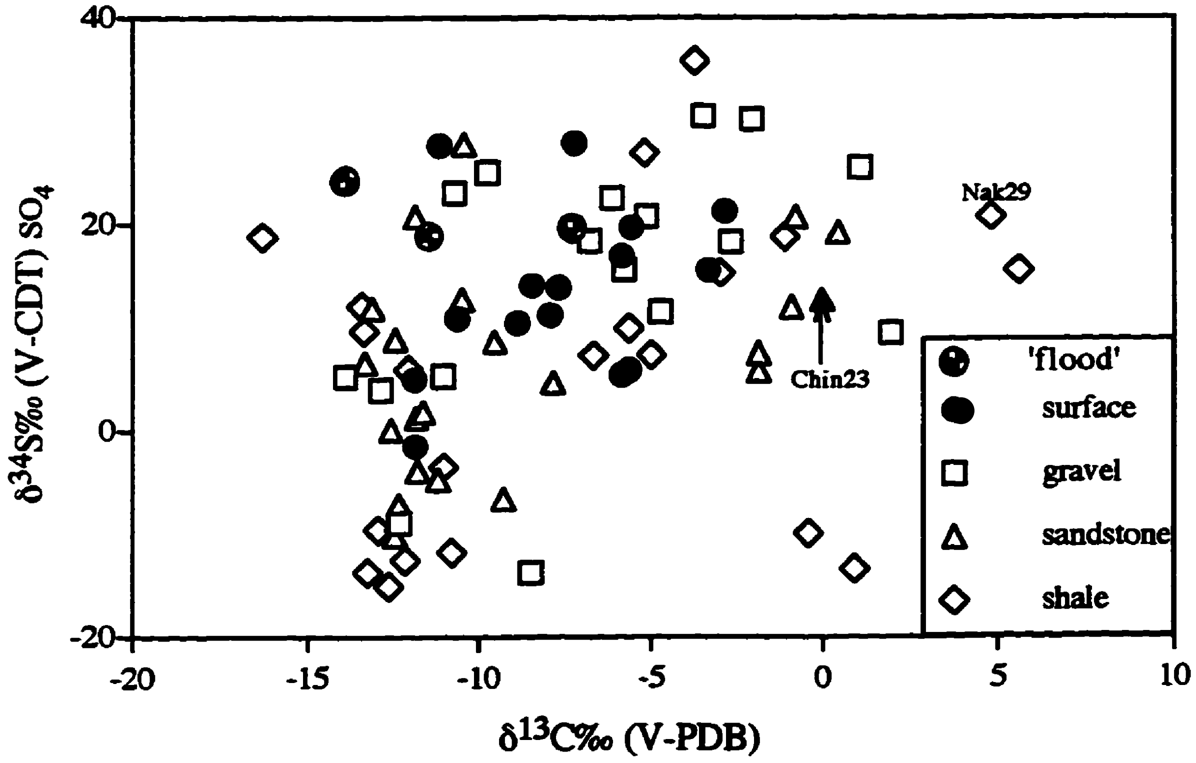


Figure 5.13. Cross plot of $\delta^{34}S$ vs. $\delta^{13}C$ separated into the different aquifer units.

This equation is a global best-fit line and may not represent the local meteoric line. It is plotted as a reference for the discussion of processes affecting the reserve waters.

When the data from this study are plotted, most of the points for both surface waters and groundwaters fall below the GMWL (Figure 5.14). One reason for the data trend below the GMWL is evaporation. Dansgaard (1964) defined a line representing evaporation as having a slope of five. Most of the samples from this study could be accounted for by a greater or lesser degree of evaporation. An evaporation line was plotted using the intercept of δD and $\delta^{18}O$ values for Calgary precipitation, -133‰ and -17.4‰ respectively, as reported by Yonge et al. (1989) and plotting a line with a slope of five through the point (dashed line on Figure 5.14). Gonfiantini et al. (1974) defined an evaporation line for a set of data as having a slope of 2.9. However, this value was calculated for an area with high evaporation rates where the groundwaters have very high TDS, reinforcing that an average equation applied to the global situation may not apply to the local region.

There is a further set of data points that have essentially the same δD value of about -154 with varying $\delta^{18}O$ values (circled region on Figure 5.14). These samples may represent water-rock interactions, a kinetic isotope effect, or mixing of waters from isotopically distinct sources. The four points circled are all samples taken from either the Bow River or the Kananaskis River at a high flow episode during late spring / early summer runoff in the summer of 1995. This was a summer of extensive flooding in southern Alberta, with large amounts of rainfall. There appears to be a dilution effect on the chemical constituents for these waters, as the TDS values of these waters are much lower than the average values for the data set and even for the surface waters in general, showing an inverse relationship between discharge and solute concentrations (Ferguson et

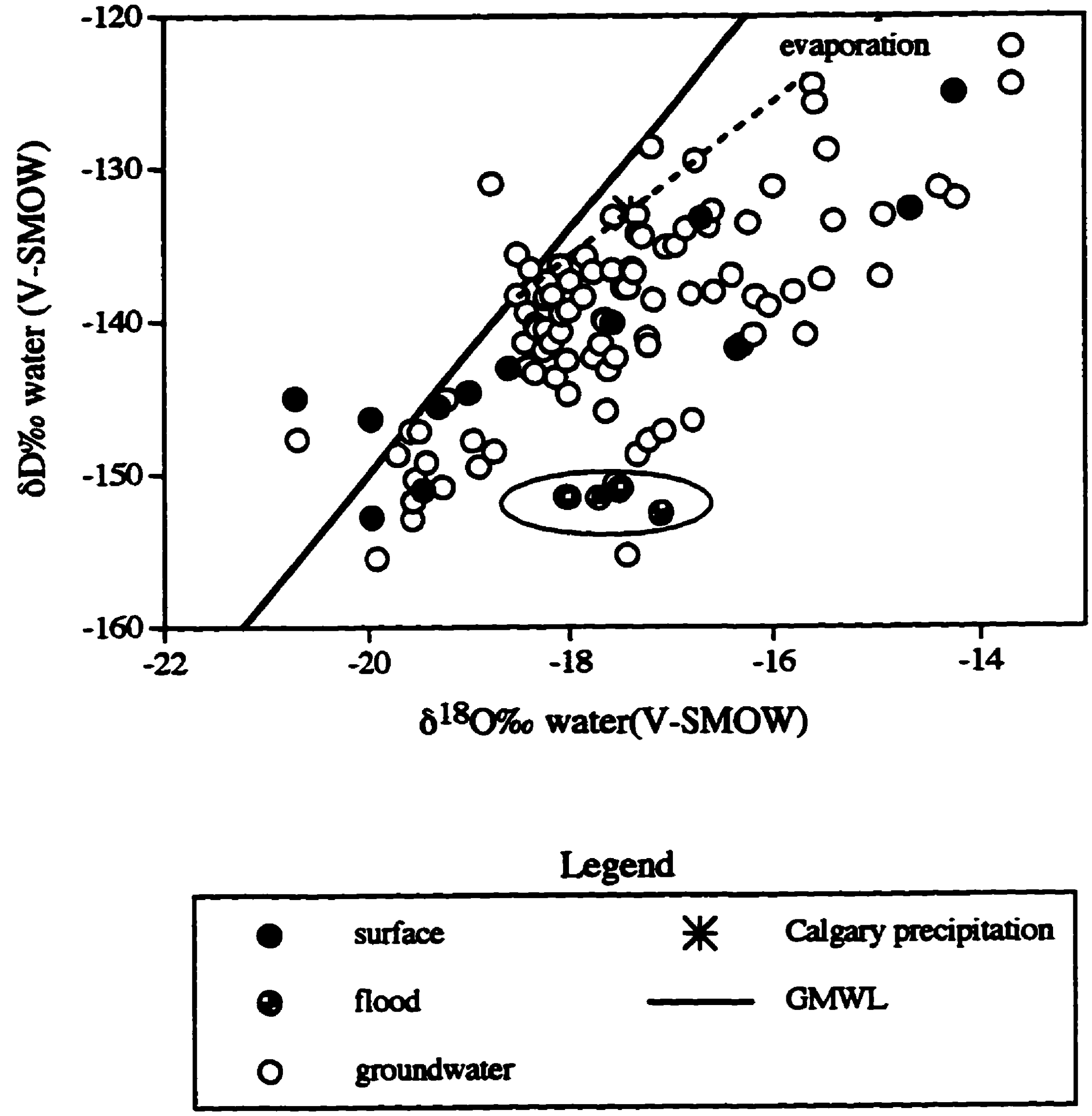


Figure 5.14. δD vs $\delta^{18}O$ of reserve waters showing the global meteoric water line and an evaroative trend for reference.

al., 1994). However, the more rain that falls in a given area, the more positive the $\delta^{18}O$ values become (Dansgaard, 1964).

When the individual groundwater aquifer units are examined (Figure 5.15), there appears to be little difference between the surface waters and various groundwaters. This supports the idea that all the water is derived from the same source. The sandstone and shale waters' best fit lines have a lower r-value and may support the idea that the shales and sandstones are subjected to more water-rock interactions than the other aquifer units. This would lead to greater chemical and isotopic variations, as seen in the data set. The shales have a much larger surface are per unit mass than the other aquifer units, creating more surfaces for exchange reactions and the shales have much lower porosity and permeability than the other aquifers, leading to slower water movement and more time in contact with the rock surface.

There is no pattern to the seasonal affect of the data when examined (Figure 5.16). Grasby et al. (in review) have values from seasonal sampling of the Bow River at Morley. These samples are also plotted to provide additional information for this study area.

5.5. Water flow patterns

Waters collected from the gravels appear to be most closely related to the surface waters based on the chemical and isotopic data from this study. This suggests a faster rate of recharge to the gravel aquifer than the sandstone and shale aquifers. Since the gravels are the shallowest unit, precipitation and surface waters are more likely to be able to enter the gravels quickly. The gravels are also located close to the rivers on the reserve (see Figure 2.2) and thus are subject to more infiltration of stream and river waters.

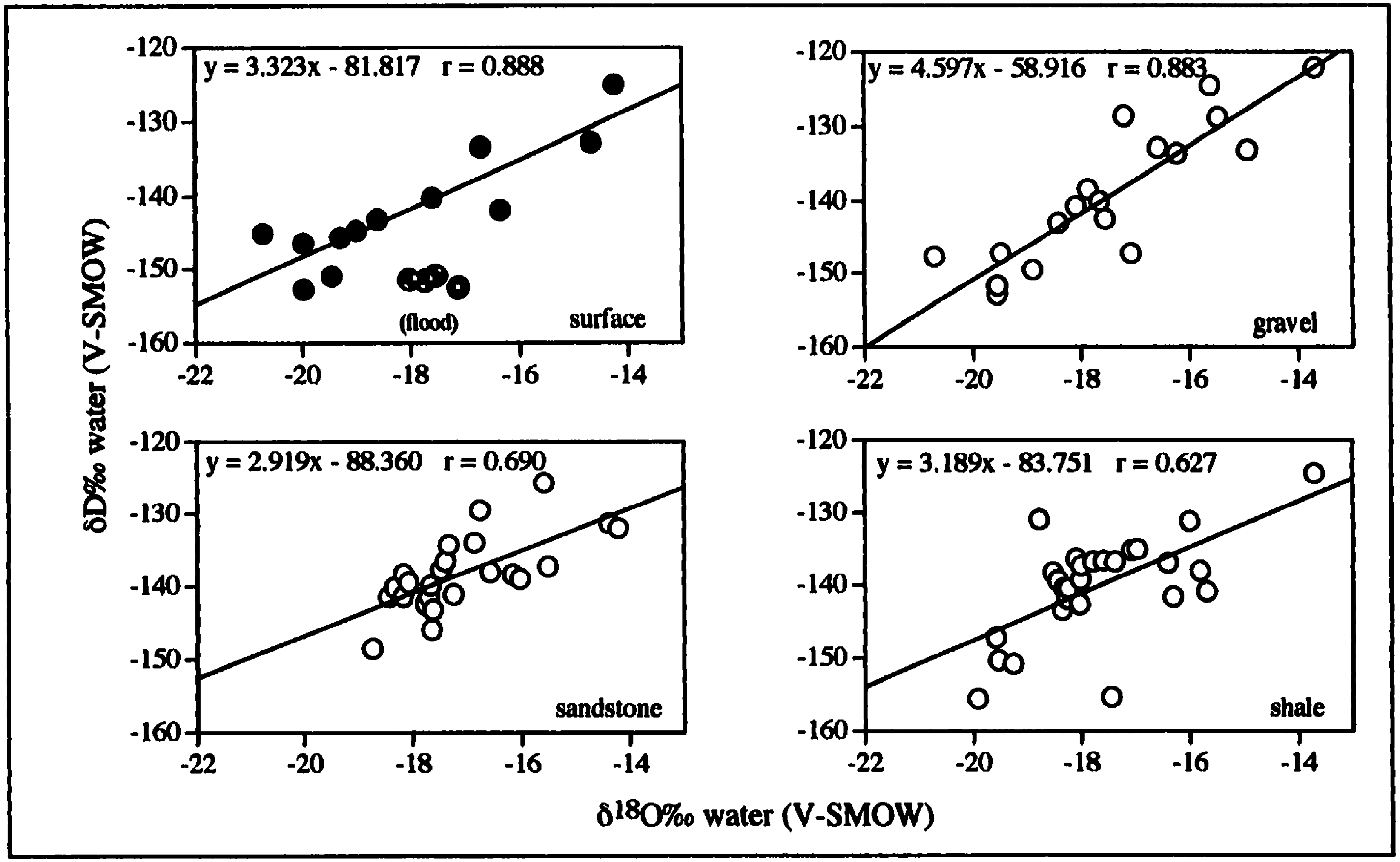


Figure 5.15. δD vs. $\delta^{18}O$ graphs for the reserve waters separated by aquifer type. The open circles on the surface water plot indicate the previously identified 'anomalous' samples.

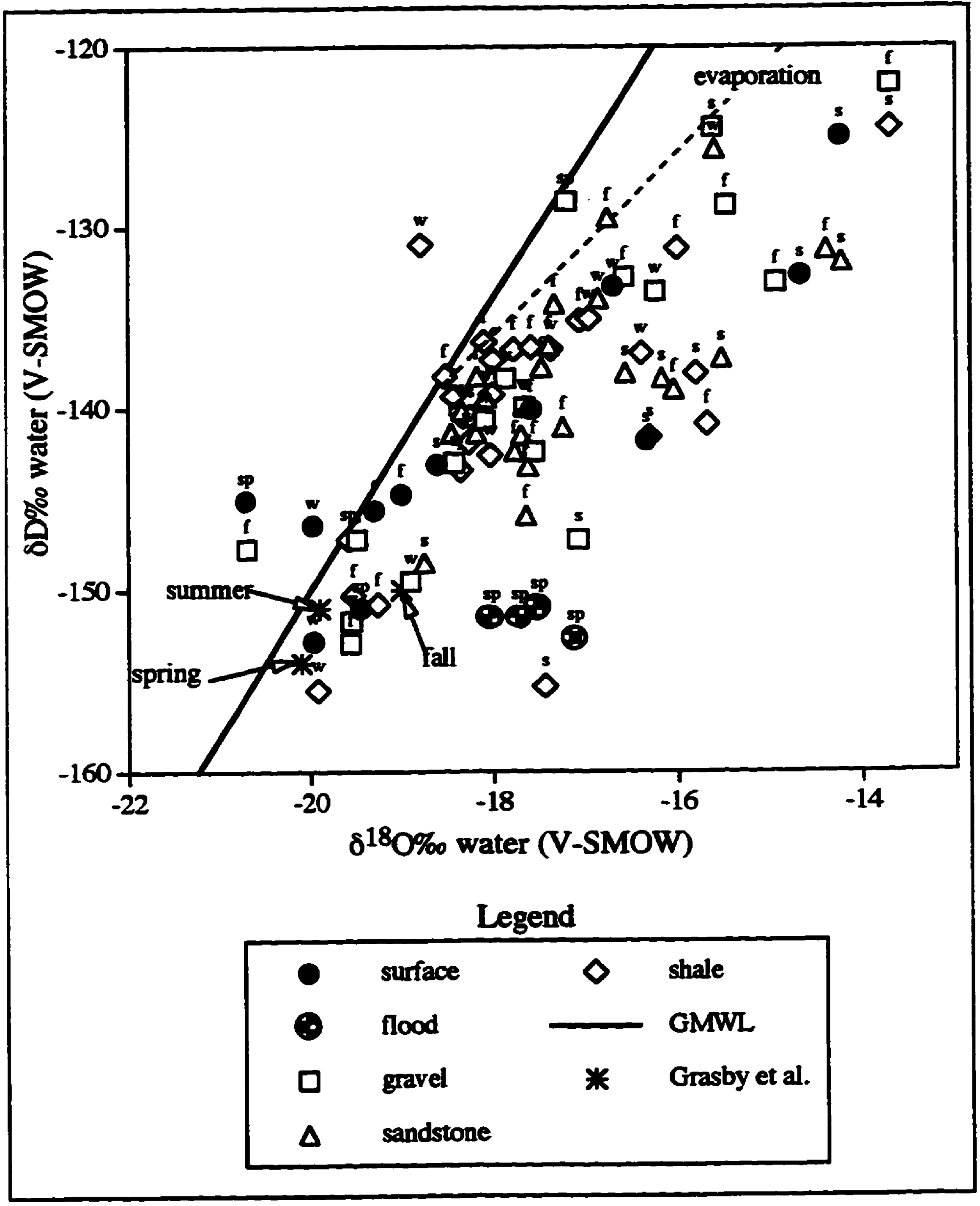


Figure 5.16. δD vs. δ^{18}O reserve samples separated into different aquifers.
Seasons indicated by s = summer, f = fall, w = winter and sp = spring.

Most of the precipitation on the reserve occurs as snowfall in the winter months. When the snow melts, the levels increase rapidly in the rivers and the flow rate increases. There is evidence to support a dilution effect on the concentration of chemical constituents in the river due to the increased flow, particularly when the snowmelt is occurring at the same time as a significant rainfall.

All the concentration and isotopic values were plotted on maps of the reserve to determine regional distribution patterns were discernible. The chemistries and isotopic values were plotted for each unit and for each season. No patterns were seen in the regional plotting of the study data.

5.6. Seasonal Differences

Many sites were sampled several times over the year in an attempt to examine any effect seasonal differences may have on the waters (Figure 2.1 shows sites with multiple samples). Tables 3.8 and 3.9 summarise the results of this aspect of the study. Most of the sites were only sampled twice as access was difficult in the winter and spring months at many of the sites. Only three sites were sampled in the winter period, and in the spring of 1996, six sites were revisited. Samples from June and early July of 1995 represent a period of extremely high water flow that was associated with high rainfall and flooding in southern Alberta.

When the data from seasonal sampling are examined, there are apparently no major seasonal differences. Many of the chemical constituents were relatively constant throughout the year. The chemical concentrations are relatively constant for the resampled sites. Fe^{2+}, Cl^- and Mn^{2+} have noticeable differences at a few sites, but there are no consistent variations. Fe was reported to vary considerably in the region west of Calgary by other researchers (Barnes and Ozoray, 1977).

The isotopic data are consistent with temperature variations. As the air temperature gets cooler, the δD values of the water should become more negative relative to the standard. This is seen for most of the sampling sites. The exceptions are sites 10, 11 and 12. These may be due to slight differences in the source of the water at these locations as compared to the rest of the waters sampled. The $\delta^{18}O$ data followed the expected behavior for the waters precipitating at different air temperatures.

A regional plot of the sample information as done for the other parameters failed to show any regional pattern in the changes seen, if any, with the seasons.

5.7. Summary

There are differences in the waters of the reserve based on their chemical and isotopic compositions. Chemical parameters can be used to determine differences between different subsurface units. The shale and sandstone aquifers tend to have high TDS concentrations and the greater range in ion concentrations overall. The surface waters have low TDS and a smaller range in the ion concentrations. The gravels resemble the surface waters most closely, suggesting that they are more directly affected by meteoric and infiltration of surface waters. The subtle differences are not resolvable using simple concentration plots or frequency distribution plots as many of the chemical components have low concentrations.

The deeper aquifers, the sandstone and shale, have higher TDS values and appear more changed by water - rock interactions that will be further examined in Chapter 6.

These processes require more time for the effects to occur, thus the deeper aquifers where the waters take longer to move through them are more likely to be influenced by water - rock dissolution and precipitation reactions.

Consideration of the isotopic data illustrates that the surface and groundwaters are closely related and all are affected by evaporation. None of the waters appear to have been strongly influenced by the bacterial reduction of sulfate, however, oxidation of pyrite may lower the $\delta^{34}S$ values. Carbon isotopes suggest there is mixing between waters from different sources.

Chapter 6

Interaction Between Groundwaters, Surface Waters and Minerals in the Study Area

6.1. Introduction

There are many factors controlling the concentrations of anions and cations in surface and subsurface waters. Weathering reactions, breaking down different bedrock types into other minerals and aqueous species release material to the water (Mather, 1994). As meteoric water filters through the surface soil and unsaturated zone, chemical evolution takes place as it reacts with the soil and aquifer minerals (Mather, 1994). Other mineral-related controls include ion exchange, occurring on clay and clay fractions in streamwaters and subsurface waters, and dissolution and precipitation of minerals. The type of bedrock present is, obviously, the key controlling factor, as all possible reactions are controlled by the initial starting material (Garrels and MacKenzie, 1967; Cleaves et al., 1970).

This chapter considers log-activity plots for dominant ions in the waters. Activity ratios of $Ca^{2+}/(H^+)^2$, $Mg^{2+}/(H^+)^2$, K^+/H^+, Na^+/H^+, $Fe^{2+}/(H^+)^2$ and silica were calculated from water analyses using the SOLMINEQ.88 (Kharaka et al., 1989) aqueous speciation and mineral solubility programme. Overlaying the activity ratios with the mineral stability fields calculated with the PTA programme (Brown et al., 1988) help to illustrate potential mineral reactions and ion exchange reactions that may influence the chemistry of the waters. Iron is not discussed, as the oxidation state of iron in minerals and waters is difficult to determine and many of the thermodynamic properties of iron minerals are not well defined.

6.2. Water Chemistries and Activity Ratios

Ion concentrations in surface waters and groundwaters are controlled by a variety of factors. With the large range for ion concentrations in the sampled waters, simple concentration plots show a greater variation than log-activity plots do. Water-rock interactions tend to influence the composition of groundwaters more than surface waters due to the longer residence time of groundwaters in the subsurface, allowing solute enrichment (Ferguson et al., 1994). If the groundwaters have sufficiently long residence time in the subsurface (time in contact with the rocks and minerals), then there is the increased possibility of interactions between the minerals of the aquifer unit(s) and the groundwaters. These mineral interactions change the ion concentrations in the water. Higher TDS values often imply a greater time in the subsurface, and this is supported by the data presented in the previous chapter, with higher TDS levels associated with the shales and sandstone units, as compared to the surface waters.

The relatively faster ion exchange reactions on clays in the surface waters may be a possible control on the composition of surface waters. More slowly occurring dissolution and reprecipitation reactions and ion-exchange reactions may be more important in groundwaters due to longer residence time for the waters and a lower water/rock ratio than for the surface waters.

All mineral stabilities were calculated using a reaction temperature of 10°C, a reasonable average temperature for groundwaters in the study area, and 1 atmosphere for pressure, as they are all shallow waters. All the reactions were written to conserve aluminum, as aluminum is extremely difficult to measure in fresh waters and the values obtained tend to be inaccurate. In addition to this, Al solubility is very low, so 'open system' behaviour is unlikely. In all cases, plausible minerals for the regional geology have been used, as the minerals considered should reflect possible minerals of the area (Miller and Drever, 1977). These mineral interactions will be presented as possible control factors on the chemical composition of the waters. Following up the water analysis with actual rock samples taken from specific aquifer units, the outcrops around the reserve, sediment from the lakes and reservoirs in the area, and the rocks west of the reserve area would help to confirm the likelihood that the pathways are reasonable and justifiable mineral reaction possibilities and strengthen the argument for a particular mineral pathway as a water chemistry control.

For this study and surrounding area, the observed bedrock compositions are limestones, dolomites, shales and sandstones with minor amounts of siltstone and minor conglomerates (Barnes and Ozoray, 1977). Only reactions among minerals stable at low temperatures are considered as part of this study, as all the waters are shallow and little heating of the waters is likely to have occurred.

6.3. Possible Weathering Patterns

Weathering tends to have a major impact on calcite, as it is very chemically reactive and there is a high rate of physical erosion in mountainous environments (Mast et al., 1990). For the waters of the reserve area, the bicarbonate ion is dominant, evidence that calcite weathering might be contributing to the composition of the waters, as bicarbonate is a byproduct of such weathering.

Limestone weathering would follow the general pattern of

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \tag{6.1}$$

while general dolomite weathering could be written as:

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \tag{6.2}$$

potentially influencing the concentration and activity of Mg^{2+}, Ca^{2+} and HCO_3^-.

Shales tend to weather to clays, albeit indirectly, and shales have high clay contents typically, so weathering is not necessary for clay to be present. Shales often have sufficient reduced sulfur and organic matter that may be oxidized which leads to a production of protons resulting in the dissolution of carbonate in the shale. Thus, sulfide oxidation and carbonate dissolution provide a ready source of Ca^{2+} for ion exchange (Cerling et al., 1989).

Cation exchange on clay minerals during the weathering of shales may occur via reactions such as:

$$(Na^+)_2 - clay + Ca^{2+} = Ca^{2+} - clay + 2\ Na^+ \tag{6.3}$$

Sandstones would likely be the least reactive aquifer material in the thesis area, based on water-rock interactions, because quartz and other silicate minerals tend to be much less soluble and reactive in waters and they are more resistant to weathering.

6.4. Possible Water - Rock Reactions

6.4.1. Log. activity Na^+/H^+ vs. log. activity K^+/H^+

Figure 6.1 shows the best correspondence between measured water compositions and the calculated mineral stability fields, with all waters on or very near mineral stability

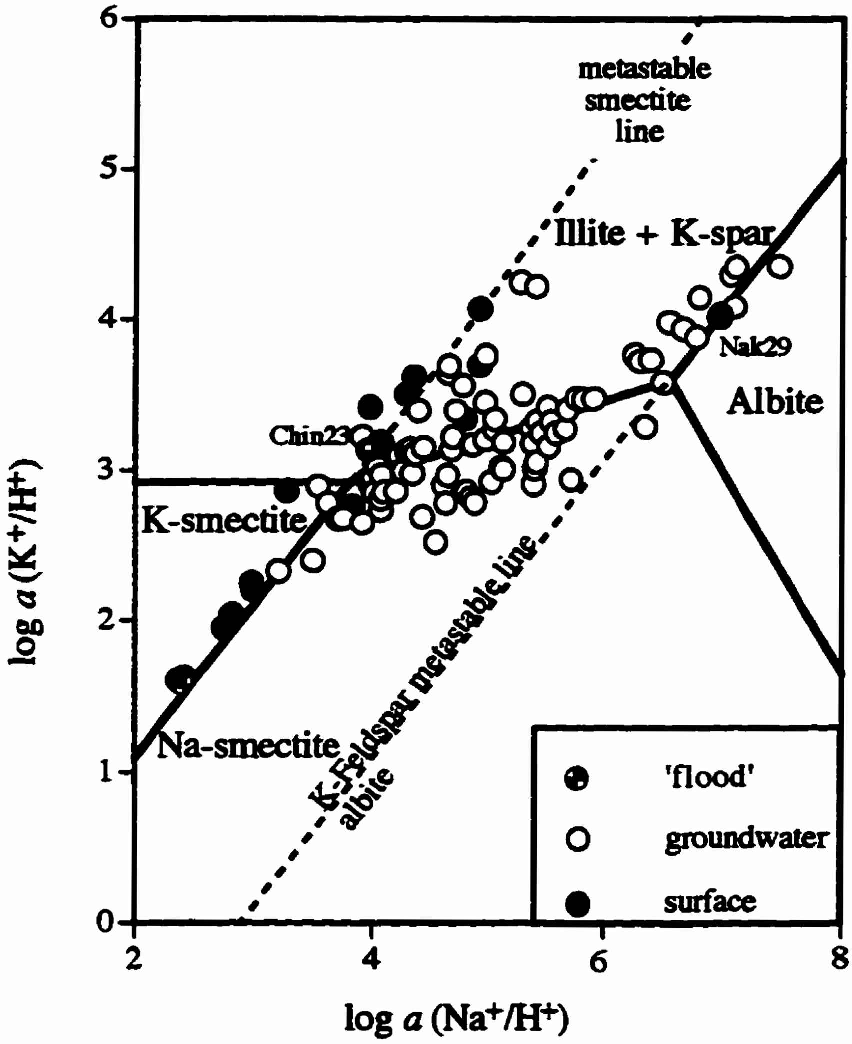


Figure 6.1. Log activity K^+/H^+ vs. Na^+/H^+ with mineral field overlays. Dashed lines indicate metastable reactions at the calculation temperature of 10°C, 1 atmosphere pressure. (Activity Na-smectite is 0.85).

lines. The surface water samples lie along the boundary between the Na-smectite and K-smectite mineral fields. This suggests that ion exchange on smectite may be a controlling factor on the chemistry of the surface waters:

$$3\ Na^+ + 10\ [K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2] = 10\ [Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2] + 3K^+ \quad (6.4)$$

Na^+ and K^+ ion exchange on clay

Short-term changes in soil solution chemistry during snowmelt may also result from the flushing of the byproducts of decomposition and mineral weathering that have increased during the summer and fall in the soils of an area (Arthur and Fahey, 1993). Thus the surface water correlation with ion exchange on clays may be due to changes in the cation exchange capacity (CEC) of the clays, perhaps linked to changes in the surface water acidity conditions.

With their longer residence time in the subsurface, the groundwaters appear to be subject to reactions that require longer reaction times than simple ion exchange reactions. The majority of the groundwater samples lie along the dissolution - precipitation boundaries between illite and K-feldspar, smectite, and albite mineral fields. The reactions represented by these mineral assemblages are:

1) $KAlSi_3O_8 + Na^+ = K^+ + NaAlSi_3O_8$ (6.5)

potassium feldspar + $Na^+ = K^+$ + albite

2) $59\ KAlSi_3O_8 + 34\ [K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2] + 8\ H_20 = 64\ K^+ + 74\ [K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2]$ (6.6)

K-feldspar + illite + water = K^+ + K-smectite

3.) $40\ H_2O + 170[K_{0.6}Mg_{.0.5}Al_{2.3}Si_{3.5}O_{10}(OH)_2] + 295\ [NaAlSi_3O_8] =$

$370\ [Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2] + 184\ Na^+ + 136\ K^+$ (6.7)

water + illite + albite = Na-smectite + Na^+ + K^+

4.) $111\ Na^+ + 40\ H2O + 170\ [K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2] + 295\ KAlSi_3O_8$

$= 370\ [Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2] + 431\ K^+$ (6.8)

Na^+ + water + illite + K-feldspar = Na-smectite + K^+

Equations 6.6 through 6.8 are stable for this pressure and temperature regime for the groundwaters. Activities used to generate the mineral stability plot were 0.95 for K-feldspar (≈ 1 which is the default value and thus the activity used is reasonable). Activity of Na-smectite used was 0.85, based on the best-fit line and would require more rigorous calculations to determine if this value is acceptable.

6.4.2. Log. activity Mg^{2+}/H^{+2} vs. log. activity Ca^{2+}/H^{+2}

The groundwater and surface water activity data plot along a linear trend (Figure 6.2). Two mineral reactions appear to be possible controls on the ion activities in the water:

1) $3\ Ca^{2+} + 20[Mg_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2]$

$= 20\ [Ca_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2] + 3\ Mg^{2+}$ (6.9)

Ca^{2+} and Mg^{2+} ion exchange on smectites:

or

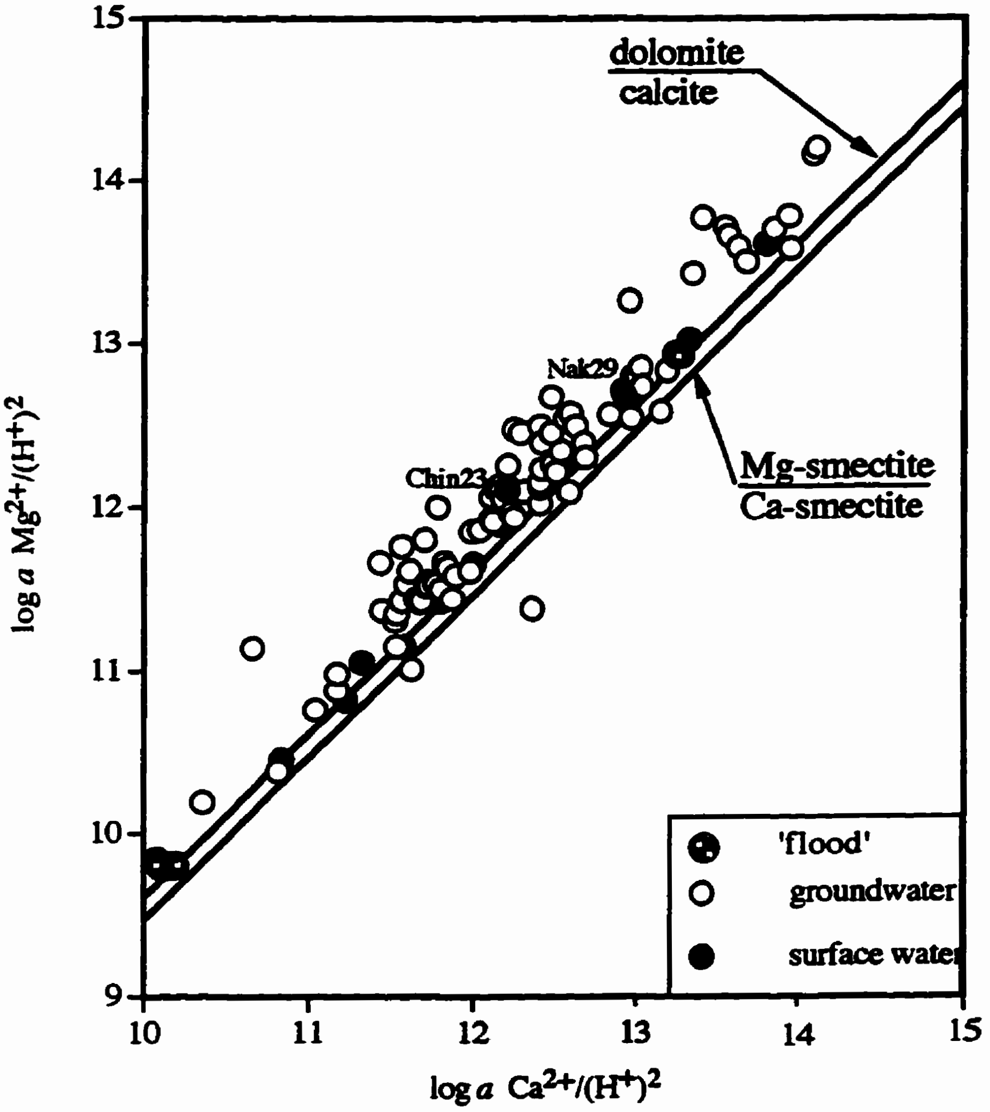


Figure 6.2. Log activity cross plot for $Mg^{2+}/(H^+)^2$ vs. $Ca^{2+}/(H^+)^2$ with mineral stability fields calculated at 10°C and 1 atmosphere pressure. Activity $Mg^{2+} = 0.35$, activity Mg-smectite = 0.60.

2) $CaMg(CO_3)_2 + Ca^{2+} + 2H^+ \;=\; 2\,Ca(CO_3) + Mg^{2+} + 2H^+$

dolomite - calcite dissolution reaction (6.10)

Both reaction choices are reasonable given the mineralogy of the rocks west of the study area. However, the rocks in the region are dominantly carbonates and thus simple dissolution of these rocks could be controlling the calcium/magnesium ratio in the waters. Most waters in this study are saturated with respect to calcite and many are saturated with respect to dolomite.

6.4.3. Other log. activity - log. activity relationships

Other plots examined include $Ca^{2+}/(H^+)^2$ vs. K^+/H^+, $Ca^{2+}/(H^+)^2$ vs. Na^+/H^+, all ion activities vs. $Fe^{2+}/(H^+)^2$ and all ions vs. activity of silica. There are no trends for the data for the Fe^{2+} plots, the $Ca^{2+}/(H^+)^2$ vs. K^+/H^+ and $Ca^{2+}/(H^+)^2$ vs. Na^+/H^+ activity plots. For all activities plotted against log activity silica, the trends are the same as the silica activity, falling in a very narrow range, about $a\ SiO_2 = 10^{-3.5}$ to $10^{-4.2}$ (e.g. act. SiO_2 vs. act. K^+/H^+, Figure 6.3). A best fit line for the surface waters gives a log silica activity of -4.0, while the groundwater samples fit a line with a log silica activity of -3.7 These values are consistent with quartz saturation.

No mineral phases were found that were consistent with the data when examining the activity of Fe. There are several reasons for this: 1. Fe has several possible oxidation states, which are difficult to determine accurately in waters; 2. minerals containing iron tend to be relatively insoluble, thus reactions with waters, particularly at low temperatures are unlikely; 3. Fe is easily affected by small changes in the pH of waters; and 4. the thermodynamic properties of low temperature iron-bearing minerals are not well known.

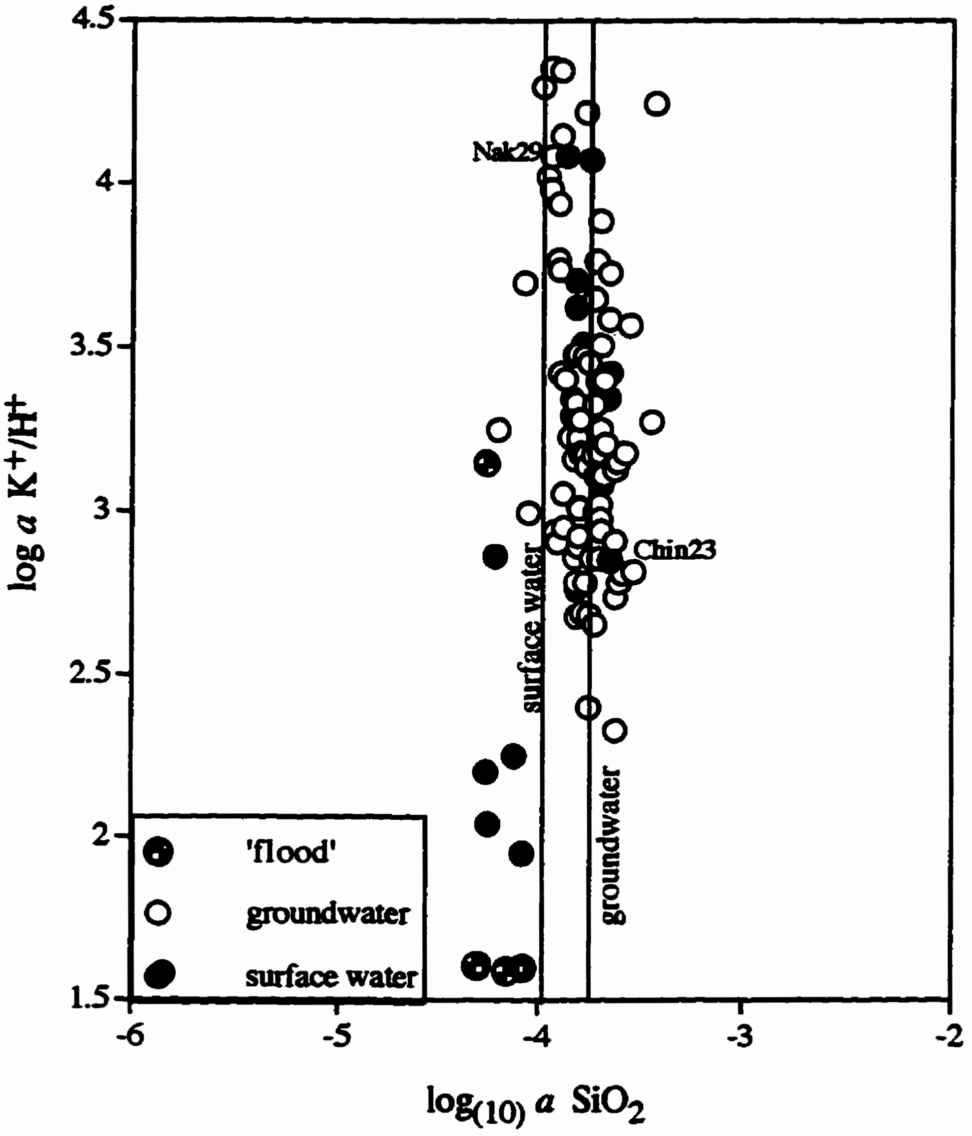


Figure 6.3. Representative activity plot of another ion activity (K^+) against silica activity at 10°C and 1 atmosphere of pressure.

6.5. Summary of Activity Data

The data presented provide an insight into the possible mineral reactions that may be occurring in the study area. As these reactions occur, the ion concentrations in the waters change as some elements are consumed and others released during the reactions. Surface water ion concentrations and activities appear to be controlled primarily by simple ion exchange on clays present in the waters, as seen in the sediment collected on the filters from some of the wells. These reactions can occur very quickly, needing little time to influence the ion levels in the surface waters.

The reactions that appear to contribute to the groundwater ion composition are a mix of quickly-occurring ion exchange reactions and slower mineral dissolution and precipitation reactions. Dominant minerals controlling the Na^+ and K^+ ion activities in the groundwaters are the illite-smectite dissolution and reprecipitation and illite - albite dissolution and reprecipitation reactions. Dissolution and reprecipitation of calcite and dolomite and the Ca^{2+} and Mg^{2+} ion exchange on smectites are both reasonable limits on the waters composition given the regional geology. More information about the detailed mineralogy of the rocks and stream sediments is required before conclusive reactions can be established.

Chapter 7

Discussion and Conclusion

7.1. Introduction

It is often difficult to determine the detailed hydrology of an alpine or subalpine area. The Stoney Indian Reservation represents this type of environment. This study used typically available water chemistry data, synthesising information from well water analyses, drillers' records and Health Canada chemical records to determine the links that exist between the various waters and the subsurface geology. Three main questions were addressed in this study: 1. Can the chemistry and isotope analyses of the water be used to characterise the nature of the subsurface geology? 2. Does the aquifer geology control the quality of drinking water on the reserve? 3. Is it possible to separate the different aquifers the water comes from on the basis of their chemical and isotopic characteristics?

7.2. Drinking Water Quality

Water quality on the reserve is generally good. Two applicable chemical parameters were considered as part of this study: aesthetic objectives (AO), parameters that make the water look or taste unpleasant but are not believed to pose a health risk; and maximum acceptable concentrations (MAC), compounds that have been determined to be harmful above a certain concentration. The nitrate concentration for one sample exceeded the MAC level of 45 mg/L. All other parameters that exceeded the government standards were aesthetic objectives. Many of the parameters that exceed recommended Health Canada concentration standards are associated with waters from shale aquifers.

The Stoney Nation and Health Canada sampled the drinking waters on the reserve for bacteriological data. There appears to be a problem with bacteria in the drinking waters of the reserve, however, how this may be linked to the geology was not able to be determined as part of this study.

7.3. Discussion.

There are several factors that would better define the hydrologic controls on the reserve waters. A sampling programme including taking sediments from the rivers and lakes of the region, in addition to fresh and weathered bedrock around the reserve would better confirm the likelihood of the mineral stability reactions proposed. The identification of weathering products would confirm (or disprove) the possible mineral dissolution - precipitation reactions that are influencing the ionic compositions of the waters in the study area.

A more frequent time series study of the surface and groundwaters would permit a better determination of details of the seasonal changes seen in the waters. In particular, accessing water directly from snowmelt would help clarify the confusion surrounding the changes in the waters associated with the melting snowpack. Good sites for long-term monitoring could include the spring on the north side of Highway 1A as it flows year-round, is easily accessible and has a high flow rate. The Bow River could be sampled up-river from where the Kananaskis River enters the Bow, at the Bow Valley Campground location. A representative group of wells from all three aquifers could be resampled to determine if there are seasonal changes that were not resolvable at the scale of sampling permitted in this study.

Additional information that would better define the groundwater movement in the area could include a short-term study measuring the static water levels of wells. This sort of data collected over a period of a few weeks would provide information about flow regimes and possible local flow patterns and discharge areas.

7.4. Summary

The three main questions posed by this study were addressed. It was determined that the chemistry and isotope analysis of the water can be used to characterise the nature of the subsurface geology An understanding of the possible geology of the aquifers can be determined based on the ion activity ratios in the water. Reasonable minerals likely to influence the ion concentrations in the surface and groundwaters include carbonate rocks containing calcite and dolomite, quartz, clays (the smectites), illite and albite. All these minerals are found in the study area. Surface water K^+, and Na^+ appear to be influenced by ion exchange reactions on smectites, while the groundwater concentrations appear to be more influenced by the dissolution and precipitation stability reactions involving illite, albite and possibly K-feldspar, for K^+ and Na^+, with calcite and dolomite dissolution reactions contributing to the Ca^{2+}, Mg^{2+} and HCO_3^{2-} concentrations and activities in the waters.

The isotopic data indicated that the waters of the reserve are subjected to evaporation, as all the δD vs. $\delta^{18}O$ data plotted in a region that lies parallel to a line with a slope of five, indicating an evaporative trend. Sulfur isotopes had a large variation in their $\delta^{34}S$ values and indicated that the sulfur is primarily derived from the rocks and mineral dissolution in the rocks. The carbon isotopes exhibited a wide range in $\delta^{13}C$ values and were useful in determining the contribution of plant matter to the dissolved carbon of the waters. Both sulfur and carbon isotopes show poor correlation to nutrient levels which suggested that the bacterial activity in the waters was not a major control on the water composition.

Aquifer geology appears to have slight control on the quality of drinking water on the reserve. The aquifer that appears to have the poorest quality of water overall is the shale. The very highest concentrations of Fe^{2+} and Mn^{2+} were from waters in the shales. These waters tend to have the greatest variations of ionic concentrations, and are distributed randomly over the reserve. Extreme differences are seen in the concentrations in very short distances, particularly for Fe^{2+}.

Is was possible to separate the different aquifers the water comes from on the basis of their chemical and isotopic characteristics, albeit on a rudimentary basis The shales and some of the sandstones had much higher TDS values than waters from gravels. The gravels looked more like the surface waters, with low TDS and less variation in the ion concentrations than the shale and sandstone aquifer waters. The groundwaters had higher concentrations of SiO_2, Na^+, Sr^{2+}, Li^+, Mn^{2+}, Fe^{2+}, Cl^- and NO_3^- than the surface waters. The surface waters had higher concentrations of K^+ and PO_4^{3-} than the groundwaters.

7.5. Conclusion

This study confirmed that it is possible to separate surface waters from different aquifer waters based on their chemistry, although the relationship is not always strong The addition of isotopic data facilitated a more complete separation of the waters from the shale, sandstone and gravel aquifers of the reserve. Evaporation and water - rock interactions, particularly between carbonate minerals, accounted for the majority of the isotopic processes affecting the waters. Mineral weathering consistent with the rocks and surficial deposits of the area were found to be possible influences on the ionic composition of the waters.

The waters subjected to the most change in composition were the groundwaters. Further work to be done in this area should include a detailed examination of the bacterial composition of the waters of the reserve, including pathogenic types that affect human health and sulfur reducing bacteria that may control the sulfur isotope composition and the presence of H_2S as a by-product in the waters.

The members of the Stoney Reserve should be assisted to determine if the water quality concerns can be mitigated with appropriate maintenance and monitoring steps. Some simple steps such as iron filters or proper sediment screens or traps may help alleviate many of the problems.

References

Aly, A., Froehlich, K., Nada, A., Awad, M., Hamza, M. and Salem, W.M. 1993. Study of environmental isotope distribution in the Aswan High Dam Lake (Egypt) for estimation of evaporation of lake water and its recharge to adjacent groundwater. Environmental Geochemistry and Health, **15(1)**: 37-49.

Aravena, R. and Sukuki, O. 1990. Isotopic evolution of river water in the northern Chile region. Water Resources Research, **26(12)**: 2887 - 2895.

Arthur, M.A. and Fahey, T.J. 1993. Controls on soil solution chemistry in a subalpine forest in north-central Colorado. Soil Science Society of America Journal, **57**: 1122-1130.

Barnes, R.G. and Ozoray, G., 1977. Hydrogeology of the Calgary - Golden area. Alberta Research Council Report 77 - 2: 38 pp.

Bartarya, S.K., Bhattacharya, S.K., Ramesh, R., and Somayajulu, B.L.K. 1995. $\delta^{18}O$ and δD systematics in the surficial waters of the Gaula river catchment area, Kumaun Himalaya, India. Journal of Hydrology, **167**: 369 - 379.

Bates, R.L. and Jackson, J.A. 1987. Glossary of Geology. American Geological Institute, 788 pp.

Boivin-Jahns, V., Ruimy, R., Bianchi, A., Daumas, S. and Christen, R. 1996. Bacterial diversity in a deep-subsurface clay environment. Applied and Environmental Microbiology, **62(9)**: 3405 - 3412.

Borneuf, D. 1983. Springs of Alberta. Earth Sciences Report 82-3, Alberta Research Council, Edmonton, Alberta: 95 pp.

Bow River Water Quality Council 1994. Preserving Our Lifeline: A Report on the State of the Bow River. Calgary, Alberta: 98pp.

Brenner, K.P., Rankin, C.C., Sivaganesan, M. and Scarpino, P.V. 1996. Comparison of the recoveries of *Escherichia coli* and total coliforms from the drinking water by the MI agar method and the U.S. Environmental Protection Agency - approved membrane filter method. Applied and Environmental Microbiology, **62(1)**: 203 - 208.

Brown, T.H., Berman, R.G. and Perkins, E.H. 1988. PTA-System (Version 2.0). GeO-Calc Software, University of British Columbia.

Cameron, E.M., Hall, G.E.M., Veizer, J. and Krouse, H.R. 1995. Isotopic and elemental hydrogeochemistry of a major river system: Fraser River, British Columbia, Canada. Chemical Geology, **122**: 149 - 169.

Cerling, T.E., Pederson, B.L. and von Damm, K.L. 1989. Sodium-calcium ion exchange in the weathering of shales: Implications for global weathering budgets. Geology, **17**: 552-554.

Cleaves, E.T., Godfrey, A.E., and Bricker, O.P. 1970. Geochemical balance of a small watershed and its geomorphic implications. Geological Society of America Bulletin, **81**: 3015-3032.

Coleman. M.L., Shepherd. T.J., Durham, J.J., Rouse, J.E. and Moore, G.R. 1982. Reduction of water with zinc for hydrogen isotope analysis. Analytical Chemistry, **54**: 993-995.

Craig, H. 1957. Isotopic standards and correction factors for mass-spectrometric analysis of carbon dioxide. Geochemica et Cosmochimica Acta, **133**: 133 - 149.

Craig, H. 1961. Isotopic variations in meteoric waters. Science, **133**: 1702-1703.

Dansgaard, W. 1964. Stable isotopes in precipitation. Tellus, **4**: 436-468.

Davis, J.S. and Keller, H.M. 1983. Dissolved loads in streams and rivers - discharge and seasonally related variations. *in* Dissolved Loads of Rivers and Surface Water Quality / Quality Relationships (Proccedings of the Hamburg Symposium, August 1983). IAHS Publ. No. 141: 79 - 89.

Davisson, M.L. and Criss, R.E. 1993. Stable isotope imaging of a dynamic groundwater system in the southwestern Sacramento Valley, California, USA. Journal of Hydrology, **144**: 213-246.

Denning, A.S., Baron. J., Mast, M.A. and Arthur, M. 1991. Hydrologic pathways and chemical composition of runoff during snowmelt in Loch Vale Watershed, Rocky Mountain National Park, Colorado, U.S.A. Water, Air, and Soil Pollution, **59**: 107-123.

Desjardins, T., Andreux, F., Volkoff, B. and Cerri, C.C. 1994. Organic carbon and ^{13}C contents in soils and soil size-fractions, and their exchanges due to deforestation and pasture installation in eastern Amazonia. Geoderma, **61**: 103-118.

Dethier, D.P. 1988. A hygrogeochemical model for stream chemistry, Cascade Range, Washington, U.S.A. Earth Surface Processes and Landforms, **13**: 321 - 333.

Drimmie, R.J., Aravena, R., Wassenaar, L.I., Fritz, P., Hendry, M.J. and Hut, G. 1991. Radiocarbon and stable isotopes in water and dissolved constituents, Milk River aquifer, Alberta, Canada. Applied Geochemistry, **6**: 381 - 392.

Environment Canada Atmospheric Science Services 1996. Precipitation data for the study area, January, 1995 through July, 1996.

Environment Canada, Surface Water Survey 1996. Water flow data for the Bow River, January, 1995 through July, 1996.

Epstein, S. and Mayeda, T. 1953. Variation of O^{18} content of waters from natural sources. Geochimica et Comochimica Acta, **4**: 213 - 224.

Ferguson, R.I., Trudgill, S.T. and Ball, J. 1994. Mixing and uptake of solutes in catchments: model development. Journal of Hydrology, **159**: 223 - 233.

Fisher, T.G. and Spooner, I. 1994. Subglacial meltwater origin and subaerial meltwater modifications of drumlins near Morley, Alberta, Canada. Sedimentary geology, **91**: 285 - 298.

Garrels, R.M. and MacKenzie, F.T. 1967. Origin of the chemical composition of some springs and lakes. *in* Equilibrium Concepts in Natural Water Systems. American Chemistry Society, Advances in Chemistry Series, **67**: 222 - 242.

Gilvear, D.J., Andrews, R., Tellam, J.H., Lloyd, J.W., and Lerner, D.N. 1993. Quantification of the water balance and hydrological processes in the vicinity of a small groundwater-fed wetland, East Anglia, UK. Journal of Hydrology, **144**: 311 - 334.

Gonfiantini, R., Dincer, T. and Derekoy, A. M. 1974. Environmental isotope hydrology in the Hodna region, Algeria. *in* Isotope Techniques in Groundwater Hydrology. Proceedings of a symposium Vienna, 11 - 15 March, 1974. Vol. 1: 293 - 314.

Grasby, S.E., Hutcheon, I. and Krouse, H.R. (in review) Assessing seasonal variation in meteoric versus groundwater inputs to the Bow River, southern Alberta, using δ^{18}O and δD. submitted to Water Resources Research, April, 1996.

Handfield, M., Simard, P. and Letarte, R. 1996. Differential media for quantitative recovery of waterborne *Aeromonas hydrophila*. Applied and Environmental Microbiology, **62(9)**: 3544 - 3547.

Harrison, R., Swift, R.S., Campbell, A.S. and Tonkin, P.J. 1990. A study of two soil development sequences located in a montane area of Cantebury, New Zealand, I. Clay mineralogy and cation exchange properties. Geoderma, **47**: 261 - 282.

Health and Welfare Canada. 1993. Guidelines for Canadian Drinking Water Quality. Minister of Supply and Services Canada, 24p.

Hitchon, B. and Krouse, H.R. 1972. Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada-III. Stable isotopes of oxygen, carbon and sulphur. Geochimica et Cosmochimica Acta, **36**: 1337 - 1357.

Isaac-Renton, J., Moorehead, W. and Ross, A. 1996. Longitudinal studies of *Giardia* contamination in two community drinking water supplies: cyst levels, parasite viability, and health impact. Applied and Environmental Microbiology, **62(1)**: 47 - 54.

Kemp, A.L.W. and Thode, H.G. 1968. The mechanism of the bacterial reduction of sulphate and of sulphite from isotope fractionation studies. Geochimica et Cosmochimica Acta, **32**: 71 - 91.

Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H. and DeBraal, J.D. 1989. SOLMINEQ.88: A computer program for geochemical modeling of water-rock interactions. U.S. Geological Survey Water-Resources Investigations Report 88-4227, 420 pp.

Klemes, V. 1990. The modelling of mountain hydrology: the ultimate challenge. *in* Hydrology of Mountainous Areas (Proceedings of the Strbske Pleso Workshop, Czechoslovakia, June 1988) IAHS Publication No. 190: 29 - 43.

Konhauser, K.O., Fyfe, W.S. and Kronberg, B.I. 1994. Multi-element chemistry of some Amazonian waters and soils. Chemical Geology, **112**: 155 - 175.

Krothe, N.C. 1982. Sulfur isotopes and the hydrochemical variations as an indicator of flow in groundwater. *in* Isotope Studies of Hydrologic Processes (E.C. Perry Jr. and C.W Montgomery, eds.), Northern Illinois University Press, pp 75 - 82.

Krouse, H.R. 1989. Sulphur isotope studies of the pedosphere and biosphere. *in* Stable Isotopes in Ecological Research (Rundel, P.W., Ehleringer, J.R. and Nagy, K.A eds.) Ecological Studies Volume 68, Springer Verlag New York Inc., U.S.A.

Lico, M.S., Kharaka, Y.K., Carothers, W.W. and Wright, V.A. 1982. Methods of collection and analysis of geopressured geothermal and oilfield waters. United States Geological Survey Water Supply Paper 2194, 21 pp.

Mast, M.A., Drever, J.I. and Baron, J. 1990. Chemical weathering in the Loch Vale watershed, Rocky Mountain National Park, Colorado. Water Resources Research, **26**(12): 2971 - 2978.

Mather, J. 1994. Relationship between rock, soil and groundwater compositions. *in* Geochemical Processes, Weathering and Ground Water Recharge in Catchments, Short Course Notes (Saether, O.M., de Caritat, P. and Sand, K., eds.) Norges Geologiske Undersokelse Report 94.080:

Maule, C.P., Chanasyk, D.S. and Muehlenbachs, K. 1994. Isotopic determination of snow-water contribution to soil water and groundwater. Journal of Hydrology, **155**: 73 - 91.

McCarthy, K.A., McFarland, W.D., Wilkinson, J.M. and White, L.D. 1992. The dynamic relationship between ground water and the Columbia River: using deuterium and oxygen-18 as tracers. Journal of Hydrology, **135**: 1 - 12.

McCrea, J.M. 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. Journal of Chemical Physics, **18**: 849 - 857.

McGregor, C.A. 1979. Ecological Land Classification and Evaluation - Ghost River Study Area. Alberta Energy and Natural Resources Report No. 116: 64pp.

Miller, W.R. and Drever, J.I. 1977. Chemical weathering and related controls on surface water chemistry in the Absaroka Mountains, Wyoming. Geochimica et Cosmochimica Acta, **41**: 1693 - 1702.

Moran, S.R. 1986. Surficial Geology of the Calgary Urban Area. Alberta Research Council, Natural Resources Division, Terrain Science Department Bulletin No. 53: 46pp.

Nowak, R.L. 1984. Report on test drilling programe conducted in the vicinity of Chiniki Village near Morley Alberta (SE-24-25-7W5). Nowak Geological Services Ltd. Balzac, Alberta, 25pp.

Nriagu, J.O., Rees, C.E., Mekhtiyeva, V.L., Lein, A.Y., Fritz, P., Drimmie, R.J., Pankina, R.G., Robinson, R.W., and Krouse, H.R. 1991. Hydrosphere. *in* Stable Isotopes in the Assessment of Natural and Anthropogenic Sulphur in the Environment (Krouse, H.R. and Grinenko, V.A., eds.), SCOPE 43, John Wilet and Sons, Chichester, England: 228 - 244.

O'Leary, M.H. 1981. Carbon isotope fractionation in plants. Phytochemistry, **20**(4): 553 - 567.

Piper, A.M. 1944. A graphical procedure in the geochemical interpretation of water analyses. American Geophysical Union Transactions, **25**: 914 - 923.

Rees, C.E. 1973. A steady-state model for sulphur isotope fractionation in bacterial reduction processes. Geochimica et Cosmochimica Acta, **37**: 1141 - 1162.

Shevalier, M. 1996. personal communication

Silar, J. 1990. Surface water and groundwater interactions in mountainous areas. *in* Hydrology of Mountainous Areas (Proceedings of the Strbske Pleso Workshop, Czechoslovakia, June, 1988) IAHS Publication No. 190: 21 - 28.

Simpson, G. 1996. personal communication

Sklash, M.G. and Farvolden R.N. 1982. The use of environmental isotopes in the study of high-runoff episodes in streams. *in* Isotope Studies of Hydrologic Processes (E.C. Perry and C.W Montgomery, eds.), Northern Illinois University Press, 65 - 74.

Sklash, M.G., Farvolden R.N and Fritz, P. 1976. A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. Canadian Journal of Earth Sciences, **13**: 271 - 283.

Stednick, J.D. 1987. The effects of hydrochemistry variability on water quality sampling frequencies in an alpine-subalpine forest basin. *in* Forest Hydrology and Watershed Management, IAHS Publication No. 167: 401 - 407.

Stevens, T.O. and McKinley, J.P. 1995. Lithoautotrophic microbial ecosystems in deep basalt aquifers. Science, **270**: 450 - 454.

Stiff, H.A. Jr. 1951. The interpretation of chemical water analysis by means of patterns. Journal of Petroleum Technology, **3(10)**: 15 - 16 and section 2, page 3.

Stottlemyer, R. and Troendle, C.A. 1992. Nutrient concentration patterns in streams draining alpine and subalpine catchments, Fraser Experimental Forest, Colorado. Journal of Hydrology, **140**: 179 -208.

Tokarsky, O. 1973. Groundwater availability in the Morley Indian Reserve, Alberta - preliminary evaluation. Alberta Research Council, Open File Report WO1973-18: 11pp.

Udea, A. and Krouse, H.R. 1986. Direct conversion of sulphide and sulphate minerals to SO_2 for isotope analyses. Geochemical Journal, **20**: 209 - 212.

van Donkelaar, C., Hutcheon, I.E. and Krouse, H.R. 1995. $\delta^{34}S$, $\delta^{18}O$, δD in shallow groundwater: tracing anthropogenic sulfate and accompanying groundwater/rock interactions. Water, Air and Soil Pollution, **79**: 279 - 298.

van Everdinger, R.O. 1972. Thermal and Mineral Springs in the Southern Rocky Mountains of Canada. Environment Canada, Water Management Service, Ottawa: 151 pp.

Veizer, J. and Hoefs, J. 1976. The nature of O^{18}/O^{16} and C^{13}/C^{12} secular trends in sedimentary carbonate rocks. Geochimica et Comochimica Acta, **40**: 1387 - 1395.

Wenner, D.B., Ketcham, P.D. and Dowd, J.F. 1991. Stable isotope composition of waters in a small Piedmont watershed. *in* A Tribute to Samuel Epstein (Taylor, H.P.Jr., O'Neil, J.R. and Kaplan, I.R. eds), the Geochemical Society , Special Publication No. 3: 195 - 203.

Williams, M., Kattelmann, R. and Melack, J. 1990. Groundwater contributions to the hydrochemistry of an alpine basin. *in* Hydrology in Mountainous Regions. I - Hydrological Measurements; the Water Cycle (Proceedings of two Lausanne Symposia, August 1990) IAHS Publication No. 193:741 - 748.

Yanagisawa, F. and Sakai, H. 1983. Thermal decomposition of barium sulfate-vanadium pentaoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements. Analytical Chemistry, **55**: 985 - 987.

Yang, C., Telmer, K. and Veizer, J. 1996. Chemical dynamics of the "St. Lawrence" riverine system: δD_{H2O}, $\delta^{18}O_{H2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}S_{sulfate}$, and dissolved $^{87}Sr/^{86}Sr$. Geochimica et Cosmochimica Acta, **60**(5): 851 - 866.

Yonge, C.J., Goldenberg, L. and Krouse, H.R. 1989. An isotope study of water bodies along a transverse of southwestern Canada. Journal of Hydrology, **106**: 245 - 255.

Yurtserver, Y. and Gat, J.R. 1981. Atmospheric waters. *in* Stable Isotope Hydrology Deuterium and Oxygen-18 in the Water Cycle. Vienna, International Atomic Energy Agency Technical Report Series No. 210: 103 - 142.