



RESULTS OF THE JULY 2011 GROUNDWATER CHEMISTRY SAMPLING STUDY ON MAYNE ISLAND, BRITISH COLUMBIA

Final Report

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EXECUTIVE SUMMARY

This study describes the results of synoptic groundwater sampling on Mayne Island in July 2011. It extends previous research conducted in 1975 by R.A. Dakin (Master of Science Thesis, University of Waterloo) on the chemistry of groundwater on Mayne Island.

Water samples were collected in July 2011 from wells volunteered by local residents under the auspices of a joint project between the Mayne Island Integrated Water Systems Society (MIIWSS) and Simon Fraser University (SFU). Water samples were analyzed for dissolved ionic species (i.e., metals and common anions) at Simon Fraser University and are interpreted herein in the context of the local hydrogeology as well as previous groundwater sampling studies (on Saturna, Hornby and Mayne Islands).

Groundwater on Mayne Island is recharged locally. During recharge, the water undergoes evapotranspiration and carbonate mineral dissolution resulting in a composition that is dominated by calcium-bicarbonate ($\text{Ca}-\text{HCO}_3$). Many groundwaters have undergone extensive cation exchange, a process whereby sodium (Na) replaces calcium (Ca) during and following the dissolution of calcite. It is suggested that groundwater flow through fractured mudstone units may be the cause for the high occurrence of cation exchange. Mature groundwaters, characterized by higher concentrations of chloride, result from mixing between the Na-rich groundwater and evolved sulphate (SO_4)-rich seawater.

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1. INTRODUCTION

1.1. BACKGROUND

The Gulf Islands (Figure 1), situated in southwestern British Columbia, support a growing population that is dependent on groundwater as a source of drinking water. For the most part, groundwater supply on these islands is derived wells completed in fractured sedimentary rock aquifers, although surficial sand and gravel deposits accessed by shallow wells provide potable water in some local areas.

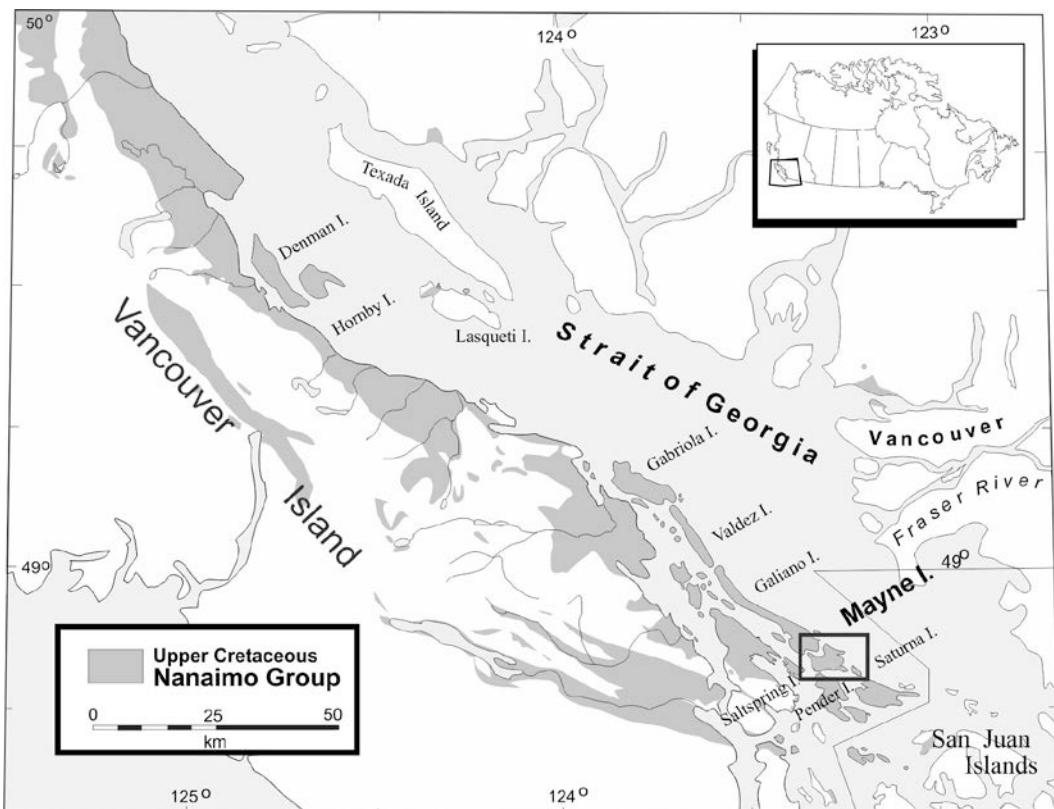


Figure 1: Location map of the southern Gulf Islands, southwestern British Columbia, Canada. Mayne Island is the focus area for this study. Also shown are areas where the Upper Cretaceous Nanaimo Group is exposed.

Development on the islands necessitates an evaluation of the long-term sustainability of groundwater resources. Sustainability of the resource is dependent upon a number of factors including the amount of recharge that is received annually by the aquifers, the geological and topographic complexity of the islands, and the water use patterns. Complicating factors include

high water usage during summer season (the population can triple during summer months), low recharge to aquifers during the summer and early fall, and residential development primarily along the coast. A confounding factor is that these coastal (island) aquifers are also potentially at increased risk of degradation from contamination due to the process of saltwater intrusion. Saltwater intrusion is a process that results in a shift of the interface that exists in a coastal aquifer between “fresh” groundwater and the ocean (Figure 2). Saltwater intrusion is known to be caused by declines in recharge (either natural or through land surface modification) or groundwater extraction. Numerous examples of coastal aquifer salinization are known around the world, and the problem is worsening (Barlow and Reichard, 2010; Bocanegra et al., 2010; Custodio, 2010; Style and Dennis, 2010; Werner 2010).

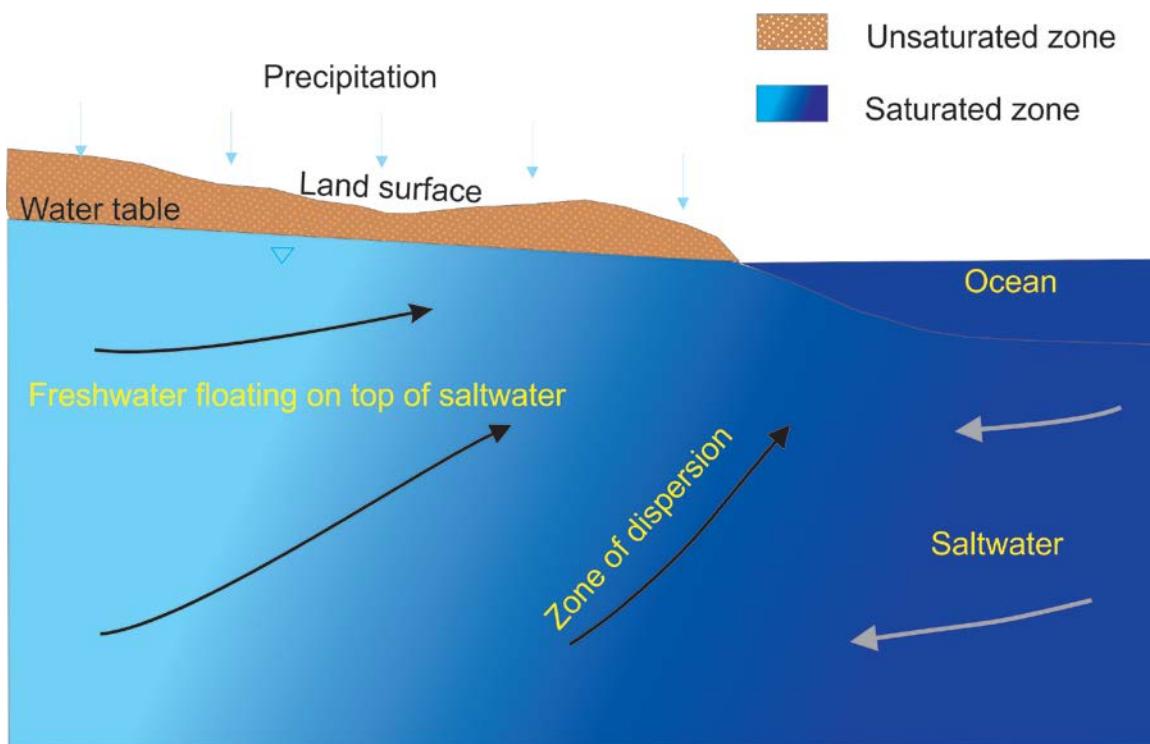


Figure 2: Saltwater-freshwater interface in a coastal aquifer. A zone of diffusion exists between the fresh and saltwater (from Liteanu, 2003).

Typically, only a portion of the total amount of rainfall infiltrates the subsurface and recharges the groundwater system. Numerous studies have aimed to estimate recharge on the Gulf Islands, but values remain highly uncertain (Liteanu, 2003; Appaih-Adjei, 2006). A rough estimate is approximately 20% of annual precipitation (Liteanu, 2003), although spatial and temporal variability can be expected on the basis of climate, topography and geology (Appaih-

Adjei, 2006). Nevertheless, the relatively low values of recharge, particularly during the summer months, present a potential problem, especially in those areas that receive relatively little recharge or where significant volumes of groundwater are extracted. Most natural hydrogeological systems maintain a balance between the amount of recharge, the amount of discharge, and the amount of water retained in storage. If no groundwater is extracted, then the system is generally in dynamic equilibrium (climate factors aside) and water input equals water output. On an island, water input (recharge) is normally limited to the island surface itself (i.e., there are no external sources), and output is to the ocean, surface streams, rivers and lakes. When groundwater is extracted from wells, the result is a shift in the natural balance. If the same amount of recharge is applied, then it can be expected that there will be either a reduction in the amount of groundwater held in storage, a reduction in the baseflow to streams, or a reduction in the amount of groundwater that discharges to the ocean. Reductions in the amount of storage result in a lowering of the water table (as evidenced by wells that run dry, pumps that must be lowered to maintain a yield and the drying up of wetlands). Reductions to stream baseflow¹ can potentially lead to dry streams, and reductions in the amount of ocean discharge can result in saltwater intrusion. Many of these impacts are manifest not only in the quantity of groundwater that is accessible for consumption, but also in the quality of groundwater that is extracted.

Increased coastal residential and recreational development on the Gulf Islands, combined with limited surface water sources, has placed increased demands on groundwater resources. Groundwater extraction in combination with high-density lot development has, in some areas (e.g. East Point on Saturna Island), resulted in unacceptable (with respect to aesthetics and human health) increases in the concentration of total dissolved solids (TDS) measured in groundwater samples (Allen and Suchy, 2001; Lapcevic and Kelly, 2010).

A further layer of complexity that characterizes the Gulf Islands is the presence of fractured sedimentary bedrock aquifers with associated fractures, faults and folds (see Section 1.3). Unlike groundwater flow through unconsolidated sediments, flow through fractured bedrock follows discrete flow paths (Allen et al., 2002). The path taken by water as it flows through bedrock is defined by the fracture aperture, orientation and interconnectedness of fractures that are hosted within the rock. Fracture zones, of which there are many on the Gulf Islands, provide preferential pathways along which water may flow (Mackie, 2002; Surrette, 2006). Because of

¹ Baseflow is maintained by groundwater discharge.

their relatively high permeability, fracture zones are also prime targets for drillers in search of potable water. It is a result of this high directional permeability that serious problems may develop if coastal aquifers are over pumped. Because fracture zones are desirable drilling targets, several wells may tap the same fracture zone if properties are located in close proximity. The combined pumping of all wells may cause seawater to be drawn into all wells in a given area. Thus, over pumping of coastal wells drilled into fractured bedrock can result in significant landward migration of saltwater into an aquifer. The presence of discrete fractures can also be expected to result in neighbouring wells having completely different hydraulic and chemical characteristics, which may complicate the interpretation of spatial data.

1.2. MAYNE ISLAND: THE STUDY AREA

This study was conducted on Mayne Island, one of the outer southern Gulf Islands. Mayne Island is located on the eastside of Active Pass directly across from Galiano Island (Figure 1). Pender Island is to the south across Navy Channel and Plumper Sound, while Saturna Island and the Canada-U.S. maritime boundary is to the southeast. Mayne Island is roughly 21 km² in area and land use is largely agricultural. Mount Parke, in the south-central heart of the island, is its highest peak at 255 m (Figure 3). The average annual rainfall is 828 mm (Environment Canada, 2011). As of 2006, the population of Mayne Island was approximately 1,112 (Statistics Canada, 2006), an increase of 26.4% since 2001. Population also increases seasonally; in particular during the summer as off island residents and tourists arrive. In comparison, Saltspring, Galiano and Saturna Islands have full-time populations of 10,500, 1,258 and 359, respectively (Statistics Canada, 2006).

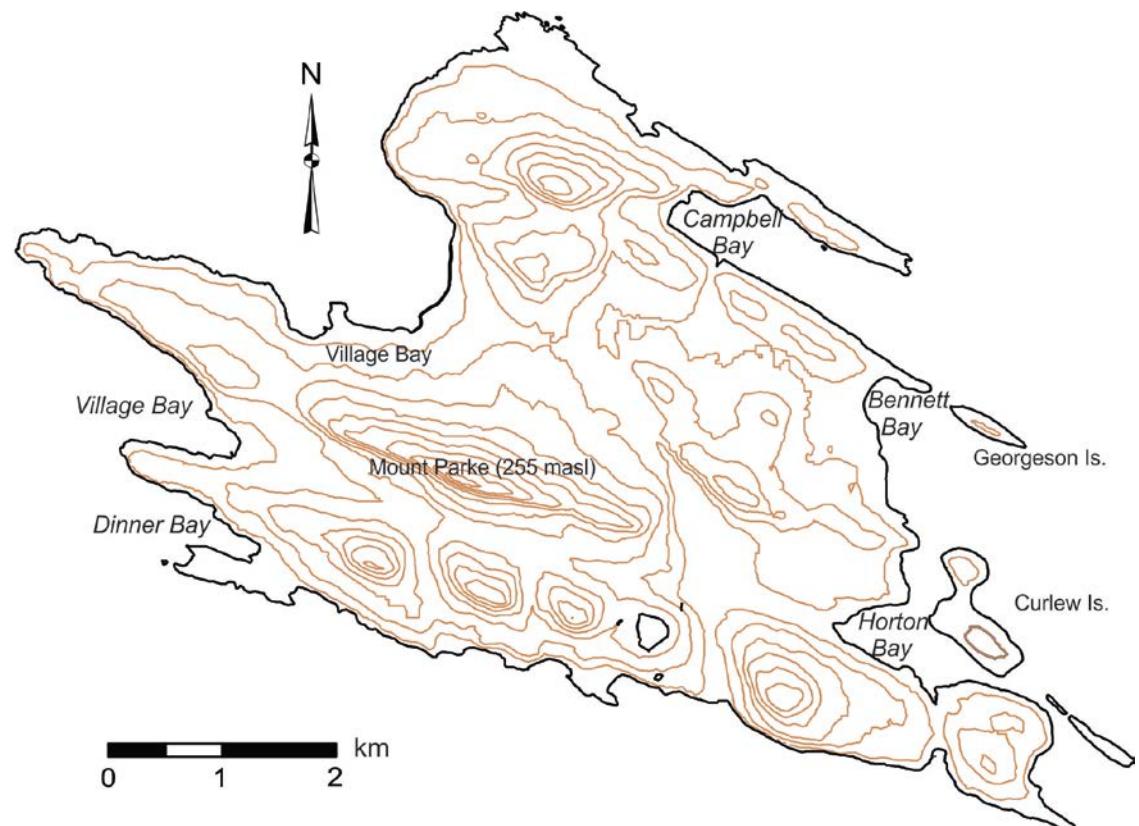


Figure 3: Topography of Mayne Island.

1.3. REGIONAL AND LOCAL GEOLOGY

Groundwater on the Gulf Islands is sourced primarily² from the fractured sedimentary rocks of the Upper Cretaceous Nanaimo Group (extent shown in Figure 1), which consist of alternating interbeds of sandstone, mudstone, and some conglomerate (Mustard, 1994). The primary porosity of the Nanaimo Group rocks is extremely low (<5% estimated from oil and gas exploration wells) (Dakin et al., 1983; England, 1990). Secondary porosity is derived primarily from fracturing that developed when the Nanaimo Group sequence was deformed by compression into a fold and thrust belt (England and Hiscott, 1991; Journeay and Morrison, 1999).

The Gulf Islands host a complex subsurface geological framework that includes numerous faults and fracture zones. Fracturing related to the deformational history is heterogeneously distributed, and has resulted in a complex structural overprint consisting of faults, joints, bedding

² Older metamorphosed igneous and sedimentary rocks are also found in Salt Spring Island.

perpendicular fractures and deformation bands that may be linked to tectonic events (Mackie, 2002). Two main hydrostructural domains have been identified: bedding-perpendicular fractures, and fault / fracture zones (Figure 4). The bedding-perpendicular domain includes two sub-domains: interbedded mudstone and sandstone (IBMS-SS) and less fractured sandstone (LFSS) (Surrette, 2006), which are differentiated on the basis of intensity of bedding perpendicular fractures. The fault zone (FZ) and IBMS-SS domains have been shown to have slightly higher permeabilities relative to the LFSS (Surrette and Allen, 2008; Surrette et al., 2008; Liteanu, 2003).

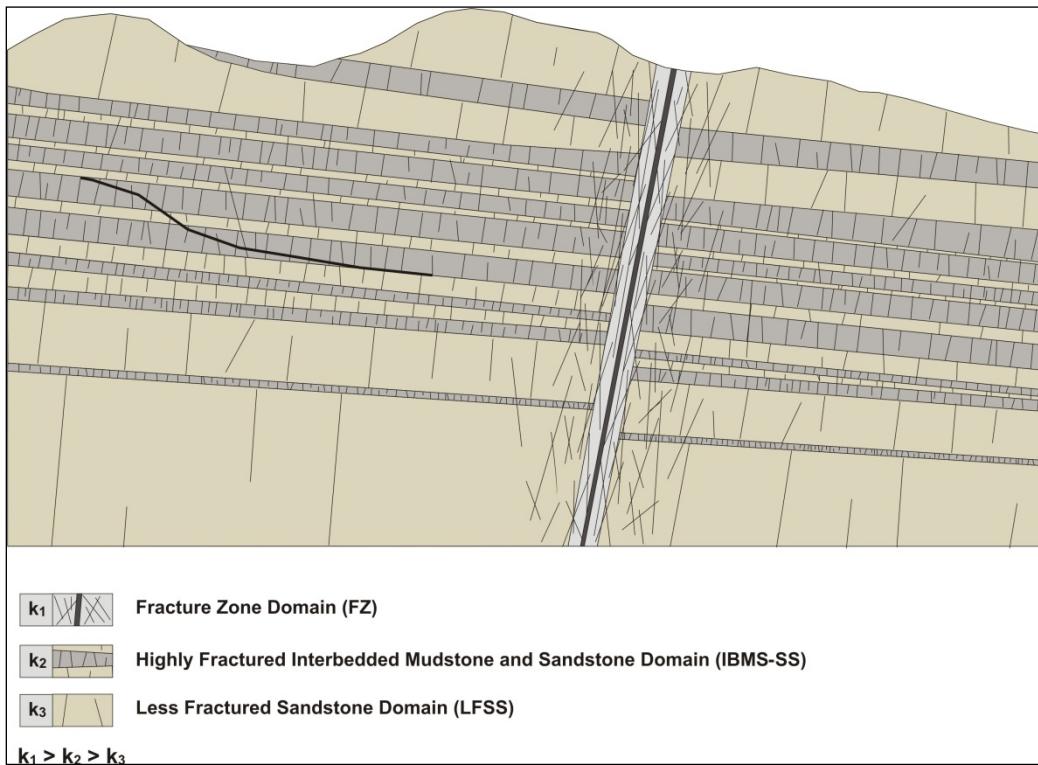


Figure 4: Hydrostructural domains of the Gulf Islands (modified from Mackie, 2002). The k values represent relative permeability.

The sedimentary rocks that comprise the Upper Cretaceous age Nanaimo Group represent the predominant rock types (lithologies; Table 1) that crop out on both the northern and southern Canadian Gulf Islands (Figure 1). The lateral extent of the seven geological formations that underlie Mayne Island (Figure 5) is variable, but well-exposed outcrop is present along most of the coastline. Pockets of surficial sediments are also present. The most recent period of glaciation (Fraser Glaciation, approximately 20,000 years BP) is generally responsible for depositing much of the surficial cover currently observed on the Gulf Islands (Clague, 1986). Due to the ongoing process erosion by wind and water, and mass wasting, much of this

unconsolidated sedimentary cover has been removed, and is only present as a thin veneer on most islands.

Table 1: Lithofacies descriptions of the Nanaimo Group strata examined in this study (after Mustard, 1994) and hydrostructural domain designations. Shaded formations are present on Mayne Island (see Figure 5).

Formation	Description	Hydrostructural Domain
Extension	Clast-supported, moderately to poorly sorted pebble to cobble conglomerate, with medium to coarse grained lithic arenite matrix. Sandstone interbeds present and increase in the upper section of formation	LFSS
Pender	Massive to thin-bedded mudstone and siltstone with interbeds of finely grained sandstone	IBMS-SS
Protection	Primarily medium- to thick-bedded sandstone with interbeds or siltstone	LFSS
Cedar District	Thin bedded silty shale, siltstone and fine grained sandstone which commonly contain carbonate concretions	IBMS-SS
de Courcy	Thick-bedded, medium to very coarse sandstone with fined grained sandstone, siltstone and mudstone interbeds.	LFSS
Northumberland	Silty shale with thin interbeds of very fine grained sandstone and siltstone; Minor thick bedded medium to coarse grained sandstone	IBMS-SS
Geoffrey	Thick bedded, medium to coarse grained sandstone, pebble to cobble conglomerate; Prominent interbeds of shale	LFSS
Spray	Mudstone and siltstone sequences with varying amounts of sandstone interbeds	IBMS-SS
Gabriola	Thick bedded, coarse to medium grained arkosic sandstone with rare laminated silty mudstone interbeds	LFSS

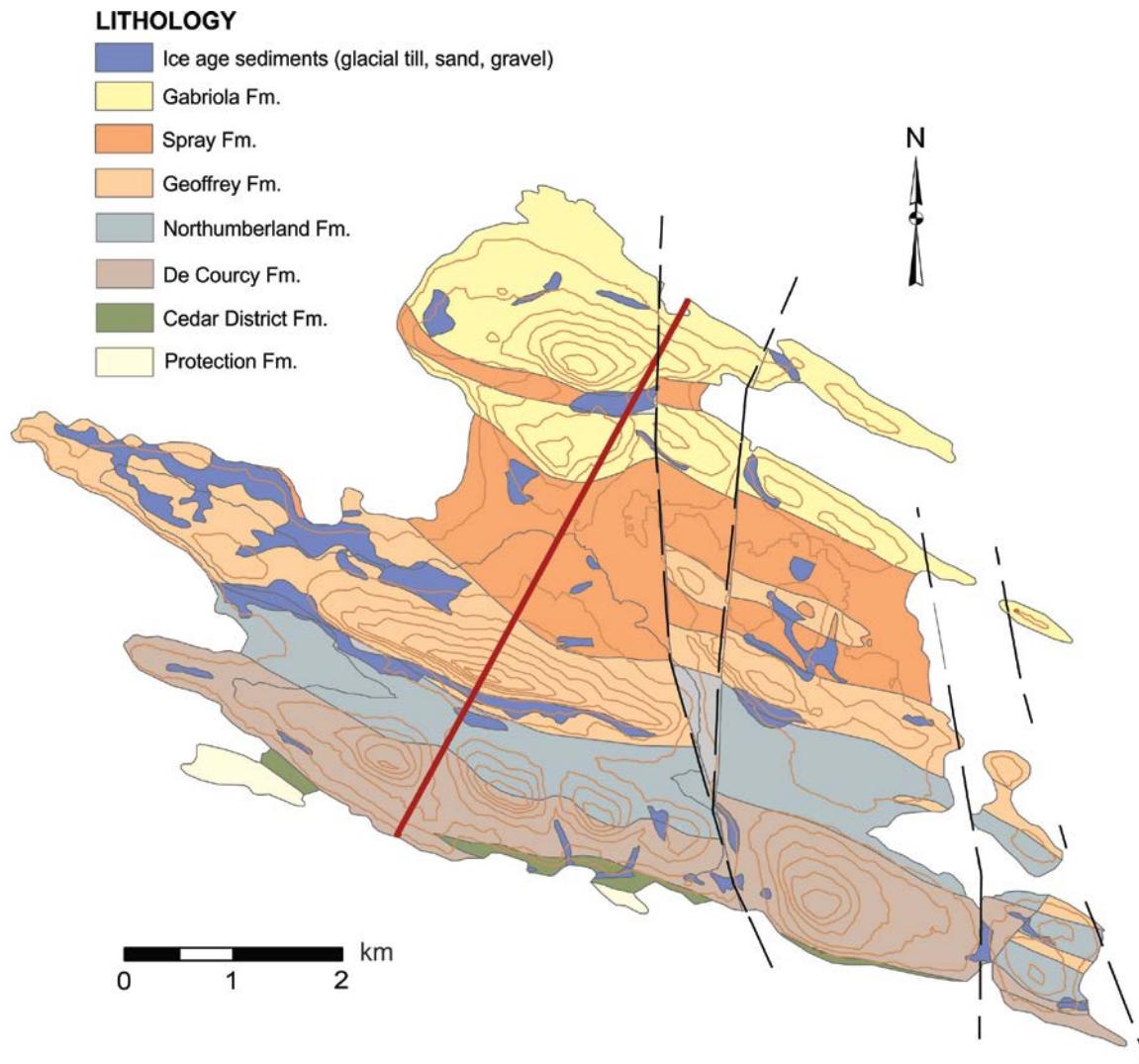


Figure 5: Geology of Mayne Island.

In general, the nature of the bedrock (as well as topography) will have an important bearing on the pattern of groundwater movement and the type of dissolved chemical constituents in groundwater (Section 4.2). Not only does each bedrock type have its own characteristic porosity, and thus, permeability, but each yields to structural deformation (i.e., fracturing) in a different way. The implication is that rock type and structure will have a significant bearing on groundwater flow. In complex geological systems, such as the Gulf Islands, where the rock type alternates between sandstone and mudstone, with transitional zones in between, and where the rocks have been subjected to different stresses associated with tectonic deformation, the groundwater flow patterns can be expected to be complex and difficult to characterize. At best, and without detailed studies on the hydrogeology, it is only possible to describe the overall

geological attributes of the system, infer the general movement of groundwater, and characterize the chemical composition of groundwater based on large-scale trends.

1.4. PREVIOUS STUDIES ON THE GROUNDWATER CHEMISTRY OF THE GULF ISLANDS

1.4.1. MAYNE ISLAND

In the 1970s, a chemical study of groundwaters on Mayne Island was conducted to determine the origin of saline groundwater (Dakin, 1975; Dakin et al., 1983). That study included sampling of a small number of wells and leaching experiments on rock chip samples collected during drilling.

Dakin et al. (1983) proposed four possible origins of saline groundwater based on chemical data for Mayne Island:

1. Soluble salts (such as halite) that are present within the sedimentary strata that now exist in zones of active groundwater flow in the bedrock.
2. Marine water trapped in fractured bedrock strata that are currently raised above present sea.
3. Ocean water intruded into bedrock aquifers under present hydrologic conditions.
4. Formational brines that flow upward from deep (>1000 m) sedimentary zones.

Dakin et al. (1983) concluded that saline groundwater on Mayne Island is of a sodium-chloride (Na-Cl) type, and that salinity is not due to the mixing of deep formation brines or due to dissolution of soluble salts. Rather the presence of Na and Cl was thought to be due to the slow diffusion of these ions through the mudstones from which they appear to be derived³. Active saline intrusion was viewed as being only a minor contributor to the overall Na and Cl concentrations.

³ The leaching experiments on rock cuttings from drilled wells confirmed that the mudstones can leach Cl and Na in the amounts needed to explain the measured pore water salinities.

1.4.2. SATURNA AND HORNBY ISLANDS

In 1997/98, a synoptic groundwater chemistry sampling study was conducted on Saturna Island (Allen and Suchy, 2001a; 2001b). Groundwater (and surface water) chemistry data were used to define the chemical evolution of groundwater on the island. The results indicated that there are basically three water types (in the most general sense) on Saturna: 1) relatively young, fresh (immature) groundwater characterized by a calcium-bicarbonate ($\text{Ca}-\text{HCO}_3$) composition and typically sampled from shallow wells; 2) a more evolved sodium-bicarbonate ($\text{Na}-\text{HCO}_3$) type groundwater, typically sampled from deeper wells; and 3) an evolved sodium-chloride ($\text{Na}-\text{Cl}$) type groundwater, found dominantly on East Point but in other isolated areas of the island. Cation exchange between Ca and Na explained the transition from a $\text{Ca}-\text{HCO}_3$ type water to a $\text{Na}-\text{HCO}_3$ type water, while mixing explained the transition from HCO_3 to Cl (salinization). Two major contributors to salinity were identified: 1) salinity due to mixing of fresh groundwater with saline groundwater resident in the rocks, and 2) salinity due to saltwater intrusion.

Not surprisingly, the two dominant mechanisms proposed are similar to those of Dakin et al. (1983) for Mayne Island. The incidence of saltwater intrusion, however, was prevalent on East Point of Saturna Island. Allen and Matsuo (2002) conducted a similar study on Hornby Island in 2000, largely finding overall similar chemical results.

1.4.3. CURRENT CONCEPTUAL MODEL FOR GROUNDWATER EVOLUTION

Dakin et al. (1983) speculated that the salt in the mudstones on Mayne Island originated as trapped marine water during periods of compaction during deep sedimentary burial in Tertiary time, or as sea water that intruded the sedimentary rocks during episodes of glacial loading and unloading during the Pleistocene when much of the island was submerged below sea level. They proposed that the present flow regime of active flushing of meteoric water (precipitation) through the aquifers began as the island emerged from below sea level at the end of the last glaciation.

The general consistency of groundwater chemistry on the Gulf Islands and its likely evolution prompted Allen (2004) to use stable isotopes of ^{18}O and ^2H in water (and ^{34}S and ^{18}O in dissolved SO_4) to verify more broadly the interpretation of the chemical evolution and proposed sources of salinity for the islands (data for Saturna and Hornby Islands were used). The results

pointed to a meteoric origin for most groundwaters. However, some groundwaters were shown to have different ^{18}O and ^2H isotopic compositions compared to current day meteoric waters, suggesting that the isotopic composition of recharge has varied. Allen (2004) speculated that some groundwaters may have been recharged during a time when it was much colder – likely during the late Pleistocene. Thus, there is isotopic evidence of old groundwaters (perhaps of Pleistocene age) in the aquifers of the Gulf Islands.

An interesting aspect of the groundwater chemistry of the Gulf Islands is that many of the groundwaters appear to be of a Na-HCO₃ type. This begs the question, where did the Na come from and why is there no Cl associated with it if the origin of the salinity is trapped saline water in the mudstones as proposed by Dakin et al. (1983) and supported by Allen and Suchy (2001b). Apart from wells near the coast that have been affected by saltwater intrusion, where did the Cl go?

Allen and Liteanu (2008) proposed that the Na and Cl were emplaced in the rocks during the late Pleistocene when the islands were submerged below sea level (one of the hypotheses of Dakin et al. 1983). Following isostatic rebound, meteoric waters began to flush the aquifers, removing the mobile Cl, but leaving the less mobile Na sorbed onto the clay particles of the mudstones. Over time, this fresh infiltrating water with a Ca-HCO₃ composition, has undergone cation exchange, gradually stripping the Na from the mudstones and giving it a Na-HCO₃ composition. Therefore, many of the groundwaters on the Gulf Islands have this composition, particularly at depths where all the Na has not been stripped off of the clay exchange sites. In some cases, this Na-rich water mixes with a Cl-rich water, either because the well is near the coast or perhaps because some remnant Cl remains in the rock. In actively flushed parts of the islands, where groundwater recharge is rapid (as would be the case near fracture zones), likely there is little Na left on clay exchange sites, and the water remains fresh, with a Ca-HCO₃ composition.

Liteanu (2003) tested the hypothesis concerning emplacement of Cl during submergence and the subsequent flushing of Cl following isostatic rebound. She showed, through modeling, that the groundwater chemistry observed today is consistent with a saltwater-freshwater interface that has varied according to the sea level history since the end of the Pleistocene. There was sufficient time during the brief period of submergence to emplace seawater in the aquifer, and there has been sufficient time to flush most of this older Cl from the aquifers.

Notwithstanding this interesting history of the evolution of groundwater on the Gulf Islands, there remain problem areas where the salinity is not related to a past period of island submergence and emergence. Areas that tend to have a higher incidence of saltwater intrusion (characterized by high Na and Cl compositions, among other constituents characteristic of seawater) are generally located near the coast, as might be expected, but particularly in areas where the topography is relatively flat (e.g., East Point on Saturna, Whaling Station Bay on Hornby). Where the topography is flat, there is only a small hydraulic gradient (and a small flux of groundwater) to literally push the saltwater interface seaward. Thus, low topography areas are particularly vulnerable to saltwater intrusion. Excessive pumping exacerbates the problem by drawing seawater inland.

1.5. PURPOSE

The purpose of this groundwater chemistry study on Mayne Island was to provide a benchmark set of data for future studies aimed at tracking changes in groundwater quality. Concern has been raised by members of the community, specifically the Mayne Island Integrated Water Systems Society (MIIWSS), about the potential for saltwater intrusion. A monitoring program is being proposed and the current study provides a synoptic (one time) view of the status of groundwater quality in wells distributed around the island.

1.5.1. STUDY OBJECTIVES

1. To acquire representative samples of groundwater for Mayne Island and to assemble a chemical database.
2. To interpret these data both within the context of previous data collected on Mayne Island (by Dakin et al., 1983) but also within the context of the proposed evolution of groundwater within the Gulf Islands region.

1.5.2. SCOPE OF WORK

The specific tasks undertaken as part of this study included:

1. Collecting groundwater samples from a representative number of appropriately distributed

- sample locations.
2. Analyzing the samples for major ion chemistry, and generating a geochemical database.
 3. Interpreting the geochemical data using a variety of chemical plotting tools.

1.6. OUTLINE OF THE REPORT

Section 1 of this report summarized the context and previous research, and the objectives of the study. Section 2 presents an overview of the methodology and results of the groundwater chemistry study on Mayne Island. Section 3 offers a brief discussion of the results, making linkages to previous studies in the Gulf Islands region. Appendix A includes a hard copy of the analytical results.

2. GEOCHEMISTRY: METHODOLOGY AND RESULTS

2.1. DATA COLLECTION

Thirty-four (34) water samples were collected during a field visit to Mayne Island in July 2011. These samples were collected from private and community wells volunteered for the study. Permission to sample was obtained by each resident and/or person responsible. Due to the inherent variability in the plumbing setup at each well, it was generally not possible to collect a sample before the water had passed through the pressure tank, but the water was allowed to flow for a minimum of 15 minutes to ensure that the fresh groundwater was flowing through the line. Stabilization was monitored using a series of physical/chemical parameters (pH, Eh (oxidation-reduction potential), DO (dissolved oxygen), temperature, EC (electrical conductivity)) measured in a flow through cell. When necessary, samples were collected after filtration systems. The locations of all samples are shown in Figure 6.

Field measurements of pH, Eh, DO, temperature and EC were recorded just prior to sampling (Appendix A). The field parameters were measured using Orion 3-Star and 5-Star temperature-compensated portable meters. Total alkalinity, measured by titration, was determined immediately upon collection of the sample. Several titrations for total alkalinity were done to ensure precision. The average alkalinity value is reported in Appendix A.

Samples were collected in 60 and 125 ml high-density polyethylene (HDPE) bottles. Metal samples were acidified to a pH of approximately 2 using measured aliquots of ultra pure nitric acid. Anion samples were not preserved but were kept cool (at approximately 4°C) in environmental coolers. Sample collection and preservation protocols for this project are in accordance with the guidelines outlined in ASTM Standards on Environment Sampling (1994). Detection limits for all analytical equipment used are summarized in Appendix A.

Analysis of major and minor components in well water samples was conducted at the groundwater chemistry laboratory at Simon Fraser University. Samples were analyzed for concentrations of anions (F, Cl, Br, NO₃, PO₄, SO₄) using a Dionex ICS-3000 SP Ion Chromatography System (IC) and for concentrations of major (Na, K, Ca, Mg, Fe) and minor (Al, As, B, Ba, Li, Mn, Mo, Si, Sr, Zn) elements using a Horiba Jobin Yvon Ultima 2 Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES).

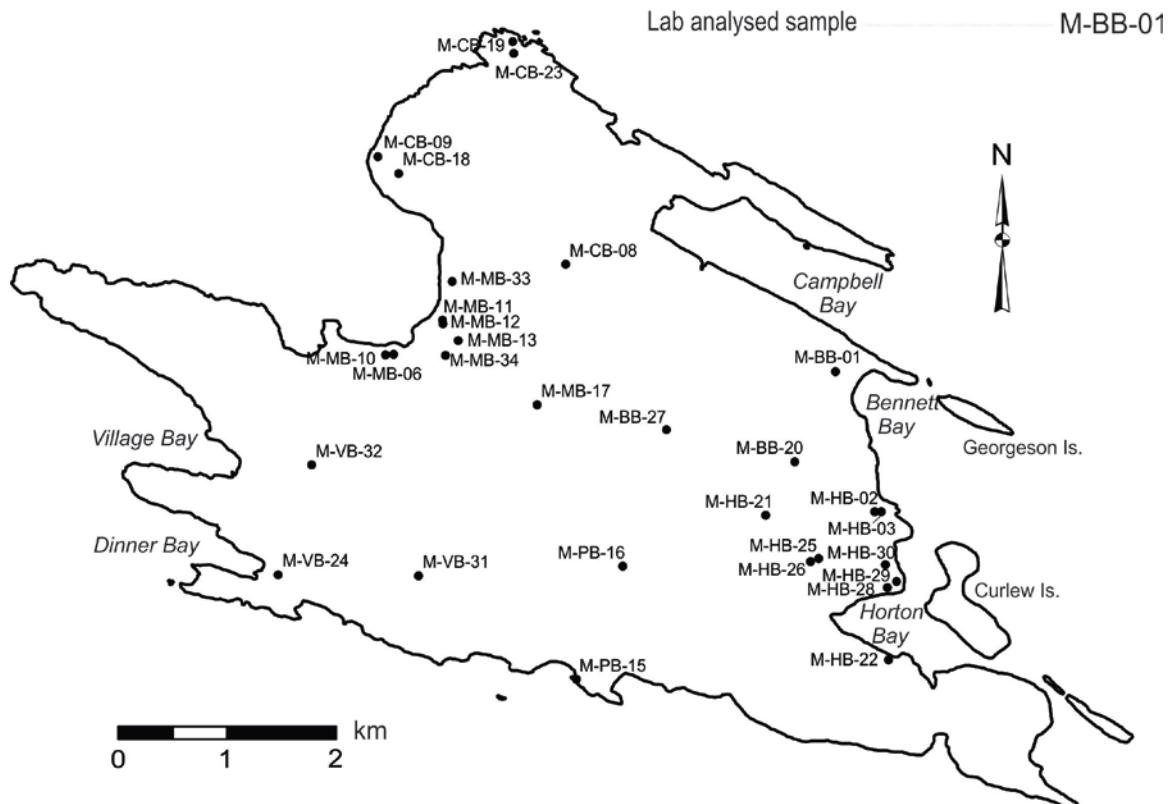


Figure 6: Sampling locations for groundwater.

Two control samples were collected for this study. C-1 is the field blank that was obtained by passing distilled water through the field equipment (beakers used for collection of field samples). C-1 was used as a check for both laboratory accuracy and proper field equipment rinsing procedures. A second control blank (C-2) of distilled water was also analyzed (i.e., one that represents the distilled water itself without having been put through the field sampling procedure). Both of these control samples indicate field contamination was minimal.

2.2. DATA ANALYSIS

Results of the analyses were entered into Microsoft Excel (2010), AquaChem v. 10 (Waterloo Hydrogeologic Inc., 2010), and PHREEQC (Parkhurst and Appelo, 1999) for generating plots used for geochemical interpretation and calculating chemical speciation and saturation indices.

Piper plots are particularly useful for showing the relative concentrations of different major dissolved species. To construct a Piper plot, the relative concentrations of three cations and three anions (expressed in milliequivalents) are calculated. Typically, Ca, Mg and Na are the cations, and HCO₃, Cl and SO₄ are the anions, although other combinations may be useful for different types of studies. For each sample, the cation composition is plotted on the left triangle and anion composition on the right, and the sample points are projected onto the diamond. Bivariate plots (or scatter plots) show the relative concentrations of two constituents for different samples. These plots are useful for visualizing trend in the data, and for illustrating key groundwater evolutionary processes. PHREEQC is a solution and chemical equilibrium software program that can be used to calculate chemical speciation (including the carbonate speciation, which is of primary importance to this work), charge balance errors, the saturation indices for various minerals, and the re-adjustment of the solution equilibrium to field conditions.

2.2.1. CHARGE BALANCE ERROR

Another important calculated value that must be considered is the charge balance error (CBE) (Freeze and Cherry, 1979):

$$CBE = \frac{\sum zm_c - \sum zm_a}{\sum zm_c + \sum zm_a} \times 100 \quad (1)$$

where z and m represent the ionic charge and molality (defined as moles/kg), respectively, of each ionic analyte. The charge balance error is one method used to assess the integrity of a sample's analysis because all solutions should be electrically neutral. For an analysis to be considered "good" it should fall in the range of $\pm 5\%$. No samples in this study had CBEs greater than $\pm 5\%$ (Table 2). High CBEs may indicate a problem with the lab analysis, or that one or more ions present were not analyzed. The absence of a given ion will result in an increase or decrease in CBE depending on the concentration of the missing ion and on its associated ionic charge. If an ion with a high concentration and ionic charge is not included in the analysis, then the associated CBE will be large. On the other hand, if an ion with a low concentration and low ionic charge is missed in the analysis, then the associated impact on CBE will be small. As such, it is very important to capture the dominant ionic species in a sample. Another consideration is that for samples with low concentrations of dissolved species, the effect of a small error in concentration is amplified.

Table 2. Charge Balance Error (CBE) summary of samples.

Sample ID	CBE %	Sample ID	CBE %	Sample ID	CBE %
M-BB-01	-0.94	M-MB-13	-2.33	M-VB-24	-0.45
M-HB-02	-1.17	M-PB-14	-0.88	M-HB-25	-2.34
M-HB-03	-0.66	M-PB-15	-2.57	M-HB-26	-2.80
M-MB-04	-1.05	M-PB-16	-1.37	M-BB-27	-3.00
M-MB-05	-2.00	M-MB-17	-3.64	M-HB-28	0.81
M-MB-06	-1.74	M-CB-18	-2.76	M-HB-29	-2.36
M-MB-07	0.13	M-CB-19	-3.56	M-HB-30	-0.20
M-CB-08	0.46	M-BB-20	-4.61	M-VB-31	0.55
M-CB-09	-3.06	M-HB-21	-3.44	M-VB-32	0.63
M-MB-10	-4.17	M-HB-22	-1.61	M-MB-33	-2.56
M-MB-11	-2.86	M-CB-23	-2.49	M-MB-34	-1.71
M-MB-12	-1.73				

* note – CBE recalculated from initial data release

The following is a summary of the analytical lab results obtained during this study and the interpretation of those results. The raw lab results were processed using AquaChem® and then partitioned into groups based on the location from which samples were collected.

2.3. RESULTS

The composition of groundwater on Mayne Island is variable. Three distinct compositions can be identified using the Piper plot (Figure 7):

- 1) Chemically young (immature) groundwaters, which plot in the middle left portion of the diamond diagram of the Piper plot;
- 2) Chemically more evolved groundwaters, which plot near the bottom of the Piper diamond; and
- 3) Evolved (mature) groundwaters, which plot more towards seawater.

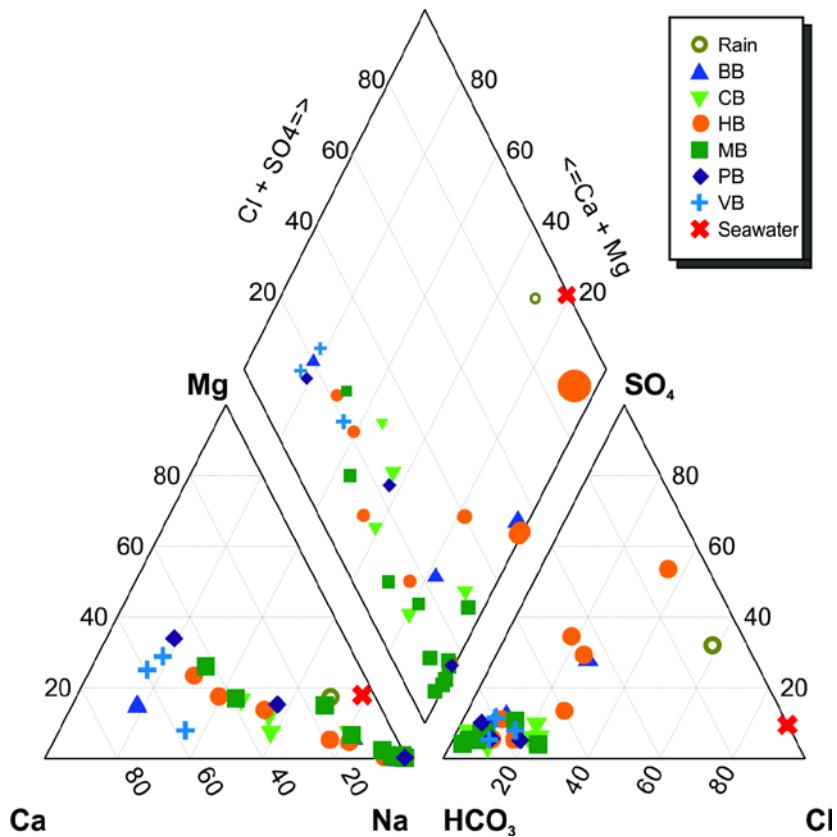


Figure 7. Piper plot of Mayne Island groundwater samples. Symbol size on the diamond is proportional to the electrical conductivity (except seawater).

A number of samples have an intermediate composition, and plot between these type waters. The position of these samples on the Piper plot reflects the relative impact of the dominant physical/chemical processes that define the three groups identified in the plot. In addition to their different plotting positions, which reflect the compositions of the samples, these samples have significant differences in measured field parameters and total concentrations of dissolved species. The symbols shown in the diamond diagram of the Piper plot (except that for seawater) are proportional to the electrical conductivity (and thus how salty the water is). The salinity increases from the chemically immature through the chemically more evolved to the evolved groundwater. The processes by which the groundwater chemistry evolves, which are reflected in the compositions of intermediate groundwater, are described under Mayne Island Groundwater Evolution (see Section 4.0).

Chemical anomalies, involving elevated levels of dissolved species such as manganese (Mn), arsenic (As), boron (B), fluoride (F) and sulphate (SO_4^{2-}), are summarized separately.

2.3.1. CHEMICALLY IMMATURE GROUNDWATER COMPOSITIONS

Chemically immature groundwaters were sampled from wells in the Village Bay, Piggott Bay and Bennett Bay regions. These wells were completed over a range of depths (i.e., from dug, shallow, mid-depth and deep wells). In general, these waters have the lowest pH, electrical conductivity (EC), total alkalinity, and major ion concentrations. The pH ranges from 5.5 to 7.7, and they are predominately Ca-HCO₃ type waters with Ca ranging from 37.5 to 55 mg/L, and with varying but lower amounts of Mg and Na. Total alkalinity ranges between 56 and 250 mg/L (as HCO₃⁻), while EC ranges between 136 µS/cm and 450 µS/cm. The composition is significantly different from that of average rainwater in the region (which plots on the opposite side of the Piper plot).

2.3.2. CHEMICALLY MORE EVOLVED GROUNDWATER COMPOSITIONS

From the chemically immature groundwater there is a transition to a more evolved groundwater composition which is dominated by Na-HCO₃. Most of the wells of this type are from around Miners Bay and are greater than 50 m deep. The samples are characterized by relatively high pH (7.2-9.4), EC (400-700 µS/cm) and alkalinity (300-375 mg/L HCO₃). Major cation concentrations are highest for Na, followed by Ca and Mg. Na varies from 113 to 146 mg/L, Ca varies from 0.5 to 5.9 mg/L and Mg varies from 0.02 to 1.4 mg/L.

2.3.3. EVOLVED GROUNDWATER COMPOSITIONS

The highly evolved groundwater composition is dominated by a Na-SO₄-Cl type. The composition is similar to seawater, but with a higher relative sulphate content. Only one well has a composition that clearly identifies it as highly evolved; however, several more fall on compositional trends that indicate the groundwater is impacted by the process resulting in this chemistry. Most of the wells that show some indication of the highly evolved composition are from around Horton Bay and inland from the southern end of Bennett Bay. All of the samples but one have high pH (>8.5), an EC range from 594-5230 µS/cm and generally high alkalinity (317-478 mg/L HCO₃). Sodium is the dominant cation, while Ca and Mg are typically low except for in the most saline sample.

2.3.4. ANOMALOUS CONCENTRATIONS

In order to examine the occurrence of anomalous concentrations of dissolved species, it is necessary to define acceptable limits. For the purposes of this study, the Canadian Drinking Water Guidelines are used for comparison. While incomplete in many respects, these guidelines offer the only means for assessing water quality. Table 3 shows the Canadian Drinking Water Guidelines and the United States Drinking Water Guidelines. Several constituents have no reported limit. It is important to note that most chemical constituents considered in this study were analyzed at detection limits that are lower than those reported in the Drinking Water Guidelines. For example, the minimum detection limit (MDL) for F (Table 3) is 0.01 mg/L and the guideline indicates that concentrations less than 1.5 mg/L are acceptable. Therefore, consideration should be given to the MDLs when evaluating anomalous concentrations of dissolved species.

- Four samples have fluoride concentrations in excess of those outlined in the Canadian Drinking Water Guidelines. Three of the four are from the highly evolved groundwater grouping. See the BC Ministry of Environment Water Stewardship Information Series (http://www.env.gov.bc.ca/wat/wq/wq_guidelines.html).
- Two samples have arsenic in excess of the Drinking Water Guidelines. See the BC Ministry of Environment Water Stewardship Information Series (http://www.env.gov.bc.ca/wat/wq/wq_guidelines.html).
- Three samples have boron in excess of the Canadian Drinking Water Guidelines. See the BC Ministry of Environment Water Stewardship Information Series (http://www.env.gov.bc.ca/wat/wq/wq_guidelines.html).

In addition Cl, SO₄, Fe, Mn and Na were found to exceed the aesthetic or operational objectives set in the Canadian Drinking Water Guidelines for a number of samples. See the BC Ministry of Environment Water Stewardship Information Series (http://www.env.gov.bc.ca/wat/wq/wq_guidelines.html).

Table 3: Range of concentration for dissolved constituents and number of samples above the Canadian Drinking Water Guidelines.

Dissolved Constituent	Drinking Water Guidelines (DWG) (mg/L)	Detection Limit (mg/L)	Range	# Samples above DWG
Fluoride	1.5	0.01	0.067 – 3.00	4
Bromide		0.01	<0.01 – 0.27	
Chloride	<=250^a	0.1	6.2 - 643	1
Nitrate	45	0.01	<0.01 - 0.82	
Sulphate	500 ^a	0.1	5.9 - 1326	1
Aluminum		0.001	<0.001 - 0.092	
Arsenic	0.01	0.002	<0.002 - 0.031	2
Barium	1	0.001	<0.001 - 0.27	
Boron	5	0.001	0.024 - 10.9	3
Calcium	200 ^a	0.1	0.5 – 65.3	
Iron	0.3^a	0.001	0.002 – 4.98	4
Magnesium	50 ^a	0.01	0.02 – 19.9	
Manganese	0.05^a	0.0001	0.001 – 0.32	12
Molybdenum		0.001	<0.001-0.002	
Phosphorous		0.1	<0.1 – 0.39	
Potassium		0.1	<0.1 – 6.5	
Silica		0.01	8.9-42.4	
Sodium	200^a	0.1	10.3 - 1104	4
Strontium		0.001	0.007 – 2.53	
Zinc	5	0.001	0.017 – 0.17	

^a – aesthetic or operational objective

3. DISCUSSION

3.1. MAJOR GEOCHEMICAL PROCESSES

There are four major natural processes that commonly contribute significantly to the chemistry of groundwater. These processes may act alone, but are more commonly observed to work in concert with one another:

- 1) Evaporation/evapotranspiration
- 2) Dissolution/precipitation of minerals
- 3) Cation exchange
- 4) Mixing

3.1.1. EVAPORATION / EVAPOTRANSPIRATION

Evaporation and/or transpiration of rainwater are very common processes that impact the composition of recharge to a groundwater system. Evaporation involves transitioning rainwater that is at the ground surface or near to the ground surface in the soil horizon from a liquid to vapour phase. Transpiration is the result of plants extracting water from the soil horizon through their roots to be used in photosynthesis. Both have the same result in that the residual water becomes more salty. However, it has to be kept in mind that rainwater starts out at very low salinity so it takes a lot of evaporation or transpiration (evapotranspiration) to have a significant effect. Usually the best way to assess the extent of evapotranspiration is to compare the Cl content of the samples with that of the rainwater. If other processes such as mixing with saltier water or dissolving of halite have not occurred, then the change in Cl reflects the amount of evapotranspiration that has taken place. Normally evapotranspiration results in an overall increase in the dissolved ions with no change in their relative amounts, so on a Piper diagram, there would be no change in the composition from the original input water it would just have a higher electrical conductivity.

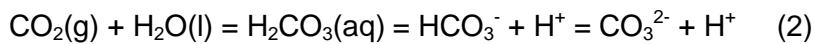
The Mayne Island groundwater samples show a range in Cl (6.2 to 643 mg/L). The average Cl content of the rain water at Saturna Island is 1.5 mg/L. The majority of the groundwater samples that are chemically immature or chemically more evolved have total Cl of 6.2 to 20 mg/L, suggesting that evapotranspiration may have concentrated the rain water by a factor 4 to 13 times. On the Piper diagram the groundwater composition is significantly altered from that of the rain water, so in addition to evapotranspiration, there must be some additional process

impacting the groundwater chemistry.

3.1.2. DISSOLUTION OF MINERALS: WITH CONSIDERATION OF THE CARBONATE SYSTEM

Chemical weathering of rock by water results in the liberation of numerous dissolved ion species (e.g., Na^+ , Ca^{2+} , SiO_2 , HCO_3^- and SO_4^{2-} ...). It is by this process that a relatively juvenile surface/soil water composition gradually becomes enriched in total dissolved solids. The rate and degree to which enrichment occurs is dependent on a number of factors including: 1) the solubility of the minerals present, 2) the temperature and pH of the water, 3) the amount of surface area available for the water to react with minerals comprising the aquifer (fractured rock in the case of the Gulf Islands), and 4) the amount of time that the water is in contact with the minerals (i.e., the residence time). One of the main drivers of chemical weathering is carbon dioxide (CO_2) which is sourced from the atmosphere and from the decay of organic material in the soil horizon and sediments. This makes understanding the controls on the CO_2 content especially important when we are trying to understand the factors that are impacting groundwater quality in a particular region.

Carbon dioxide and carbonate equilibria exercise a dominant control on the evolution of groundwater. Carbonate equilibria pertain to the complex interplay between CO_2 (gas), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) in aqueous solution. These species are related to each other by the following equation:



which shows that there is a strong relationship between the concentration or fugacity (f) of CO_2 (g), the pH and the amount of HCO_3^- and CO_3^{2-} present in a groundwater. The availability of CO_2 (i.e., as measured by the partial pressure of CO_2 ($p\text{CO}_2$)) dictates whether or not a groundwater evolves under open or closed conditions. $p\text{CO}_2$ for the atmosphere is $10^{-3.5}$ Bar, while $p\text{CO}_2$ is slightly higher in the soil horizon due to the production of CO_2 , and is generally about $10^{-1.5}$ Bar.

Open system evolution of groundwater involves a constant source of CO_2 during dissolution of mineral species, while closed system evolution involves the eventual isolation of a groundwater from a source of CO_2 . Open system conditions result in a moderate increase in HCO_3^- with a small increase in pH. Since many mineral weathering or dissolution reactions use hydrogen ions

(H^+), the result is that more and more HCO_3^- is produced from the constant or fixed source of CO_2 as minerals react. At the pH values commonly encountered in groundwater (pH=6.5-9.1), HCO_3^- is the dominant carbonate species present. The lack of a CO_2 source, as is the case with closed system conditions, means that the carbonate equilibrium is shifted to the right in equation (2) as H^+ is consumed by mineral dissolution reactions (especially calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$)). This results in a more significant increase in the pH as there is no longer any buffering from the constant or fixed source of CO_2 . An open system is typically one that is in contact with the soil horizon or organic rich sediments, whereas closed systems usually reflect conditions where the groundwater is isolated from either the soil horizon or atmosphere and does not occur in sediments that have abundant organic matter.

Carbonate minerals have a relatively high solubility and rapid dissolution rates when compared to other common minerals that make up the sediments and rocks found in the Gulf Island groundwater systems. The dissolution of carbonate minerals is generally considered to be a primary source of Ca^{2+} , HCO_3^- , and sometimes Mg^{2+} , in groundwater. This composition is reflected on a Piper Plot (Figure 8). If we start with the original rainwater composition, the chemically immature groundwater composition is achieved by dissolving carbonate minerals in or near to the soil horizon at fixed CO_2 content.

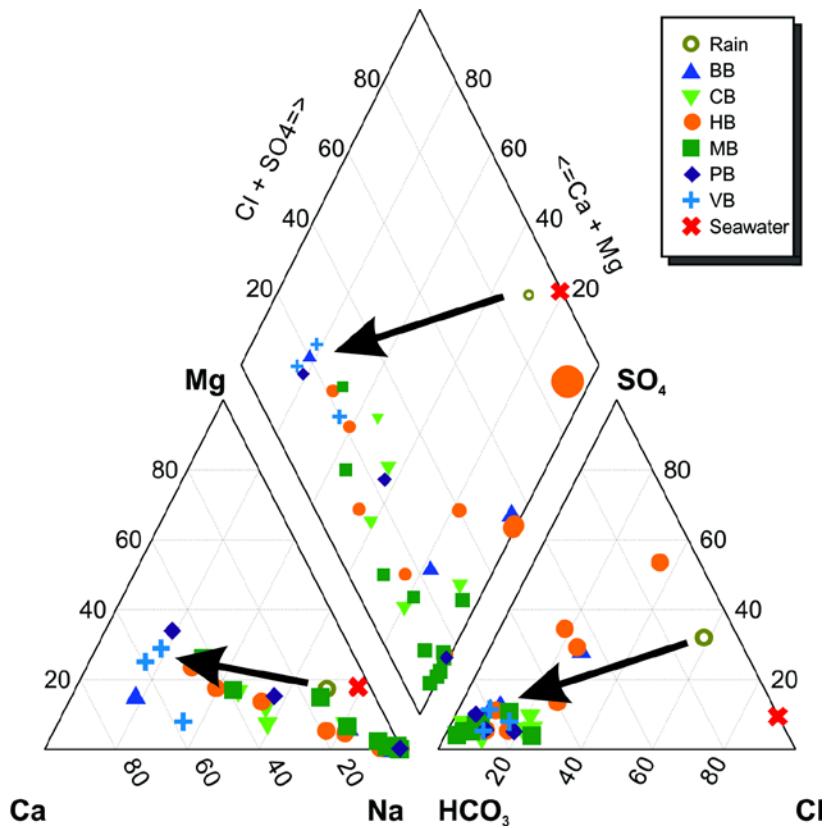


Figure 8. Piper plot showing the effect of carbonate dissolution on the composition of groundwater that initially had a rainwater composition.

In the absence of other minerals, the concentrations of Ca, Mg and HCO_3^- will increase until the groundwater becomes saturated with respect to calcite and/or dolomite and dissolution ceases. The low concentrations of Mg in water samples collected on Mayne Island, similar to low concentrations on Hornby and Saturna Islands (Allen and Suchy, 2001), probably indicate that the dissolution of dolomite is of minor importance.

Figure 9 is a graph of the Calcite Saturation Index versus pH for all samples, differentiated on the basis of their sample area. The Calcite Saturation Index is a measure of how close the sample chemical composition is to being at equilibrium with the mineral calcite. Values below 0 indicate that the water is undersaturated with respect to the mineral and would be able to dissolve the mineral if it came in contact with some. For values greater than 0 the water is supersaturated and could precipitate the mineral. At a saturation index of 0, the water is considered to be at equilibrium with respect to that mineral so neither dissolution nor precipitation is expected to occur. In general, we consider saturation indices to reflect equilibrium with respect to the mineral phase at values of 0 ± 0.5 .

Groundwaters from Mayne Island are generally undersaturated with respect to calcite at low pH and saturated with respect to calcite at high pH. The low pH likely reflects that the water has elevated pCO₂ and potentially reduced access to calcite for dissolution. The high pH waters, especially at pH>8, most likely reflect closed system conditions. The plot shows that the groundwaters of Mayne Island have a composition that is changed from the input rainwater, in part, through the dissolution of calcite. Plots of other dissolved constituents indicate that although other mineral weathering reactions may be occurring, the dominant impact of weathering on the water chemistry is calcite dissolution.

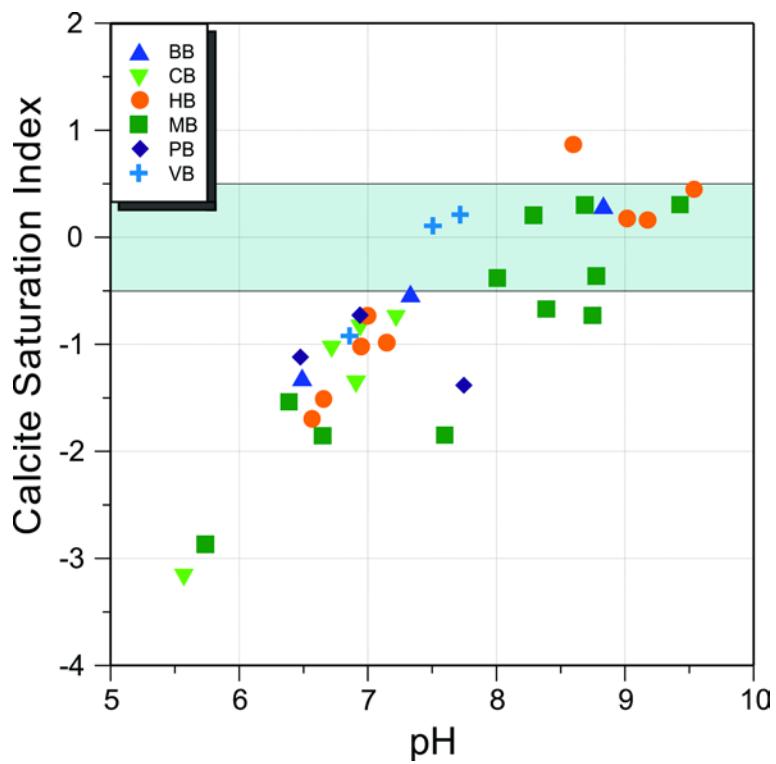


Figure 9. Graph of Calcite Saturation Index vs pH showing groundwater samples from the different Mayne Island study locations. The area in blue highlights the samples considered to be in equilibrium with calcite.

3.1.3. CATION EXCHANGE

Cation exchange is a process whereby cations dissolved in the water are swapped or exchanged for cations that are associated with mineral surfaces. Exchangeable cations commonly occur on clays and other minerals that harbour a negative charge, either structurally

or on their surfaces, and can be responsible for significant control on the relative concentrations of the major cations Na, Ca, Mg and K of groundwater. In order for cation exchange to be possible there has to be a significant number of exchange sites present and the exchangeable composition of those sites has to be set by water with a chemistry different from that of the recharging groundwater. The process is commonly observed in groundwater systems that were once dominated by seawater and that subsequently have freshwater recharge flowing through. This is the case with the Gulf Islands where not only were the original sediments that make up the bedrock deposited in marine conditions, but the islands themselves were submerged below sea level at various times during glaciation over the past 2 million years (and most recently during the Pleistocene). Seawater results in a dominance of Na on the exchange sites because of the high concentration of Na in seawater. This, combined with the fact that there is a preference for Ca and Mg over Na at low salinity, results in substantial changes in groundwater composition through the process of cation exchange.

Immature groundwater in sedimentary aquifers is commonly characterized as Ca-HCO₃ in composition. However, if a suitable exchange media is present in the subsurface (e.g., mudstone interbeds and stringers within otherwise coarse-grained materials) and the exchange media was equilibrated with seawater, there can be a significant increase in the relative amount of dissolved Na present, due to cation exchange. The degree to which the exchange of Ca (and Mg) with Na occurs is dependent on the surface area available for exchange, the cation exchange capacity (CEC) of the exchange media (e.g., CEC varies for different clay minerals), residence time, and the concentration of the solutions involved. Large mineral surface areas and long residence times favour the cation exchange process (Stumm and Morgan, 1996). Based on these criteria, it would be expected that chemically mature waters that have evolved for extended periods of time would tend to show the strongest signs of cation exchange. From a geologic point of view, increased reaction surface area could be accommodated by groundwater flow through pervasively fractured shale units.

The more evolved groundwater samples from Mayne Island show a compositional trend that is consistent with cation exchange of Na for Ca (and Mg) (Figure 10). The data trend from the immature groundwater composition in the diamond down to the Na-HCO₃ chemistry in the lower point of the figure. There is very little change in the relative anion content, reflecting the fact that the process directly impacts the cation composition and has no effect on the anions. The change in the Na content is made apparent in Figure 11. There is very little change in the Cl, but

a significant increase in the Na, especially for the Marina Bay samples. The change in composition is not through evaporation or mixing with seawater (arrow in Figure 11 shows an evapotranspiration or mixing trend).

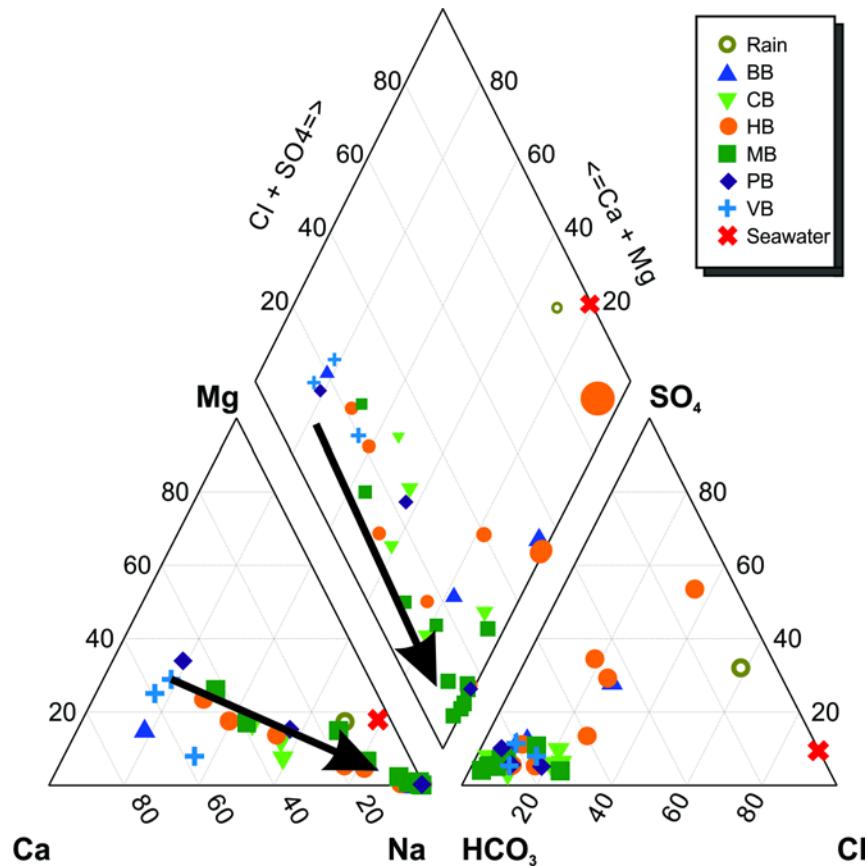


Figure 10. Piper diagram showing the direction of groundwater composition evolution that occurs through the process of cation exchange (black arrows).

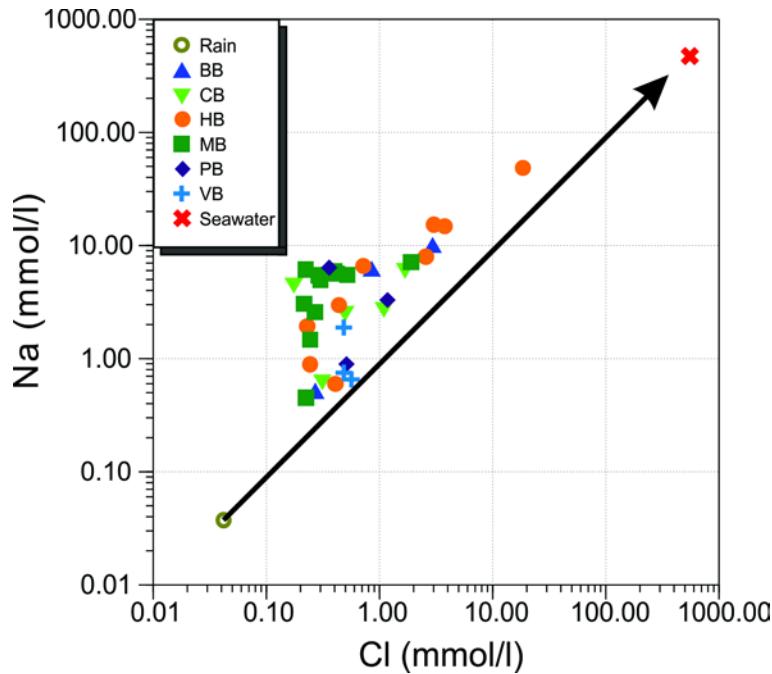
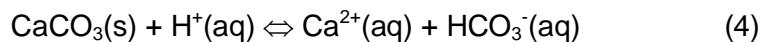
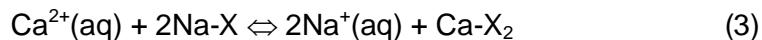


Figure 11. Na vs Cl plot showing the non-linear relation between Na and Cl at low concentrations. Arrow indicates the trend if mixing with seawater or evapotranspiration of the input rainwater dominates.

Cation exchange often takes place in conjunction with calcite dissolution. The result is an increase in Na and HCO_3^- and decrease in Ca. The reaction is described in the following equations:



Where the X stands for exchange site, (s) refers to solid and (aq) aqueous. Cation exchange involves the exchange of Ca^{2+} ions for Na^+ ions at negatively charged exchange sites on suitable exchange media (e.g., montmorillonite clays). Therefore Na^+ is added to the solution at the expense of Ca^{2+} (Equation 3). The removal of Ca^{2+} results in a shift to the right in Equation 4. This shift occurs in an attempt to reestablish the Ca^{2+} lost by cation exchange at the expense of calcite (CaCO_3). Dissolution continues as long as there is a source of calcite and H^+ . The liberation of Na^+ and simultaneous removal of Ca^{2+} from solution generally results in an increase in the HCO_3^- concentration and increase in pH, as cation exchange occurs. The relative increase of Na to HCO_3^- should be 2:1 if this mechanism is correct, and 1:1 for a system that is open to CO_2 . Figure 12 shows that the increase in Na relative to HCO_3^- is approximately 2:1.

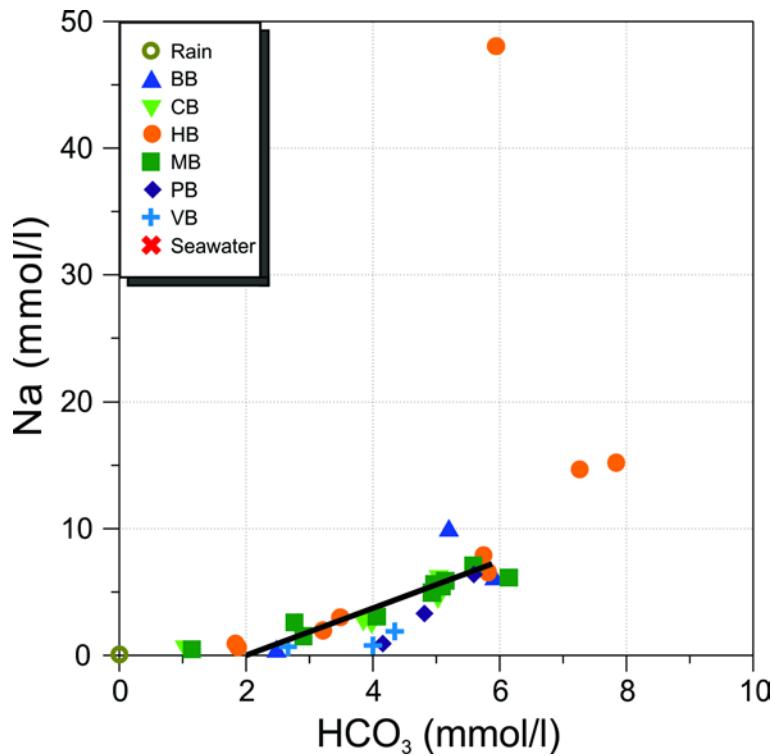


Figure 12. Plot of Na vs HCO_3 showing the general 2:1 increase in the concentration of Na relative to HCO_3 .

3.1.4. MIXING

The last major process that can influence the chemical evolution of groundwater is mixing, and particularly, its relevance to saltwater intrusion. Mixing involves combining two waters of different chemical, and sometimes, physical characters. The resulting composition is a hybrid of the two starting compositions, and that hybrid may subsequently dissolve or precipitate minerals that were previously at equilibrium within both waters. A common example of mixing involves waters from different groundwater systems (e.g., shallow and deep). The net result is water with a new chemical composition that represents the different properties of the end member waters. Another example of mixing observed in coastal aquifers is salinization by active saltwater intrusion. During this process, saline groundwater, present at depth or intruded into the freshwater lens, mixes with fresh water. This process may be accelerated in certain areas by concentrated groundwater pumping from coastal aquifers.

The role of mixing in the evolution of groundwater composition often can be assessed by assuming that the Cl content behaves conservatively (not involved in any reactions). Figure 11 in combination with the Piper plot (Figure 13) provides a good indicator of mixing. Both diagrams show that there is a strong linear correlation marking the increase of Cl and the trend is towards a seawater type composition. In the case of Mayne Island, this end member composition appears to be a modified seawater composition that has an elevated SO₄ content (data sit above the lines in Figure 14). This suggests that seawater has entered the system and interacted with the minerals that occur in the rock units in such a way as to increase the relative amount of sulfate. One of the common reactions that can result in an increase in sulfate is pyrite dissolution through oxidation. The data indicate that seawater has entered the aquifer system, reacted with pyrite, or has been affected by oxidized pyrite and then mixed with the freshwater recharge for a number of the samples, especially those from Horton Bay. It is also clear that the majority of samples show elevated sulfate content that likely relates to the oxidation process described above.

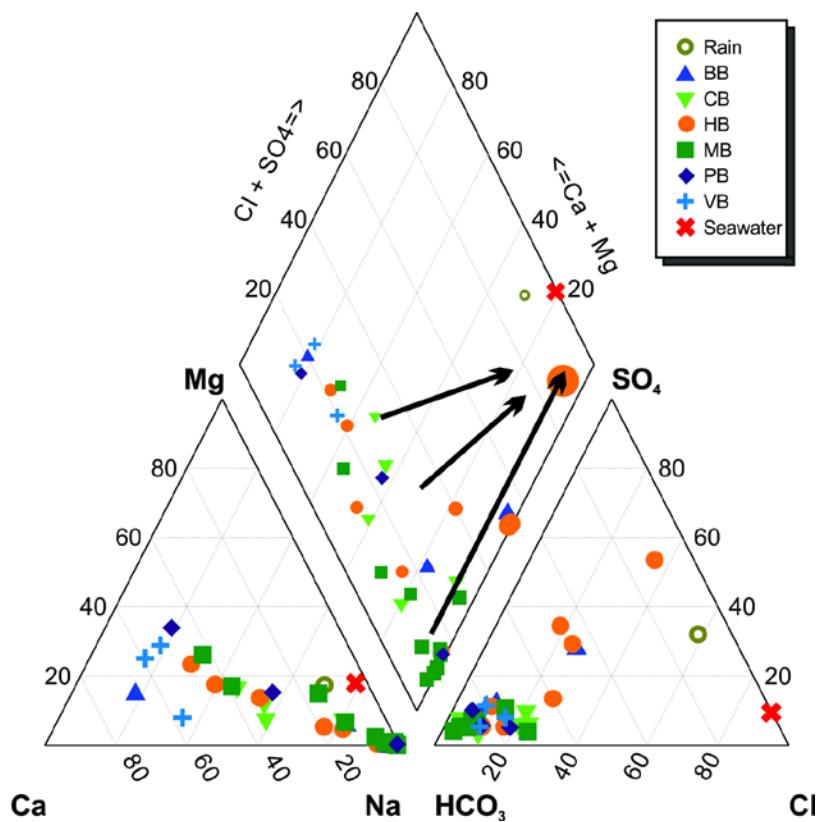


Figure 13. Piper plot showing the effect of mixing on the composition of the Mayne Island groundwater samples. Arrows point toward the fluid composition of the saline end member. The multitude of arrows indicates that mixing may occur at any time during recharge.

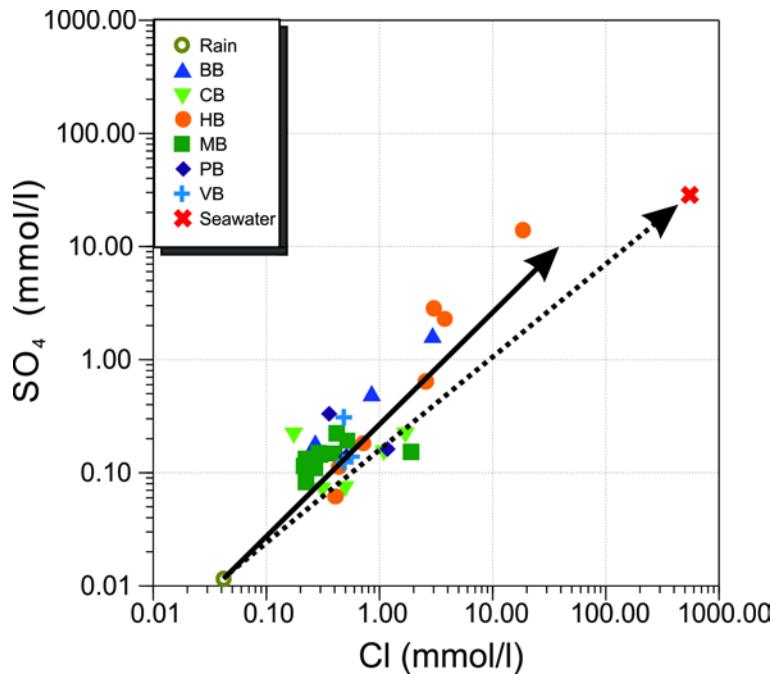


Figure 14. Scatter plot showing SO_4 vs Cl. The two lines indicate the how the composition would evolve if just evapotranspiration occurred (solid line) and mixing with seawater (dotted line).

3.2. GENERAL EVOLUTION OF GROUNDWATER

In previous studies on Saturna and Hornby Islands, groundwater was generally observed to follow two linked evolutionary trajectories (Allen and Suchy, 2001): 1) cation-exchange (Na enrichment), followed by 2) simple mixing with Cl-rich water (salinization). Simple mixing of fresh groundwater (Ca-rich) and seawater (i.e., direct salinization without significant cation exchange) was observed locally (e.g., East Point, Saturna Island).

Groundwater chemical evolution on Mayne Island appears to follow similar trends, although of the waters sampled, none appears to represent direct salinization by modern seawater. All of the groundwaters sampled show evidence of evapotranspiration to some degree, in conjunction with and subsequent to the evapotranspiration, carbonate dissolution has resulted in changes in the composition of the recharge water. The carbonate dissolution results in groundwater with a $\text{Ca}-\text{HCO}_3$ type composition, when this groundwater encounters cation exchange sites along a flow path, exchange of Ca^{2+} for 2Na^+ results in $\text{Na}-\text{HCO}_3$ type water. As the Ca content decreases through cation exchange, carbonate dissolution occurs as a coupled reaction,

increasing the HCO_3 content. The resultant $\text{Na}-\text{HCO}_3$ type water is the more evolved groundwater identified in the Piper plot. Mixing of some of the recharging groundwater with an altered seawater end member is the primary process impacting the salinity of the Mayne Island groundwater. The altered seawater has elevated SO_4 content that likely reflects interaction with the rocks prior to the mixing.

There does appear to be some correlation between the degree of impact of the varying controlling processes and the bedrock type. The bedrock composition (Northumberland, Spray and Cedar District Formations) with higher clay contents identified through a greater proportion of shaly and silty interlayers coincides with the groundwater displaying the more evolved composition. The west side of the island has the highest salinities in this study and similar observations were made by Dakin et al. (1983).

3.2.1. SALTWATER INTRUSION

Although there are a number of groundwater samples that display elevated salinity, there does not appear to be any evidence of saltwater intrusion currently taking place. However, the evolved groundwater samples show that there is some mixing occurring between the recharging fresh groundwater and a saline groundwater that has an origin as seawater. The composition of the seawater end member suggests that it is a groundwater that has experienced a more significant residence time and may be representative of the leading edge of a saline intrusion.

3.2.2. ORIGIN OF DISSOLVED SPECIES

Specific sources of dissolved species, such as Na, Ca, Mg, Cl, Fe, Mn and SO_4 , etc., would require a detailed examination of not only the geology (by undertaking whole rock geochemistry and mineralogy), but also the geological history of the region. It is beyond the scope of work for this project to identify all the potential sources of dissolved species. However, the composition of groundwater is primarily a function of the geological units through which it flows, the residence time, the presence of mudstone units, the proximity to the ocean, the orientation of fault and fracture systems, the geological history, and possibly the depth of wells.

Understanding the origin of dissolved species is a focus of ongoing study. It is speculated that

the many wells tap into saline water at depth, and that this saline water is coincident with the current freshwater-saltwater interface beneath the island. Over the past 10,000 years or so, following glacial rebound of the Gulf Islands, seawater has been flushed out of the islands, and has been largely replaced by relatively fresh water, particularly at high elevation. Because seawater is present at depth beneath all islands it is difficult to say if this is remnant seawater or present day seawater. The dynamics of this system are not fully understood, but are the focus of ongoing research.

Regardless of the age of the saline water at depth, the chemistry of the groundwater for a proportion of the wells indicates mixing with seawater. Furthermore, the observed distribution of dissolved constituents in groundwater, such as manganese, fluoride and boron, may be linked to the complex geological history of rebound, and may in fact, be associated with old seawater incursion.

4. CONCLUSIONS

Concern has been raised by members of the community of Mayne Island, specifically the Mayne Island Integrated Water Systems Society (MIIWSS), about the potential for saltwater intrusion in the island aquifers. The current study provides a synoptic (one time) view of the status of groundwater quality in wells distributed around the island. Thirty-four (34) water samples were collected during a field visit to Mayne Island in July 2011. These samples were collected from private and community wells volunteered for the study. This report provides a benchmark set of data for future studies aimed at tracking changes in groundwater quality.

Results of the groundwater chemistry study are consistent with both previous research on Mayne Island by Dakin et al. (1983) and similar groundwater sampling studies on Saturna Island (Allen and Suchy, 2001a; 2001b) and Hornby Island (Allen and Matsuo, 2002). Three distinct compositions can be identified using the Piper plot (Figure 7):

- Chemically young (immature) groundwaters, which plot in the middle left portion of the diamond diagram of the Piper plot;
- Chemically more evolved groundwaters, which plot near the bottom of the Piper diamond; and
- Evolved (mature) groundwaters, which plot more towards seawater.

Based on Cl concentrations in groundwater relative to rain water, all of the groundwaters sampled show evidence of some evapotranspiration, which may have concentrated the rain water by a factor 4 to 13 times.

Considering a starting composition for rainwater, the chemically **immature groundwater** composition is achieved by dissolving carbonate minerals in or near to the soil horizon at fixed CO₂ content. Carbonate dissolution results in groundwater with a Ca-HCO₃ type.

Cation exchange (Ca exchanging for Na) is identified as a dominant geochemical process during the evolution of groundwater. When immature groundwater encounters cation exchange sites along a flow path, there is an exchange of Ca for Na. This results in groundwater with a Na-HCO₃ type, which is the **more evolved groundwater** identified in the Piper plot.

Mature groundwaters, characterized by higher concentrations of chloride, result from mixing between the Na-HCO₃ groundwater and saline groundwater at depth, associated with either modern seawater or remnant seawater. Mixing of some of the recharging groundwater with an altered seawater end member is the primary process impacting the salinity of the Mayne Island groundwater. The altered seawater has elevated SO₄ content that likely reflects interaction with the rocks prior to the mixing.

Although there are a number of groundwater samples that display elevated salinity, there does not appear to be any evidence of saltwater intrusion currently taking place.

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