



**GEOLOGICAL SURVEY OF CANADA  
OPEN FILE 7406**

**Aqueous Geochemistry of the Englishman River Watershed,  
Parksville, British Columbia for use in assessment of potential  
surface water-groundwater interaction**

**S.K. Provencher, B. Mayer, S.E. Grasby**

**2013**



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## **Abstract**

The population in the Englishman River Watershed (ERW) in Parksville, BC is over 50% reliant on groundwater. Increasing development pressures have raised local, provincial and federal government concerns over sustainability of water resources. The Englishman River is viewed as a significant water source to support future growth and economic development. Managing long-term sustainable use of water resources of this watershed is imperative for both ecologic health and economic prosperity. As water demand pressures grow, sustainable water management requires knowledge of the degree of surface water-groundwater (SW/GW) interaction within a watershed. Geochemical methods can provide valuable information on seasonal aquifer contribution and SW/GW interactions. Developing geochemical tools that can place constraints on these complex systems will aid development of hydrogeological models, which can be used to support decision makers in water allocation.

This open file provides initial geochemical results from a groundwater well and river sampling program in the Englishman River watershed carried out in 2010-2011.

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# **1 Introduction**

## **1.1 Project Rationale**

The purpose of the Englishman River study is to assess the nature and extent of surface water-groundwater interaction in the Englishman River Watershed on Vancouver Island, southern British Columbia, using geochemical and isotopic parameters. Increasing population, development, existing industrial and commercial land use practices, combined with the impacts of changing climate puts sustainable water resource supplies at risk. The river provides a significant source of drinking water to the city of Parksville (~11,000 inhabitants) and nearby local communities and has immense value to fisheries, with chinook, chum, coho, sockeye and pink salmon; cutthroat, rainbow, and steelhead trouts all present at some point in the river during the year (FISS, 2006). The Englishman River has been identified as having recurring inadequate water flow that affects fish populations according to the Fish Protection Act (FPA) (FISS, 2006; Barlak *et al.*, 2010).

## **1.2 Previous Work**

There are currently? no peer-reviewed publications on the geochemistry or hydrogeology of the ERW. Initiatives from the BC Ministry of Environment were undertaken to assess surface water quality within the watershed (Barlak *et al.*, 2010). The purpose of the study was to accumulate baseline data necessary to assess the current state of the river water quality, establish ambient water quality objectives, and provide future monitoring recommendations (Barlak *et al.*, 2010). Mid Vancouver Island Habitat Enhancement Society (MVIHES) is a community organization, which worked in

conjunction with GW Solutions Consulting to assess the extent of surface water-groundwater interaction within the ERW. The report (Wendling, 2012) reveals that increasing interaction between groundwater and surface water occurs as you move downstream. It was also shown that bedrock aquifers within the watershed provide 30 to 40% of the baseflow in dry summer months.

#### **1.4 Objectives**

The objective of the Englishman River study is to provide a comprehensive? geochemical analysis of the ERW. The sub-objectives include: to determine the sources of solutes in both surface water and groundwater, to identify rock-water interactions, and to provide valuable geochemical information that can aid in current attempts to assess the extent of surface water-groundwater interaction within the watershed. The purpose of this Open File is to provide geochemical results from sampling campaigns carried out in 2010-2011.



## **2 Study Area**

### **2.1 Location and Basin Profile**

The Englishman River Watershed is located south west of the City of Parksville on Vancouver Island, British Columbia. The Englishman River is 39 km in length and flows in an easterly direction from its headwaters on Mount Arrowsmith (elevation 1819 m), and discharges in the strait of Georgia, north of Craig Bay. The total drainage area of the watershed is 324 km<sup>2</sup>. Most licensed water demand occurs in the lower part of the Englishman River and in its tributary Morison Creek (Environment Canada, 1994). The watershed of Morison Creek is 48.60 km<sup>2</sup> and comprises 15% of the total Englishman River Watershed. Swayne Creek and Digby Creek are tributaries of Morison Creek. Tributaries of Swayne Creek include: Pollard Creek, Dayton Brook, and Connell Creek are tributaries. The largest tributary to the Englishman River is the South Englishman River and constitutes 77.76 km<sup>2</sup>, or 24% to the total watershed (Barlak *et al.*, 2010).

### **2.2 Climate**

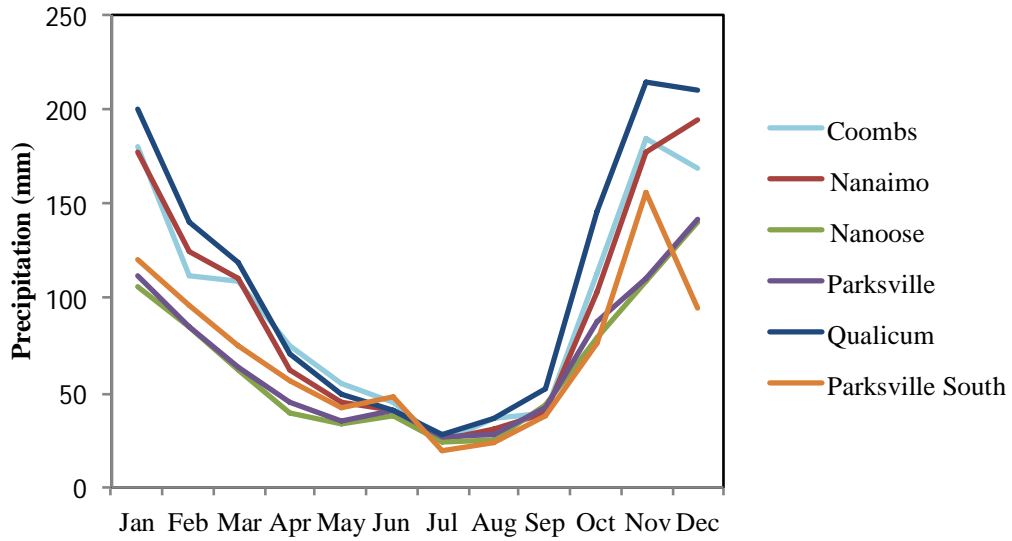
Vancouver Island is considered a subtropical and temperate rainforest environment and is part of the temperate rainforest of Cascadia, a bioregion defined by the watersheds of the rivers flowing into the Pacific Ocean through North America's temperate rain forests (Environment Canada, 2012a). The climate of the ERW is characterized by mild, wet winters; and warm, dry summers. The mountain ranges to the west create a rainshadow affecting the eastern slopes of the central Vancouver Island.

Unfortunately, there are no active climate stations within the ERW, so data from historical and nearby active stations were used to delineate climatic conditions. There are six climate stations located within or near the study area, which were either historically active or are still actively recording temperature and precipitation data (Table 1; Figure 1, 2; Environment Canada 2012a). Average annual precipitation within the study area is ~1000 mm and mean annual temperature is ~9.3 °C, with mean annual maximum and minimum temperatures of ~14 °C and ~5 °C respectively (Table 1; Environment Canada, 2012a).

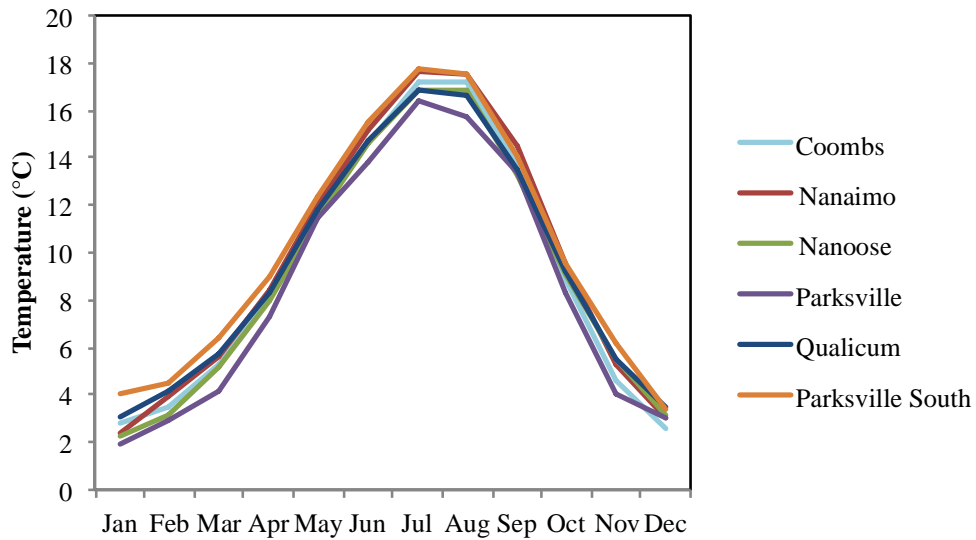
**Table 1:** Historical climate data displaying mean annual temperatures and precipitation from various climate stations within or near the ERW (Environment Canada, 2012a).

| Climate Station  | Observation Period | Mean Annual Temperature<br>(°C) | Mean Annual Precipitation<br>(mm) |
|------------------|--------------------|---------------------------------|-----------------------------------|
| Parksville       | 1916-1960          | 8.5                             | 818.7                             |
| Parksville South | 1993-1967          | 10.0                            | 845.6                             |
| Nanaimo          | 1946-2006          | 9.6                             | 1132.1                            |
| Nanoose          | 1912-1939          | 9.2                             | 785.8                             |
| Qualicum         | 1963-2006          | 9.4                             | 1305.3                            |
| Coombs           | 1961-2006          | 9.1                             | 1139.8                            |

Hudson (2000) revealed through studies on the south coast of BC that between 0-300, 300-800, and above 800 m.a.s.l. correspond to the rain dominated, rain on snow, and snow dominated zones respectively. Approximately 30% of the ERW lies within the rainfall dominated zone, 60% in the rain on snow zone, and only 10% in the snow dominated zone. Therefore, the ERW is a rain driven hydrologic system, influenced by heavy rainfall in fall and winter months and a dry summer season (Figure 1; Wade *et al.*, 2001; Environment Canada, 2012a).



**Figure 1:** Historical mean monthly precipitation values for Coombs, Nanaimo, Nanoose, Parksville, Qualicum, and Parksville South stations (1971-2000 period, data from Environment Canada, 2012a).



**Figure 2:** Historical mean monthly temperature values for Coombs, Nanaimo, Nanoose, Parksville, Qualicum, and Parksville South stations (1971-2000 period).

### 2.3 Bedrock Geology

The East-central coast of Vancouver Island is underlain predominately by the Nanaimo group, which is Upper Cretaceous in age with a total thickness close to 5000 m (Fyles, 1963; Mustard, 1994).

The Nanaimo group is characterized by a series of alternating layers of conglomerate, sandstone, siltstone, and mudstone sediments deposited mostly under marine conditions, largely as submarine fans, offshore from coastal shelf deposits (Mustard, 1994). The remaining bedrock within the study area is from the Wrangellia Terrane, which is most commonly characterized by widespread exposures of Triassic flood basalts and complementary intrusive rocks (Jones *et al.*, 1977). The Upper Triassic Vancouver Group of the Wrangellia Terrane underlies much of the study area, and outcrops on Mt. Arrowsmith. The Group is subdivided into a thick basaltic volcanic package called the Karmutsen Formation and an upper sedimentary package designated as the Quatsino Formation. The Karmutsen Formation form pillowed flows, pillow breccias, and breccias interbedded with massive flows and sills (Massey *et al.*, 1995). These sequences are predominantly extrusive, marine sequences locally exceeding 6000 m in thickness.

The Quatsino Formation is characterized by massive, thickly bedded, black micritic limestone. Northeast of the Karmutsen and Quatsino outcrops, outcrops of Jurassic Island Intrusions and Westcoast Crystalline Complex (WCC) are observed. The WCC includes granitic rocks that are intrusive equivalents of the Bonanza Formation (which does not outcrop in the study area), and form intrusions, which are dominantly

equigranular quartz diorite to granodiorite, rich in mafic inclusions (Massey *et al.* 1995; Massey and Friday, 1987).

Sicker and Buttle Lake Groups of the Wrangellia Terrane underlie the study area to the Southeast and outcrop in areas of Mt. Arrowsmith. The Sicker and Buttle Lake Groups are the oldest rocks of Vancouver Island and range from Middle Devonian to Lower Permian in age. The Devonian Sicker Group is a thick package of lower greenschist facies, metavolcanic and volcanoclastic rocks that formed in an oceanic island environment (Massey *et al.*, 1995). The Buttle Lake Group is characterized by epiclastic and bioclastic limestone sedimentary sequences ranging from Mississippian to Early Permian in age (Greene *et al.*, 2004; Massey *et al.*, 1995; Massey and Friday, 1987).

## **2.4 Surficial Geology**

The glacial history of Vancouver Island was affected by at least three glaciations. Surficial deposits from the Pleistocene include the Quadra Sands, which are described as glacio-fluvial sands, and the Vashon Drift, characterized as glacial tills (Clague, 1977; Fyles, 1963). The Holocene deposits are comprised of marine, fluvial, and lacustrine deposits relating to prior sea levels called the Capilano Sediments and as well as Salish sediments relating to deposits during present sea levels (Fyles 1963; Howes, 1983). Salish sediments make up the surficial sediments of the easternmost coast, where the Englishman River discharges into the Strait of Georgia. The Quadra Sands are found outcropped in small areas North and South of the Englishman River but are a dominant lithology of the aquifers within the study area (Fyles 1963; Howes, 1983). The Quadra Sands are described as well sorted, distinctive white sands that can exceed 75 m in

thickness. The sands are characterized as remarkably uniform, with horizontal stratification and extensive cross bedding (Fyles 1963; Clague 1977).

## **2.5 Hydrogeology**

There are six aquifers within the ERW, which have been mapped with the BC Aquifer Classification System (Kreye *et al.*, 2001). Bedrock and surficial geology mapping, well lithology records, and hydrogeological reports were used to delineate aquifer boundaries. The aquifers are further classified based on their level of development and vulnerability to contamination from the surface (Kreye *et al.*, 2001). Three aquifers in the ERW are shown to be at risk due to dropping groundwater levels and/or localized contamination, and four aquifers within the watershed are classified as moderately vulnerable (Table 2; Kreye *et al.*, 2001).

Four of the six aquifers within the ERW consist of unconsolidated, surficial sediments (three consisting of Quadra Sand and one of Salish Sediments) and two consist of fractured bedrock from the Nanaimo Group (Table 2; BC Ministry of Environment, 2012). The highest yielding wells are those completed within sand, gravel glacial outwash, post-glacial fluvial deposits, as well as those completed in major faults or fractures in bedrock (Yorath, 2005). Unconfined aquifers consisting of coarse surficial sediments are those with the highest vulnerability to contamination (Denny *et al.*, 2006). Main characteristics of all six aquifers within the ERW are presented in Table 2. Note that only the 4 km<sup>2</sup> aquifer #0221 was classified by the province as highly vulnerable.

**Table 2:** Characteristics of mapped aquifers in the Englishman River Watershed (BC? Ministry of Environment, 2012).

| Aquifer | Aquifer Materials | Demand   | Productivity | Vulnerability | Size (km <sup>2</sup> ) | Stratigraphic Unit | Water Use |
|---------|-------------------|----------|--------------|---------------|-------------------------|--------------------|-----------|
| 0209    | Sand and Gravel   | Low      | Moderate     | Low           | 10.7                    | Quadra Sand        | Multiple  |
| 0214    | Bedrock           | Low      | Low          | Moderate      | 30.4                    | Nanaimo Group      | Domestic  |
| 0216    | Sand and Gravel   | Moderate | Moderate     | Moderate      | 25.5                    | Quadra Sand        | Multiple  |
| 0219    | Sand and Gravel   | Moderate | Moderate     | Low           | 37.8                    | Quadra Sand        | Domestic  |
| 0220    | Bedrock           | Low      | Low          | Moderate      | 59.2                    | Nanaimo Group      | Multiple  |
| 0221    | Sand and Gravel   | Moderate | High         | High          | 4                       | Salish Sediments   | Domestic  |

The MOE BC has a voluntary program for water well drillers to submit a well report, which is available on the WELLS database (Denny *et al.*, 2006). There are over 250 wells in the provincial database that are located within the ERW; although the number of wells is likely much higher. Well reports outline details such as well location, depth, lithology, and an estimate of flow rate. Without mandatory submission governed by the MOE, accurate aquifer demand estimates prove to be difficult (Kreye *et al.*, 2001).

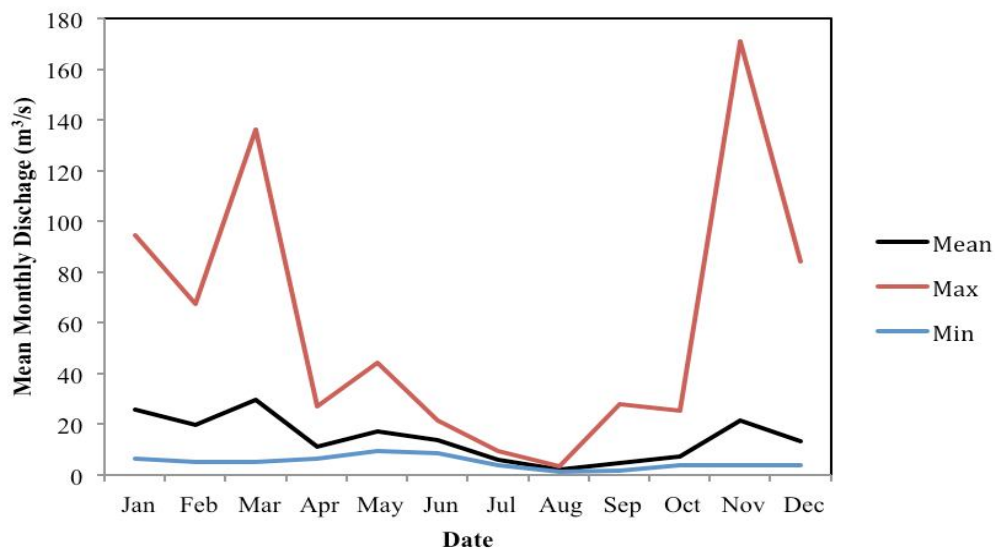
## 2.6 Hydrology

There are seven lakes in the watershed: Arrowsmith, Fishtail, Rowbotham, Healy, Shelton, Marshall, and Hidden lakes. The Englishman River originates from Arrowsmith Lake on Mt. Arrowsmith, which is used as a reservoir for the Arrowsmith dam. The dam has a live storage volume of 9 000 000 m<sup>3</sup> of water and stores heavy winter rain and melting snow. During the dry season (summer and early fall), 50% of the storage volume is available for release into the river (Boom and Bryden, 1994).

There is one hydrometric station located on the Englishman River, approximately 200 m upstream of the estuary. Historical hydrometric data is available from 1913 to 2010 and real-time hydrometric data from 2011-present (Environment Canada, 2012 b,

c). Historical data include monthly maximum, minimum and mean discharge values and real-time data is recorded hourly throughout the day. The mean annual discharge of the Englishman River, based on data from 1915 to 2011, is 13.6 m<sup>3</sup>/s. (Figure 3 and 4;).

Analyzing the hydrometric data, maximum discharge rates occur during November, when precipitation is typically greatest, and during March when snowmelt contributes to discharge. Minimum discharge rates typically occur during late August and September when precipitation is minimal (Figure 3 and 4; Environment Canada, 2012a,b,c).



**Figure 3:** Minimum, maximum and average monthly discharge data for Englishman River near Parksville (Water Survey Canada Station 08HB002) for the 1913 -2011 period (Environment Canada, 2012b).



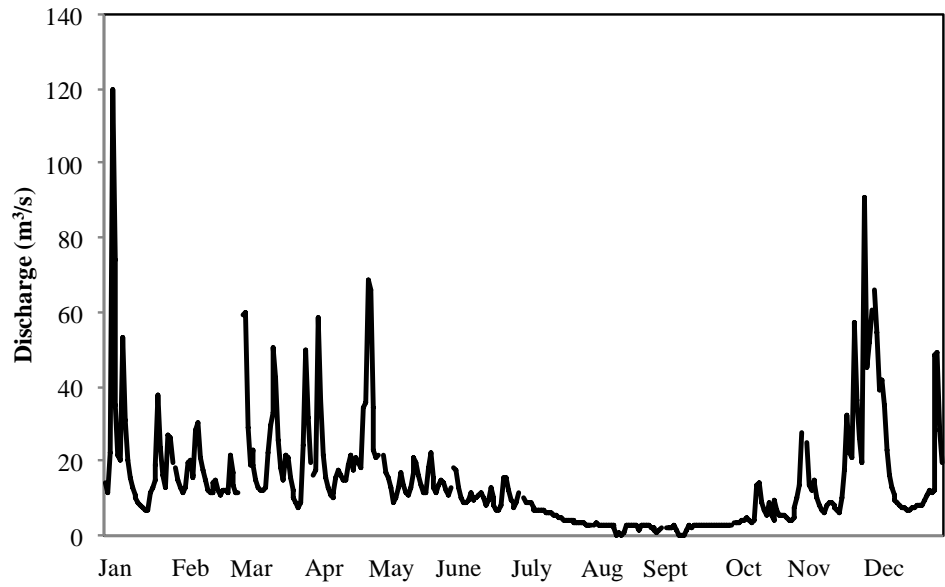


Figure 4: Average daily discharge data for Englishman River near Parksville (Water Survey Canada)

## **3 Data Collection and Methodology**

### **3.1 Data Collection**

Fifty groundwater samples were collected from the ERW in July 2011 from residential, commercial, and city wells. For groundwater samples, pH, electrical conductivity (EC), dissolved oxygen (DO) and temperature were measured using a Thermo Scientific Orion 5 Star multiprobe electrode. The pH probe was calibrated prior to sampling with pH 4, pH 7, and pH 10 standards. To ensure representative aquifer readings, the probe was placed in a flow through cell and water was pumped from the well until parameters stabilized.

Surface water samples were collected from the Englishman River over five sampling trips during August 2010, October 2010, February 2011, May 2011, and July 2011. Parameters that were measured directly in the field include: pH, EC, DO, and temperature using a Thermo Scientific Orion 5 Star multiprobe electrode. Probes were immersed directly in the sample water and values were recorded once readings stabilized.

Water was collected for cation, anion and alkalinity measurements. All samples were vacuum filtered in the field through a 0.45  $\mu\text{m}$  cellulose acetate filter and containers were filled to overflowing, creating a positive meniscus, ensuring minimal exposure to atmospheric oxygen. Treatment of the samples and the volume of the containers used for collection depend on the analysis. Cation, anion, and alkalinity samples were collected in

125 ml Nalgene bottles, pre-rinsed with sample water. The cation samples were acidified using concentrated nitric acid. All samples were quickly sealed and refrigerated at 4 °C until analyzed.

### **3.2 Analytical methods and techniques**

Alkalinity, cation, trace elements, and anion analyses of samples were conducted at the Geological Survey of Canada Laboratories in Ottawa. Anions were measured using Ion Chromatography (IC-110). The cations were measured using Inductively Coupled Plasma emission spectrometry (ICP-ES).

Duplicate samples of cations, anions, and alkalinity were analyzed by the Applied Geochemistry Group, Department of Geoscience, University of Calgary. The cation samples were measured using a Perkin Elmer Analyst 100 atomic absorption spectrometer. Anion analyses were conducted using a Dionex ICS 2000 Column Suppression Ion Liquid Chromatograph. Alkalinity was measured with an automated titrator (Orion 960) using 0.01M sulfuric acid. The inflection point in the titration curve gives the alkalinity of the sample reported in  $\text{HCO}_3^-$  (mg/L). For duplicate analyses, the mean values were reported. Accuracy of the analytical analysis was tested using a charge balance equation where reliable measurements yield a  $\pm 5\%$  charge balance.

## **4 Major Ion Chemistry**

### **4.1 Major Cations**

#### **4.1.1 Surface Water**

Ca, Na, K, and Mg concentrations of surface water samples had overall average values of 7.00, 3.64, 0.160, and 0.920 mg/L respectively. Maximum concentrations occurred in Summer 2010, where minimum values occurred in Fall 2010. Surface water samples had low overall variations in Ca, Mg, and K concentrations with standard deviations of 1.60, 0.990, and 0.320 mg/L respectively. Na concentrations varied the most with a standard deviation of 7.99 mg/L. This can be attributed to one sample site near the confluence of the Englishman River with saline water from the Strait of Georgia (with Na concentrations of 66.5 mg/L) ; Na concentrations can vary widely depending on the level of the tide (Table 3).

#### **4.1.2 Groundwater**

Ca, Na, K, and Mg concentrations of groundwater samples had average values of 18.1, 16.1, 0.580 and 6.10 mg/L respectively. Cation concentrations are much more variable in groundwater samples as compared to surface water samples with standard deviations of 14.1, 33.4, and 6.00 mg/L for Ca, Na, and Mg respectively. Cation concentration is highly dependent on the aquifer medium and residence time. Varying well depths (2 to 60 m) and aquifer lithologies also explain the variation seen in the

groundwater samples (Table 4).

**Table 3:** Statistical summary of cation concentrations of surface water samples.

| <b>Sampling Period</b> | <b>Statistic</b> | <b>Ca<br/>mg/L</b> | <b>Mg<br/>mg/L</b> | <b>Na<br/>mg/L</b> | <b>K<br/>mg/L</b> |
|------------------------|------------------|--------------------|--------------------|--------------------|-------------------|
| Summer 2010            | Mean             | 9.78               | 1.21               | 4.78               | 0.192             |
|                        | Min              | 8.99               | 0.787              | 4.51               | 0.0900            |
|                        | Max              | 12.1               | 3.20               | 6.79               | 0.393             |
|                        | $\sigma$         | 0.794              | 0.601              | 0.589              | 0.0928            |
| Fall 2010              | Mean             | 6.45               | 1.15               | 5.89               | 0.276             |
|                        | Min              | 4.84               | 0.485              | 1.07               | 0.0860            |
|                        | Max              | 10.3               | 8.25               | 66.5               | 2.66              |
|                        | $\sigma$         | 1.41               | 1.90               | 16.2               | 0.635             |
| Winter 2011            | Mean             | 6.36               | 1.04               | 4.31               | 0.179             |
|                        | Min              | 5.88               | 0.674              | 2.66               | 0.0840            |
|                        | Max              | 7.11               | 3.41               | 23.2               | 0.994             |
|                        | $\sigma$         | 0.469              | 0.689              | 5.44               | 0.236             |
| Spring 2011            | Mean             | 5.85               | 0.601              | 1.51               | 0.0914            |
|                        | Min              | 5.52               | 0.527              | 1.35               | 0.0740            |
|                        | Max              | 6.36               | 0.673              | 1.67               | 0.130             |
|                        | $\sigma$         | 0.207              | 0.0507             | 0.112              | 0.0167            |
| Summer 2011            | Mean             | 6.55               | 0.615              | 1.72               | 0.0701            |
|                        | Min              | 6.29               | 0.513              | 1.53               | 0.0500            |
|                        | Max              | 6.95               | 0.718              | 1.99               | 0.0870            |
|                        | $\sigma$         | 0.236              | 0.0756             | 0.155              | 0.0129            |
| Overall                | Mean             | 7.00               | 0.923              | 3.64               | 0.162             |
|                        | Min              | 4.84               | 0.485              | 1.07               | 0.0500            |
|                        | Max              | 12.1               | 8.25               | 66.5               | 2.66              |
|                        | $\sigma$         | 1.60               | 0.993              | 7.99               | 0.321             |

**Table 4:** Statistical summary of cation concentrations of groundwater samples (from 50 wells).

| <b>Sample ID</b> | <b>Ca<br/>mg/L</b> | <b>Mg<br/>mg/L</b> | <b>Na<br/>mg/L</b> | <b>K<br/>mg/L</b> |
|------------------|--------------------|--------------------|--------------------|-------------------|
| Mean             | 18.1               | 6.10               | 16.1               | 0.583             |
| Min              | 0.320              | 0.0536             | 1.76               | 0.100             |
| Max              | 69.4               | 25.4               | 169                | 1.68              |
| $\sigma$         | 14.2               | 6.00               | 33.4               | 0.392             |

## **4.2 Major Anions**

### **4.2.1 Surface Water**

Cl, HCO<sub>3</sub>, SO<sub>4</sub>, and NO<sub>3</sub> concentrations of surface water samples had overall average values of 6.96, 19.7, 1.90 and 0.260 mg/L respectively (Table 7). Again, maximum concentrations occurred in Summer 2010, where minimum values occurred in Fall 2010. Surface water samples had large variations in sodium concentrations, which can be attributed to one sample site near the confluence of the Englishman River with the Straight of Georgia, suggesting an influx of seawater (Table 5). Bicarbonate concentrations exhibited moderate variability with a standard deviation of 4.10 mg/L. Surface waters had very low ranges of both sulphate and nitrate with standard deviations of 1.92 and 0.710 mg/L respectively; due to low overall concentrations of both ions in surface water (Table 5).

### **4.2.2 Groundwater**

Cl, HCO<sub>3</sub>, SO<sub>4</sub>, and NO<sub>3</sub> concentrations of groundwater samples had average values of 14.4, 96.0, 4.37 and 1.28 mg/L respectively (Table 6). Anion concentrations are highly variable in groundwater samples with standard deviations of 28.8, 77.6, 3.78, and 3.94 mg/L for Cl, HCO<sub>3</sub>, SO<sub>4</sub>, and NO<sub>3</sub> respectively (Table 6). The observed variability is due to varying well depths aquifer lithologies.

**Table 5:** Statistical summary of anion concentrations of surface water samples.

| <b>Sampling Period</b> | <b>Statistic</b> | <b>Cl<br/>mg/L</b> | <b>HCO<sub>3</sub><br/>mg/L</b> | <b>SO<sub>4</sub><br/>mg/L</b> | <b>NO<sub>3</sub><br/>mg/L</b> |
|------------------------|------------------|--------------------|---------------------------------|--------------------------------|--------------------------------|
| Summer 2010            | Mean             | 11.2               | 25.5                            | 2.09                           | 0.187                          |
|                        | Min              | 10.9               | 20.6                            | 1.34                           | 0.000                          |
|                        | Max              | 13.2               | 42.5                            | 3.43                           | 1.12                           |
|                        | $\sigma$         | 0.584              | 5.28                            | 0.709                          | 0.282                          |
| Fall 2010              | Mean             | 9.92               | 17.6                            | 2.61                           | 0.0469                         |
|                        | Min              | 1.48               | 12.7                            | 1.10                           | 0.000                          |
|                        | Max              | 111                | 21.2                            | 16.5                           | 0.0900                         |
|                        | $\sigma$         | 27.0               | 3.05                            | 3.71                           | 0.0278                         |
| Winter 2011            | Mean             | 7.74               | 18.5                            | 2.26                           | 0.0984                         |
|                        | Min              | 4.50               | 16.8                            | 1.75                           | 0.000                          |
|                        | Max              | 40.7               | 19.9                            | 6.77                           | 0.196                          |
|                        | $\sigma$         | 9.51               | 0.835                           | 1.30                           | 0.0603                         |
| Spring 2011            | Mean             | 2.61               | 17.1                            | 1.56                           | 0.966                          |
|                        | Min              | 2.33               | 15.7                            | 1.35                           | 0.229                          |
|                        | Max              | 2.89               | 17.8                            | 3.18                           | 4.65                           |
|                        | $\sigma$         | 0.201              | 0.601                           | 0.472                          | 1.45                           |
| Summer 2011            | Mean             | 3.30               | 19.9                            | 0.990                          | 0.00971                        |
|                        | Min              | 2.81               | 18.4                            | 0.799                          | 0.000                          |
|                        | Max              | 3.83               | 21.4                            | 1.13                           | 0.0290                         |
|                        | $\sigma$         | 0.373              | 0.849                           | 0.114                          | 0.0118                         |
| Overall                | Mean             | 6.96               | 19.7                            | 1.90                           | 0.262                          |
|                        | Min              | 1.48               | 12.7                            | 0.799                          | 0.000                          |
|                        | Max              | 111                | 42.5                            | 16.5                           | 4.65                           |
|                        | $\sigma$         | 13.5               | 4.10                            | 1.92                           | 0.728                          |

**Table 6:** Statistical summary of anion concentrations of groundwater samples (from 50 wells).

| <b>Sample ID</b> | <b>Cl<br/>mg/L</b> | <b>HCO<sub>3</sub><br/>mg/L</b> | <b>SO<sub>4</sub><br/>mg/L</b> | <b>NO<sub>3</sub><br/>mg/L</b> |
|------------------|--------------------|---------------------------------|--------------------------------|--------------------------------|
| Mean             | 14.4               | 96.0                            | 4.37                           | 1.28                           |
| Min              | 1.56               | 18.9                            | 0.282                          | 0.000                          |
| Max              | 197                | 391                             | 20.1                           | 25.7                           |
| $\sigma$         | 28.8               | 77.6                            | 3.78                           | 3.94                           |

### **4.3 Combined Cations and Anions**

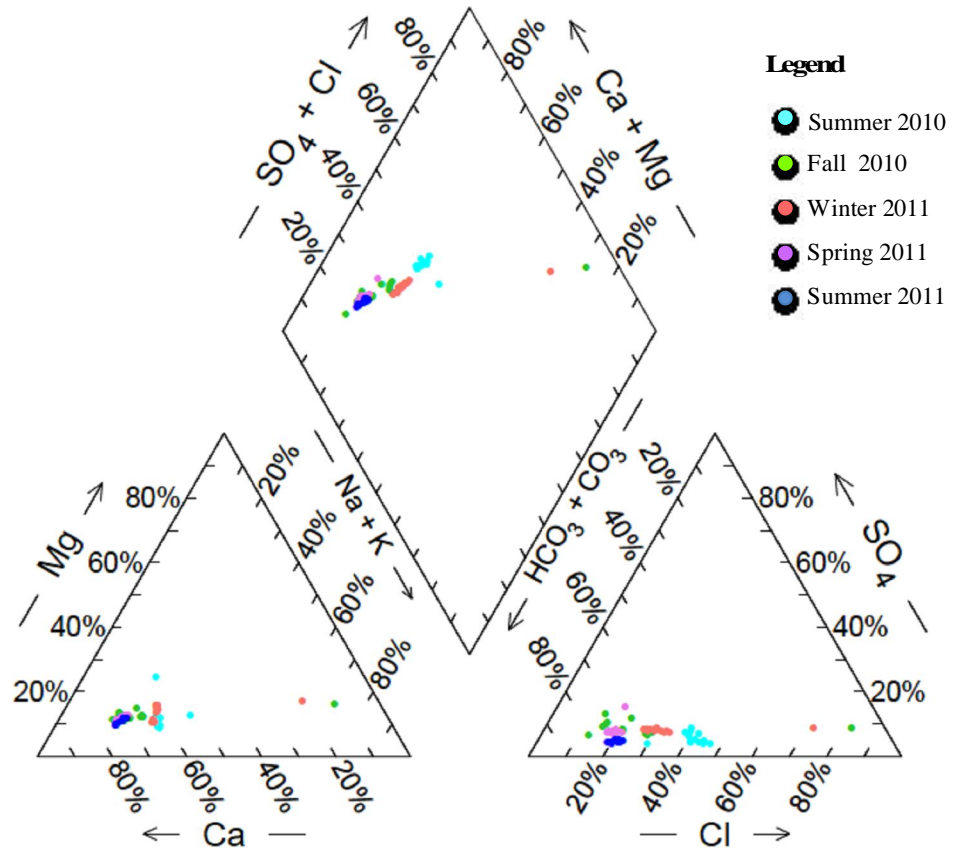
#### **4.3.1 Surface Water**

Data from 98% of the surface water data depict water types ranging from Ca-HCO<sub>3</sub>-Cl to Ca-HCO<sub>3</sub>, where 2% are Na-Cl water type (Figure 5). The two water samples displaying a Na-Cl water type are located in close proximity to the estuary, suggesting mixing of seawater. Temporal variation in the surface water is observed; summer 2010 depicts a water type of Ca-HCO<sub>3</sub>-Cl, where in Fall 2010, Spring 2011, and Fall 2011 a Ca-HCO<sub>3</sub> water type is observed.

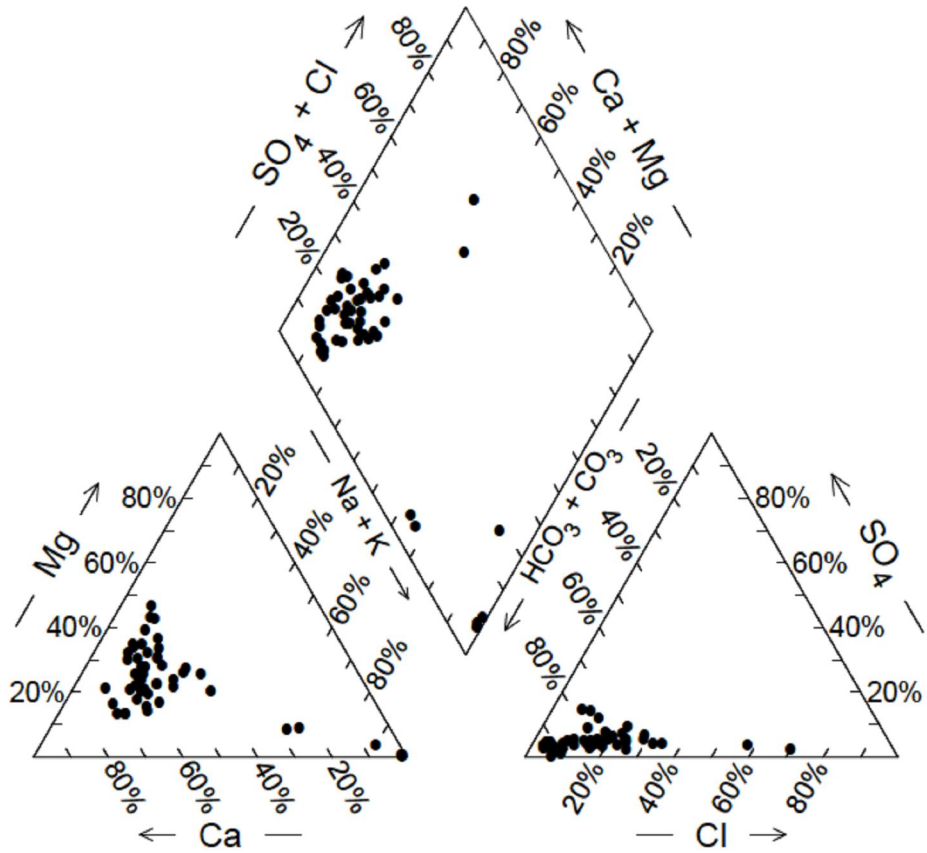
#### **4.3.2 Groundwater**

The groundwater data display highly mineralized water with large variability when compared to surface water samples (Figure 6). Of the groundwater samples, 86% have a Ca-Mg-HCO<sub>3</sub>-Cl water type, where 10% and 4% have a Na-HCO<sub>3</sub> and Ca-Na-HCO<sub>3</sub>-Cl water type respectively.





**Figure 5:** Piper diagram of surface water samples depicting temporal variation.



**Figure 6:** Piper diagram of groundwater samples.

**Table 7:** Chemical analyses of surface water samples within the ERW over five sampling periods.

| Sample ID | Sampling Period | Ca mg/L | Mg mg/L | Na mg/L | K mg/L | Cl mg/L | HCO <sub>3</sub> mg/L | SO <sub>4</sub> mg/L | NO <sub>3</sub> mg/L | Sample ID | Sampling Period | Ca mg/L | Mg mg/L | Na mg/L | K mg/L | Cl mg/L | HCO <sub>3</sub> mg/L | SO <sub>4</sub> mg/L | NO <sub>3</sub> mg/L |
|-----------|-----------------|---------|---------|---------|--------|---------|-----------------------|----------------------|----------------------|-----------|-----------------|---------|---------|---------|--------|---------|-----------------------|----------------------|----------------------|
| 10SKP-01  | Summer-10       | 9.82    | 1.19    | 4.54    | 0.144  | 11.0    | 25.3                  | 3.43                 | 0.0780               | 11SKP-38  | Winter-11       | 6.05    | 0.903   | 2.74    | 0.115  | 4.83    | 16.8                  | 1.83                 | 0.139                |
| 10SKP-02  | Summer-10       | 9.84    | 1.20    | 4.68    | 0.215  | 10.9    | 26.8                  | 2.97                 | 0.116                | 11SKP-39  | Winter-11       | 5.93    | 0.874   | 2.72    | 0.120  | 4.83    | 18.3                  | 1.87                 | 0.113                |
| 10SKP-03  | Summer-10       | 9.38    | 1.36    | 6.79    | 0.387  | 13.2    | 27.6                  | 2.99                 | 0.0400               | 11SKP-40  | Winter-11       | 6.37    | 0.863   | 2.90    | 0.124  | 5.21    | 18.8                  | 2.03                 | 0.159                |
| 10SKP-04  | Summer-10       | 10.5    | 1.23    | 4.93    | 0.171  | 10.9    | 25.5                  | 2.30                 | 0.000                | 11SKP-41  | Winter-11       | 5.89    | 0.857   | 2.74    | 0.109  | 4.85    | 17.2                  | 1.93                 | 0.150                |
| 10SKP-05  | Summer-10       | 9.79    | 1.14    | 4.78    | 0.230  | 11.0    | 25.3                  | 3.02                 | 0.0400               | 11SKP-42  | Winter-11       | 6.60    | 0.674   | 2.94    | 0.0980 | 5.62    | 18.4                  | 1.86                 | 0.0580               |
| 10SKP-06  | Summer-10       | 9.97    | 1.16    | 4.74    | 0.211  | 11.0    | 25.1                  | 1.62                 | 0.155                | 11SKP-43  | Winter-11       | 7.02    | 0.728   | 3.23    | 0.0860 | 6.28    | 19.3                  | 1.99                 | 0.0770               |
| 10SKP-07  | Summer-10       | 10.0    | 1.16    | 4.61    | 0.143  | 11.3    | 25.7                  | 1.68                 | 0.0750               | 11SKP-44  | Winter-11       | 7.08    | 0.780   | 3.19    | 0.0840 | 6.27    | 19.9                  | 2.00                 | 0.0850               |
| 10SKP-08  | Summer-10       | 9.52    | 0.918   | 4.61    | 0.153  | 10.9    | 23.7                  | 1.82                 | 0.0970               | 11SKP-45  | Winter-11       | 7.11    | 0.719   | 3.30    | 0.0880 | 6.56    | 19.5                  | 2.04                 | 0.0710               |
| 10SKP-09  | Summer-10       | 8.99    | 0.833   | 4.51    | 0.100  | 11.0    | 21.5                  | 1.60                 | 0.141                | 11SKP-47  | Spring-11       | 6.36    | 0.673   | 1.67    | 0.108  | 2.84    | 17.6                  | 1.49                 | 4.65                 |
| 10SKP-10  | Summer-10       | 9.02    | 0.787   | 4.54    | 0.168  | 11.1    | 22.0                  | 1.40                 | 0.137                | 11SKP-48  | Spring-11       | 5.88    | 0.648   | 1.62    | 0.0830 | 2.78    | 17.6                  | 3.18                 | 0.293                |
| 10SKP-11  | Summer-10       | 9.26    | 0.808   | 4.56    | 0.0900 | 11.3    | 20.6                  | 1.34                 | 0.347                | 11SKP-49  | Spring-11       | 5.83    | 0.654   | 1.64    | 0.130  | 2.84    | 17.6                  | 1.47                 | 0.229                |
| 10SKP-13  | Summer-10       | 12.1    | 3.20    | 4.57    | 0.393  | 11.1    | 42.5                  | 1.94                 | 1.12                 | 11SKP-50  | Spring-11       | 5.93    | 0.650   | 1.61    | 0.0840 | 2.72    | 17.4                  | 1.57                 | 0.239                |
| 10SKP-14  | Summer-10       | 9.51    | 1.03    | 4.56    | 0.148  | 11.4    | 23.7                  | 1.63                 | 0.0670               | 11SKP-51  | Spring-11       | 6.07    | 0.655   | 1.63    | 0.0990 | 2.84    | 17.4                  | 1.48                 | 0.250                |
| 10SKP-15  | Summer-10       | 9.17    | 0.867   | 4.58    | 0.135  | 11.5    | 22.4                  | 1.55                 | 0.198                | 11SKP-52  | Spring-11       | 5.77    | 0.642   | 1.60    | 0.0830 | 2.89    | 16.7                  | 1.41                 | 0.271                |
| 10SKP-16  | Fall-10         | 7.67    | 0.857   | 2.76    | 0.140  | 5.16    | 20.9                  | 2.14                 | 0.0650               | 11SKP-53  | Spring-11       | 5.69    | 0.595   | 1.46    | 0.0910 | 2.48    | 16.7                  | 1.46                 | 0.340                |
| 10SKP-17  | Fall-10         | 7.21    | 0.841   | 2.64    | 0.123  | 5.05    | 18.8                  | 1.76                 | 0.000                | 11SKP-54  | Spring-11       | 5.59    | 0.578   | 1.42    | 0.0820 | 2.42    | 15.7                  | 1.38                 | 0.271                |
| 10SKP-18  | Fall-10         | 10.3    | 8.25    | 66.5    | 2.66   | 111     | 20.7                  | 16.5                 | 0.0270               | 11SKP-55  | Spring-11       | 5.77    | 0.555   | 1.35    | 0.0810 | 2.37    | 17.8                  | 1.37                 | 0.237                |
| 10SKP-19  | Fall-10         | 7.08    | 0.822   | 2.66    | 0.118  | 5.26    | 21.2                  | 1.76                 | 0.0250               | 11SKP-56  | Spring-11       | 5.52    | 0.573   | 1.41    | 0.0830 | 2.43    | 16.2                  | 1.40                 | 0.268                |
| 10SKP-20  | Fall-10         | 7.22    | 0.827   | 2.67    | 0.117  | 5.13    | 19.9                  | 1.62                 | 0.0270               | 11SKP-57  | Spring-11       | 5.89    | 0.552   | 1.50    | 0.119  | 2.59    | 16.8                  | 1.41                 | 0.313                |
| 10SKP-21  | Fall-10         | 6.32    | 0.677   | 1.85    | 0.115  | 3.18    | 18.7                  | 1.70                 | 0.0430               | 11SKP-58  | Spring-11       | 5.89    | 0.527   | 1.39    | 0.0740 | 2.57    | 17.3                  | 1.35                 | 0.246                |
| 10SKP-22  | Fall-10         | 7.16    | 0.978   | 2.28    | 0.149  | 3.92    | 20.6                  | 2.87                 | 0.0700               | 11SKP-59  | Spring-11       | 5.94    | 0.538   | 1.40    | 0.0750 | 2.46    | 17.4                  | 1.42                 | 2.41                 |
| 10SKP-23  | Fall-10         | 6.11    | 0.644   | 1.83    | 0.0950 | 3.10    | 17.8                  | 1.64                 | 0.000                | 11SKP-60  | Spring-11       | 5.78    | 0.572   | 1.45    | 0.0870 | 2.33    | 16.7                  | 1.38                 | 3.50                 |
| 10SKP-24  | Fall-10         | 6.48    | 0.620   | 1.75    | 0.0930 | 2.87    | 17.4                  | 1.55                 | 0.0460               | 11SKP-70  | Summer-11       | 6.32    | 0.654   | 1.69    | 0.0840 | 3.44    | 20.5                  | 1.04                 | 0.000                |
| 10SKP-25  | Fall-10         | 6.23    | 0.636   | 1.86    | 0.0890 | 3.12    | 17.7                  | 1.56                 | 0.0450               | 11SKP-71  | Summer-11       | 6.33    | 0.654   | 1.67    | 0.0780 | 3.25    | 19.3                  | 1.08                 | 0.0240               |
| 10SKP-26  | Fall-10         | 6.80    | 0.626   | 1.87    | 0.0930 | 3.06    | 18.9                  | 1.62                 | 0.0380               | 11SKP-72  | Summer-11       | 6.36    | 0.657   | 1.71    | 0.0870 | 3.11    | 19.4                  | 1.12                 | 0.0200               |
| 10SKP-27  | Fall-10         | 4.88    | 0.562   | 1.09    | 0.145  | 1.48    | 13.4                  | 1.93                 | 0.0900               | 11SKP-100 | Summer-11       | 6.89    | 0.711   | 1.91    | 0.0800 | 3.74    | 20.7                  | 1.13                 | 0.0200               |
| 10SKP-28  | Fall-10         | 4.84    | 0.526   | 1.09    | 0.145  | 1.51    | 12.8                  | 1.22                 | 0.0390               | 11SKP-101 | Summer-11       | 6.95    | 0.718   | 1.99    | 0.0830 | 3.83    | 20.7                  | 1.11                 | 0.000                |
| 10SKP-29  | Fall-10         | 4.89    | 0.550   | 1.13    | 0.142  | 1.55    | 12.9                  | 1.41                 | 0.0790               | 11SKP-102 | Summer-11       | 6.88    | 0.712   | 1.94    | 0.0800 | 3.75    | 21.4                  | 1.10                 | 0.0230               |
| 10SKP-30  | Fall-10         | 5.09    | 0.485   | 1.07    | 0.0860 | 1.52    | 16.5                  | 1.10                 | 0.0790               | 11SKP-117 | Summer-11       | 6.70    | 0.646   | 1.80    | 0.0740 | 3.54    | 20.6                  | 1.02                 | 0.0200               |
| 10SKP-31  | Fall-10         | 4.98    | 0.534   | 1.17    | 0.111  | 1.57    | 12.7                  | 1.41                 | 0.0780               | 11SKP-118 | Summer-11       | 6.70    | 0.619   | 1.80    | 0.0730 | 3.57    | 20.4                  | 0.968                | 0.000                |
| 11SKP-32  | Winter-11       | 6.05    | 0.961   | 2.66    | 0.152  | 4.50    | 18.8                  | 1.96                 | 0.000                | 11SKP-119 | Summer-11       | 6.57    | 0.602   | 1.77    | 0.0670 | 3.52    | 19.9                  | 1.01                 | 0.000                |
| 11SKP-33  | Winter-11       | 6.23    | 1.01    | 2.73    | 0.145  | 4.51    | 18.8                  | 1.89                 | 0.154                | 11SKP-120 | Summer-11       | 6.56    | 0.565   | 1.66    | 0.0640 | 3.14    | 19.9                  | 0.799                | 0.0290               |
| 11SKP-34  | Winter-11       | 6.83    | 3.41    | 23.2    | 0.994  | 40.7    | 18.5                  | 6.77                 | 0.196                | 11SKP-121 | Summer-11       | 6.34    | 0.513   | 1.53    | 0.0500 | 2.86    | 19.2                  | 0.868                | 0.000                |
| 11SKP-35  | Winter-11       | 6.03    | 0.954   | 2.66    | 0.130  | 4.61    | 18.2                  | 1.75                 | 0.0440               | 11SKP-122 | Summer-11       | 6.29    | 0.516   | 1.53    | 0.0540 | 2.81    | 18.4                  | 0.893                | 0.000                |
| 11SKP-36  | Winter-11       | 5.88    | 0.938   | 2.66    | 0.148  | 4.67    | 18.5                  | 1.94                 | 0.000                | 11SKP-123 | Summer-11       | 6.41    | 0.537   | 1.56    | 0.0550 | 2.82    | 19.5                  | 0.905                | 0.000                |
| 11SKP-37  | Winter-11       | 6.02    | 0.941   | 2.71    | 0.116  | 4.86    | 17.7                  | 1.81                 | 0.131                | 11SKP-124 | Summer-11       | 6.38    | 0.513   | 1.55    | 0.0530 | 2.85    | 18.8                  | 0.825                | 0.000                |

**Table 8:** Chemical analyses of groundwater samples within the ERW.

| Sample ID | Ca<br>mg/L | Mg<br>mg/L | Na<br>mg/L | K<br>mg/L | Cl<br>mg/L | HCO <sub>3</sub><br>mg/L | SO <sub>4</sub><br>mg/L | NO <sub>3</sub><br>mg/L | Sample ID | Ca<br>mg/L | Mg<br>mg/L | Na<br>mg/L | K<br>mg/L | Cl<br>mg/L | HCO <sub>3</sub><br>mg/L | SO <sub>4</sub><br>mg/L | NO <sub>3</sub><br>mg/L |
|-----------|------------|------------|------------|-----------|------------|--------------------------|-------------------------|-------------------------|-----------|------------|------------|------------|-----------|------------|--------------------------|-------------------------|-------------------------|
| 11SKP-61  | 8.11       | 1.62       | 2.65       | 0.267     | 2.45       | 32.1                     | 1.14                    | 0.0700                  | 11SKP-89  | 18.2       | 5.38       | 5.30       | 0.237     | 8.93       | 75.3                     | 2.69                    | 0.696                   |
| 11SKP-62  | 53.6       | 19.5       | 10.3       | 0.598     | 37.8       | 210                      | 8.37                    | 7.45                    | 11SKP-90  | 7.14       | 0.850      | 2.05       | 0.115     | 4.35       | 21.6                     | 1.18                    | 0.0640                  |
| 11SKP-63  | 8.52       | 1.87       | 2.45       | 0.202     | 4.33       | 30.3                     | 2.28                    | 0.0230                  | 11SKP-91  | 7.16       | 0.851      | 2.06       | 0.108     | 4.31       | 21.7                     | 1.21                    | 0.0780                  |
| 11SKP-64  | 8.60       | 2.11       | 2.67       | 0.198     | 5.05       | 31.5                     | 2.20                    | 0.0270                  | 11SKP-92  | 11.4       | 3.39       | 3.55       | 0.271     | 6.76       | 47.0                     | 1.48                    | 0.0750                  |
| 11SKP-65  | 43.2       | 14.4       | 7.28       | 0.835     | 10.5       | 199                      | 7.76                    | 0.000                   | 11SKP-93  | 10.3       | 1.94       | 26.5       | 0.499     | 2.01       | 106                      | 3.36                    | 0.000                   |
| 11SKP-66  | 22.1       | 12.4       | 5.51       | 0.778     | 3.90       | 131                      | 4.79                    | 0.000                   | 11SKP-94  | 0.320      | 0.0536     | 31.2       | 0.100     | 3.15       | 75.4                     | 0.282                   | 0.0200                  |
| 11SKP-67  | 5.45       | 0.925      | 1.76       | 0.163     | 2.71       | 18.9                     | 1.26                    | 0.0450                  | 11SKP-95  | 9.40       | 1.67       | 3.76       | 1.56      | 2.06       | 34.6                     | 5.16                    | 4.72                    |
| 11SKP-68  | 35.7       | 6.57       | 4.48       | 0.777     | 9.21       | 115                      | 17.3                    | 0.000                   | 11SKP-96  | 5.17       | 1.02       | 1.89       | 0.290     | 1.89       | 20.6                     | 1.81                    | 0.000                   |
| 11SKP-69  | 8.43       | 3.12       | 135        | 0.697     | 58.3       | 278                      | 7.06                    | 0.000                   | 11SKP-97  | 15.7       | 5.71       | 10.3       | 0.476     | 13.0       | 70.2                     | 5.54                    | 2.72                    |
| 11SKP-73  | 15.5       | 3.90       | 8.95       | 0.270     | 15.4       | 52.5                     | 2.86                    | 7.75                    | 11SKP-98  | 15.4       | 3.79       | 6.36       | 0.862     | 9.70       | 37.7                     | 2.53                    | 25.7                    |
| 11SKP-74  | 10.8       | 1.23       | 2.65       | 0.174     | 1.56       | 41.8                     | 0.734                   | 0.000                   | 11SKP-99  | 17.8       | 4.79       | 5.66       | 0.333     | 8.43       | 74.3                     | 2.15                    | 0.000                   |
| 11SKP-75  | 5.44       | 1.14       | 1.89       | 0.203     | 3.87       | 19.0                     | 1.01                    | 0.0400                  | 11SKP-103 | 5.92       | 1.46       | 2.50       | 0.204     | 4.01       | 20.6                     | 2.25                    | 1.08                    |
| 11SKP-76  | 9.17       | 2.03       | 28.4       | 0.502     | 2.30       | 105                      | 2.44                    | 0.000                   | 11SKP-104 | 12.8       | 3.31       | 3.35       | 0.252     | 6.18       | 49.0                     | 2.57                    | 0.920                   |
| 11SKP-77  | 6.48       | 0.901      | 2.68       | 0.151     | 2.95       | 23.9                     | 1.34                    | 0.000                   | 11SKP-105 | 11.3       | 2.22       | 2.97       | 0.264     | 7.69       | 38.3                     | 2.45                    | 0.000                   |
| 11SKP-78  | 7.42       | 1.12       | 2.94       | 0.263     | 3.08       | 28.5                     | 1.35                    | 0.000                   | 11SKP-106 | 1.84       | 0.562      | 169        | 0.775     | 16.9       | 391                      | 3.36                    | 0.000                   |
| 11SKP-79  | 44.3       | 16.0       | 16.7       | 1.39      | 53.2       | 163                      | 8.50                    | 0.000                   | 11SKP-107 | 11.9       | 2.98       | 3.62       | 0.310     | 9.60       | 37.2                     | 3.07                    | 2.23                    |
| 11SKP-80  | 33.0       | 12.0       | 12.3       | 1.21      | 17.1       | 158                      | 7.92                    | 0.000                   | 11SKP-108 | 11.0       | 3.17       | 10.8       | 0.498     | 25.5       | 29.3                     | 2.29                    | 2.39                    |
| 11SKP-81  | 14.2       | 4.08       | 7.69       | 0.846     | 9.46       | 62.3                     | 3.70                    | 0.382                   | 11SKP-109 | 22.9       | 12.7       | 4.95       | 0.654     | 8.80       | 124                      | 6.52                    | 0.000                   |
| 11SKP-82  | 17.9       | 5.98       | 7.58       | 0.821     | 11.2       | 79.8                     | 3.52                    | 0.000                   | 11SKP-110 | 30.5       | 19.1       | 5.83       | 0.794     | 16.5       | 155                      | 20.1                    | 0.000                   |
| 11SKP-83  | 19.5       | 7.99       | 6.97       | 0.918     | 6.10       | 102                      | 4.62                    | 0.000                   | 11SKP-111 | 34.8       | 13.2       | 5.86       | 1.03      | 15.8       | 153                      | 6.19                    | 2.42                    |
| 11SKP-84  | 16.5       | 5.61       | 10.4       | 0.948     | 11.6       | 77.2                     | 4.86                    | 3.98                    | 11SKP-112 | 31.3       | 12.3       | 6.71       | 1.68      | 13.9       | 147                      | 7.11                    | 0.000                   |
| 11SKP-85  | 0.944      | 0.310      | 115        | 0.464     | 15.4       | 262                      | 2.49                    | 0.000                   | 11SKP-113 | 69.4       | 25.4       | 59.3       | 0.754     | 197        | 134                      | 8.73                    | 0.603                   |
| 11SKP-86  | 33.9       | 10.3       | 5.98       | 1.02      | 8.57       | 152                      | 3.91                    | 0.000                   | 11SKP-114 | 31.3       | 14.7       | 6.66       | 0.951     | 18.6       | 152                      | 6.50                    | 0.0960                  |
| 11SKP-87  | 13.7       | 1.95       | 2.67       | 0.365     | 2.02       | 52.8                     | 1.52                    | 0.000                   | 11SKP-115 | 24.0       | 11.0       | 7.90       | 0.926     | 3.94       | 136                      | 5.34                    | 0.000                   |
| 11SKP-88  | 17.4       | 5.67       | 4.22       | 0.326     | 9.56       | 69.5                     | 5.73                    | 0.481                   | 11SKP-116 | 28.7       | 10.5       | 8.31       | 0.840     | 3.21       | 152                      | 6.02                    | 0.000                   |



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