HYDROGEOCHEMICAL EVOLUTION AND ARSENIC MOBILIZATION IN CONFINED AQUIFERS FORMED WITHIN GLACIOMARINE SEDIMENTS

by

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ABSTRACT

The hydrogeochemical evolution and arsenic mobilization mechanisms in groundwater occurring in confined aquifers formed within glaciomarine sediments in the Lower Fraser Valley, British Columbia, are addressed. Methodology includes analysis of chemical and isotopic composition of groundwater, and mineralogical and chemical analysis of sediment samples sourced from core. Groundwater in confined aquifers is Na-HCO_3 or Na-Cl type, basic and reduced; whereas groundwater in unconfined aquifers is Ca-Mg-HCO_3 type, near neutral and oxidized. The chemistry of groundwater in confined aquifers is controlled by cation exchange, dissolution of carbonate minerals, silicate mineral weathering, and mixing with saline connate water suggesting freshening conditions. Arsenic release occurs as groundwater flows through glaciomarine sediments; its mobility is favoured by basic pH and reducing groundwater conditions. Possible arsenic release mechanisms are iron (hydr)oxide reduction and sulphide oxidation. A method of spatially representing likelihood of arsenic occurrence in groundwater based on geochemical interpretation and available data is presented.

Keywords: Groundwater; hydrogeochemistry; freshening; arsenic; likelihood of occurrence

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1: INTRODUCTION

Arsenic is a known carcinogen and poses serious risks to human health if ingested. Exposure to arsenic in drinking water is a known cause of a number of diseases, including skin cancer, hypertension, diabetes, vascular disease, neurological disorders and reproductive problems (Hopenhayn, 2006). The World Health Organization (WHO) and the Canadian Drinking Water Guidelines for arsenic are 10 µg/l (WHO, 2006; Health Canada, 2008); however, studies have shown that even this guideline amount exceeds tolerable cancer risks when considering long term exposure (Lindberg and Vahter, 2006).

Groundwater is often more vulnerable to arsenic contamination than surface water due to interactions of groundwater with aquifer minerals and the higher potential in aquifer environments for the generation of conditions that favour arsenic release (Smedley, 2006). Occurrences of arsenic at concentrations above the WHO guideline have been reported in a wide variety of groundwater environments (Smedley and Kinniburgh, 2002). These include mine sites (e.g., Williams, 2001; Woo and Choi, 2001), geothermal waters (e.g., Aiuppa et al., 2003; Arnórsson, 2003), bedrock aquifers (e.g., Lipfert et al., 2006; Peters and Blum, 2003; Smedley et al., 2007), and unconsolidated sedimentary aquifers (e.g., Bhattacharya et al., 1997; Smedley et al., 2002). Unconsolidated sedimentary aquifers have been of interest to researchers in particular, because arsenic has been reported at elevated levels in groundwater occurring within sediments with relatively low arsenic content (Smedley and Kinniburgh, 2002; Hering and Kneebone, 2002). The finding that large areas of Bangladesh and West Bengal, India have groundwater with arsenic at concentrations above drinking water guidelines (Chatterjee et al., 1995; Bhattacharya et al., 1997; BGS and DPHE, 2001), where 57 million people are believed to be exposed to groundwater with elevated arsenic concentrations, has prompted studies of arsenic occurrence and mobilization in unconsolidated sedimentary aquifers in a variety of settings. These include organic-rich aquifers in tropical regions (McArthur et al., 2004; Buschmann et al., 2007), evaporative semi-arid environments (Smedley et al., 2003; Deng et al., 2009), and aquifers formed in glaciated areas in the interior of North America (Warner, 2001; Erickson and Barnes, 2005).

Locally, elevated arsenic concentrations have been reported in groundwater in southwestern British Columbia. In Chilliwack, water samples analysed for 8 out of 18 wells were found to have arsenic concentrations above 10 µg/l (Graham, 2006). Groundwater with elevated arsenic was sampled predominantly from the Chilliwack-Rosedale aquifer, which is formed by young fluvial sediments (Graham, 2006). In Mission, 9 out of 20 wells were found to have arsenic above 10 µg/l. Wells with elevated arsenic in Mission were completed in granitic bedrock (Zubel, 2002). Bolton and Beckie (2011) addressed arsenic sources and mobilization mechanisms in groundwater sourced from Fraser River delta sediments. Arsenic concentrations in groundwater peaked at 32 µg/l in saline groundwaters. High concentrations of iron (up to 230 mg/l) and bicarbonate, and the presence of phosphate and ammonia in solution indicated that arsenic is released through reductive dissolution of iron oxide minerals. Reducing conditions were interpreted to occur as a result of oxidation of organic matter (Bolton and Beckie, 2011). Outside the Fraser Valley, elevated arsenic concentrations in groundwater have been reported on Bowen Island, where arsenic is associated with sulphide mineralization in bedrock (Boyle et al., 1998), and in the Powell River and Sunshine Coast regions, where high water pH associated with basaltic bedrock facilitates the mobility of arsenic, fluoride and boron (Mattu and Schreider, 2000).

Elevated arsenic has also been reported in groundwater occurring in aquifers confined by glaciomarine sediments in a coastal region, Lower Fraser Valley of British Columbia (Wilson et al., 2008). This is a groundwater environment that is very different from other environments mentioned above where processes resulting in elevated arsenic have been addressed. Wilson et al. (2008) sampled 98 wells in Langley and Surrey, and found that 45 wells have arsenic concentrations above the Canadian guideline. Positive relationships of arsenic with PO_4, Na, K, Cl, B, Mo, specific conductance, pH and well depth were found. Wilson et al. (2008) suggested that arsenic is most likely associated with sediments of marine origin since some of the parameters found to relate to arsenic, such as Na, K, Cl and B, are indicators of marine sedimentary deposits. They suggested that the relationship between arsenic and well depth infers that arsenic is sourced naturally, as deep wells are, in general, less sensitive to contamination from land use activities. They also found that elevated arsenic tends to occur in confined aquifers formed within marine sediments. Although the study of Wilson et al. (2008) delineated the spatial distribution of arsenic in groundwater in Langley and Surrey, the specific mechanisms by which the arsenic is mobilized and the physical and chemical groundwater conditions favouring arsenic mobility were not identified.

This thesis focuses on arsenic mobilization processes as well as chemical and physical groundwater conditions favouring arsenic mobility in the aquifers confined by glaciomarine sediments in Langley and Surrey, British Columbia.

1.1 Arsenic sources, speciation and mobility

Arsenic is an ubiquitous element in the environment that occurs naturally in rocks, sediments, soils, surface water and groundwater. It is a major constituent in more than 200 minerals, including arsenic oxides, as arsenolite (As_2O_3) and scorodite ($FeAsO_4.2H_2O$), and the sulphide ore forming minerals arsenopyrite (FeAsS), arsenian pyrite ($Fe(S,As)_2$), realgar (AsS) and orpiment (As_2S_3) (O'Day, 2006). Arsenic may also occur as impurities in a wide variety of minerals, often attaining higher concentrations (up to 100 g/kg) in sulphide and oxide minerals (Smedley and Kinniburgh, 2002). Although arsenic concentrations in most groundwaters are below the 10 µg/l WHO guideline, arsenic has been reported to occur naturally in groundwater at concentrations as high as 5300 µg/l (Smedley et al., 2002). Arsenic release to solution often takes place through some form of solid-aqueous solution interaction or microbial reduction process (BGS and DPHE, 2001; Lloyd and Oremland, 2006). As porosity typically accounts for a small portion of the total volume of aquifer media (Freeze and

Cherry, 1979), dissolution of only a relatively small amount of arsenic from solids is needed for groundwater to acquire elevated arsenic concentrations (Hering and Kneebone, 2002).

One control on the fate of arsenic, as well as other minor and trace elements in groundwater, is sorption promoted by surfaces of solids (as minerals and organic matter). Adsorption may take place through two different mechanisms: outer-sphere complexation (also referred to as non-specific adsorption) and inner-sphere complexation (or specific adsorption). With outer-sphere complexation, an electrostatic attraction occurs between a charged solid surface and an oppositely charged ion in solution. The adsorbed ion resides in solution at some distance from the solid surface, being easily displaced. With inner-sphere complexation, a coordinative complex is formed between the aqueous species and the mineral surface. Inner-sphere complex bonds are stronger than outer-sphere complexes, resulting in them being more difficult to break (Stollenwerk, 2002; Cheng et al., 2009). The pH of groundwater is a major control on the sorption of minor and trace elements. Under acidic conditions, sorption sites are occupied by protons, causing the surface of minerals to be generally positively charged; whereas under basic conditions the low concentration of protons causes the mineral surfaces to be negatively charged (Dzombak and Morel, 1990; Drever, 2002). As a result of this pH control on the charge of solid surfaces, anionic species tend to be adsorbed to surfaces at low pH and desorbed and mobilized at high pH; while cationic species are adsorbed to surfaces at high pH and mobilized at low pH (Dzombak and Morel, 1990).

Speciation of arsenic is an important control on its sorption behaviour. Dissolved arsenic species in groundwater occur dominantly as the inorganic oxidized form arsenate [As(V)] and the inorganic reduced form arsenite [As(III)]. Arsenic speciation redox reactions are commonly promoted by microbes (Lloyd and Oremland, 2006). Arsenate reduction to arsenite may be mediated by the ArsC arsenate reductase protein found in the cytoplasms of microbial cells, or may occur through the respiration of dissimilatory arsenate-reducing prokaryotes under anaerobic conditions (Lloyd and Oremland, 2006). Arsenite oxidation to arsenate is mediated by arsenite-oxidising bacteria that couple the oxidation of arsenite to the reduction of oxidants, such as oxygen and nitrate (Lloyd and Oremland, 2006). Organic arsenic, typically in the form of methylated arsenic compounds (produced by fungi as a detoxification strategy), may be found in surface water; however, they rarely occur at significant concentrations in groundwater (Francesconi and Kuehnelt, 2002).

Arsenic forms oxyanion complexes in aqueous solutions. In the typical pH range of natural waters (4 - 9; Hem, 1992) arsenate occurs in solution dominantly as the negatively charged species $H_2AsO_4^-$ and $HAsO_4^{2-}$, while arsenite occurs dominantly as the uncharged species $H_3AsO_3^0$ (Figure 1-1). Due to its negative charge, arsenate adsorption is greatest under acidic conditions and gradually decreases with increasing pH. Laboratory studies have shown that arsenate desorption from minerals such as amorphous Fe-hydroxide (Pierce and Moore, 1982; Raven et al., 1998), goethite (Bowell, 1994), gibbsite (Manning and Goldberg, 1996a), hematite (Xu et al., 1988), and clay minerals (Frost and Griffin, 1977; Xu et al., 1988) is greatest at basic water pH. Likewise, arsenic desorption has been interpreted as a process resulting in elevated arsenic concentrations in basic groundwater in the natural environment (Robertson, 1989; Del Razo et al., 1990; Smedley et al., 2002). As the dominant aqueous arsenite species is uncharged, arsenite adsorption peaks at the point of zero charge (pzc; often under near neutral pH) of solids surface (Pierce and Moore, 1982). The uncharged nature of arsenite species also results in it typically being less prone to adsorption than arsenate, making it a more mobile arsenic form (Pierce and Moore, 1982; Bowell, 1994; Stollenwerk, 2002). As a result of the sorption behaviour, arsenic is typically mobile in solution under basic pH or reducing conditions (Smedley and Kinniburgh, 2002).

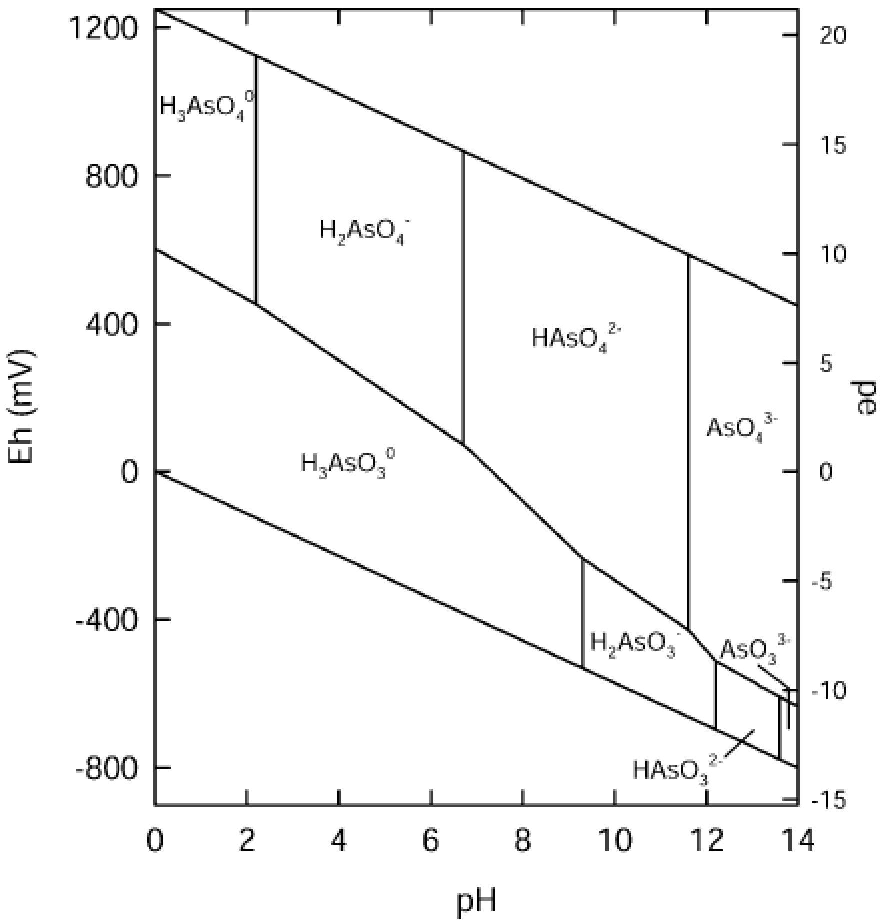

Figure 1-1. Eh-pH diagram for aqueous arsenic species at 25 ºC and 1 bar pressure.

Other anionic species in solution may compete for adsorption sites with arsenate. This can prevent arsenic from adsorbing to the solids' surfaces, which enhances arsenic mobility (a process referred in hydrogeochemistry as competitive adsorption). In particular, phosphorus and arsenic have similar chemical properties (they are both Group V elements), and thus strongly compete for adsorption sites. Laboratory studies have demonstrated that arsenate adsorption on ferrihydrite (Jain and Loeppert, 2000), goethite (Gao and

Mucci, 2001), gibbsite (Manning and Goldberg, 1996a) and clay minerals (Manning and Goldberg, 1996b) was significantly reduced in the presence of competing phosphate at elevated concentrations. Competitive adsorption of arsenate with phosphate has also been interpreted as a possible contributor to arsenic mobility in groundwater (Hundal et al., 2007; Rowland et al., 2008; Ujević et al., 2010). The presence of other anionic aqueous species at elevated concentrations in solution, such as bicarbonate (Appelo et al., 2002; Anawar et al., 2004), sulphate (Xu et al., 1988; Wilkie and Hering, 1996; Jain and Loeppert, 2000), silicic acid (Swedlund and Webster, 1999) and molybdate (Roy et al., 1986; Manning and Goldberg, 1996a; Manning and Goldberg, 1996b) has been interpreted to possibly enhance arsenic mobility through competitive adsorption.

Another major process resulting in the release of arsenic to solution is the dissolution of arsenic bearing minerals. The iron oxide and hydroxide minerals, ferrihydrite, goethite, lepidocrocite and hematite, are commonly found in oxidized sediments (Appelo and Postma, 2006). These minerals are a major source of arsenic due to their abundance in sediments and strong binding affinity (Smedley and Kinniburgh, 2002). Dissolution of oxide minerals takes place at increasing reducing conditions that are often triggered by oxidation of organic matter (Appelo and Postma, 2006). The reductive dissolution of oxide minerals has been described as a major process of arsenic release in groundwater (Stüben et al., 2003; Buschmann et al., 2007; Ujević et al., 2010)**,** especially in arsenic-rich groundwater of southeast Asia (McArthur et al., 2004; von Brömssen et al., 2007; Eiche et al., 2008; Rowland et al., 2008). The concurrent release of arsenic and iron to solution via the dissolution of arsenic bearing iron oxide and hydroxide minerals has been interpreted to result in a positive correlation between arsenic and iron concentrations in groundwater (McArthur et al., 2004). However, in several study areas, decoupling of arsenic and iron is instead observed (e.g. Islam et al., 2004; Horneman et al., 2004; Kelly et al., 2005). Decoupling of arsenic and iron in groundwater in environments where iron oxide dissolution is occurring has been interpreted to take place as a result of iron re-adsorption to mineral surfaces, or re-precipitation of Fe^{2+} as different oxide or carbonate minerals (Horneman et al., 2004; Charlet and Polya, 2006).

Arsenic may also be released to solution through the oxidative dissolution of arsenic bearing sulphide minerals. Although this process is typically reported in mine drainage environments (Williams, 2001; Morin and Calas, 2006; Cheng et al., 2009), the oxidation of sulphides is recognized as a mechanism of arsenic release to groundwater in natural environments (Nesbitt et al., 1995; Craw et al., 2003; Yunmei et al., 2004). Sulphide minerals are not stable under oxidizing conditions; hence, their dissolution is promoted by oxidants as O_2, Fe^{3+}, $Fe(OH)_3$ and NO_3. Although the oxidation of sulphides results in the release of iron to solution, correlation of arsenic and iron content in groundwater should not be expected as iron tends re-precipitate as iron oxides or hydroxides in the presence of oxidants (Cheng et al., 2009). A concurrent increase in the sulphate concentration in groundwater with depletion in the ^{34}S and ^{18}O concentrations of dissolved sulphate is an indicator of oxidative sulphide dissolution in water (van Everdingen and Krouse, 1985; Clark and Fritz, 1997).

1.2 Research purpose and objectives

The purpose of this research is to address arsenic mobilization mechanisms and conditions favouring arsenic mobility in groundwater found in confined aquifers in a coastal temperate region that was previously glaciated. This groundwater environment was chosen for investigation as most published studies on arsenic occurrences in groundwater in sedimentary environments have been conducted in organic-rich tropical environments (as in southeast Asia) or in evaporation dominated semi-arid regions, while less attention has been given to arsenic occurrences in coastal areas that have been impacted by sea level change associated with glaciation.

It is also a purpose of this research to address the hydrogeochemical evolution of the studied groundwater environment. This is done in order to evaluate how groundwater in confined aquifers acquires chemical conditions that favour arsenic mobility. The studied aquifers are confined by sediments that were deposited under seawater during a period of local marine transgression (see Chapter 2). As these aquifers are currently occupied by fresh groundwater, it is possible that the chemistry of groundwater in confined aquifers is controlled by processes as cation exchange, carbonate mineral dissolution and mixing, which are typically associated with coastal freshening environments (i.e. where fresh groundwater flushes seawater; Chapelle and Knobel, 1983; Edmunds and Walton, 1983; Bishop and Lloyd, 1990; Appelo, 1994). The occurrence of these processes and their controls to groundwater chemistry is addressed in this research.

The research objectives are:

1. To assess the hydrogeochemical evolution of groundwater occurring in confined aquifers formed within glaciomarine sediments. More specifically, to evaluate how processes associated with freshening environments such as cation exchange, mineral dissolution and precipitation, and silicate mineral weathering control the chemistry of groundwater in these environments;
2. To determine if arsenic release and mobility are enhanced in aquifers confined by glaciomarine sediments;
3. To assess the arsenic sources in the glaciomarine sediments and their controls on arsenic concentrations in groundwater;
4. To address arsenic release processes and chemical conditions favouring mobility in the studied environment; and,
5. To provide a method of spatially representing the likelihood of arsenic occurrences in different aquifers based on geochemical interpretation and observed data.

1.3 Scope of work

The main tasks that are involved in this work are:

1. Review the Quaternary geology, hydrogeological data, lithological logs, and previously collected groundwater chemistry data, and develop a conceptual model of the hydrogeochemistry of the study area;

2. Conduct an groundwater sampling program in the study area targeted to obtain representative samples and analyse collected samples for chemical and stable isotopic parameters;
3. Conduct chemical and mineralogical analyses on sediment core samples sourced from the study area;
4. Analyse collected data in order to identify the physical and chemical processes controlling the chemical and isotopic composition as well as the fate of arsenic in the studied groundwater;
5. Classify aquifers mapped in the study area based on likelihood of arsenic occurrence at elevated concentrations in groundwater, and produce a map showing the potential spatial distribution of arsenic in these aquifers.

1.4 Thesis outline

The format of this thesis is as three introductory chapters, followed by three stand alone papers, and overall conclusions and recommendations.

Chapter 1: Introduction

Introduction and rationale for the research. The purpose and objectives, along with the scope of the work are presented.

Chapter 2: Study area

Detailed overview of the study area. Geology, hydrogeology and climate are described.

Chapter 3: Methodology

Description of sampling and analytical methods used in this research.

Chapter 4 (paper): Hydrogeochemical evolution in a freshening environment in coastal glaciated region.

In this paper, the hydrogeochemical evolution of a groundwater system in a glaciated coastal region (Township of Langley and City of Surrey, Lower Fraser Valley of British Columbia) is described. A detailed discussion of mixing, cation exchange, carbonate mineral dissolution and silicate mineral weathering controls on groundwater chemistry is presented. The stoichiometry of the reactions are carefully analysed in order to interpret trends in the groundwater chemistry data. Logarithmic activity diagrams are used to address mineral weathering controls on groundwater chemistry. The contents of this chapter will be submitted as a paper to the Applied Geochemistry journal. Portions of the content in this chapter were included in an extended abstract and presentation at the 13th Water Rock Interaction (WRI-13) conference in Guanajuato, Mexico, in 2010.

Chapter 5 (paper): Arsenic mobilization under freshening conditions in confined aquifers formed within glaciomarine deposits.

Sources of arsenic in sediments and causes of the occurrence of arsenic at elevated concentration in the groundwater system are investigated in this paper. Relationships of arsenic concentrations in groundwater with chemical indicators of processes interpreted to take place in a freshening environment are described. Possible arsenic release processes, like desorption from mineral surfaces and dissolution of arsenic bearing minerals are assessed. The contents of this chapter were submitted as a paper for a special edition of Applied

Geochemistry on arsenic geochemistry. Portions of the content of this chapter were included in poster presentations at the Joint Assembly conference in Toronto and at the International Applied Geochemistry Symposium (IAGS) in Fredericton (both in 2009), and in an extended abstract and presentation at 13th Water Rock Interaction (WRI-13) conference in Guanajuato, Mexico, in 2010.

Chapter 6 (paper): A methodology for spatially representing the likelihood of occurrence of natural contaminants in groundwater.

A method for classifying aquifers based on the likelihood of occurrence of a hazardous constituent in groundwater, and spatially representing these aquifers on a map is presented in this paper. A case study demonstrates the method for showing the likelihood of occurrence of arsenic in different aquifers within the study area. The classification of aquifers by likelihood of arsenic occurrence is done based on geochemical and hydrogeological interpretations presented in the two previous chapters and groundwater chemistry data collected through this research and previous work. The contents of this chapter were presented at the 63rd Canadian Water Resource Association Conference in Vancouver, BC, 2010.

Chapter 7: Conclusions and recommendations

This chapter presents the conclusions from each chapter and recommendations for future research.

2: STUDY AREA

The study area includes the Township of Langley and the eastern portion of the City of Surrey (more specifically the Nickomekl-Serpentine Valley, including Cloverdale), in the Lower Fraser Valley of British Columbia (Figure 2-1). The population of the Township of Langley is over 100,000 people (Township of Langley, 2007), and the population of Cloverdale, in the City of Surrey, is approximately 50,000 people (BC Stats, 2005). In the Township of Langley, approximately 18,000 residents rely on private wells and community wells as source of water, while 82,000 residents use water supplied through the Greater Vancouver Water District and16 wells owned by the Township (Township of Langley, 2007).

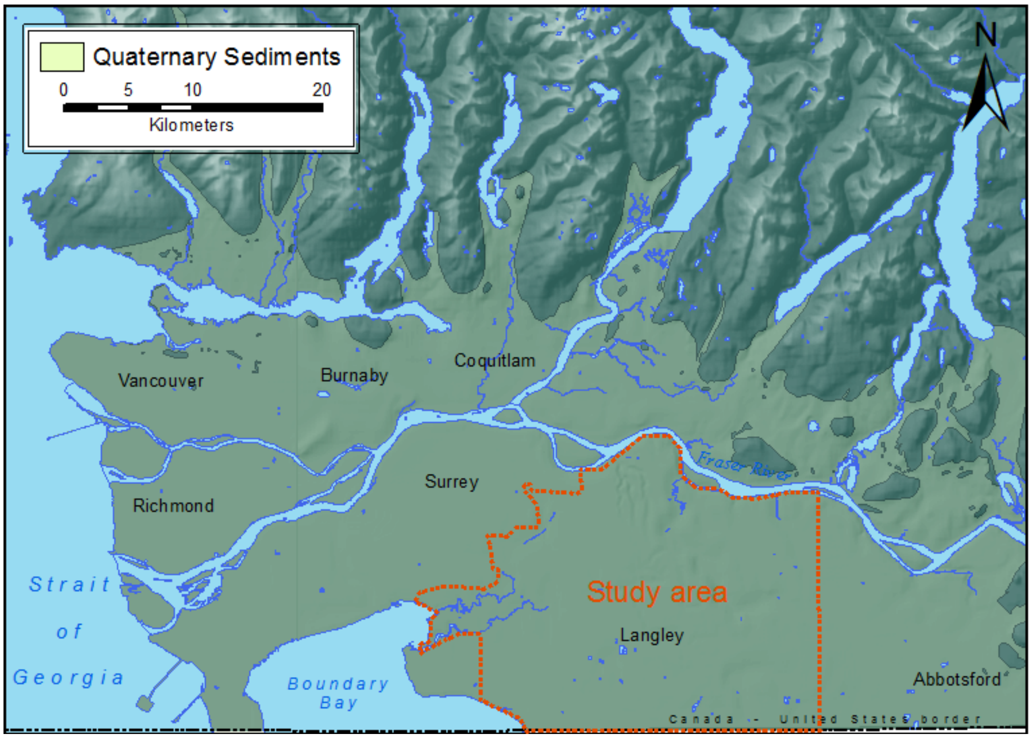

Figure 2-1. Study area for this research includes the Township of Langley and the eastern portion of the City of Surrey in the Lower Fraser Valley, British Columbia.

2.1 Physiography

The 3500 km^2 Lower Fraser Valley is a triangular shaped valley that extends from the city of Vancouver to the town of Agassiz (both in British Columbia), and to the City of Bellingham, Washington State, United States. The Lower Fraser Valley is bordered by the Cascade Mountains to the east and southeast, the Coastal Mountains to the north, and the Strait of Georgia to the west. On the Canadian side, the Lower Fraser Valley is cut by the Fraser River, which flows in an east to west direction. Surface elevations in Langley and Surrey range from 2 to 125 metres above sea level (masl).

2.2 Climate

The Lower Fraser Valley is situated in a temperate climate region. Average monthly temperatures in Langley range from +2.2 ^{o}C in January to +17.0 ^{o}C in August. The annual average rainfall is nearly 1500 mm and the average annual snowfall is 68 cm. Highest precipitation occurs from November to March (140-200 mm/month), while the lowest precipitation amounts occur from June to September (50-75 mm/month) (Environment Canada, 2008).

2.3 Geology and Hydrogeology

The bedrock geology of the Lower Fraser Valley consists of a sedimentary sequence comprised of clastic sedimentary rocks that were deposited within the Georgia Basin (Mustard and Rouse, 1994) overlying igneous basement rocks (Monger and Journeay, 1994). The bedrock is overlain by a sequence of surficial sediments up to 300 m thick, including sediments deposited near the margins of Pleistocene glaciers as well as sediments deposited post-glaciation (Clague, 1994). During the Fraser Glaciation (most recent advance of the Cordilleran Ice Sheet), a series of glaciation and deglaciation events, as well as marine transgression and regression, occurred in the Fraser Valley (Clague and James, 2002). This resulted in the deposition of a complex sequence of glacial, glaciofluvial, glaciomarine and fluvial sediments (Armstrong, 1976). The Quaternary geology of the study area is composed mainly of the following units: the Vashon Drift, the Capilano Sediments, the Fort Langley Formation, the

Sumas Drift and the Salish Sediments (see Quaternary geology map of the study area; Figure 2-2). Details concerning the sedimentary sequence are provided by Armstrong and Hicock (1980) and Clague (1994), and are summarized here.

- Sediments of the Vashon Drift were deposited by re-advancing ice following an interglacial period. These sediments are composed of lodgement till with interbeds of glaciolacustrine laminated stony silt, as well as glaciofluvial sandy gravel, gravelly sand outwash and ice-contact deposits.
- The Capilano Sediments and the Fort Langley Formation are marine and glaciomarine sediments that were deposited during ice retreat in isostaticaly depressed lowlands. The Capilano Sediments were deposited beyond the retreating ice margin and are composed of marine silt loam to clay loam, raised beach and deltaic sand, and fluvial deposits. The Fort Langley Formation was deposited in areas of fluctuating ice margin and is composed of glaciomarine clayey silt, lodgement and flow till, as well as outwash and ice-contact gravel and sand.
- The Sumas Drift was deposited as a result of a brief ice advance, near the end of the Fraser Glaciation, which extended as far as the eastern portion of the Township of Langley. Sumas Drift sediments are composed of outwash, ice-contact and deltaic sand and gravel with till lenses.
- The Salish Sediments are post-glacial and were deposited as a result of the formation and growth of the Fraser River floodplain and delta.

- Fraser River Sediments are deltaic and distributary channel fill sediments (Armstrong and Hicock, 1980; Clague, 1994).

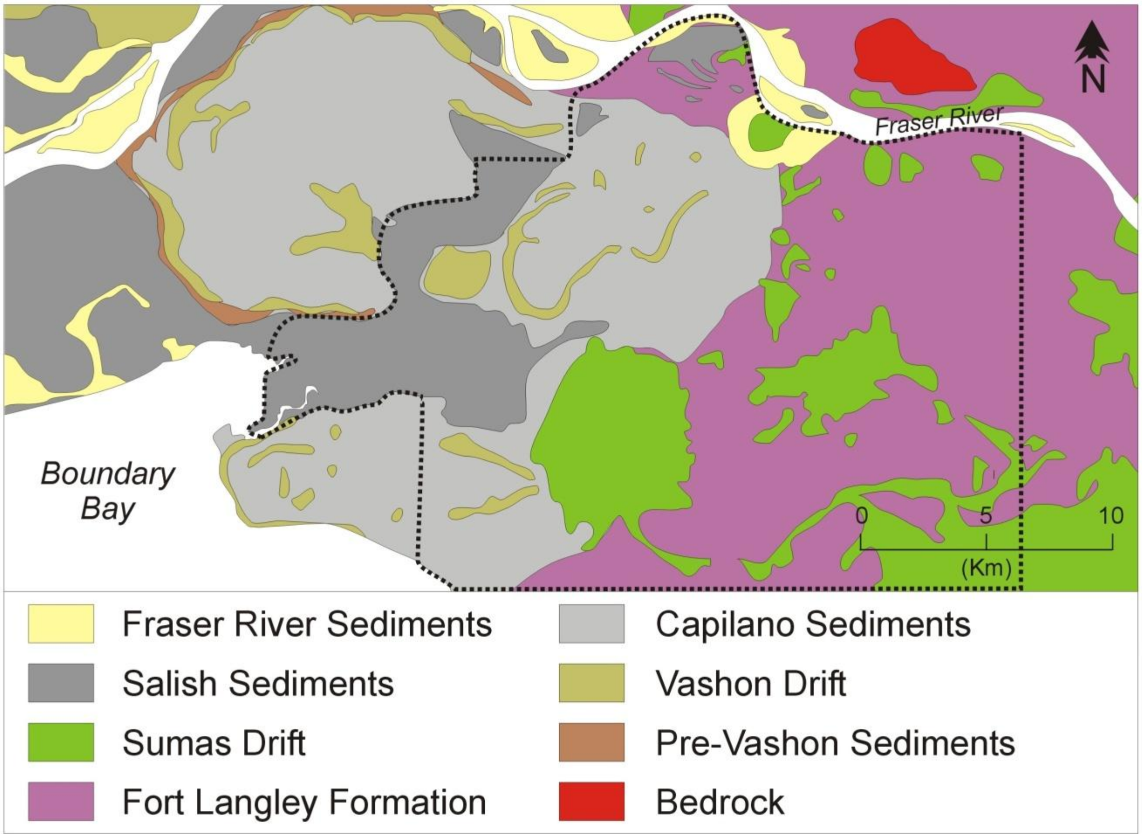

Figure 2-2. Simplified Quaternary geology map of the study area (modified from Armstrong and Hicock, 1980). Study area of research is outlined by dashed lines.

A total of 45 permeable units forming 18 major aquifers were mapped in this study area (Golder Associates Ltd., 2005). These aquifers can be separated into two groups: confined aquifers formed within glaciomarine and marine sediments (Capilano Sediments and Fort Langley Formation), and unconfined aquifers formed in near surface glaciofluvial sand and gravel (Sumas Drift). Detailed descriptions of the physical characteristics of these aquifers are provided by Halstead (1986) and Kreye and Wei (1994). The confined aquifers are formed in estuarine conditions, as fine to medium grained sand lenses or till diamictons; these are overlain and underlain by grey to blue-grey glaciomarine and marine clays and silts deposited during periods of marine transgression. These clay and silt deposits act as confining units. Lithological logs of wells show that the confined aquifers occur at depths ranging from 100 m to as shallow as 10 m below surface. Unconfined aquifers are comprised of reddish-brown deltaic and glaciofluvial sands and gravels that were deposited on top of glaciomarine sediments (Halstead, 1986; Kreye and Wei, 1994).

A groundwater flow model of the study area was produced by Golder Associates Ltd. (2005). The model suggests that the general groundwater flow direction in this area is southeast to northwest, following the topography of the terrain. Groundwater in shallow unconfined aquifers reaches the confined aquifers by flowing vertically downward through the confining units formed by glaciomarine silts and clays. Halstead (1986) suggested that groundwater occurring in deep confined aquifers should have considerable residence time.

In the described hydrogeological setting it is likely that groundwater chemistry in confined aquifers is controlled by processes related to water-rock interactions with salt water aquifers. Wilson et al. (2008) noted that groundwater in confined aquifers have high sodium content, while Halstead (1986) observed that in some deep confined aquifers groundwater also has high salinity and chloride content. These observations indicate that groundwater chemistry may be controlled by processes associated with freshening environments, as cation exchange and mixing with saline end-member. In addition, most confining units and aquifer forming sediments were deposited near the margin of glaciers. Glacially transported sediments typically have a high concentration of geochemically reactive phases, which favours the occurrence of mineral weathering reactions in glaciated environments (Anderson et al., 1997; Anderson et al., 2000; Cooper et al., 2002). This suggests that mineral weathering may also be an important control on groundwater chemistry. The occurrence of these processes and their controls on groundwater chemistry are evaluated in detail in Chapter 4 of this thesis.

3: METHODOLOGY

3.1 Field Methods

3.1.1 Installation of sampling equipment and field analysis of general water parameters

A total of 46 public and privately owned wells were selected for sampling. Of these, 41 are private wells and 5 are government owned observation wells. Private well water samples were collected from taps or access points as close as possible to the source well. Water treatment systems (e.g. filters, reverse osmosis, etc.) were avoided by collecting the sample from a pre-treatment access point, or the treatment systems were turned off prior to sampling. Observation wells were accessed with the assistance of British Columbia Ministry of Environment staff. Sampling at these wells was conducted using a Grundfos 3 inch submersible pump.

Installation of sampling equipment consisted of connecting an Eijkelkamp Agrisearch Equipment flow cell to the sampling tap using a hose. Another hose was connected to the flow cell in order to conduct water flowing out of the cell. Water parameters (pH, Eh, temperature, electrical conductivity (EC) and dissolved oxygen (DO)) were measured with probes inserted in the flow cell. This configuration ensured minimum exposure of the groundwater to the atmosphere (as contact with atmospheric gases can result in changes to some water parameters, such as pH, DO and Eh; Drever, 2002). Calibration of probes was done prior to sampling. Probes used were: Thermo Orion 01301MD Electrical Conductivity probe, Thermo Orion 08301MD Dissolved Oxygen probe, Thermo Orion 9678BNWP Redox/ORP probe (for Eh analysis) and Thermo Orion 9107BNMD pH probe. Electrical conductivity, dissolved oxygen and Eh probes were used connected to a Thermo Orion 5 Star meter, while the pH probe was used connected to a Thermo Orion 4 Star meter. The electrical conductivity probe was calibrated against 12.9 µS/cm and 1413 µS/cm standards, the dissolved oxygen probe was calibrated in water-saturated air in a calibration chamber with a water reservoir, the redox/ORP probe was calibrated against a Thermo Orion ORP 420 +/- 3 mV at 25 °C standard, and the pH probe was calibrated against Anachemia pH 4, pH 7 and pH 10 standards. Temperature was measured with the pH probe.

Once the flow cell was connected to the tap and the probes were calibrated and inserted into the flow cell, water was allowed to run. Readings of electrical conductivity, dissolved oxygen, Eh, pH and temperature were recorded on a sampling sheet every three to five minutes. Water was allowed to run until no significant change was observed with these parameters over the previous two to three readings (i.e. the probes were stabilized). This was done in order to ensure that water flowing through the cell was sourced directly from the aquifer and not from water that had been stagnant in the well and pipes. Probes typically took 15 to 30 minutes to stabilize in private wells, and 30 minutes to two hours to stabilize in observation wells. The last readings taken with the probes were recorded as the final values of pH, Eh, dissolved oxygen, electrical conductivity and temperature.

3.1.2 Collection and preservation of samples

Groundwater samples were collected after the stabilization of probes. All samples collected were filtered using a QED Environmental Systems disposable filter with 30 cm^2 area and 0.45 micron pore size. Sample bottles were washed with a filtered sample three times prior to sample collection. Water samples collected for the analysis of concentrations of cations were acidified with 0.5 ml ultrapure nitric acid and stored in 125 ml bottles. Samples collected for analysis of concentrations of anions were stored unacidified in 60 ml bottles. Samples collected for analysis of sulphur and oxygen stable isotopes of sulphate were acidified with 1.0 ml ultrapure nitric acid, mixed with $BaCl_2$ in order to precipitate $BaSO_4$, and stored in 1 litre bottles. Samples collected for analysis of carbon stable isotopes were mixed with $SrCl_2$ and 0.5 ml 1M NaOH in order to precipitate $SrCO_3$, and stored in 250 ml bottles.

3.1.3 Preservation and separation of arsenate and arsenite

Arsenate and arsenite species are redox sensitive and subject to rapid changes when exposed to the atmosphere (Samanta and Clifford, 2005). For this reason, preservation and separation of arsenic species were conducted on site. Preservation of arsenic species was done using method of Samanta and Clifford (2005), which prevents arsenic speciation from occurring for as long as 3 months. Filtered groundwater was collected and stored in 125 ml amber bottles.

These bottles were used in order to block UV illumination, which has been observed to enhance arsenite oxidation (Samanta and Clifford, 2005). A total of 1.25 ml of 50 mg/g ethylenediaminetetraacetate (EDTA) solution and 1.25 ml of 1.7M acetic acid solution were added to the collected sample. The EDTA solution preserves arsenic species from undergoing speciation and sequesters all the Fe, Mn and Al cations, which avoids precipitation of their corresponding oxyhydroxides that could provide sorption sites for arsenate species. The acetic acid solution keeps samples at a pH around 3.70, where the dominant arsenate species is the anionic $H_2AsO_4^-$ and the dominant arsenite species is the uncharged $H_3AsO_3^0$.

Although the preservation method applied has been reported to efficiently prevent arsenic speciation from occurring over a sufficiently long period, arsenic species separation was done in the field in order to ensure that minimum speciation occurred before separation. Arsenic species separation was done using the anion-exchange method, originally suggested by Ficklin (1983) and modified by Miller et al. (2000). Preparation of anion exchange columns was done in the laboratory prior to sampling. A Bio-Rad 1-X8 anion exchange resin with 50-100 mesh, purchased in the chloride form, was converted to acetate form. This was done by mixing three times 32.5 grams of dry resin with 900 litres of 1M NaOH solution for an hour, washing the resin with deionised water, mixing it three times with 120 ml of 1N acetic acid solution for an hour, and washing it again with deionised water. A total of 3 ml of resin converted to acetate form was added to each Bio-Rad econocolumn used. This amount of resin provided an anion exchange capacity of 3.6 meq to the column according to the resin manual (Bio-Rad, 1997). One anion-exchange column was used per sample. In the field, 30 ml of the EDTA preserved sample was injected in the anion-exchange column and collected in a bottle down flow from the column. During injection, anionic arsenate species is adsorbed by the anion-exchange resin, while the uncharged arsenite species is not adsorbed and allowed to flow through the column. The solution collected down flow from the column should only contain arsenite. The arsenite solution was analysed in the groundwater geochemistry laboratory at Simon Fraser University using a Horiba Jobin Yvon Ultima 2 Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES) with matrix corrections applied to calibration standards. The results are reported in As (III) per cent.

3.1.4 Alkalinity titration

Alkalinity titrations in triplicate were carried out using the methyl orange indicator solution method. Two drops of methyl orange were added to 10 ml of filtered groundwater sample. A Hach digital titrator was used to slowly add aliquots of 0.1 M HCl solution to the sample. This was done until the sample turned from an orange to a pink colour. The titrator has a counter that keeps track of the amount of solution added, with each click of the titrator counter being equal to 1.25 µl of solution added. The number of clicks of the titrator at the time the solution changed colour was recorded on the sampling sheet. The following formula for the reaction is assumed to take place when HCl is added to the sample:

$$HCO_3 + HCl \rightarrow H_2CO_3 + Cl^- \qquad (3.1)$$

As one mol of HCO_3 is converted to H_2CO_3 for every mol of HCl that is added, and considering that titration was done using a 0.1 M acid solution in 10 ml sample, the following formula was used to convert the number of clicks of the titrator to alkalinity (as HCO_3) in mg/l:

$$Alkalinity\ as\ HCO_3\ (mg/l) = no. of\ clicks * 1.25\ ul\ per\ click * 10^{-7} (converts\ to\ mol\ of\ HCO_3) * 61.01714\ (gfw\ of\ HCO_3) * 10^{5}\ (converts\ to\ mg/l) \quad (3.2)$$

3.1.5 Spectrophotometry

Concentrations of redox sensitive species NH_3, S^{2-} and Fe^{2+} in well water samples were determined using a Hach DR 2800 spectrophotometer. All spectrophotometry analyses were done using filtered samples. The methylene blue method was used to determine S^{2-} concentration (Hach, 2008a). A total of 10 ml of deionised water was used for blank preparation, while 10 ml of sample was used for sample preparation. 1 ml of Sulphide 1 reagent (containing sulphuric acid) and 1 ml of Sulphide 2 reagent (containing potassium dichromate) were added to both the blank and the sample. These were shaken and left waiting for 5 minutes. The blank was inserted in the spectrophotometer cell for zeroing. The prepared sample was inserted in the spectrophotometer cell following zeroing and the concentration of S^{2-} in µg/l was read (method detection limit is 5 ug/l). Concentration of Fe^{2+} was determined using the phenanthroline method for powder pillows (Hach, 2008b). Ferrous iron reagent (containing 1, 10-Phenanthroline and sodium bicarbonate) powder was added to a 25 ml sample. The sample was shaken and left for 3 minutes. Pure deionised water was inserted in the spectrophotometer cell for zeroing. The prepared sample was then inserted in the spectrophotometer cell and the concentration of Fe^{2+} in mg/l read (method detection limit is 0.02 mg/l). Concentration of NH_3 was determined using the salicylate method for powder pillows (Hach, 2008c). A total of 10 ml of deionised water was used for blank preparation, while 10 ml of sample was used for sample preparation. Ammonia salicylate reagent powder (containing sodium tartrate and sodium citrate) was added to both the sample and the blank. These were shaken and left waiting for 3 minutes. Ammonia cyanurate powder was then added to both the sample and the blank. These were shaken again and left for 15 minutes. The prepared blank was inserted in the spectrophotometer cell for zeroing. The prepared sample was then inserted in the spectrophotometer cell and the concentration of NH_3 in mg/l was read (method detection limit is 0.01 mg/l).

3.2 Laboratory methods

3.2.1 Groundwater

3.2.1.1 Concentration of elements

Analysis of major and minor elements in well water samples was conducted at the groundwater chemistry laboratory at Simon Fraser University. Samples were analysed for concentrations of anions (F, Cl, Br, NO_3, PO_4, SO_4) using a Dionex ICS-3000 SP Ion Chromatography System (IC) and for concentrations of major (Na, K, Ca, Mg) and minor (Al, As, B, Ba, Fe, Li, Mn, Mo, Si, Sr, Zn) cations using a Horiba Jobin Yvon Ultima 2 Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES). Samples were analysed for additional trace and minor elements (Ag, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Ga, Hf, In, La, Nb, Ni, Pb, Rb, Sb, Se, Sn, Ta, Te, Th, Tl, U, V, W, Y, Zn, Zr) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at ALS Chemex Laboratories in Vancouver. Complete analytical results are provided in the Appendix of this thesis. The error for results obtained through IC, ICP-AES and ICP-MS methods is +/- 3%. The detection limit of the analysis of each constituent is provided in the Appendix of this thesis.

3.2.1.2 Stable Isotopes

Barium sulphate and strontium carbonate precipitates were filtered from field preserved samples using a 0.45 micron cellulose acetate filter, oven dried and submitted to the Isotope Science Laboratory at the University of Calgary for analysis of sulphur and oxygen stable isotopes of sulphate as well as for carbon stable isotopes of dissolved inorganic carbon (DIC). Sulphur isotope ratios of precipitated barium sulphate were analysed using a Continuous Flow-Isotope Ratio Mass Spectrometry (CF-EA-IRMS). Results are reported relative to V-CDT. The error for δ^{34}S results is reported by the laboratory as +/- 0.25 ‰ based on daily reproducibility tests. Oxygen isotope ratios of precipitated barium sulphate were analysed by Thermal Conversion (pyrolysis) – Continuous Flow – Isotope Ratio Mass Spectrometry. Accuracy and precision of δ^{18}O of $BaSO_4$ is reported by the laboratory as generally better than ±0.3‰ (one standard deviation based on n = 50 lab standards). Carbon stable isotope measurements were performed on field precipitated strontium carbonate using a VG 903 Dual-Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) in the Isotope Science Laboratory at the

University of Calgary. Results are reported relative to V-PDB. The error for $\delta^{13}C$ results is +/- 0.2 per mil. This value is the reported precision and accuracy as 1 sigma (n=10) laboratory standards.

3.2.2 Sediment

A total of 29 sediment samples taken from three cores of wells completed in or near the study area were available for chemical and mineralogical analyses.

3.2.2.1 Mineralogical analyses

Quantitative X-Ray Powder Diffraction (XRD) analysis using the Rietveld Method (Rietveld, 1969) was conducted at the University of British Columbia on four glaciomarine clay and silt sediment (confining units) samples and one fine grained sand unit (a confined aquifer) extracted from these wells. Samples were reduced to the optimum grain-size range for quantitative X-ray analysis (<10 μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 7 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKa radiation on a Bruker D8 Focus Bragg-Brentano diffractometer, equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

3.2.2.2 Concentration of elements

Sediments samples were submitted to ALS Chemex Laboratories in Vancouver for analysis of concentrations of elements. All 29 sediment samples were analysed for total extractable concentration of 51 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr) using Aqua regia digestion and ICP-MS, near total concentration of 48 elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr) using four acids digestion (HF - HNO_3 – $HCLO_4$ digestion; HCl leach) and ICP-MS, and concentrations of additional 38 minor and trace elements (Ag, Ba, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr) using lithium metaborate fusion and ICP-MS. These samples were also analysed using Loss-on-Ignition, and for total organic carbon and total sulphur by Leco Furnace. Whole rock analysis (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, Cr_2O_3, TiO_2, MnO, P_2O_5, SrO, BaO) was conducted on sediment samples using lithium metaborate / lithium tetraborate fusion with ICP-MS. Complete analytical results are provided in the Appendix of this thesis.

3.2.2.3 Selected extractions

Twelve core samples were analysed using selected extractions in the groundwater geochemistry laboratory at Simon Fraser University in order to quantify various pools of solid phase arsenic in the sediment. A summary of the selected extractions steps applied to the sediment samples is displayed in Table 3-1. The first four extraction steps were done using the method by Keon et al. (2001), while the fifth extraction step is a method by Wenzel et al. (2001). These selected extraction steps were used in the study by Bolton and Beckie (2011), which investigated arsenic sources and mobilization mechanisms in groundwater sourced from Fraser River delta sediments.

Table 3-1. Summary of selected extraction steps applied to sediment core samples.

Step	Target Phase	Procedure	Possible extraction mechanism
1	Ionically bound and pore water	1 M $MgCl_2$, pH 8, room temp., 2 - 2 h repetitions, 1 DIW rinse at end	Anion exchange for Cl for As, possible Mg-As complex formed
2	Strongly adsorbed	1 M NaH_2PO_4, pH 5, room temp., 1 - 16 h then 1 - 24 h repetition, 1 DIW rinse at end	Anion exchange of PO4 for AsO_4 and AsO_3
3	Coprecipitated with carbonates, Mn oxides and very amorphous Fe oxyhydroxides	1 M HCl, room temp., 1 – 1 h repetition, 1 DIW rinse at end	Proton dissolution, Fe-Cl complexation
4	Coprecipitated with amorphous Fe oxyhydroxides	0.2 M ammonium oxalate/oxalic acid + 0.1 M NaH_2PO_4, pH 3.25, room temp., in the dark, 1 – 1 h repetition, 1 DIW rinse at end	Ligand-promoted dissolution
5	Coprecipitated with crystaline Fe oxyhydroxides	0.2 M ammonium oxalate/oxalic acid + 0.1 M ascorbic acid, pH 3.25, water bath at 96 °C, 1 – 30 min repetition, 1 DIW rinse at end	Reduction of Fe(III) to Fe(II)
6	Coprecipitated with As oxides and sulphides	Aqua regia + ICP-MS	
7	Total As	Four acids + ICP-MS	

The sediment core samples and all necessary equipment were transferred to an anaerobic chamber which was purged with nitrogen gas. The liner of each core sample was cut open and each sample was collected from the centre of the core, away from possible contamination effects associated with the core liner. For each sediment core sample, two duplicate samples of approximately 0.4 gram equivalent dry mass was collected and used in the selected extractions. Selected extraction steps 1 to 5 outlined in Table 3-1 were completed in the anaerobic chamber. All of the extractant solutions were prepared with deionised water (DIW), and the pH of each solution was adjusted with environmental grade hydrochloric acid (HCl) or sodium hydroxide (NaOH). The prepared extractant solutions were de-oxygenated by bubbling nitrogen gas through them prior to being transferred to the anaerobic chamber. Upon completion of each extraction step, the samples were centrifuged for 30 minutes. The extractant solutions were decanted into 60 ml syringes and filtered with 0.45 µm cellulose acetate syringe filters into HDPE sample bottles. Extractants from steps 1, 2, 4 and 5 were preserved with nitric acid (HNO_3). Extractant solutions were analysed for concentrations of dissolved arsenic in the groundwater geochemistry laboratory at Simon Fraser University by ICP-AES. Arsenic calibration standards used in the analyses by ICP-AES were prepared using the extractant solutions in order to account for matrix corrections. The detection limit obtained for steps 1, 2, 3 and 5 using this method was <1.0 mg/kg of As, while the detection limit obtained for step 4 was of <10 mg/kg of As. This high detection limit in extraction step 4 was the result of matrix effects and sample dilution that needed to be performed in order to avoid analytical problems with the ICP-AES. Results for steps 6 and 7 were recorded from arsenic concentration results from Aqua regia and four acids digestion with ICP-MS analyses conducted at ALS Chemex laboratories (described in Section 3.2.2.3).

4: HYDROGEOCHEMICAL EVOLUTION IN A FRESHENING ENVIRONMENT IN A COASTAL GLACIATED REGION

4.1 Introduction

The term "freshening" is employed in hydrogeochemistry to refer to groundwater environments where fresh groundwater displaces seawater. The chemistry of groundwater in a freshening environment is controlled by cation exchange reactions promoted by exchange sites on clays and organic matter. The main governing reaction in this type of groundwater environment is the exchange of calcium and magnesium ions from fresh groundwater for sodium present on the seawater equilibrated cation exchange complex of the aquifer (Appelo and Postma, 2006). This process is evidenced through the occurrence of Na-HCO_3 type groundwater in environments where fresh Ca-HCO_3 or Ca-Mg-HCO_3 type water is recharged (as observed in the studies of Foster, 1950; Lawrence et al., 1976; Chapelle and Knobel, 1983; Edmunds and Walton, 1983; Bishop and Lloyd, 1990; Appelo, 1994; Allen and Suchy, 2001, among others). Na-Cl type groundwater may also be found as a result of mixing with saline water that has not been completely displaced out of the aquifer (Edmunds and Walton, 1983). In environments where sufficient fresh water has flushed the aquifer, differences in selectivity leads to ion chromatography patterns with sequential yields of Ca -HCO_3, Mg-HCO_3 and Na-HCO_3 groundwaters at increasing distances from the recharge area (Valocchi et al., 1981; Appelo, 1994;

Lambrakis, 2006). Variations in the concentrations of cations in solution caused by cation exchange reactions have been interpreted to trigger mineral dissolution and precipitation. For example, the removal of calcium and magnesium from solution in a freshening system results in the dissolution of carbonate minerals and, consequently, increases in groundwater pH, alkalinity and dissolved inorganic carbon (DIC) (Lee and Strickland, 1988; Bishop and Lloyd, 1990; McMahon and Chapelle, 1991; Appelo, 1994).

The role of silicate mineral weathering controls on groundwater chemistry has not been described in detail in previous studies done on the hydrogeochemical evolution of aquifers in freshening systems. One exception is the study by Chapelle and Knobel (1983), which discussed weathering of glauconite in a freshening environment; however, these authors did not provide details on the hydrogeochemical evidence for this process. Mineral weathering should be an important control on the chemistry of groundwater occurring in glaciated regions, as glacially-transported sediments typically have a high proportion of geochemically-reactive mineral phases (Anderson et al., 1997; Anderson et al., 2000; Cooper et al., 2002). The role of silicate mineral weathering in the hydrogeochemical evolution of freshening environments should be carefully addressed, as weathering of silicates also results in the addition of cations to solution and in increases in groundwater pH and alkalinity.

In this study, the hydrogeochemical evolution of groundwater occurring in a coastal setting, comprised of unconfined aquifers formed within glaciofluvial sediments and aquifers confined by glaciomarine sediments, is addressed. The main processes considered are carbonate mineral dissolution, cation exchange, mixing with saline water, and weathering of silicate minerals. Carbonate mineral dissolution and cation exchange reactions are assessed by comparing trends in the groundwater chemical data with the stoichiometry of governing reactions and using carbon stable isotopes of DIC. Mixing is addressed through geochemical analysis in combination with the post-glacial history of this region. Possible reactive silicate phases contributing to weathering reactions are evaluated through XRD analyses conducted on confining units and aquifer-forming sediments. Hydrogeochemical evidence for silicate weathering controls on groundwater chemistry is evaluated using activity diagrams.

4.2 Study area

The study area is located in the Township of Langley and the eastern portion of the City of Surrey in the Lower Fraser Valley, British Columbia, Canada (Figure 4-1). The groundwater system consists of aquifers formed in Quaternary unconsolidated sediments that are several hundreds of meters thick and that overlie Tertiary bedrock (Halstead, 1986). The geological history of the Quaternary period in the Fraser Valley has been described by Clague (1994) and Clague and James (2002). Unconsolidated sediments in this region were deposited dominantly during and since the most recent Cordilleran ice sheet advance in the Late Pleistocene (Armstrong, 1976). This period was characterized by a series of glaciation and deglaciation events that took place in the Fraser Valley, during which glacial and glaciofluvial sediments were deposited. Thickening and expansion of glaciers led to a progressive isostatic depression of the land by as much as 300 meters below present day sea-level. The depressed land was submerged beneath the sea, resulting in the deposition of glaciomarine and marine sediments in the region. Rapid deglaciation triggered isostatic rebound of the land and relative sea-level regression at the end of the Pleistocene (Clague and James, 2002). This was followed by deposition of Late Pleistocene glaciofluvial sediments and Holocene deltaic and fluvial sediments (Clague and James, 2002). The surficial geology of the Lower Fraser Valley is therefore formed by a complex sequence of glacial, glaciofluvial, glaciomarine, marine and post-glacial fluvial unconsolidated sediments (Armstrong and Hicock, 1980).

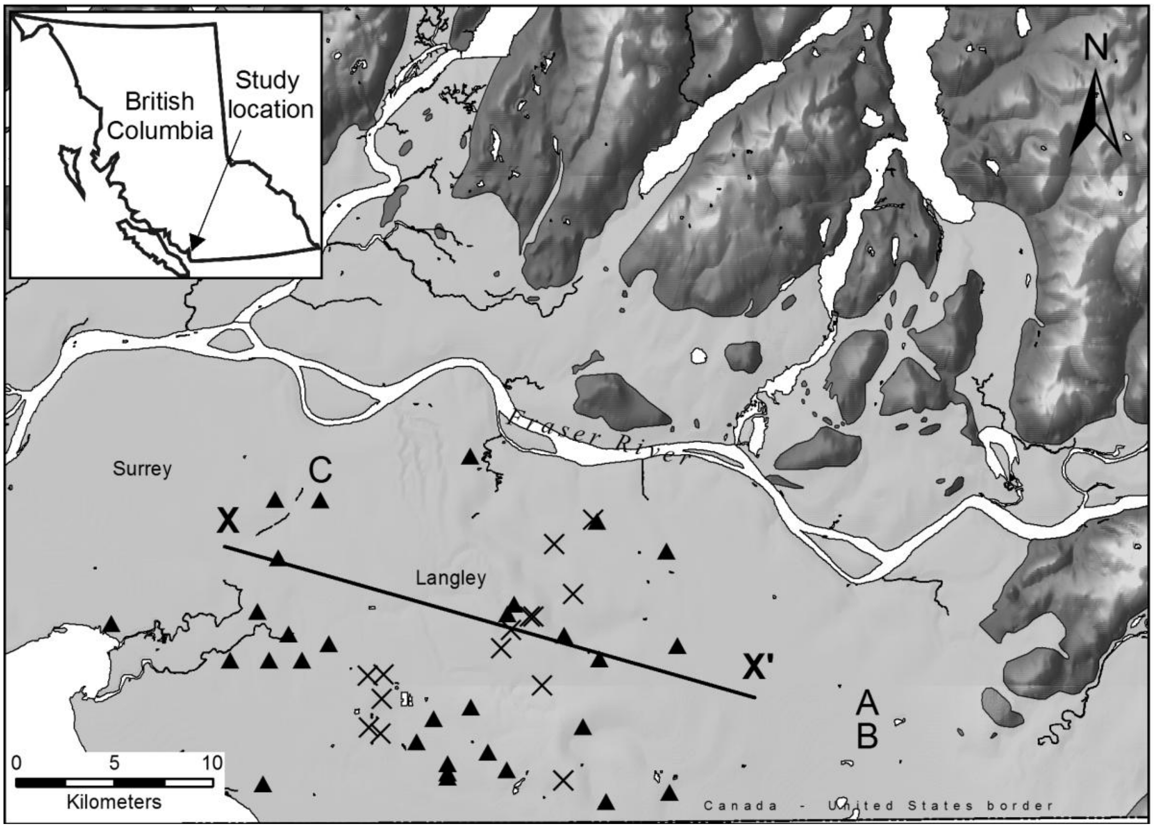

Figure 4-1. The study area is located in the Township of Langley and the eastern portion of the City of Surrey, in the Lower Fraser Valley of British Columbia, Canada. Groundwater sampling locations are marked as crosses for samples sourced from unconfined aquifers, and as triangles for samples sourced from confined aquifers. Letters A, B and C represent the locations of wells at which sediment core samples were taken. The cross-section for Figure 4-2 is shown from X-X'.

A total of 45 permeable units forming 18 major aquifers have been mapped in this study area (Golder Associates Ltd., 2005). These aquifers can be separated into two groups: confined aquifers formed within glaciomarine and marine sediments, and unconfined aquifers formed in areas of higher elevation above present sea level in near surface glaciofluvial sand and gravel deposited on top of glaciomarine sediments (Figure 4-2). Detailed descriptions of the physical characteristics of these aquifers are provided by Halstead (1986) and

Kreye and Wei (1994). The confined aquifers comprise estuarine deposits, as fine to medium grained sand lenses, or till diamictons, and are overlain and underlain by glaciomarine and marine clays and silts that were deposited during periods of marine transgression. These clay and silt deposits act as confining units. Lithological logs of wells show that the top of some of the confined aquifers are as deep as 100 meters below surface, and are overlain by a monotonous sequence of stony grey clays that outcrop at the surface. Deeper confined aquifers are known to exist in this area; however, these are rarely explored, as the shallower aquifers supply sufficient groundwater to residents. Other confined aquifers occur at depths as shallow as 10 meters below surface. Unconfined aquifers are comprised of reddish-brown deltaic and glaciofluvial sands and gravels that were deposited on top of the glaciomarine sediments (Halstead, 1986; Kreye and Wei, 1994).

A groundwater flow model of the study area was produced by Golder Associates Ltd. (2005). The model suggests that the general groundwater flow direction in this area is southeast to northwest. Groundwater in unconfined aquifers is recharged by rain water at the surface. Groundwater that reaches the glaciomarine sediments and confined aquifers is recharged either from the overlying unconfined aquifers (where present) and down through the sequence of deeper deposits, or directly through the glaciomarine sediments where these are exposed at surface (Figure 4-2). Many of the low lying wells that source water from deep confined aquifers are artesian, suggesting that recharge to these aquifers occurs at higher elevation – i.e., the Toth flow model of topography driven recharge (Toth, 1962). Halstead (1986) suggested that groundwater occurring in deep confined aquifers should have a considerable residence time.

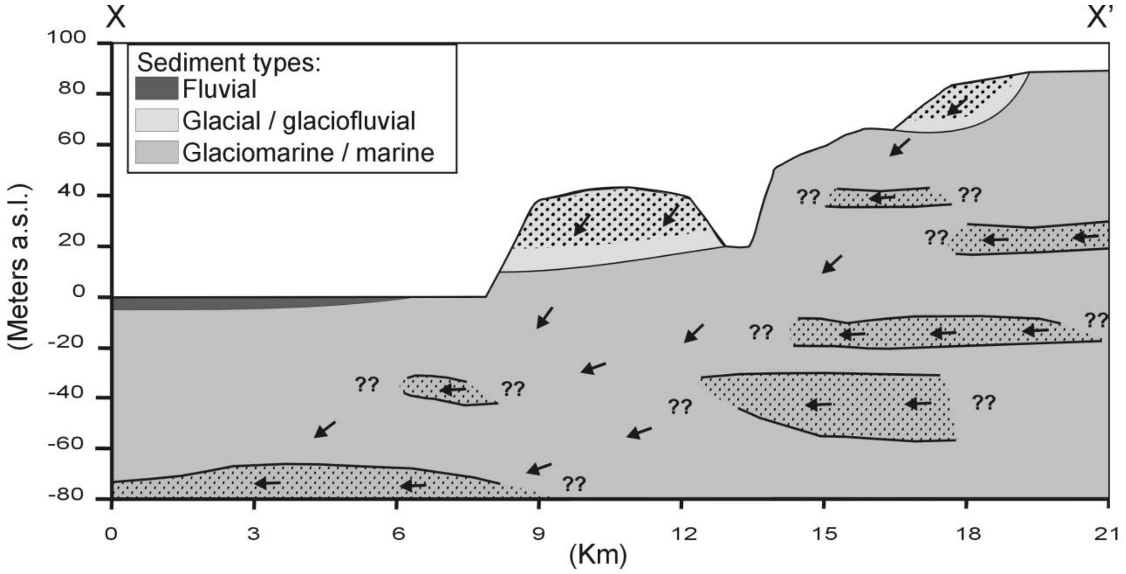

Figure 4-2. Schematic cross section of the study area (location of cross-section shown on Figure 4-1). Aquifers (represented with a dotted pattern in this figure) can be separated into two groups: Unconfined aquifers comprise near surface glaciofluvial sand and gravel, and confined aquifers comprise deeper estuarine deposits and till that are overlain and interbedded with glaciomarine silt and clay. A groundwater flow model suggests that the general groundwater flow direction (represented as arrows) in this area is southeast to northwest. Groundwater reaches deep confined aquifers by flowing from unconfined aquifers through confining units and other confined aquifers (Golder Associates Ltd., 2005).

4.3 Methodology

Analysis of historical groundwater geochemistry data was conducted prior to sampling for this study. Two datasets were examined: the British Columbia Environmental Monitoring System (EMS) database and data collected through the study of Wilson et al. (2008). A total of 46 publically and privately owned wells were selected for sampling. Wells were selected with the objective of including a representative number of samples from each groundwater environment in the study area. Thus, 15 wells source groundwater from unconfined aquifers formed in glaciofluvial deposits, and 31 wells source groundwater from aquifers confined by glaciomarine and marine clays and silts. The sampling locations are distributed across the entire study area, rather than being located solely along a specific flow path of a single aquifer.

Private well water samples were collected from taps or access points as close to the source well as possible. Water treatment systems (e.g. filters, reverse osmosis, etc.) were avoided by collecting the sample from a pre-treated access point, or the treatment systems were turned off prior to sampling. Public monitoring well samples were collected using a Grundfos 3 inch submersible pump. Temperature, pH, Eh, electrical conductivity and dissolved oxygen were monitored using Thermo Orion meters and probes placed within an Eijkelkamp flow through cell. Upon stabilization of the monitored parameters a QED Environmental Systems polyethersulfane 0.45 micron in-line disposable filter was attached and samples were collected for analysis of stable isotopes and concentrations of dissolved constituents. Well water samples were analyzed on site for alkalinity by titration and for redox sensitive constituents (NH_3, S^{2-} and Fe^{2+}) using a Hach DR2800 spectrophotometer. Samples collected for analysis of cation concentrations were acidified to $pH < 3$ with ultrapure HNO_3.

Analysis of major and minor elements was conducted in the groundwater geochemistry laboratory at Simon Fraser University. Samples were analysed for concentrations of anions (F, Cl, Br, NO_3, PO_4, SO_4) using a Dionex ICS-3000 SP Ion Chromatograph (IC) and for concentrations of major (Na, K, Ca, Mg) and minor (Al, As, B, Ba, Fe, Li, Mn, Mo, Si, Sr, Zn) cations using a Horiba Jobin Yvon Ultima 2 Inductively Couple Plasma Atomic Emission Spectrometer (ICP-AES). The saturation indexes of minerals and the activities of aqueous species were calculated using PHREEQC with the Wateq4f thermodynamic database (Parkhurst and Appelo, 1999). The chemical composition of average rainfall was determined from the Environment Canada Saturna Island Station *CAPMoN* (Canadian Air and Precipitation Monitoring Network) dataset available online (Environment Canada, 2011). Precipitation chemistry data were culled based on completeness of analyses, and bicarbonate content was estimated based on charge balance. Carbon stable isotope measurements were performed on field precipitated strontium carbonate using a VG 903 Dual-Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) in the Isotope Science Laboratory at the University of Calgary. All stable isotope results are reported in ‰ relative to the VPDB (Vienna Peedee Belemnite) standard. The error for $\delta^{13}C$ results is +/- 0.2 per mil. This value is the reported precision and accuracy as 1 sigma (n=10) laboratory standards.

Sediment samples taken from three cores from wells drilled within or near the study area were available for mineralogical analysis. Quantitative X-Ray Powder Diffraction (XRD) analysis using the Rietveld method (Rietveld, 1969) was conducted at the University of British Columbia on four glaciomarine clay and silt sediment (confining units) samples and one fine grained sand unit (a confined aquifer) extracted from the cores. Samples were reduced to the optimum grain-size range for quantitative X-ray analysis (<10 μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 7 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKa radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with a Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. The organic matter content of sediment samples was determined using a LECO elemental analyzer, conducted at ALS Chemex Laboratories in Vancouver. Complete analytical results are provided in the Appendix of this thesis.

4.4 Results

A clear difference is observed between the major element chemistry of groundwater occurring in glaciofluvial unconfined aquifers and aquifers confined by glaciomarine clays. Unconfined aquifer samples are of Ca-Mg-HCO_3 type, whereas confined aquifer samples have a range in composition, going from Ca-Mg-HCO_3 to Na-HCO_3 and then to Na-Cl (as observed in the Piper diagram; Figure 4-3). Most confined aquifer samples are a Na-HCO_3 type, while eight samples collected from deep confined aquifers are a Na-Cl type.

Other differences in the chemistry of groundwater sourced from confined and unconfined aquifers are observed (Table 4-1). Specifically, Ca-Mg-HCO_3 groundwater sourced from unconfined aquifers has relatively low salinity, near neutral pH (mostly 6.0 to 7.7), low alkalinity (35 mg/l to 135 mg/l as HCO_3), mostly oxidizing conditions, with Eh ranging from 150 mV to 350 mV (SHE), and ferrous iron and ammonia occurring below method detection limits in most samples. Conversely, Na-HCO_3 and Na-Cl confined aquifer samples have higher salinity, basic pH, higher alkalinity and reducing conditions, with Eh values as low as -45 mV (SHE), ferrous iron and ammonia occurring above detection limits in most samples, and hydrogen sulphide present in some samples. In addition, Na-Cl samples display higher salinity than the Na-HCO_3 samples.

The four glaciomarine clay and silt confining unit sediment samples (RCA-01, RCA-09, RCA-28, RCA-29) have similar mineralogy (Table 4-2). XRD analysis results show that these sediments have a relatively high proportion of primary silicate minerals such as plagioclase (~40%), quartz (~25%), amphibole (actinolite; ~7%), chlorite (~11%) and orthoclase (~4%). Carbonate (calcite and dolomite; ~3.5%) and sulphide (pyrite; ~0.2%) minerals also constitute a noticeable proportion of the minerals in these sediments, while kaolinite/lizardite appears in minor amounts. The fine grained sand confined aquifer sample (RCA-07) has a similar mineralogy to the clay and silt samples, although with higher quartz content (42%) and lower amphibole (3.6%), chlorite (5.0%) and illite/muscovite (5.6%) contents. The organic matter content of sediment samples ranges from 0.04% to 0.54%.

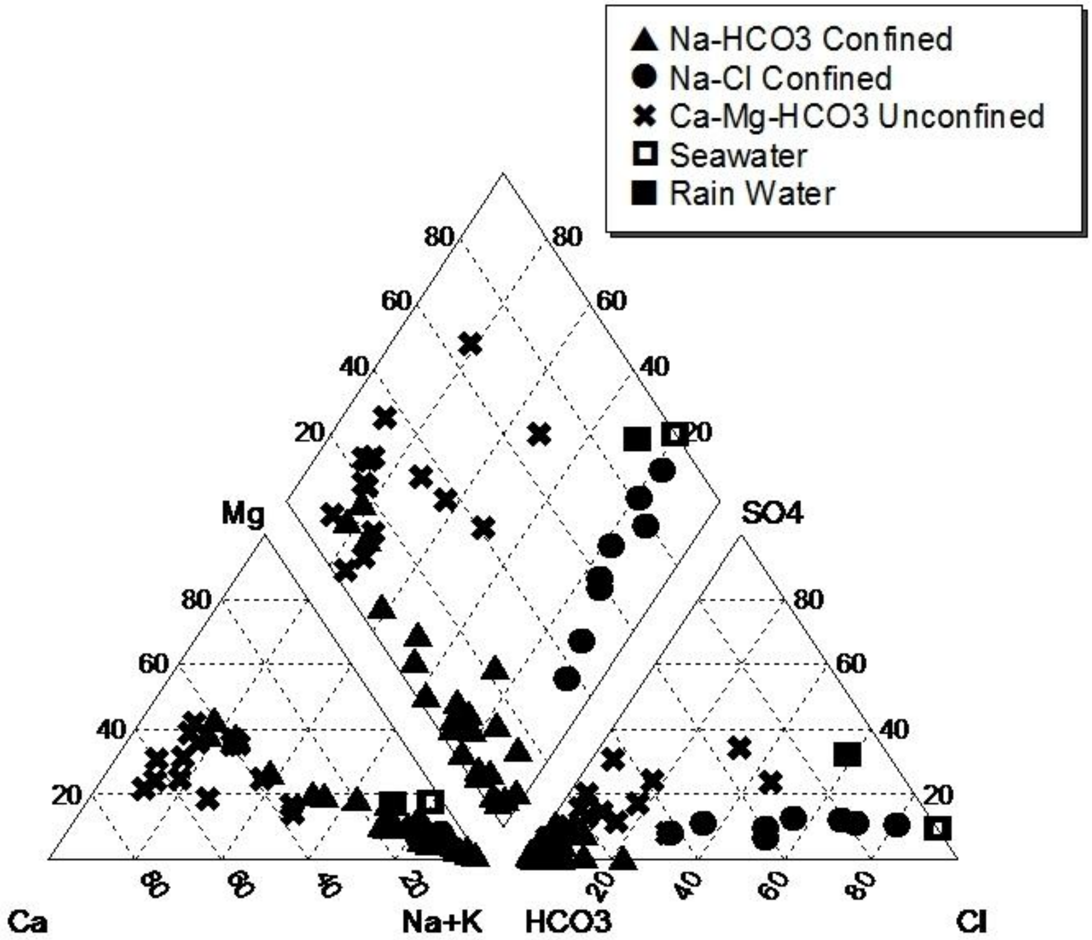

Figure 4-3. Piper diagram showing different groundwater types. Unconfined aquifer samples are a Ca-Mg-HCO_3 type while confined aquifers are Na-HCO_3 and Na-Cl types. Included is the average rainfall composition from the Saturna Island station and average seawater composition (Drever, 2002).

Table 4-1. Major cations and anions, pH, Eh, field measured redox sensitive species, and δ^{13}C results for well water samples.

Sample no.	Sample Type*	pH	Eh (mV)	K (mg/l)	Na (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)	Si (mg/l)	Fe^{2+} (mg/l)	NH_3 (mg/l)	S^{2-} (µg/l)	$\delta^{13}C_{DIC}$ ‰
01	U - $CaMgHCO_3$	7.0	164	1.7	6.6	23.6	11.5	15	14	117	16.6	1.78	0	0	-16.0
02	U - $CaMgHCO_3$	5.9	349	1.1	10.0	29.1	7.5	20	29	36	10.5	0.02	0		-20.3
03	U - $CaMgHCO_3$	6.1	337	2.2	14.4	10.1	2.4	6.7	12	39	5.5	0.01	0		-18.5
04	U - $CaMgHCO_3$	8.6	107	2.8	7.8	28.6	10.1	5.2	21	133	8.5	0.02	0.14		-13.9
05	U - $CaMgHCO_3$	7.7	148	1.3	5.0	8.1	4.6	1.0	0.6	80	11.0	0.35	0.03	0	-18.9
06	U - $CaMgHCO_3$	7.3	271	2.9	8.9	56.3	17.3	5.2	43	115	9.7	0	0.01		-14.4
07	U - $CaMgHCO_3$	6.4	374	1.0	11.5	20.5	4.2	9.3	12	59	6.8	0.05	0		-18.0
08	U - $CaMgHCO_3$	7.7	234	1.4	7.9	11.1	6.1	1.3	3.9	72	11.7	0	0		-18.2
09	U - $CaMgHCO_3$	8.7	76	1.3	3.5	22.2	4.2	2.7	16	76	9.2	0.01	0		-12.9
10	C - $NaHCO_3$	8.4	319	5.1	21.4	12.1	5.1	1.8	7.7	114	13.1	0.01	0.06	0	-12.7
11	U - $CaMgHCO_3$	6.8	336	1.1	5.3	25.3	5.8	7.2	13	86	11.4	0.01	0		-16.8
12	U - $CaMgHCO_3$	6.4	328	1.1	14.7	14.0	5.4	17	6.2	63	7.7	0.49	0	0	-19.7
13	C - NaCl	8.7	61	11.5	261	32.6	11.6	302	91	288	9.1	0.18	0.2	14	-15.3
14	C - NaCl	8.5	44	6.4	141	12.4	5.5	141	23	187	11.0	0.06	0.19	24	-17.3
15	C - $NaHCO_3$	9.0	236	4.1	104	12.2	3.9	28	1.8	281	7.5	0.06	0.21	0	-18.0
16	C - NaCl	8.9	192	7.7	197	9.7	3.2	98	33	332	14.4	0.03	0.07	1	-12.5
17	C - $NaHCO_3$	8.6	277	6.7	76.9	7.9	2.3	1.6	4.5	236	13.5	0.01	0.09	0	-16.4
18	C - $NaHCO_3$	8.7	245	4.7	72.9	15.1	5.3	2.5	4.7	260	10.1	0.03	0.11	0	-15.1
19	C - $NaHCO_3$	8.4	95	1.8	94.7	6.1	2.6	1.8	10	272	11.1	0.07	0.02	6	-16.8
20	C - $NaHCO_3$	8.6	145	3.1	106	4.4	1.6	2.4	2.7	303	9.1	0.03	0.1	3	-15.3
21	C - $NaHCO_3$	7.9	89	1.9	10.0	22.8	14.5	6.1	5.2	142	12.4	0.26			-19.4
22	C - $NaHCO_3$	8.1	92	9.1	122	20.2	16.3	7.6	21	421	12.8	0.09			-15.7
23	C - $NaHCO_3$	9.2	187	4.5	83.7	3.3	2.0	9.0	18	186	8.7	0.01	0.14	0	-14.6
24	C - NaCl	8.7	78	9.8	473	58.1	21.4	755	132	137	6.0	0.12	0.48	1	-16.5
25	C - $NaHCO_3$	8.5	71	6.5	162	14.2	14.3	3.5	3.1	539	10.9	0.07	0.19	0	-12.3
26	C - $NaHCO_3$	8.1	72	2.3	21.4	9.7	4.3	1.7	2.1	107	11.7	0.12	0.05	6	-17.4
27	C - $NaHCO_3$	8.2	123	2.2	12.1	10.8	4.8	0.9	3.0	87	12.5	0.03	0.04	1	-17.6
28	C - $NaHCO_3$	7.6	161	1.4	7.6	11.2	6.8	1.1	8.0	82	10.5	0.2	0.05	3	-19.0
29	U - $CaMgHCO_3$	7.6	307	1.7	7.2	25.2	13.9	2.0	8.5	153	8.0	0.01	0	0	-18.9
30	C - $NaHCO_3$	8.6	77	5.8	83.1	11.2	6.0	4.8	11	264	13.8	0.03	0.21	0	-14.3
31	C - $NaHCO_3$	8.2	319	8.0	62.3	18.3	10.5	3.4	0.5	277	16.9	0.01	0	0	-18.4
32	C - $NaHCO_3$	6.9	361	1.6	5.7	14.1	7.4	5.3	5.6	78	14.1	0	0.01		-17.4
33	U - $CaMgHCO_3$	7.7	306	1.6	8.8	13.7	7.2	2.9	8.1	87	11.6	0.02	0		-18.6
34	C - $NaHCO_3$	8.7	76	4.4	76.6	5.7	3.0	0.7	2.7	235	13.7	0.06	0.11	0	-12.3
35	C - $NaHCO_3$	8.5	149	7.0	47.5	11.1	3.9	4.1	2.1	172	14.4	0.02	0.3	0	-16.5
36	C - $NaHCO_3$	8.5	167	7.7	54.2	10.9	4.0	8.5	3.3	176	14.0	0.01	0.07	0	-15.4
37	C - NaCl	8.5	-26	16.0	439	25.0	21.2	598	140	319	10.7	0.3	0.32	13	-15.8
38	C - $NaHCO_3$	9.3	-47	3.4	103	1.9	0.9	7.2	2.3	264	11.0	0.04	0.17	9	-14.8
39	C - $NaHCO_3$	8.3	63	2.5	88.5	1.5	1.5	0.8	3.9	235	14.9	0.14	0.23	17	-14.6
40	C - $NaHCO_3$	8.7	4	4.8	64.1	11.5	5.4	31	0.1	177	15.4	0.06	0.48	3	-15.5
41	U - $CaMgHCO_3$	5.9	387	31.8	18.0	23.9	6.6	34	24.3	41	5.4	0.05	0.02		-20.8
42	U - $CaMgHCO_3$	6.9	341	2.1	10.4	29.0	13.2	6.3	14.2	111	9.0	0.01	0.01		-17.6
44	C - NaCl	8.3	327	14.3	347	41.7	18.6	534	109	235	10.5	0.01	0.01	0	-17.0
45	C - $NaHCO_3$	8.8	-31	5.0	248	1.7	1.6	35	0.4	638	7.6	0.15	0.15	44	-11.5
46	C - NaCl	8.8	-29	2.4	137	7.8	3.5	92	38	226	10.3	0.03	0.12	3	-17.5
47	C - NaCl	8.6	252	12.4	236	26.6	7.8	244	61	320	16.5	0.02	0.13	0	-15.2

* U - Unconfined aquifer; C - Confined aquifer

Table 4-2. XRD results for sediments analysed.

Mineral *Sediment Type*	*Ideal Formula*	*RCA-01* *Silt/ Clay*	*RCA-09* *Silt/ Clay*	*RCA-28* *Silt/ Clay*	*RCA-29* *Silt/ Clay*	*RCA-07* *Fine Sand*
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	7.0	7.6	7.5	7.2	3.6
Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	9.2	12.7	11.4	11.6	5.0
Illite/Muscovite	$K_{0.65}Al_{2.0}Al_{0.65}Si_{3.35}O_{10}(OH)_2$/ $KAl_2(AlSi_3O_{10})(OH)_2$	8.0	9.4	8.4	10.2	5.6
Quartz	SiO_2	27.8	23.5	25.7	25.6	42.0
Dolomite	$CaMg(CO_3)_2$	1.1	0.9	1.0	0.9	1.1
Calcite	$CaCO_3$	2.5	2.2	1.7	2.5	1.2
Pyrite (maximum)	FeS_2	0.3	0.1	0.2	0.2	0.2
Albite low An0	$NaAlSi_3O_8$	12.7	11.3	11.7	12.2	14.3
Oligoclase An16	$(Na_{0.84}Ca_{0.16})Al_{1.16}Si_{2.84}O_8$	7.3	8.1	8.4	8.1	6.0
Oligoclase An25	$(Na_{0.75}Ca_{0.25})Al_{1.25}Si_{2.75}O_8$	19.4	19.2	19.6	17.0	17.9
Orthoclase	$KAlSi_3O_8$	3.9	4.0	3.8	3.9	2.6
Magnetite	Fe_3O_4	0.6	0.7	0.7	0.6	0.2
Lizardite or Kaolinite	$Mg_3Si_2O_5(OH)_4$/ $Al_2Si_2O_5(OH)_4$	0.1	0.1		0.1	0.2
Total		100.0	100.0	100.0	100.0	100.0
Total Plagioclase		39.4	38.7	39.7	37.2	38.1

4.5 Discussion

In this section, the evolution of groundwater throughout the system is discussed. First, a conceptual model is proposed, followed by evidence from the hydrogeochemistry to support this conceptual model.

4.5.1 The conceptual model for groundwater evolution

The chemistry of Ca-Mg-HCO_3 groundwater found in unconfined aquifers is largely controlled by rain water composition, and typical processes related to recharge in glacial sediments, which can range in composition from till to glaciofluvial sediments. Groundwater in unconfined aquifers has higher concentrations of calcium, magnesium, bicarbonate and sulphate as well as higher sulphate to chloride ratios than average rain water composition collected from the Saturna Island Station (which is likely representative of water that recharges the unconfined aquifers). This suggests that water-rock interactions play a significant role during recharge through the soil zone, but also that these processes continue to modify the water chemistry in this shallow environment. The Ca-Mg-HCO_3 type groundwater in these unconfined aquifers represents the composition of groundwater recharging the underlying glaciomarine sediments and confined aquifers.

Groundwater in confined aquifers appears to have undergone a more complex series of chemical reactions, spanning cation exchange, mixing, and water-rock interaction. As noted above, there are two dominant water types: Na-HCO_3 and Na-Cl. The high sodium content of groundwater in confined aquifers relative to Ca-Mg-HCO_3 groundwater recharging the glaciomarine sediments indicates that groundwater chemistry is evolving along a freshening system, as demonstrated throughout the paper. The Piper diagram (Figure 4-3) shows a gradual increase in sodium content relative to calcium and magnesium from a Ca-Mg-HCO_3 type to a Na-HCO_3 type, indicating possible cation exchange control. Fresh groundwater sourced from unconfined aquifers has a significantly lower salinity than seawater. Low groundwater salinity should favour the occupancy of calcium and magnesium on exchange sites in exchange for sodium (Appelo and Postma, 2006), as fresh groundwater flows through glaciomarine sediments that were previously submerged by seawater. The Na-Cl groundwater samples plot on the Piper diagram (Figure 4-3) along a mixing line, which trends from a Na-HCO_3 water composition towards average seawater composition (composition from Drever, 2002). This suggests that mixing of Na-HCO_3 groundwater with a seawater type end member may yield saline Na-Cl groundwater. A detailed discussion on carbonate dissolution, cation exchange, mixing and weathering processes taking place in this study area follows.

4.5.2 Carbonate dissolution and cation exchange

The dissolution of carbonate minerals has been interpreted to be a process commonly resulting in increases in the dissolved inorganic carbon (DIC) of groundwater in freshening environments (Lee and Strickland, 1988; Bishop and Lloyd, 1990; Appelo, 1994). The dissolution of carbonate minerals can be recognized by an increase in pH occurring concurrent with increases in the DIC and enrichment in the ^{13}C of DIC of water (Clark and Fritz, 1997).

As shown in the Piper plot (Figure 4-3), rain water in the region of the study area has a Na-Cl composition, while groundwater in unconfined aquifers acquires a Ca-Mg-HCO_3 composition. The majority of groundwater samples sourced from unconfined aquifers with pH below 7.5 have DIC increasing from 1.9 to approximately 2.6 mmol/l at increasing pH (Figure 4-4A). Concurrent to this increase in DIC, there is a stoichiometric increase in Ca^{2+} and Mg^{2+} (Figure 4-4B). These samples also become enriched in ^{13}C at increasing pH (Figure 4-4C), suggesting that carbonate dissolution is taking place in the unconfined aquifers and adding DIC, Ca^{2+} and Mg^{2+} to solution. Most groundwater samples sourced from unconfined aquifers are undersaturated with respect to calcite indicating that calcite dissolution has a thermodynamic driver (Figure 4-4D). That not all of the samples are at calcite saturation suggests that calcite might not have a ubiquitous presence. The increase in DIC in these low pH samples is marginal (approximately 0.7 mmol/l), which indicates that carbonate mineral dissolution in unconfined aquifers occurs in a system closed to soil zone CO_2 (Figure 5-6 in Clark and Fritz, 1997). A limited supply of CO_2, the source of H^+ driving carbonate dissolution, results in lower amounts of dissolution but a much larger change in the $\delta^{13}C$ as additional carbon is sourced only from carbonate (marine calcite $\delta^{13}C \sim 0$ ‰). The increase in DIC is proportionately large (from 1.9 mmol/l to 2.6 mmol/l) and the $\delta^{13}C$ values increase from ~ -20 to -14.4 ‰ because only up to 25% of the total DIC comes from the carbonate dissolution reaction. There are two unconfined samples at pH > 8 that have enriched ^{13}C content but similar or lower DIC than the lower pH samples. The low DIC in these two high pH samples further supports that carbonate dissolution in unconfined aquifers occurs and the system is closed to CO_2 because an open system would result in higher DIC. There are two unconfined samples that defy the trend, with relatively low DIC and $\delta^{13}C$ at pH ~7.7. These may reflect an area that is undergoing little carbonate dissolution resulting in a $\delta^{13}C$ very similar to the initial low pH soil water.

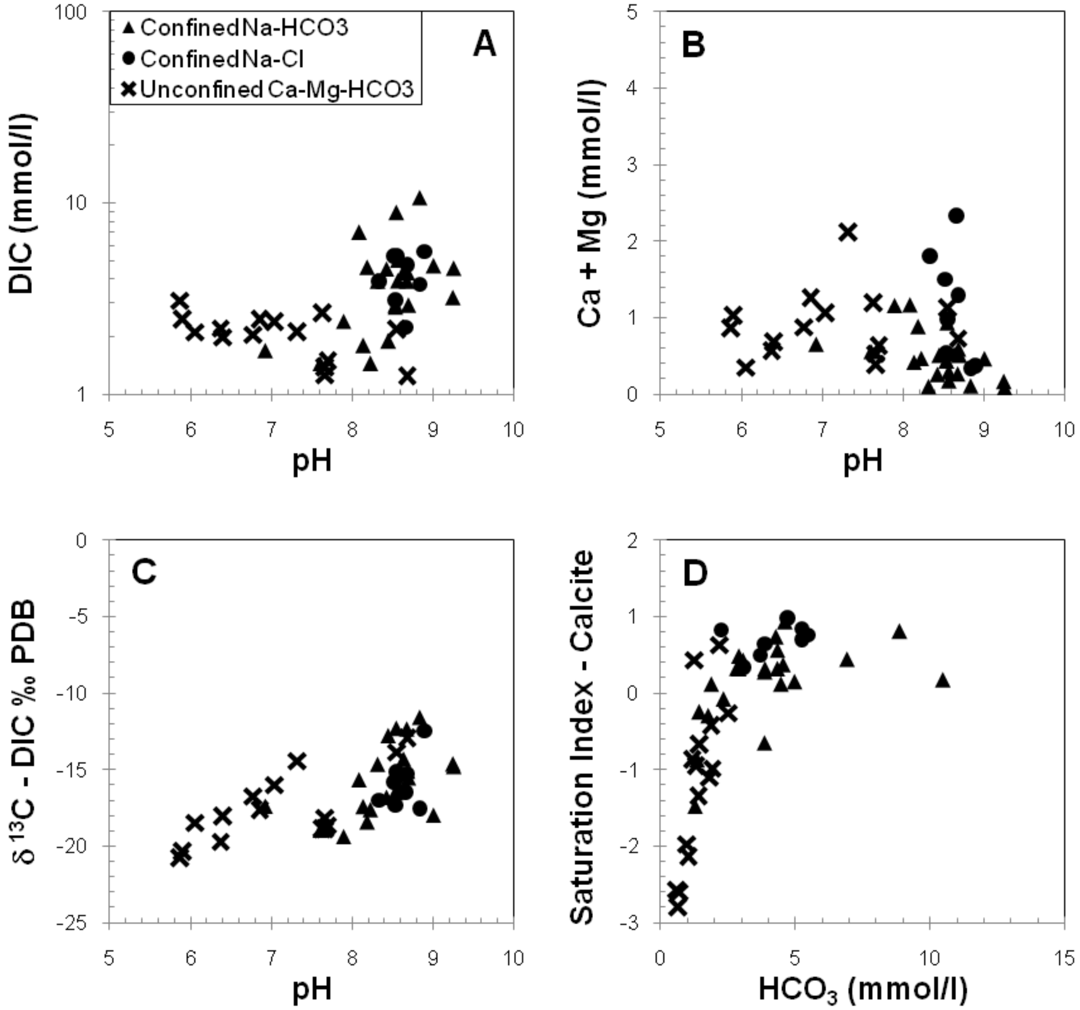

Figure 4-4. Scatter plots comparing (A) DIC, (B) Ca + Mg and (C) δ^{13}C of DIC with pH, and comparing bicarbonate concentrations with the saturation index of calcite (D). A marginal increase in DIC occurring concurrent to increases in Ca + Mg and in δ^{13}C of DIC at increasing pH indicates that carbonate dissolution in a system closed to soil CO_2 is occurring in unconfined aquifers. A sharp increase in DIC and increases in δ^{13}C of DIC at increasing pH indicates that carbonate dissolution in a system open to CO_2 occurs in confined aquifers.

Most groundwater in the confined aquifers has higher bicarbonate content than groundwater in unconfined aquifers (Table 4-1), and nearly all samples sourced from confined aquifers are saturated or supersaturated with respect to calcite (Figure 4-4D). A positive relationship exists between the pH of groundwater in confined aquifers with DIC (Figure 4-4A) and $\delta^{13}C$ of DIC (Figure 4-4C). In addition, the XRD analysis indicates sediment samples sourced from confining units and confined aquifers contain calcite and dolomite (Table 4-2). All of these observations suggest that the relatively high alkalinity and DIC of groundwater in the confined aquifers are a result of carbonate mineral dissolution. Clark and Fritz (1997) noted that in systems open to CO_2, carbonate dissolution results in a sharp increase in the DIC in groundwater. The significantly higher DIC of some groundwater sourced from confined aquifers (up to 10.7 mmol/l) with respect to the DIC in groundwater in unconfined aquifers is evidence that carbonate dissolution in groundwater in confined aquifers occurs in a system open to CO_2. As noted by McMahon and Chapelle (1991) and Chapelle and McMahon (1991), carbon may be added to water via oxidation of organic matter coupled with reduction reactions. The active breakdown of organic matter, evidenced through the reduction of iron oxide minerals and sulphate (discussed in detail in Chapter 5), is a mechanism through which CO_2 may be added to solution. The lower Eh and higher concentrations of the reduced species Fe^{2+}, NH_3 and S^{2-} in groundwater in confined aquifers, in comparison to groundwater in unconfined aquifers, indicate that reduction reactions occur in confining units and/or in confined aquifers. These observations indicate that carbonate dissolution occurs in confined aquifers in a system open to CO_2 as a result of addition of CO_2 through reduction reactions.

Groundwater samples sourced from unconfined aquifers have bicarbonate concentrations at around 1 mmol/l, while Na-HCO_3 samples from confined aquifers have bicarbonate concentrations of up to 10.5 mmol/l (Table 4-1). This represents an up to ten fold increase in the bicarbonate content in confined aquifers. As mentioned, this significant increase in the DIC (and consequently in the bicarbonate content) of groundwater in the confined aquifers is interpreted to be a result of carbonate mineral dissolution. Marine calcite typically has $\delta^{13}C$ around 0 ‰ (Clark and Fritz, 1997). If all the bicarbonate that is added to the groundwater was purely derived from calcite dissolution, the $\delta^{13}C$ of bicarbonate-rich groundwater occurring in confined aquifers should be approaching 0 ‰. This is not observed as the sample most enriched in the heavier isotope, which is also the sample with highest bicarbonate concentration (10.5 mmol/l), has a $\delta^{13}C$ value of -11.5 ‰. The relatively low $\delta^{13}C$ of high bicarbonate water can be explained though the net reaction of carbonate dissolution trigged by CO_2 with cation exchange (shown below) which shows that a portion of the HCO_3 added to water is sourced from dissolved CO_2. Between a pH of 7.5 and 8, the confined aquifer samples have $\delta^{13}C$ values that are similar to the low pH unconfined samples. The DIC of these samples is the same as or lower than the low pH unconfined samples indicating no carbon is being added and that the majority of the DIC occurs as HCO_3 in a closed system.

Carbonate mineral dissolution is triggered in freshening systems by the removal of calcium and magnesium from solution via cation exchange (McMahon and Chapelle, 1991). The stoichiometry of the net reaction (which incorporates carbonate mineral dissolution and cation exchange reactions), which is thought to control the groundwater chemistry in the confined aquifers and that yields Na-HCO_3 water, is given as (McMahon and Chapelle, 1991):

$$CaCO_3 + CO_2 + H_2O + 2Na\text{-}X \rightarrow\ 2Na^+ + 2HCO_3^- + Ca\text{-}X_2 \qquad (4.1)$$

Where M-X represents the cations (M) associated with the exchanger (X).

A positive correlation between calcium and/or magnesium with bicarbonate should be expected in groundwater occurring in environments where calcite dissolution is taking place and where there is no major sink of calcium, magnesium or bicarbonate. However, there is no correlation between calcium and magnesium with bicarbonate concentrations in groundwater sourced from confined aquifers (Figure 4-5A), where carbonate mineral dissolution is interpreted to be a control to water chemistry. The concentrations of sodium and bicarbonate in Na-HCO_3 type water correlate at a nearly one-to-one ratio (slope of 1.02; R^2=0.92; Figure 4-5B). This correlation has been observed previously in freshening environments (Chapelle and Knobel, 1983; McMahon and Chapelle, 1991) and is explained by Equation 4.1. As calcium is released through calcite dissolution it undergoes cation exchange. For every mole of calcium that occupies exchange sites, two moles of sodium are added to solution. Since the net reaction also results in the addition of two moles of bicarbonate to solution, sodium and bicarbonate concentrations in the Na-HCO_3 groundwater in the confined aquifers correlate at a one-to-one ratio. Although it has been noted that chloride has likely been flushed out of the environments where Na-HCO_3 groundwater occurs, the release of sodium from exchange sites should be expected as it typically takes a far greater water volume to completely flush sodium out of exchange sites than to flush seawater from porous space (Appelo and Postma, 2006). Because calcium is removed from solution through the exchange reaction, no correlation between calcium and bicarbonate should be expected in Na-HCO_3 groundwater. The observed one-to-one correlation of sodium and bicarbonate should still hold if dolomite dissolution is assumed to be taking place, as the same amount of sodium and bicarbonate is added to solution:

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O + 4Na\text{-}X \rightarrow Ca\text{-}X_2 + Mg\text{-}X_2 + \boldsymbol{4Na^+} + \boldsymbol{4HCO_3^-} \qquad (4.2)$$

The concentrations of both calcium and sodium in Na-Cl groundwater increase independently of HCO_3. The Na-Cl groundwater is mixing with a saline end member (as discussed later), which results in the increase in concentrations of these elements (there is also a positive correlation between calcium and chloride concentrations in Na-Cl groundwater; not shown in plots presented). Increases in HCO_3 concentrations in Ca-Mg-HCO_3 groundwater occur independently of Na but show a linear dependence on Ca+Mg at pH between 6 and 7.5. Carbonate dissolution is taking place in both the unconfined and confined aquifers resulting in a strong control on the pH and bicarbonate content. Although cation exchange may occur in the unconfined aquifers, it is clear that this process does not control the water chemistry as significantly as it does in the confined aquifers as unconfined aquifers are not a freshening system.

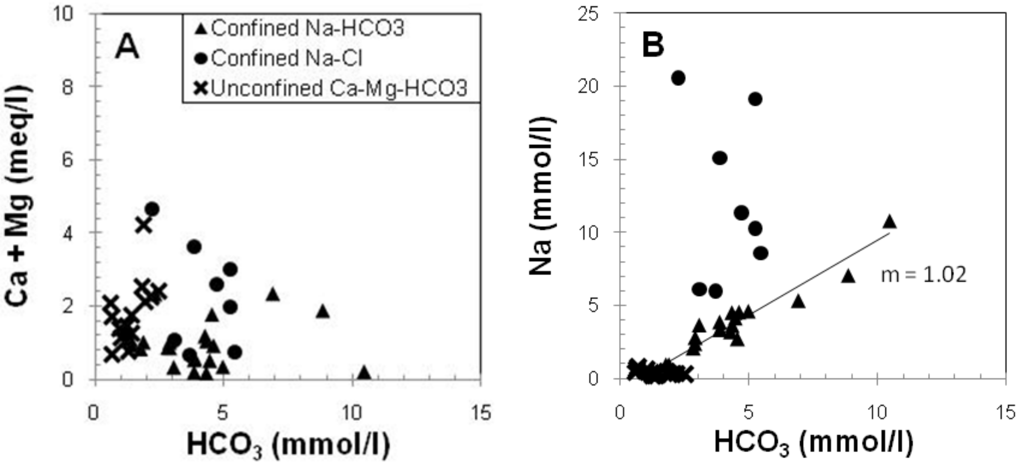

Figure 4-5. Scatter plots comparing concentrations of (A) calcium + magnesium and (B) sodium with bicarbonate. Ca+Mg increase with increasing HCO_3 in the majority of the unconfined aquifers indicating carbonate dissolution. A strong positive correlation is observed between sodium and bicarbonate in Na-HCO_3 groundwater. This is interpreted to be a result of a combination of calcite dissolution coupled with cation exchange reactions.

Appelo (1994) and Lambrakis (2006) suggest that chromatography effects should be observed in freshening aquifers as a result of differences in ion selectivity. However, no Mg-HCO_3 or Ca-HCO_3 type groundwater is observed in the studied aquifers. This is possibly a result of the distribution of sampling points not being along a flow path and that exchange reactions occur relatively quickly so the chromatographic pattern may only occur in the upper portion of the confining units.

4.5.3 Mixing

Na-Cl water samples have the highest salinity, and the major element chemistry converges on the average seawater composition in the Piper diagram

(Figure 4-3). The near linear trend is an indicator that groundwater of this type is derived from mixing with a seawater-like end member. This interpretation is supported with Na/Cl scatter plots (Figure 4-6), which show a strong positive correlation of sodium and chloride in Na-Cl samples forming a mixing line trending towards seawater composition. There are two possible origins for the saline end member of the mixing trend observed with Na-Cl groundwater: Modern seawater intruding the aquifer (as the study area is located in a coastal region), or older seawater that has not been completely flushed out of the confined aquifers and the surrounding low permeability glaciomarine sediments. Seawater could be present within the glaciomarine and marine sediments as it may be trapped in the pore space since sediment deposition during the Late Pleistocene; while it could have also been emplaced in low lying areas during periods of marine inundation. All but one of the Na-Cl type samples is sourced from the deepest confined aquifer amongst all aquifers sampled in this study, while the one other Na-Cl sample is sourced from the second deepest aquifer sampled. Fresh groundwater recharges from the surface at high elevation and reaches the deep confined aquifers by flowing through the low permeability clay- and silt-rich units and other confined aquifers, as shown in the schematic cross-section (Figure 4-2). The low permeability of confining units suggests that there is a low flux of recharge water to these deep aquifers; therefore, remnant seawater-like water may be present. Modern seawater intrusion is observed in Fraser River delta sediments (Neilson-Welch and Smith, 2001; Bridger and Allen, 2006); however, the Fraser River delta is located outside (towards the west) of the study area. In addition, a modern intrusion of seawater to clay-rich sediments should result in reverse cation exchange (release of calcium to solution while sodium occupies exchange sites), which would yield Ca-Cl groundwater (Appelo and Postma, 2006); however, no Ca-Cl type groundwater is found in the study area. These observations suggest that the mixing trend observed with Na-Cl samples reflects the incomplete flushing of remnant seawater trapped in the sediments rather than mixing with modern seawater currently intruding the aquifers.

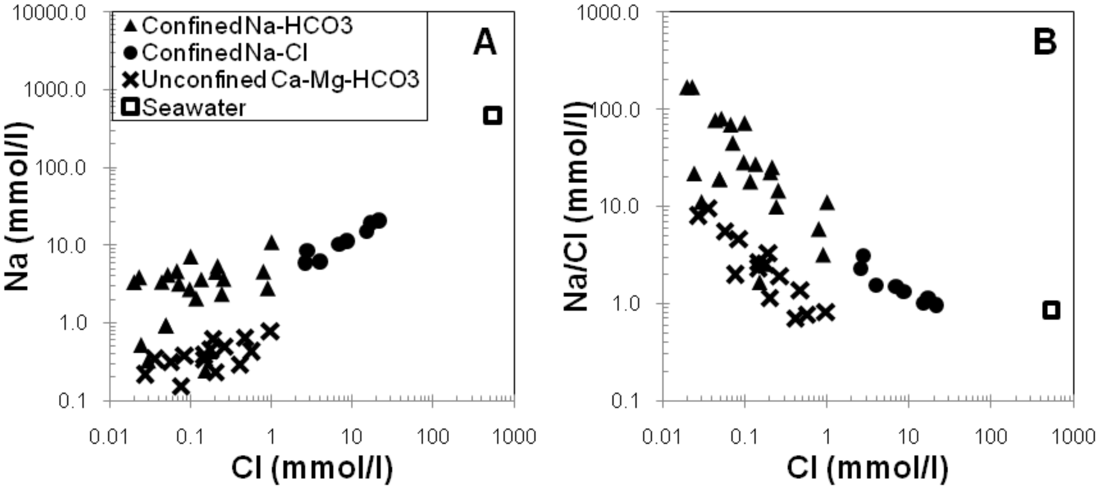

Figure 4-6. Scatter plots comparing the concentrations of sodium and chloride in the study area for the different type waters. A strong correlation between sodium and chloride trending towards average seawater composition (according to Drever, 2002) is apparent in Na-Cl groundwater.

Na-HCO_3 and Ca-Mg-HCO_3 samples plot along apparent mixing trends in the Na/Cl plots. There is a slight positive trend of sodium with chloride in Ca-Mg-HCO_3 samples. It is difficult to attribute the increase in chloride of the Ca-Mg-HCO_3 groundwater in the unconfined aquifers to mixing with modern seawater as the bottom of unconfined aquifers are at least 10 meters above present sea level. However, as the unconfined aquifers are formed by glaciofluvial sediments, it is possible that at least portions of the unconfined aquifers were at some point submerged by seawater. In this case, groundwater could be mixing with trapped seawater within the glaciofluvial sediments since the last period of major sea level transgression in the Late Pleistocene. However, this is unlikely as the unconfined aquifers are located close to the recharge area and they are formed by highly permeable sediments (sand and gravel); hence any seawater that may have previously occupied these aquifers has probably been completely flushed out of these aquifers. The observed variations in the chloride content of Ca-Mg-HCO_3 groundwater in unconfined aquifers may be a result of evapotranspiration in the soil horizon, as shown by a marginal increase in chloride and sodium. This would be in agreement with Hendry et al. (1986), who observed that processes associated with recharge in glacial deposits may include oxidation of reduced sulphur, dissolution of carbonate minerals at elevated pCO_2, evapotranspiration-related processes, and cation exchange.

The apparent mixing trend in Na-HCO_3 samples could be a result of mixing with seawater (as suggested for Na-Cl groundwater), as Na-HCO_3 groundwater occurs within low permeability sediments that were deposited in marine conditions and may have experienced periods of submersion subsequent to deposition. If this was the case, an increase in the chloride content of Na-HCO_3 groundwater with respect to Ca-Mg-HCO_3 groundwater would be expected. This is not observed as Ca-Mg-HCO_3 and Na-HCO_3 samples have the same range of chloride concentrations, while they also have relatively low chloride concentrations (less than 1.0 mmol/l). However, there is no evidence to support an unequivocal interpretation that the variable chloride content is the result of the initial input water recharging the confined aquifers from the unconfined system or whether it is from mixing through incomplete flushing of the confining units and confined aquifers.

4.5.4 Mineral weathering

The relationship between an aqueous solution and the associated mineral phases can be assessed using mineral stability diagrams (Helgeson et al., 1969). In surface and near surface environments, weathering and diagenesis are the principal processes that affect aqueous solution composition. Although many of these reactions are irreversible, comparing real systems to ideal thermodynamic equilibrium models enables evaluation of changes in solution composition that are the product of mineral-solution interactions (Helgeson et al., 1969).

Aquifer-forming and confining unit sediments in the study area are composed of considerable amounts of reactive silicate minerals like amphibole (actinolite), chlorite (clinochlore) and plagioclase (Table 4-2). The presence of these reactive minerals in the sediments may facilitate silicate weathering reactions, making mineral weathering another possible driver of the observed basic groundwater pH and solution chemistry evolution. In order to evaluate the role of mineral weathering in controlling the groundwater composition, activity diagrams were generated using the ACT2 module of Geochemist’s Workbench (Bethke, 1994) with the thermo.com.V8.R6 database, a modified form of the

EQ3/EQ6 database (Delany and Lundeen, 1990) (Figures 4-7; 4-8; 4-9). Activities for dissolved species in each groundwater sample were determined using PHREEQC (Parkhurst and Appelo, 1999).

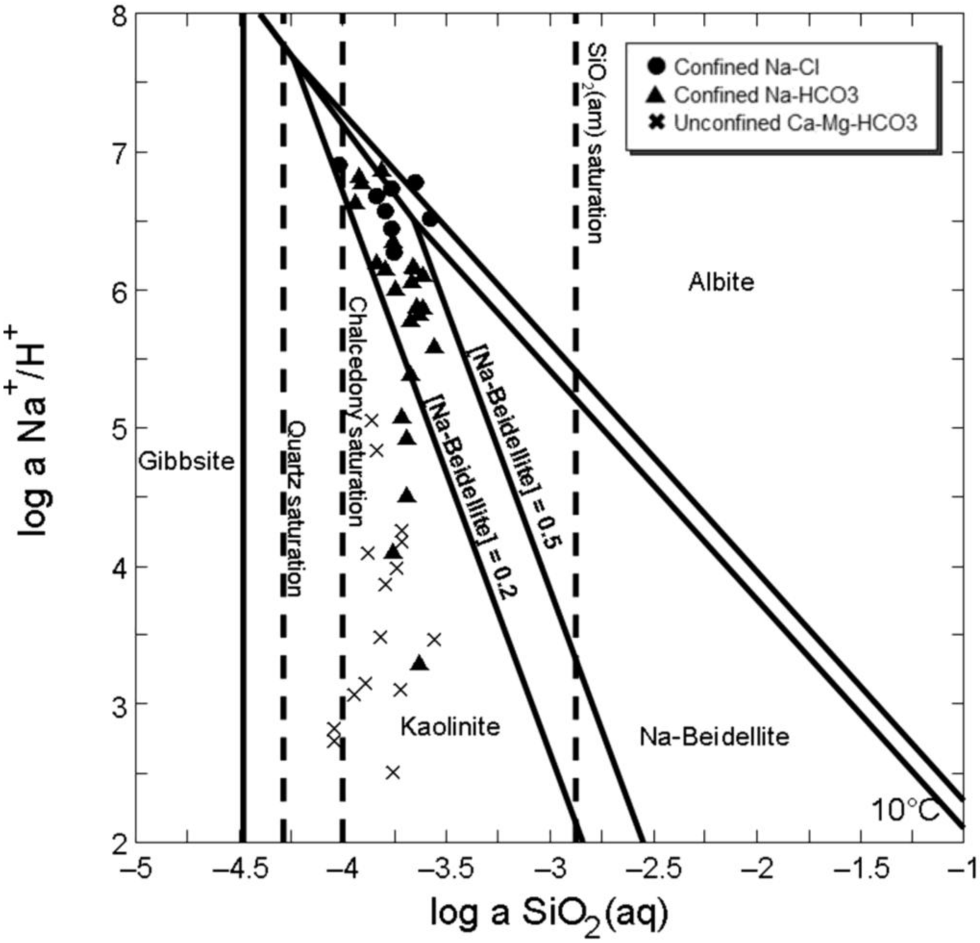

Figure 4-7. SiO_2 - Na^+/H^+ logarithm activity diagram at T=10°C. Equilibrium curves for Na-silicate minerals are presented as solid lines and saturation curves for silica polymorphs are presented as dashed lines. $Na-HCO_3$ and Na-Cl type groundwaters sampled from confined aquifers plot along the Na-beidellite – kaolinite, the albite – Na-beidellite or the albite – kaolinite equilibrium curves, while most $Ca-Mg-HCO_3$ type waters sampled from the unconfined aquifers plot in the kaolinite field.

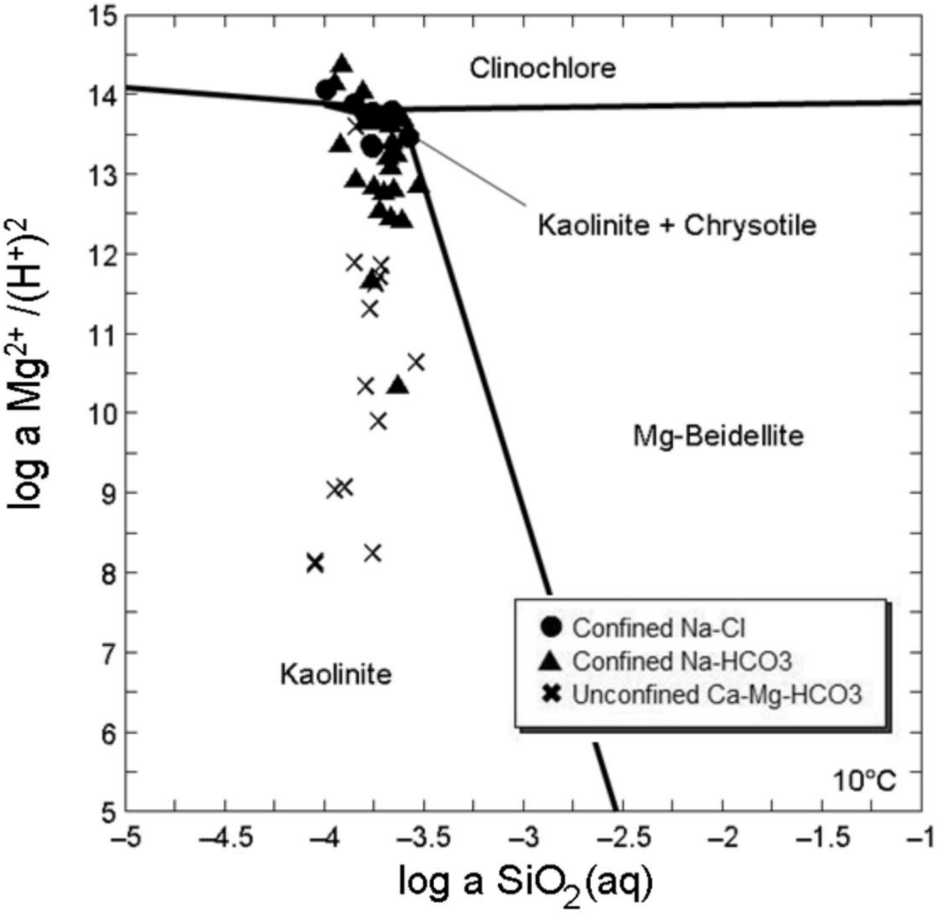

Figure 4-8. SiO_2 - $Mg^{2+}/(H^+)^2$ logarithm activity diagram at T=10°C and Mg-beidellite activity = 0.82. Chrysotile is used in this plot in the place of lizardite. Some Na-Cl and Na-HCO_3 samples plot near the clinochlore – kaolinite + chrysotile equilibrium curve, suggesting that clinochlore weathering may be a control on the chemistry of these waters. The fact that many Na-HCO_3 samples do not plot along equilibrium curves suggests that two different Mg-rich minerals (actinolite and chlinochlore) are weathering and controlling groundwater chemistry.

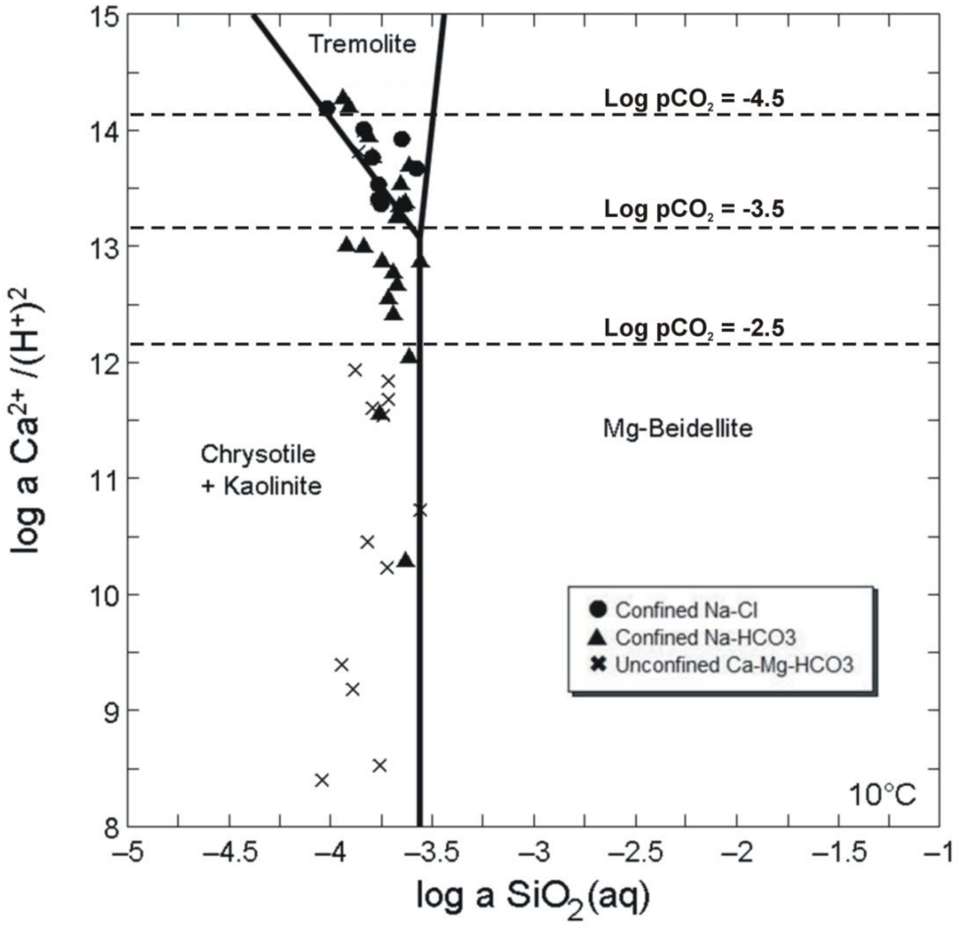

Figure 4-9. SiO_2 - $Ca^{2+}/(H^+)^2$ logarithm activity diagram at T=10°C and Mg-beidellite activity = 0.82. Chrysotile is used in place of lizardite. Most Na-HCO_3 and Na-Cl samples plot along the tremolite – chrysotile + kaolinite curve. Some Na-HCO_3 samples plot parallel to and below the tremolite-chrysotile curve suggesting amphibole of variable composition may be present. Na-HCO_3 and Na-Cl samples also plot within the area defined by the calcite solubility curves at log pCO_2 of -2.5 to -4.5.

Smectite clay mineral phases are represented in the activity diagrams, as smectite is a weathering product of aluminosilicate minerals. Mixed composition solid solution mineral phases like smectite are challenging to represent on mineral stability diagrams. Helgeson et al. (1969) suggest the use of thermodynamic end members to approximate solid solution phases and recommend beidellite to represent smectite in these diagrams. Beidellite, as defined in the thermo.com.V8.R6 database, has the general formula $A^{x}_{0.33/x}Al_2(Al_{0.33}Si_{3.67})O_{10}(OH)_{2;}$ here, Al^{3+} is substituted into the tetrahedral layers of the clay structure generating the layer charge, while the A site represents the exchangeable interlayer charge balancing cations commonly in the form of Na^+,K^+,Ca^{2+}, and Mg^{2+}. The fact that the only variable in the beidellite formula, as given, is the composition of the A site facilitates the calculation of the activity of end members when producing activity diagrams. Unrealistic results may be produced when solid solution minerals are represented in activity plots as their hypothetical end member, as these minerals are likely not occurring as a pure end member in the environment (Aagaard and Helgeson, 1983). This discrepancy between the solid solution mineral occurring in the environment and end member minerals described in thermodynamic databases has to be accounted for when producing activity diagrams. This was done by representing smectite as beidellite with an activity calculated using the ideal mixing model equation proposed by Helgeson and Aagaard (1985) (assuming an intracrystaline standard state):

$$a_i = k_i \prod_s \prod_j X_{j,s}^{v_{s,j,i}} \qquad (4.3)$$

where a_i is the activity of the *i*th thermodynamic component (end member) of a solid solution, k_i represents a constant relating to the inter- and intracrystaline standard states of for the *i*th component, $X_{j,s}$ stands for the mole fraction of the *j*th atom on the *i*th site, and $v_{j,s,i}$ refers to the stoichiometry number of these sites occupied by the *j*th atom in one mole of the *i*th component. The k_i term can be expressed as (Helgeson and Aagaard, 1985):

$$k_i = \prod_s \prod_j X_{j,s,i}^{-v_{s,j,i}} \qquad (4.4)$$

where $X_{j,s,i}$ represents the mole fraction of the *j*th atom on the *s*th sites in one mole for the *i*th thermodynamic component. If Na-beidellite, Mg-beidellite, Ca-beidellite and K-beidellite are selected as the component end members, the only variable is the exchangeable cation (A site in the beidellite formula given above) and equation 4.4 reduces down to consideration of a single mixing site. The calculation of the activities of the Na- and Mg-beidellite thermodynamic components of a beidellite solid solution was done by applying equation 4.3:

$$a_{Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2} = k(X_{Na,A})^{0.33} \qquad (4.5)$$

$$a_{Mg_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2} = k(X_{Mg,A})^{0.165} \qquad (4.6)$$

where $X_{Na,A}$ and $X_{Mg,A}$ refer to the corresponding mole fractions of Na and Mg in the interlayer site. The beidellite end-members are perfectly ordered on the A site, thus k = 1 and equations 4.5 and 4.6 are reduced to:

$$a_{Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2} = (X_{Na,A})^{0.33} \qquad (4.7)$$

$$a_{Mg_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2} = (X_{Mg,A})^{0.165} \qquad (4.8)$$

PHREEQC was used to evaluate the distribution of the potential mole fraction composition of Na, K, Ca and Mg on the interlayer site of beidellite by equilibrating each groundwater sample with 1 mole of exchanger. A wide range of calculated Na-beidellite activities was found using this method (from 0.14 to 0.77), with most groundwater samples having a value between 0.2 and 0.5. For this reason, equilibrium curves for Na-beidellite at activities of 0.2 and 0.5 are used in the SiO_2 - Na^+/H^+ activity diagram. A much narrower range of Mg-beidellite activities was calculated, with both the median and the mean in Na-HCO_3 samples being 0.82, and in Na-Cl samples being 0.80. Therefore, an activity of 0.82 for Mg-beidellite was used in the SiO_2 - $Mg^{2+}/(H^+)^2$ and SiO_2 - $Ca^{2+}/(H^+)^2$ activity diagrams.

Aluminum activity in all activity diagrams was initially set by kaolinite solubility and is conserved between reactions. Lizardite ($Mg_3Si_2O_5(OH)_4$) was one of the authigenic minerals found in the XRD analyses of sediment samples. No thermodynamic data for lizardite was found in the databases provided with Geochemist's Workbench, PHREEQC, or in the literature. Geochemical modelling of systems that include lizardite is often carried out using chrysotile thermodynamic data as surrogate (Evans, 2004; Frost and Beard, 2007). For this reason chrysotile, a high temperature polymorph of lizardite, was used. The chlorite to chrysotile weathering reaction can be written as (log Ks of reactions provided in this chapter are for T = 10 °C as all field measured groundwater temperatures were near 10 °C):

$$Mg_5Al_2Si_3O_{10}(OH)_8 + 10H^+ \leftrightarrow Mg_3Si_2O_5(OH)_4 + 2Mg^{2+} + 7H_2O + SiO_{2(aq)} + 2Al^{3+}$$

$$Log\ K\ (10\ ℃) = 40.5963 \qquad (4.9)$$

The above reaction (Equation 4.9) cannot be represented in the SiO_2 - $Mg^{2+}/(H^+)^2$ logarithm activity diagram as it produces free Al^{3+}, which is an ion that is not included in the axis of the activity diagram. In order to represent chrysotile, the free Al^{3+} in Equation 4.14 was substituted with kaolinite:

$$2Mg_5Al_2Si_3O_{10}(OH)_8 + 14H^+$$
$$\leftrightarrow\ Mg_3Si_2O_5(OH)_4 + 2Al_2Si_2O_5(OH)_4 + 7Mg^{2+} +\ 9H_2O$$
$$Log\ K\ (10\ ℃) =\ 97.279 \qquad (4.10)$$

As a result, chrysotile + kaolinite and Mg-beidellite fields are used in order to assess weathering of chlorite. Tremolite was used to represent actinolite as it is a calcium-rich amphibole mineral phase available in the thermo.com.V8.R6 database. Calcite saturation curves at different CO_2 partial pressures (log pCO_2= -2.5, -3.5 and -4.5) are represented in Figure 4-9 to evaluate the role of calcite dissolution/precipitation on solution composition.

Nearly all of the groundwater samples plot to the right of the chalcedony saturation curve (Figure 4-7). A tendency for dissolved silica activities in low temperature groundwater to exceed quartz saturation is commonly observed (Hem, 1992; Gislason et al., 1993; Abercrombie et al., 1994; Chapelle, 2003). Although arguments are made that primary silicate weathering to clay minerals may be the origin of the narrow range of silica activities in groundwater (Davis, 1964; Abercrombie et al., 1994), it may also be possible that the weathering reaction at the mineral surface is a control (Zhu et al., 2006; Daval et al., 2010). Zhu et al. (2006) describe feldspar mineral grain surfaces of the Navajo Sandstone as consisting of a Si enriched amorphous layer partially coated by a thin kaolinite layer and a continuous layer of smectite. The presence of this series of mineral phases suggests that metastable phases may be common in weathering and diagenetic environments, and the resultant impact on fluid chemistry could be sufficient to drive activity relationships to display equilibrium or near-equilibrium conditions.

The silica content of groundwater is almost certainly the result of weathering reactions taking place in the unconfined and confined aquifers in this study area. Samples that plot below the equilibrium curves for weathering reactions shown in the diagrams, which are mostly samples sourced from unconfined aquifers, have a slightly acidic to neutral pH that is largely controlled by the partial pressure of CO_2. As a result of CO_2 influence on pH, these samples plot in the kaolinite stability field in Figure 4-7 and Figure 4-8 and in the chrysotile + kaolinite stability field in Figure 4-9, far from univariant equilibrium curves.

As calcite saturation is approached in groundwater in confined aquifers, pH increases, and water-rock interaction becomes the dominant mechanism influencing pH and the silica activity. As a result, the majority of the Na-HCO_3 and all of the Na-Cl samples plot along the albite – kaolinite univariant equilibrium curve or within Na-beidellite (smectite) – kaolinite and albite – Na-beidellite (smectite) univariant equilibrium curves (Figure 4-7). Although mixing and cation exchange play a significant role in the chemical evolution of groundwater in the confined aquifers, the relationship between dissolved Na, pH and silica content is controlled by weathering of feldspar to kaolinite and/or smectite. Likewise, a significant number of samples collected from groundwater occurring in confined aquifers plot along the tremolite – chrysotile + kaolinite and the tremolite – smectite univariant equilibrium curves (Figure 4-9). This indicates that the chemistry of groundwater in confined aquifers is also, in part, controlled by weathering reactions involving amphibole and lizardite or smectite.

A group of Na-HCO_3 type samples with $Ca^{2+}/(H^+)^2$ ratios ranging from 12.4 to 13.0 plot parallel to and below the tremolite – chrysotile + kaolinite equilibrium curve. As mentioned, tremolite is a calcium-rich actinolite end member. If a solid solution actinolite mineral phase with differing calcium, magnesium or iron mole fractions were considered, rather than a pure tremolite end member, tremolite would be represented with an activity lower than 1. This would result in an expansion of the tremolite field in the diagram and Na-HCO_3 samples with lower $Ca^{2+}/(H^+)^2$ ratio would plot closer to the tremolite – chrysotile + kaolinite equilibrium curve. Hence, the lower Ca^{2+}/H^+ ratio of some Na-HCO_3 type samples possibly reflects weathering of amphiboles with variable composition. The mineral composition of the glaciomarine sediments is the result of glacial erosion of numerous rock types that occurred along the path of the glaciers feeding into the Fraser Valley; hence it is very unlikely the sediments are sourced from a single amphibole composition.

Some groundwater samples sourced from confined aquifers plot in the SiO_2 - $Mg^{2+}/(H^+)^2$ diagram near the clinochlore – kaolinite + chrysotile equilibrium curve, suggesting possible chlorite weathering controls on the chemistry of these waters (Figure 4-8). However, several samples sourced from confined aquifers plot in the kaolinite field, indicating that clinochlore weathering is not a clear control on these samples. This is different than what is observed in Figure 4-7, where the majority of samples sourced from confined aquifers plot along univariant equilibrium curves (Figure 4-7). One reason for the lack of correlation between the aqueous fluid composition and the mineral phases modelled may be that there are two primary mineral phases that contain significant proportions of Mg (clinochlore and actinolite) in the sediments (Table 4-2), and both of these phases are reactive in weathering environments. With two minerals likely weathering and controlling the relationship between dissolved Mg, pH and silica, groundwater samples end up not plotting along specific univariant equilibrium curves in the SiO_2 - $Mg^{2+}/(H^+)^2$ diagram.

Na-Cl and Na-HCO_3 samples plot within the calcite saturation curves for a log pCO_2 range from -2.5 to -4.5, in agreement with the interpretation that calcite dissolution plays a role in the confined aquifers. At the same time, a significant portion of Ca-Mg-HCO_3 groundwater samples plot below the calcite saturation curve for a log pCO_2 of -2.5. The majority of unconfined aquifer samples have been shown to be undersaturated with respect to calcite and thus are not expected to plot on the calcite saturation curves.

The addition of solutes through mineral weathering should not alter the one-to-one correlation observed between sodium and bicarbonate. Balanced weathering reactions involving albite add the same amount (in moles) of sodium and bicarbonate to solution, as carbonic acid is converted to bicarbonate (shown in bold below).

- Albite weathering to Na-beidellite (smectite): (4.11)

$$7NaAlSi_3O_8 + 6H_2CO_3 + 20\ H_2O$$

$$\leftrightarrow 3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 10H_4SiO_4 + \mathbf{6HCO_3^-} + \mathbf{6Na^+}$$

- Albite weathering to kaolinite: (4.12)

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9\ H_2O$$

$$\leftrightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + \mathbf{2HCO_3^-} + \mathbf{2Na^+}$$

- Na-beidellite (smectite) weathering to kaolinite: (4.13)

$$6Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 2H_2CO_3 + 23H_2O$$

$$\leftrightarrow 7Al_2Si_2O_5(OH)_4 + 8H_4SiO_4 + \mathbf{2HCO_3^-} + \mathbf{2Na^+}$$

The correlation between sodium and bicarbonate should also be preserved during weathering of silicate minerals containing calcium and magnesium, as these ions are exchanged with sodium on clay sites after being added to solution. This is demonstrated below with an example of the weathering reaction of tremolite to produce chrysotile (or lizardite), followed by cation exchange:

- Tremolite weathering to chrysotile (or lizardite): (4.14)

$$Ca_2Mg_5Si_8O_{22}(OH)_2 + 8H_2CO_3 + 9H_2O$$

$$\leftrightarrow 6H_4SiO_4 + 2Ca^{2+} + 2Mg^{2+} + Mg_{\mathbf{3}}Si_2O_5(OH)_4 + \mathbf{8HCO_3^-}$$

- Cation exchange: (4.15)

$$2Ca^{2+} + 2Mg^{2+} + 8Na\text{-}X \rightarrow 2Ca\text{-}X_2 + 2Mg\text{-}X_2 + \mathbf{8Na^+}$$

As shown above, the two moles of calcium and the two moles of magnesium added to solution through the weathering of tremolite (Equation 4.14) are exchanged by eight moles of sodium (Equation 4.15). The end result is that the same amounts of sodium and bicarbonate are added to solution. These reactions show that mineral weathering should not affect cation exchange trends in groundwater data, despite being a process that can exert an important control on other water parameters such as pH, dissolved silica content and alkalinity.

4.6 Conclusions

The hydrogeochemical evolution of groundwater occurring in unconfined glaciofluvial aquifers and aquifers confined by glaciomarine sediments was described. Groundwater occurring in unconfined aquifers formed by glaciofluvial sediments is a Ca-Mg-HCO_3 type with low salinity and alkalinity, and has a slightly acidic to neutral pH. The hydrogeochemistry of the unconfined aquifers is controlled by rain water composition, and carbonate and silicate weathering. The unconfined aquifers appear to be closed with respect to soil zone CO_2 (as evidenced by ^{13}C results), which results in a marginal increase in DIC.

As fresh groundwater flows through glaciomarine clay- and silt-rich sediments and reaches the confined aquifers its chemistry evolves through a complex sequence of reactions controlled by mixing and water rock interactions associated with freshening processes. The occurrence of cation exchange reactions is recognized in the major cation chemistry as groundwater in the confined aquifers is of Na-HCO_3 type. In deep confined aquifers, where saline water has not been completely flushed out of the aquifer, groundwater is more saline and is Na-Cl type as a result of mixing with a seawater-like end member. Carbonate mineral dissolution is favoured by the removal of calcium and magnesium from solution through cation exchange and the generation of CO_2 likely through organic matter oxidation. This is evidenced by a concurrent increase in DIC and $\delta^{13}C$ of DIC in basic water, and calcite reaching saturation in groundwater sourced from confined aquifers. A strong one-to-one correlation between sodium and bicarbonate concentrations in Na-HCO_3 groundwater is explained through the stoichiometry of the coupled reaction of cation exchange and calcite or dolomite dissolution, which results in the addition of the same amount of sodium and bicarbonate to solution.

Samples sourced from glaciomarine sediments have a significant amount of the relatively reactive silicate minerals, amphibole, plagioclase and chlorite based on XRD analysis. The presence of these minerals in the sediments facilitates weathering reactions and enhances weathering controls on groundwater chemistry in the confined aquifers. This is apparent in activity diagrams, which demonstrate that samples sourced from confined aquifers plot along univariant equilibrium curves for silicate weathering reactions. Most samples sourced from unconfined aquifers plot far from equilibrium curves as they have a slightly acidic to neutral pH that is largely controlled by the partial pressure of CO_2. Groundwater in confined aquifers is fairly basic ($pH > 8$), which is a condition interpreted to be acquired as a result of carbonate dissolution and silicate mineral weathering.

In summary, groundwater chemistry in the study area evolves from being controlled by precipitation input, evapotranspiration, and minor water-rock interaction in unconfined aquifers to being controlled by mineral weathering, mixing and cation exchange, processes commonly associated with freshening environments, in confined aquifers. The groundwater changes from a Ca-Mg-HCO_3 composition to a Na-HCO_3 groundwater and, finally, in the deep confined aquifers, a Na-Cl composition from mixing with a seawater-like end member that has not been completely flushed out of the aquifer.

5: ARSENIC MOBILIZATION UNDER FRESHENING CONDITIONS IN CONFINED AQUIFERS FORMED WITHIN GLACIOMARINE DEPOSITS

5.1 Introduction

Exposure to arsenic in drinking water is a known cause of a number of diseases, including skin cancer, lung cancer and hypertension (Hopenhayn, 2006). The finding that large areas of Bangladesh and West Bengal, India have groundwaters with arsenic at concentrations above drinking guidelines (Bhattacharya et al., 1997; BGS and DPHE, 2001) has prompted studies of arsenic occurrence and mobilization in unconsolidated sediment aquifers in a variety of different settings. These include organic-rich aquifers in tropical regions (McArthur et al., 2004; Buschmann et al., 2007), evaporative semi-arid environments (Smedley et al., 2003; Deng et al., 2009), and aquifers formed in glaciated areas in the interior of North America (Warner, 2001; Erickson and Barnes, 2005).

Natural occurrences of elevated arsenic concentrations in groundwater are commonly the result of factors influencing arsenic mobilization and the concentration of arsenic sources in sediments and rocks (Smedley and Kinniburgh, 2002). Arsenic may be mobilized via desorption from mineral surfaces caused by reduction of arsenate to arsenite (which is a more mobile arsenic form) or desorption of arsenate at elevated pH (Pierce and Moore, 1982; Cullen and Reimer, 1989; Bowell, 1994; Smedley and Kinniburgh, 2002). In addition, the presence of anionic species such as phosphate, bicarbonate and sulphate at elevated concentrations may favour arsenic mobilization through competitive adsorption (Xu et al., 1988; Wilkie and Hering, 1996; Jain and Loeppert, 2000; Appelo et al., 2002; Anawar et al., 2004; Hundal et al., 2007; Rowland et al., 2008; Ujević et al., 2010). Arsenic may also be mobilized through arsenic bearing mineral dissolution reactions mediated by a change in the redox state. This commonly happens via reductive dissolution of oxides and oxyhydroxides (Stüben et al., 2003; Charlet and Polya, 2006; Buschmann et al., 2007) or oxidative dissolution of sulphide minerals (Nesbitt et al., 1995; Craw et al., 2003; Yunmei et al., 2004).

Many of the conditions that favour arsenic mobility are found in freshening groundwater environments characterized by aquifers where fresh groundwater flushes seawater, typical of coastal regions (Appelo and Postma, 2005). The hydrogeochemistry of freshening environments is controlled by cation exchange reactions that are evidenced through the occurrence of Na-HCO_3 type groundwater in environments where fresh Ca-HCO_3 or Ca-Mg-HCO_3 type water is recharged (as observed in the studies of Foster, 1950; Lawrence et al., 1976; Chapelle and Knobel, 1983; Edmunds and Walton, 1983; Bishop and Lloyd, 1990; Appelo, 1994 among others). Variations in the concentrations of cations in solution resulting from cation exchange reactions in freshening systems have been interpreted to trigger mineral dissolution and precipitation which in turn exert controls on water pH (Bishop and Lloyd, 1990; Appelo, 1994). At the same time, reducing conditions may be attained in freshening environments at increasing distances from recharge (Bishop and Lloyd, 1990). The mobility of metals and metalloids in solution is strongly controlled by water pH and redox through processes as adsorption and desorption, speciation and dissolution of minerals (Drever, 2002). Although papers have been published on the natural occurrence of metals and metalloids in coastal aquifers (e.g. Almeida et al., 2004; O'Shea et al., 2007), few studies have linked processes associated with freshening environments and their controls on groundwater chemistry to the mobility of metals and metalloids. One example is the study by Haque et al. (2008) that addressed arsenic mobilization in the Aqua aquifer, Maryland, USA, where freshening processes had been previously assessed by Chapelle and Knobel (1983). Haque et al. (2008) found that arsenic was mobilized through desorption and dissolution of arsenic bearing iron oxyhydroxides. These reactions were interpreted to be favoured by basic and reducing conditions acquired through freshening and increasing groundwater residence time downgradient from the recharge area. In another study, Ravenscroft and McArthur (2004) found that the mobilization of boron in aquifers in Michigan and different regions of Bangladesh occurred concurrent to freshening processes. This was evidenced by a strong positive correlation between sodium and boron concentrations in water.

This study was carried out in response to observations by Wilson et al. (2008) that arsenic concentrations exceed Canadian and International drinking water guidelines in 43% of groundwaters sampled in the Lower Fraser Valley of British Columbia. Wilson et al. (2008) found elevated arsenic concentrations in groundwater associated with marine and glaciomarine sediments in this area. The high arsenic concentrations were correlated with a number of variables indicative of marine influence on groundwater composition consistent with the coastal setting of the study area. However, Wilson et al. (2008) did not identify the mechanisms by which the arsenic was mobilized. In the present study, arsenic mobilization in coastal aquifers formed within glaciomarine clays and silts in a temperate climatic region is addressed. The objectives are to determine whether groundwater chemical conditions attained through freshening processes favour the mobility of arsenic, and what the specific arsenic mobilization processes in this environment are. Freshening processes are evidenced through increases in alkalinity and sodium concentrations occurring concurrent to decreases in the concentrations of calcium and magnesium (see Chapter 4). Conditions favouring arsenic mobility are addressed by comparing arsenic concentrations to pH, concentrations of other metalloids and redox sensitive parameters. Groundwater samples were also analysed for arsenic speciation in order to further evaluate redox controls on the mobility of arsenic. Sediment core samples were analysed using selective extractions in order to determine arsenic sources in specific mineral phases. As arsenic is found to occur in sulphide minerals, the role of redox of sulphur species on arsenic mobilization is discussed in detail using sulphur and oxygen stable isotopes of sulphate.

5.2 Study area

The study area is located in the Township of Langley and the eastern portion of the City of Surrey in the Lower Fraser Valley, British Columbia, Canada

(Figure 5-1). The groundwater system consists of aquifers formed in Quaternary unconsolidated sediments that are several hundreds of meters thick and that overlie Tertiary bedrock (Halstead, 1986). The geological history of the Quaternary period in the Fraser Valley has been described by Clague (1994) and Clague and James (2002). Unconsolidated sediments in this region were deposited during and since the most recent Cordilleran ice sheet advance in the Late Pleistocene (Armstrong, 1976). This period was characterized by a series of glaciation and deglaciation events that took place in the Fraser Valley, during which glacial and glaciofluvial sediments were deposited. Thickening and expansion of glaciers led to a progressive isostatic depression of the land by as much as 300 meters below present day sea-level, resulting in the deposition of glaciomarine and marine sediments in the region. Rapid deglaciation triggered isostatic rebound of the land and relative sea-level regression at the end of the Pleistocene. This was followed by deposition of Late Pleistocene glaciofluvial sediments and Holocene deltaic and fluvial sediments (Clague and James, 2002). The surficial geology of the Lower Fraser Valley is therefore formed by a complex sequence of glacial, glaciofluvial, glaciomarine, marine and post-glacial deltaic and fluvial unconsolidated sediments (Armstrong and Hicock, 1980).

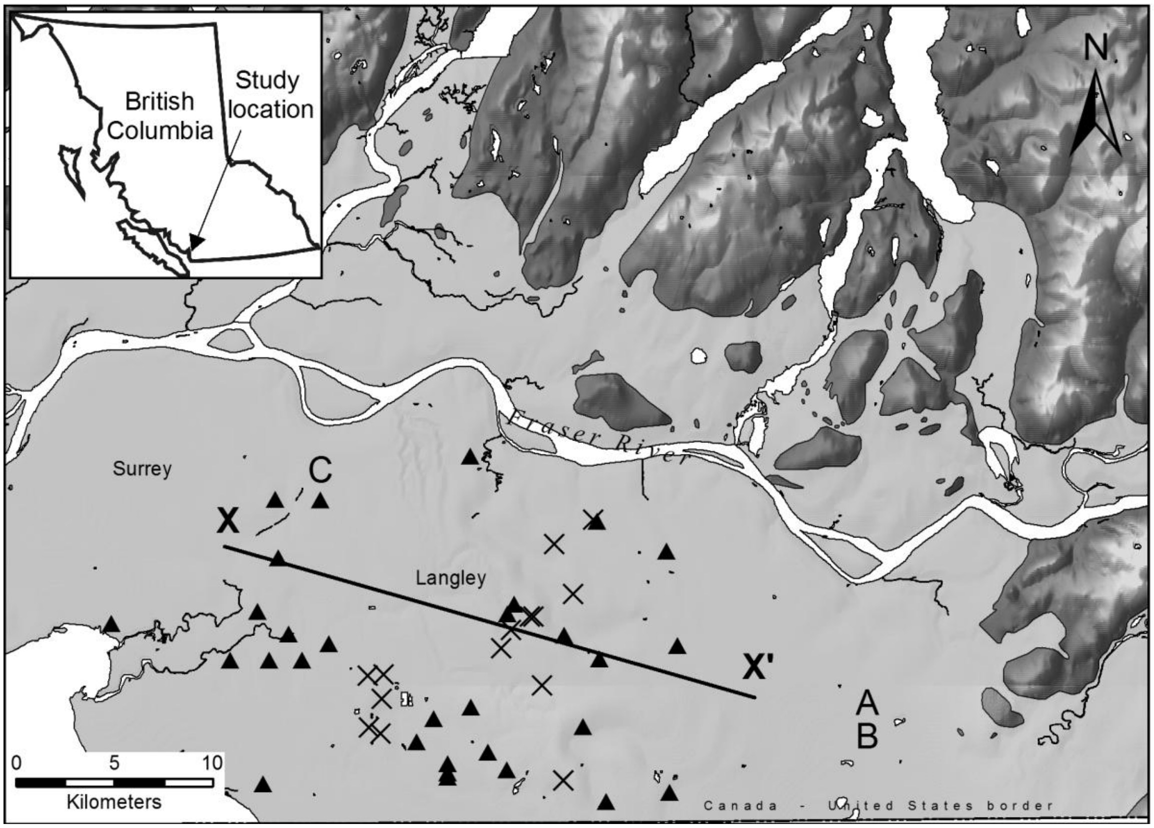

Figure 5-1. The study area is located in the Township of Langley and the eastern portion of the City of Surrey, in the Lower Fraser Valley of British Columbia, Canada. Groundwater sampling locations are marked as crosses for samples sourced from unconfined aquifers, and as triangles for samples sourced from confined aquifers. Letters A, B and C represent the locations of wells at which sediment core samples were taken. The cross-section for Figure 5-2 is shown from X-X'.

A total of 45 permeable units forming 18 major aquifers have been mapped in this study area (Golder Associates Ltd., 2005). These aquifers can be separated into two groups: confined aquifers formed within glaciomarine and marine sediments, and unconfined aquifers formed in near surface glaciofluvial sand and gravel (Figure 4-2). Detailed descriptions of the physical characteristics of these aquifers are provided by Halstead (1986) and Kreye and Wei (1994). The confined aquifers comprise estuarine deposits, as fine to medium grained sand lenses, or till diamictons, and are overlain and underlain by grey to blue-grey glaciomarine and marine clays and silts that were deposited during periods of marine transgression. These clay and silt deposits act as confining units. Lithological logs of wells show that the confined aquifers occur at depths ranging from 100 m to as shallow as 10 m below surface. Unconfined aquifers are comprised of reddish-brown deltaic and glaciofluvial sands and gravels that were deposited on top of the glaciomarine sediments (Halstead, 1986; Kreye and Wei, 1994).

A groundwater flow model of the study area was produced by Golder Associates Ltd. (2005). The model suggests that the general groundwater flow direction in this area is southeast to northwest. Groundwater in unconfined aquifers is recharged by rain water at the surface. Groundwater that reaches the glaciomarine sediments and confined aquifers is recharged either from the overlying unconfined aquifers (where present) and down through the sequence of deeper deposits, or directly through the glaciomarine sediments where these are exposed at surface (Figure 4-2). Many of the low lying wells that source water from deep confined aquifers are artesian, suggesting that recharge to these aquifers occurs at higher elevation – i.e., the Toth flow model of topography driven recharge (Toth, 1962). Halstead (1986) suggested that groundwater occurring in deep confined aquifers should have a considerable residence time.

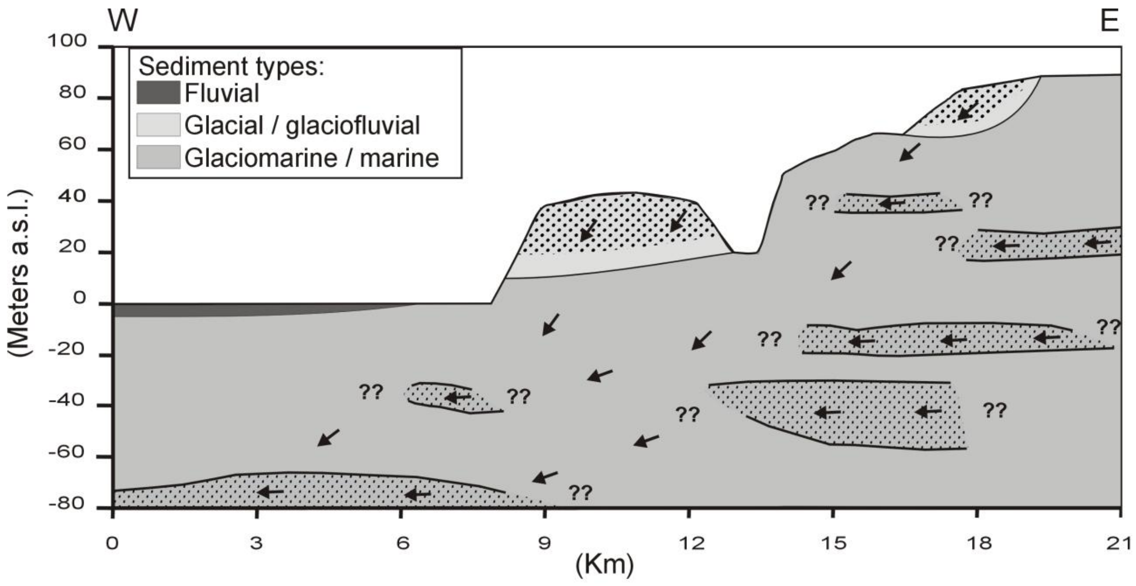

Figure 5-2. Schematic cross section of the study area (location of cross-section shown on Figure 5-1). Aquifers (represented with a dotted pattern in this figure) can be separated into two groups: Unconfined aquifers comprise near surface glaciofluvial sand and gravel, and confined aquifers comprise deeper estuarine deposits and till that are overlain and interbedded with glaciomarine silt and clay. A groundwater flow model suggests that the general groundwater flow direction (represented as arrows) in this area is southeast to northwest. Groundwater reaches deep confined aquifers by flowing from unconfined aquifers through confining units and other confined aquifers (Golder Associates Ltd., 2005).

5.3 Methodology

A total of 46 publically and privately owned wells were selected for sampling. Wells were selected with the objective of including a representative number of samples from each groundwater environment in the study area. Thus, 15 wells source groundwater from unconfined aquifers formed in glaciofluvial deposits, and 31 wells source groundwater from aquifers confined by glaciomarine and marine clays and silts (Figure 5-1).The sampling locations are distributed across the entire study area, rather than being located solely along a specific flow path of a single aquifer.

Private well water samples were collected from taps or access points as close to the source well as possible. Water treatment systems (e.g. filters, reverse osmosis, etc.) were avoided by collecting the sample from a pre-treatment access point, or the treatment systems were turned off prior to sampling. Public monitoring well samples were collected using a Grundfos 3 inch submersible pump. Temperature, pH, Eh, conductivity and dissolved oxygen were monitored using Thermo Orion meters and probes placed within an Eijkelkamp flow through cell. Upon stabilization of the monitored parameters a QED Environmental Systems polyethersulfane 0.45 micron in-line disposable filter was attached and samples were collected for analysis of stable isotopes and concentrations of dissolved constituents. Well water samples were analyzed on site for alkalinity by titration and for redox sensitive constituents (NH_3, S^{2-} and Fe^{2+}) using a Hach DR2800 spectrophotomenter. Samples collected for analyses of cation concentrations were acidified to $pH < 3$ with ultrapure HNO_3.

Analysis of major and minor elements was conducted in the groundwater geochemistry laboratory at Simon Fraser University. Samples were analysed for concentrations of anions (F, Cl, Br, NO_3, PO_4, SO_4) using a Dionex ICS-3000 SP Ion Chromatograph (IC) and for concentrations of major (Na, K, Ca, Mg, Fe) and minor (Al, As, B, Ba, Li, Mn, Mo, Si, Sr, Zn) cations using a Horiba Jobin Yvon Ultima 2 Inductively Couple Plasma Atomic Emission Spectrometer (ICP-AES). Samples were analysed for additional trace and minor elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at ALS Chemex Laboratories in Vancouver. The saturation indexes of minerals and the activities of aqueous species were calculated using PHREEQC (Parkhurst and Appelo, 1999). Sulphur and oxygen stable isotopes of sulphate were performed on field precipitated barium sulphate at the Isotope Science Laboratory at the University of Calgary. Sulphur isotope ratios of precipitated barium sulphate were analysed using a Continuous Flow-Isotope Ratio Mass Spectrometry (CF-EA-IRMS). The error for $\delta^{34}S$ results is reported by the laboratory as +/- 0.25 ‰ based on daily reproducibility tests. Oxygen isotope ratios of precipitated barium sulphate were analysed by Thermal Conversion (pyrolysis) – Continuous Flow – Isotope Ratio Mass Spectrometry. Accuracy and precision of $\delta^{18}O$ of $BaSO_4$ is reported by the laboratory as generally better than ±0.3‰ (one standard deviation based on n = 50 lab standards). Results for ^{34}S are standardized relative to VCDT and for ^{18}O are standardized relative to V-SMOW.

Arsenate and arsenite species separation was conducted in the field using dedicated anion exchange columns previously prepared in the laboratory (method originally suggested by Ficklin, 1983 and later modified by Miller et al., 2000). A Bio-Rad 1-X8 anion exchange resin with 50-100 mesh, in the chloride form, was converted to acetate form prior to sampling. A total of 3 ml of resin converted to acetate form was added to each Bio-Rad econocolumn used. This amount of resin provided an anion exchange capacity of 3.6 meq calculated to be in excess of fluid anion concentrations (Bio-Rad, 1997). In the field, arsenate and arsenite species were preserved using the method of Samanta and Clifford (2005) prior to separation. Filtered groundwater was collected and stored in 125ml amber bottles. These bottles were used to block UV illumination, which has been observed to enhance arsenite oxidation (Samanta and Clifford, 2005). A total of 1.25 ml of 5% ethylenediaminetetraacetate (EDTA) solution and 1.25 ml of 1.7M acetic acid solution were added to the collected sample. The EDTA solution was preserves arsenic species from undergoing speciation and sequesters all the Fe, Mn and Al cations, which avoids the precipitation of corresponding oxyhydroxides that could provide sorption sites for arsenate species (Samanta and Clifford, 2005). The acetic acid solution keeps samples at a pH of around 3.70, where the dominant arsenate species is the anionic $H_2AsO_4^-$ and the dominant arsenite species is the uncharged $H_3AsO_3^0$. A total of 30 ml of the EDTA preserved sample was injected in the anion-exchange column and collected in a bottle down flow from the column. These were analysed in the groundwater geochemistry laboratory at Simon Fraser University by ICP-AES. The results are reported in As (III) per cent.

Twelve core samples were analysed using selected extractions in the groundwater geochemistry laboratory at Simon Fraser University in order to quantify various pools of solid phase arsenic in the sediment. A summary of the selected extractions steps applied to the sediment samples is displayed in Table 5-1. The first four extraction steps were done using the method by Keon et al. (2001), while the fifth extraction step is a method by Wenzel et al. (2001).

The sediment core samples and all necessary equipment were transferred to an anaerobic chamber which was purged with nitrogen gas. For each sediment core sample, two duplicate samples of approximately 0.4 gram equivalent dry mass was collected and used in the selected extractions. Selected extraction steps 1 to 5 outlined in Table 5-1 were completed in the anaerobic chamber. All of the extractant solutions were prepared with deionised water (DIW) and the pH of each solution was adjusted with environmental grade hydrochloric acid (HCl) or sodium hydroxide (NaOH). The prepared extractant solutions were de-oxygenated by bubbling nitrogen gas through them prior to being transferred to the anaerobic chamber. Upon completion of each extraction step, the samples were centrifuged for 30 minutes. The extractant solutions were decanted into 60 ml syringes and filtered with 0.45µm cellulose acetate syringe filters into HDPE sample bottles. Extractants from steps 1, 2, 4 and 5 were preserved with nitric acid (HNO_3). Extractant solutions were analysed for concentrations of dissolved arsenic in the groundwater geochemistry laboratory at Simon Fraser University by ICP-AES. Arsenic calibration standards used in the analyses by ICP-AES were prepared using the extractant solutions in order to account for matrix corrections. The detection limit obtained for steps 1, 2, 3 and 5 using this method was <1.0 mg/kg of As, while the detection limit obtained for step 4 was <10 mg/kg of As.

Thirty sediment core samples (including the twelve sediment samples analysed using selected extractions) were analysed for total extractable arsenic and other 50 elements using Aqua regia digestion and ICP-MS, and total arsenic using four acids digestion (HF - HNO_3 – $HClO_4$ digestion; HCl leach) and ICP-MS at ALS Chemex Laboratories in Vancouver (selected extraction steps 6 and 7 respectively; Table 5-1). These samples were also analysed for total organic carbon by Leco Furnace at ALS Chemex Laboratories. Complete analytical results are provided in the Appendix of this thesis.

Table 5-1. Summary of selected extraction steps applied to sediment core samples.

Step	Target Phase	Procedure	Possible extraction mechanism
1	Ionically bound and pore water	1 M $MgCl_2$, pH 8, room temp., 2 - 2 h repetitions, 1 DIW rinse at end	Anion exchange for Cl for As, possible Mg-As complex formed
2	Strongly adsorbed	1 M NaH_2PO_4, pH 5, room temp., 1 - 16 h then 1 - 24 h repetition, 1 DIW rinse at end	Anion exchange of PO4 for AsO_4 and AsO_3
3	Coprecipitated with carbonates, Mn oxides and very amorphous Fe oxyhydroxides	1 M HCl, room temp., 1 – 1 h repetition, 1 DIW rinse at end	Proton dissolution, Fe-Cl complexation
4	Coprecipitated with amorphous Fe oxyhydroxides	0.2 M ammonium oxalate/oxalic acid + 0.1 M NaH_2PO_4, pH 3.25, room temp., in the dark, 1 – 1 h repetition, 1 DIW rinse at end	Ligand-promoted dissolution
5	Coprecipitated with crystaline Fe oxyhydroxides	0.2 M ammonium oxalate/oxalic acid + 0.1 M ascorbic acid, pH 3.25, water bath at 96 °C, 1 – 30 min repetition, 1 DIW rinse at end	Reduction of Fe(III) to Fe(II)
6	Coprecipitated with As oxides and sulphides	Aqua regia + ICP-MS	
7	Total As	Four acids + ICP-MS	

5.4 Results

5.4.1 Groundwater

Analytical results are presented in Table 5-2. Major ion chemistry data for groundwater samples are available in Chapter 4. A brief overview of the major ion chemistry is given here to enable integration of the sample water types with this study. Unconfined aquifer samples are of Ca-Mg-HCO_3 type. Most confined aquifer samples are Na-HCO_3 type, while eight samples collected from a deep confined aquifer are Na-Cl water type. Ca-Mg-HCO_3 groundwater sourced from unconfined aquifers has relatively low salinity, near neutral pH (mostly 6.0 to 7.7), low alkalinity (35 mg/l to 135 mg/l as HCO_3) and mostly oxidizing conditions, with Eh ranging from 150 mV to 350 mV (SHE), and ferrous iron and ammonia occurring below method detection limits in most samples. Conversely, Na-HCO_3 and Na-Cl confined aquifer samples have higher salinity, basic pH, higher alkalinity and reducing conditions, with Eh values being as low as -45 mV (SHE), ferrous iron and ammonia above detection limits in most samples, and hydrogen sulphide present in some samples.

Table 5-2 Field measured redox sensitive species, pH, Eh, minor element, As(III) and stable isotopes of sulphate results for well water samples. Sample types are described Chapter 4. As(III) results are only available for samples with total arsenic concentration above 10 µg/l.

Samp. no.	Sample Type*	pH	Eh (mV)	Fe^{2+} (mg/l)	NH$_3$-N (mg/l)	S^{2-} (µg/l)	PO$_4$ (mg/l)	As (µg/l)	As(III) (%)	B (µg/l)	F (mg/l)	Mn (µg/l)	Mo (µg/l)	Cu (µg/l)	Pb (µg/l)	Zn (µg/l)	$\delta^{34}S_{SO4}$ ‰	$\delta^{18}O_{SO4}$ ‰
01	U - $CaMgHCO_3$	7.0	164	1.78	0	0	< 0.1	5.5		11	0.09	227	5.1	0.8	< 0.2	< 1		
02	U - $CaMgHCO_3$	5.9	349	0.02	0		< 0.1	< 1		53	0.01	4.7	< 1	43.6	3.0	30	8.0	6.7
03	U - $CaMgHCO_3$	6.1	337	0.01	0		< 0.1	< 1		37	0.03	0.8	< 1	71.3	1.3	19	6.4	4.5
04	U - $CaMgHCO_3$	8.6	107	0.02	0.14		< 0.1	5.6		14	0.05	74	< 1	0.3	< 0.2	< 1		
05	U - $CaMgHCO_3$	7.7	148	0.35	0.03	0	< 0.1	< 1		6	0.11	128	< 1	0.3	< 0.2	< 1		
06	U - $CaMgHCO_3$	7.3	271	0	0.01		< 0.1	3.4	29	9	< 0.01	12	< 1	1.5	< 0.2	41	2.6	0.3
07	U - $CaMgHCO_3$	6.4	374	0.05	0		< 0.1	1.8	39	57	0.06	8.2	1.0	< 0.3	< 0.2	< 1	0.1	3.5
08	U - $CaMgHCO_3$	7.7	234	0	0		0.2	< 1		13	0.09	1.1	< 1	< 0.3	< 0.2	2		
09	U - $CaMgHCO_3$	8.7	76	0.01	0		< 0.1	7.9	71	7	0.07	87	< 1	< 0.3	< 0.2	< 1	-10.6	-3.6
10	C - $NaHCO_3$	8.4	319	0.01	0.06	0	0.7	12.4	35	41	0.12	53	1.8	< 0.3	0.3	3		
11	U - $CaMgHCO_3$	6.8	336	0.01	0		< 0.1	< 1		7	0.05	6.5	< 1	10.5	0.5	34	-2.9	3.8
12	U - $CaMgHCO_3$	6.4	328	0.49	0	0	< 0.1	3.6	100	31	0.03	94	< 1	< 0.3	< 0.2	< 1	6.3	4.5
13	C - NaCl	8.7	61	0.18	0.2	14	< 0.1	25.0	68	356	0.15	43	33.1	0.6	< 0.2	1	19.0	11.5
14	C - NaCl	8.5	44	0.06	0.19	24	2.7	6.8	100	203	0.27	33	13.0	0.6	< 0.2	3	32.9	12.7
15	C - $NaHCO_3$	9.0	236	0.06	0.21	0	0.3	21.3	57	208	< 0.01	16	40.4	1.4	0.9	7	74.1	
16	C - NaCl	8.9	192	0.03	0.07	1	1.3	54.8	23	452	0.40	11	18.5	1.5	0.2	3	21.0	13.9
17	C - $NaHCO_3$	8.6	277	0.01	0.09	0	1.3	30.7	29	198	0.45	20	7.3	0.6	0.2	4		
18	C - $NaHCO_3$	8.7	245	0.03	0.11	0	3.5	19.3	55	242	0.37	59	8.3	2.2	< 0.2	< 1	11.5	9.0
19	C - $NaHCO_3$	8.4	95	0.07	0.02	6	4.3	15.6	100	213	0.79	35	6.9	1.1	< 0.2	11	2.8	10.1
20	C - $NaHCO_3$	8.6	145	0.03	0.1	3	5.2	18.8	68	262	0.78	36	11.4	1.4	< 0.2	1	16.3	
21	C - $NaHCO_3$	7.9	89	0.26			0.4	3.5	42	8	0.16	288	< 1	0.4	0.3	2	8.5	7.2
22	C - $NaHCO_3$	8.1	92	0.09			2.3	27.7	71	276	0.43	214	21.7	0.8	0.4	27	14.8	12.3
23	C - $NaHCO_3$	9.2	187	0.01	0.14	0	1.1	23.1	77	131	0.22	15	6.8	0.4	< 0.2	1	9.4	11.2
24	C - NaCl	8.7	78	0.12	0.48	1	< 0.1	21.8	94	241	0.08	71	36.0	< 0.3	< 0.2	11	27.7	13.3
25	C - $NaHCO_3$	8.5	71	0.07	0.19	0	5.5	18.2	100	431	0.55	48	17.9	< 0.3	< 0.2	38	9.7	10.9
26	C - $NaHCO_3$	8.1	72	0.12	0.05	6	1.2	9.2	66	53	0.16	60	2.7	< 0.3	< 0.2	4	16.8	18.3
27	C - $NaHCO_3$	8.2	123	0.03	0.04	1	0.5	4.6	61	25	0.10	49	1.1	0.4	< 0.2	1		
28	C - $NaHCO_3$	7.6	161	0.2	0.05	3	< 0.1	< 1		12	0.02	35	< 1	1.8	< 0.2	2	-13.3	1.2
29	U - $CaMgHCO_3$	7.6	307	0.01	0	0	< 0.1	< 1		10	< 0.01	4.2	< 1	5.4	0.2	2	-3.1	0.4
30	C - $NaHCO_3$	8.6	77	0.03	0.21	0	3.5	21.9	45	224	0.39	49	11.0	1.5	< 0.2	< 1	17.1	13.1
31	C - $NaHCO_3$	8.2	319	0.01	0	0	2.5	23.9	28	140	0.28	10	26.7	1.1	< 0.2	9		
32	C - $NaHCO_3$	6.9	361	0	0.01		< 0.1	5.0	51	11	0.03	0.6	1.4	33.8	< 0.2	2	3.6	3.1
33	U - $CaMgHCO_3$	7.7	306	0.02	0		< 0.1	5.0	20	8	0.04	0.8	1.5	10.3	< 0.2	3		
34	C - $NaHCO_3$	8.7	76	0.06	0.11	0	5.8	29.2	62	292	0.65	35	6.6	1.1	< 0.2	2	10.3	
35	C - $NaHCO_3$	8.5	149	0.02	0.3	0	1.9	27.5	100	96	0.27	25	5.1	0.7	< 0.2	2		
36	C - $NaHCO_3$	8.5	167	0.01	0.07	0	2.1	30.0	54	105	0.30	26	5.1	< 0.3	< 0.2	1		
37	C - NaCl	8.5	-26	0.3	0.32	13	< 0.1	44.4	100	410	0.32	71	24.0	< 0.3	< 0.2	1	31.4	16.4
38	C - $NaHCO_3$	9.3	-47	0.04	0.17	9	4.9	20.8	55	334	0.71	10	11.0	4.5	0.2	1	33.9	14.4
39	C - $NaHCO_3$	8.3	63	0.14	0.23	17	19.5	26.9	79	396	2.09	49	4.9	25.1	2.3	27	5.6	8.6
40	C - $NaHCO_3$	8.7	4	0.06	0.48	3	0.9	1.7		90	0.20	40	2.6	0.5	< 0.2	8		
41	U - $CaMgHCO_3$	5.9	387	0.05	0.02		< 0.1	3.6		14	0.01	85	< 1	58.0	2.1	22		
42	U - $CaMgHCO_3$	6.9	341	0.01	0.01		< 0.1	1.8		19	0.04	0.4	< 1	1.6	0.7	10		
44	C - NaCl	8.3	327	0.01	0.01	0	< 0.1	19.6	0	266	0.28	67	24.1	1.8	0.2	30	23.2	14.8
45	C - $NaHCO_3$	8.8	-31	0.15	0.15	44	8.2	33.0	49	1051	1.72	23	16.6	1.4	0.2	14	25.2	
46	C - NaCl	8.8	-29	0.03	0.12	3	1.2	10.6	56	167	0.28	23	11.3	0.7	0.3	4	25.2	15.1
47	C - NaCl	8.6	252	0.02	0.13	0	< 0.1	47.8	44	446	0.31	40	26.9	2.8	1.7	11	22.7	13.3

* U - Unconfined aquifer; C - Confined aquifer

Arsenic concentrations in the unconfined aquifer samples range from below detection limit (< 1.0 µg/l) to 7.9 µg/l (Table 5-2; i.e. no samples were above the Canadian drinking water guideline for arsenic of 10 µg/l). Samples collected from confined aquifers have higher arsenic concentrations, ranging from below detection to 54.8 µg/l (Table 5-2), and with mean and median concentrations of 21.1 µg/l and 21.2 µg/l, respectively. No significant difference in arsenic concentration exists between Na-HCO_3 and Na-Cl groundwaters, the two water types in the confined aquifers. The median arsenic concentration in Na-HCO_3 groundwater type is 20.8 µg/l, while the median concentration in Na-Cl type is 23.4 µg/l. Arsenite constitutes a significant portion of total arsenic, with a percentage of total arsenic ranging from 29 % to 100 % (with one outlier with 0 % As (III)), and a mean and median of 60.7 % and 59.0 %, respectively.

Other anions and oxyanions also have higher concentrations in groundwater from confined aquifers compared to unconfined aquifers. Most samples sourced from unconfined aquifers have molybdenum below detection (< 0.2 µg/l), while the mean molybdenum concentration in confined aquifer samples is 13.1 µg/l. Boron concentrations range from 6 µg/l to 57 µg/l in unconfined aquifer samples, and from 8 µg/l to 1.1 mg/l with a median of 212 µg/l in confined aquifer samples. Fluoride concentrations range from below detection (< 0.01mg/l) to 0.11 mg/l in unconfined aquifer samples, and from < 0.01 mg/l to 2.08 mg/l in confined aquifer samples. Most samples collected from unconfined aquifers have phosphate below detection (< 0.1 mg/l), while samples sourced from confined aquifers have phosphate at concentrations as high as 19.5 mg/l (Table 5-2).

Minor cationic constituents are mostly at low concentrations in groundwater samples, with a slight tendency for higher concentrations in groundwater in unconfined aquifers. Copper concentrations in unconfined aquifer samples range from below detection (< 0.3 µg/l) to 71.3 µg/l with a median of 5.4 µg/l, and range from < 0.3 µg/l to 33.8 µg/l with a median of 1.1 µg/l in confined aquifer samples. Lead concentrations in unconfined aquifer samples range from below detection (< 0.2 µg/l) to 3.0 µg/l with a median of 1.0 µg/l, and range from < 0.2 µg/l to 2.3 µg/l with a median of 0.3 µg/l in confined aquifer samples. Zinc concentrations are generally slightly higher in groundwater in confined aquifer samples. Median zinc concentration in unconfined aquifer samples is 2.0 µg/l and in confined aquifer samples is 3.0 µg/l (Table 5-2).

5.4.2 Sediments

Selected extractions, total extractable arsenic (by Aqua Regia), total arsenic (by Four Acids) and total organic carbon results are displayed in Table 5-3. Selected extraction and total arsenic results are also shown along with a simplified lithological log in Figure 5-3 (note that extraction steps with results that are below detection limit are not displayed in Figure 5-3. Summary of selected extraction and total arsenic results. Total arsenic content in sediments ranges from 5.0 mg/kg to 17.2 mg/kg. This range is not particularly high if compared to typical concentrations in unconsolidated sediments and soils worldwide, which range from 3 mg/kg to 10 mg/kg (Smedley and Kinniburgh, 2002). The highest percentages of arsenic were extracted during the Aqua Regia step (43 % to 72 %) in sediment samples sourced from wells A and B, while a significant percentage of arsenic was also extracted on the HCl step (13 % to 38 %; step 3) on the same samples. Unfortunately the detection limit for step 4 (10 mg/kg) is too high for the observed arsenic concentrations in sediment samples. This high detection limit in step 4 was the result of matrix effects and sample dilution that needed to be performed in order to avoid analytical problems with the ICP-AES. The selected extraction results nonetheless suggests that arsenic in sediments occurs dominantly in sulphide or arsenic oxide minerals, while a significant proportion of arsenic is also available in manganese oxides or very amorphous iron oxyhydroxides. Well C results differ from those of wells A and B, as results for NaH_2PO_4 (step 2) and Oxalic acid + ascorbic acid (step 5) steps were above detection. This suggests that there is also a noticeable proportion of arsenic present adsorbed to mineral surfaces and coprecipitated with crystalline iron oxyhydroxides in well C sediments. However, the sediment samples from well C were from dried cuttings and it is likely that extensive oxidation of any reduced species may have altered the distribution of arsenic between the different phases.

Table 5-3. Selected extractions, total extractable arsenic and selected elements (Aqua Regia), total arsenic (Four Acids) and total organic carbon results for sediment core samples. Selected extraction steps 1 to 5 are described in Table 5-1.

Samp. no.	Arsenic - Selected Extractions								Aqua Regia Digestion			
	Step 1 (mg/kg)	Step 2 (mg/kg)	Step 3 (mg/kg)	Step 4 (mg/kg)	Step 5 (mg/kg)	Aqua Regia (ppm)	Four Acids (ppm)	TOC (%)	Cu (ppm)	Mo (ppm)	Pb (ppm)	Zn (ppm)
01	-	-	-	-	-	12.2	13.4	0.41	35.6	0.82	4.9	69
03	-	-	-	-	-	7.5	7.9	0.33	31.8	0.78	3.8	57
04	-	-	-	-	-	9.1	10.9	0.54	38.0	0.84	4.6	71
05	-	-	-	-	-	6.3	6.4	0.29	38.4	0.70	4.8	70
06	-	-	-	-	-	7	8.6	0.16	19.0	0.63	2.7	42
07	< 1	< 1	1.3	< 10	< 1	6.4	9.6	0.19	16.2	0.57	2.2	32
08	-	-	-	-	-	8.7	9.9	0.29	48.2	0.72	6.0	88
09	< 1	< 1	3.4	< 10	< 1	7.8	9	0.32	42.4	0.81	5.3	78
10	< 1	< 1	3.0	< 10	< 1	7.6	7.9	0.38	38.8	0.79	4.5	71
11	< 1	< 1	1.2	< 10	< 1	3.7	5	0.04	15.3	0.28	2.2	35
12	< 1	< 1	2.4	< 10	< 1	6.6	7.3	0.44	36.4	0.90	4.3	66
13	-	-	-	-	-	6.5	7.4	0.43	54.1	0.80	5.2	77
14	< 1	< 1	1.5	< 10	< 1	5.9	6.2	0.39	29.7	0.79	3.4	54
15	-	-	-	-	-	6.5	8.5	0.29	17.9	0.60	2.6	36
16	-	-	-	-	-	13.6	17.2	0.33	77.9	1.15	10.0	142
17	< 1	2.0	4.0	< 10	1.1	9.7	12.2	0.28	65.3	1.19	9.6	132
18	-	-	-	-	-	9.5	11.4	0.36	55.0	0.95	7.1	108
19	-	-	-	-	-	9.9	11.6	0.47	60.4	1.70	8.3	114
20	< 1	1.4	3.3	< 10	1.3	9.3	11.4	0.49	55.3	1.07	6.7	103
21	-	-	-	-	-	9	12	0.38	53.0	0.99	6.7	95
22	-	-	-	-	-	5.7	6.6	0.23	26.1	0.59	3.5	47
23	-	-	-	-	-	7.3	8	0.24	38.3	0.82	4.6	64
24	-	-	-	-	-	4.1	5.6	0.18	27.9	1.10	3.9	52
25	-	-	-	-	-	5	6.6	0.21	33.8	5.88	5.0	67
26	< 1	< 1	2.7	< 10	< 1	6.7	7.9	0.29	43.5	0.73	5.2	78
27	< 1	< 1	1.6	< 10	< 1	5	5.9	0.19	21.7	0.56	2.6	40
28	< 1	< 1	2.8	< 10	< 1	6.4	8.3	0.28	40.8	0.70	5.2	75
29	< 1	< 1	3.3	< 10	< 1	8.6	9.7	0.44	41.1	0.93	5.1	77
30	-	-	-	-	-	8.8	10.6	0.43	48.9	0.90	5.9	92

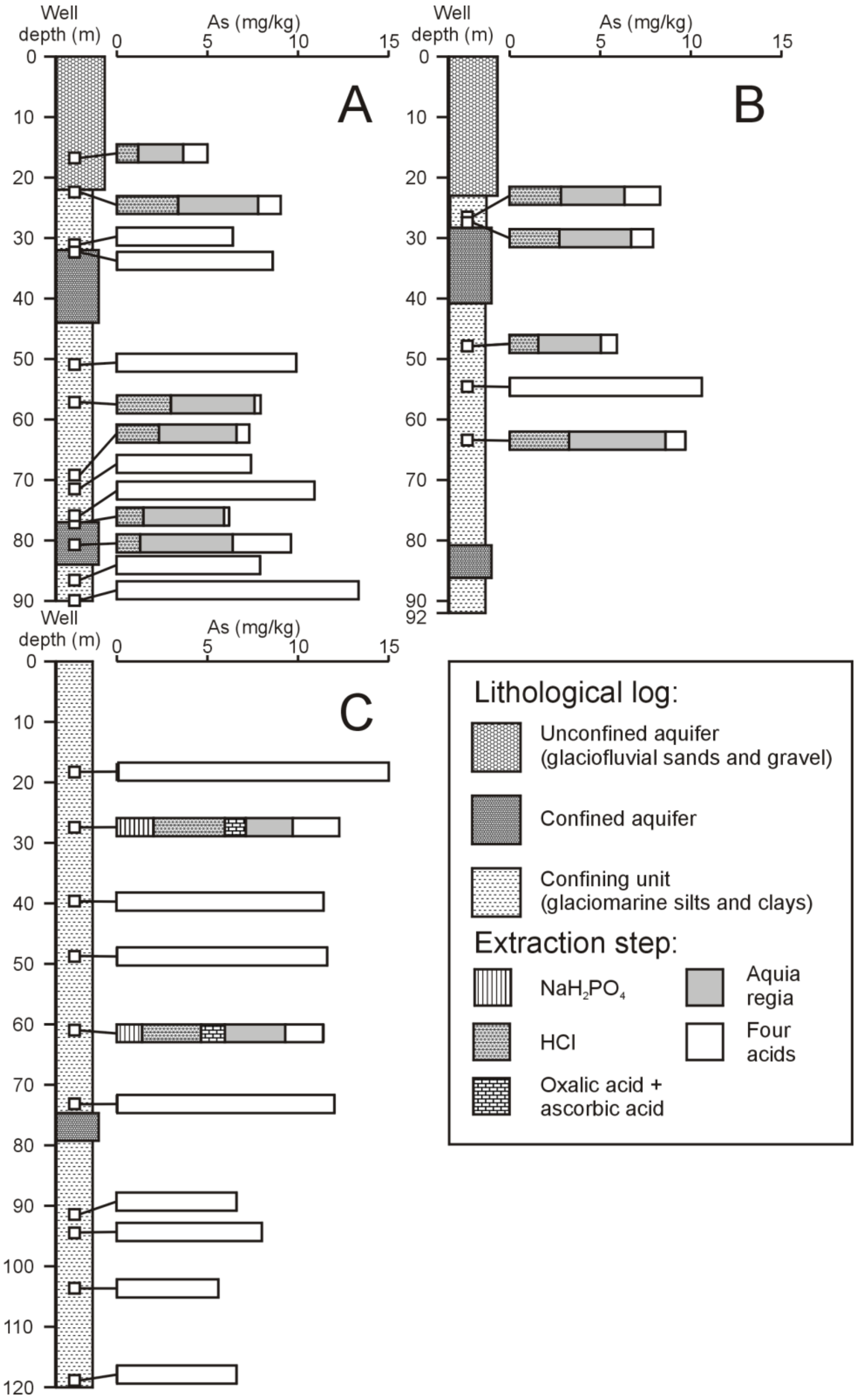

Figure 5-3. Summary of selected extraction and total arsenic results of sediment core samples with simplified lithological logs of wells. Lithological information for well A is simplified from GW Solutions (2009) and for well B from Kalwij Water Dynamics (2010). In the majority of samples, most arsenic was extracted on Aqua Regia and HCl and steps. This indicates that arsenic is hosted dominantly in sulphide minerals, while a significant portion is also in very amorphous iron oxyhydroxides or magnesium oxides.

Total extractable (using aqua regia digestion) copper concentrations in sediments range from 15.3 ppm to 77.9 ppm, molybdenum concentrations range from 0.28 ppm to 1.70 ppm (with one outlier sample at 5.88 ppm), lead concentrations range from 2.2 ppm to 10 ppm and zinc concentrations range from 32 to 142 ppm (Table 5-3). The mineralogy of sediment samples is determined Chapter 4 through XRD analysis. The samples contain both sulphide (pyrite) and oxide minerals (magnetite). This supports the selected extraction results, which show that arsenic occurs in both oxyhydroxide and sulphide minerals. The total organic carbon content in sediment samples ranges from 0.04 % to 0.49 %. The relatively low organic carbon content in the sediments indicates that it is unlikely that arsenic is associated with organic carbon.

5.5 Discussion

5.5.1 Hydrogeochemistry

The hydrogeochemistry of the groundwater system is discussed in detail in Chapter 4. The chemistry of groundwater in unconfined aquifers is interpreted to be controlled mainly by rain water composition and processes related to recharge in till deposits. Hendry et al. (1986) observed that processes associated with recharge in till deposits may include oxidation of reduced sulphur, dissolution of carbonate minerals at elevated pCO_2, evapotranspiration, and cation exchange. Groundwater samples sourced from unconfined aquifers have relatively low salinity and are mostly oxidizing. This suggests that groundwater occurring in unconfined aquifers has undergone little water-rock interaction. The chemistry of groundwater occurring in confined aquifers is controlled by freshening processes (i.e. fresh groundwater flushing a salt water aquifer) promoted during recharge through the glaciomarine silts and clays, and associated water-rock interactions. Freshening processes are characterized in the studied system by increases in sodium accompanied by increases in bicarbonate concentrations caused by dissolution of carbonate minerals, and subsequent cation exchange reactions and an enrichment in the $\delta^{13}C$ of dissolved inorganic carbon (DIC). The addition of bicarbonate through this process causes groundwater in confined aquifers to acquire a basic pH and high alkalinity. In addition, the presence of reactive silicate minerals in the aquifer and confining unit sediments facilitates silicate weathering reactions. The primary drivers of the more reducing conditions in groundwater in confined aquifers appears to be the organic matter occurring in the glaciomarine sediments and the presence of dissolved organic acids (formic and acetic) that are recognized as distinct peaks (not quantified) in ion chromatography. The occurrence of saline Na-Cl groundwater type was interpreted to be the result of mixing of the Na-HCO_3 groundwater with connate seawater-like end member.

5.5.2 Arsenic release in glaciomarine sediments

Confined aquifers occur within glaciomarine sediments where the dominant processes controlling the major ion chemistry of groundwater is cation exchange promoted by clays. When the sediments where submerged beneath the sea, they acquired sodium on exchange sites. Chloride was also present at high concentration in solution. Subsequently, fresh water flushed the chloride relatively rapidly, and continues to remove sodium from the exchange sites by replacing it with calcium and magnesium. This results in groundwater in confined aquifers having a relatively high Na/(Ca+Mg) ratio (see Chapter 4). Unconfined aquifers are formed in glaciofluvial sediments that were deposited after the last period of marine transgression in the study area and they do not constitute a freshening environment. For this reason, groundwater occurring in unconfined aquifers is a Ca-Mg-HCO_3 type, with a relatively low Na/(Ca+Mg) ratio. In this setting, it is suggested that if a minor element reaches elevated concentrations only in groundwater with a high Na/(Ca+Mg) ratio, it is highly likely that this element is mobilized in glaciomarine sediments and not in glaciofluvial sediments.

A positive relationship exists between arsenic concentrations and the Na/(Ca+Mg) ratio in groundwater. Arsenic concentrations of all samples with a Na/(Ca+Mg) ratio (in mmol/l) below 1.8 are below the Canadian Drinking Water Guideline (10 µg/l), while nearly all samples with a higher Na/(Ca+Mg) ratio have arsenic at concentrations above 10 µg/l (Figure 5-4). This indicates that arsenic is likely released to solution as groundwater flows through the glaciomarine sediments and while processes associated with freshening environments (as cation exchange) take place. Low arsenic concentrations in groundwater with low Na/(Ca+Mg) ratios indicates that little or no arsenic release occurs outside the glaciomarine sediments. Some samples tagged as being sourced from confined aquifers have low arsenic concentrations and low Na/(Ca+Mg) ratios (Figure 5-4). The lithological logs indicate that these samples were collected from wells completed in aquifers that are overlain by a relatively thin (few meters thick) layer of silt and clay. This differs from the logs of most wells sourcing groundwater in confined aquifers that have a thick (up to 70 meters) monotonous layer of clay and silt overlying the aquifer. As water flows through a thinner layer of clay to reach the aquifer it does not acquire a strong freshening chemical signature (i.e. it remains with a relatively low Na/(Ca+Mg) ratio). At the same time, water interacts less with glaciomarine sediments, which results in lower arsenic concentrations. One sample lies outside the described relationship as it has a Na/(Ca+Mg) ratio that is typical of groundwater in confined aquifers (5.46) but a low arsenic concentration (2 μg/l; Figure 5-4). This sample has one of the highest chloride concentrations (31.3 mg/l) among all samples tagged as being Na-HCO_3 type. This suggests that the relatively high sodium concentration of this sample is a result of mixing with saline water rather than a strong cation exchange control to its chemistry.

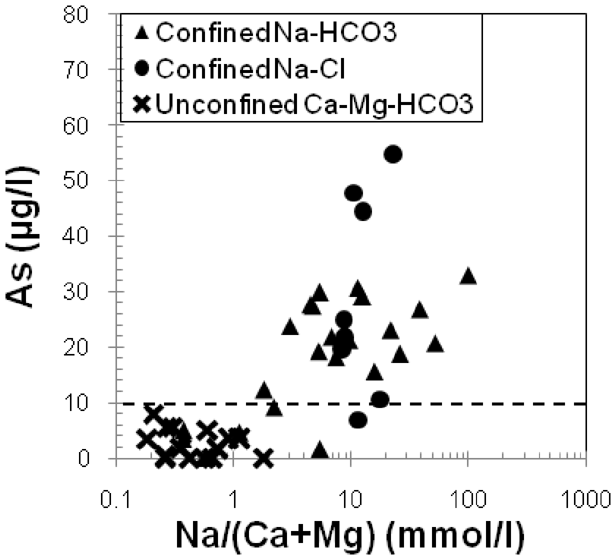

Figure 5-4. Scatter plot comparing Na/(Ca+Mg) ratios (in mmol/l) to arsenic concentrations in groundwater. Dashed lines indicates the Canadian Drinking Water Guideline for arsenic (10 µg/l). The positive relationship indicates that arsenic release to groundwater occurs in a freshening setting.

Another process, related to freshening, is mixing with residual seawater. This yields saline Na-Cl type groundwater in the deepest confined aquifer. If the residual seawater end member has lower arsenic concentrations than fresh groundwater, arsenic concentrations in Na-Cl samples would necessarily be lower than in the Na-HCO_3 samples as a result of dilution. On the other hand, if the concentrations of anionic species phosphate and sulphate were to increase as a result of mixing with saline water, arsenic mobility could be enhanced due to competitive adsorption (as observed by Xu et al., 1988; Wilkie and Hering, 1996; Jain and Loeppert, 2000; Hundal et al., 2007; Rowland et al., 2008; Ujević et al., 2010). There is no relationship between arsenic with chloride (assumed to be a conservative element during mixing), sulphate or phosphate (Figure 5-5). This suggests that mixing is not enhancing arsenic mobility through competitive adsorption, while it is also not diluting arsenic concentrations. The lack of relationship between arsenic and chloride indicates that conditions for arsenic mobility are the result of water-rock interactions that control the pH and redox of the system. This results in saline Na-Cl groundwater having similar arsenic concentrations to those of the Na-HCO_3 groundwater. In the subsequent sections, conditions favouring arsenic mobility and arsenic release processes in confined aquifers are addressed.

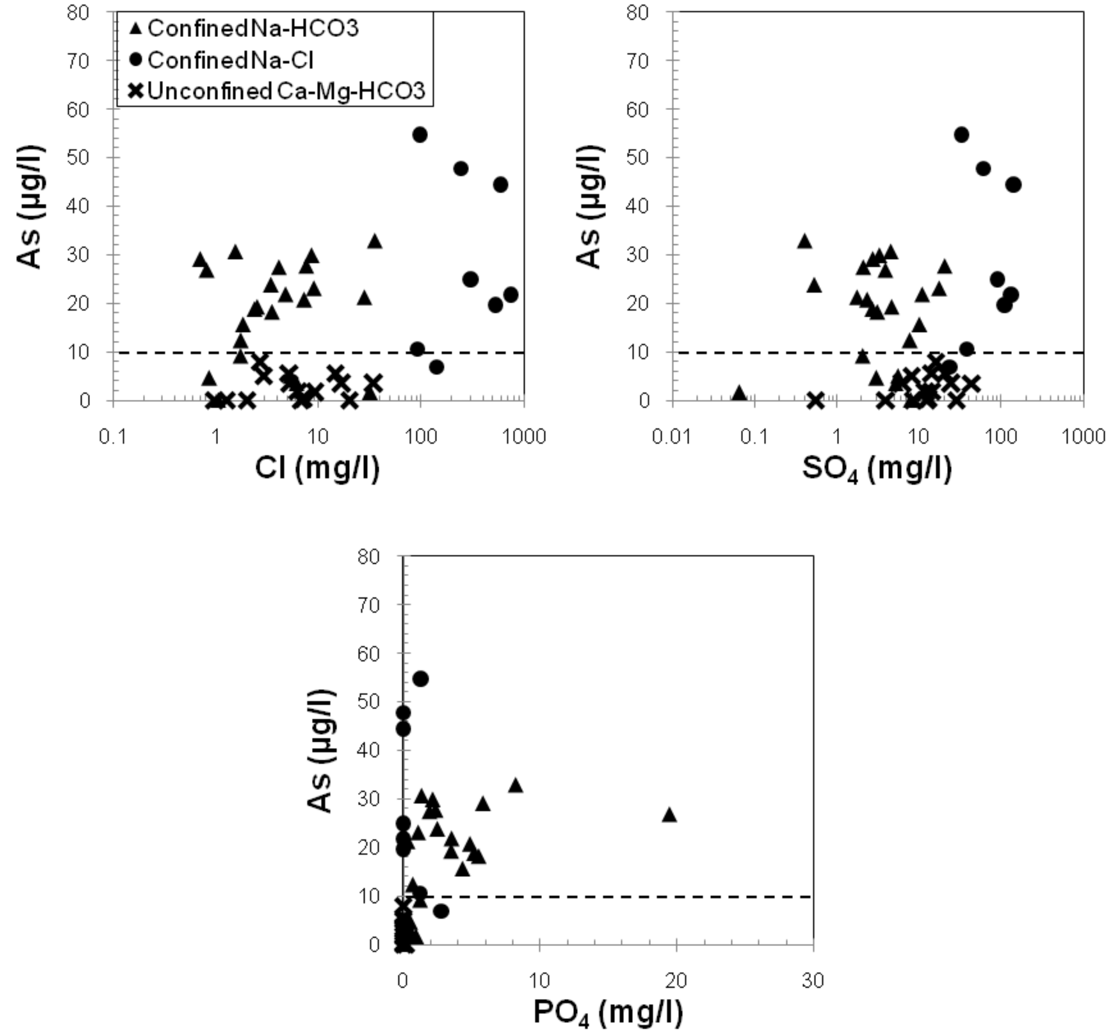

Figure 5-5. Scatter plots comparing arsenic concentrations with chloride, sulphate and phosphate concentrations. Dashed lines indicate the Canadian Drinking Water Guideline for arsenic (10 µg/l). Lack of clear relationships in these plots indicates that arsenic mobility is not enhanced by mixing with saline water or by competitive adsorption with other anions.

5.5.3 Groundwater conditions for arsenic mobility

The electrical charge of mineral surfaces and of dissolved arsenic species may prevent arsenic adsorption at specific groundwater chemical conditions and favour arsenic mobility. Adsorption of dissolved arsenate species (which occurs dominantly with a negative charge at pH > 2.3) is greatest under acidic conditions and gradually decreases at increasing pH as mineral surfaces also become negatively charged (Pierce and Moore, 1982; Bowell, 1994; Stollenwerk, 2002). Under reducing conditions, arsenic adsorption is not favoured as the reduced arsenic species, arsenite, is uncharged and less prone to undergo adsorption than arsenate (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). As a result, arsenic is typically mobile in solution at basic pH or reducing conditions (Smedley and Kinniburgh, 2002).

Selected extraction results indicate that no significant proportion of arsenic occurs adsorbed to mineral surfaces in the sediments (steps 1 and 2 of selected extractions; Table 5-3). This suggests that mineral surfaces are not effectively removing arsenic from solution. Groundwater occurring in confined aquifers is basic and reduced, which are conditions achieved as a result of processes related to freshening environments as described previously. The chemistry of groundwater in unconfined aquifers differs from groundwater in confined aquifers as it is mostly neutral and oxidized. A positive relationship between arsenic and pH (Figure 5-6) indicates that arsenic mobility in confined aquifers is favoured by basic pH. All samples with pH below 8 have arsenic at concentrations below the drinking water guideline (10 µg/l), whereas most samples with pH above 8 have arsenic above the guideline (Figure 5-6). Still, not all confined groundwater samples with a pH above 8 have elevated arsenic concentrations. This shows that the addition of arsenic to water and its mobility cannot be explained solely by the pH of groundwater. These high pH samples with low arsenic concentrations have a low Na/(Ca+Mg) ratio; hence they have not undergone significant interaction with glaciomarine sediments. A negative relationship between As (III)/As_{TOTAL} and Eh indicates that arsenic mobility is also favoured at increasing reducing conditions as a result of speciation to arsenite (Figure 5-6). Under basic conditions, other anionic dissolved species should also have their mobility favoured (as observed previously by Smedley et al., 2002) as they have similar sorption behaviour as arsenic (Drever, 2002). This is observed with molybdenum, fluoride and phosphate, all of which show a positive relationship with pH (Figure 5-6). The relationship of pH with boron is slightly different than with As, Mo, F and PO_4. Boron concentrations are relatively moderate (14 µg/l to 56 µg/l) at a pH below 7, lowest (6 µg/l to 12 µg/l) at a pH range of 7 to 8, and highest (up to 1.05 mg/l) at a pH above 8. Goldberg and Glaubig (1985) observed that boron adsorption to amorphous iron and aluminum oxides is highest at a pH range of 7 to 8. The very high boron concentrations in basic Na-HCO_3 and Na-Cl type groundwaters is also likely tied to a marine influence, as boron concentrations in seawater (~ 5 mg/l) is typically much higher than in freshwater (Parks and Edwards, 2005). However, it is unlikely that high boron concentrations in groundwater are directly caused by mixing with saline water, as there is no correlation between boron and chloride in the groundwater data.

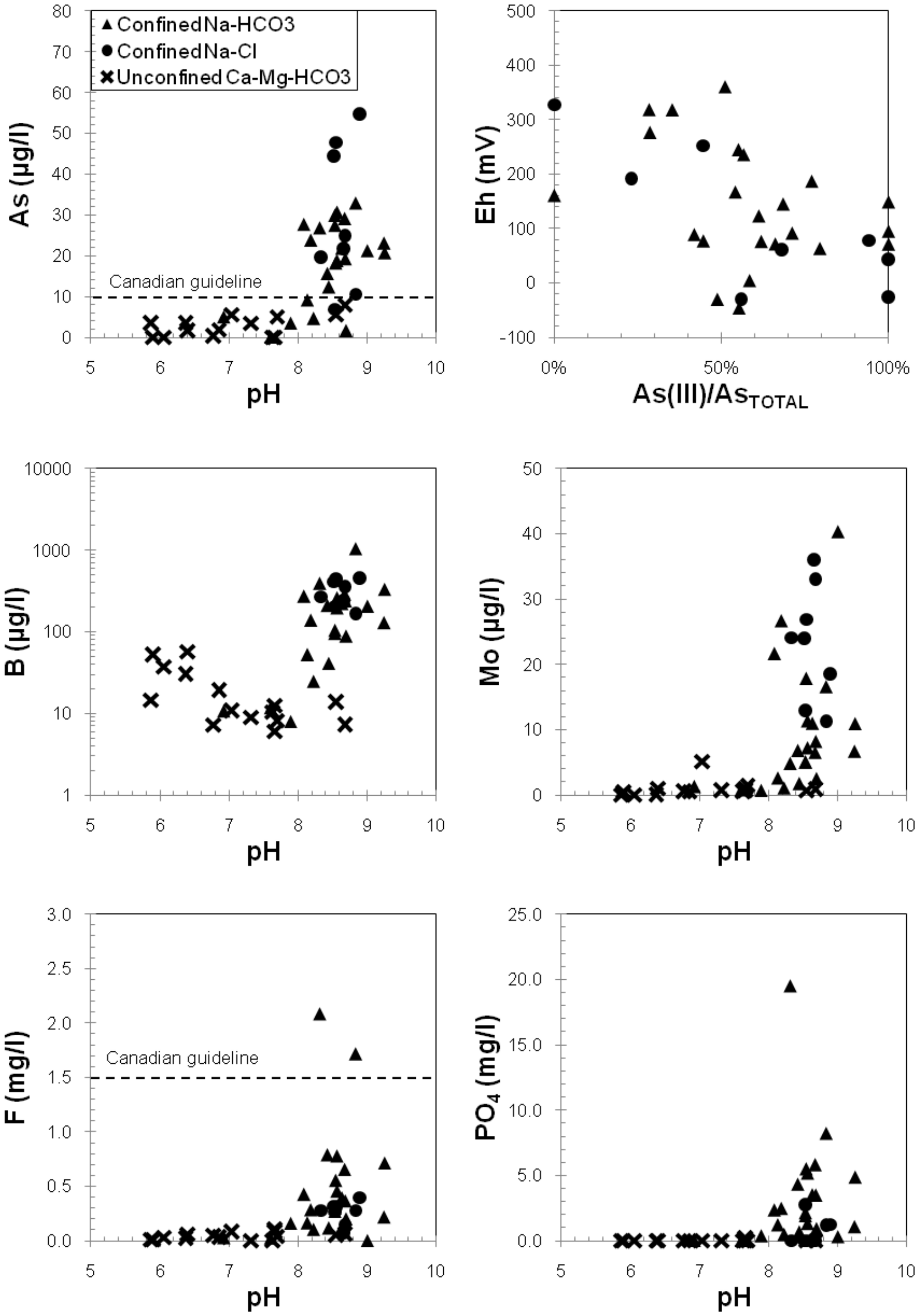

Figure 5-6. Scatter plots comparing arsenic, boron, molybdenum, fluoride and phosphate concentrations with pH, and As(III)/As$_{TOTAL}$ with Eh. Increases in the concentrations of As, B, Mo, F, and PO$_4$ at pH > 8 indicate that their mobility is favoured at basic pH. The negative relationship of As(III)/As$_{TOTAL}$ with Eh suggests that arsenic mobility is favoured at increasing reducing conditions through speciation to arsenite.

Unlike anions and oxyanions, cationic metals tend to be less mobile at basic pH as their adsorption to negatively charged surfaces is favoured (Dzombak and Morel, 1990; Drever, 2002). For this reason, cationic metals including lead, copper and zinc remain at low concentrations in basic groundwater occurring in the confined aquifers. This demonstrates the role of pH and redox on the mobility of arsenic in groundwater. Arsenic concentrations in sediments positively correlates with copper, lead, zinc and molybdenum concentrations (determined using aqua regia digestion); with copper and zinc occurring at higher concentrations than arsenic in sediments (see results section). If cationic metals occur in sediments in the same mineral pools as arsenic and other anionic occurring elements, mineral dissolution should result in the release of both anion and cation species to solution. Yet, the pH and redox of groundwater in confined aquifers keep arsenic and other anions mobile in solution, while any cationic metals released via mineral dissolution are prone to be immobilized through adsorption.

5.5.4 Arsenic release via oxide and oxyhydroxide minerals dissolution

Up to 4 mg/kg of arsenic was extracted from sediments in step 3 of the selected extractions (Table 5-3). This indicates that a significant proportion of arsenic occurs structurally within manganese oxide and amorphous iron oxyhydroxide minerals. Hence, one possible mechanism of arsenic release to solution is via the reductive dissolution of oxide and oxyhydroxide minerals.

Although no clear relationship exists between total arsenic and measured Eh (Figure 5-7), the fact that all samples with Eh above 330 mV have arsenic below the guideline indicates that mobilization is not favoured under oxidizing conditions. Platinum electrode measured Eh values are usually not in agreement with calculated Eh using the Nerst equation for individual redox couples. In fact, redox disequilibrium is the norm in most systems, so there is no absolute Eh that represents the full range of redox couples (Lindberg and Runnells, 1984). However, the measured Eh using a platinum electrode is often consistent with the calculated Eh for iron redox couples if iron is present in sufficient quantities (Lindberg and Runnells, 1984). For this reason, low concentrations of arsenic in samples with elevated Eh most likely indicates that arsenic mobilization is not favoured where Fe^{3+} or $Fe(OH)_3$ species predominate over Fe^{2+}. Ammonia and phosphate are two products of organic matter oxidation (Murray et al., 1978). The presence of phosphate and ammonia in groundwater samples (Table 5-2) indicates that reducing conditions are likely attained via oxidation of organic matter. Hydrogen sulphide gas may be produced if sulphate is an oxidant involved in the organic matter oxidation reaction (Murray et al., 1978). The occurrence of groundwater samples with detectable ammonia and no detectable hydrogen sulphide gas (Table 5-2), and the fact that groundwater in confined aquifers is mostly anoxic, may suggest that ferric iron, rather than sulphate, is utilized by bacteria in the oxidation of organic matter. However, most samples with detectable ammonia are relatively enriched in ^{34}S of SO_4 (above 8.0 ‰; Table 5-2). This is indicative that ammonia is produced during sulphate reduction (bacterial sulphate reduction is addressed later in the chapter), and that sulphate is also an important oxidant of organic matter. The low hydrogen sulphide gas content in some ammonia rich samples may be a result of precipitation with Fe^{2+} to form sulphide minerals.

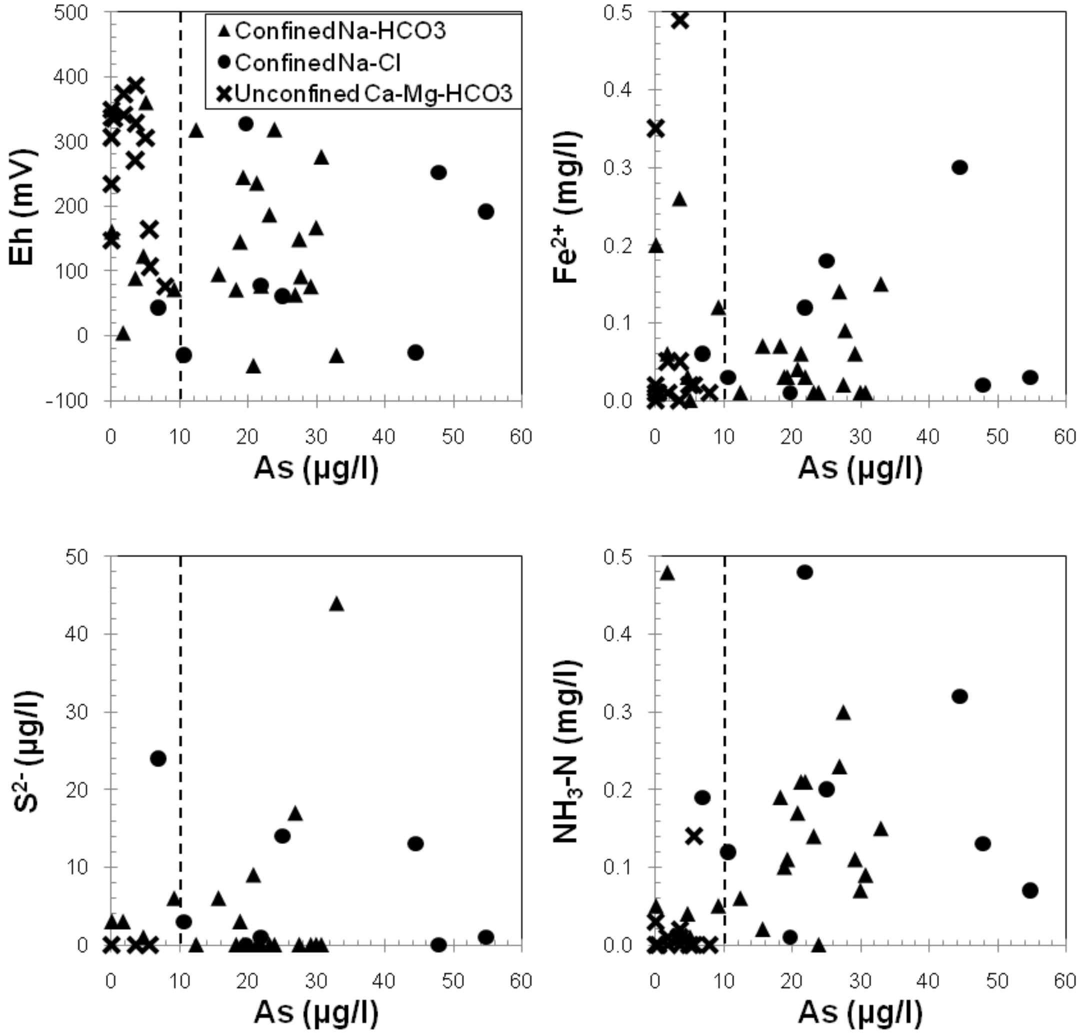

Figure 5-7. Scatter plots comparing arsenic concentrations with Eh and the concentrations of redox sensitive species. Dashed lines indicate the Canadian Drinking Water Guideline for arsenic (10 µg/l). No samples with Eh above 330 mV have arsenic above the guideline, while general positive relationships exist between arsenic and redox sensitive species. These trends indicate that reducing conditions in groundwater in confined aquifers favour arsenic mobilization.

Groundwater samples with relatively high Fe^{2+}, NH_3 and S^{2-} concentrations tend to have elevated arsenic (Figure 5-7). This suggests that at increasing reducing conditions these reduced species are produced and arsenic is released to groundwater. Strong positive correlations between arsenic and NH_3 and S^{2-} should not be expected to be processes resulting in arsenic release in reducing environments, as the reduction of arsenate to arsenite and the dissolution of As-bearing (hydr)oxide minerals typically occur at a higher redox state than bacterial sulphate reduction driving the oxidation of organic matter and the resultant formation of ammonia and hydrogen sulphide gas (Appelo and Postma, 2005). It has been observed that redox reactions involving As(V)/As(III) and Fe(III)/Fe(II) redox couples occur at similar pH and redox potential (Cherry et al., 1979). This, in theory, should result in strong positive correlations between arsenic and iron reduced species in groundwater at increasing reducing conditions. However, it has been noted that the redox potential of arsenic and iron redox couples often do not agree as dissolved species in low temperature water tend to be far from redox equilibrium (Lindberg and Runnells, 1984; Holm and Curtiss, 1989). Hence, a strong correlation between arsenic and iron should not be expected here either. Nonetheless, general positive relationships of arsenic with Fe^{2+}, NH_3 and S^{2-} indicate that arsenic is mobilized at increasing reducing conditions, even though these relationships are not strongly correlated.

At increasing reducing conditions, oxide and oxyhydroxide minerals may dissolve and release arsenic hosted in them to groundwater (Smedley and Kinniburgh, 2002). In study areas where arsenic has been interpreted to be released via oxide reductive dissolution, as in Southeast Asia, groundwater acquires elevated iron concentrations. Eiche et al. (2008) reports iron at concentrations as high as 20 mg/l in groundwater in Vietnam, McArthur et al. (2004) reports iron at 13.7 mg/l in West Bengal, India, Rowland et al. (2008) reports 14.5 mg/l in Cambodia, and von Brömssen et al. (2007) reports 14.2 mg/l in Bangladesh. Yet, iron concentrations in groundwater occurring in confined aquifers in the study area described in this paper (up to 0.37 mg/l) are much lower than the high arsenic groundwaters of Southeast Asia. One fundamental difference between the groundwater environment described in this chapter and the environment in Southeast Asia, which may result in this disparity in iron concentrations, is the redox state of sediments prior to deposition. Sediments in Southeast Asia were previously oxidized as they were transported downstream and exposed to the atmosphere from the Himalayas by rivers. They are subjected to reducing conditions in lower topographic areas due to high organics, which results in extensive iron oxide reductive dissolution and, consequently, groundwater with high iron concentrations (Mukherjee et al., 2009; Fendorf et al., 2010). The glaciomarine sediments in the study area of this research were glacially eroded and transported from bedrock. It is likely that they were exposed to more reducing conditions (XRD analysis reported that major iron oxide in sediments is magnetite; see Chapter 4) than the fluvial sediments of Southeast Asia during transportation. This would result in sediments in this study area having less iron sources available as oxide and oxyhydroxide minerals. In addition, high arsenic groundwater in the described environment in this study has basic pH (up to 9.2), while the pH in groundwaters of Southeast Asia is mostly neutral (Stüben et al., 2003; McArthur et al., 2004; Buschmann et al., 2007; Rowland et al., 2008). Basic pH coupled with high bicarbonate content (up to 637 mg/l) of groundwater may facilitate the removal of iron from solution through the precipitation of carbonate minerals. Charlet and Polya (2006) and Horneman et al. (2004) noted that decoupling of iron and arsenic release during iron oxide dissolution might be caused by adsorption of Fe^{2+} to mineral surfaces, or reprecipitation of Fe^{2+} as different oxide or carbonate minerals. While Fe^{2+} adsorption should be favoured at basic water pH (Liger et al., 1999; Appelo et al., 2002), groundwater in confined aquifers reaches siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) saturation at decreasing Eh (Figure 5-8). This indicates that iron and manganese can be removed from solution through reprecipitation as carbonate minerals.

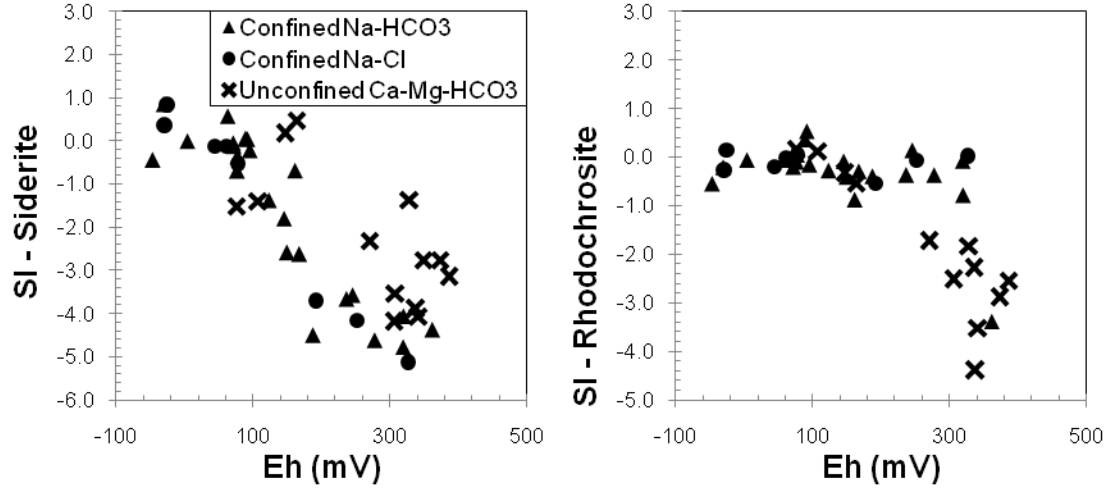

Figure 5-8. Scatter plots comparing Eh with the saturation indices of siderite ($FeHCO_3$) and rhodochrosite ($MnHCO_3$). Saturation with respect to these minerals is reached at decreasing Eh. Manganese and iron may reprecipitate as carbonate minerals following reductive dissolution of oxide and oxyhydroxide minerals. This results in groundwater with low Mn and Fe concentrations.

No siderite or rhodochrosite were detected (although detection limits may be as high as 1%) in confined aquifer or confining unit sediments through XRD analysis, while dolomite (0.9 % to 1.1 %) and calcite (1.7 % to 2.5 %) were reported to occur in the sediments (see Chapter 4). Iron and manganese removal through reprecipitation as carbonate minerals would more likely occur as impurities in calcite and dolomite, than as pure iron or manganese carbonate phases.

Despite low iron and manganese concentrations in groundwater, it is likely that arsenic release in the studied environment occurs through the dissolution of manganese or iron oxide and oxyhydroxide minerals. Iron and manganese remain at low concentrations in groundwater as they may be removed from solution via adsorption to mineral surfaces or reprecipitation as carbonate minerals.

5.5.5 Sulphur redox and arsenic mobilization

Sediment selective extraction results indicate that a significant proportion of arsenic in the sediments is hosted in sulphide minerals (aqua regia extraction; step 6; Table 5-3). This is supported by XRD analyses (see Chapter 4) which reports that pyrite is present in the sediments. Arsenic release to groundwater is potentially tied to the redox of sulphur species, as arsenic may be mobilized via the oxidative dissolution of arsenic bearing sulphide minerals.

The sulphate content of the three different groundwater types recognized in the studied area is distinct. The mean and median sulphate concentration in Ca-Mg-HCO_3 type groundwater occurring unconfined aquifers are 0.16 mmol/l and 0.13 mmol/l, respectively (n = 15). Na-HCO_3 type groundwater occurring in confined aquifers has generally a lower sulphate content, with mean and median sulphate concentrations of 0.056 mmol/l and 0.034 mmol/l, respectively (n = 23). This indicates that there is a net sulphate loss in groundwater as it flows from unconfined aquifers to confined aquifers through the glaciomarine sediments. Na-Cl type groundwater occurring in confined aquifers has a much higher sulphate content than the two other water types, with mean and median sulphate concentrations of 0.82 mmol/l and 0.79 mmol/l, respectively (n = 8).

The sulphate content in groundwater occurring in unconfined aquifers may reflect input from sea salt and oxidized dimethylsulphide in rain water, oxidation of reduced sulphur in till, concentration through evapotranspiration, and biologic sulphur cycling in the soil horizon (Hendry et al., 1986; Mayer et al., 1995). The atmospheric isotopic composition of sulphate in Langley varies diurnally, with an average δ^{34}S over a 16 days period of +6.6 ‰ and an average δ^{18}O over the same period of +10.0 ‰ (Norman et al., 2006). Heavy isotope depleted δ^{34}S and δ^{18}O values in groundwater samples sourced from unconfined aquifers (the most depleted sample has δ^{34}S and δ^{18}O of -10.6 ‰ and -3.6 ‰, respectively) with respect to atmospheric values possibly reflects an oxidation of reduced sulphur control on dissolved sulphate. However, it is difficult to determine precisely the sources of sulphate in groundwater in the unconfined aquifers due to the number of different processes that may be contributing sulphate. All of the unconfined aquifer samples, except one, have δ^{34}S and δ^{18}O values lower than the average atmospheric input suggesting that biological sulphur cycling in the soil and oxidation of sulphides dominate during recharge.

The generally lower sulphate content of Na-HCO_3 type groundwater occurring in confined aquifers is a result of bacterial sulphate reduction. Groundwater in confined aquifers is under reducing conditions, as indicated by the presence of reduced species ferrous iron, ammonia, hydrogen sulphide gas and arsenite in solution. The presence of hydrogen sulphide gas in groundwater in confined aquifers is an indicator of microbially mediated sulphate reduction. Groundwater of Na-HCO_3 type is generally more enriched in ^{34}S of SO_4 than Ca-Mg-HCO_3 type groundwater. A sulphate reduction trend is observed for most samples of Na-HCO_3 water type, with samples becoming increasingly enriched at decreasing sulphate concentrations (Figure 5-9). A linear sulphate reduction trend would indicate that sulphate reduction occurs in a closed system (i.e. there are no other sources and sinks of sulphate), and that reaction follows a Rayleigh-type distillation (Strebel et al., 1990; Clark and Fritz, 1997). However, groundwater samples were collected from various aquifers across the study area; hence samples are not sourced from along a single groundwater flow path. For this reason, the initial sulphate composition prior to reduction may be different for each sample. This results in the non-linear sulphate reduction trend in Figure 5-9. During sulphate reduction there is an enrichment in ^{18}O of the residual sulphate that is initially 2.5 to 4 times lower than the ^{34}S enrichment through intermediate species, such as sulphate-enzyme complexes as well as sulphite, which exchange oxygen with water and re-oxidize to sulphate (Fritz et al., 1989). Hence, a positive relationship of $\delta^{34}S$ and $\delta^{18}O$ of SO_4 is also indicative of sulphate reduction.

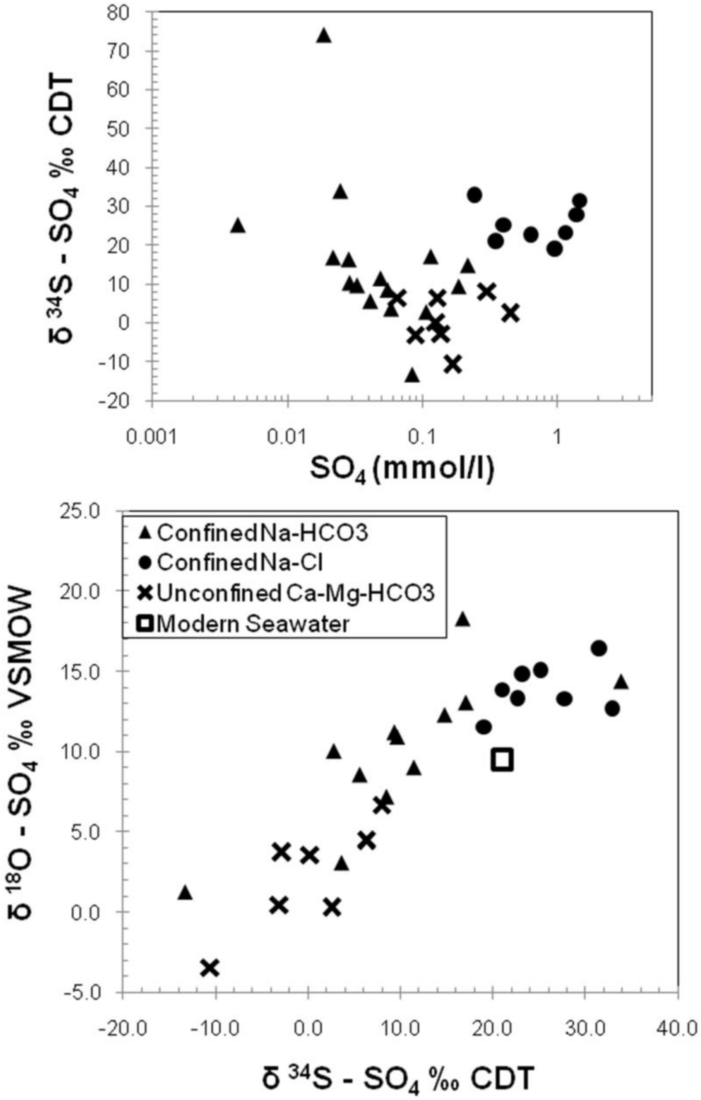

Figure 5-9. Scatter plots comparing sulphate concentrations with $\delta^{34}S$ of SO_4 and $\delta^{34}S$ with $\delta^{18}O$ of SO_4. The negative relationship of $\delta^{34}S$ of SO_4 and sulphate concentrations and positive relationship of $\delta^{34}S$ with $\delta^{18}O$ of SO_4 indicate sulphate reduction controls on Na-HCO_3 type groundwater. The sulphate content of Na-Cl is controlled by mixing with saline water. Samples of Na-Cl are more enriched in sulphate stable isotopes than modern seawater, which indicates that this groundwater type has also undergone sulphate reduction.

Several of the Na-Cl waters have ^{34}S contents that are enriched relative to seawater sulphate (Figure 5-9). A linear sulphate reduction trend is not apparent in the $\delta^{34}S$ of Na-Cl samples as the sulphate concentrations of Na-Cl type groundwater is also controlled by mixing with saline water. Mixing controls on sulphate concentrations are apparent through the strong positive correlation between chloride and sulphate in this groundwater type (Figure 5-10). Na-Cl type samples are generally enriched by about 5 ‰ to 6 ‰ in ^{18}O and by up to 11 ‰ in ^{34}S of SO_4 with respect to modern seawater ($\delta^{34}S$ of SO_4 = 21 ‰ and $\delta^{18}O$ of SO_4 = 9.5 ‰; Clark and Fritz, 1997). This, along with the presence of hydrogen sulphide in all but two samples, indicates that Na-Cl type groundwater has also undergone sulphate reduction. Variability in the both the $\delta^{34}S$ and $\delta^{18}O$ may occur as a result of mixing between seawater and different fresh water end-members and because at later stages of sulphate reduction ^{34}S is enriched at a constant $\delta^{18}O$ (Fritz et al., 1989). Some Na-HCO_3 and Ca-Mg-HCO_3 type waters appear to be on a similar mixing trend as Na-Cl type samples in Figure 5-10, as they approach a typical Na-Cl type composition. These samples plot in the $\delta^{34}S$ of SO_4 / SO_4 scatter plot in between the sulphate reduction trend and Na-Cl type samples (Figure 5-9). This indicates that their $\delta^{34}S$ of SO_4 are also possibly controlled by some degree of mixing.

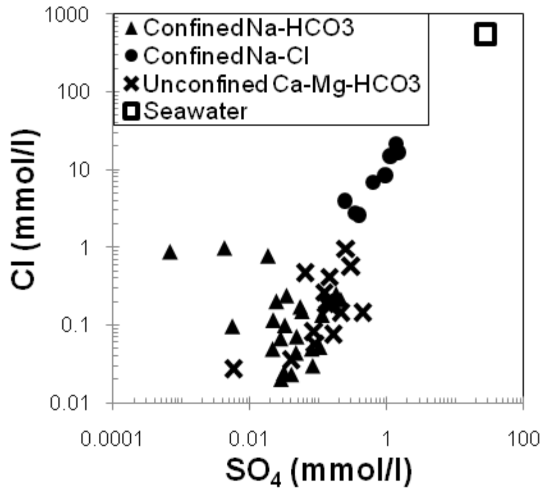

Figure 5-10. Scatter plot comparing chloride and sulphate concentration in groundwater. A strong positive correlation in Na-Cl type groundwater is evidence that high sulphate concentrations of this water type are a result of mixing with connate seawater type end-member. No relationship is observed with most Ca-Mg-HCO_3 and Na-HCO_3 type samples, which indicates that their sulphate content is not controlled by mixing. Some Ca-Mg-HCO_3 and Na-HCO_3 type samples appear to be on a trend approaching typical Na-Cl type composition. This may indicate some mixing control on sulphate concentration, which may result in these samples plotting closer to modern seawater composition in Figure 5-9.

Sulphur redox reactions in the confined aquifers are dominated by sulphate reduction. In this environment it is highly unlikely that arsenic is being released to solution via sulphide oxidation. Groundwater in unconfined aquifers is relatively depleted in ^{34}S and ^{18}O of SO_4, which may be an indicator of sulphide oxidation (Figure 5-9). However, this groundwater has low arsenic concentrations, which indicates that if sulphide oxidation is taking place in unconfined aquifers it is not adding significant amounts of arsenic to groundwater. Arsenic release to solution only occurs as groundwater flows through glaciomarine sediments exposed to reducing conditions. Arsenic release via sulphide oxidation may take place early, as relatively oxidized groundwater in unconfined aquifers encounters glaciomarine sediments exposed to reducing conditions. At this point, sulphide mineral oxidation could occur resulting in arsenic release to solution. As groundwater flows deeper into the glaciomarine sediments it becomes increasingly reducing. This would trigger sulphate reduction and cause dissolved sulphate to become enriched in ^{34}S and ^{18}O, while halting sulphide oxidation. If this hypothesis stands, groundwater in confined aquifers would be enriched in ^{34}S and ^{18}O while having elevated arsenic concentrations, as observed.

Hydrogen sulphide gas produced through sulphate reduction is known to promote arsenic removal from water in reducing environments through the precipitation of arsenic bearing sulphides (Carbonell-Barrachina et al., 2000). A lack of relationship between arsenic concentrations in groundwater and δ^{34}S of SO_4, and a general positive relationship of arsenic and hydrogen sulphide gas (Figure 5-7) indicate that if sulphide mineral precipitation is occurring in sulphate reducing groundwater it is not effectively precipitating arsenic from solution. Zhu et al. (2008) observed that since arsenic and sulphur can substitute for each other in the pyrite structure (Savage et al., 2000) and form arsenopyrite-like solids (Blanchard et al., 2007), hydrogen sulphide gas might promote arsenic mobilization in the presence of an oxidant through sulphide-arsenide exchange. Although samples with elevated hydrogen sulphide gas tend to have elevated arsenic (Figure 5-7), there are samples that are relatively oxidizing (Eh above 300 mV) for sulphate reduction and have no detected hydrogen sulphide gas that also have elevated arsenic concentrations. This indicates that if sulphide-arsenide exchange is occurring, it is not a major process resulting in arsenic mobility.

5.6 Conclusions

Unconfined aquifers formed by glaciofluvial sediments have arsenic below drinking water guidelines (10 μg/l); whereas most samples collected from confined aquifers occurring within glaciomarine sediments have arsenic above 10 μg/l. A positive relationship between arsenic concentration and Na/(Ca+Mg) ratio in groundwater indicates that arsenic release to solution occurs in a freshening environment in the glaciomarine sediments which host the confined aquifers. Mixing with connate saline water does not appear to enhance or prevent arsenic mobility. The Na-Cl groundwater type has similar arsenic concentrations as Na-HCO_3 type groundwater, while there is no relationship between arsenic and chloride concentration. Positive relationships of pH with arsenic and other anion and oxyanion forming constituents, such as molybdenum, phosphate, fluorite and boron, indicates that the mobility of these constituents in confined aquifers is favoured by basic pH. Reducing conditions of confined aquifers also favours arsenic mobility through speciation to arsenite (a more mobile arsenic form), as evidenced by a negative relationship of Eh with percent arsenite of total arsenic.

Selective extractions of sediment core suggest that significant portions arsenic in sediments occurs in two distinct mineral pools: sulphide minerals, and manganese oxides or iron oxyhydroxides. Hence, there are two possible mechanisms for arsenic release to solution: oxidative dissolution of sulphides, or reductive dissolution of oxides and oxyhydroxides. At increasing reducing conditions observed in confined aquifers, the dissolution of oxides and oxyhydroxides should be favoured. Positive relationships of arsenic with the reduced species Fe^{2+}, NH_3 and S^{2-} indicate that arsenic may be mobilized through dissolution of oxides and oxyhydroxides. Iron concentrations in groundwater remain at relatively low levels, despite possible iron oxide dissolution. This may be a result of Fe^{2+} adsorption being favoured at basic pH or iron reprecipitation as minerals. Groundwater achieves saturation with respect to siderite at low Eh, which suggests that iron may precipitate from solution as carbonate minerals. The presence of hydrogen sulphide gas in some samples, a negative relationship of $\delta^{34}S$ of SO_4 with sulphate concentration, and a positive relationship of $\delta^{34}S$ with $\delta^{18}O$ of SO_4 indicate that groundwater in confined aquifers is undergoing bacterial sulphate reduction. In this setting, sulphide mineral oxidation may only contribute to arsenic release early in the system. This would happen as relatively oxidized groundwater sourced from unconfined aquifer encounters reduced glaciomarine sediments, resulting in oxidation of sulphides. As groundwater flows through the glaciomarine sediments, it becomes increasingly reduced, triggering sulphate reduction. This results in groundwater with a sulphate reducing isotopic signature and elevated arsenic concentrations. The presence of hydrogen sulphide gas does not appear to remove arsenic from solution through the precipitation of arsenic bearing sulphides, as samples with high hydrogen sulphide gas content also have elevated arsenic concentrations. At the same time, arsenic release via sulphide-arsenide exchange (suggested by

Zhu et al., 2008) does not seem to be an important mechanism as elevated arsenic is found in groundwater with no detectable hydrogen sulphide gas.

6: A METHODOLOGY FOR SPATIALLY REPRESENTING THE LIKELINESS OF OCCURRENCE OF NATURAL CONTAMINANTS IN GROUNDWATER

6.1 Introduction

Some natural constituents found in groundwater are harmful to human health when they are present at elevated concentrations. The distribution of these constituents in groundwater is often controlled by a number of different factors: their sources in rocks and sediments; from biogeochemical reactions, and; by mass distribution in flowing groundwater (Appelo and Postma, 2006). Appropriate representation of the spatial distribution of these hazardous groundwater constituents is essential for water resources management.

Maps are a valuable tool for displaying water quality information in an accessible format that allows the visualization of spatial patterns and determination of areas of concern. The production of groundwater quality maps typically requires extensive geochemical surveys, which should be conducted following up-to-date sampling protocols and analytical methods. Unfortunately, groundwater chemistry data available for many regions are insufficient for the production of detailed maps (Vasak et al., 2006). Some of the challenges associated with using groundwater datasets include an insufficient number of samples collected, poor spatial distribution of sample locations, constituents with an elevated method detection limit, and uncertainty in the quality of the data. In addition, some regions have complex hydrogeology, with several aquifers of differing physical and chemical properties occurring within a relatively small area. For these reasons, maps showing only raw concentration data may not appropriately represent occurrences of a hazardous constituent in groundwater over the entire region.

A few methods for spatially representing occurrences of hazardous groundwater constituents have been developed with the objective of tackling challenges associated with limited groundwater quality datasets. The International Groundwater Resources Assessment Centre (IGRAC) has produced maps at global and continental scales, highlighting regions with high probability of occurrence of hazardous substances at excessive concentration in groundwater (Vasak et al., 2006). The IGRAC has produced maps at a global scale with countries colour-coded based on the number of occurrences of constituents, such as arsenic, fluoride and nitrate at excessive concentrations in groundwater (Vasak et al., 2006). In another approach, the IGRAC used hydrogeological, geological, geochemical and climate information as indicators of probability of occurrence of arsenic and fluoride in groundwater and showed this information in maps at a continental scale (Brunt et al., 2004a; Brunt et al., 2004b). This allowed the production of more detailed maps where the demarcation of affected areas was refined. Payne and Woessner (2010) developed a method of classifying aquifers based on the following components: geological framework, aquifer productivity, groundwater quality, groundwater/surface exchange, and depth to groundwater. In this method, the classified aquifers are represented at a watershed scale. The groundwater quality component is defined based on the specific conductance of groundwater (an indicator of salinity), and whether the groundwater is suitable for domestic supply, irrigation uses, commercial and industrial uses, and wildlife and livestock uses. Hence, the approach of Payne and Woessner (2010) assesses the overall groundwater quality rather than occurrences of a specific hazardous constituent of concern. Stuyfzand (1999) developed a method of mapping and diagnosing major factors accounting for regional variations in hydrogeochemistry by addressing the spatial distribution of hydrosomes (defined as a coherent, three-dimensional unit of groundwater with a specific origin) and hydrogeochemical facies (as defined by Back, 1961; see below) within each hydrosome. Stuyfzand (1999) classified hydrosomes by assessing the evolution of different hydrogeochemical parameters (pH, Eh, as well as concentrations of major and redox sensitive constituents in groundwater) along specific groundwater flow directions. This method was used to produce maps highlighting the different hydrosomes and hydrosomes complexes (set of various adjancent hydrosomes with similar origin and recharge area) in The Netherlands (Mendizabal et al., 2011). One aspect that is missing in the methods of mapping groundwater quality described above is the representation of uncertainty in the maps produced. As mentioned, limited groundwater chemistry datasets result in uncertainties on understanding of occurrences and spatial distribution of constituents in groundwater. Although the authors of the methods described above recognize that uncertainty in the data is an issue, they did not attempt to incorporate spatial representation of uncertainty in their methods. As uncertainty plays a role in decision-making, it would be beneficial to government authorities and interest parties if uncertainty in interpretation and data available was captured in groundwater quality map.

Other groundwater quality classification approaches have been proposed. For example, in a benchmark paper, Back (1961) determined hydrogeochemical facies based on the relative concentration of major cations and anions in groundwater. This approach is commonly used in groundwater investigations (e.g. Chapelle and Knobel, 1983; Appelo, 1994; Jones et al., 1999; Stuyfzand, 1999; Lambrakis, 2006). Groundwater quality has also been classified based on other chemical parameters, like concentrations of different redox sensitive constituents (Stumm, 1984), alkalinity (Mendizabal et al., 2011) and age (as young groundwater is sensitive to recent anthropogenic pollutants; Mendizabal and Stuyfzand, 2009). These studies provided important advances to the classification of groundwater quality as the fate of harmful metals and metalloids in groundwater is strongly controlled by factors as pH, Eh and alkalinity, while the concentrations of major concentrations are good indicators for the hydrogeochemical evolution of groundwater (Appelo and Postma, 2006). However, these criteria do not fully assess groundwater quality as it pertains to human or ecosystem health as several minor and trace metals and metalloids are known to be deleterious when occurring at relatively low concentrations in groundwater (e.g. above a few micrograms per litre (ug/l)). One method that classifies water quality based on the concentrations of harmful constituents in Canada is the Water Quality Index (CCME WQI) developed by the the Canadian

Council of Ministers of the Environment. A CCME WQI is assigned to each sampling location and is calculated based on the number of constituents that occur above given objectives (e.g. drinking water guidelines) in that location, the frequency at which constituents are above these objectives over time, and the amount by which constituents are above the objectives (Canadian Council of Ministers of the Environment, 2001)**.** The CCME WQI was applied to evaluate groundwater quality in the study area considered here; Langley Township, BC (Norman et al., submitted). As the CCME WQI requires a very extensive water chemistry dataset (for example, there is a requirement of at least four samples collected per year at any given sampling location), limitations in datasets are a major barrier to a detailed representation of the spatial distribution of the CCME WQI of groundwater (as noted by Norman et al., submitted).

The objective of this study is to introduce and test a method of classifying aquifers and spatially representing the likelihood of occurrence of a specific hazardous constituent in groundwater at the scale of a municipality or watershed. Two components are used to classify the aquifers: 1) interpretations provided through hydrogeochemical studies and 2) raw groundwater chemistry data. Geochemical interpretations are incorporated to account for aquifers with insufficient groundwater chemistry samples. Aquifers and data points are classified based on data quality and confidence of interpretation (or uncertainty), as groundwater information available for each aquifer within a given study area may vary. The approach consists of a series of steps for generating maps that highlight different groundwater chemical environments in the study area, geochemical interpretation for likelihood of occurrence of a hazardous constituent, confidence of interpretation, and raw concentration data. These maps are then superimposed to produce a map showing the likelihood of occurrence of a hazardous constituent of interest for each aquifer of a study area. In this paper, this method is applied to represent likelihood of arsenic occurrence in groundwater in confined and unconfined aquifers in Langley and Surrey, British Columbia. In the study area, arsenic occurs naturally at elevated concentrations in groundwater as a result of water-rock interactions within aquifers and confining units, and groundwater chemical conditions that favour arsenic mobility in solution (see Chapter 5). Interpretations provided from geochemical studies and raw arsenic concentration data are used to classify each aquifer based on the likelihood of arsenic occurrence in groundwater. The final map produced may assist water managers in identifying areas of greater concern regarding arsenic occurrences in groundwater.

6.2 Case study: Arsenic in groundwater in Langley and Surrey, British Columbia

The Township of Langley (ToL) and the City of Surrey are located in the Lower Fraser Valley of British Columbia (Figure 6-1). The population is over 100,000, of which approximately 18,000 residents rely on groundwater from private wells and community wells as source of water (Township of Langley, 2007). The hydrogeology of the region consists of a complex network of confined and unconfined aquifers occurring in marine, glaciomarine, glaciofluvial and post-glacial Quaternary sediments that are several hundreds of metres thick and that overlie Tertiary bedrock (Halstead, 1986). A total of 45 permeable units forming 18 major confined and unconfined aquifers have been identified in this area (Golder Associates Ltd., 2005). These aquifers differ from each other in a variety of physical and chemical characteristics, as they are formed by different sediment types, have variable natural water quality, and have different levels of vulnerability to contaminants that may be introduced at the land surface (Halstead, 1986). Golder Associates Ltd. (2005) produced a detailed three-dimensional model of the various aquifers for the ToL. The aquifers were classified as unconfined, confined and deep confined (Figure 6-2; aquifers shown in 2-D plan view). Aquifers polygons in the City of Surrey were produced as part of a study by Kreye and Wei (1994), which mapped and classified many aquifers throughout British Columbia. As the study by Kreye and Wei (1994) was at a provincial scale, the geographical limits of the aquifers in Surrey are defined with less detail than those in the ToL (Figure 6-2).

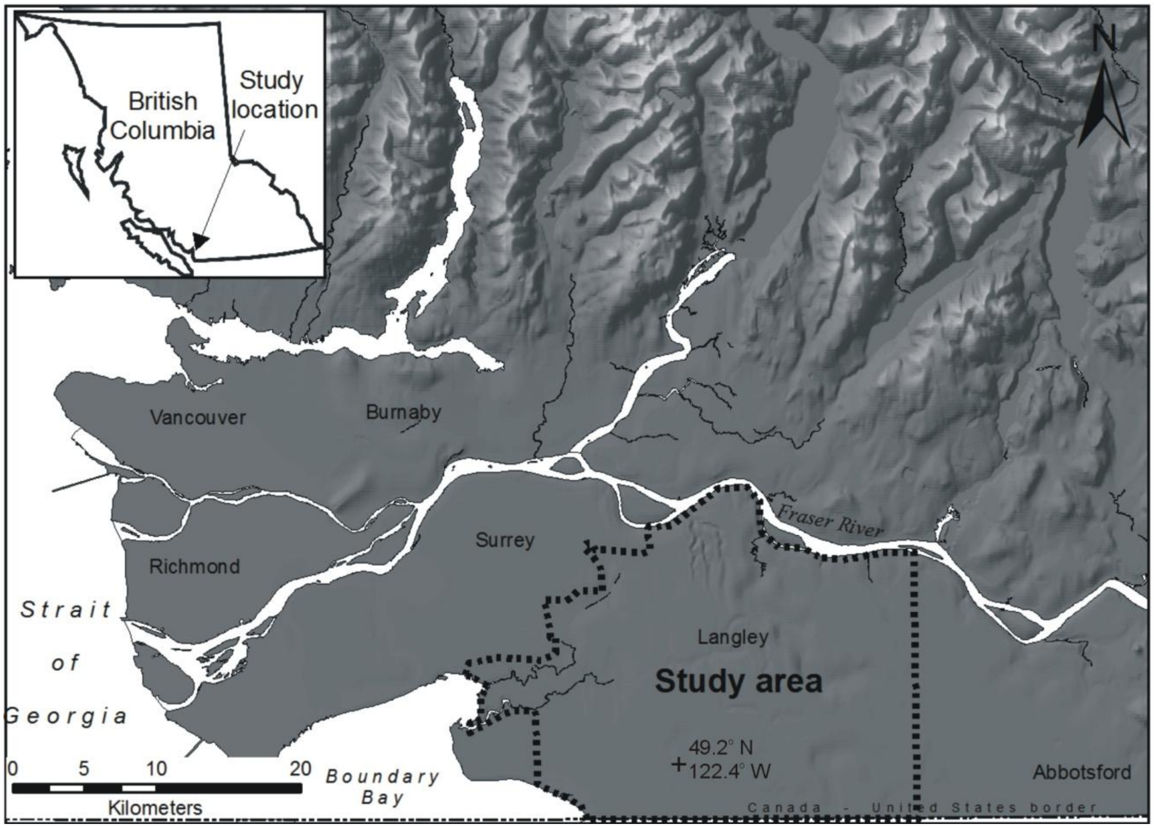

Figure 6-1. Study area is located in the Township of Langley and the eastern portion of the City of Surrey, British Columbia, Canada.

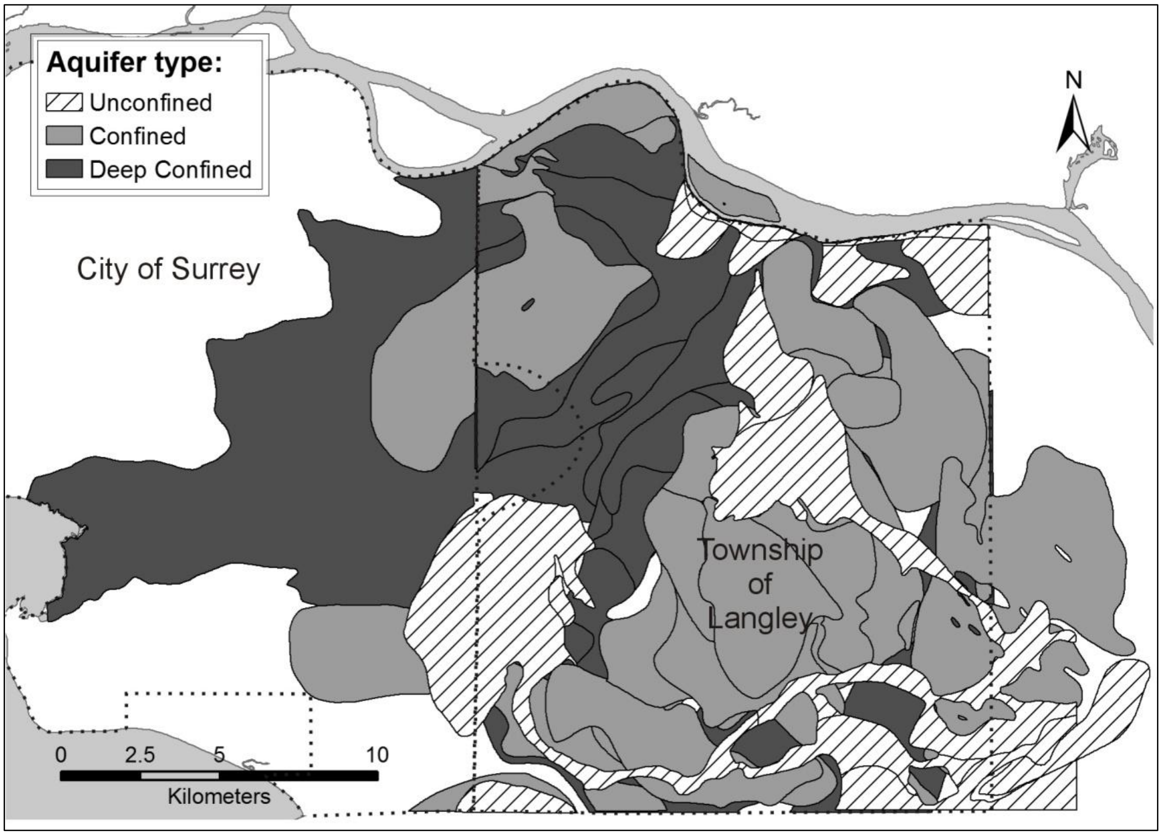

Figure 6-2. **A plan view aquifer polygon map of the study area assembled using data from Kreye and Wei (1994) and Golder Associates Ltd. (2005). The groundwater system consists of unconfined aquifers formed in glaciofluvial sediments and a series of overlying confined sand aquifers formed in pockets within low permeability glaciomarine deposits. Golder Associates Ltd. (2005) further subdivided confined aquifers as deep confined and confined (or shallow confined) aquifers.**

6.2.1 Hydrogeochemistry and arsenic occurrence in groundwater in Langley and Surrey

The hydrogeochemistry of groundwater in Langley and Surrey is discussed in detail in Chapter 4. Two distinct groundwater chemical environments are found in Langley and Surrey. One environment is characterized by groundwater occurring in unconfined aquifers formed by glacial and glaciofluvial sediments, while a second environment is characterized by groundwater in confined aquifers formed within glaciofluvial sediments. Groundwater in unconfined aquifers is Ca-Mg-HCO_3 type, has a mostly neutral pH, oxidizing conditions, and low salinity. Groundwater in confined aquifers is either Na-HCO_3 or Na-Cl type, has basic pH, reducing conditions, and relatively high salinity. Groundwater chemistry in unconfined aquifers is controlled by rain water composition, anthropogenic inputs at the surface (e.g., nitrate), and processes related to recharge in glacial deposits. In confined aquifers, groundwater chemistry is controlled by extensive water-rock interactions, such as cation exchange reactions, carbonate mineral dissolution and silicate mineral weathering.

A major water quality issue in Langley and Surrey is natural arsenic contamination to groundwater. Wilson et al. (2008) sampled 98 randomly selected wells in this area and found that 43 had arsenic concentrations above the Canadian Drinking Water Guideline (10 µg/l). Exposure to arsenic in drinking water is a known cause of a number of diseases, including skin cancer, lung cancer and hypertension (Hopenhayn, 2006). Natural occurrences of elevated arsenic concentrations in groundwater are commonly the result of concentrations of arsenic species in sediments and rocks, and microbial and chemical factors influencing arsenic mobilization (Smedley and Kinniburgh, 2002). Arsenic may occur naturally in several different mineral phases; however, the highest concentrations are usually found in oxides, oxyhydroxydes and sulphides (Smedley and Kinniburgh, 2002). Arsenic release to solution may occur through desorption from mineral surfaces (Pierce and Moore, 1982; Bowell, 1994), reductive dissolution of oxide and oxyhydroxide minerals (Stüben et al., 2003; Buschmann et al., 2007), and oxidative dissolution of sulphide minerals (Nesbitt et al., 1995; Craw et al., 2003; Yunmei et al., 2004). Arsenic mobility in solution is typically controlled by sorption and is greatest at basic pH or reducing conditions (Pierce and Moore, 1982; Cullen and Reimer, 1989; Bowell, 1994; Smedley and Kinniburgh, 2002). Processes and conditions causing arsenic to occur naturally at elevated concentration in groundwater in Langley and Surrey are addressed in Chapter 5. Arsenic concentrations in most samples sourced from confined aquifers are above 10 µg/l, while concentrations in all samples collected from unconfined aquifers were below 10 µg/l. The occurrence of elevated arsenic in groundwater with a relatively high sodium concentration (indicative of groundwater flowing through glaciomarine sediments) indicates that most arsenic addition to solution takes place in glaciomarine sediments that form confining units. Arsenic is mobile in groundwater in confined aquifers as a result of its basic pH and reducing conditions. Conversely, near neutral pH and oxidizing conditions of groundwater in unconfined aquifers does not favour arsenic mobility. Possible arsenic release processes are reductive dissolution of iron oxyhydroxides or manganese oxides, and oxidative dissolution of sulphide minerals.

6.3 Methodology

In the method presented, a map is produced where aquifer polygons are classified and colour-coded based on the likelihood of occurrence of a hazardous constituent of interest at elevated concentrations in groundwater. In this particular case study, the contaminant of interest is arsenic, and groundwater is considered to have elevated arsenic if the concentration is above the Canadian Drinking Water Guideline for arsenic (10 µg/l). Aquifers are classified using two sources of information: 1) Raw concentration data for the constituent of interest, and 2) interpretations provided through the geochemical study, which considered the mechanisms that likely result in the occurrence of this contaminant at elevated concentrations in groundwater.

The method involves four steps. In step 1, a map delineating different groundwater chemical environments in the study area is produced. Step 2 consists of classifying each groundwater environment defined in the first step as having a high or low likelihood of occurrence of the constituent of interest at elevated concentrations. At this step, aquifer classification is done based solely on interpretations provided with the geochemical study. In step 3, the confidence of the interpretation for the different aquifers in the study area is evaluated based on data and information available for each aquifer. Finally, in step 4, the various maps produced in steps 1-3 are superimposed with the raw concentration data. The final map displays a spatial representation of the likelihood of occurrence of the contaminant of interest at elevated concentration in groundwater and the confidence of the interpretation for each aquifer. Sample locations are colour-coded based on the concentration of the constituent of interest.

Aquifer polygons produced by Kreye and Wei (1994) and Golder Associates Ltd. (2005) are used in the production of maps for Langley and Surrey. There are four different groundwater chemistry datasets available for this particular study area, all of which include arsenic concentration as one of the measured parameters. One dataset consists of water quality data collected during the study presented in Chapter 5, which focused on arsenic occurrences in groundwater in the study area. This dataset has 46 water well sampling locations, sourcing both confined and unconfined aquifers. It is the most complete of the four available datasets in terms of chemical parameters measured, as it contains major and minor elements, and some trace elements, as well as field measured parameters including pH, Eh, conductivity, temperature, dissolved oxygen, and redox sensitive species (arsenite, ferrous iron, ammonia and hydrogen sulphide gas). It is also the dataset with the best data quality, as it used the most up to date sampling and analytical methods. A second dataset consists of water quality data collected during a study by Wilson et al. (2008). It includes data from 98 sampling wells, sourcing both confined and unconfined aquifers. A total 51 parameters, including major and minor elements, are included in this dataset; however, it lacks field measured parameters as samples were submitted for analysis by well owners (conductivity and pH were measured in the laboratory). A third dataset is the Environmental Monitoring System (EMS) dataset maintained by the British Columbia Ministry of Environment (MoE). It contains samples collected periodically as part of the groundwater sampling program conducted by the MoE, as well as other unknown sources. A total of 35 sampling locations from the study area are included in the EMS dataset. These are mostly sourced from unconfined aquifers, with few samples sourced from confined aquifers. Data completeness is quite variable in the EMS dataset, as some samples contain more than 40 measured inorganic parameters, while some samples have only 10 parameters. The fourth database is the ToL's Private Well Network (PWN). It contains 1045 samples in the ToL only, with some samples sourced from the same well. Each sample has up to 37 parameters analysed; however, data completeness is very variable in this dataset. Sampling and analytical methods used with the PWN dataset are unknown. It is likely that most samples in the PWN were collected by well owners and submitted to a laboratory for analysis; however, no information is given on the sampling method to verify its appropriateness. For this reason, the PWN is considered to be the dataset with the poorest data quality among the four datasets available for the study.

Details on each of the four steps of the mapping method are discussed in detail in the sections below. The specific criteria used in the production of maps for the case study of arsenic in groundwater in Langley and Surrey are also discussed below.

6.3.1 Step 1: Represent different groundwater environments

Some study areas may have a variety of different aquifers and a restricted number of sampling locations. Trying to evaluate likelihood of occurrence of a constituent in groundwater within each individual aquifer may be a too complex task. One source of difficulty is the lack of a representative number of samples with good quality data for each aquifer. The mechanisms resulting in the occurrence of a contaminant may be well understood for one aquifer, from which several groundwater samples were collected, but these mechanisms may be unknown for aquifers where few or no samples were taken. This could result in a very low confidence in the assignment of likelihood of occurrence of a constituent in aquifers with few samples. On the other hand, mechanisms resulting in the occurrence of a constituent may be the same in nearby aquifers with similar physical and chemical characteristics. In this case, it may not be necessary to have a large number of samples collected from a particular aquifer in order to estimate the likelihood of occurrence of a constituent, if there are enough samples collected from nearby aquifers with similar chemical and physical properties.

In step 1, different aquifers are grouped into unique “groundwater zones”. This is done in order to simplify the task of assigning likelihood of occurrence of a constituent in step 2. Grouping of aquifers into zones is done based on physical and chemical properties that are common among a given set of aquifers. Physical and chemical properties used as criteria for grouping aquifers should be relevant to the occurrence of the contaminant in groundwater, according to what is described in the geochemical study. For example, consider a hypothetical study area where some aquifers are formed by sediment type A, while other aquifers are formed by sediment type B. If a geochemical study demonstrates that the aquifer-forming sediment is a major control on the occurrence of the contaminant of interest in groundwater, then aquifers formed by sediment type A should be grouped in a separate zone than aquifers formed by sediment type B. However, if there is no indication that aquifer-forming sediments are a control on the occurrence of the contaminant, sediment type should not be used as a criterion when grouping aquifers into zones. Some examples of physical and chemical properties of aquifers that may be used as criteria for grouping aquifers are listed below:

- Unconfined aquifers versus confined aquifers
- Sediment or rock types forming aquifers and confining units
- Geographical location of aquifers
- Depth from surface to aquifers
- Vulnerability to contaminants introduced at surface
- Groundwater chemistry (this may include a number of different criteria, such as redox potential, pH, salinity, concentration of specific constituents, etc.)

Based on results presented in Chapter 4 regarding groundwater environments in Langley and Surrey (see Section 6.2.1), two groundwater zones are identified in the case study. One groundwater zone (Zone 1) is comprised of all unconfined aquifers, while a second zone (Zone 2) consists of all confined aquifers. The physical and chemical characteristics of each of these two groundwater zones are summarized in Table 6-1; they are also displayed on a colour-coded map (Figure 6-3). In the model by Golder Associates Ltd. (2005) confined aquifers are further subdivided into deep confined aquifers and confined (or shallow confined) aquifers based on their depth from surface (Figure 6-2). This division is not described in the geochemical study as being relevant to the occurrence of arsenic in groundwater, as chemical and other physical properties of deep and shallow confined aquifers are similar. For this reason, the classification used by Golder Associates Ltd. (2005) for confined aquifers is not used in this case study.

Table 6-4. Physical and chemical properties of the two defined groundwater zones in Langley and Surrey.

Groundwater zone	**Zone 1**	**Zone 2**
Aquifer type	Unconfined aquifers	Confined aquifers
Sediment type	Glacial and glaciofluvial sediments	Till and estuarine deposits; formed within glaciomarine sediments
Groundwater chemistry	Near neutral pH, oxidized, low salinity	Basic pH, reduced, high salinity

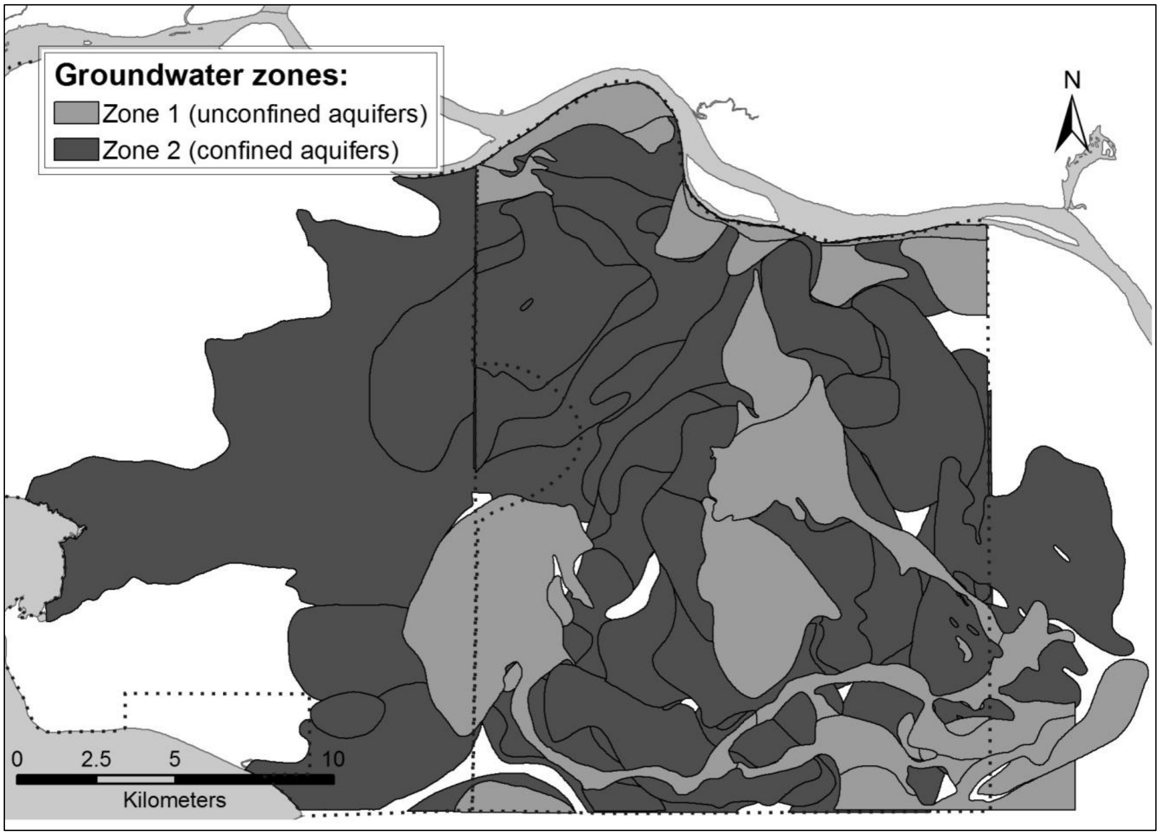

Figure 6-3. Map showing aquifers classified based on their groundwater zone. Zone 1 is comprised of all unconfined aquifers, whereas Zone 2 is comprised of all confined aquifers. These two zones were determined based on the two distinct groundwater environments described in Chapter 5.

6.3.2 Step 2: Represent interpretation spatially

Step 2 consists of assigning each groundwater zone defined in step 1 as either ‘likely’ or ‘unlikely’ in having the constituent of interest occurring in groundwater. This assignment is done based solely on interpretations provided by the geochemical study. Raw concentration data are not used in this step. The assignment of a constituent as ‘likely’ or ‘unlikely’ occurring is applied to the entire area of each groundwater zone, and not to portions of zones. If it appears that the constituent of interest is likely occurring in part of a zone, but unlikely occurring in another part of the same zone, then step 1 should be revisited. In this case, the groundwater zone in question should be divided into two or more zones.

As described in Section 6.2.1, it was determined that there is no tendency for arsenic to occur at elevated concentrations in groundwater in unconfined aquifers (see Chapter 5). It was also determined that there is a tendency for arsenic to occur at elevated concentrations in groundwater in confined aquifers as a result of processes described above. Hence, Zone 1 (all unconfined aquifers) is assigned as having arsenic unlikely occurring in groundwater, while Zone 2 (all confined aquifers) is assigned as having arsenic likely occurring in groundwater (Figure 6-4)**.** A small proportion (7 out of 31 samples) of groundwater samples collected through this research sourced from confined aquifers had arsenic below the drinking guideline. In Chapter 5, it is suggested that these low arsenic samples in the confined aquifers occur as a result of specific characteristics of the locality where the samples was taken; as being overlain by a thinner confining unit than the low permeability sediments confining most confined aquifers. These local characteristics were not interpreted to exist across an entire aquifer or region of the study area. For this reason, it is not necessary to redefine Zone 2 (confined aquifers) based on the few samples with low arsenic levels.

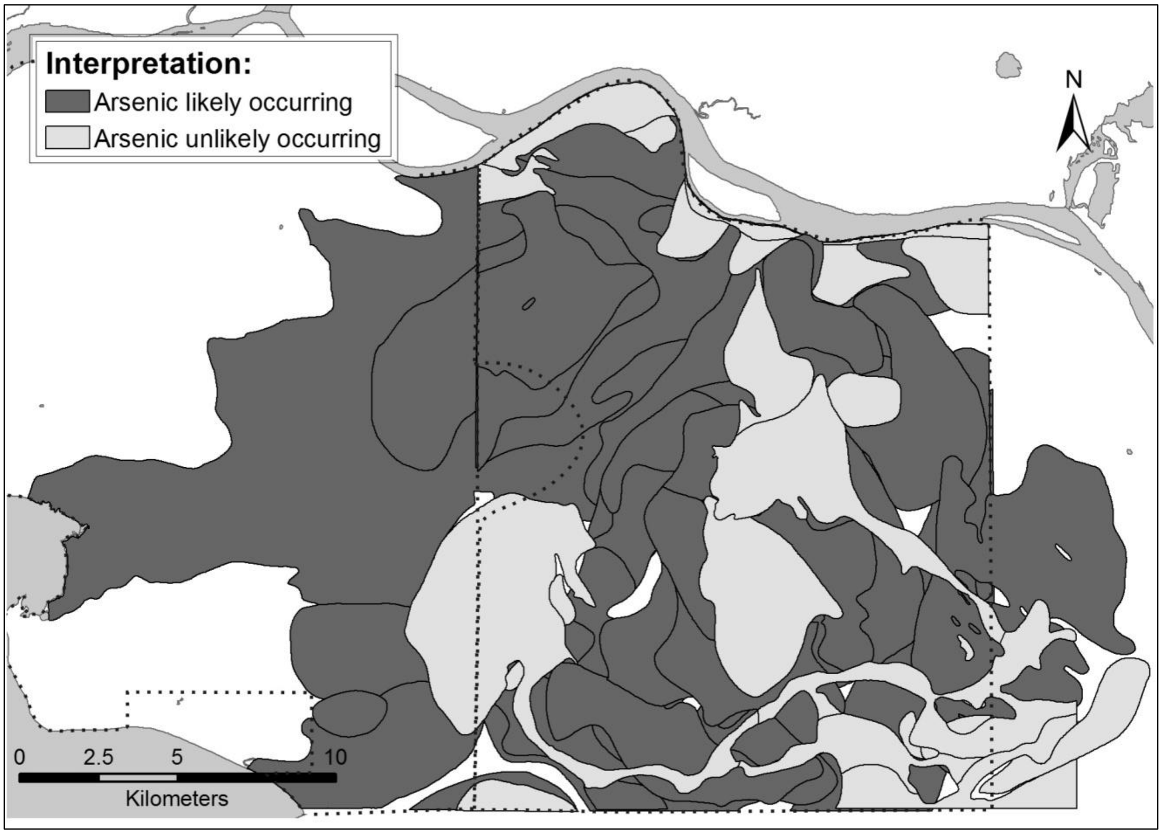

Figure 6-4. Based on interpretations provided through the geochemical study (Chapter 5), Zone 1 (unconfined aquifers) is assigned as having arsenic unlikely occurring in groundwater, while zone 2 (confined aquifers) is assigned as having arsenic likely occurring in groundwater.

6.3.3 Step 3: Represent confidence of interpretation spatially

In step 3, different levels of confidence in the geochemical interpretation are represented on a map. This representation is done based on availability of groundwater chemistry data within each aquifer. This step is taken in order to represent uncertainty in the geochemical interpretation as it pertains to likelihood of contamination. Three levels of confidence are used: high, medium and low confidence. High confidence is assigned as points on a map, while medium and low levels of confidence are assigned to aquifer polygons. High confidence points are assigned at every sampling location where the data collected are of a satisfactory quality. Medium confidence is assigned to aquifer polygons where there is sufficient groundwater chemistry data available, and the hydrogeological and geochemical controls on groundwater quality are well understood. Low confidence is assigned to areas with insufficient or no groundwater chemistry data available, or where the hydrogeology and hydrogeochemistry are poorly understood. The assignment of areas with medium or low confidence is independent of the groundwater zones assigned in step 1. Hence, it is possible for parts of a groundwater zone to be assigned a low level of confidence of interpretation, and other parts of the same zone assigned a medium level of confidence. Note that assigning confidence is at the discretion of the mapper, in that some determination of what constitutes sufficient data available or well understood hydrogeology and hydrogeochemistry is needed.

As mentioned, there are four groundwater chemistry datasets available for this study. Of these, the methods used for collecting and analysing samples are known for the datasets collected through this research and by Wilson et al. (2008), and for the majority of the data in the EMS dataset. The methods applied to collect the data for the PWN dataset are unknown as discussed above. Thus, data points sourced for the first three datasets are assigned high confidence data points, while data points from the PWN dataset are assigned low confidence and are not included as points in the confidence map.

In order to determine which aquifer polygons should be assigned medium or low confidence, it is necessary to consider the criteria that were used to design the groundwater sampling program. When conducting a groundwater geochemistry study, it is important to know the source aquifer for each sample. This is done to attribute differences in the water chemistry to specific aquifers. As described above, some portions of the study area have up to four recognized aquifers stacked on top of each other. This presents a challenge when conducting a groundwater geochemistry study, as in these regions it may not be possible to determine the source aquifer. In other regions of the study area there are fewer aquifers and, as such, it is easier to determine the source aquifer. Only those wells with a known source aquifer were selected for sampling in the geochemical study (Chapter 5). For this reason, more samples were collected from major aquifers that spatially dominate the study area than from smaller, less well defined aquifers. Consequently, there is higher confidence of interpretation of causes of arsenic occurrences in some the major aquifers than in most small aquifers.

A major confined aquifer in the west of the study area, a group of confined aquifers in the south, and two major unconfined aquifers in the center of the study area are assigned medium confidence of interpretation for the reasons described above. The remaining aquifers are assigned low confidence of interpretation (Figure 6-5). It is noted that most high confidence points (i.e., the sampling locations from the three reliable datasets) lie within the areas of the aquifer polygons identified as medium confidence of interpretation aquifers, whereas few high confidence points are located within the low confidence aquifer polygons.

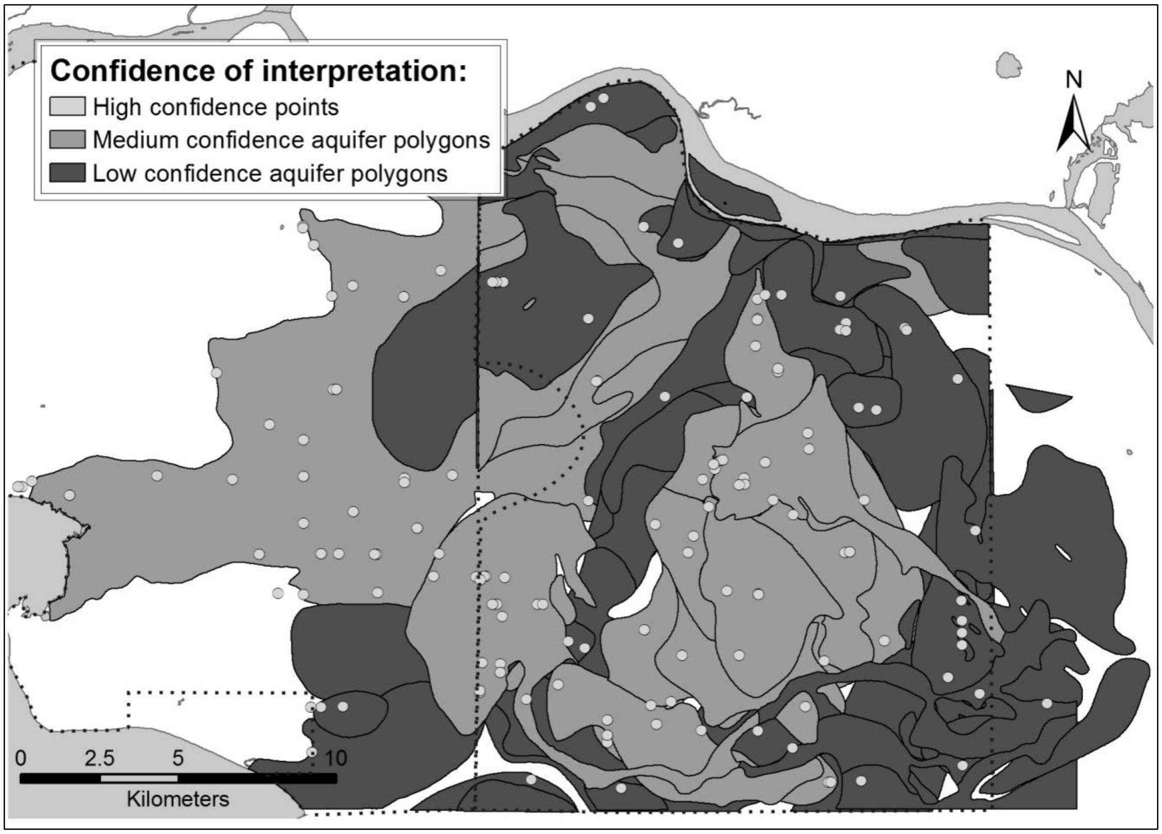

Figure 6-5. Confidence of interpretation map. Sample locations sourced from data collected through this research, by Wilson et al. (2008) and, the EMS dataset are identified as high confidence points. Aquifers with many samples deriving from these datasets are classified medium confidence of interpretation, while aquifers with few samples are classified low confidence of interpretation.

6.3.4 Step 4: Represent likelihood of mobilization spatially

In step 4, the raw concentration data of the constituent of interest are superimposed over the interpretation map produced in step 2 and the confidence of interpretation map produced in step 3. The result of this superimposition (the final product) is a map showing aquifer polygons that are colour-coded based on likelihood of occurrence of the constituent of interest, with a hatch pattern coded based on the confidence of interpretation. Colour, shape or size coded data points may be displayed on the map based on the concentration of the constituent of interest.

Likelihood of occurrence of a constituent is determined based on the superimposed raw concentration data with the interpretation map. Three levels of likelihood of occurrence are assigned to aquifer polygons on the map: high, medium and low. High level of likelihood is assigned to aquifer polygons displayed on the interpretation map (step 2) as having the constituent of interest likely occurring, and that have the vast majority of its data points at concentrations above the guideline. Medium level of likelihood is assigned to aquifer polygons displayed in the interpretation map as having the constituent of interest likely occurring, and that have a significant number of data points at concentrations below the guideline. Low level of likelihood is assigned to aquifers that are both interpreted to not have the constituent likely occurring, and that also have most of the data points at concentrations below the guideline. One possibility not considered in the categorization above is for aquifers interpreted as to have the constituent unlikely occurring (in step 2) that have a significant number of data points with concentrations above the guideline. In this case, step 2 (representation of interpretation spatially) should be revisited, as the aquifer in question may need to be assigned as being likely contaminated.

6.3.5 Likelihood of Arsenic Occurrence Map: Langley and Surrey

The likelihood of arsenic occurrence map for Langley and Surrey consists of the superimposed interpretation map, the confidence of interpretation map, and the data points from three reliable datasets (Figure 6-6). All samples sourced from unconfined aquifers have arsenic at concentrations below the Drinking Water Guideline (10 ug/l). In step 2, these aquifers were classified as having arsenic unlikely occurring in groundwater; hence these unconfined aquifers all have a low likelihood of arsenic occurrence in the final map (Figure 6-6). In step 2, all confined aquifers were classified as having arsenic likely occurring in groundwater. Most of the samples sourced from the major confined aquifer in the west of the study area have arsenic at concentrations above the guideline. Likewise, a significant number of samples collected from a confined aquifer in the south of the study area have arsenic above the guideline. These aquifers are classified as high likelihood of arsenic occurrence in groundwater (Figure 6-6). The confined aquifers located in the center and in the east of the study area contain a number of samples with arsenic above the guideline, but also a significant number of samples with arsenic at concentrations below the guideline. For this reason, they are classified as medium likelihood of arsenic occurrence. Finally, there are some deep confined aquifers that lie in between the major deep confined aquifer in the west of the study area and the confined aquifers in the center of the study area that are classified as medium likelihood of arsenic occurrence. These deep confined aquifers were identified as having a low confidence of interpretation due to few sample locations. The fact that these aquifers are deep and confined possibly indicates that they have similar conditions as the major deep confined aquifer in the west, which was classified as high likelihood of arsenic occurrence. The few samples collected from these aquifers have arsenic at concentrations above the guideline value. For these reasons these aquifers are classified as high likelihood of arsenic occurrence (Figure 6-6).

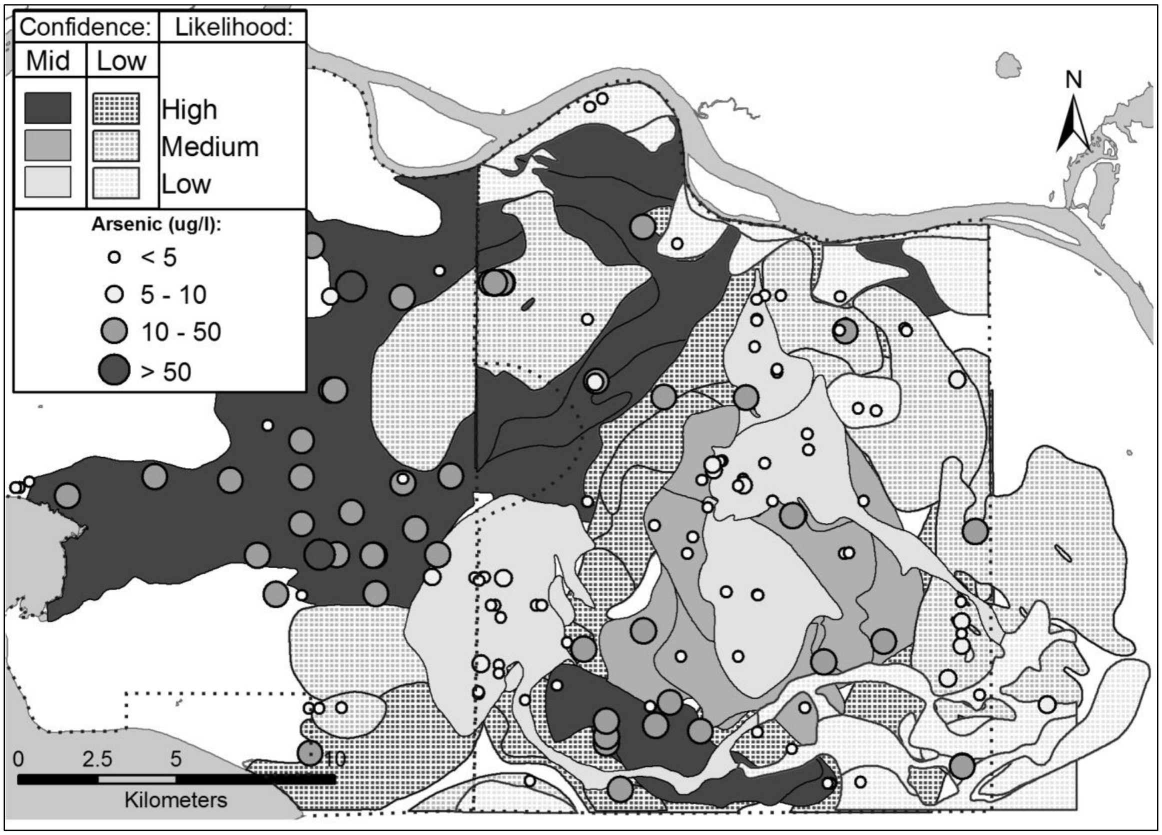

Figure 6-6. Map showing likelihood of arsenic occurrence in groundwater in aquifers in Langley and Surrey. Arsenic concentration data points are sourced from this research, Wilson et al. (2008), and the EMS dataset. This is the final product of the method presented.

Although the PWN dataset has lower data quality than the other datasets available, it has a far greater number of sample locations. The PWN dataset is used to suggest arsenic occurrences in portions of the study area where there are few samples from the other three datasets. A map was produced with the PWN raw arsenic concentration data superimposed over the classified aquifer polygons (Figure 6-7). As mentioned, there is no well depth information in the PWN dataset. Hence, the PWN is not useful for determining arsenic occurrences in areas where there are several aquifers present, because in these areas it is not possible to determine the source aquifer. As an example, there are a few samples in the PWN dataset located in the center of the study area that have elevated arsenic. It is not known if these samples were collected from the unconfined aquifer or from one of the underlying confined aquifers. Nevertheless, the PWN data are used to infer arsenic occurrences in areas where one aquifer predominates.

The PWN dataset contains a number of samples in the area of the deep confined aquifers in the center of the study area. These confined aquifers are interpreted to have arsenic likely occurring in groundwater; however, there is a low confidence of interpretation because the other three datasets available had very few samples from these aquifers. The vast majority of samples in the PWN dataset sourced from the area of these confined aquifers have arsenic at concentrations above 10 µg/l. This suggests that the assignment of these aquifers as having a high likelihood of arsenic occurring in groundwater is likely correct. Most other samples in the PWN with elevated arsenic lie in areas outside and around the major unconfined aquifer in the center of the study area. There are also a number of samples in the PWN dataset in the area around the major unconfined aquifer in the center of the study area with arsenic concentrations below 10 µg/l. This indicates that classifying the confined aquifers in this area as medium likelihood of arsenic occurring in groundwater is appropriate.

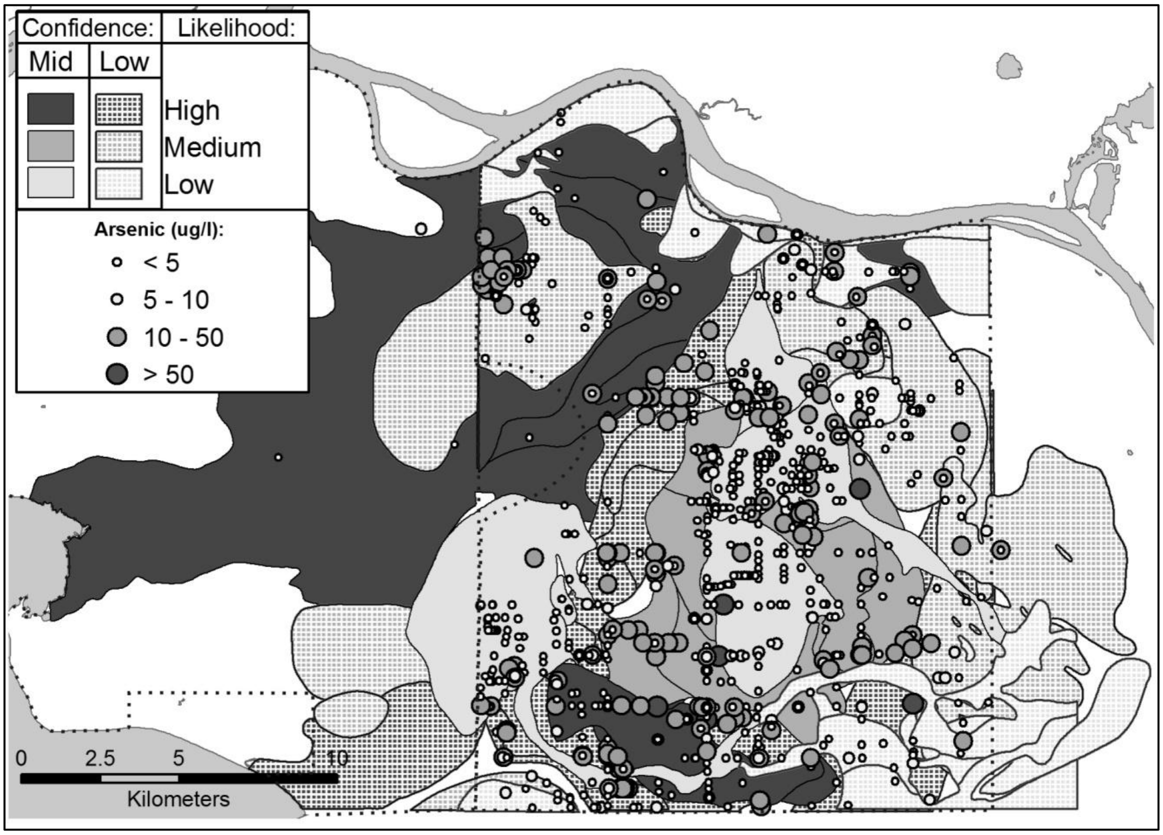

Figure 6-7. Township of Langley's Private Well Network (PWN) data points superimposed over aquifer polygons and coded based on likelihood of arsenic occurrence and confidence of interpretation. PWN data are used to evaluate arsenic occurrences in aquifers with few data points from the other datasets. PWN data show that elevated arsenic is concentrated in Langley in confined aquifers located around a main unconfined aquifer in the center of the study area.

6.4 Conclusions

A method is presented for classifying aquifers based on the likelihood of occurrence of a hazardous constituent of interest in groundwater, and spatially representing this classification on a map. The method incorporates confidence of geochemical interpretation for the different aquifers in a case study area based on availability of data and information on each aquifer. The method may be of use to water managers as it provides a spatial representation of aquifers of concern and areas where further sampling or study may be needed.

The method is tested in Langley and Surrey, British Columbia. A geochemical interpretation based on available data guided the production of a likelihood of arsenic occurrence in groundwater map in aquifers. Unconfined aquifers in the study area are classified as low likelihood of arsenic occurrence, while confined aquifers are classified as high likelihood. Arsenic concentration data collected through this research, by Wilson et al. (2008), and data available through the BC MOE EMS dataset are used to evaluate likelihood of arsenic occurrence in the different aquifers. A major confined aquifer in the west of the study area and some confined aquifers in the south are classified as high likelihood of arsenic occurrence. These aquifers are interpreted to have arsenic likely occurring in their groundwater, and the vast majority of samples sourced from them have arsenic concentrations above the Canadian Drinking Water Guideline (10 µg/l). Other confined aquifers are interpreted to have arsenic likely occurring, but a significant number of samples sourced from them have arsenic at concentrations below 10 µg/l. For this reason, these aquifers are classified as medium likelihood of arsenic occurrence. Unconfined aquifers have no samples with arsenic above the guideline. Therefore, these unconfined aquifers are classified as low likelihood of arsenic occurrence.

7: CONCLUSIONS AND RECOMENDATIONS

7.1 Conclusions

The hydrogeochemical evolution of groundwater occurring in a coastal setting, comprised of unconfined aquifers formed by glacial and glaciofluvial sediments and in aquifers confined by marine and glaciomarine sediments was addressed. The groundwater chemistry in the study area evolves from being controlled by atmospheric precipitation input, evapotranspiration, and minor water-rock interaction in unconfined aquifers to being controlled by mineral weathering, mixing and cation exchange, processes commonly associated with freshening environments, in confined aquifers. The groundwater changes from a Ca-Mg-HCO_3 composition to a Na-HCO_3 groundwater and, finally, in the deep confined aquifers, a Na-Cl composition from mixing with a seawater-like end member that has not been completely flushed out of the aquifer.

Groundwater in unconfined aquifers formed by glaciofluvial sediments is Ca-Mg-HCO_3 type, has relatively low salinity and alkalinity, has a slightly acidic to near neutral pH and is oxidized. The chemistry of groundwater in unconfined aquifers is controlled by rain water composition, and carbonate dissolution and silicate weathering in a system closed with respect to soil CO_2.

As groundwater flows through the glaciomarine sediments and reaches the confined aquifers its chemistry evolves through a sequence of mixing and water-rock interactions associated with freshening processes. Groundwater in confined aquifers first gradually evolves from a Ca-Mg-HCO_3 composition to Na-HCO_3, and then to Na-Cl. Groundwater in confined aquifers has higher salinity and alkalinity than in unconfined aquifers, has basic pH and is reduced. The gradual increase in sodium content in Na-HCO_3 groundwater is indicative of cation exchange. The release of sodium from exchange sites in exchange for calcium and magnesium is favoured as fresh groundwater flows through clay-rich sediments that were previously submerged by seawater. Carbonate mineral dissolution is driven by the removal of calcium and magnesium from solution through cation exchange and the generation of CO_2 likely through organic matter oxidation. The coupled cation exchange and carbonate dissolution reaction results in the addition of sodium and bicarbonate to solution. Groundwater with a Na-Cl composition occurs in deep confined aquifers as a result of mixing with a seawater-like end member that has not been completely flushed out of the aquifers.

Samples sourced from glaciomarine sediments have a significant amount of the relatively reactive silicate minerals, amphibole, plagioclase and chlorite based on XRD analysis. The presence of these minerals in the sediments facilitates weathering reactions and enhances weathering controls on groundwater chemistry in the confined aquifers. This is evidenced with activity diagrams, which demonstrate that samples sourced from confined aquifers plot along univariant equilibrium curves for silicate weathering reactions. Most samples sourced from unconfined aquifers plot far from equilibrium curves as they have a slightly acidic to neutral pH that is largely controlled by the partial pressure of CO_2. Groundwater in confined aquifers is fairly basic (pH > 8), which is a condition interpreted to be acquired as a result of carbonate dissolution and silicate mineral weathering.

Arsenic release processes and groundwater conditions favouring arsenic mobility were addressed in the system described above. Arsenic concentrations in most samples sourced from confined aquifers were above the Canadian Drinking Water Guideline (10 µg/l); whereas concentrations in all samples sourced from unconfined aquifers were below 10 µg/l. A positive relationship between arsenic concentrations and the Na/(Ca+Mg) ratio in groundwater indicates that arsenic release to solution likely occurs in glaciomarine sediments concurrent with cation exchange reactions. Positive relationships of pH with arsenic and other anions and oxyanions, such as molybdenum, phosphate, fluorite and boron, indicate that the mobility of these constituents in confined aquifers is favoured by basic pH. This happens as adsorption of anionic species to mineral surfaces is not favoured under basic pH. Reducing conditions of confined aquifers also favours arsenic mobility through speciation to arsenite (a more mobile arsenic form), as evidenced by a negative relationship of Eh with percent arsenite of total arsenic. Selected extractions applied to sediment core samples indicate that arsenic occurs in sediments predominantly in sulphide minerals, and in manganese oxides or iron oxyhydroxides. The occurrence of elevated arsenic in samples with relatively high concentrations of the reduced species Fe^{2+}, NH_3 and S^{2-} suggest that arsenic release occurs at increasingly reducing conditions. Despite likely arsenic release via iron oxyhydroxide reductive dissolution, iron remains at relatively low concentrations in groundwater (up to 0.37 mg/l) possibly as a result of iron adsorption and iron reprecipitation as carbonate minerals favoured by basic pH and high alkalinity. The presence of hydrogen sulphide in some samples, a negative relationship of $\delta^{34}S$ of SO_4 with sulphate concentrations, and a positive relationship of $\delta^{34}S$ with $\delta^{18}O$ of SO_4 indicate that groundwater in confined aquifers are undergoing or have experienced bacterial sulphate reduction. Arsenic may be mobilized through sulphide oxidation early in the system, where relatively oxidized groundwater encounters reduced glaciomarine sediments prior to sulphate reduction. Hence, the two possible mechanisms for arsenic release in the studied system is the reductive dissolution of arsenic bearing oxides and oxyhydroxides, and the oxidation of sulphide minerals during recharge into the confined system.

Results and interpretation obtained from this study were used to produce maps highlighting the likelihood of arsenic occurrences at concentrations above 10 µg/l in the different aquifers of Langley and Surrey. The method used to produce the maps incorporated confidence of geochemical interpretation for the different aquifers of the study area based on availability of data and information on each aquifer. A major confined aquifer in the west of the study area and some confined aquifers in the south are classified as having a high likelihood of arsenic occurrence. These aquifers are interpreted to have arsenic likely occurring in the groundwater, and the vast majority of samples sourced from them have arsenic concentrations above 10 µg/l. Other confined aquifers are interpreted to have arsenic likely occurring, but a significant number of samples sourced from them have arsenic at concentrations below 10 µg/l. For this reason, these aquifers are classified as having a medium likelihood of arsenic occurrence. Unconfined aquifers have no samples with arsenic above the guideline. Therefore, these unconfined aquifers are classified as low likelihood of arsenic occurrence. The maps produced may be of use to water managers as they provide a spatial representation of aquifers of concern and areas where further sampling or study may be needed.

7.2 Recommendations

The results of this study have led to the following recommendations for further work:

- Perform a detailed flow through column study that evaluates the hydrogeochemical evolution of groundwater and arsenic release at the contact between glaciofluvial sediments exposed to oxidizing conditions and glaciomarine sediments exposed to reducing conditions. Although sulphate stable isotope data indicated that groundwater in confined aquifers are sulphate reducing, it is suggested that a possible mechanism for arsenic release is the oxidation of arsenic bearing sulphides early in the system and prior to sulphate reduction. The column study could help elucidate if sulphide oxidation is indeed taking place as oxidized groundwater in confined aquifers reaches glaciomarine sediments.

- As mentioned in the Study Area (Chapter 2) section of this thesis, arsenic is reported at elevated concentrations in groundwater in other localities of the Lower Fraser Valley and south-western British Columbia. The specific mechanisms of arsenic release and mobility may have not been fully evaluated at some of these areas. Groundwater chemistry data from these areas should be analysed in order to evaluate if the conditions leading to elevated arsenic in these areas are the same as in Langley and Surrey. If so, the method used to classify aquifers based on likelihood of arsenic occurrence presented on Chapter 6 could be applied to classify aquifers in these other localities.
- Geochemical modelling codes (as PHREEQC) may be used to further evaluate and confirm the occurrence of some of the processes interpreted to be taking place in the studied system. For example, inverse modelling could be used to evaluate coupled reactions of cation exchange with carbonate mineral dissolution, discussed in Chapter 4. In another exercise, one dimensional transport model of a freshening system similar to the model presented by Appelo (1994) could be developed incorporating surface and mineral phases reactions in order to further evaluate controls to the mobility of arsenic as well as precipitation and dissolution of carbonate minerals.

- Sediment samples were analysed for a number of different chemical parameters that were not used in the discussion in this thesis due to lack of time. These parameters should be used to better describe the confining units and aquifer forming sediments and to further evaluate the occurrence of arsenic as well as other metals and metalloids in the sediments. For example, Pearce Element Ratio (PER; Pearce, 1968) analysis has been used to assess fractionation, alteration and weathering of minerals in sediments and rocks (as shown in a number of studies, e.g. Kumar, 2003; Murphy and Stanley, 2007; Urqueta et al., 2009). PER analysis could be used to infer the clay versus feldspar content in sediments, as clay minerals have a lower concentration of the major elements K, Ca, Mg and Na than feldspars. This would allow the determination of possible tendencies for arsenic and other elements to occur at greater concentrations in clay rich sediments.

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APPENDIX A: COMPLETE ANALYTICAL RESULTS

Table A-1. Field measured parameters and Ion Chromatography (IC) results for well water samples.

Sample no.	pH	Eh (mV)	Temp. (°C)	Cond. (μS/cm)	D.O. (mg/l)	Fe^{2+} (mg/l)	NH_3-N (mg/l)	S^{2-} (μg/l)	HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	PO_4 (mg/l)	Br (mg/l)	F (mg/l)
D.L.						0.01	0.01	1		0.1	0.1	0.01	0.1	0.01	0.01
01	7.0	164	10.0	221	0.17	1.78	0	0	117	15	14	0.08	< 0.1	0.02	0.09
02	5.9	349	12.3	257	6.36	0.02	0		36	20	29	50	< 0.1	0.01	0.01
03	6.1	337	12.7	137	7.84	0.01	0		39	6.7	12	22	< 0.1	0.02	0.03
04	8.6	107	10.0	224	0.13	0.02	0.14		133	5.2	21	0.15	< 0.1	0.04	0.05
05	7.7	148	11.3	89	1.01	0.35	0.03	0	80	1.0	0.6	< 0.01	< 0.1	< 0.01	0.11
06	7.3	271	9.4	431	3.52	0	0.01		115	5.2	43	102	< 0.1	0.01	< 0.01
07	6.4	374	11.2	180	9.54	0.05	0		59	9.3	12	28	< 0.1	0.01	0.06
08	7.7	234	9.2	120	2.01	0	0		72	1.3	3.9	2.12	0.2	0.02	0.09
09	8.7	76	10.2	143	0.18	0.01	0		76	2.7	16	<0.01	< 0.1	< 0.01	0.07
10	8.4	319	10.6	176	4.01	0.01	0.06	0	114	1.8	7.7	0.02	0.7	< 0.01	0.12
11	6.8	336	11.1	175	6.31	0.01	0		86	7.2	13	7.69	< 0.1	0.02	0.05
12	6.4	328	10.5	174	8.14	0.49	0	0	63	17	6.2	12.27	< 0.1	0.02	0.03
13	8.7	61	9.8	1443	0.56	0.18	0.2	14	288	302	91	4.59	< 0.1	0.68	0.15
14	8.5	44	10.3	725	0.18	0.06	0.19	24	187	141	23	0.07	2.7	0.38	0.27
15	9.0	236	9.9	492	1.48	0.06	0.21	0	281	28	1.8	0.17	0.3	0.23	< 0.01
16	8.9	192	9.9	897	4.20	0.03	0.07	1	332	98	33	0.44	1.3	0.35	0.40
17	8.6	277	11.1	345	0.76	0.01	0.09	0	236	1.6	4.5	0.19	1.3	0.09	0.45
18	8.7	245	11.2	377	0.30	0.03	0.11	0	260	2.5	4.7	0.39	3.5	0.09	0.37
19	8.4	95	9.5	399		0.07	0.02	6	272	1.8	10	0.42	4.3	< 0.01	0.79
20	8.6	145	10.8	440	0.28	0.03	0.1	3	303	2.4	2.7	0.37	5.2	< 0.01	0.78
21	7.9	89	10.7	227		0.26			142	6.1	5.2	0.06	0.4	0.05	0.16
22	8.1	92	9.6	642		0.09			421	7.6	21	<0.01	2.3	0.20	0.43
23	9.2	187	10.8	365	0.12	0.01	0.14	0	186	9.0	18	0.67	1.1	< 0.01	0.22
24	8.7	78	7.8	270	0.22	0.12	0.48	1	137	755	132	<0.01	< 0.1	9.91	0.08
25	8.5	71	10.5	720	0.29	0.07	0.19	0	539	3.5	3.1	2.01	5.5	< 0.01	0.55
26	8.1	72	8.9	159		0.12	0.05	6	107	1.7	2.1	0.06	1.2	0.05	0.16
27	8.2	123	9.0	128	0.79	0.03	0.04	1	87	0.9	3.0	0.12	0.5	< 0.01	0.10
28	7.6	161	9.1	132	0.35	0.2	0.05	3	82	1.1	8.0	0.14	< 0.1	< 0.01	0.02
29	7.6	307	9.6	218		0.01	0	0	153	2.0	8.5	3.32	< 0.1	0.06	< 0.01
30	8.6	77	11.0	410		0.03	0.21	0	264	4.8	11	0.35	3.5	0.10	0.39
31	8.2	319	11.0	387		0.01	0	0	277	3.4	0.5	0.87	2.5	0.10	0.28
32	6.9	361	10.6	146		0	0.01		78	5.3	5.6	4.53	< 0.1	0.05	0.03
33	7.7	306	11.0	149		0.02	0		87	2.9	8.1	2.37	< 0.1	0.05	0.04
34	8.7	76	10.0	338	0.04	0.06	0.11	0	235	0.7	2.7	0.32	5.8	0.03	0.65
35	8.5	149	10.2	274	0.96	0.02	0.3	0	172	4.1	2.1	0.20	1.9	0.02	0.27
36	8.5	167	10.5	298	1.62	0.01	0.07	0	176	8.5	3.3	0.06	2.1	0.04	0.30
37	8.5	-26	9.5	2527	0.27	0.3	0.32	13	319	598	140	0.12	< 0.1	2.62	0.32
38	9.3	-47	12.0	431		0.04	0.17	9	264	7.2	2.3	0.60	4.9	0.04	0.71
39	8.3	63	13.9	349	0.43	0.14	0.23	17	235	0.8	3.9	0.14	19.5	< 0.01	2.09
40	8.7	4	10.2	365	0.19	0.06	0.48	3	177	31	0.1	0.06	0.9	0.10	0.20
41	5.9	387	11.0	366	2.25	0.05	0.02		41	34	24.3	<0.01	< 0.1	< 0.01	0.01
42	6.9	341	10.6	265	3.10	0.01	0.01		111	6.3	14.2	<0.01	< 0.1	0.02	0.04
44	8.3	327	9.1	2123		0.01	0.01	0	235	534	109	<0.01	< 0.1	2.37	0.28
45	8.8	-31	9.9	993		0.15	0.15	44	638	35	0.4	<0.01	8.2	0.17	1.72
46	8.8	-29	9.1	665	0.26	0.03	0.12	3	226	92	38	1.24	1.2	0.57	0.28
47	8.6	252	10.3	1287		0.02	0.13	0	320	244	61	3.12	< 0.1	1.86	0.31

* U - Unconfined aquifer; C - Confined aquifer; D.L. - Detection limit

Table A-2. Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES) results for well water samples.

Sample no.	K (mg/l)	Na (mg/l)	Ca (mg/l)	Mg (mg/l)	Si (mg/l)	Al (µg/l)	As (µg/l)	B (µg/l)	Ba (µg/l)	Fe (mg/l)	Li (µg/l)	Mn (µg/l)	Mo (µg/l)	S (mg/l)	Sr (µg/l)	Zn (µg/l)
D.L.	0.1	0.1	0.1	0.1	0.1	1.00	1	1	1	0.01	0.1	0.1	1	0.1	1	1
01	1.7	7	24	11	16.6	1.17	5.5	11	12	4.25	2.9	227	5.1	5.2	82	< 1
02	1.1	10	29	8	10.5	1.24	< 1	53	5	0.11	0.4	4.7	< 1	10.9	260	30
03	2.2	14	10	2	5.5	3.78	< 1	37	35	0.01	0.5	0.8	< 1	5.0	72	19
04	2.8	8	29	10	8.5	2.16	5.6	14	7	0.04	2.1	74	< 1	7.4	84	< 1
05	1.3	5	8	5	11.0	5.37	< 1	6	3	0.89	0.6	128	< 1	0.1	29	< 1
06	2.9	9	56	17	9.7	< 1.00	3.4	9	30	0.02	3.3	12	< 1	15.7	180	41
07	1.0	11	21	4	6.8	< 1.00	1.8	57	9	0.05	0.5	8.2	1.0	5.0	104	< 1
08	1.4	8	11	6	11.7	2.16	< 1	13	6	0.00	0.7	1.1	< 1	1.8	45	2
09	1.3	3	22	4	9.2	1.62	7.9	7	5	0.03	1.9	87	< 1	6.5	59	< 1
10	5.1	21	12	5	13.1	1.46	12.4	41	40	0.05	0.5	53	1.8	3.2	49	3
11	1.1	5	25	6	11.4	< 1.00	< 1	7	10	0.00	1.0	6.5	< 1	5.5	92	34
12	1.1	15	14	5	7.7	< 1.00	3.6	31	7	0.57	1.1	94	< 1	2.8	100	< 1
13	11.5	261	33	12	9.1	1.94	25.0	356	30	0.16	1.8	43	33.1	39.6	266	1
14	6.4	141	12	5	11.0	2.87	6.8	203	11	0.08	0.4	33	13.0	10.9	88	3
15	4.1	104	12	4	7.5	1.79	21.3	208	4	0.20	1.2	16	40.4	1.0	60	7
16	7.7	197	10	3	14.4	2.55	54.8	452	13	0.02	1.9	11	18.5	15.3	83	3
17	6.7	77	8	2	13.5	2.08	30.7	198	5	0.01	1.3	20	7.3	2.3	51	4
18	4.7	73	15	5	10.1	1.88	19.3	242	9	0.07	0.9	59	8.3	2.4	75	< 1
19	1.8	95	6	3	11.1	3.26	15.6	213	3	0.13	1.1	35	6.9	4.9	30	11
20	3.1	106	4	2	9.1	1.16	18.8	262	3	0.03	1.0	36	11.4	1.4	27	1
21	1.9	10	23	15	12.4	< 1.00	3.5	8	10	0.24	2.3	288	< 1	2.3	62	2
22	9.1	122	20	16	12.8	< 1.00	27.7	276	19	0.10	0.8	214	21.7	9.2	133	27
23	4.5	84	3	2	8.7	3.71	23.1	131	2	0.03	0.9	15	6.8	8.3	21	1
24	9.8	473	58	21	6.0	< 1.00	21.8	241	41	0.22	3.7	71	36.0	53.9	424	11
25	6.5	162	14	14	10.9	2.86	18.2	431	15	0.09	0.9	48	17.9	1.8	106	38
26	2.3	21	10	4	11.7	0.38	9.2	53	15	0.13	1.5	60	2.7	1.1	45	4
27	2.2	12	11	5	12.5	< 1.00	4.6	25	14	0.03	0.9	49	1.1	1.6	46	1
28	1.4	8	11	7	10.5	2.09	< 1	12	12	0.14	< 0.1	35	< 1	3.8	50	2
29	1.7	7	25	14	8.0	1.90	< 1	10	6	0.01	2.0	4.2	< 1	3.7	66	2
30	5.8	83	11	6	13.8	1.88	21.9	224	10	0.12	1.4	49	11.0	5.6	68	< 1
31	8.0	62	18	11	16.9	10.39	23.9	140	20	0.03	13.8	10	26.7	0.3	119	9
32	1.6	6	14	7	14.1	< 1.00	5.0	11	3	< 0.01	1.4	0.6	1.4	2.0	57	2
33	1.6	9	14	7	11.6	< 1.00	5.0	8	5	0.01	1.1	0.8	1.5	2.8	62	3
34	4.4	77	6	3	13.7	4.56	29.2	292	4	0.07	0.8	35	6.6	1.1	36	2
35	7.0	48	11	4	14.4	< 1.00	27.5	96	10	0.01	1.2	25	5.1	0.8	69	2
36	7.7	54	11	4	14.0	0.44	30.0	105	10	0.02	1.5	26	5.1	1.3	72	1
37	16.0	439	25	21	10.7	< 1.00	44.4	410	41	0.37	4.0	71	24.0	51.4	304	1
38	3.4	103	2	1	11.0	4.30	20.8	334	3	0.03	0.7	10	11.0	1.1	17	1
39	2.5	89	1	2	14.9	11.79	26.9	396	11	0.35	1.0	49	4.9	1.7	18	27
40	4.8	64	12	5	15.4	< 1.00	1.7	90	13	0.07	1.1	40	2.6	0.1	80	8
41	31.8	18	24	7	5.4	20.56	3.6	14	348	0.05	0.8	85	< 1	9.2	226	22
42	2.1	10	29	13	9.0	1.08	1.8	19	10	< 0.01	2.4	0.4	< 1	4.9	107	10
44	14.3	347	42	19	10.5	< 1.00	19.6	266	38	0.01	4.0	67	24.1	42.5	390	30
45	5.0	248	2	2	7.6	14.13	33.0	1051	13	0.22	0.7	23	16.6	0.7	19	14
46	2.4	137	8	3	10.3	1.54	10.6	167	6	0.11	1.1	23	11.3	15.1	57	4
47	12.4	236	27	8	16.5	< 1.00	47.8	446	23	0.01	3.0	40	26.9	24.4	213	11

D.L.- Detection limit

Table A-3. Arsenic speciation and stable isotopes results for well water samples.

Sample no.	As(III) (%)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{34}S_{SO4}$ (‰)	$\delta^{18}O_{SO4}$ (‰)
01		-16.0		
02		-20.3	8.0	6.7
03		-18.5	6.4	4.5
04		-13.9		
05		-18.9		
06	29	-14.4	2.6	0.3
07	39	-18.0	0.1	3.5
08		-18.2		
09	71	-12.9	-10.6	-3.6
10	35	-12.7		
11		-16.8	-2.9	3.8
12	100	-19.7	6.3	4.5
13	68	-15.3	19.0	11.5
14	100	-17.3	32.9	12.7
15	57	-18.0	74.1	
16	23	-12.5	21.0	13.9
17	29	-16.4		
18	55	-15.1	11.5	9.0
19	100	-16.8	2.8	10.1
20	68	-15.3	16.3	
21	42	-19.4	8.5	7.2
22	71	-15.7	14.8	12.3
23	77	-14.6	9.4	11.2
24	94	-16.5	27.7	13.3
25	100	-12.3	9.7	10.9
26	66	-17.4	16.8	18.3
27	61	-17.6		
28		-19.0	-13.3	1.2
29		-18.9	-3.1	0.4
30	45	-14.3	17.1	13.1
31	28	-18.4		
32	51	-17.4	3.6	3.1
33	20	-18.6		
34	62	-12.3	10.3	
35	100	-16.5		
36	54	-15.4		
37	100	-15.8	31.4	16.4
38	55	-14.8	33.9	14.4
39	79	-14.6	5.6	8.6
40		-15.5		
41		-20.8		
42		-17.6		
44	0	-17.0	23.2	14.8
45	49	-11.5	25.2	
46	56	-17.5	25.2	15.1
47	44	-15.2	22.7	13.3

Table A-4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) results for well water samples.

Sample no.	Ag (µg/l)	Al (µg/l)	As (µg/l)	B (µg/l)	Be (µg/l)	Bi (µg/l)	Ca (µg/l)	Cd (µg/l)	Ce (µg/l)	Co (µg/l)	Cr (µg/l)	Cs (µg/l)	Cu (µg/l)	Fe (µg/l)
D.L	0.06	50	10	10	0.3	0.1	200	0.1	0.02	0.1	1	0.01	0.3	20
01	<0.06	<50	<10	10	<0.3	<0.1	>10000	0.1	0.06	0.6	<1	0.01	0.8	3790
02	<0.06	<50	<10	50	<0.3	<0.1	>10000	<0.1	0.02	1.2	1	0.01	43.6	140
03	<0.06	<50	<10	30	<0.3	<0.1	9700	<0.1	0.03	0.1	<1	0.01	71.3	20
04	<0.06	<50	10	10	<0.3	<0.1	>10000	0.1	<0.02	<0.1	<1	0.01	0.3	70
05	<0.06	<50	<10	10	<0.3	<0.1	7700	0.4	0.02	0.1	<1	0.01	0.3	860
06	<0.06	<50	<10	10	<0.3	<0.1	>10000	0.2	<0.02	0.1	<1	0.01	1.5	90
07	<0.06	<50	<10	50	<0.3	<0.1	>10000	<0.1	0.05	0.2	<1	0.02	<0.3	60
08	<0.06	<50	<10	10	<0.3	<0.1	>10000	0.1	<0.02	<0.1	<1	<0.01	<0.3	20
09	<0.06	<50	<10	10	<0.3	<0.1	>10000	0.2	<0.02	<0.1	<1	0.01	<0.3	40
10	<0.06	<50	10	40	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	<0.01	<0.3	60
11	<0.06	<50	<10	10	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	<0.01	10.5	20
12	<0.06	<50	<10	30	<0.3	<0.1	>10000	0.1	<0.02	0.3	<1	<0.01	<0.3	510
13	<0.06	<50	30	340	<0.3	<0.1	>10000	<0.1	<0.02	0.1	<1	0.01	0.6	180
14	<0.06	<50	10	190	<0.3	<0.1	>10000	<0.1	0.02	0.1	<1	0.01	0.6	90
15	<0.06	<50	20	180	<0.3	<0.1	>10000	0.3	<0.02	0.1	<1	0.01	1.4	200
16	<0.06	<50	50	420	<0.3	<0.1	9600	<0.1	<0.02	0.1	<1	<0.01	1.5	20
17	<0.06	<50	30	180	<0.3	<0.1	7600	0.1	<0.02	<0.1	<1	0.03	0.6	20
18	<0.06	<50	20	230	<0.3	<0.1	>10000	<0.1	0.03	0.1	<1	<0.01	2.2	70
19	<0.06	<50	20	200	<0.3	<0.1	6100	<0.1	0.03	<0.1	<1	<0.01	1.1	130
20	<0.06	<50	20	250	<0.3	<0.1	4400	<0.1	0.03	0.1	<1	<0.01	1.4	30
21	<0.06	<50	10	10	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	0.01	0.4	260
22	<0.06	<50	20	270	<0.3	<0.1	>10000	<0.1	<0.02	0.2	<1	<0.01	0.8	110
23	<0.06	<50	20	130	<0.3	<0.1	3300	<0.1	0.02	<0.1	<1	<0.01	0.4	20
24	<0.06	<50	30	270	<0.3	<0.1	>10000	0.1	<0.02	0.1	1	0.02	<0.3	290
25	<0.06	<50	20	450	<0.3	<0.1	>10000	0.1	0.07	0.3	<1	<0.01	<0.3	90
26	<0.06	<50	10	60	<0.3	<0.1	9200	<0.1	<0.02	<0.1	<1	0.01	<0.3	130
27	<0.06	<50	10	30	<0.3	<0.1	9900	<0.1	<0.02	<0.1	<1	<0.01	0.4	30
28	<0.06	<50	<10	10	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	0.01	1.8	140
29	<0.06	<50	<10	10	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	2	<0.01	5.4	30
30	<0.06	<50	20	200	<0.3	<0.1	>10000	<0.1	0.02	<0.1	<1	0.01	1.5	130
31	<0.06	<50	20	140	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	<0.01	1.1	30
32	<0.06	<50	<10	10	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	<0.01	33.8	<20
33	<0.06	<50	<10	10	<0.3	<0.1	>10000	0.1	<0.02	<0.1	<1	<0.01	10.3	<20
34	<0.06	<50	20	270	<0.3	<0.1	5800	<0.1	0.14	<0.1	<1	<0.01	1.1	70
35	<0.06	<50	30	90	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	0.01	0.7	20
36	<0.06	<50	30	100	<0.3	<0.1	>10000	0.2	<0.02	<0.1	<1	0.01	<0.3	30
37	<0.06	<50	40	420	<0.3	<0.1	>10000	<0.1	<0.02	0.1	<1	0.01	<0.3	390
38	<0.06	<50	20	320	<0.3	<0.1	2100	<0.1	0.11	0.1	<1	0.01	4.5	30
39	0.15	<50	30	390	<0.3	0	1600	0.2	0.49	0.1	1	<0.01	25.1	490
40	<0.06	<50	<10	90	<0.3	<0.1	>10000	0.1	<0.02	0.1	<1	0.01	0.5	70
41	<0.06	<50	<10	20	<0.3	<0.1	>10000	<0.1	0.49	0.2	<1	0.11	58	60
42	<0.06	<50	<10	20	<0.3	<0.1	>10000	<0.1	<0.02	<0.1	<1	<0.01	1.6	30
44	<0.06	<50	20	270	<0.3	<0.1	>10000	<0.1	<0.02	0.1	<1	0.01	1.8	50
45	<0.06	<50	30	>1000	<0.3	<0.1	1800	<0.1	0.26	0.1	2	0.01	1.4	240
46	<0.06	<50	10	170	<0.3	<0.1	8400	<0.1	<0.02	0.1	<1	0.02	0.7	120
47	<0.06	<50	40	440	<0.3	<0.1	>10000	<0.1	<0.02	0.1	<1	0.01	2.8	40

D.L.-Detection limit

Table A-5. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) results for well water samples (continued).

Sample no.	Ga (µg/l)	Hf (µg/l)	Hg (µg/l)	In (µg/l)	K (µg/l)	La (µg/l)	Li (µg/l)	Mg (µg/l)	Mn (µg/l)	Mo (µg/l)	Na (µg/l)	Nb (µg/l)	Ni (µg/l)	P (µg/l)
D.L.	0.05	0.05	0.2	0.04	60	0.02	10	4	0.1	1	300	0.02	0.5	100
01	<0.05	<0.05	<0.2	<0.04	1450	0.04	<10	8360	235	<1	5900	<0.02	1.2	100
02	<0.05	<0.05	<0.2	<0.04	990	0.06	<10	7010	5.1	<1	8900	<0.02	1.1	<100
03	<0.05	<0.05	<0.2	<0.04	2020	0.08	<10	2350	1.0	<1	>10000	<0.02	0.5	<100
04	<0.05	<0.05	<0.2	<0.04	2530	<0.02	<10	7860	79	1	7000	<0.02	<0.5	100
05	<0.05	<0.05	<0.2	<0.04	1160	<0.02	<10	4380	126	1	4300	<0.02	0.6	100
06	<0.05	<0.05	<0.2	<0.04	2630	<0.02	<10	>10000	13	<1	8200	<0.02	1.5	<100
07	<0.05	<0.05	<0.2	<0.04	870	0.10	<10	4230	8.2	1	10000	<0.02	<0.5	<100
08	<0.05	<0.05	<0.2	<0.04	1270	<0.02	<10	5920	0.3	1	6100	<0.02	<0.5	100
09	<0.05	<0.05	<0.2	<0.04	1230	<0.02	<10	4130	86	1	2600	<0.02	<0.5	<100
10	<0.05	<0.05	<0.2	<0.04	4730	<0.02	<10	4930	53	2	>10000	<0.02	0.9	200
11	<0.05	<0.05	<0.2	<0.04	960	<0.02	<10	5490	6.5	<1	4600	<0.02	1.2	<100
12	<0.05	<0.05	<0.2	<0.04	1040	<0.02	<10	5200	95	<1	>10000	<0.02	1.4	<100
13	<0.05	<0.05	<0.2	<0.04	>10000	<0.02	<10	>10000	48	37	>10000	<0.02	1.8	300
14	<0.05	<0.05	<0.2	<0.04	5590	<0.02	<10	5600	35	15	>10000	<0.02	<0.5	1100
15	<0.05	<0.05	<0.2	<0.04	3440	<0.02	<10	3850	17	42	>10000	<0.02	0.9	500
16	<0.05	<0.05	<0.2	<0.04	7080	<0.02	<10	3230	12	20	>10000	<0.02	1.6	700
17	<0.05	<0.05	<0.2	<0.04	6510	<0.02	<10	2350	20	8	>10000	<0.02	<0.5	500
18	<0.05	<0.05	<0.2	<0.04	4530	0.02	<10	5330	62	9	>10000	<0.02	0.8	1000
19	<0.05	<0.05	<0.2	<0.04	1770	<0.02	<10	2710	35	8	>10000	<0.02	<0.5	1300
20	<0.05	<0.05	<0.2	<0.04	3070	0.02	<10	1720	37	13	>10000	<0.02	0.8	1600
21	<0.05	<0.05	<0.2	<0.04	1840	<0.02	<10	>10000	300	1	>10000	<0.02	0.8	200
22	<0.05	<0.05	<0.2	<0.04	8870	<0.02	<10	>10000	233	24	>10000	<0.02	1.0	900
23	<0.05	<0.05	<0.2	<0.04	4310	<0.02	<10	2070	16	8	>10000	<0.02	<0.5	400
24	<0.05	<0.05	<0.2	<0.04	6920	<0.02	<10	>10000	85	42	>10000	<0.02	1.6	200
25	<0.05	<0.05	<0.2	<0.04	6450	0.04	<10	>10000	54	20	>10000	<0.02	1.1	1900
26	<0.05	<0.05	<0.2	<0.04	2220	<0.02	<10	4270	61	3	>10000	<0.02	<0.5	400
27	<0.05	<0.05	<0.2	<0.04	2100	<0.02	<10	4730	48	2	>10000	<0.02	<0.5	200
28	<0.05	<0.05	<0.2	<0.04	1320	<0.02	<10	6610	36	1	7200	<0.02	<0.5	<100
29	<0.05	<0.05	<0.2	<0.04	1650	<0.02	<10	>10000	4.4	1	7000	<0.02	0.8	<100
30	<0.05	<0.05	<0.2	<0.04	5340	<0.02	<10	5890	50	12	>10000	<0.02	<0.5	1000
31	<0.05	<0.05	<0.2	<0.04	7770	<0.02	<10	8560	0.7	20	>10000	<0.02	0.5	700
32	<0.05	<0.05	<0.2	<0.04	1500	<0.02	<10	7310	0.6	<1	5400	<0.02	2.2	<100
33	<0.05	<0.05	<0.2	<0.04	1540	<0.02	<10	7060	0.9	1	8400	<0.02	<0.5	100
34	<0.05	<0.05	<0.2	<0.04	4200	0.07	<10	3110	36	7	>10000	<0.02	0.8	1700
35	<0.05	<0.05	<0.2	<0.04	6630	<0.02	<10	3960	27	6	>10000	<0.02	0.6	600
36	<0.05	<0.05	<0.2	<0.04	7050	<0.02	<10	4110	28	6	>10000	<0.02	0.5	600
37	<0.05	<0.05	<0.2	<0.04	>10000	<0.02	<10	>10000	82	28	>10000	<0.02	1.4	700
38	<0.05	<0.05	<0.2	<0.04	3260	0.05	<10	1060	11	12	>10000	<0.02	0.7	1400
39	<0.05	<0.05	<0.2	<0.04	2330	0.28	<10	1640	51	7	>10000	0.06	1.0	5600
40	<0.05	<0.05	<0.2	<0.04	4450	<0.02	<10	5600	42	2	>10000	<0.02	<0.5	400
41	<0.05	<0.05	<0.2	<0.04	>10000	0.44	<10	6370	87	<1	>10000	<0.02	0.9	<100
42	<0.05	<0.05	<0.2	<0.04	1970	<0.02	<10	>10000	0.5	<1	>10000	<0.02	1.8	<100
44	<0.05	<0.05	<0.2	<0.04	>10000	<0.02	<10	>10000	76	28	>10000	<0.02	1.4	300
45	0	<0.05	<0.2	<0.04	4560	0.13	<10	1760	25	21	>10000	0.03	0.6	2800
46	<0.05	<0.05	<0.2	<0.04	2140	<0.02	<10	3740	25	12	>10000	<0.02	0.5	700
47	<0.05	<0.05	<0.2	<0.04	>10000	<0.02	<10	8760	45	29	>10000	<0.02	1.5	400

D.L.- Detection limit

Table A-6. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) results for well water samples (continued).

Sample no.	Pb (µg/l)	Se (µg/l)	Zn (µg/l)	Rb (µg/l)	Sb (µg/l)	Sn (µg/l)	Sr (µg/l)	Ta (µg/l)	Te (µg/l)	Th (µg/l)	Tl (µg/l)	U (µg/l)	V (µg/l)	W (µg/l)	Y (µg/l)	Zr (µg/l)
D.L.	0.2	10	2	0.1	0.1	0.3	0.1	0.01	10	0.01	0.04	0.01	1	0.2	0.03	0.05
01	<0.2	<10	<2	1	<0.1	<0.3	90	<0.01	<10	<0.01	<0.04	0.02	<1	<0.2	0.12	<0.05
02	3	<10	31	1	<0.1	<0.3	274	0.01	<10	<0.01	<0.04	0.01	<1	<0.2	0.31	<0.05
03	1.3	<10	19	2.3	<0.1	<0.3	79	<0.01	<10	<0.01	<0.04	0.01	<1	<0.2	0.15	<0.05
04	<0.2	<10	<2	0.7	<0.1	<0.3	92	<0.01	<10	<0.01	<0.04	0.03	<1	<0.2	<0.03	<0.05
05	<0.2	<10	<2	0.5	0.1	<0.3	33	<0.01	<10	<0.01	<0.04	0.01	<1	0.6	<0.03	<0.05
06	<0.2	<10	46	0.8	0.7	<0.3	202	<0.01	<10	<0.01	<0.04	1.20	2	<0.2	<0.03	<0.05
07	<0.2	<10	<2	1.5	0.1	<0.3	113	<0.01	<10	<0.01	<0.04	0.01	1	<0.2	0.25	<0.05
08	<0.2	<10	<2	0.1	0.1	<0.3	49	<0.01	<10	<0.01	<0.04	0.09	5	<0.2	<0.03	<0.05
09	<0.2	<10	<2	0.9	<0.1	<0.3	66	0.01	<10	<0.01	<0.04	0.01	<1	<0.2	<0.03	<0.05
10	0.3	<10	3	0.5	<0.1	<0.3	56	<0.01	<10	<0.01	<0.04	0.05	<1	0.6	<0.03	<0.05
11	0.5	<10	34	1.4	<0.1	<0.3	98	0.01	<10	<0.01	<0.04	0.07	<1	<0.2	<0.03	<0.05
12	<0.2	<10	<2	0.4	<0.1	<0.3	108	<0.01	<10	<0.01	<0.04	0.01	<1	<0.2	0.03	<0.05
13	<0.2	<10	<2	1.1	0.1	<0.3	292	<0.01	<10	<0.01	<0.04	3.47	<1	1.3	<0.03	<0.05
14	<0.2	<10	3	1.1	<0.1	<0.3	100	<0.01	<10	<0.01	<0.04	0.02	1	2.4	0.03	0.05
15	0.9	<10	7	0.7	<0.1	<0.3	65	0.01	<10	<0.01	<0.04	0.04	1	1.6	<0.03	0.07
16	0.2	<10	3	0.9	0.1	<0.3	94	<0.01	<10	<0.01	<0.04	0.74	1	5.5	<0.03	<0.05
17	0.2	<10	4	1.2	0.1	<0.3	57	<0.01	<10	<0.01	<0.04	1.12	1	3.4	<0.03	<0.05
18	<0.2	<10	<2	0.7	<0.1	<0.3	85	<0.01	<10	<0.01	<0.04	0.12	1	2.0	<0.03	<0.05
19	<0.2	<10	10	0.1	<0.1	<0.3	34	<0.01	<10	<0.01	<0.04	0.04	1	0.5	0.04	<0.05
20	<0.2	<10	<2	0.4	<0.1	<0.3	33	<0.01	<10	<0.01	<0.04	0.23	<1	1.7	0.03	<0.05
21	0.3	<10	2	0.1	0.1	<0.3	71	<0.01	<10	<0.01	<0.04	0.07	1	<0.2	<0.03	<0.05
22	0.4	<10	29	0.8	0.1	<0.3	159	<0.01	<10	<0.01	<0.04	0.14	1	0.5	0.03	<0.05
23	<0.2	<10	<2	0.6	<0.1	<0.3	26	<0.01	<10	<0.01	<0.04	0.04	<1	1.2	<0.03	<0.05
24	<0.2	10	12	1.2	<0.1	<0.3	533	<0.01	<10	<0.01	<0.04	0.05	<1	0.5	<0.03	<0.05
25	<0.2	<10	3	1.0	0.1	<0.3	130	<0.01	<10	<0.01	<0.04	0.01	1	4.0	0.04	0.10
26	<0.2	<10	3	1.0	<0.1	<0.3	51	<0.01	<10	<0.01	<0.04	0.02	<1	0.2	<0.03	<0.05
27	<0.2	<10	2	0.7	<0.1	<0.3	50	0.01	<10	<0.01	<0.04	0.01	<1	0.3	<0.03	<0.05
28	<0.2	<10	2	0.3	<0.1	<0.3	55	<0.01	<10	<0.01	<0.04	0.11	1	<0.2	<0.03	<0.05
29	0.2	<10	2	0.1	0.1	<0.3	78	0.01	<10	<0.01	<0.04	0.46	1	<0.2	<0.03	<0.05
30	<0.2	<10	2	1.0	<0.1	<0.3	78	0.01	<10	<0.01	<0.04	0.03	1	2.0	<0.03	0.07
31	<0.2	<10	7	1.4	<0.1	<0.3	129	<0.01	<10	<0.01	<0.04	0.03	<1	0.9	<0.03	<0.05
32	<0.2	<10	2	0.1	<0.1	<0.3	62	<0.01	<10	<0.01	<0.04	0.19	3	<0.2	<0.03	<0.05
33	<0.2	<10	2	0.1	0.1	<0.3	68	<0.01	<10	<0.01	<0.04	0.20	4	<0.2	<0.03	<0.05
34	<0.2	<10	2	0.8	0.1	<0.3	41	<0.01	<10	<0.01	<0.04	0.06	1	2.4	0.07	0.14
35	<0.2	<10	3	0.8	<0.1	<0.3	77	<0.01	<10	<0.01	<0.04	0.25	<1	1.9	<0.03	<0.05
36	<0.2	<10	<2	0.9	<0.1	<0.3	78	0.01	<10	<0.01	<0.04	0.25	<1	2.0	<0.03	<0.05
37	<0.2	10	<2	1.7	0.1	<0.3	365	<0.01	<10	<0.01	<0.04	2.48	<1	2.3	<0.03	<0.05
38	0.2	<10	2	0.5	0.1	<0.3	21	<0.01	<10	<0.01	<0.04	0.13	2	2.4	0.09	0.16
39	2.3	<10	5	0.2	0.1	<0.3	19	<0.01	<10	0.1	<0.04	0.05	5	2.5	0.51	1.02
40	<0.2	<10	5	1.5	<0.1	<0.3	88	<0.01	<10	<0.01	<0.04	<0.01	<1	0.9	<0.03	0.06
41	2.1	<10	21	24.1	0.1	<0.3	240	<0.01	<10	<0.01	0.1	0.02	<1	<0.2	0.50	<0.05
42	0.7	<10	10	<0.1	0.1	<0.3	123	<0.01	<10	<0.01	<0.04	0.18	1	<0.2	<0.03	0.19
44	0.2	<10	33	2.0	0.1	<0.3	434	<0.01	<10	<0.01	<0.04	1.96	<1	1.2	<0.03	<0.05
45	0.2	<10	2	0.6	0.3	<0.3	24	<0.01	<10	0.0	<0.04	0.13	8	6.2	0.39	1.31
46	0.3	<10	5	0.8	0.1	0.5	67	0.01	<10	<0.01	<0.04	0.04	<1	0.9	<0.03	0.06
47	1.7	<10	12	1.8	0.1	<0.3	248	<0.01	<10	<0.01	<0.04	0.59	1	3.2	0.03	<0.05

D.L.- Detection limit

Table A-7. Aqua regia extraction with ICP-MS results for sediment samples.

Sample no.	Ag ppm	Al %	As ppm	Au ppm	B ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Ce ppm	Co ppm	Cr ppm	Cs ppm	Cu ppm	Fe %	Ga ppm	Ge ppm
D.L.	0.01	0.01	0.1	0.2	10	10	0.05	0.01	0.01	0.01	0.0	0.1	1	0.05	0.2	0.01	0.05	0.05
01	0.08	1.80	12.2	<0.2	<10	100	0.29	0.09	1.43	0.18	17.9	13.5	47	0.92	35.6	3.02	5.93	0.07
03	0.07	1.63	7.5	<0.2	<10	110	0.26	0.07	1.32	0.18	15.9	12.3	41	0.72	31.8	2.78	5.53	0.08
04	0.09	1.97	9.1	<0.2	<10	130	0.32	0.10	1.49	0.20	20.3	14.4	46	1.04	38.0	3.14	6.31	0.08
05	0.08	1.98	6.3	<0.2	<10	120	0.28	0.10	1.18	0.18	16.4	13.7	38	0.94	38.4	3.12	6.01	0.07
06	0.06	1.28	7.0	<0.2	<10	60	0.16	0.06	0.87	0.12	8.4	6.6	19	0.33	19.0	2.00	4.33	0.06
07	0.05	1.09	6.4	<0.2	<10	60	0.17	0.05	0.91	0.10	9.0	6.5	25	0.33	16.2	1.72	3.79	0.06
08	0.10	2.41	8.7	<0.2	<10	140	0.33	0.13	1.16	0.19	19.0	16.9	44	1.20	48.2	3.67	7.09	0.08
09	0.09	2.17	7.8	<0.2	<10	130	0.31	0.13	1.27	0.19	17.8	15.4	42	1.07	42.4	3.39	6.47	0.08
10	0.08	1.94	7.6	<0.2	<10	100	0.35	0.10	1.24	0.16	17.4	15.0	46	1.06	38.8	3.16	6.43	0.08
11	0.04	1.27	3.7	<0.2	<10	60	0.17	0.04	0.46	0.08	8.8	5.9	18	0.35	15.3	1.71	3.85	0.05
12	0.09	1.74	6.6	<0.2	<10	120	0.29	0.08	1.49	0.21	19.2	13.7	45	0.86	36.4	3.00	5.87	0.09
13	0.09	1.80	6.5	<0.2	<10	120	0.27	0.08	1.46	0.20	18.9	13.8	46	0.90	54.1	3.01	5.71	0.08
14	0.07	1.50	5.9	<0.2	<10	110	0.25	0.06	1.36	0.18	16.4	12.1	41	0.72	29.7	2.56	5.12	0.08
15	0.04	1.04	6.5	<0.2	<10	70	0.16	0.06	1.01	0.12	11.3	7.1	29	0.39	17.9	1.70	3.49	0.05
16	0.13	4.03	13.6	<0.2	10	220	0.52	0.22	1.10	0.24	22.6	25.6	66	2.38	77.9	5.11	11.9	0.11
17	0.14	3.69	9.7	<0.2	10	200	0.46	0.21	1.00	0.20	22.1	22.6	57	2.04	65.3	4.85	10.75	0.10
18	0.11	3.00	9.5	<0.2	<10	180	0.37	0.16	1.24	0.17	19.7	19.9	52	1.55	55.0	4.12	8.61	0.09
19	0.14	3.11	9.9	<0.2	10	140	0.44	0.18	0.93	0.16	21.9	20.9	51	1.75	60.4	4.32	9.48	0.10
20	0.11	2.84	9.3	<0.2	<10	140	0.42	0.14	1.51	0.16	22.8	19.9	60	1.53	55.3	4.12	8.88	0.09
21	0.09	2.75	9.0	<0.2	<10	140	0.38	0.15	1.33	0.18	21.8	17.4	52	1.58	53.0	3.80	8.21	0.08
22	0.06	1.67	5.7	<0.2	<10	90	0.23	0.08	1.09	0.10	17.3	9.7	31	0.69	26.1	2.62	5.09	0.06
23	0.08	2.22	7.3	<0.2	<10	150	0.3	0.10	1.13	0.14	18.8	13.3	36	0.99	38.3	3.06	6.75	0.07
24	0.06	1.94	4.1	<0.2	<10	110	0.25	0.08	0.99	0.13	17.7	10.6	34	0.77	27.9	2.67	5.88	0.06
25	0.07	2.34	5.0	<0.2	<10	140	0.31	0.10	1.02	0.11	19.0	13.2	94	0.96	33.8	3.04	6.66	0.07
26	0.09	2.21	6.7	<0.2	<10	130	0.31	0.11	1.21	0.19	17.9	15.3	41	1.07	43.5	3.35	6.61	0.08
27	0.05	1.21	5.0	<0.2	<10	70	0.18	0.05	0.85	0.12	11.3	8.2	25	0.47	21.7	2.04	3.94	0.06
28	0.10	2.12	6.4	<0.2	<10	120	0.29	0.11	1.19	0.18	17.4	14.6	39	1.01	40.8	3.19	6.27	0.08
29	0.09	2.10	8.6	<0.2	<10	120	0.35	0.11	1.39	0.18	19.9	15.7	49	1.17	41.1	3.28	6.41	0.09
30	0.10	2.55	8.8	<0.2	<10	140	0.39	0.13	1.37	0.20	21.4	17.9	54	1.44	48.9	3.74	7.78	0.09

D.L.- Detection limit

Table A-8. Aqua regia extraction with ICP-MS results for sediment samples (continued).

Sample no.	Hf ppm	Hg ppm	In ppm	K %	La ppm	Li ppm	Mg %	Mn ppm	Mo ppm	Na %	Nb ppm	Ni ppm	P ppm	Pb ppm	Rb ppm	Re ppm	S %	Sb ppm
D.L.	0.02	0.01	0.01	0.01	0.2	0.1	0.0	5	0.1	0.0	0.1	0.2	10	0.2	0.1	0.001	0.01	0.05
01	0.35	0.04	0.03	0.24	8.6	14.6	1.2	541	0.8	0.1	0.2	46.5	830	4.9	9.9	0.001	0.09	0.39
03	0.31	0.03	0.03	0.19	7.5	12.7	1.0	480	0.8	0.1	0.2	40.1	730	3.8	8.1	0.001	0.12	0.34
04	0.39	0.04	0.03	0.24	9.6	17.1	1.2	593	0.8	0.1	0.2	47.1	810	4.6	11.0	0.001	0.07	0.41
05	0.33	0.03	0.03	0.25	7.8	15.6	1.2	562	0.7	0.1	0.1	37.3	750	4.8	10.9	0.001	0.10	0.31
06	0.16	0.02	0.02	0.11	3.8	9.3	0.7	382	0.6	0.1	0.2	15.8	470	2.7	4.2	0.001	0.18	0.27
07	0.16	0.02	0.01	0.11	4.1	8.5	0.6	300	0.6	0.1	0.2	25.4	390	2.2	4.1	<0.001	0.09	0.25
08	0.39	0.04	0.03	0.34	9.0	19.6	1.5	678	0.7	0.1	0.1	45.3	830	6.0	13.9	0.001	0.07	0.31
09	0.34	0.04	0.03	0.28	8.5	17.5	1.3	611	0.8	0.1	0.1	43.1	810	5.3	12.0	0.001	0.08	0.32
10	0.35	0.04	0.03	0.25	8.3	17.0	1.3	573	0.8	0.1	0.2	49.4	700	4.5	11.1	0.001	0.08	0.37
11	0.16	0.02	0.01	0.10	4.1	8.5	0.6	289	0.3	0.1	0.1	15.9	390	2.2	4.1	<0.001	0.01	0.19
12	0.37	0.03	0.03	0.21	9.2	14.3	1.1	552	0.9	0.1	0.2	45.8	840	4.3	9.3	0.001	0.08	0.38
13	0.37	0.04	0.03	0.21	9.0	15.0	1.2	554	0.8	0.1	0.2	46.3	840	5.2	9.7	0.001	0.09	0.37
14	0.34	0.03	0.02	0.17	7.7	11.4	1.0	465	0.8	0.1	0.2	45.3	710	3.4	7.7	0.001	0.09	0.34
15	0.22	0.02	0.02	0.11	5.2	8.3	0.7	302	0.6	0.1	0.2	31.0	470	2.6	4.3	<0.001	0.07	0.26
16	0.34	0.06	0.06	0.67	10.6	36.2	2.4	957	1.2	0.8	0.1	68.8	770	10.0	24.8	0.002	0.09	0.44
17	0.33	0.05	0.05	0.61	10.4	32.3	2.2	892	1.2	0.7	0.1	56.4	840	9.6	22.8	0.002	0.08	0.41
18	0.32	0.04	0.04	0.49	9.3	26.4	1.8	803	1.0	0.6	0.1	56.4	820	7.1	18.7	0.002	0.09	0.37
19	0.38	0.06	0.04	0.52	10.3	29.6	1.9	730	1.7	0.6	0.3	51.7	830	8.3	21.6	0.002	0.41	0.37
20	0.38	0.05	0.04	0.43	10.8	24.5	1.8	765	1.1	0.4	0.2	62.8	890	6.7	17.5	0.001	0.08	0.43
21	0.32	0.04	0.04	0.41	10.3	23.5	1.6	724	1.0	0.3	0.2	48.5	860	6.7	17.4	0.001	0.07	0.44
22	0.26	0.02	0.02	0.20	8.3	11.2	0.8	424	0.6	0.2	0.2	25.1	690	3.5	9.0	0.001	0.05	0.27
23	0.28	0.03	0.03	0.27	9.0	16.1	1.0	549	0.8	0.2	0.2	32.8	670	4.6	12.2	0.001	0.04	0.35
24	0.26	0.02	0.02	0.24	8.6	12.5	0.8	485	1.1	0.2	0.2	24.3	620	3.9	10.7	<0.001	0.04	0.28
25	0.3	0.02	0.03	0.28	9.1	16.1	1.1	598	5.9	0.2	0.2	30.1	660	5.0	13.2	0.001	0.04	0.23
26	0.36	0.05	0.03	0.28	8.4	17.6	1.3	607	0.7	0.1	0.1	41.4	800	5.2	12.2	0.001	0.09	0.30
27	0.21	0.02	0.02	0.15	5.2	8.8	0.7	323	0.6	0.1	0.2	24.7	480	2.6	5.6	0.001	0.12	0.24
28	0.32	0.04	0.03	0.26	8.3	16.3	1.3	587	0.7	0.1	0.1	39.7	790	5.2	11.5	0.001	0.09	0.30
29	0.38	0.04	0.03	0.27	9.5	18.7	1.4	620	0.9	0.2	0.1	52.0	810	5.1	11.8	0.001	0.09	0.39
30	0.39	0.04	0.04	0.35	10.1	22.5	1.6	704	0.9	0.2	0.1	57.1	830	5.9	14.9	0.001	0.10	0.42

D.L.- Detection limit

Table A-9. Aqua regia extraction with ICP-MS results for sediment samples (continued).

Sample no.	Sc ppm	Se ppm	Sn ppm	Sr ppm	Ta ppm	Te ppm	Th ppm	Ti %	Tl ppm	U ppm	V ppm	W ppm	Y ppm	Zn ppm	Zr ppm
D.L.	0.1	0.2	0.2	0.2	0.01	0.01	0.2	0.005	0.02	0.05	1	0.05	0.05	2	0.5
01	6.8	0.4	0.5	72.2	<0.01	0.02	2.1	0.154	0.11	0.59	70	0.15	9.86	69	14.3
03	6.3	0.5	0.4	68.0	<0.01	0.02	1.8	0.145	0.09	0.74	67	0.12	9.46	57	12.7
04	7.4	0.4	0.5	81.1	<0.01	0.02	2.1	0.162	0.11	0.52	72	0.10	11.05	71	15.9
05	6.8	0.4	0.4	67.4	<0.01	0.03	2.1	0.144	0.10	0.54	72	0.08	9.55	70	13.7
06	4.0	0.3	0.3	40.8	<0.01	0.02	0.9	0.100	0.05	0.24	47	0.14	5.86	42	5.2
07	4.0	0.2	0.3	43.2	<0.01	0.01	0.9	0.098	0.05	0.26	44	0.14	5.81	32	5.8
08	8.1	0.4	0.5	73.2	<0.01	0.03	2.5	0.165	0.13	0.59	82	0.10	10.70	88	16.7
09	7.4	0.4	0.5	71.4	<0.01	0.04	2.3	0.149	0.12	0.60	76	0.09	10.05	78	15.1
10	7.3	0.4	0.5	63.6	<0.01	0.03	2.0	0.141	0.11	0.48	71	0.08	9.40	71	15.2
11	3.9	0.2	0.2	38.5	<0.01	0.01	1.0	0.091	0.05	0.29	42	0.10	5.68	35	5.4
12	6.8	0.4	0.5	75.9	<0.01	0.02	2.0	0.168	0.11	0.60	72	0.09	10.55	66	15.6
13	6.9	0.4	0.5	76.2	<0.01	0.02	2.0	0.162	0.10	0.58	70	0.09	10.35	77	15.2
14	5.9	0.4	0.4	72.1	<0.01	0.02	1.7	0.138	0.09	0.58	60	0.12	9.14	54	14.1
15	4.1	0.2	0.3	54.8	<0.01	0.01	1.2	0.100	0.06	0.39	43	0.32	6.17	36	7.6
16	13.9	0.5	0.8	85.4	<0.01	0.06	3.3	0.200	0.21	0.90	112	0.09	13.45	142	15.5
17	12.4	0.4	0.7	78.2	<0.01	0.06	3.3	0.203	0.19	0.82	105	0.11	13.00	132	14.9
18	10.1	0.4	0.6	76.7	<0.01	0.04	2.7	0.183	0.16	0.68	91	0.11	11.40	108	14.7
19	11.1	0.6	0.6	70.3	<0.01	0.06	2.9	0.183	0.15	1.00	96	0.11	12.75	114	16.6
20	10.4	0.5	0.6	77.7	<0.01	0.03	2.9	0.185	0.15	0.64	92	0.09	12.65	103	17.6
21	9.7	0.5	0.6	77.2	<0.01	0.03	3.0	0.185	0.15	0.73	93	0.13	11.80	95	13.1
22	5.9	0.3	0.4	71.9	<0.01	0.01	2.1	0.146	0.08	0.60	70	0.12	9.17	47	9.7
23	6.9	0.3	0.5	82.5	<0.01	0.02	2.5	0.159	0.12	0.60	73	0.12	9.64	64	11.2
24	6.0	0.2	0.5	72.3	<0.01	0.01	2.3	0.147	0.11	0.55	66	0.10	8.68	52	10.0
25	7.1	0.2	0.5	80.4	<0.01	0.02	2.8	0.155	0.13	0.59	71	0.09	9.45	67	12.1
26	7.4	0.4	0.4	72.5	<0.01	0.03	2.2	0.155	0.11	0.61	77	0.09	10.15	78	15.1
27	4.2	0.3	0.3	49.8	<0.01	0.02	1.4	0.103	0.07	0.39	52	0.09	6.23	40	8.1
28	7.1	0.4	0.5	70.5	<0.01	0.03	2.4	0.150	0.11	0.59	76	0.08	9.92	75	14.0
29	7.8	0.4	0.5	72.2	<0.01	0.02	2.3	0.157	0.12	0.58	76	0.09	10.75	77	16.0
30	9.1	0.5	0.6	75.1	<0.01	0.03	2.5	0.168	0.13	0.65	85	0.09	11.65	92	17.3

D.L.- Detection limit

Table A-10. Four acids extraction with ICP-MS results for sediment samples.

Sample no.	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Ce ppm	Co ppm	Cr ppm	Cs ppm	Cu ppm	Fe %	Ga ppm	Ge ppm	Hf ppm	In ppm
D.L.	0.01	0.01	0.2	10	0.05	0.01	0.01	0.02	0.01	0.1	1	0.05	0.2	0.01	0.05	0.05	0.1	0.005
01	0.08	7.50	13.4	540	1.03	0.10	3.36	0.22	33.4	18.1	89	1.84	37.1	4.08	18.10	0.10	1.5	0.057
03	0.08	7.24	7.9	510	0.87	0.08	3.27	0.22	30.3	15.8	87	1.38	31.6	3.83	16.50	0.12	1.3	0.048
04	0.12	7.53	10.9	580	0.99	0.10	3.19	0.27	33.6	18.9	82	2.07	40.8	4.06	19.40	0.13	1.6	0.057
05	0.08	7.76	6.4	550	0.84	0.10	3.18	0.20	29.4	16.4	68	1.76	37.0	4.20	17.15	0.09	1.3	0.050
06	0.06	7.00	8.6	500	0.83	0.06	2.72	0.16	21.3	10.0	39	0.85	20.3	2.98	15.25	0.07	0.8	0.044
07	0.07	6.64	9.6	470	0.89	0.06	2.64	0.15	22.3	10.0	56	0.89	17.1	2.58	14.85	0.09	0.9	0.036
08	0.11	7.94	9.9	580	1.11	0.13	2.98	0.23	32.6	21.0	73	2.39	50.5	4.77	19.75	0.11	1.6	0.061
09	0.10	7.92	9.0	570	1.09	0.11	3.21	0.22	33.6	20.0	72	2.30	46.2	4.55	19.60	0.10	1.5	0.061
10	0.10	7.73	7.9	550	1.15	0.09	2.93	0.18	31.4	18.1	83	2.20	40.5	4.10	18.10	0.11	1.5	0.053
11	0.05	6.89	5.0	490	0.76	0.04	2.22	0.11	19.1	8.2	35	0.87	16.2	2.42	14.75	0.07	0.7	0.033
12	0.09	7.46	7.3	560	1.04	0.08	3.34	0.22	33.9	17.8	84	1.78	36.4	3.98	18.45	0.09	1.6	0.055
13	0.08	7.63	7.4	570	1.05	0.08	3.39	0.23	35.1	18.2	89	1.84	37.3	4.14	18.35	0.10	1.7	0.052
14	0.10	7.40	6.2	550	0.98	0.06	3.41	0.22	32.5	16.3	88	1.46	31.6	3.62	17.60	0.10	1.4	0.048
15	0.07	6.95	8.5	500	0.99	0.05	2.96	0.16	24.0	11.3	63	0.98	18.3	2.57	15.90	0.08	1.0	0.035
16	0.14	9.05	17.2	700	1.20	0.20	1.99	0.27	27.9	29.3	78	4.98	85.4	6.02	25.10	0.12	1.6	0.078
17	0.15	9.00	12.2	700	1.33	0.19	2.13	0.24	31.9	26.5	73	4.15	70.5	5.76	24.10	0.12	1.5	0.072
18	0.13	8.58	11.4	650	1.17	0.15	2.78	0.21	31.0	24.0	75	3.16	59.4	5.22	21.90	0.13	1.4	0.063
19	0.17	8.43	11.6	620	1.20	0.16	2.20	0.19	32.3	24.6	73	3.67	65.1	5.28	22.50	0.13	1.6	0.067
20	0.13	8.18	11.4	610	1.16	0.14	2.91	0.20	34.0	23.4	87	3.17	58.2	5.11	21.40	0.12	1.8	0.067
21	0.17	8.20	12.0	630	1.07	0.15	2.97	0.27	25.3	19.5	78	2.51	60.2	4.91	21.60	0.12	1.5	0.062
22	0.05	7.24	6.6	500	0.91	0.07	3.12	0.11	30.0	12.1	59	1.15	23.9	3.55	14.90	0.09	1.0	0.042
23	0.08	7.49	8.0	590	1.07	0.09	2.87	0.18	32.0	16.3	59	1.85	37.0	3.84	17.95	0.09	1.3	0.047
24	0.07	7.60	5.6	580	1.04	0.08	2.96	0.15	33.6	14.1	57	1.45	28.6	3.65	17.35	0.09	1.3	0.045
25	0.08	7.85	6.6	630	1.19	0.09	2.90	0.14	33.6	17.5	86	1.92	36.5	4.10	18.95	0.09	1.5	0.054
26	0.11	8.02	7.9	570	1.08	0.11	3.17	0.24	34.5	20.1	72	2.26	44.6	4.43	19.95	0.11	1.5	0.058
27	0.06	7.31	5.9	490	0.80	0.06	3.03	0.17	27.7	12.6	55	1.09	23.6	3.15	16.20	0.09	1.0	0.042
28	0.11	8.02	8.3	570	1.01	0.17	3.23	0.24	34.3	19.4	71	2.10	43.2	4.42	19.15	0.11	1.5	0.060
29	0.10	7.69	9.7	580	0.99	0.10	3.14	0.22	36.0	19.5	88	2.33	43.6	4.42	18.55	0.11	1.7	0.054
30	0.11	8.12	10.6	610	1.16	0.12	2.92	0.25	33.2	22.1	86	2.73	52.3	4.78	20.20	0.15	1.7	0.061

D.L.- Detection limit

Table A-11. Four acids extraction with ICP-MS results for sediment samples (continued).

Sample	K	La	Li	Mg	Mn	Mo	Na	Nb	Ni	P	Pb	Rb	Re	S	Sb	Sc	Se	Sn
no.	%	ppm	ppm	%	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm
D.L.	0.01	0.5	0.2	0.01	5	0.05	0.01	0.1	0.2	10	0.5	0.1	0.002	0.01	0.05	0.1	1	0.2
01	1.16	14.9	22.5	1.72	786	1.05	2.27	7.0	52.6	870	8.1	33.9	0.002	0.08	1.00	17.0	1	1.0
03	1.03	13.8	17.1	1.54	747	0.91	2.24	6.1	43.5	750	6.8	31.1	0.002	0.10	0.81	16.7	1	0.9
04	1.21	15.0	22.7	1.73	797	1.07	2.27	7.7	54.6	860	8.1	37.7	0.002	0.06	0.97	18.0	1	1.1
05	1.13	13.1	19.5	1.68	839	0.87	2.19	5.5	38.8	790	7.5	31.6	0.002	0.09	0.79	16.3	1	1.0
06	0.93	9.7	14.4	1.06	668	0.79	2.43	3.5	20.0	530	5.7	24.8	0.002	0.17	1.05	13.7	1	0.7
07	0.87	10.4	15.0	1.01	529	0.69	2.35	3.4	30.2	430	5.5	25.8	<0.002	0.08	0.73	12.3	1	0.6
08	1.26	14.3	26.0	1.98	933	0.97	2.03	6.3	49.8	880	9.6	36.4	0.002	0.06	0.88	18.8	1	1.1
09	1.22	15.0	24.5	1.88	883	1.13	2.11	6.4	49.4	850	8.5	37.3	0.002	0.08	0.93	18.7	1	1.1
10	1.22	14.4	24.3	1.78	794	0.96	2.15	6.2	53.7	750	7.7	40.0	<0.002	0.06	0.95	16.4	1	1.0
11	0.92	8.9	12.4	0.85	502	0.35	2.46	3.0	17.9	420	5.3	24.3	<0.002	<0.01	0.63	11.2	1	0.6
12	1.14	15.3	21.4	1.64	771	1.06	2.33	7.8	51.1	880	7.6	34.3	0.002	0.07	0.96	16.8	1	1.1
13	1.16	16.1	21.9	1.75	799	1.05	2.33	7.5	53.7	890	7.6	36.2	0.002	0.08	0.98	16.8	1	1.1
14	1.06	15.1	18.1	1.56	708	1.00	2.31	6.6	51.4	770	7.1	32.2	0.002	0.08	0.91	15.8	1	0.9
15	0.95	11.3	14.6	1.12	519	0.78	2.46	4.3	36.8	520	6.0	28.4	<0.002	0.06	0.76	12.6	1	0.7
16	1.84	11.9	49.8	2.75	1100	1.38	2.36	6.5	74.4	820	12.2	53.8	0.003	0.08	1.41	22.3	1	1.4
17	1.73	14.2	43.2	2.57	1060	1.49	2.35	6.4	62.5	870	11.7	57.2	0.003	0.07	1.15	22.0	1	1.3
18	1.49	13.8	34.2	2.27	1020	1.14	2.48	6.1	62.2	860	10.2	46.5	0.002	0.08	1.03	19.8	1	1.2
19	1.59	14.2	38.2	2.30	921	1.95	2.32	6.7	57.3	890	11.2	53.4	0.003	0.39	1.07	21.0	1	1.3
20	1.46	15.0	33.5	2.22	950	1.31	2.18	7.7	67.9	930	9.2	47.2	0.002	0.07	1.18	19.8	1	1.3
21	1.41	10.8	30.8	2.08	987	1.20	2.24	6.3	55.6	910	16.9	35.6	0.002	0.06	1.29	19.8	2	1.2
22	0.99	13.9	13.2	1.22	694	0.65	2.33	4.9	26.1	720	6.6	26.8	<0.002	0.04	0.67	14.4	1	0.8
23	1.19	14.4	20.9	1.40	783	0.97	2.15	5.7	34.9	690	7.9	36.8	0.002	0.03	0.88	16.1	1	1.1
24	1.18	15.5	17.1	1.27	772	1.62	2.35	5.4	27.5	680	7.8	34.2	0.002	0.03	0.78	15.2	1	0.9
25	1.27	15.0	21.9	1.50	876	4.13	2.22	6.6	34.2	720	8.5	38.9	0.002	0.03	0.76	16.6	1	1.1
26	1.20	15.5	24.1	1.83	873	0.96	2.12	6.4	47.8	840	8.9	38.7	0.002	0.07	0.92	19.3	1	1.1
27	0.97	13.0	14.0	1.16	629	0.66	2.43	4.2	29.6	520	6.5	27.3	0.002	0.11	0.72	14.1	1	0.8
28	1.19	15.6	22.5	1.78	873	0.95	2.18	6.3	45.2	820	8.6	36.2	0.002	0.08	0.90	18.7	1	1.1
29	1.26	16.0	25.2	1.89	856	1.17	2.23	7.3	58.6	870	8.1	36.5	<0.002	0.07	1.01	17.4	1	1.1
30	1.38	14.8	28.0	2.05	909	1.18	2.14	7.3	63.7	880	8.6	43.9	<0.002	0.10	1.06	20.0	1	1.1

D.L.- Detection limit

Table A-12. Four acids extraction with ICP-MS results for sediment samples (continued).

Sample	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y	Zn	Zr
no.	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
D.L.	0.2	0.05	0.05	0.2	0.005	0.02	0.1	1	0.1	0.1	2	0.5
01	408	0.46	0.05	3.1	0.455	0.26	1.2	124	1.1	16.9	84	50.4
03	389	0.40	<0.05	2.7	0.426	0.22	1.0	119	0.7	16.8	71	42.9
04	392	0.51	<0.05	3.2	0.453	0.27	1.0	123	0.8	18.0	86	58.3
05	392	0.37	0.05	2.6	0.421	0.22	1.0	127	1.0	16.7	87	41.4
06	360	0.24	<0.05	1.7	0.298	0.18	0.7	93	0.9	14.5	56	26.0
07	373	0.24	<0.05	1.8	0.272	0.19	0.8	82	1.0	12.7	44	27.2
08	374	0.44	0.06	3.2	0.452	0.28	1.2	140	1.1	18.2	104	50.8
09	387	0.44	0.05	3.1	0.449	0.27	1.1	135	1.1	18.8	96	51.7
10	373	0.41	<0.05	2.8	0.402	0.25	1.0	121	1.0	16.6	86	50.4
11	361	0.21	<0.05	1.5	0.246	0.18	0.6	77	0.8	12.2	45	23.4
12	410	0.51	<0.05	2.9	0.472	0.24	1.1	122	1.0	17.5	83	55.5
13	414	0.50	<0.05	3.0	0.471	0.25	1.1	125	1.1	17.8	84	55.6
14	428	0.44	<0.05	2.7	0.426	0.21	1.2	113	1.0	16.4	71	49.3
15	427	0.30	<0.05	1.9	0.290	0.20	0.9	80	1.2	13.3	47	32.9
16	292	0.43	0.08	3.3	0.442	0.43	1.4	165	1.3	17.3	157	53.0
17	317	0.42	0.09	3.6	0.451	0.43	1.2	162	1.4	18.7	144	49.7
18	356	0.40	0.07	3.3	0.439	0.33	1.1	150	1.2	17.8	124	46.4
19	318	0.45	0.08	3.5	0.442	0.33	1.4	154	1.1	19.1	129	54.8
20	345	0.52	0.05	3.4	0.472	0.32	1.1	147	1.2	18.7	117	60.6
21	377	0.46	0.07	2.7	0.460	0.33	1.1	151	0.8	18.5	110	49.7
22	403	0.34	<0.05	2.8	0.361	0.17	1.0	108	0.9	15.6	61	31.6
23	381	0.38	<0.05	3.2	0.365	0.25	1.1	115	0.9	16.0	75	39.3
24	398	0.39	<0.05	3.3	0.356	0.23	1.1	108	1.0	15.9	67	38.2
25	403	0.45	<0.05	3.5	0.386	0.27	1.2	117	1.0	16.9	83	47.7
26	391	0.42	<0.05	3.3	0.435	0.28	1.2	131	1.1	19.3	92	49.4
27	416	0.29	<0.05	2.3	0.333	0.19	0.8	98	0.8	14.7	56	30.9
28	399	0.45	0.07	3.3	0.431	0.26	1.1	132	1.0	19.0	92	47.5
29	387	0.48	<0.05	3.7	0.457	0.27	1.1	128	0.9	17.0	94	55.3
30	371	0.48	0.07	3.3	0.455	0.30	1.2	140	0.8	18.2	109	58.4

D.L.- Detection limit

Table A-13. Lithium metaborate/lithium tetraborate fusion with ICP-AES whole rock analysis and loss on ignition results for sediment samples.

Sample no.	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	Cr_2O_3 %	TiO_2 %	MnO %	P_2O_5 %	SrO %	BaO %	LOI %
D.L.	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
01	62.4	14.35	6.03	4.76	2.92	3.22	1.38	0.02	0.81	0.11	0.20	0.05	0.07	4.91
03	64.1	13.65	5.66	4.68	2.64	3.22	1.22	0.02	0.77	0.10	0.17	0.05	0.06	3.49
04	60.8	14.65	6.00	4.56	2.95	3.23	1.46	0.02	0.80	0.11	0.20	0.05	0.07	3.71
05	61.0	14.85	6.23	4.54	2.85	3.11	1.34	0.01	0.76	0.12	0.20	0.05	0.07	4.70
06	69.0	13.35	4.29	3.84	1.80	3.50	1.11	0.01	0.52	0.09	0.10	0.04	0.06	1.61
07	70.3	12.30	3.66	3.61	1.72	3.35	1.03	0.01	0.47	0.07	0.10	0.04	0.06	1.40
08	57.9	15.40	7.07	4.25	3.38	2.89	1.54	0.01	0.81	0.13	0.20	0.04	0.07	5.59
09	58.8	15.00	6.58	4.51	3.14	2.98	1.44	0.01	0.79	0.12	0.19	0.04	0.07	5.08
10	62.8	14.55	6.01	4.13	2.98	3.10	1.46	0.02	0.71	0.11	0.16	0.04	0.07	4.80
11	71.7	13.55	3.49	3.13	1.43	3.55	1.10	0.01	0.43	0.07	0.09	0.04	0.06	0.50
12	61.6	14.40	5.93	4.79	2.81	3.35	1.39	0.02	0.84	0.11	0.19	0.05	0.07	4.09
13	61.4	14.35	5.98	4.78	2.91	3.29	1.38	0.02	0.83	0.11	0.19	0.05	0.07	4.91
14	63.2	13.70	5.25	4.75	2.64	3.28	1.25	0.02	0.75	0.10	0.16	0.05	0.07	4.37
15	69.8	12.85	3.65	4.06	1.91	3.48	1.12	0.01	0.52	0.07	0.11	0.05	0.06	2.42
16	50.5	17.45	8.56	2.86	4.63	3.20	2.25	0.01	0.75	0.15	0.18	0.04	0.09	10.00
17	53.8	17.30	8.45	3.04	4.31	3.34	2.09	0.01	0.78	0.14	0.18	0.04	0.08	7.50
18	55.1	16.15	7.48	3.86	3.76	3.47	1.78	0.01	0.76	0.14	0.18	0.04	0.08	6.61
19	55.4	16.15	7.68	3.08	3.86	3.27	1.90	0.01	0.76	0.12	0.18	0.04	0.07	7.41
20	56.1	15.45	7.42	4.07	3.75	3.08	1.76	0.02	0.82	0.13	0.21	0.04	0.07	6.59
21	58.2	15.55	7.05	4.17	3.40	3.14	1.70	0.01	0.79	0.13	0.19	0.04	0.07	4.70
22	65.5	14.00	5.20	4.44	2.12	3.47	1.22	0.01	0.66	0.10	0.16	0.05	0.06	4.00
23	62.8	14.75	5.75	4.13	2.45	3.20	1.48	0.01	0.67	0.11	0.14	0.05	0.07	4.91
24	64.2	14.20	5.15	4.03	2.10	3.28	1.38	0.02	0.61	0.10	0.14	0.05	0.07	3.30
25	62.0	14.95	5.93	4.05	2.56	3.01	1.50	0.01	0.70	0.12	0.15	0.05	0.07	3.70
26	59.7	14.95	6.53	4.50	3.10	2.92	1.39	0.01	0.80	0.12	0.17	0.05	0.07	5.36
27	69.0	13.70	4.55	4.25	1.98	3.37	1.13	0.01	0.62	0.08	0.11	0.05	0.06	1.91
28	59.8	14.75	6.41	4.49	3.00	2.91	1.35	0.01	0.79	0.12	0.17	0.05	0.07	4.56
29	59.3	14.45	6.51	4.41	3.23	2.96	1.46	0.02	0.83	0.12	0.18	0.05	0.07	4.10
30	57.2	14.65	6.72	3.96	3.38	2.80	1.55	0.02	0.79	0.12	0.18	0.04	0.07	6.38

D.L.- Detection limit

Table A-14. Lithium metaborate fusion with ICP-MS results for sediment samples

Sample no.	Ag ppm	Ba ppm	Ce ppm	Co ppm	Cr ppm	Cs ppm	Cu ppm	Dy ppm	Er ppm	Eu ppm	Ga ppm	Gd ppm	Hf ppm	Ho ppm	La ppm	Lu ppm
D.L.	1	0.5	0.5	0.5	10	0.01	5	0.05	0.03	0.03	0.1	0.05	0.2	0.01	0.5	0.01
01	<1	582	34.8	17.8	110	1.62	39	3.73	2.25	1.16	17.4	3.91	3.4	0.76	17.2	0.32
03	<1	539	31.3	15.4	110	1.25	32	3.55	2.18	1.05	15.6	3.67	3.5	0.77	15.4	0.31
04	<1	629	33.3	18.1	100	1.80	40	3.72	2.20	1.12	17.7	3.85	3.1	0.76	16.2	0.32
05	<1	555	29.4	16.5	80	1.62	38	3.61	2.21	1.03	16.1	3.79	3.7	0.73	14.3	0.34
06	<1	516	23.2	9.3	50	0.75	22	2.97	1.85	0.88	14.1	2.78	2.4	0.63	11.6	0.28
07	<1	464	17.9	8.9	80	0.70	17	2.27	1.47	0.73	12.7	2.23	2.1	0.48	8.6	0.23
08	<1	605	33.2	20.6	90	2.14	52	3.83	2.36	1.12	18.5	3.97	3.2	0.78	16.1	0.34
09	<1	589	32.8	19.0	90	1.91	45	3.68	2.26	1.12	17.4	3.85	3.0	0.75	15.9	0.32
10	<1	575	30.1	18.4	110	1.94	42	3.60	2.24	1.07	17.4	3.67	2.9	0.73	15.0	0.34
11	<1	506	20.2	7.9	40	0.79	17	2.43	1.53	0.82	14.0	2.39	2.0	0.52	10.2	0.23
12	<1	611	34.1	17.5	110	1.54	39	3.73	2.19	1.16	17.0	3.93	3.1	0.74	16.8	0.32
13	<1	586	32.6	17.0	100	1.53	37	3.55	2.16	1.12	16.2	3.61	3.2	0.73	16.0	0.30
14	<1	480	25.4	12.9	90	1.02	27	2.82	1.73	0.89	13.3	2.87	2.7	0.58	12.5	0.24
15	<1	514	23.6	9.7	80	0.79	19	2.51	1.52	0.81	13.4	2.58	2.3	0.51	11.7	0.22
16	<1	728	30.5	27.6	90	4.14	84	3.77	2.34	1.05	22.9	3.76	2.8	0.79	15.0	0.36
17	<1	712	30.7	24.4	80	3.38	68	3.79	2.31	1.06	20.7	3.81	2.7	0.81	14.7	0.36
18	<1	666	30.1	21.8	90	2.63	57	3.59	2.26	1.06	19.3	3.65	2.6	0.74	14.5	0.33
19	<1	650	33.2	22.9	90	3.03	63	3.93	2.42	1.10	19.9	4.05	2.9	0.82	16.3	0.36
20	<1	642	34.5	22.5	100	2.82	59	3.96	2.43	1.19	19.9	4.03	3.1	0.82	17.1	0.35
21	<1	645	34.5	20.4	90	2.53	55	4.06	2.47	1.16	19.3	4.01	3.0	0.84	17.0	0.37
22	<1	525	32.8	12.6	80	1.13	28	3.57	2.24	1.05	15.3	3.54	3.7	0.74	16.1	0.34
23	<1	587	30.1	14.3	60	1.46	35	3.21	1.92	0.97	14.9	3.31	2.9	0.64	14.9	0.30
24	<1	590	32.5	13.2	110	1.25	29	3.26	2.01	1.04	15.8	3.35	3.3	0.69	16.0	0.30
25	<1	618	31.5	16.1	100	1.62	36	3.29	2.06	0.98	16.9	3.52	3.2	0.69	15.5	0.31
26	<1	574	30.0	18.7	90	1.88	44	3.62	2.25	1.08	17.5	3.98	3.4	0.74	14.2	0.34
27	<1	495	24.4	11.8	80	0.99	22	2.74	1.71	0.90	14.7	2.93	3.3	0.59	11.9	0.25
28	<1	538	28.5	17.2	90	1.69	39	3.41	2.08	1.03	16.3	3.61	3.1	0.70	13.7	0.30
29	<1	601	34.2	19.8	110	2.09	44	3.72	2.22	1.12	17.8	4.09	3.8	0.75	16.5	0.34
30	<1	592	30.4	20.3	100	2.36	48	3.55	2.19	1.05	17.9	3.86	3.3	0.72	14.8	0.31

D.L.- Detection limit

Table A-15. Lithium metaborate fusion with ICP-MS results for sediment samples (continued).

Sample no.	Mo ppm	Nb ppm	Nd ppm	Ni ppm	Pb ppm	Pr ppm	Rb ppm	Sm ppm	Sn ppm	Sr ppm	Ta ppm	Tb ppm	Th ppm	Tl ppm	Tm ppm	U ppm
D.L.	2	0.2	0.1	5	5	0.03	0.2	0.03	1	0.1	0.1	0.01	0.05	0.5	0.01	0.05
01	<2	7.7	17.1	61	8	4.47	35.7	3.80	1	414	0.5	0.64	3.41	<0.5	0.32	1.40
03	<2	6.7	16.0	54	7	3.98	29.9	3.60	1	399	0.4	0.59	3.18	<0.5	0.32	1.28
04	<2	7.6	17.0	59	8	4.34	38.2	3.76	1	403	0.5	0.62	3.39	<0.5	0.31	1.35
05	<2	5.9	15.2	43	8	3.85	31.7	3.42	1	374	0.4	0.59	3.07	<0.5	0.33	1.27
06	<2	3.6	11.4	23	7	2.94	24.2	2.61	1	370	0.2	0.46	2.14	<0.5	0.27	0.91
07	<2	3.4	9.2	31	6	2.32	22.7	2.06	1	368	0.2	0.36	1.69	<0.5	0.21	0.79
08	<2	6.7	16.9	57	9	4.30	39.4	3.84	1	381	0.4	0.65	3.75	<0.5	0.32	1.46
09	<2	6.7	17.1	53	8	4.24	36.6	3.86	1	384	0.4	0.62	3.38	<0.5	0.31	1.36
10	<2	6.7	15.4	61	8	3.91	38.6	3.40	1	379	0.4	0.60	3.25	<0.5	0.33	1.29
11	<2	3.1	10.5	22	5	2.67	24.4	2.25	<1	381	0.2	0.41	1.86	<0.5	0.22	0.84
12	<2	8.2	17.3	58	8	4.35	35.1	3.94	1	422	0.5	0.63	3.26	<0.5	0.30	1.40
13	<2	7.6	16.9	58	7	4.22	33.3	3.76	1	399	0.5	0.61	3.16	<0.5	0.30	1.34
14	<2	5.9	13.0	45	6	3.27	25.4	2.88	1	356	0.4	0.46	2.56	<0.5	0.24	1.16
15	<2	4.3	12.0	37	6	3.07	24.8	2.59	1	408	0.3	0.43	2.10	<0.5	0.22	0.95
16	<2	6.6	16.1	81	12	3.98	62.6	3.53	1	294	0.4	0.61	4.36	<0.5	0.32	1.70
17	<2	6.5	16.0	67	11	4.05	55.8	3.64	1	315	0.4	0.64	3.97	<0.5	0.33	1.48
18	<2	6.3	15.7	68	10	3.91	45.9	3.56	1	354	0.4	0.60	3.60	<0.5	0.31	1.35
19	2	6.7	17.1	61	10	4.31	52.7	3.91	1	323	0.4	0.66	4.21	<0.5	0.36	1.71
20	<2	8	18.0	74	9	4.49	48.9	4.00	1	352	0.5	0.64	3.99	<0.5	0.33	1.46
21	<2	7.2	17.5	59	10	4.48	47.1	4.05	1	369	0.4	0.66	4.04	<0.5	0.36	1.51
22	<2	5.8	16.2	33	7	4.21	28.7	3.59	1	406	0.4	0.59	3.25	<0.5	0.32	1.37
23	<2	5.8	14.9	36	7	3.77	34.4	3.23	1	360	0.4	0.53	3.55	<0.5	0.29	1.30
24	6	6.2	15.7	31	8	4.14	34.1	3.33	1	401	0.4	0.56	3.64	<0.5	0.28	1.30
25	3	6.5	16.2	40	8	4.02	42.4	3.40	1	375	0.4	0.58	3.66	<0.5	0.30	1.27
26	<2	6.3	16.3	54	8	3.97	37.9	3.73	1	369	0.4	0.63	3.18	<0.5	0.32	1.31
27	<2	4.4	12.9	36	6	3.19	27.2	2.78	1	400	0.3	0.48	2.30	<0.5	0.25	1.05
28	<2	5.9	15.5	49	7	3.74	34.7	3.55	1	351	0.4	0.60	2.91	<0.5	0.30	1.20
29	<2	7.8	18.2	68	8	4.45	42.4	3.94	1	368	0.5	0.65	3.51	<0.5	0.32	1.47
30	<2	7.3	16.5	69	9	4.00	44.9	3.66	1	335	0.5	0.62	3.34	<0.5	0.31	1.36

D.L.- Detection limit

Table A-16. Lithium metaborate fusion with ICP-MS results for sediment samples (continued).

Sample no.	V ppm	W ppm	Y ppm	Yb ppm	Zn ppm	Zr ppm
D.L.	5	1	0.5	0.03	5	2
01	137	2	20.9	2.03	96	123
03	130	2	19.9	2.01	84	124
04	136	2	20.4	2.01	97	111
05	133	2	20.2	2.11	92	136
06	101	2	16.4	1.73	64	87
07	87	2	13.3	1.39	53	74
08	153	2	21.9	2.17	117	112
09	143	2	20.6	2.01	106	108
10	137	2	20.2	2.04	96	107
11	84	1	14.1	1.45	55	67
12	139	2	20.8	1.94	98	111
13	132	2	19.6	2.01	94	113
14	102	2	15.3	1.62	68	93
15	86	2	14.0	1.39	55	80
16	182	2	21.1	2.22	161	94
17	170	2	21.1	2.25	150	93
18	156	2	20.3	2.05	127	93
19	163	2	22.0	2.22	137	105
20	159	2	22.4	2.15	127	110
21	158	2	22.6	2.19	116	106
22	120	2	20.2	2.08	71	137
23	114	2	17.3	1.86	79	102
24	115	2	18.4	1.94	76	115
25	117	2	17.9	1.96	80	110
26	138	2	19.5	2.07	93	118
27	103	2	15.0	1.66	56	118
28	129	2	18.2	1.93	91	107
29	138	2	19.9	2.07	94	137
30	138	2	19.2	1.98	100	119

D.L.- Detection limit

Table A-17. Total carbon and total sulphur by LECO furnace results for sediment samples.

Sample no.	C %	S %
D.L.	0.01	0.01
01	0.41	0.08
03	0.33	0.09
04	0.54	0.06
05	0.29	0.08
06	0.16	0.14
07	0.19	0.08
08	0.29	0.05
09	0.32	0.07
10	0.38	0.05
11	0.04	0.01
12	0.44	0.07
13	0.43	0.07
14	0.39	0.07
15	0.29	0.05
16	0.33	0.07
17	0.28	0.06
18	0.36	0.07
19	0.47	0.33
20	0.49	0.06
21	0.38	0.05
22	0.23	0.04
23	0.24	0.04
24	0.18	0.02
25	0.21	0.03
26	0.29	0.08
27	0.19	0.10
28	0.28	0.07
29	0.44	0.07
30	0.43	0.09

D.L.- Detection limit

Table A-18. Selected extraction results for sediment samples (see Section 3.2.2.3 for description of extraction steps).

Samp. no.	Step 1 (mg/kg)	Step 2 (mg/kg)	Step 3 (mg/kg)	Step 4 (mg/kg)	Step 5 (mg/kg)
01	-	-	-	-	-
03	-	-	-	-	-
04	-	-	-	-	-
05	-	-	-	-	-
06	-	-	-	-	-
07	< 1	< 1	1.3	< 10	< 1
08	-	-	-	-	-
09	< 1	< 1	3.4	< 10	< 1
10	< 1	< 1	3.0	< 10	< 1
11	< 1	< 1	1.2	< 10	< 1
12	< 1	< 1	2.4	< 10	< 1
13	-	-	-	-	-
14	< 1	< 1	1.5	< 10	< 1
15	-	-	-	-	-
16	-	-	-	-	-
17	< 1	2.0	4.0	< 10	1.1
18	-	-	-	-	-
19	-	-	-	-	-
20	< 1	1.4	3.3	< 10	1.3
21	-	-	-	-	-
22	-	-	-	-	-
23	-	-	-	-	-
24	-	-	-	-	-
25	-	-	-	-	-
26	< 1	< 1	2.7	< 10	< 1
27	< 1	< 1	1.6	< 10	< 1
28	< 1	< 1	2.8	< 10	< 1
29	< 1	< 1	3.3	< 10	< 1
30	-	-	-	-	-