GROUNDWATER – SURFACE WATER INTERACTIONS IN THE SALMON RIVER WATERSHED, BC: INTEGRATING SPECTROSCOPY, ISOTOPES, WATER QUALITY, AND LAND USE ANALYSES

by

TRUDY LYNN NAUGLER

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Resource Management and Environmental Studies)

THE UNIVERSITY OF BRITISH COLUMBIA

July 2007

ABSTRACT

Understanding the sources and pathways of water pollutants is critical for protecting freshwater resources. Relationships between water quality and land use can be obscured by variable land use, seasonal variability, and interactions between surface water and groundwater. This research combines the tools of fluorescence spectroscopy, nitrate stable isotopes and water chemistry to better understand land use impacts on water quality.

The Hopington aquifer, one of the most vulnerable aquifers in the Lower Fraser Valley, is a source of drinking water for the Township of Langley. This aquifer is also responsible for maintaining the summer stream flow in the Salmon River, a productive Coho salmon stream. Elevated nitrates in both ground and stream water are a concern. Twelve stream sites and eleven groundwater wells were sampled during 2006 to try and "fingerprint" different water sources. Samples were analyzed for: uv-visible absorbance, fluorescence, DOC, nutrients (ammonium, nitrate, ortho-phosphate), chloride, trace elements, and nitrate-isotopes ($\delta^{18}0$ and $\delta^{15}N$). The combination of these tools provided a more detailed look at the groundwater – surface water interactions and helped track pollutants within the system.

Nitrate concentrations in the Salmon River increase where it cuts through the Hopington aquifer; concentrations peak in August when groundwater makes up the greatest proportion of the stream flow. Humic-like fluorescence was able to measure this groundwater influence because groundwater has much lower fluorescence. Nitrate-isotopes showed that inorganic fertilizers were not a dominant source, but that soil N, septic tank leakage, and manure were possible sources. Stream sites influenced by groundwater had an isotopic fingerprint similar to nearby wells, showing that the nitrate source(s) were the same. A GIS-based land use analysis suggested that agricultural land use was having the greatest impact on local water quality, especially on surface waters in the wet season. Protein-like fluorescence showed potential as a tool for pollution monitoring and should be explored further.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND COMMON TERMS

Abbreviation	Explanation
BMP	Beneficial management practice
CA	Contributing area
CDOM / FDOM	Chromophoric / fluorescing dissolved organic matter
CFC	Chlorofluorocarbons
CV	Coefficient of variation
DOC / TOC	Dissolved / total organic carbon
DOM	Dissolved organic matter
GIS	Geographic information system
ICP-AES	Inductively-coupled plasma atomic emission spectroscopy
LRL	Lowest readable limit
NO_X	Nitrous oxides
OM	Organic matter
PARAFAC	Parallel factor analysis
SRP	Soluble reactive phosphorus
TS	Total solids
UV	Ultraviolet
VSMOW	Vienna standard mean ocean water
VLSAP	Vienna standard light antarctic precipitation
λ_{ex} / λ_{em}	Excitation wavelength, emission wavelength
‰	Permil

ACKNOWLEDGEMENTS

First and foremost, I wish to thank Dr. Hans Schreier. He has been an enthusiastic and supportive supervisor throughout the whole process and his wealth of knowledge and experience have been inspiring. I would also like to acknowledge and thank my other committee members, Dr. Les Lavkulich and Dr. Ken Hall, as well as Gwynn Graham who was the external examiner.

This document came to exist only because of the help and support of many colleagues and friends. I am indebted to those who helped me in the field and the lab: Gina Bestbier, Sandra Brown, Dulcie Chan, Carol Dyck, Janet Gabites, Oh Iwata, Jennifer MacDonald, Sheena Pappas, Mandeep Purewall, Fred Rosell, and Jamie Ross. I am also very thankful for the support and encouragement of Jen Karmona, Alice Cohen, Stephanie Lepsoe, and Hillary Uren. Thanks are also due to Lisa Belanger and Roberta Nouri for their support.

Finally, I would like to acknowledge NSERC who provided funding and the Canadian Water Network.

1. INTRODUCTION

1.1. Research context

Understanding the sources and pathways of water pollutants is critical for protecting freshwater resources. Relationships between water quality and land use can be obscured by many factors such as heterogeneous land use, seasonal variability, and interactions between surface water and groundwater. This thesis uses the tools of fluorescence spectroscopy, nitrate stable isotopes and water chemistry to better understand land use impacts on water quality in the Salmon River watershed.

The Salmon River Watershed is located in the township of Langley, east of Vancouver, BC. The watershed originates in Aldergrove and cuts through the Hopington aquifer, one of the most vulnerable aquifers in the Lower Fraser Valley (LFV). The Hopington aquifer maintains the summer stream flow in the Salmon River, a productive salmon stream. Where the stream is influenced by groundwater, nitrate concentrations peak in August when flow is at its lowest and groundwater is providing a large proportion of the stream flow. The Hopington aquifer is also a drinking water source and there is concern about elevated nitrate concentrations in some wells. Understanding the nitrate dynamics is important for the health of both the ecosystem and the residents in this area.

1.2. Previous studies

Previous studies in this watershed have revealed elevated nitrate concentrations in both the stream and groundwater (Beale, 1976; Carmichael, Wei, & Ringham, 1995; Cook, 1994; Wernick, 1996; Wernick, Cook, & Schreier, 1998). A thesis by Beale (1976) was the first major study in the area and looked at trace metals and nutrients as indicators of water and sediment quality. Building on this work, Cook (1994) and Wernick (1996) used geographic information systems (GIS) to try and link water quality and land use. Elevated nitrate levels in the Salmon River system have been attributed to high animal unit densities (agricultural activities) and high septic system density (Wernick et al., 1998). Previous studies, however, have had difficulty conclusively linking land use activities to

stream water quality due to watershed heterogeneity, time lag considerations, and variable land use within the designated source areas (Cook, 1994; Wernick, 1996). Pollutant sourcing is further complicated by groundwater influence.

The Hopington aquifer has been studied on several occasions. In 2000, Gartner Lee did a report for the Township of Langley that sought to better understand the aquifer water balance, vulnerability, groundwater quality, and options for protection of this resource. The report also confirmed previous findings that the shallow, unconfined aquifer regions are highly vulnerable to contamination from livestock activities and septic systems (Gartner Lee Limited, 2000). A comprehensive study done by Golder Associates (2005) provided more detailed information about the aquifers in the Township of Langley. This report showed that the Hopington aquifer, which was previously considered as one permeable unit, has several sections (Golder Associates, 2004).

1.3. Research objectives

The overall aim of this thesis is to further explore the interactions between groundwater and surface water by applying tools not previously used. The thesis also seeks to further investigate nitrate sources in the study area, relating sources to land use activities. More specifically, the research objectives are:

1. To spatially and seasonally investigate nitrate sources that impact groundwater and stream water in the Salmon River Watershed using:
    a. fluorescence spectroscopy
    b. nitrate stable isotope analysis ($\delta^{18}O$ and $\delta^{15}N$ of nitrate)
    c. water chemistry (nutrients and dissolved elements)
    d. land use analysis (GIS)
2. To determine differences in water quality and impacts between the three groundwater aquifer units that make up the Hopington aquifer (A, B, and C).
3. To examine the impact of groundwater on the stream flow and water quality using fluorescence, isotope analysis, and water chemistry.
4. To relate land use activities to the groundwater and surface water quality.

1.4. Thesis organization

The next three chapters provide further background information and a framework for the thesis work. Chapter 2 reviews some of the theory and literature relevant to this study. Chapter 3 gives an overview of field and laboratory methods used. Chapter 4 provides site-specific information and background data; this includes climate data, stream discharge, stream temperature, and land use. Chapters 5, 6, and 7 present the results for nitrate dynamics, water chemistry (nutrients and dissolved elements), and spectral analyses, respectively. Discussion of seasonal trends, groundwater – surface water interactions, and land use relationships are addressed within each chapter. The final chapter is an integrated discussion of the results and the compatibility of the techniques that were used.

2. BACKGROUND

2.1. Linking land use and water quality

It is intuitive that land use activities impact local water quality. Surface water can be affected by point source pollution, runoff, and diffuse sources. Groundwater can also be impacted by contaminants that percolate through the soil to aquifers; shallow and unconfined aquifers are particularly vulnerable to land use impacts. Although these connections make sense it can be difficult to prove the link between water quality degradation and particular activities on the land surface. Anthropogenic activities associated with agriculture (Allan, Erickson, & Fay, 1997; Berka, Schreier, & Hall, 2001; Cuffney, Meador, Porter, & Gurtz, 2000; Poor & McDonnell, 2007) and urban (Sliva & Williams, 2001; Wang, 2001) land uses are most often implicated in having a negative impact on local water quality.

There are various challenges that may be encountered when trying to connect land use and water quality: heterogeneous land use, diffuse sources and/or multiple sources, spatial scale (e.g. riparian zone vs. whole catchment influence), seasonality, time-lag, groundwater – surface water interactions, data availability and resolution, lack of supporting information (e.g. residence time for aquifers, soil types). This section will give an overview of some studies that have looked at land use impacts and the difficulties in uncovering causal relationships.

Season is very important because both land use activities and hydrological pathways vary with season. Berka et al. (2001) found that relationships between water quality data and land use were stronger in the wet season. Similarly, Sliva and Williams (2001), found that water quality was better explained by landscape in the spring and fall than in the summer. Such a trend can not necessarily be extrapolated to any watershed, as the processes there may be different. For subcatchments in central Michigan, landscape factors accounted for more variation in streamwater chemistry in the summer than the autumn (Johnson, Richards, Host, & Arthur, 1997). On a smaller time scale, there is variability between and during storm events; relating storm event water quality to land use (McFarland & Hauck, 1999; Poor & McDonnell, 2007) has similar challenges, but deals with different processes.

In discussions of land use, spatial scale is critical. Land use and landscape influence is scale dependent (Allan et al., 1997; Hunsaker & Levine, 1995; Johnson et al., 1997). Depending on the season and what is being measured, the entire catchment landscape may have significant influence or perhaps only 100 m on each side of a river (Johnson et al., 1997). Allan et al. (1997) found that organic matter inputs to the stream were mostly influenced by local conditions (e.g. vegetative cover at site), but nutrients and sediment delivery were influenced by regional conditions (land use/cover and landscape features both upstream and lateral to stream sites. Overall, the extent of agricultural land at the subcatchment scale was the best single predictor of local stream conditions (Allan et al., 1997). Using multiple regression, Sliva and Williams (2001) found that the catchment land use generally gave slightly better correlations with water quality (water chemistry) than a 100 m buffer. Thus, depending on the quality measure, the scale of landscape and land use influence will vary.

Correlations between land use and water quality measurements vary depending on the site and the analysis methods used. Urban land use has been found to be positively correlated with Cu^{+2}, Cl^{-}, TS, and NH_4^{+} (Sliva & Williams, 2001), and soluble reactive phosphorus (SRP) (Osborne & Wiley, 1988) in streams. During storm events in an agriculture dominated catchment, SRP increased with the % fields that applied dairy waste above the sampling site; ammonium and nitrate concentrations were positively correlated with the % intensive agriculture and milking cow density (McFarland & Hauck, 1999). Percentage agricultural land use is often positively related to stream nitrate-N concentrations (King et al., 2005; Osborne & Wiley, 1988; Poor & McDonnell, 2007), while forested land can be associated with low nitrate concentrations in streams (Poor & McDonnell, 2007). Houlahan and Findlay (2004) found that nitrogen and phosphorus in wetland water were negatively correlated to forest cover; this relationship could be interpreted as (a) the forest is acting as a sink for nutrients, or (b) forest cover is a surrogate for agricultural activity (Houlahan & Findlay, 2004). All these relationships vary depending on nutrient and manure input, type of soil, distance from the stream, surface and subsurface conditions, rainfall events and antecedence soil moisture conditions.

Land use or land cover analyses are often done using class percentages, but this means that the categories are not independent predictors, there is collinearity; for example, a decrease in agricultural land will necessarily be reflected by an increase in another category (e.g. forest cover). Collinearity is one of the spatial issues that should be addressed when trying to link land use to stream indicators (King et al., 2005). King (2005) addresses 3 other challenges in addition to collinearity of land cover/use classes: (a) spatial autocorrelation (land-cover patches may correspond to physical characteristics of the landscape) (b) "intercorrelations and spatial autocorrelation of abiotic intermediaries between land cover and stream biota" (c) spatial arrangement of land cover. Distance weighting is a possible way to deal with this final challenge, but techniques for this are not refined yet (King et al., 2005).

Correlations, regression, multiple regression, and nutrient budgets are tools commonly applied to look at land use and water quality interactions. Water quality measures most often include chemical, physical, and sometimes microbiological parameters. When assessing stream water quality, biological indicators are a very important component and should not be overlooked (Cuffney et al., 2000; Wang, 2001) as the biological impact of water quality may not be fully represented by just chemical or physical measurments (Wang, 2001).

Geographic information systems (GIS) is an important spatial analysis tool (Johnson & Gage, 1997); the use and application of GIS has been increasing since its development as a tool in the natural sciences in the 1980-1990s (Tsihrintzis, Hamid, & Fuentes, 1996). GIS has enabled an empirical approach to non-point source pollution through analysis of land use and land cover (Osborne & Wiley, 1988). With such a powerful tool, it is important to ensure that quality data is used and that the resolution and detail of spatial data is appropriate for the application (Sliva & Williams, 2001). It is also critical to objectively consider challenges such as spatial autocorrelation and spatial arrangement of land cover (King et al., 2005). Ideally, the thoughtful use of GIS and these other tools will help inform land use planning so as to really make a difference in water quality (Osborne & Wiley, 1988; Wang, 2001).

2.2. Nitrate

Anthropogenic activities can release excess nutrients to the environment that are damaging to ecosystems and potentially harmful to human health (Chambers et al., 2001; Schindler, Dillon, & Schreier, 2006). Excess nitrogen is a growing environmental concern in Canada. Chamber et al. (2001) estimated that in 1996, 0.3 million tonnes of N entered fresh, ground, and coastal waters because of anthropogenic activities; the greatest point source was municipal sewage. In 1996, almost 2 million tonnes of N was applied to cropland as fertilizer, manure and biosolids (Chambers et al., 2001). The lower Fraser Valley in B.C. is an area of particular concern with both the agricultural sector and human population experiencing growth (Schindler et al., 2006).

Canadian lakes and rivers usually have nitrate levels of less than 0.9 mg NO_3-N/L (surface waters with higher levels are often eutrophic). If there is no anthropogenic influence, dissolved nitrate in groundwater is usually less than 3 mg NO_3-N/L (Environment Canada, 2003).

2.2.1. Nitrogen cycle and nitrate sources

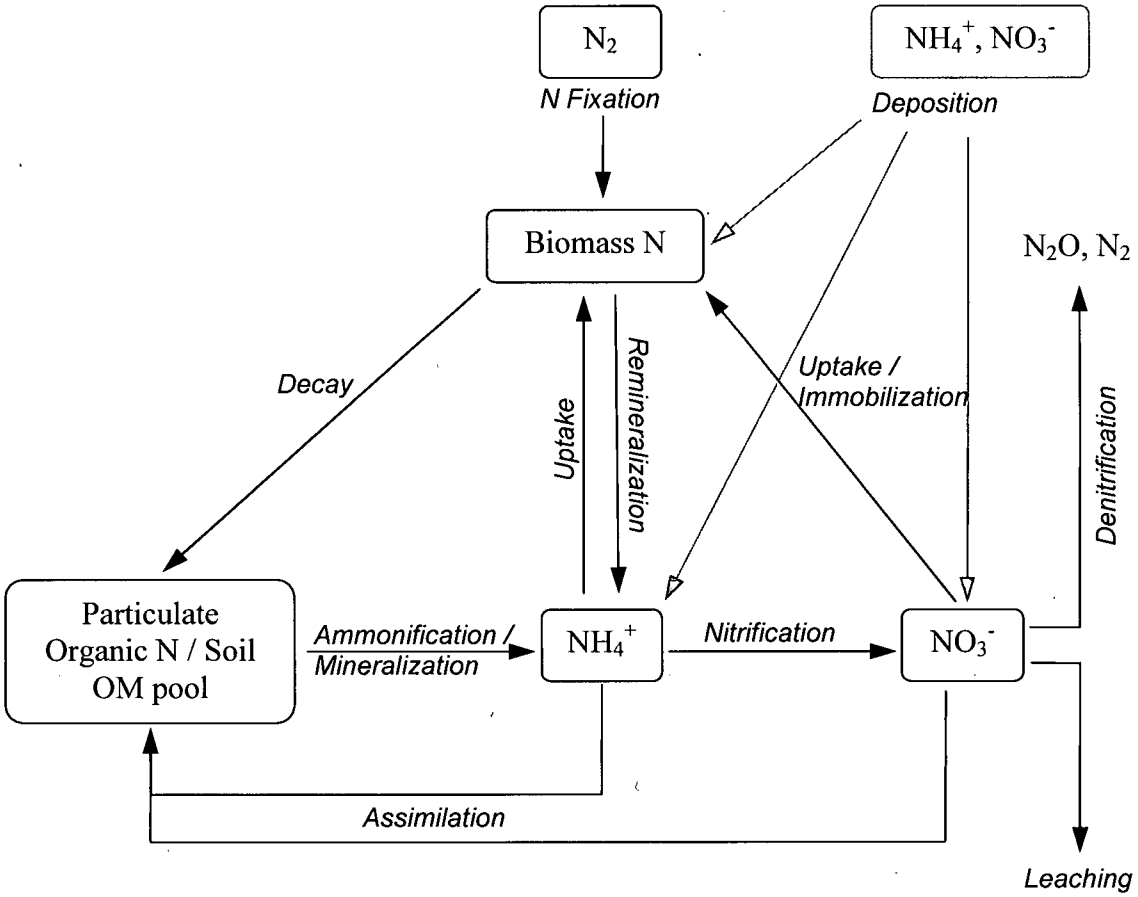

Figure 2.1 Nitrogen Cycle; showing key sources, sinks, and processes.

Atmospheric NO_X (primarily from vehicle emissions) and NH_3 (biggest contributor is agriculture) both contribute to water pollution with nitrate and ammonium (Schindler et al., 2006). Both dry deposition and wet deposition (precipitation) are of concern. Other major anthropogenic sources of nitrate to water are: agricultural runoff (manure and fertilizer applied to land, animal feedlots), industrial effluent, domestic wastewater, septic systems, urban runoff, and landfill leachate (Environment Canada, 2003; Jin, Chen, Wang, & Ogura, 2004). Nitrate may also come from native soil organic matter or geologic sources (Jin et al., 2004). In Canada, most occurrences of elevated nitrates in ground water are in agricultural areas; fertilizer use and manure production have been increasing, leading to more direct movement of N to water (Schindler et al., 2006). Nutrient contents of manure vary according to animal source (e.g. broiler chicken

litter 29 kg N/t; pig and cattle manure 6 kg N/t) and can vary within species depending on diet and other factors (Environment Canada, 2003).

The primary losses from the nitrogen cycle are due to leaching, volatilization (gaseous losses), and erosion. Nitrate is an anion and thus is not readily adsorbed by soil (clay) particles – this means that leaching and surface runoff are important processes for nitrate contamination of ground and surface water.

2.2.2. Factors affecting N export and loss

In water, biotic processes (assimilation, N fixation, nitrification, denitrification, ammonification, decomposition of OM) determine the fate of nitrate (see Figure 2.1). Rates of biological processes are affected by pH, temperature, and O_2 availability (Environment Canada, 2003). Leaching and runoff of fertilizer (inorganic or manure) is affected by the form, timing, and amounts, as well as the weather during and after application. Vegetation, soil characteristics (soil OM, depth, texture), watershed geology, and land use history will also affect how much N is lost after fertilization (Schoenholtz, 2004).

Nitrogen dynamics within a watershed are heavily dependent on the specific land use activities and management. Nitrate is often supply limited (Burns, 2005) and may therefore have a "dilution" pattern during storm events where nitrate concentrations decrease with increasing stream discharge (Poor & McDonnell, 2007). If nitrate concentrations in a catchment are transport-limited, stream nitrate concentrations may mimic a storm hydrograph, increasing with flow rates (a "concentration" pattern) (Poor & McDonnell, 2007). Although some generalization can be made, each system has unique conditions and concerns.

2.2.3. Health and environmental concerns

The Canadian drinking water quality guideline (FPT Committee on Drinking Water, 2007) and B.C. water quality criteria for drinking water (Nordin & Pommen, 1986) are both 10 mg/L NO_3^--N (45 mg/L NO_3^-); the B.C. criteria for recreation and aesthetics is also 10 mg/L (maximum). The guideline for drinking water quality is based on

observations of methemoglobinemia, but there was no safety factor used (Manassaram, Backer, & Moll, 2006). The foremost concern regarding nitrate exposure through drinking water is for infants.

Methemoglobinemia was first reported by Comly (1945), who made the connection between two infant cyanosis cases and the high-nitrate well water being used to make their formula(Comly, 1945). One nitrite ion can react with two hemoglobin molecules to form methemoglobin, which can not carry oxygen because the iron molecule was oxidized (Comly, 1945). The infant can start to turn blue from lack of oxygen, thus the common name blue baby syndrome. This problem is not seen in adults.

Nitrate is a normal part of the human diet, but adults are not immune to high nitrate exposure through drinking water. There is concern that nitrate might act as a procarcinogen and it has been associated with gastric cancer (Cantor, Shy, & Chilvers, 1996); nitrate is reduced to nitrite in the body and can react with other compounds to form *N*-nitroso compounds, which may play a role in gastric carcinogenesis (Nomura, 1996). "Brain cancer, bladder cancer, and non-Hodgkin's lymphoma are also of interest, although there is less evidence" (Cantor et al., 1996). There is some evidence of adverse reproductive effects (spontaneous abortions, intrauterine growth restriction, and birth defects) occurring with high nitrate levels in drinking water, but evidence is not yet strong enough to assert a causal relationship (Manassaram et al., 2006).

Aquatic life can be affected by high nitrate concentrations in stream water, although ammonia and nitrite[1] are more toxic. Freshwater invertebrates, freshwater fish (especially the egg stage), and amphibians are all sensitive to nitrate exposure (Environment Canada, 2003). The mechanism of toxicity in aquatic organisms may be due to methaemoglobin formation or osmoregulation difficulties due to high salt concentrations that may be associated with the nitrate (Environment Canada, 2003). The potential for eutrophication is another concern related to excess nitrate (N) in surface water; excessive algal growth (eutrophication) reduces dissolved oxygen and in extreme cases can cause fish kills.

[1] Nitrite is quite toxic to salmonids, which has resulted in more investigations than for nitrate, which is not as toxic (Nordin and Pommen 1986).

There is a Canadian interim water quality guideline of 13 mg/L (3 mg/L NO_3-N) for the protection of aquatic life[2] (Environment Canada, 2003). To protect fresh water aquatic life, the B.C. water quality criteria is 200 mg/L NO_3^--N as a maximum concentration and 40 mg/L NO_3^--N (or less) as a 30-day average[3] (Nordin & Pommen, 1986). The B.C. criteria specify 100 mg/L NO_3^--N as the maximum concentration for livestock watering and wildlife (Nordin & Pommen, 1986).

2.3. Nitrate stable isotopes

Kendall (1998) gives 3 potential complications in trying to relate groundwater and surface water nitrates and the contribution from different sources: (1) possibility of multiple sources (2) overlapping point and non-point sources (3) biogeochemical processes. Isotopes can offer a means of source identification by unique isotopic composition of different nitrate sources, and when both ^{18}O and ^{15}N of nitrate are used, biological cycling can sometimes be identified (Kendall, 1998).

2.3.1. Notation

Atmospheric nitrogen is the standard used for reporting nitrogen isotopic ratios ($\delta^{15}N_{Air\ N2}$ = 0 ‰). A ratio of 1/272 ($^{15}N/^{14}N$) is used as the constant for atmospheric N_2 (Coplen, Krouse, & Bohlke, 1992). The delta (δ) notation is commonly used and this value reflects a relative enrichment or depletion in ^{15}N, compared to the standard (see Equation 2.1); δ values are normally reported in permil (‰). The same notation and units apply to $^{18}O/^{16}O$, but the standard used for $\delta^{18}O$ is Vienna standard mean ocean water (VSMOW).

---

[2] Selected to protect "all stages of freshwater life against the adverse effects of the nitrate ion"; based on the lowest observable effect concentration reported for the Pacific treefrog, multiplied by a safety factor of 0.1. (Environment Canada, 2003)

[3] Calculated from at least 5 weekly samples.

$$\delta^{15}N\ (in\ ‰) = \left[\frac{\left(\frac{^{15}N}{^{14}N}\right)_{sample}}{\left(\frac{^{15}N}{^{14}N}\right)_{Air\ N_2\ (std)}} - 1 \right] 1000$$

Equation 2.1. Calculating delta (δ) value for ^{15}N.

2.3.2. **Sources and fractionation**

Fractionation of isotope composition between different nitrogen compounds is the basis for using ^{15}N as a tool in hydrology (Clark & Fritz, 1997). Fractionation processes result in a range of $\delta^{15}N$ values for different sources of nitrate (see Figure 2.2). On the basis of different sources producing nitrate with distinct $\delta^{15}N$, nitrate-N isotopes have been used to distinguish the pollution source for both ground and surface water (Heaton, 1986). While some sources have overlapping $\delta^{15}N$ ranges, there is a clear distinction between inorganic fertilizers and animal waste / septic. Fertilizers produced from atmospheric nitrogen have a $\delta^{15}N$ close to 0‰[4] because there is very little fractionation associated with the process. Animal waste (manure and septic) has higher $\delta^{15}N_{NO3}$ values.

[4] $\delta^{15}N_{NO3}$ = -1.6 to +5.6‰ (Vitoria, Otero, Soler, & Canals, 2004)

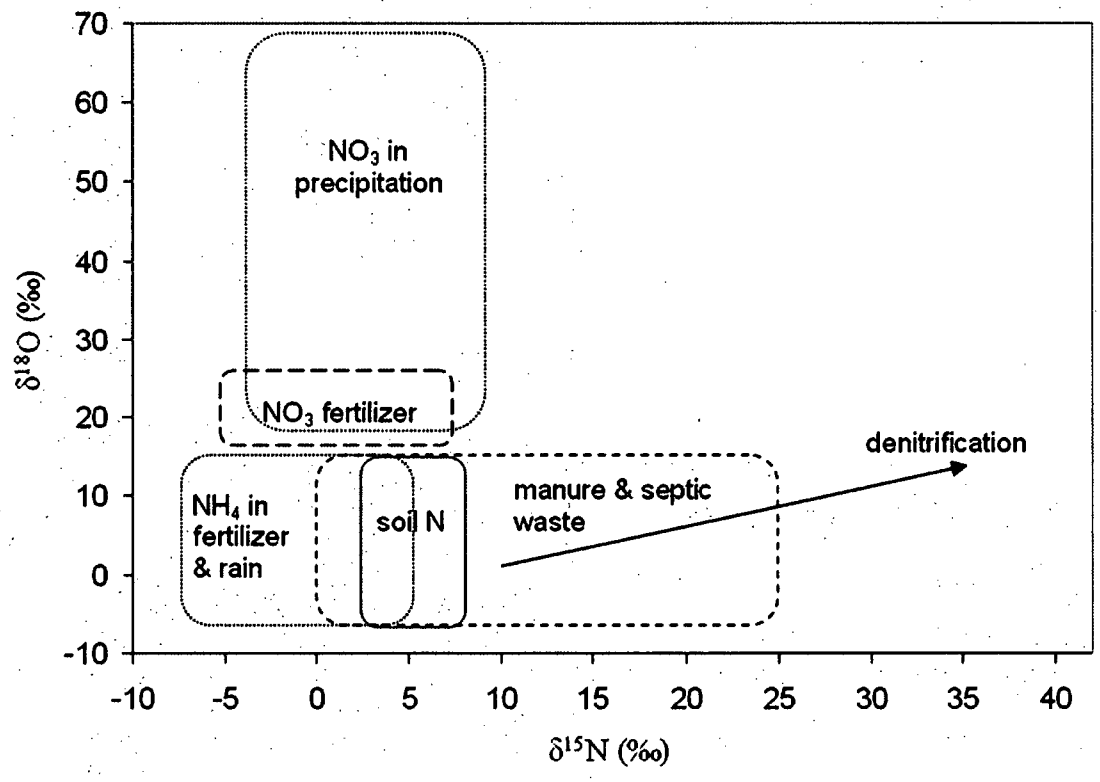

Figure 2.2. Typical range of $\delta^{15}N$ and $\delta^{18}O$ values of nitrate for different sources. Modified from Kendall (1998).

Denitrification (and other processes) can change the original $\delta^{15}N$ signature. Figure 2.3 outlines the different processes that affect the N isotopic composition. Fractionation within the food web is proportional to the tropic level of organisms. The low ^{15}N content in primary producers is magnified by 10 ‰ or more by higher consumers; the catabolic reaction of amino acids produces NH_4^+ that is depleted in ^{15}N by several permil, therefore the solid waste (manure) is enriched in ^{15}N (Clark & Fritz, 1997). Thus fractionation enables the distinction of sources, but it can also confuse the isotopic signature and obscure the source. For example, a $\delta^{15}N_{NO3}$ value of 15‰ may directly reflect the isotopic signature of the nitrate source (e.g. animal manure), but the same value could also result if an isotopically "lighter" source (e.g. synthetic fertilizer) had been subject to denitrification. The denitrification process favours isotopically light nitrogen (^{14}N) and thus the remaining nitrate pool is left isotopically enriched in ^{15}N (higher

$^{15}N/^{14}N$ ratio than before, and therefore greater $\delta^{15}N$ value). It is not possible to distinguish between these two possibilities using only $\delta^{15}N_{NO3}$.

The ability to measure ^{18}O of nitrate has broadened the use of ^{15}N as a tracer because, when used together, ^{15}N and ^{18}O can help identify denitrification and distinguish different nitrate origins (Clark & Fritz, 1997). The oxygen atoms of nitrate are also fractionated during denitrification, but the fractionation of N and O happen in a predictable way, with approximately a 2:1 ratio (see the arrow in Figure 2.2). Similar to nitrogen, most biological processes favour the lighter isotope (^{16}O), thus uptake, absorption/desporption, and denitrification will leave the residual nitrate enriched in ^{18}O (Kendall, 1998). Therefore, the relative $\delta^{15}N$ and $\delta^{18}O$ of nitrate (with decreasing nitrate concentrations) can help determine the presence of dentrification.

The $\delta^{18}O_{NO3}$ can also help further distinguish nitrate sources (see Figure 2.2). The oxygen atoms in synthetic nitrate fertilizers come from atmospheric O_2 ($\delta^{18}O$ = +23 ‰) (Kendall, 1998); there is minimal fractionation of ^{18}O with nitrification, thus the fertilizers will have a $\delta^{18}O_{NO3}$ reflecting this origin ($\delta^{18}O_{NO3}$ = +18.0 to +25.1‰) (Vitoria et al., 2004). Biologically formed nitrate has 2 molecules of oxygen from water (depleted in ^{18}O, relative to O_2) and one from atmospheric O_2 (Clark & Fritz, 1997; Kendall, 1998). If there is no fractionation involved with this process, a typical range of $\delta^{18}O$ for soil nitrate would be -10 to +10 ‰ (Kendall, 1998).

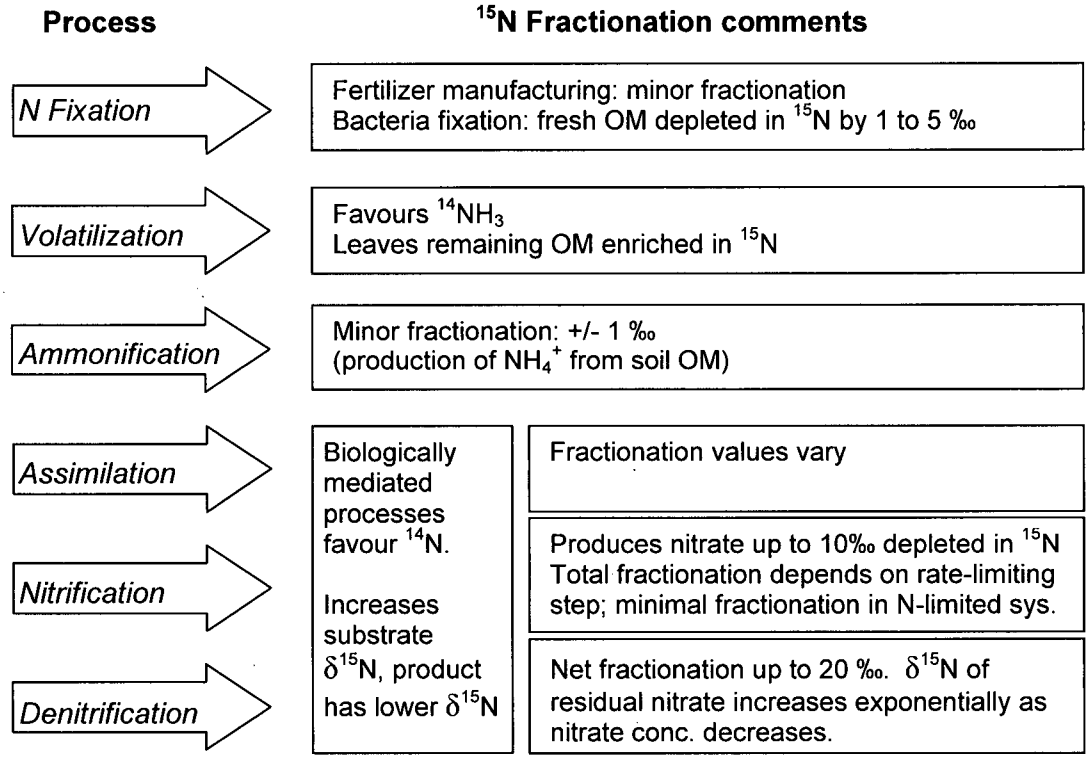

Figure 2.3. Processes affecting N isotopic composition.
(Clark & Fritz, 1997; Kendall, 1998)

2.3.3. Application and use of nitrate isotopes

Nitrate isotope analyses should be interpreted in combination with other data and measurements (water chemistry, hydrological conditions, etc) and care must be taken not to over-interpret the isotope values (Kendall, 1998). For example, under biologically active conditions, the original O-isotope ratio of fertilizers can be masked by mineralization – immobilization turnover (microbial immobilization – mineralization – nitrification), thus results could be misinterpreted even if a dual isotope approach has been used (Mengis, Walther, Bernasconi, & Wehrli, 2001). Despite such challenges, the use and application of nitrate-isotopes to look at nitrogen cycling and sources has been growing.

Nitrate isotopes techniques have been applied to both groundwater (Jin et al., 2004; Mitchell, Babcock, Gelinas, Nanus, & Stasney, 2003; Panno, Hackley, Hwang, & Kelly, 2001; Seiler, 2005; Verstraeten, Fetterman, Meyer, Bullen, & DSebree, 2005;

Wassenaar, Hendry, & Harrington, 2006) and surface water (Kellman & Hillaire-Marcel, 2003; Panno, Hackley, Kelly, & Hwang, 2006; Townsend-Small et al., 2007) studies. The primary goal of most studies was to determine the primary source of nitrate contamination. Nitrate isotopes have also been used to look at decadal trends in an aquifer to assess the effectiveness of beneficial management practices (BMPs) for reducing nitrate contamination in the aquifer (Wassenaar, 1995; Wassenaar et al., 2006). Studies have been done both in agriculture-dominated areas (Kellman & Hillaire-Marcel, 2003; Mehnert et al., 2007; Wassenaar, 1995) and in residential or urban contexts (Jin et al., 2004; Silva et al., 2002; Verstraeten et al., 2005), as well as areas with mixed use and multiple potential sources of nitrate (Seiler, 2005; Townsend-Small et al., 2007). Various scales have also been investigated from a groundwater assessment in a 10 km^2 area (Mitchell et al., 2003) to basin scale investigations (Mississippi River Basin, >34000 km^2, (Chang, Kendall, Silva, Battaglin, & Campbell, 2002)).

There has been varying levels of success in applying the isotope techniques. Panno et al. (2001) found that the nitrate isotopic data (N and O of NO_3) were the most definitive for sourcing the nitrate and determining that significant denitrification was taking place. Jin et al. (2004) used only $\delta^{15}N_{NO3}$ and had difficulty assessing the presence or extent of denitrification in the study area. Similarly, Kellman and Hillaire-Marcel (2003) found that denitrification limited the practical application of $\delta^{15}N_{NO3}$ measurements.

A dual isotope approach (analyzing both N and O isotopes of nitrate) can help determine if denitrification is taking place and help in distinguishing nitrate sources; use of $\delta^{18}O$ can be critical in separating isotopic signatures (Chang et al., 2002). Combining nitrate-isotopes with other chemical and hydrologic data can provide even more information (Seiler, 2005; Verstraeten et al., 2005). Silva et al. (2002) found that Cl and $\delta^{18}O_{NO3}$ helped to distinguish sewage impact during stream baseflow. A septic contaminant plume has been successfully delineated from surrounding groundwater using $\delta^{15}N$ of nitrate and groundwater $\delta^{18}O$ (Aravena, Evans, & Cherry, 1993). Seiler (2005) combined $\delta^{15}N_{NO3}$ and $\delta^{11}B$ to look at groundwater contaminant sources and processes and this approach was generally successful; denitrification blurred the original isotopic signature of N sources and thus some of the isotopic data on its own was inconclusive.

The presence of anthropogenic compounds (e.g. caffeine, CFCs) can be used to support isotopic data (Seiler, 2005).

2.4. Water quality: nutrients and dissolved elements

Although nitrate is the primary water quality concern being addressed in this thesis, other nutrients and dissolved elements were also used. These other measurements were included to help distinguish between different water sources, to potentially help indicate contaminant sources, and as measures of general water quality. The Canadian and BC (Ministry of Water Land and Air Protection) drinking water quality guidelines for selected parameters are shown in Table 2.1 (BC Ministry of Water Land and Air Protection, 1999; Butcher, 1988; FPT Committee on Drinking Water, 2007; Moss & Nagpal, 2003; Nagpal, 2001; Nagpal, Levy, & MacDonald, 2003; Nordin, 1985; Nordin & Pommen, 1986; Singleton, 1987).

Geologic materials and atmospheric deposition are both potential sources of trace metals. Agricultural activities can be a non-point source of trace metal contamination, as can stormwater runoff in urban areas (Ritter et al., 2002). Trace metal compounds are added to livestock feed (Al, Cu, Fe, Mn, Zn, As) and may be directly applied to fields with fertilizer or pesticide applications; Zn and Cu are most commonly associated with livestock manure (Smith, 2004). Fertilizer and manure applications to agricultural fields are also a source of nutrients and can result in N and P contamination of waterways. The greatest concern with excess phosphorus is eutrophication, but this is generally only applicable to lakes as in streams there are other factors besides P that are important for algal growth (Nordin, 1985).

Table 2.1. Canadian and BC water quality guidelines, selected parameters.

Parameter	*(units)*	*Canadian drinking water quality guideline**		***Drinking water***	***Freshwater aquatic life***	***Livestock water supply***	***Recreation & aesthetics***
				BC MWLAP water quality guidelines			
Al	mg/L	0.1/0.2**		0.2 †	0.1 † (pH>6.5)	5 (total)	0.2 †
Ba	mg/L	1	HB				
B	mg/L	5	IMAC	5	1.2	5	n/a
Cu	mg/L	≤1.0	AO	0.5	variable	0.3	1.0
Cl⁻	mg/L	≤250	AO	250	150 ††	600	none
Fe	mg/L	≤0.3	AO				
Mn	mg/L	≤0.05	AO		variable		
Na	mg/L	≤200	AO				
Zn	mg/L	≤5.0	AO	5	variable	2	5
Total P	µg/L			10	5-15 (lakes)		10 (lakes)
pH		6.5-8.5					

* HB = health based guideline; IMAC = health-based guideline developed as an interim maximum acceptable concentration; AO = aesthetic objective

** Operational guidance value for drinking water treatment plants using Al-based coagulants.

† Dissolved, †† 30 day average

Variable Cu, Mn, and Zn guidelines for aquatic life depend on water hardness.

Urban stormwater runoff can contain trace metals from vehicle exhaust, wear of automobile components, building exteriors, atmospheric deposition, commercial business, and public infrastructure (drain systems and sanitary sewers) (Minton, 2005). Nutrients can also come from some of these sources as well as landscape maintenance, wildlife, and pets. Road salt is the primary concern for chloride contamination of fresh waters, but sewage is a possible source too (Nagpal et al., 2003).

Various elements have both natural and anthropogenic sources. Boron is an essential trace element that is found naturally in groundwater (World Health Organization, 2006); B is found in cleaning products (soap, detergents) and sewage effluent may increase B levels in surface water (Nagpal et al., 2003; World Health Organization, 2006). Barium is used in some industrial applications, but its presence in water is usually from natural sources. The most common source of elevated copper and zinc in drinking water is from corrosion of plumbing; pipes can be a source of iron too, but Fe is also naturally

present in many fresh waters (World Health Organization, 2006). Manganese is another metal that is naturally present in many waters, but it is also present in various products and as an additive to gasoline (Methylcyclopentadienyl Manganese Tricarbonyl, MMT) (World Health Organization, 2006).

2.5. Absorption and fluorescence spectroscopy

Natural waters contain dissolved organic matter (DOM), produced by the degradation of terrestrial and aquatic organic material. A fraction of the DOM is optically active, with strong absorption in the UV range (CDOM, chromophoric DOM). Some of the CDOM also has fluorescence properties (FDOM). It is this absorption of light and fluorescence of DOM that enable the use of absorption and fluorescence spectroscopy to investigate the source and characteristics of CDOM in natural waters. With improved analytical technology, the application of spectroscopy to quantitative and qualitative studies of OM in natural waters, and as a tool for water quality assessment has increased in recent years.

The concentration, composition, and chemistry of DOM are variable and depend on a range of factors (e.g. allochthonous vs autochthonous OM source, temperature, pH, photolytic and microbiological degradation) (Leenheer & Croue, 2003). Fluorophores in CDOM are generally divided into two groups "humic-like" and "protein-like" (Leenheer & Croue, 2003). Humic-like fluorescence occurs in a region very similar to that for humic and fulvic acids. Protein-like fluorescence peaks are very similar to those for the aromatic amino acids tyrosine (λ_{em} 300-305 nm) and tryptophan (λ_{em} 340-350 nm) at excitation wavelengths 220 nm and 275 nm (Coble, 1996; Reynolds, 2003). Reynolds (2003) found that tryptophan-like fluorescence was in fact correlated to the presence of free tryptophan in lake water samples.

Fluorescence emission spectra can be collected for a variety of excitation wavelengths and these spectra combined into an excitation-emission matrix (EEM) to more fully characterize water samples. An example EEM is shown in Figure 2.4. Apart from the fluorescence peaks, there are two major features on the EEM both of which are scatter lines. Incident light is either absorbed by the water sample or transmitted; light can

also be scattered by molecules and particles in the water sample. Scattering results in energy being detected (as an emission) at the same wavelength as the excitation; this is Raleigh-Tyndall scattering and shows up as a prominent line across the EEM. Raman scattering (another feature on the EEM) is the result of energy loss to molecules and subsequent scattering; this energy loss is to molecular rotation and vibration and does not cause an excited state.

Fluorescence spectroscopy is generally more sensitive than absorption for detecting natural organic matter. Absorption at 254 nm (A_{254}) is often considered a rough indicator of overall DOM concentrations. A_{254} is also used as a measure for the potential of inner-filtering, which results in a non-linear relationship between fluorescence intensity and chromophore concentration. Inner-filtering occurs when other compounds in solution absorb the incident or emitted light, resulting in lower fluorescence intensity. If A_{254} is greater than 0.3, correction for inner-filtering effects should be made (Ohno, 2002). Serial dilutions can be done to show the level of quenching (Baker & Spencer, 2004).

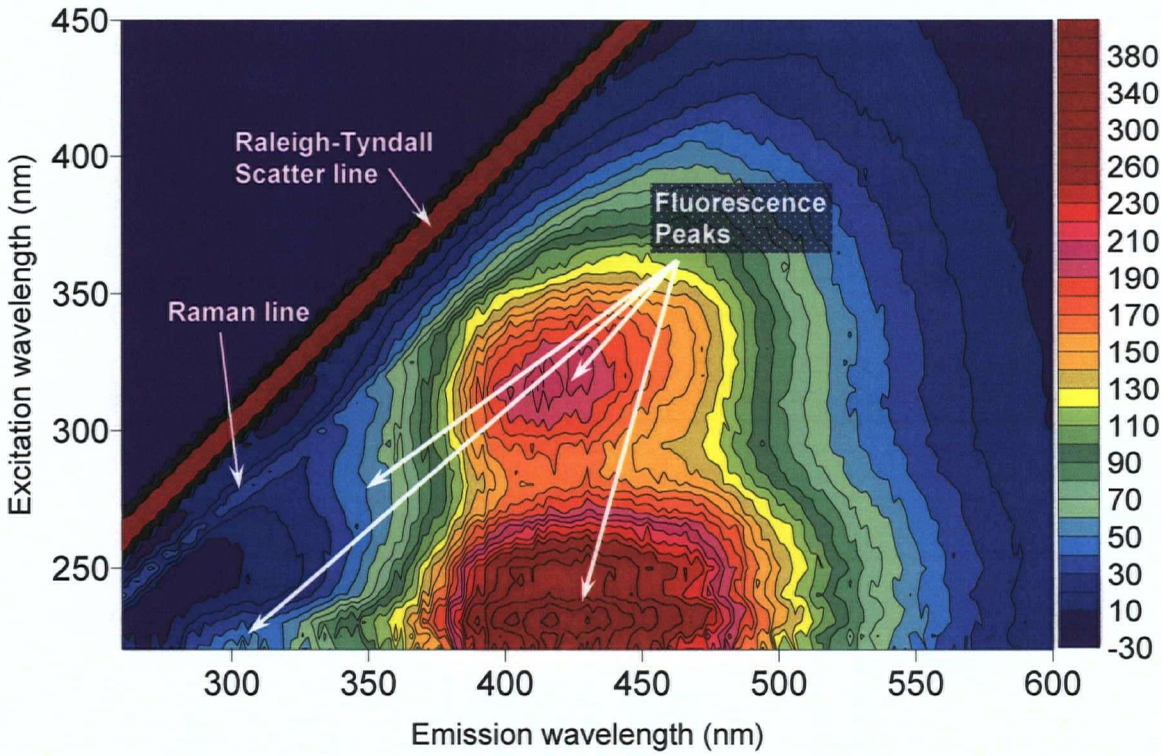

Figure 2.4. Example EEM showing scatter lines and fluorescence peaks.
Note that the contour interval is 10 units up to 240, after which it is 20 units.

2.5.1. Limitations and advantages

The main limitation of absorption spectroscopy is that multiple peaks from different chromophores may be overlapping and unresolved in the scan. Fluorescence EEMs can provide some more information, but may not resolve the overlapping peaks for different compounds. There are several important benefits of spectral analyses over traditional water quality monitoring: (1) rapid analysis (2) small sample volumes (3) high sensitivity (4) minimal sample preparation (5) no reagents (6) non-destructive analysis (7) potential for real-time monitoring. (Ross, 2006).

2.5.2. Applications

Fluorescence and absorption spectroscopy have been used to investigate DOM source and characteristics in both marine (Coble, 1996; McKnight et al., 2001; Sierra, Giovanela, Parlanti, & Soriano-Sierra, 2005; Stedmon & Markager, 2005) and freshwater environments. The mix of fluorophores causing humic-like fluorescence varies between freshwater and marine environments (Coble, 1996). The following discussion focuses on application of these tools in freshwater environments.

There have been several studies seeking to distinguish and track different DOM sources using spectroscopy. Using optical characteristics, it was possible to characterize the DOM from different catchments in the River Tyne catchment (Northern England) and then differentiate them within the estuary (Baker & Spencer, 2004). EEMs have been used to "fingerprint" two rivers and look at mixing below their confluence (Yan, Li, & Myrick, 2000), to discriminate between DOM of seven tributaries in a small catchment (70% of samples were correctly classified) (Baker, 2002), and to distinguish between DOM from marine, terrestrial, and, anthropogenic sources (Spencer et al., 2007). Relationships between anthropogenic impact and protein-like fluorescence can even be seen at the larger catchment scale (>1000 km^2) (Baker, Inverarity, & Ward, 2005). On a much smaller scale, the sources of stormflow in a forested catchment were estimated using fluorescence spectroscopy (Katsuyama & Ohte, 2002). Fluorescence and absorbance have also been used to dissolve OM source via end member mixing analysis (Hur, Williams, & Schlautman, 2006).

Assessing anthropogenic impact on water quality has been an important impetus in developing some of the spectrophometric techniques. Studies have tried to characterize a variety of waste types and circumstances. Farm wastes (silage liquor, pig and cattle slurry, and sheep barn waste) all have high tryptophan-like fluorescence and could potentially "leave a signature" during a pollution event in a river (Baker, 2002). Landfill leachate is characterized by intense fluorescence at 220-230 nm (excitation) and 340-370 nm (emission), which is sometimes called a XOM peak (Baker, 2005; Baker & Curry, 2004); leachate contamination from different landfills can be discriminated (Baker & Curry, 2004) and the leachate can be detected at downstream sites even when diluted 100-1000 times (Baker, 2005). Work has also been done to detect sewage (Baker, 2001; Baker, Inverarity, Charlton, & Richmond, 2003) and domestic waste (Galapate et al., 1998; Westerhoff, Chen, & Esparza, 2001) impacts on rivers.

Excitation-emission matrices contain a lot of information and there are many possibilities for analyzing the data. Approaches range from simply taking the maximum or average fluorescence intensity for selected peaks, to multivariate techniques that use the dataset itself to differentiate between regions of fluorescence. Parallel factor analysis (PARAFAC) is an increasingly popular tool to pair with fluorescence EEMs. The size of the sample set helps determine how many fractions or groups of fluorophores can be resolved (Holbrook, Yen, & Grizzard, 2006). Using 55 samples, Holbrook et al. (2006) identified only three fluorophore moieties (identified as humic-like, fulvic-like, and protein-like). Using 90 samples from a Danish estuary in the summer season, 5 fractions were found (Stedmon, Markager, & Bro, 2003) and by expanding the sampling to a full year and taking more than 1200 samples, 8 fractions could be identified from the same estuary (Stedmon & Markager, 2005). EEMs combined with PARAFAC analysis are a fast and effective way to characterize the fluorescent fraction of DOM (Stedmon & Markager, 2005). A synchronous or single fluorescence scan can also provide useful information (Galapate et al., 1998; Sierra et al., 2005), depending on the intention. Principal components analysis has been used to explore relationships between the spectral properties and geochemical parameters (Baker, 2005).

There are several exciting areas where spectroscopy applications will continue to develop. Thermal fluorescence properties (especially for tryptophan) have potential to

help source/fingerprint DOM and provide additional structural information (Baker, 2005). Relationships between fluorescence and other water quality measures (Baker & Inverarity, 2004) could allow fluorescence to be used as an indicator for monitoring human impact and be of great help to watershed managers (Holbrook et al., 2006). Portable spectrophotometers give results very close to a bench instrument (Baker et al., 2005; Baker et al., 2004) and allow convenient measurement without delay, thereby minimizing sample degradation. At some point in the future, realtime monitoring may be possible.

2.6. Anthropogenic compounds for source tracking

In terms of pollutant source tracking, there are limitations to the tools that have been discussed in this chapter. Fluorescence signatures can overlap between sources and nitrate isotopes are not able to distinguish between manure and septic sources. Trace metals and other water chemistry may help to distinguish between some sources. Sometimes the presence of anthropogenic compounds can help to confirm or support a certain pollutant source. Seiler (2005) used the presence of caffeine to verify that wastewater was the nitrate source in a contaminated aquifer. Pharmaceuticals in waste water can migrate to unconfined aquifers; carbamezepine, sulfamethoxazole, and nicotine were detected in an unconfined sand and gravel aquifer that was influenced by a high school septic tank (Godfrey, Woessner, & Benotti, 2007). In addition to nitrate isotopes, Verstraeten et al. (2005) used DOC, coliphages B isotopes, antibiotics and other drugs as tracers for septic influence on shallow sand-point and cased wells; coliphage, sulfamethoxazole, trimethoprim, caffeine, acetaminophen, and 1,7-dimethylxanthine (a caffeine metabolite) showed up in at least two of the 19 wells sampled. It is better to use a multi-tracer technique for septic influence instead of only measuring nitrate concentration and bacteria.

3. METHODS

3.1. Introduction

This chapter outlines the sampling sites, sampling occasions, methods for sample collection in the field, and collection of other site specific data. Procedures for chemical and spectroscopic analysis of water are explained. An overview of data analysis principles is also provided.

3.2. Sampling sites: selection and location

Research for this thesis was conducted in the Township of Langley, specifically in the Salmon River Watershed and in the area overlying the Hopington aquifers. The Salmon watershed originates near Aldergrove and flows into the Fraser River at Fort Langley. It is a relatively flat watershed, having only 140 m elevation difference between headwaters and mouth. In the middle section of the watershed, the river crosses the Hopington aquifer, one of the most sensitive unconfined aquifers in the Lower Fraser Valley. More detail on these areas can be found in Chapter 4. A total of 12 stream sites and 11 wells were used for sampling, as shown in Figure 3.1 and Figure 3.2.

Stream sites were primarily selected because previous studies collected samples at the same locations, therefore background data was available for the sites and this particular study can be more easily incorporated into the sum of information for the area. Each of the major tributaries to the Salmon River (Coghlan Creek, Davidson Creek, Union Creek) are included in sampling network. Stream sites were also selected to include headwater sites on the Salmon River and Coghlan Creek that were "before"[5] the Hopington aquifer. Coghlan Creek Site 3 (C3), was the only site not used in previous studies; it was selected to assure that there was a sample further upstream prior to interaction with the Hopington aquifer.

[5] Throughout this thesis, "before" the Hopington aquifer refers to stream sites that are not impacted by groundwater from the Hopington aquifer because they are in the headwaters before the stream cuts through the aquifer.

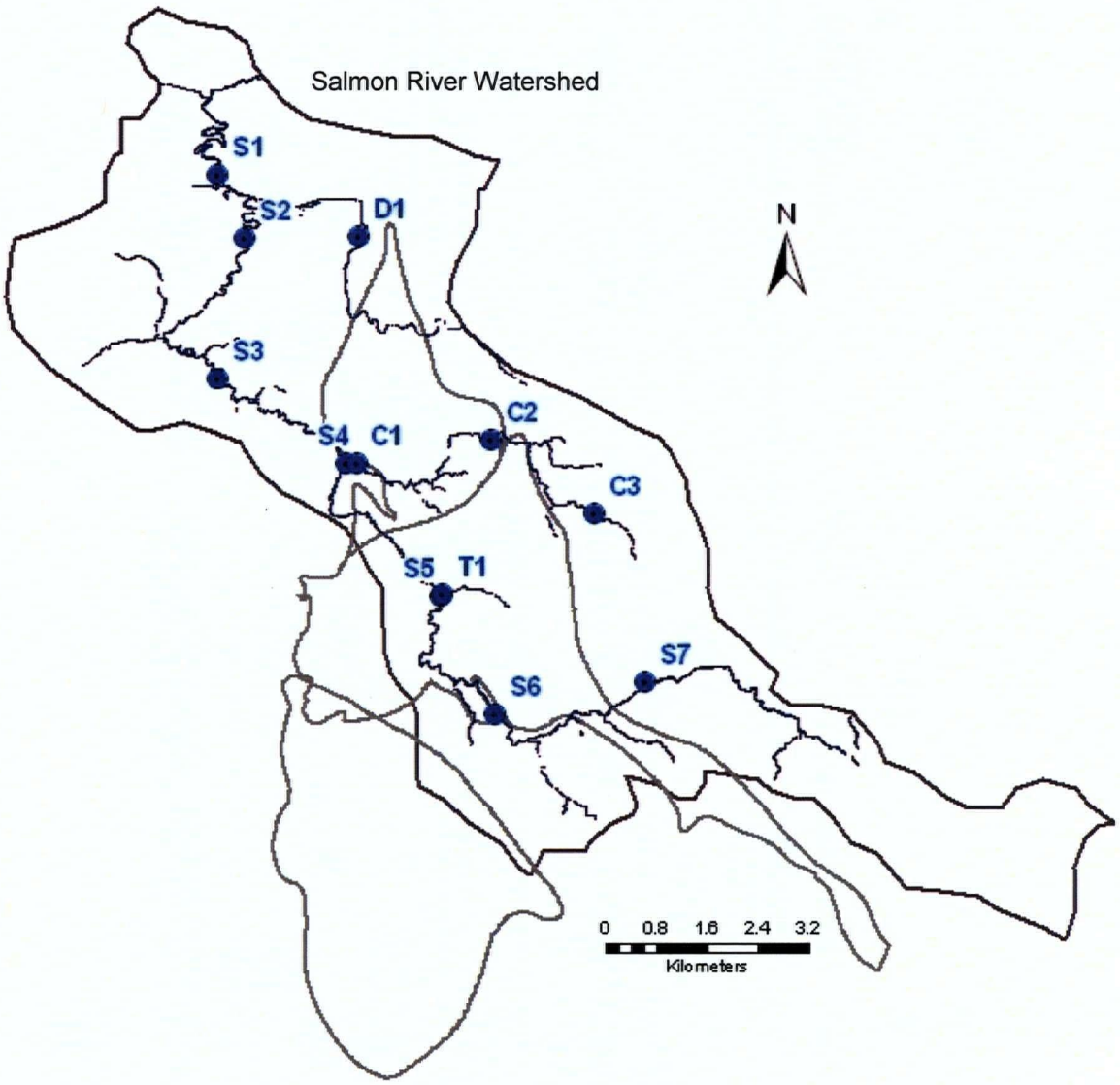

Figure 3.1 Map of Salmon River Watershed and Hopington aquifers showing stream sampling sites

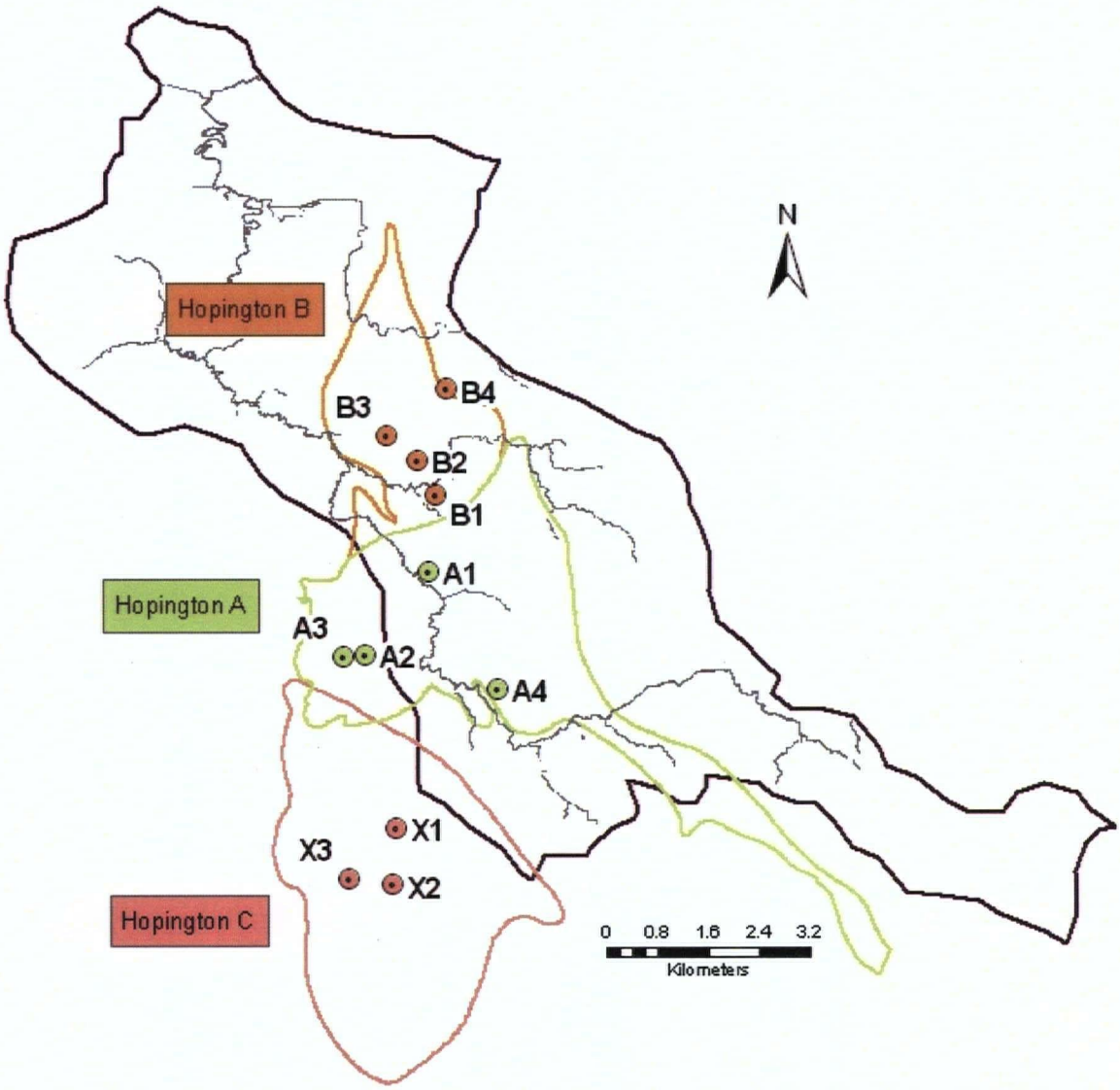

Figure 3.2. Map of Salmon River Watershed and Hopington aquifers showing well sampling sites.

Groundwater wells were selected based on several criteria. Firstly, wells known to have high nitrate levels were preferred because the nitrate concentration in local groundwater is one of the key issues addressed through this research. More specifically, the nitrate isotope analysis is only feasible with higher nitrate concentrations. Another deciding factor in selecting well sites for sampling was the interest of well owners and their willingness to participate. Contact with willing participants was facilitated by staff at the Township of Langley and the BC Ministry of Environment. Two of the wells used were Ministry of Environment monitoring wells; these sites were sampled during the biannual monitoring and sampling done by the Ministry itself.

The key sampling was done on 6 occasions in 2006; sampling dates are outlined in Table 3.1 along with the analyses included in that round of sampling. On each sampling occasion 1 groundwater site and 1 surface water site (randomly selected) were sampled and analyzed in triplicate. For isotope analyses, only 1 site in total was selected for triplicate analysis.

It should be noted that well A3 and X3 were added late; A3 was included in all well sampling occasions from March 2006 onward, but well X3 was only sampled in August 2006. Preliminary sampling was done September 6, 2005. Well B4 and all stream sites except C3 were analyzed for nutrients and selectively for $\delta^{18}O$ - H_2O; these preliminary values were included in the analysis when applicable. Ministry of Environment monitoring wells (Well A2 and X2) were only sampled in February and August, coinciding with sampling by the Ministry. Table 3.2 outlines which analyses were used for samples from the different sites. Nutrient, spectral, DOC/TOC, and ICP analyses were done for all sites. The isotope analysis was not done on all sites; stream sites S3 and C2 were excluded from water isotope analysis because it was not felt they were critical sites for this purpose. Sites for nitrate-isotope analysis were selected so there were three well sites on each of the Hopington A and B aquifers; stream sites were chosen to represent upstream, mid-stream, and downstream areas of the system. A complete sampling outline, including replicates, can be found in Appendix A.

Table 3.1 Sampling dates and types of sampling done

Date	Nutrients[+]	Spectral	DOC/TOC	ICP[^]	H_20 isotope*	NO_3 isotope	Comments
6-Sep-05	✓				✓		Selective preliminary sampling
22-Feb-06	✓	✓			✓		
28-Mar-06	✓	✓					$^{18}O - H_2O$ for 2 wells missed in Feb
30-May-06	✓	✓	✓	✓	✓	✓	
26-Jul-06	✓	✓					
21-Aug-06	✓	✓	✓	✓	✓	✓	
17-Oct-06	✓	✓					Stream sites only

[+] nitrate, ammonium, ortho-phosphate, chloride

* $\delta^{18}O$ and $\delta^{2}H$ of H_20; underlined symbol (✓) indicates that only $\delta^{18}O$ was measured

[^] trace elements and metals, as noted in text

Table 3.2 Sites selected for different types of analysis

Site	Nutrients	Spectral	DOC/TOC	ICP	H_20 isotope	NO_3 isotope
STREAM						
Sal 1	✓	✓	✓	✓	✓	✓
Sal 2	✓	✓	✓	✓	✓	×
Sal 3	✓	✓	✓	✓	×	×
Sal 4	✓	✓	✓	✓	✓	✓
Sal 5	✓	✓	✓	✓	✓	×
Sal 6	✓	✓	✓	✓	✓	×
Sal 7	✓	✓	✓	✓	✓	✓
Cog 1	✓	✓	✓	✓	✓	✓
Cog 2	✓	✓	✓	✓	×	×
Cog 3	✓	✓	✓	✓	✓	✓
Trib 1	✓	✓	✓	✓	✓	✓
Dav 1	✓	✓	✓	✓	✓	✓
WELLS						
A1	✓	✓	✓	✓	✓	✓
A2	✓	✓	✓	✓	✓	×
A3	✓	✓	✓	✓	✓	✓
A4	✓	✓	✓	✓	✓	✓
B1	✓	✓	✓	✓	✓	×
B2	✓	✓	✓	✓	✓	✓
B3	✓	✓	✓	✓	✓	✓
B4	✓	✓	✓	✓	✓	✓
X1	✓	✓	✓	✓	✓	✓
X2	✓	✓	✓	✓	✓	×
X3	✓	✓	✓	✓	✓	×

3.3. Field sampling and methods

3.3.1. General protocol

Bottles[6] used for water sample collection were acid washed [7] prior to use. On site, containers were rinsed a minimum of 3 times with the well or stream water being sampled.

[6] General purpose plastic bottles.
[7] 3-4 hours immersed in ~3 M HCl solution, then rinsed with distilled water.

Samples for water isotope analysis ($\delta^{18}O/\delta^{2}H$) were sampled separately with alternate protocol. Samples were kept in a cooler until returned to the lab, then refrigerated until further processing. Specific conductivity and temperature were measured in situ using a handheld Yellow Springs Instrument (YSI) Model 30 salinity, conductivity and temperature instrument.

Table 3.3 Summary of grab samples taken in the field

Sample size	Analyses	Notes
500 mL	Nutrients, spectral, ICP	
250 mL	DOC/TOC	
20 mL	Water isotope	Filtered onsite (Whatman 42), directly into 20mL HDPE scintillation vial with cone cap.
1 – 5 L	Nitrate isotope	Volume dependent on nitrate concentration

3.3.2. Instream thermistors

HOBO® Water Temp Pro data loggers (Onset Part # H20-001) were used to record stream water temperatures. A set of thermistors was deployed in the fall of 2005 for another study and five of these loggers were used to continue measurements. All loggers were removed from the streams on October 17, 2006. Loggers were attached to a cinderblock using wire and the whole block put in the stream; the logger at stream site C1 (Coghlan Creek, Williams Park) was attached to the gabion basket along the southern bank. Temperature measurements were recorded every 15 minutes. Daily averages were calculated upon return to the lab.[8]

3.4. Lab methods

3.4.1. Nutrients and chloride

Within 24 hours of sample collection, a 30 mL subsample was filtered (Whatman 42); the filtered sample was refrigerated until analysis, which was done within 48 hours of collection. Nutrient analyses were done done at the UBC Soil Chemistry Laboratory using a Lachat QuikChem FIA+ 8000 autoanalyzer. Methods and detection limits for each

[8] A complete summary of thermistor activities, including deployment dates and problems, can be found in Appendix B.

nutrient are listed in Table 3.4. A standard was run after every 10 samples for quality control.

Table 3.4. Method and detection limits for nutrient analyses.

Parameter	Detection limit (mg/L)	QuikChem Method #
NO_3^- - N	0.05	12-107-04-1-B
NH_4^+ - N	0.1	10-107-06-2-A
PO_4^{-3} - P	0.02	10-115-01-1-A
Cl^-	6.0	10-117-07-1-A

3.4.2. ICP, metals and trace elements

Approximately 150 mL of solution was gravity filtered (Whatman 42) and 4 drops of concentrated nitric acid (trace metal grade) was added to the filtrate. 100 mL of the acidified solution was pipetted into a clean 100 mL beaker and then reduced on a hotplate to approximately 30 mL. After cooling, the concentrated sample was quantitatively transferred to a 50 mL volumetric flask and made up to volume; 30 mL of the resultant solution was refrigerated until analysis (done within 3 weeks of collection date). Samples were run using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Samples were concentrated, as described above, to increase the number of results above detection limits (see Appendix C). Two blanks (de-ionized water) were processed simultaneously with samples.

3.4.3. DOC/TOC

Approximately 100 mL was filtered through 0.3 μm glass filter and transferred to a clean 100 mL container that was rinsed with the sample. Both the filtered and unfiltered samples were then frozen until analysis. Analysis was done by the UBC Civil Environmental Engineering Laboratory on a Dohrmann Phoenix 8000 UV-Persulfate TOC analyzer using a persulfate-ultraviolet oxidation method[9].

[9] Method 5310 C. Persulfate-Ultraviolet Oxidation Method.(Eaton, Clesceri, & Greenberg, 1995)

3.4.4. Water isotopes

Samples were taken as noted in Table 3.3. Isotope analysis of water for $\delta^{18}O$ and $\delta^{2}H$ was performed by the Pacific Center for Isotopic and Geochemical Research (PCIGR) in the Department of Earth and Ocean Sciences, UBC. The laboratory used a Finnigan Delta XL Plus mass spectrometer in continuous flow mode.[10] Results are reported in the ™ notation, measured in permil (‰) relative to the Vienna Standard Light Antarctic Precipitation (VSLAP) and Vienna Standard Mean Ocean Water (VSMOW) standards.

3.4.5. Nitrate isotopes

The volume of sample collected for nitrate isotope analysis depended on the nitrate concentration (as estimated from the most recent samples taken) so that sufficient nitrate would be collected for the analysis (see Table 3.5). Samples were processed as quickly as possible upon return to the lab.

Table 3.5 Guideline for sample volume required for nitrate isotope analysis.

NO_3^- - N concentration (mg/L)	Sample volume collected (L)
< 0.5	4
0.5 – 4	2
> 4	1

Samples were emptied into a 2 L beaker, 1 mL of 3M HCl was added for each liter of sample and left to sit for about 10 minutes to decarbonate. One mL of 10% $BaCl_2$ was added to each sample to precipitate SO_4^{-2} as $BaSO_4$. Samples were then filtered using a Buchner funnel with Whatman 42 filter paper (2.5 μm particle retention), under vacuum. The filtrate was then put through a Millipore membrane filter (disposable Stericup® / Steritop® Filter Unit, Durapore (PVDF) membrane, 0.45 μm pore size). Filtered samples were sealed and refrigerated until passed through the resin cartridges.

Pre-packed anion columns were purchased from BIO-RAD (Poly Prep® AG1-X8 resin, 200-400 mesh). Figure 3.1 shows the set-up used to pass the sample through the column (Silva et al., 2000). The filtered sample water was loaded into the separatory

[10] Further details of the instrumentation can be found in Appendix D.

funnel and the stopcock and vacuum adjusted to get a flow rate of less than 10 mL/min. After the designated sample volume had passed through the cartridge (and leaving some liquid in the column), the columns were capped and shipped to the Isotope Science Laboratory (ISL) at the University of Calgary. At the ISL, the nitrate was eluted off the column (by gravity, using 15 mL of 3M HCl and 2 mL de-ionized water) and processed according to the silver nitrate technique described by Silva et al. (2000).

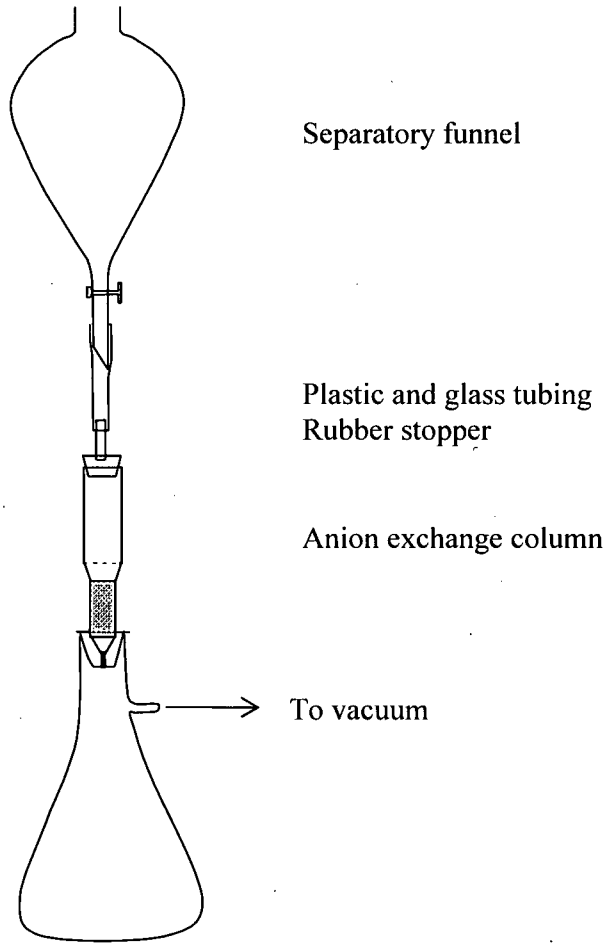

Figure 3.3 Schematic diagram of laboratory set up to pass water samples for nitrate isotope analysis through the anion exchange resin.

3.4.6. Spectroscopy - absorbance and fluorescence

All spectral analysis was done within 36 hours of sampling. Approximately 40 mL of sample was centrifuged[11] at 10100 g for 30 minutes to remove particulates; the supernatant was immediately transferred with a disposable-pipet to avoid re-suspension and the samples were refrigerated if not being analyzed that day. Two blanks (de-ionized water) were processed with each batch of samples. Quartz cuvettes with a 1 cm pathlength were used for all measurements.

Absorption analysis was done using a Varian Cary4000 UV-Vis Spectrophotometer. Absorption was measured between 700 nm and 200 nm with 1 nm intervals and a scan rate of 600 nm/min. The temperature was set at 25°C and monitored through the block (cell holder). A baseline correction was applied so that the de-ionized water blank was automatically subtracted from each field sample.

Fluorescence analysis was done using a Varian Cary Eclipse Fluorescence Spectrophotometer. An excitation-emission matrix (EEM) was collected using emissions from 260-600 nm (2 nm data interval) and excitations 230-450 nm (5 nm increments). Both the excitation and emission slit setting were 5 nm. Scanning rate was manually set at 1200 nm/min with a 0.1 second averaging time. Excitation and Emission filters were set to auto, the PMT detector voltage was 775 volts. Temperature (22°C) was monitored through the cell holder block.

The fluorescence EEMs for de-ionized water blanks were averaged to create a "combined blank" for each day that samples were run; this EEM was subtracted from field samples. No correction for inner-filtering effects was made.[12] A check for instrument stability was performed each day by monitoring the de-ionized water fluorescence intensity for 350 nm/397 nm (excitation/emission). This point falls on the Raman water line and can be used to measure instrument drift. Significant drift was observed over the

[11] Beckman J2-21M/E Centrifuge, JA-17 fixed angle router, 50 mL capped centrifuge tubes.

[12] Only 5 samples in the main data set had absorption at 254 nm > 0.3; absorption above this level may indicate DOM concentration high enough to cause inner-filtering (Ohno 2002), resulting in artificially low fluorescence intensities. Appendix J shows results from a dilution test, with the conclusion that results in this sample set are valid without correcting for inner-filtering effects.

course of this research and so a correction factor was applied, allowing fluorescence intensities to be compared across the entire data set.[13]

3.5. Hydrometric and climate data

Daily stream discharge (m^3/sec) information was obtained through the Hydrometric Program of the Water Survey of Canada.[14] The "Salmon River at 72 Ave, Langley", station number 08MH090, corresponds to stream site S3. Climate data from the Abbotsford Airport meteorological station was obtained from the Environment Canada Weather Office (Climate ID 1100030).[15]

3.6. Land Use

A digital land use and land cover map for the Salmon River watershed and the area above the Hopington aquifers was created using ArcView GIS 9 (version 9.1). A 1989 land use and land cover map (hard copy)[16] was digitized and used as a base for polygon shapes and land use / land cover designations. Modifications and updates were made based on interpretation of 2005 orthophotos and knowledge of the study area. See Chapter 4 for more details on land use for the study area.

3.7. Data analysis

Sampling dates were divided into a wet and dry season based on stream discharge and precipitation. The "wet season" included February, March, May, and October sampling occasions; the "dry season" included September, July, and August. To avoid

---

[13] The de-ionized water blanks were averaged for a given date; from this "combined blank" the fluorescence intensities at ex/em 350/396 nm and 350/398 nm were averaged to approximate the ex/em pair 350/397 nm on the Raman line of water. This point on the Raman line was scaled to an intensity of 20 units and the factor from this calculation became the correction factor for that day. The EEM for each field sample was multiplied by the correction factor for the day it was run.

[14] Archived data available online: http://www.wsc.ec.gc.ca/

[15] Data accessed online at: http://www.climate.weatheroffice.ec.gc.ca/

[16] Present land use in rural Langley, interpreted from 1984 air photos and updated by field check to September 1989.

pseudoreplication, a "site-season average" was calculated for each stream site resulting in one value per site per season; a seasonal division was not made for groundwater samples and so reference to a "site-season average" for wells refers to one average for all samples. Site-season averages were used for correlations with land use and some other statistical analyses. Within this report, the text accompanying any statistical output should specify if values have been averaged for sites or not.

There is sometimes a designation of stream site position ("before", "over", and "after" the aquifer) referring to whether the stream has flowed through the Hopington aquifer boundaries or not. Stream sites included in the "before" group were S6, S7, C3. Sites included in the "over" aquifer group were S4, S5, C1, C2, T1. Sites included in the "after" group were S1, S2, S3, D1.

All statistical analyses were done using SPSS 15.0. Most variables were not normally distributed and so non-parametric methods were applied. Spearman rank correlations were used to look at associations between variables. The Mann Whitney test was used to look at differences between groups. Visual inspection of boxplots was also used as a tool for comparison between groups. All 2-dimensional graphs were made using SPSS or Excel; contour and 3D plots of fluorescence data were generated using Surfer (version 8.05).

4. CLIMATE, HYDROLOGY & LAND USE

4.1. Introduction

This chapter gives a general overview of the study area and provides a framework for the thesis research. The first few sections look at general characteristics and data (climate, precipitation, stream discharge). Some stream temperature data, which was collected for this research, is given. Finally, land use and land cover data is considered.

4.2. Study area

4.2.1. Township of Langley

The Township of Langley, located east of Vancouver, has a population of about 99,000 (Township of Langley). Approximately 81% of the population is serviced by municipal water from local groundwater wells and from the Greater Vancouver Water District. The remaining 18% of the population has a private water supply (private wells, community wells, other sources); in 2005, it was estimated that there were 5000 private groundwater wells. There is a heavy dependence on groundwater resources within the township; within the research area for this thesis (Salmon River Watershed and Hopington Aquifers) residents have private wells and there are two small community well networks that provide water for approximately 200 people (Township of Langley). Almost all residents in the study area are on septic systems.

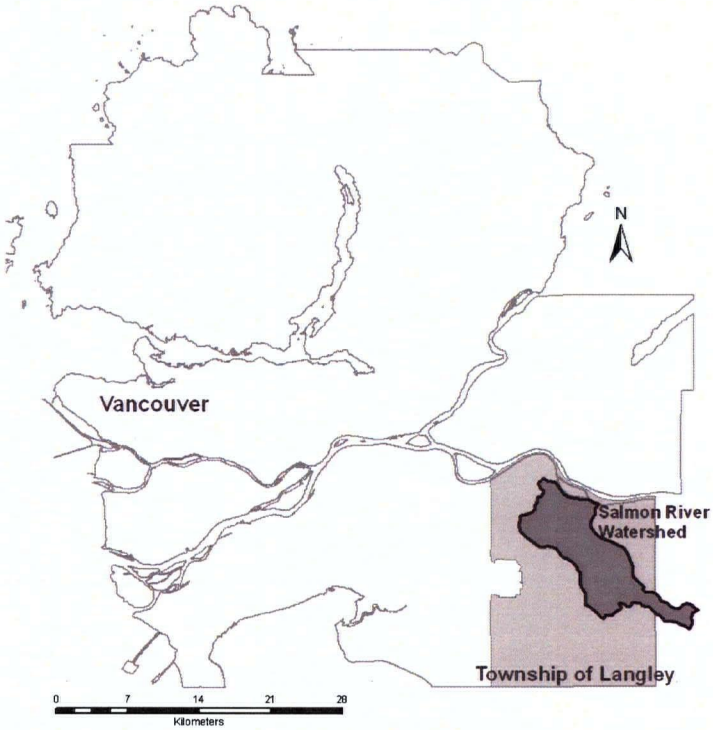

Figure 4.1. Location of the Township of Langley and the Salmon River Watershed within the Township.

4.2.2. **Hopington Aquifer**

Within the B.C. aquifer classification system, the Hopington aquifer (Aq. No 35) is described as a gravel and sand aquifer with multiple water uses, regional quality concerns and regional quantity concerns (British Columbia Ministry of Environment). It is one of 14 unconsolidated aquifers that have been given the Classification of IA (Berardinucci & Ronneseth, 2002) and are the highest priority for management and protection. The "IA" classification indicates that there is high water demand relative to availability (I) and that the aquifer is highly vulnerability to contamination (A) (Berardinucci & Ronneseth, 2002). The classification together with other criteria are used to assign ranking values to the aquifers; the Hopington Aquifer has the highest possible ranking value (21), indicating the highest management priority.[17]

The Hopington aquifer was defined as a single unit in several other reports and studies (Carmichael et al., 1995; Gartner Lee Limited, 2000; Li & Schreier, 2004; Wernick et

[17] Online aquifer classification database available at:
http://aardvark.gov.bc.ca/apps/wells/jsp/common/aquifer_report.jsp

al., 1998) and the BC aquifer classification mapping (British Columbia Ministry of Environment) also refers to the Hopington as one unit. The groundwater modeling done by Golder Associates (2005) for the Township of Langley redefined the Hopington aquifer as three units and this delineation was used for this thesis.

According to Golder (2005), the Hopington C permeable unit is part of the Fort Langley Formation, which consists of glaciomarine clays, ice contact and glaciofluvial deltaic sands and gravels, and till (Golder Associates, 2005). Hopington C consists of prograding sand and gravel of the Fort Langley Formation. Deposits are up to 50 m thick, and are overlain (and interbedded) with glaciomarine silts and locally till. It is considered a shallow semi-confined aquifer, with the permeable unit being locally exposed at the surface. Connection with Hopington A is weak, but the base of Hopington C is connected to West of Aldergrove A / South of Hopington A aquifer units, forming a vertically continuous permeable unit.

The Hopington A and B aquifers are composed of sediments deposited during the Fraser Glaciation. Part of the Sumas Drift, the Hopington A and B permeable units consist of glaciofluvial deltaic sands and gravels. The sand and gravel deposits of the Hopington A permeable unit are up to 40 m thick and the wedge-shaped unit thickens in a northwesterly direction. The top of the Hopington A forms a level surface at about 85 m elevation. The southeast extension of the Hopington A permeable unit is connected to the Abbotsford A aquifer. Hopington A is also weakly connected with Hopington B and C. The Hopington B is a sand and gravel wedge up to 50 m thick, thickening in a westerly direction. The top forms a level surface at about 55 m elevation. Hopington B is weakly connected on Aldergrove D in addition to Hopington A. (Golder Associates, 2005)

The Hopington A and B aquifers are hydraulically connected to the Salmon River and Nicomekl River (west of the Salmon) (Golder Associates, 2005). A report by Gartner Lee (2000) suggests that groundwater provides 30% of the annual flow in the Salmon River and that in August the Hopington aquifer contributes 58% of the Salmon River's baseflow. Calculations of baseflow in the Salmon River using the U.S. EPA method were in agreement with those from other studies (Golder Associates, 2005). Figure 4.2 shows the general directions of groundwater flow and areas of significant discharge to the surface.

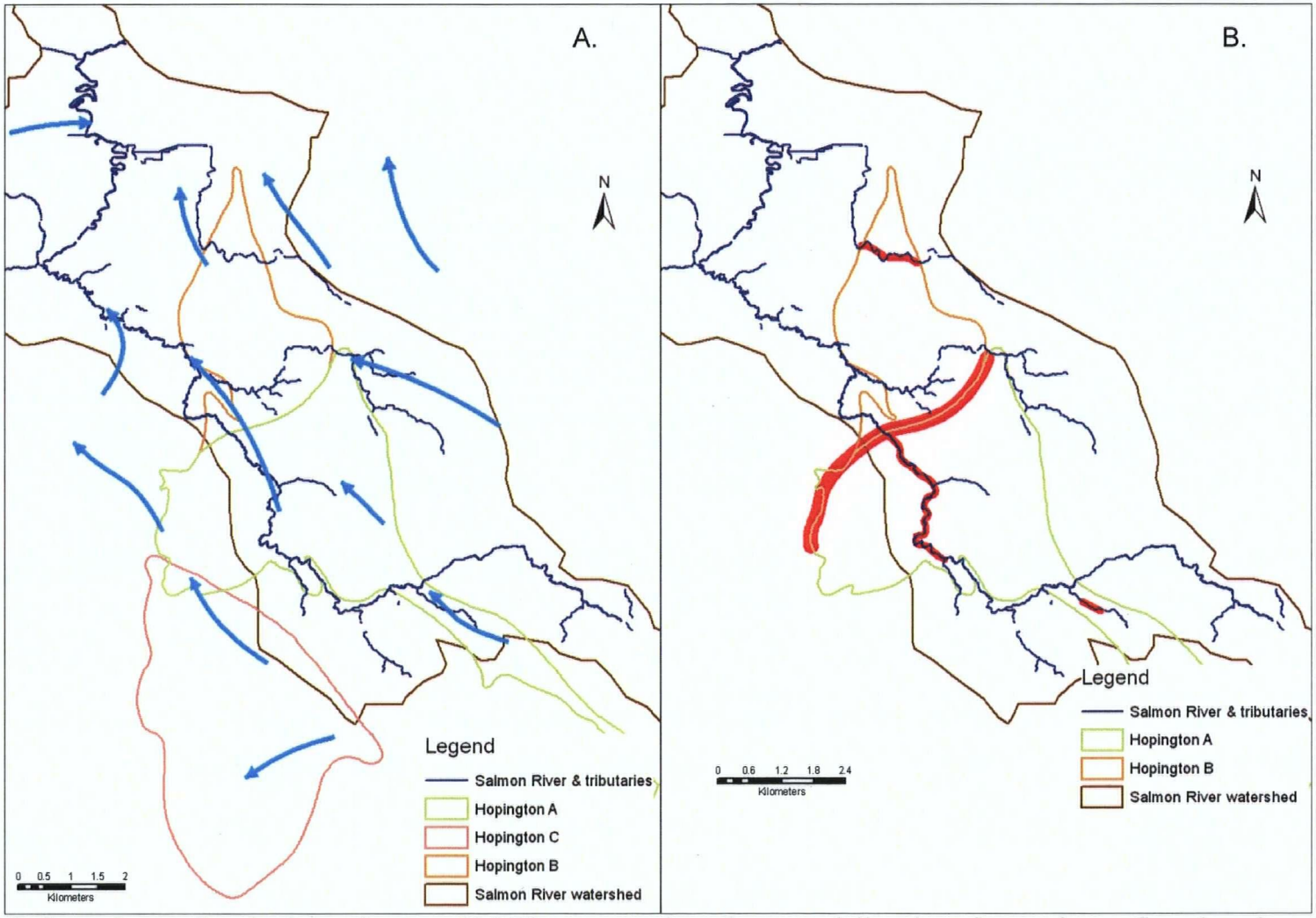

Figure 4.2. Groundwater flow in the study area. (A.) Blue arrows show the general direction of groundwater flow; based on the water table contours predicted by the calibrated model developed by Golder Associates (2005), Figure 58. (B.) Red bands highlight areas of groundwater discharge from the Hopington A and B aquifers; modified from Figure 47 by Golder Associates (2005).

4.2.3. **Salmon River Watershed**

The Salmon River Watershed covers 80 km^2. It includes 25% of the Township of Langley's land base; the upper headwaters of the mainstem are located in Matsqui. The watershed drains into the Fraser River at Fort Langley. Coghlan Creek, Davidson Creek, and Union Creek are tributaries of the Salmon River. As per its name, the Salmon River is a productive spawning and rearing area for Coho salmon as well as steelhead trout and cutthroat trout. There are at least 15 species of fish in the Salmon River including the endangered salish sucker (Watts, 1992).

Figure 4.3. Salmon River watershed boundary and main stream channels, with 2005 orthophoto.

4.3. Precipitation and stream discharge

Climate data was from Environment Canada, as discussed in the Methods section. Figure 4.4 shows the precipitation and stream discharge normals for the period 1971-2000 and 1960-2005, respectively. 2006 was a year of hydrologic extremes. Precipitation was very high in January and November, but July and August had very little precipitation (see Figure 4.5). In late January and November of 2006 the Salmon River stream discharge exceeded the previous maximum, while baseflow from July through October was extremely low (see Figure 4.6).

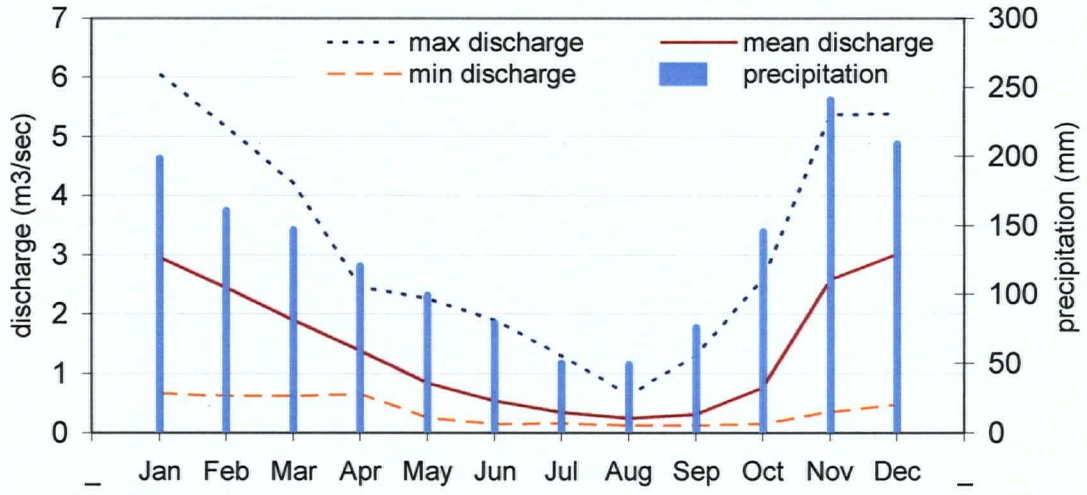

Figure 4.4. Summary of monthly discharge for Salmon River (site S3, 1960-2005) and mean monthly precipitation (Abbotsford, 1971-2000)

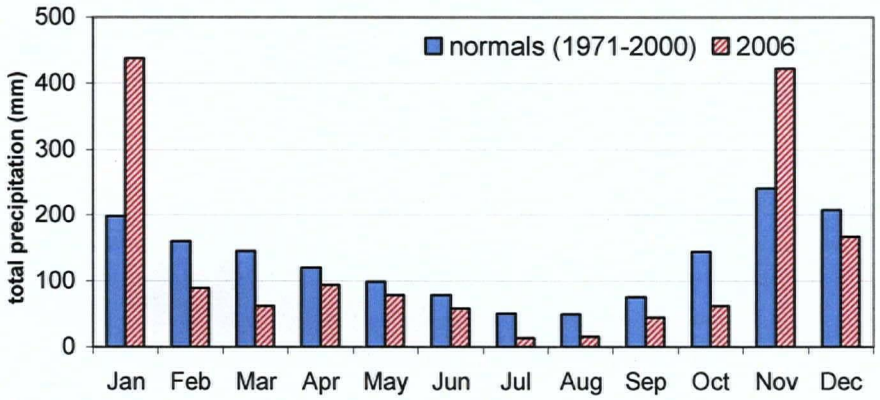

Figure 4.5. Total precipitation in 2006 compared with the normals for 1971-2000.

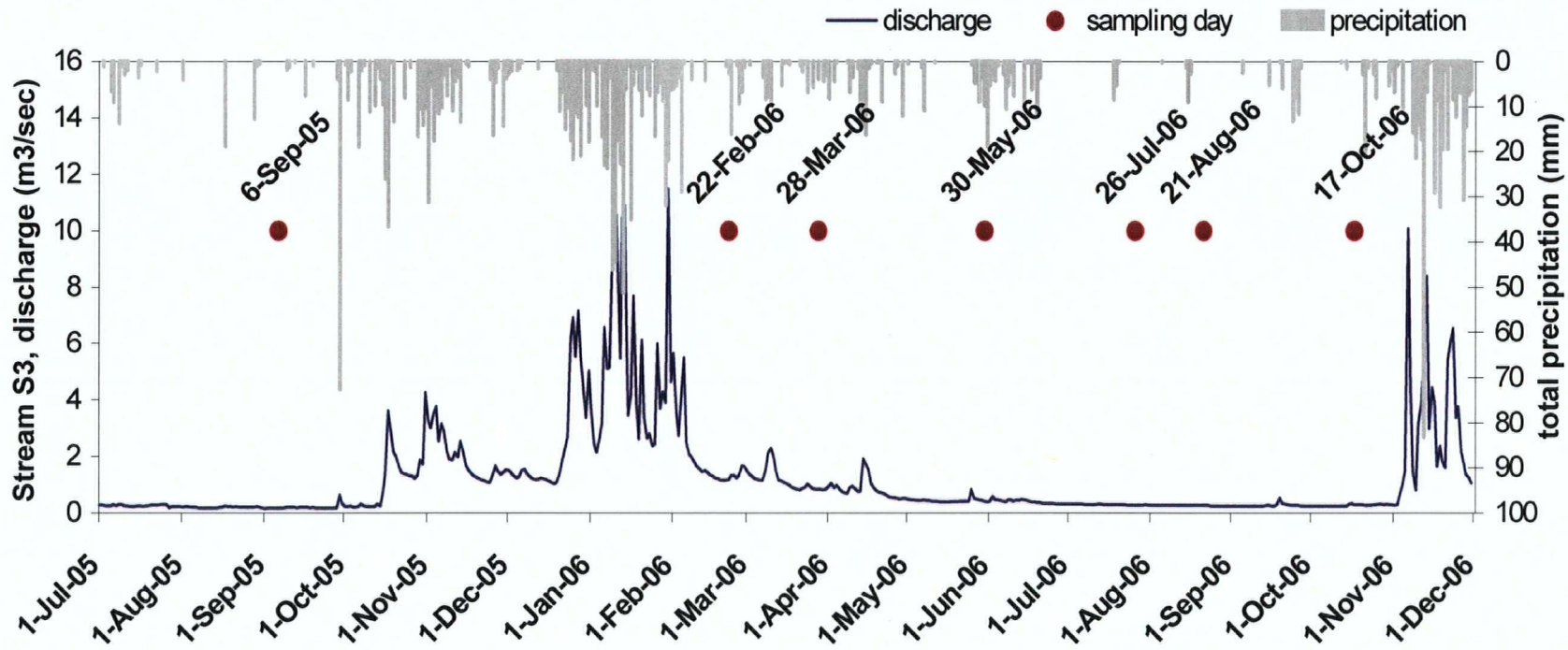

Figure 4.6. Precipitation, stream discharge, and sampling occasions, July 2005 to December 2006. Precipitation is for Abbotsford Airport climate station; discharge (m^3/s) is for stream site S3.

Table 4.1. Total precipitation on sampling days and up to 4 days prior to sampling.

	Precipitation (mm)				
Sampling Date	Day of	24h	48h	72h	96h
September 6, 2005	0.0	0.0	0.0	0.0	0.0
February 20, 2006	0.0	0.0	0.0	0.0	0.0
February 22, 2006	2.6	1.0	1.0	1.0	1.0
March 28, 2006	3.9	0.0	5.7	5.7	12.5
May 30, 2006	0.0	0.8	4.9	8.7	14.0
July 26, 2006	0.0	0.0	0.0	0.0	0.0
August 21, 2006	0.0	0.0	0.0	0.0	0.0
October 17, 2006	0.0	1.2	22.0	24.8	24.8

4.4. Stream temperature

The sites for which water temperature data was collected include: S1, S4, S6, C1, D1. As mentioned in the methods section (and detailed in Appendix B) there were some problems and gaps in collection of stream temperature data using in-stream thermistors and data loggers. There may also have been some effect from the thermistors being in various positions in the stream channel (e.g. some were more shaded than others in an attempt to "hide" them and prevent vandalism or theft). As a result, care must be taken not to over-interpret the data, but some general trends can be observed.

Figure 4.7 shows the mean daily water temperature for each of the sites monitored. It should be noted that the stream locations with expected groundwater influence (S4, C1, D1) had lower temperatures than the headwater site (S6) and the downstream site (S1). The greatest temperature spread occurred from June to September during low stream flow and higher ambient temperatures. The Coghlan site (C1) had temperatures similar to S1 during the winter, but had the lowest stream temperatures overall, which might be attributed to significant groundwater inputs. The mouth of the Salmon (S1) had the highest temperature overall, which was expected; stream temperature typically increases in a downstream direction and flow at this site was significantly reduced because of a pumping station.

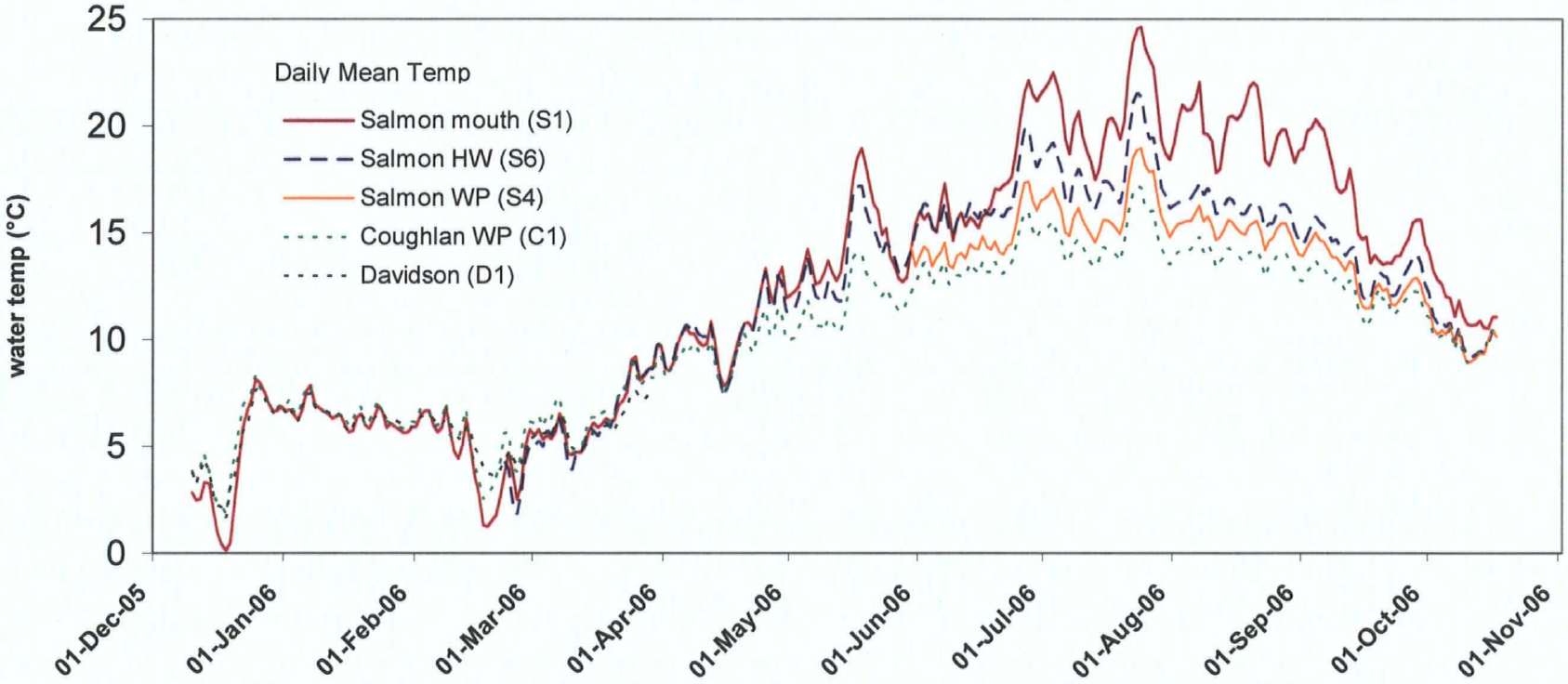

Figure 4.7. Daily mean water temperature for selected sites in Salmon River Watershed.

4.5. Land use and land cover

The land use data and map will be referred to in various discussions throughout this thesis. There will also be reference to uses that are more specific than the categories (e.g. an equestrian facility or dairy operation instead of "animal agriculture"). The intent is for the land use to help explain and link results from the other measurements and tools.

4.5.1. Description of land use and land cover categories

The categories used for land cover and land use are described in Table 4.2 and Table 4.3.

Table 4.2. Description of land cover categories.

Land Cover Category	*Included*	*Notes*
Grass/veg	Annually cultivated crops, grasses, legumes, improved grass, unimproved grassland, other non-woody plants.	Agriculture, recreational fields, lawns, unused fields
Woody veg	Mature trees (planted and irregularly spaced), small/immature trees and shrubs (planted and irregularly spaced), vines	Horticulture plantings and unused, treed areas.
Bare	Rock surfaces (natural and man made), unconsolidated material (natural and man made)	Bare soil, cleared land, extraction activities
Constructed	Buildings/structures and surfaces (pavement)	Impervious surfaces
Water		Ponds and reservoirs Stream channels not included.

Table 4.3. Description of land use categories and subcategories.

LU Category	*Sub-category**	
Agriculture	Crops/arable	Grain, forage, pasture
		Vegetables
		Fuit, nut, berry production
	Livestock activities	Animal housing and holding
		Dairy, beef, poultry, horses, sheep, other
	Greenhouses/	Greenhouse vegetables, flowers, ornamentals
	nurseries/horticulture	Christmas tree farms
		Ornamental shrubs and trees
	Other	Sod production
		Mushroom production
		Storage (crops, machinery, tools)
		Other site agriculture
	Unused/vacant	
Residential		Single family, multiple dwellings, mobile homes, group homes
Commercial/	Commercial	Wholesale, retail, commercial services
Industrial/	Industrial	Raw material processing, other processing
Institutional		Extraction activities
		Energy and heat generation
	Civic/institutional	Protective and custodial services
		Educational services
		Religious activities
		Waste disposal/treatment
	Storage activities	Tank/reservoir storage
		Storing vehicles, equipment, other
Transport		Transportation (road, rail, air) activities
		Communication activities
Recreation	Golf courses	
	Parks/playing fields	
	Other	Trail use, camping, historical areas, outdoor viewing of animals
Other	Vacant/unused	No perceived activity
		Land in transition
		Former forestry, extraction, dwelling, institutional activities
	Other	Forestry activities
		Wildlife/fisheries related activities
		Ecological research, conservation, flood control and drainage

* Subcategories listed here were defined in the GIS database, but may be generalized into larger groups in land use summaries. Greenhouses/nurseries/horticulture, Other, and Unused subcategories are sometimes grouped as "other agriculture". "Unclassified agriculture" applies to areas with no subcategory as the specific agricultural activities could not be identified.

4.5.2. **Contributing areas and buffer zones**

Contributing areas (CAs) and buffer zones were used to summarize the land use and land cover data. The buffers or contributing areas were unioned with the original land use/cover layer and then the areas summed by category for each CA and buffer. These summaries were used for calculating correlations with other parameters. Contributing areas for each stream sampling site were defined as the land surface that would contribute runoff from precipitation to the stream, upstream of the sampling area until the next sampling site. CAs were delineated using a contour map of elevation (2 m contours), Figure 4.8A shows the resulting areas.

Stream buffers of 50 m and 100 m (on either side of the bank) were generated in ArcMap. In summarizing land use/cover for stream buffer zones, the buffers were limited to the extent of the contributing areas. Circular buffers for wells had a radius of 100 m and 500 m. These circular buffers did not take into account groundwater flow direction or capture zones. Figure 4.8B shows an example of stream and well buffers within the CAs for stream sites C1 and S4.

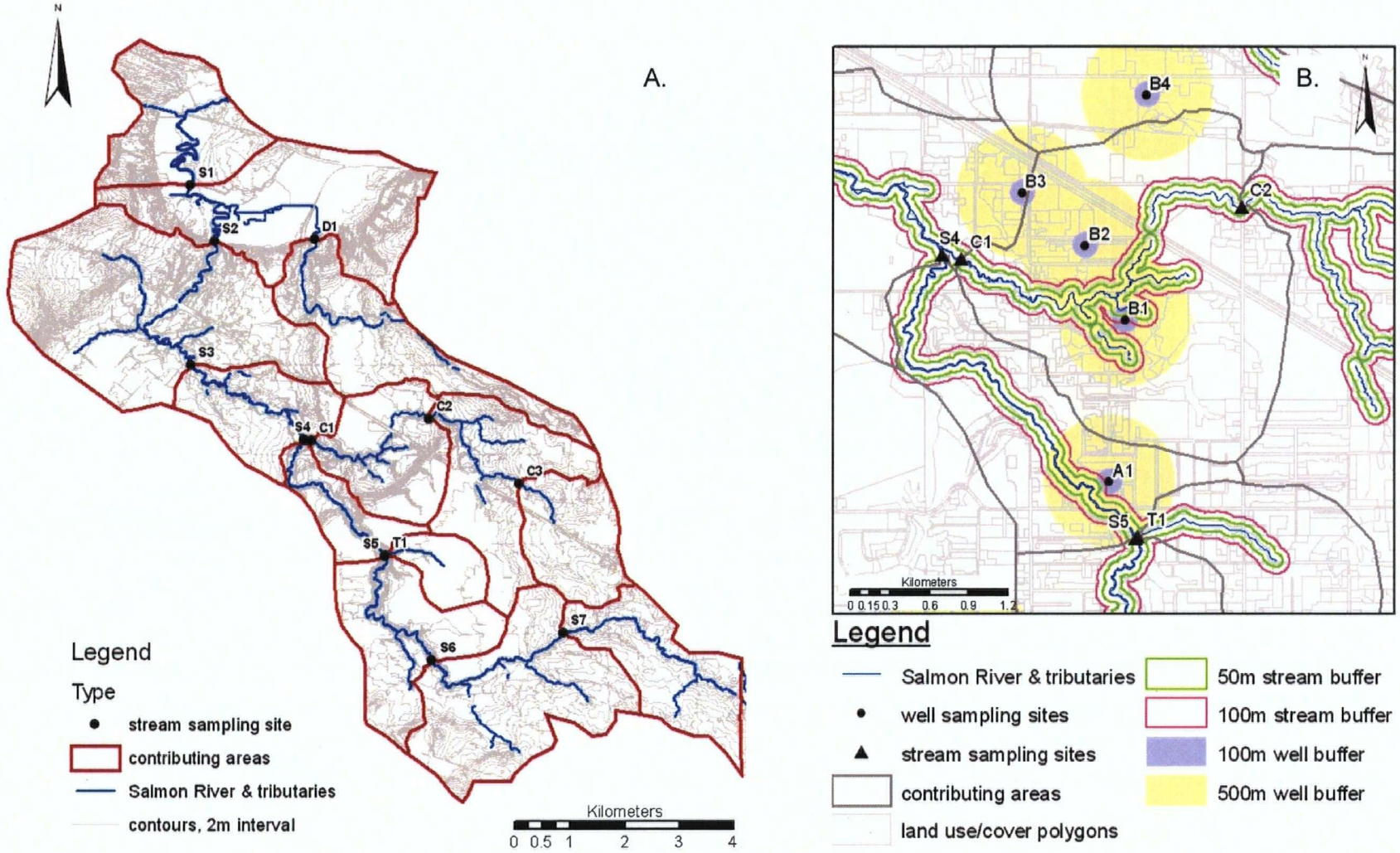

Figure 4.8. Contributing areas and buffer zones used for land use and land cover summaries. (A.) Contributing areas for each stream site. (B.) Example of stream and well buffers.

4.5.3. **Results**

Figure 4.9 and Figure 4.10 show a visual summary of the land use and land cover results. Table 4.4, Table 4.5, and Table 4.6 summarize the land use and land cover for the Salmon River watershed and the land area above the Hopington aquifers.[18] Approximately 50% of the Salmon River watershed area is involved in some agricultural use. Compared to the land use above Hopington A and B, Hopington C has the highest percentage of agricultural land use (58%) and the highest arable and livestock agricultural categories (42% and 10%, respectively). Hopington B has a higher percentage of the land in agricultural use than Hopington A (51% compared to 38%), but A has more residential use (29% compared to 14% for Hopington B).

The land use values within a 100 m buffer of the well (and perhaps even within 500 m) are somewhat biased due to the well selection. Wells were not randomly selected and most wells are private residential wells and will therefore reflect this with a seemingly high value in the residential category for land use. Therefore, some caution must be exercised when interpreting any correlations or making broader inferences regarding land use impacts on the groundwater, especially for the immediate vicinity of sampling sites. Table 4.7 gives a land use summary for 100 m buffers around the wells sampled.

Several wells stand out from the others when looking through the land use summary tables. Well A2 shows a 34% recreation land use within the 100 m buffer zone, this area is a sports / playing field beside a public school. Well B4 is predominately surrounded by agriculture, as it is located on the site of a horse show stadium facility; in this case, the "unclassified agriculture" is associated with this horse facility, but does not have an explicit pasture or animal housing use. The "other agriculture" in the buffer zone of Well X2 is land adjoining the nearby greenhouse / horticulture operation, but which is used for storage and other activities besides production.

For the stream sites, the percent land uses for the contributing areas and 100 m buffer zones are quite similar. Table 4.8 gives land use percentages for a 100 m buffer upstream of each surface water sampling site. S1, S6, C2 have a high proportion of

[18] A summary for all CAs and buffer areas can be found in Appendices F and G.

agriculture, especially in the 100 m buffer zone; most of this is crops / arable. Residential land use is high for T1 and S5, but very low for S7, D1, and S6 (S2, S4, C2 also <10% residential). S4 has very high "other" land use and woody vegetation cover (especially for 100m buffer). The comm/ind/inst land use (21-25%) near site S7 is a school and a base for armed forces. The "recreation" near S1 is a golf course and near S7 is a zoo. Williams Park increases recreation values for S3 and S4. T1 has high constructed cover (33%) due to lots of housing; S4 also has higher constructed cover in the CA (26%), mostly from housing, but only 6% within the 100 m buffer.

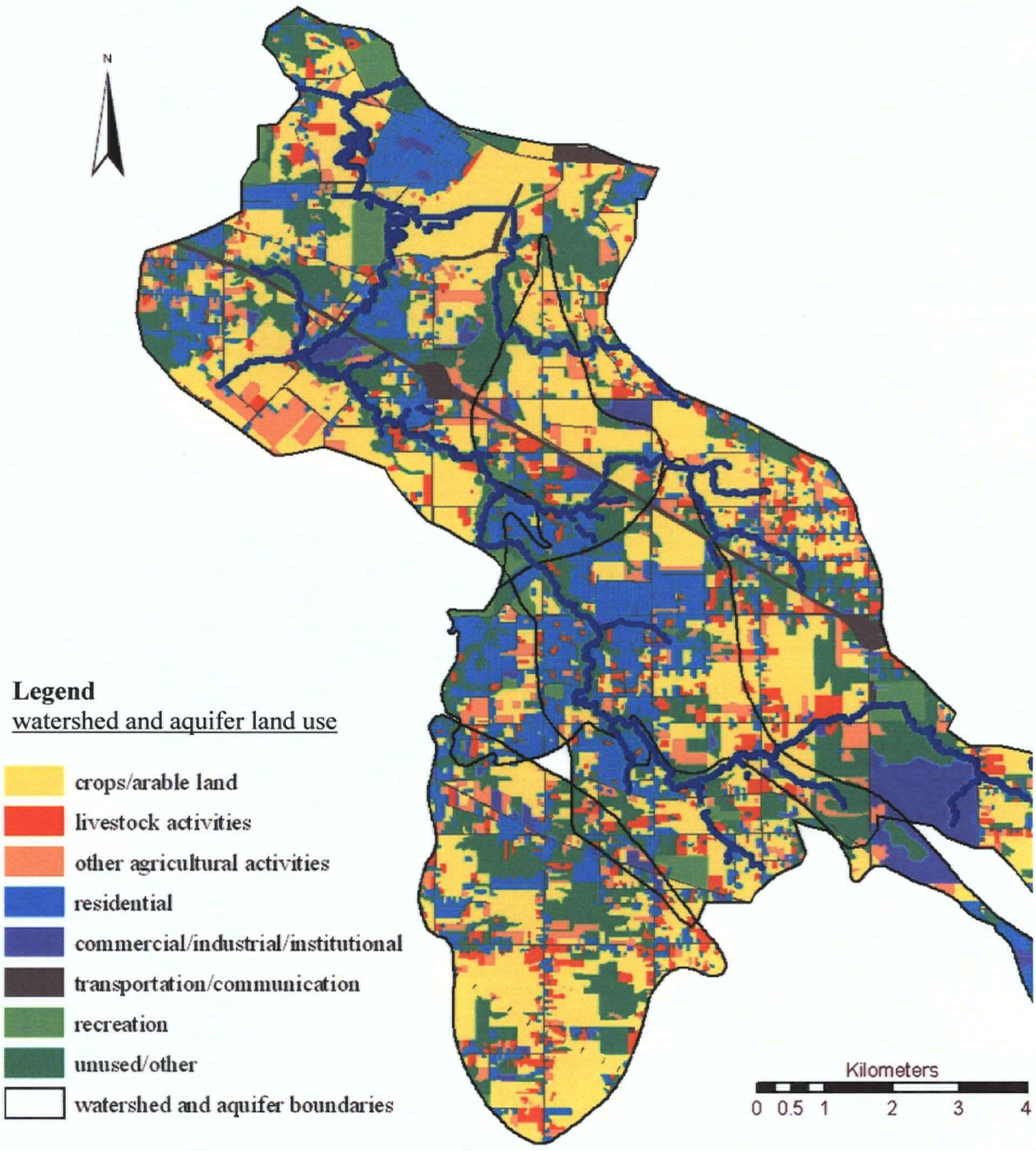

Figure 4.9. Map of land use within the study area.

Table 4.4. Summary of land use in the Salmon River watershed and above the Hopington aquifers.

	Land Use Category (% of total area)						Total Area
	agriculture	residential	com/ind/inst	transport	recreation	other	(km^2)
Salmon Watershed	49.6	15.6	4.0	7.0	3.3	20.5	73.56
Hopington A	37.5	29.1	5.7	7.2	1.8	18.7	16.39
Hopington B	50.6	13.9	2.6	7.1	2.2	23.6	7.06
Hopington C	58.3	14.0	2.8	4.0	0.3	20.6	16.46

Table 4.5. Breakdown of the agricultural land use component for land in the Salmon River watershed and above the Hopington aquifers.

	Land Use Category (% of total area)							Total Area
	crops/arable	livestock	hort/grnhse	other ag	unused	unclass ag	Ag. Total	(km^2)
Salmon Watershed	35.2	6.7	2.1	0.6	2.5	2.3	49.6	73.56
Hopington A	22.8	5.6	4.2	0.7	2.4	1.7	37.5	16.39
Hopington B	36.9	6.5	2.8	1.3	1.7	1.5	50.6	7.06
Hopington C	41.6	9.7	1.8	0.4	1.4	3.4	58.3	16.46

Table 4.6. Summary of land cover in the Salmon River watershed and above the Hopington aquifers.

	Land Cover Category (% of total area)					Total Area
	grass/veg	woody veg	bare	constructed	water	(km^2)
Salmon Watershed	52.1	29.4	3.8	14.4	0.3	73.56
Hopington A	42.6	33.0	2.8	20.4	1.1	16.39
Hopington B	47.7	36.8	3.8	11.1	0.6	7.06
Hopington C	55.0	25.5	7.4	11.8	0.2	16.46

Table 4.7. Summary of land use in 100 m buffer zone around well sampling sites

	Land Use Category, % of total buffer area (31400m^2)					
	agriculture	residential	com/ind/inst	transport	recreation	other
WELL A1	24.5	42.9	0.0	4.3	0.0	28.3
WELL A2	53.8	11.9	0.0	0.7	33.6	0.0
WELL A3	53.5	23.7	0.0	8.8	0.0	14.1
WELL A4	48.1	39.3	0.0	12.5	0.0	0.0
WELL B1	0.0	56.4	0.0	13.0	0.0	30.6
WELL B2	8.5	81.3	0.5	9.7	0.0	0.0
WELL B3	33.4	49.5	0.0	16.6	0.0	0.5
WELL B4	98.4	1.6	0.0	0.0	0.0	0.0
WELL X1	34.4	38.2	0.0	9.0	0.0	18.4
WELL X2	54.0	32.0	0.0	12.6	0.0	1.4
WELL X3	28.1	32.5	0.0	0.0	0.0	39.4

Table 4.8. Summary of land use for 100 m buffer areas above streams sampling locations.

	Land Use Category (% of total area)						Total Area
	agriculture	residential	com/ind/inst	transport	recreation	other	(km^2)
100m Buffer							
S1	80.1	3.6	0.0	3.6	10.7	1.9	1.15
S2	30.2	9.1	3.8	7.1	0.6	49.2	1.69
S3	27.2	16.4	0.2	4.8	6.2	45.1	0.88
S4	3.3	9.5	1.5	2.9	5.4	77.3	0.71
S5	7.1	36.0	0.0	4.6	0.0	52.3	0.92
S6	59.8	6.8	1.1	2.1	1.4	28.8	1.46
S7	33.6	3.8	20.6	3.9	13.9	24.2	1.15
C1	12.9	21.9	1.6	3.6	0.4	59.6	0.91
C2	71.2	9.3	0.9	3.7	0.0	14.9	1.03
C3	22.3	14.4	1.6	8.0	0.0	53.8	0.24
T1	7.9	42.0	4.1	10.1	4.6	31.3	0.24
D1	33.0	8.1	0.9	2.3	0.0	55.8	1.02

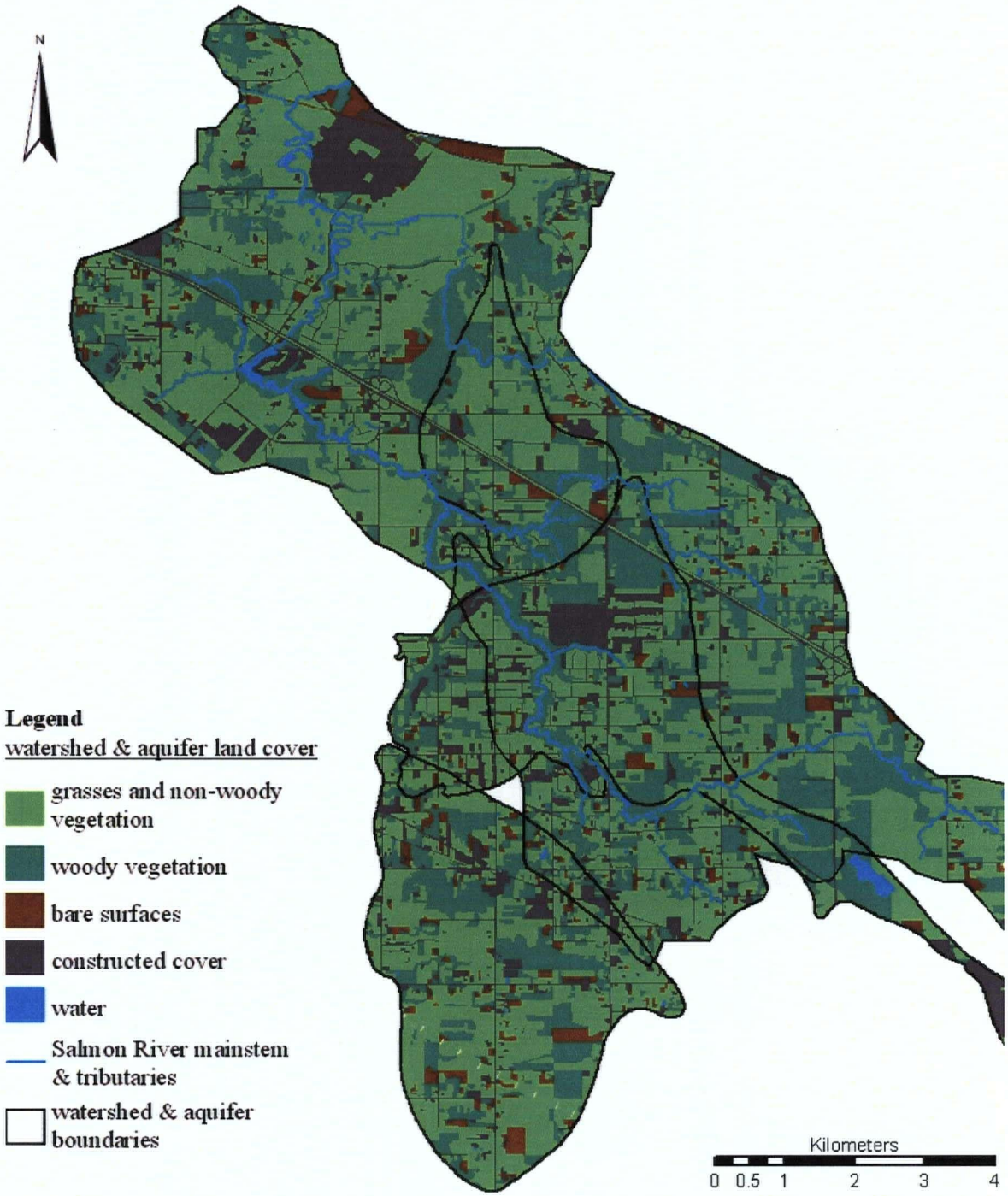

Figure 4.10. Map of land cover within the study area.

4.6. Conclusions

The hydrology of the study area and the stream temperature data set a background for further investigation of the groundwater – stream water interactions. The land use data described here provides a spatial context to understand relationships between the activities in the area and the groundwater and surface water quality. The land use is dominated by agriculture (50% of land area), which can impact local water resources through additions of nutrients, bacteria (from animal waste) and pharmaceuticals. Although residential land area is only about 16%, the use of septic tanks is a potential concern, especially on the unconfined Hopington A and B aquifers.

5. NITRATE AND NITRATE ISOTOPES

5.1. Introduction

Nitrate trends in the Salmon River Watershed have been documented in a number of studies, as discussed in Chapters 1 and 5. It has been known for some years that there are localized areas of groundwater with elevated nitrates, which are indicative of anthropogenic impacts. The data collected for this thesis confirms the established trends for nitrate in the streams and that some wells have nitrate concentrations exceeding the Canadian drinking water guideline. This thesis seeks to extend the previous knowledge of nitrate dynamics to the broader context of groundwater-surface water interactions. Furthermore, the source of nitrates are investigated through the use of stable nitrate isotopes ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) and the inclusion of other measures (e.g. dissolved elements) as discussed in other chapters.

This chapter will outline the spatial and seasonal nitrate trends in stream water, and also the status of nitrate concentrations in the wells sampled. Nitrate isotope results will be presented and discussed in terms of nitrate source and nitrogen transformations. These trends and results provide a context for the subsequent chapters that look at other measures, with the hope of complimenting and further extrapolating the results discussed here.

5.2. Methods

Laboratory methods are outlined in Chapter 3. Sampling for nitrate-isotopes was done in May and August 2006. August was selected to represent low-flow "dry season" conditions where groundwater discharge to the stream would have maximum impact. May was selected because it was still in the wet season, but stream discharge was low enough so that groundwater discharge would have a measurable impact on stream water chemistry. For isotope analysis, one site was randomly selected for sampling in triplicate for each date. For the nitrate analysis, one stream and one well site was sampled in triplicate on each sampling date.

5.3. Range and variability of measurements

Both stream and groundwater samples had a range of nitrate concentrations. Table 5.1 gives some summary statistics for both the nitrate concentrations and nitrate-isotope results. In total, 6 well and 6 stream samples were replicated (triplicate); the average standard deviation for the replicate samples was 0.043 mg/L and average CV was 8.0%.

For nitrate-isotope analyses stream site C1 and well B4 were sampled in triplicate in May and August, respectively. The $\delta^{18}O$ measurement was more variable than the $\delta^{15}N$. Laboratory methods had an accuracy of 0.2 and 0.5‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively. The replicate samples in May had a standard deviation of 0.04 and 0.98‰ and the August replicates had a standard deviation of 0.002 and 0.43‰ ($\delta^{15}N$ and $\delta^{18}O$, respectively).

Table 5.1. Summary statistics for stream and groundwater nitrate concentrations and nitrate-isotopes ($\delta^{15}N$, $\delta^{18}O$).

	N	Mean	Median	Min	Max	Std. Dev
All samples						
NO_3^--N conc (mg/L)	125	4.9	2.9	0.0	26.6	5.6
$\delta^{15}N$-nitrate (‰)	26	9.8	10.1	5.7	14.8	2.4
$\delta^{18}O$-nitrate (‰)	25	1.3	-0.4	-3.4	15.1	4.7
Stream samples						
NO_3^--N conc (mg/L)	80	2.4	2.2	0.0	5.8	1.5
$\delta^{15}N$-nitrate (‰)	12	10.9	10.9	8.6	12.8	1.1
$\delta^{18}O$-nitrate (‰)	11	1.8	-0.3	-1.1	15.1	4.6
Groundwater samples						
NO_3^--N conc (mg/L)	45	9.3	9.5	0.0	26.6	7.4
$\delta^{15}N$-nitrate (‰)	14	8.9	8.4	5.7	14.8	2.8
$\delta^{18}O$-nitrate (‰)	14	0.9	-0.8	-3.4	12.3	4.9

5.4. Stream nitrate dynamics

Nitrate concentrations were quite high at some sites, but always met the BC water quality nitrate guidelines for any specified use (drinking, recreation, aquatic life, livestock and irrigation water) (Nordin & Pommen, 1986). Stream nitrate dynamics in the Salmon River watershed are influenced by a combination of land use, season, precipitation pattern,

and groundwater influence. For the purpose of exploring the importance of each of these factors, sampling events were divided into 2 "seasons" – wet and dry. September, July, and August samples were grouped into the dry season because stream discharge was low at these times and there were no substantial precipitation events prior to the sampling day. February, March, May, and October samples were grouped into the wet season based on stream discharge and antecedent precipitation. This seasonal distinction was helpful in considering probable nitrate pathways and sources. Figure 5.1 graphically shows the nitrate concentrations for each sampling site, distinguishing between the wet and dry seasons.

A Mann-Whitney test was used to check for significant differences between seasonal nitrate concentrations at each site. Sites can be split into 3 categories of seasonal nitrate trends: wet season > dry season, dry season > wet season, and no seasonal difference (see Table 5.2). Each of these patterns says something about the nitrate sources and transport.

The upper-Salmon River sites (S7 and S6) had significantly[19] higher nitrate concentrations in the wet season, which is the norm for streams in the Lower Fraser Valley not influenced by groundwater. This suggests that additional nitrate was reaching these stream locations through overland runoff or transport due to the increased precipitation during the wet months. Upstream of site S7 there was a zoo and there was a horse farm very close to the sampling station, as well as other agricultural land uses in the contributing area. This site also has a beaver dam just above the sampling point. In between these two sites there were numerous farms, and agricultural land use dominates the contributing area of site S6 (53%), likely contributing nitrate through leaching or runoff from animal wastes. These activities were likely contributing to the higher nitrates during the wet season. These headwater sites had some of the lowest nitrate concentrations measured in streams, but the seasonal nitrate trends supported impacts and sources from nearby land uses as mentioned above.

[19] P-value = 0.034 for STR 09, 10, 08; p-value = 0.064 for HS 07

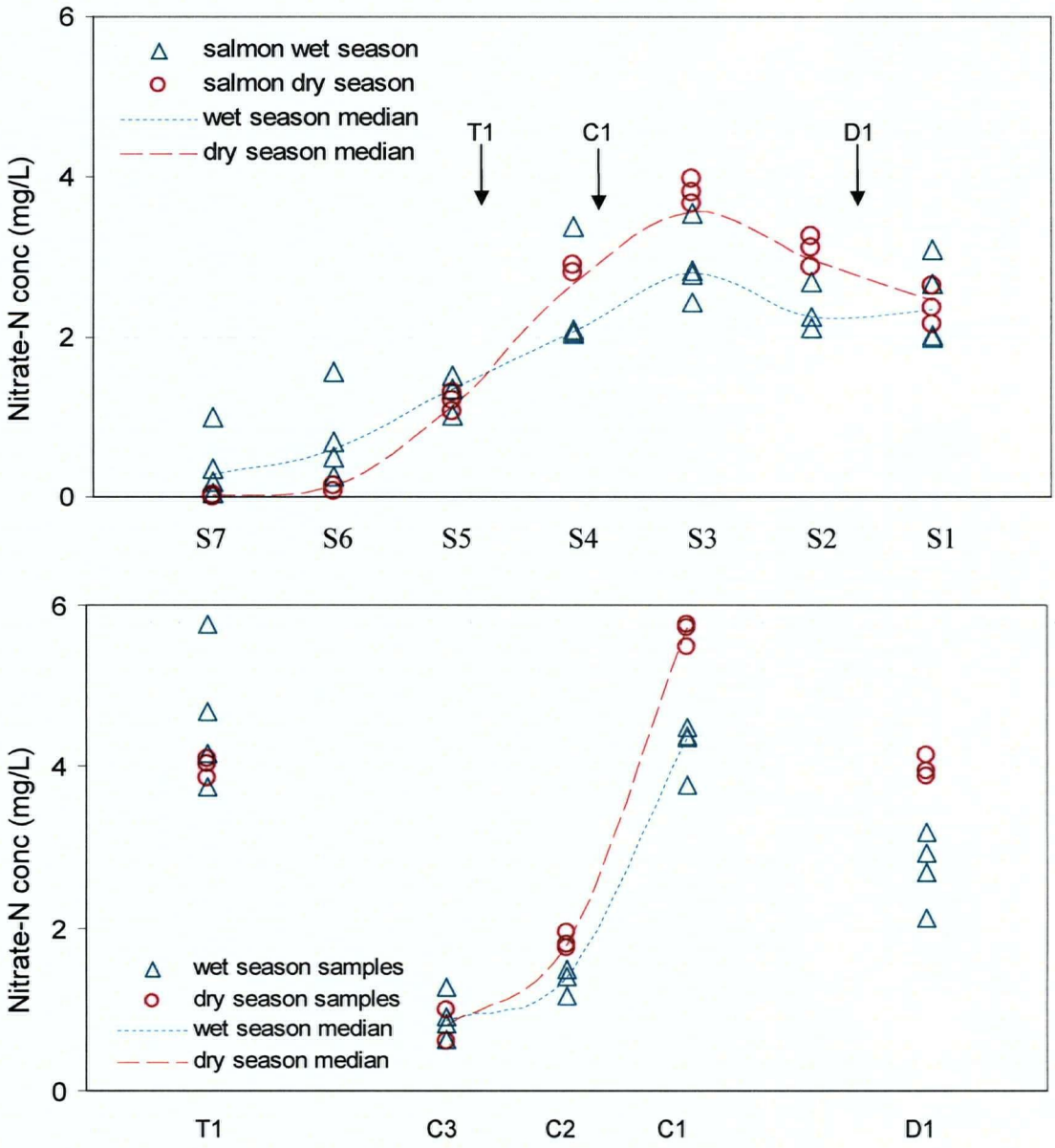

Figure 5.1. Stream nitrate concentrations, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

Table 5.2 Summary of seasonal differences in nitrate concentration for stream sites.

	Seasonal nitrate concentration of stream water		
	Dry > Wet	Dry < Wet	No difference
Salmon	*"after" aquifer* S3*	*"before" Hopington A* S6* S7*	*"over" Hopington AB* S4, S5 *Near river mouth* S1, S2
Coghlan	*"over" Hopington B* C1* C2**		*"before" Hopington AB* C3
Davidson	*"after" Hopington B* D1*		
Union Creek			*"over" Hopington A* T1
Source & Pathway	Input from groundwater during dry season (low flow) is key nitrate source/pathway, which is diluted during higher flow.	Precipitation and runoff flushes nitrates from land surface or shallow storage into the streams. Agricultural runoff and animal waste are primary sources.	Different seasonal sources with proportionate contributions, mixing and multiple sources, or continuous source.

* p-value 0.057 for Mann-Whitney test
** p-value 0.100 for Mann-Whitney test

Site T1 had higher nitrates during several wet season sampling occasions, although the seasonal difference was not statistically significant overall. Agricultural runoff and septic system leaching were both potential sources of nitrate for this site. In the last decade, agricultural land has been developed for residential use and during the transition period piles of manure and farm wastes may have been buried (Stjepovic, 2007). This buried waste may be a source of nitrates and groundwater quality problems. Site T1 had some of the highest nitrate levels measured in stream water.

The lower-Salmon River site S3, lower-Coghlan sites C2 and C1, and the Davidson Creek (D1) had significantly higher nitrate concentrations in the dry season compared to the wet. These sites were all influenced by groundwater contribution from the Hopington A and B aquifers. This nitrate "source" would have been subject to dilution during the wet season, thus the lower concentrations. The decrease in the wet-

season concentrations was not in proportion to the increase in discharge because there would be other nitrate sources in addition to groundwater inputs.

It might be expected that Salmon site S4, which is on the edge of the Hopington A aquifer, might exhibit a similar seasonal trend, but the difference was not statistically significant. Most likely, the nitrate from upstream was "supplementing" the groundwater nitrate contribution so that the overall seasonal difference in concentration was minimal at this site. The February sample was the highest for any date and so perhaps precipitation had flushed nitrate-rich runoff or leachate into the stream. Union Creek (T1), which joins the Salmon River upstream of site S4, also had the highest nitrate concentrations in February, thus this tributary may have contributed to the nitrate rise.

Sites S5, S2, S1, and C3 had no difference between seasonal nitrate concentrations. Sites S2 and S1 were the furthest downstream and thus would have a mix of groundwater and surface water inputs, which confuses the seasonal trend, although visual inspection of the graphs shows site S2 to have had higher nitrates in the dry season, reflecting the groundwater input upstream. Site S5 has cut through the Hopington B aquifer and was likely influenced by groundwater, but the upstream nitrate sources were not diluted enough to show any seasonal differentiation. Site C3 had nitrate concentrations less than 2mg/L and was not influenced by the aquifer. There was no difference between seasonal concentrations of nitrate at C3 and so perhaps the mixed land use was resulting in a steady, but minimal nitrate contribution throughout the year.

Testing for seasonal differences between grouped stream samples[20] supports the interpretation of groundwater influence at individual sites and summarized in Table 5.2. The "before" aquifer sites (not influenced by groundwater) had significantly higher nitrate in the wet season (p-value 0.016, N=12, 8 for wet, dry season). Stream sites over the Hopington aquifers had no seasonal difference (N=18, 15 for wet, dry), but the dry season nitrate concentrations were higher for the stream sites after the aquifer (p-value 0.009, N=15 for both seasons). There were also significant differences between the different stream positions relative to the aquifer position (see

[20] Site-season average was used for each site.

Figure 5.2). For the seasons grouped together and for seasons tested separately, the before-aquifer sites had significantly lower nitrate concentrations than the over or after sites (p-value 0.000); there was no significant difference between the over and after sites.

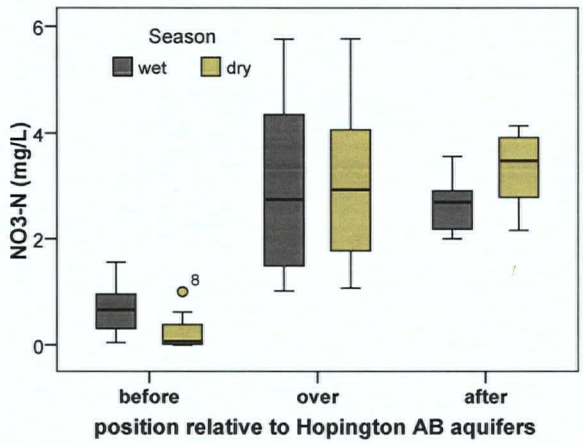

Figure 5.2. Boxplot of stream water nitrate concentrations, grouped by position relative to the Hopington aquifer. n = 20, 33, and 17 for before, over and after, respectively. Boxplots show the median, interquartile range, 95% confidence intervals, outliers (O).

5.5. Groundwater nitrate dynamics

Groundwater nitrate concentrations ranged from zero (wells in Hopington C) to 27 mg/L (well A3). Hopington C wells had lower nitrate levels that those in A and B; Hopington A wells were more variable than those sampled in B (Figure 5.3). Using one mean value for each well, Hopington B wells had significantly higher nitrate than Hopington C wells (p-value 0.057), but no other differences were significant. If all observations are included Hopington A and C were also significantly different, however the difference may be false due to pseudo-replication. Figure 5.4 shows the range for each well sampled within Hopington A and B.

Seasonally, the nitrate ranges for each aquifer are consistent, but the nitrate concentration of several individual wells fluctuated with season. Well B3 had higher values in the wet season; this well was fairly shallow (26 m) compared to others and may be subject to contamination with the winter rains. There were chicken barns and other agricultural activities nearby that could be a source. Wells A1 and A4 had higher values in the dry season. Low-nitrate recharge from surface waters and precipitation during the

winter and spring may have had a dilution effect. Both these wells are quite close to the channel of the Salmon River and may have been influenced by stream water (lower nitrate concentration) during the winter months.

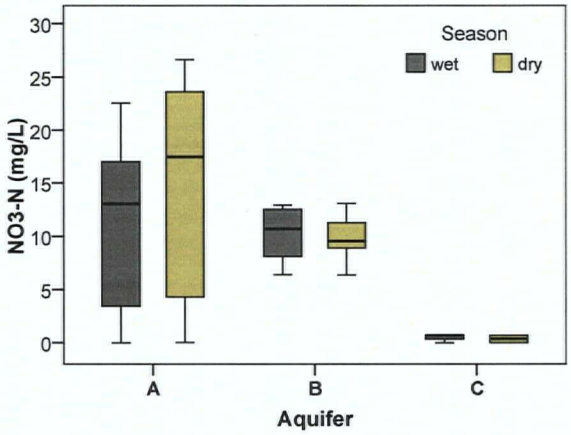

Figure 5.3. Boxplot of groundwater nitrate concentrations, by Hopington aquifer. n = 17, 20, and 8 for A, B, and C, respectively. Boxplots show the median, interquartile range, 95% confidence intervals, outliers (O).

Well depth and nitrate concentration was not necessarily related, with some of the deep wells having very high nitrate concentrations. For example, well B4 was 74 m deep and had 10.0 mg NO_3^--N/L (mean of 5 sampling occasions). The Canadian and B.C. drinking water guideline for nitrate-N is 10 mg/L (FPT Committee on Drinking Water, 2006; Nordin & Pommen, 1986). Five wells exceeded this guideline on at least one sampling occasion (see Figure 5.4). This is a health concern for some residents, especially those with very small children, and is also of concern because it may be indicative of other water quality problems.

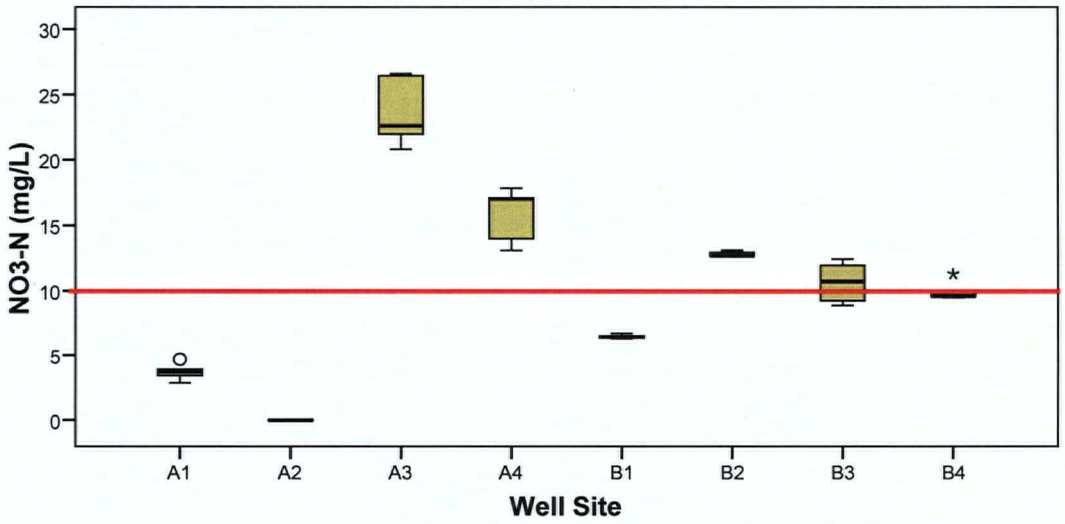

Figure 5.4. Boxplot of nitrate concentrations for wells sampled in Hopington A and B aquifers. The red line represents the drinking water quality guideline of 10 mg/L of NO_3^--N. Boxplots show the median, interquartile range, 95% confidence intervals, outliers (O), and extreme values (*).

5.6. Nitrate isotopes

Nitrate isotope values ranged from 5.7 to 14.8 ‰ for $\delta^{15}N$ and -3.4 to 15.1 ‰ for $\delta^{18}O$ of nitrate. This was a fairly narrow range of values considering the potential spread (Figure 5.5), indicating a limited range of sources or else mixing that has moderated any extreme values. The oxygen values are particularly tight in range, with all values except those for well A3 falling between -3.4‰ and 3.9‰; Well A3 had values of 12.3‰ and 10.9‰ in May and August, respectively. In August stream site T1 also had a higher $\delta^{18}O$ value, but this was attributed to contamination of the $AgNO_3$ precipitate and so the value was discarded. Stream site C3 was only analyzed in May because the nitrate concentration was too low in August.

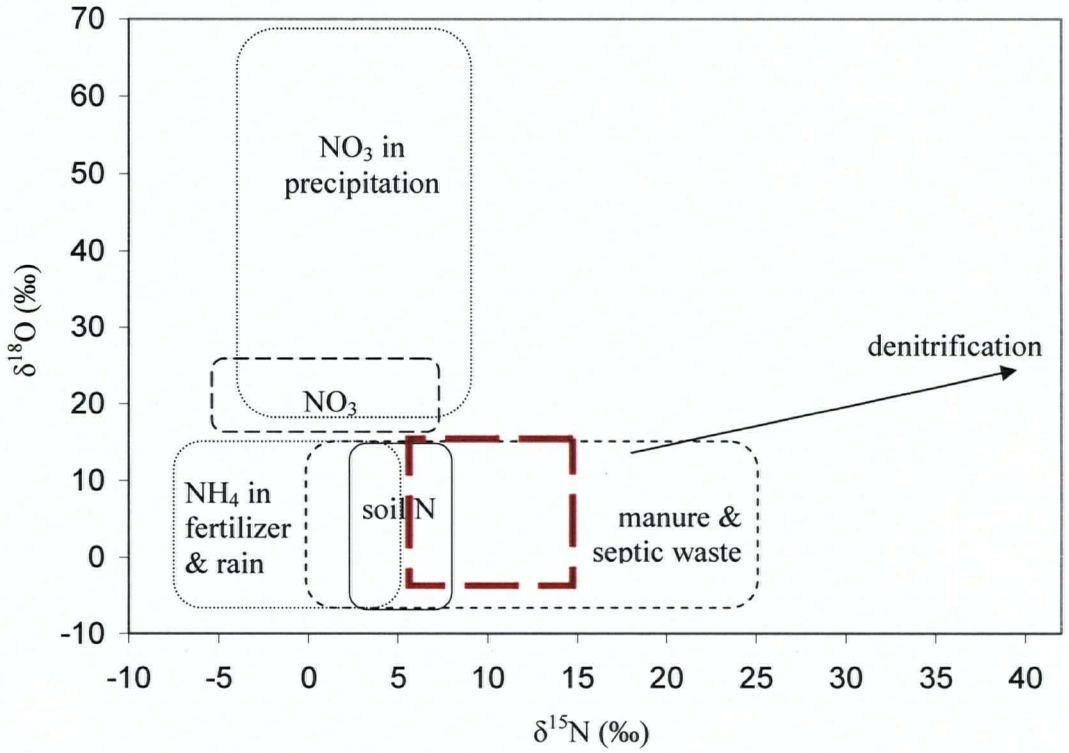

Figure 5.5. Schematic of typical $\delta^{15}N$ and $\delta^{18}O$ values of nitrate for different sources. Red box shows the range of sample values. Modified from Kendall (1998).

The most important factors affecting the nitrate-isotope values are (a) the source of the N and O atoms and (b) the oxidation / reduction reactions (e.g. nitrification / denitrification) that have occurred. The $\delta^{18}O_{NO3}$ values may be low because the original source (e.g. manure) had a low value, which would be directly reflected in the data if there were no transformations or fractionations. The nitrate may have been involved in mineralization-immobilization turnover, which would have obscured the $\delta^{18}O$ of the original source (Mengis et al., 2001). The low oxygen values may also have been from nitrification of ammonia (e.g. ammonia fertilizers); microbial nitrification uses 2 atoms from water and 1 from oxygen (Kendall, 1998). Surface and groundwater samples from this study had $\delta^{18}O_{H20}$ values from -11.99‰ to -6.16‰, with a median of -10.23‰ (n=59). Assuming a value of +23‰ for O_2, and assuming no fractionation with the microbial process, $\delta^{18}O_{NO3}$ values between -0.3 and +3.6‰ would be expected. This corresponds well to the actual values measured for samples. It was assumed that fractionation of N-isotopes from nitrification processes was limited because ammonium concentrations were

low in water samples. The maximum ammonium-N concentration was 0.7 mg/L (well A1, August) and the median value was less than 0.1 mg/L. This indicated that nitrification occurred to completion and fractionation of N-isotopes was therefore limited.

5.6.1. **Nitrate source**

Values for $\delta^{15}N_{NO3}$ were mostly within the ranges for soil nitrogen, manure, and septic waste. Figure 5.6 shows the N and O isotope values plotted against each other. All stream samples fall within the range for a manure or septic source, as did the majority of groundwater samples. Well samples had slightly lower δ15N values, and wells A3, A4, and X1 fell within the range where soil N and manure-septic sources overlapped. These ranges gave a rough idea of source, but were not definitive on their own; the sampled nitrate could have been from a mixture of sources that together resulted in the measured isotope value. Overall, the results do not point to inorganic fertilizers as a main source because $\delta^{18}O_{NO3}$ values are lower than would be expected and $\delta^{15}N_{NO3}$ values higher than those reported for fertilizers.

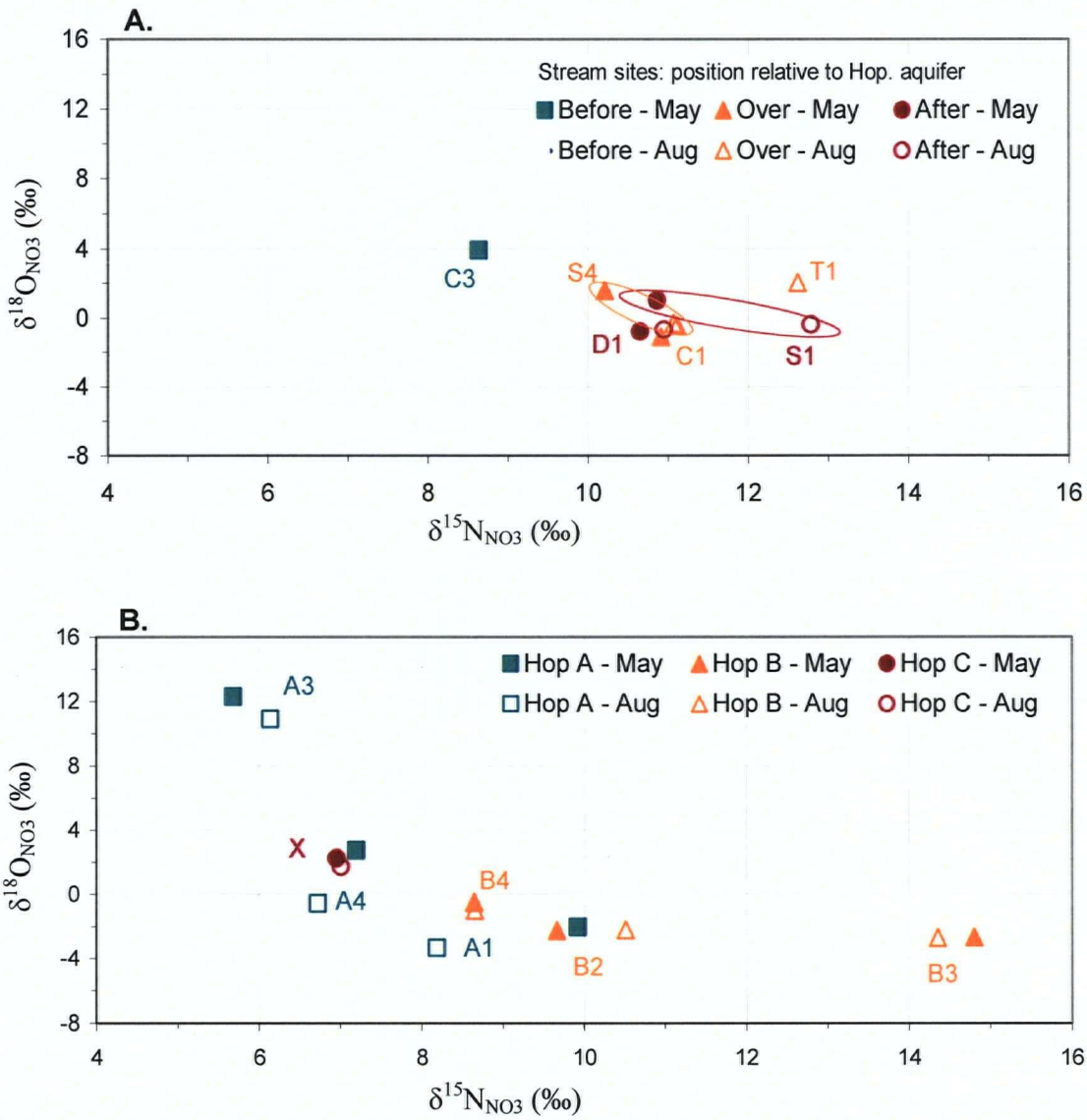

Figure 5.6. Plot of nitrate-isotope results (A.) Stream sites by position relative to aquifer and sampling date. (B.) Well samples by aquifer and sampling date. Note that two sites only have only one valid sampling date: T1 (Aug), C3 (May).

Wells A3 and B3 stand out from the others in Figure 5.6, B. Well A3 had the lowest $\delta^{15}N_{NO3}$ and the highest $\delta^{18}O_{NO3}$ values of any sample; values were consistent for both sampling occasions. The isotope values fit with the source being a mix of NO_3 and reduced-N fertilizer (Mengis et al., 2001; Panno et al., 2006). This particular site seems to be the exception with regards to having a prominent fertilizer-related nitrate source. Within the 100 m buffer of the well, 53% of land use was agricultural. There was berry

and horticulture production within 500 m of this site, greenhouses south of the property, and there was also some animal holding areas less than 100 m north. Nitrate levels at this well have been high since it was drilled in 1973 (B.C. Ministry of Environment WELLS database – version 2.3.6). Well A2 was of similar depth (25.5 m) to well A3 (21.5 m) and in very close proximity, however this site had very low nitrates. Thus, high nitrates at well A3 seem to be a localized problem.

Nitrate isotope values for well B3 also stood out from the others, having the highest $\delta^{15}N_{NO3}$ values of any sample (+14.8‰ and +14.4‰). Well B3 was 26 m deep. Nearby land use included chicken barns less than 200 m away in both north and south directions, as well as horse farms close by; there is also some residential land use. This well may represent another area of localized nitrate contamination, but this time from manure and/or septic sources. Nearby wells B2 and B4 were much deeper (57 m and 74 m, respectively) and had lower $\delta^{15}N_{NO3}$ values, although all had similar nitrate concentrations.

Some of the groundwater sites and the stream sites which had strong groundwater influence from the Hopington aquifers had similar isotope values, suggesting a similar source or combination of sources. Wells B2, B4, and A1 (May) plot very close to D1, S4, and C1 (see Figure 5.6). In both May and August, well B2 (57 m depth), which was very close to stream site C1, had very similar values to the groundwater-influenced stream sites. Well B4 also had a similar seasonal difference to the stream sites D1, S4, and C1. Values for the groundwater influenced sites were quite constant, but because more data for the other sites was not obtained, comments regarding their stability relative to non-groundwater influenced sites can not be made. Overall, however, this nitrate-isotope data provides additional evidence to suggest that the NO_3^- in the streams is coming from groundwater inputs (Hopington aquifer).

Stream site S1 and well A1 showed the most pronounced difference between the two sampling dates. The change for site S1 probably reflected a seasonal change in inputs between site S4 and the river's mouth. The contributing areas for S1, S2, and S3 are all dominated by agricultural land use and given the $\delta^{15}N_{NO3}$ value, manure is a likely nitrate source. In May, well A1 (33 m deep) had higher $\delta^{15}N_{NO3}$ than in August. The May value was close to stream water values, while August was more similar to other wells. This well

was very close to the stream and may be influenced by the stream water during the wet season. Both seasonal changes and absolute values have some contribution to make in understanding nitrate sources. It is also important to consider the potential for denitrification, which alters the isotopic signature of the remaining nitrate and thus effects the interpretation.

5.6.2. **Denitification**

One of the benefits of using the dual isotope approach (^{15}N and ^{18}O of nitrate) is the potential to identify if dentrification is happening, which causes fractionation. Denitrification leaves the remaining pool of nitrate enriched in $\delta^{15}N$, thus a plot of nitrate concentration vs. $\delta^{15}N_{NO3}$ would show a negative trend. Groundwater samples from the Hopington A aquifer were the only set that showed a negative trend (see Figure 5.7). The Hopington B wells have similar nitrate values, but a range of $\delta^{15}N_{NO3}$; these wells may have different nitrate sources or combinations of sources that still result in the same nitrate concentration. Stream samples show no trend toward denitrification and even have a slightly positive trend. Neither separating the streams by position nor differentiating between sampling occasions offered more explanatory power.

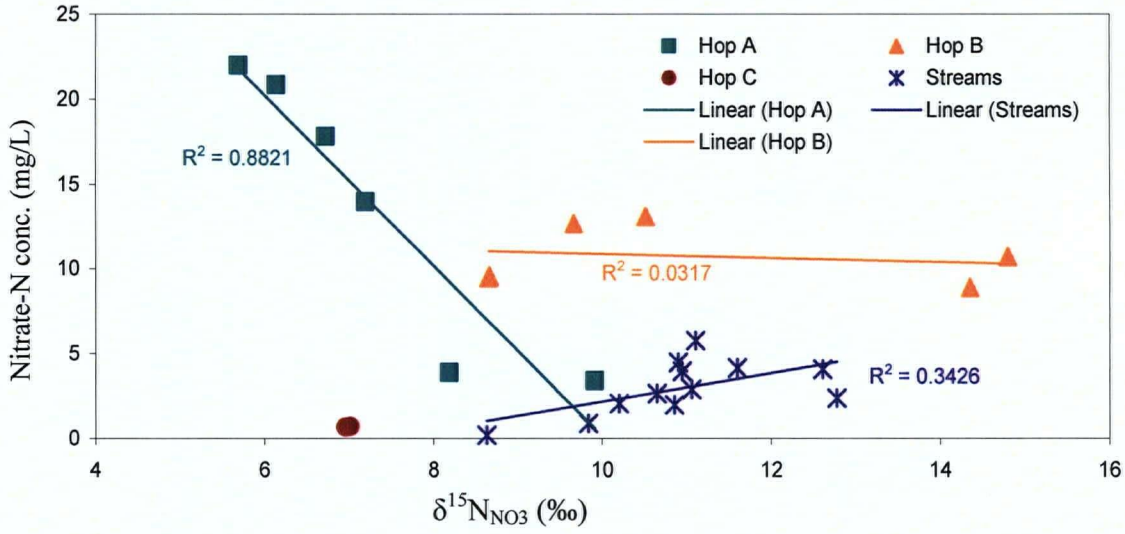

Figure 5.7. Nitrate-N isotope values vs. nitrate concentration, all samples.

There were other factors besides the $^{15}N\text{-}NO_3$ relationship, that suggested denitrification was not prominant. There was limited organic carbon available, which would limit denitrification; median DOC/TOC for Hopington A and B wells was 0.41/0.52 mg/L and 0.25/0.29 mg/L (Hop. A, n=7; Hop. B, n=8). Thus the organic carbon was slightly higher in Hopington B than A, but still very low. Furthermore, anaerobic conditions would not dominate in the unconfined Hopington A and B aquifers, thus extensive denitrification would not be expected. Finally, most $\delta^{18}O_{NO3}$ values were low, which does not support denitrification; denitrification generally results in $\delta^{18}O_{NO3}$ enrichment, roughly in a 1:2 ratio with $\delta^{15}N$ enrichment (Kendall, 1998).

5.7. Groundwater – surface water interactions

Spatial and seasonal nitrate concentrations in the stream water suggested that high-nitrate groundwater was being discharged to the Salmon River and its tributaries as they cut through the Hopington A and B aquifers. There was also some evidence of surface water influence on well water quality, as mentioned for wells A1 and A4. Nitrate-isotope data confirmed that the nitrate sources were similar for groundwater and groundwater-influenced portions of the stream network.

5.8. Land use and nitrate

There were no significant correlations between land use and nitrate concentrations. This was not surprising given that stream nitrates were a mix of groundwater input (whose nitrate origin was not necessarily related to nearby land use) and more direct sources that might relate to land use nearby. Using spatial trend analysis, both septic system density and animal unit density have been useful in understanding stream nitrate dynamics in the Salmon watershed (Wernick et al., 1998). Nitrate-isotope values supported the assertion that septic and manure were the primary sources of nitrates.

Looking at specific land uses and conditions near individual sampling sites was useful in understanding land use – water quality interaction. For example, knowing that stream site S7 had a local beaver dam and that a zoo and livestock activities were

upstream offered more insight than the percent area under agriculture. Taking a closer look at historical land use may be helpful for understanding potential groundwater nitrate sources and expansion of nitrate plumes.

5.9. Conclusions

Streamwater nitrate concentrations in the Salmon River watershed increased in a downstream direction, peaking over the Hopington A and B aquifers. Groundwater nitrate-N concentrations ranged from 0 - 26.6 mg/L, with 5 of the 11 wells sampled exceeding the dinking water guideline for nitrate. High-nitrate groundwater discharge to the streams is a key source of nitrates in the stream; a similar source was confirmed by the nitrate-isotope values. Nitrate-isotopes suggested that septic and manure were the dominant source of nitrates; there was no evidence of significant denitrification within the system.

6. NUTRIENTS, METALS AND TRACE ELEMENTS

6.1. Introduction

This chapter will address concentrations of phosphate, ammonium, chloride, and the dissolved elements measured by ICP (Al, B, Ba, Ca, Fe, K, Mg, Mn, Na, Si, Sr, Zn). The spatial and seasonal trends for surface water samples will be considered. The utility of these parameters in distinguishing between different groundwaters (Hopington A, B and C aquifers) will be addressed, as well as the characterization of groundwater discharge to the streams. Finally, there will be some discussion on possible sources of these dissolved chemicals as related to land use.

6.2. Methods

Methods for sample collection and laboratory analysis can be found in Chapter 3. Phosphate, ammonium, and chloride were measured on all sampling occasions and the data were analyzed using non-parametric significance tests. Scatter plots showing stream site measurements include all data points and thus there is no variance shown, but the standard deviation for replicate samples is reported and this gives some indication of variation for a given site and instrument variability.

Analysis for dissolved elements measured by ICP was done twice (May and August 2006), resulting in a limited number of replicates for statistical analysis. No tests for statistical differences were done; graphs showing the median and max-min range are shown to give some indication of potential differences. Scatter graphs are used to show downstream trends and to show any differences between the two sampling dates; all data points are represented in these graphs, site variability and instrument error are accounted for through replicate samples. Values below the lowest readable limit for the ICP-AES analysis were assigned a value of zero.

6.3. Chloride, phosphate, and ammonium

6.3.1. Surface water - spatial and seasonal trends

Chloride

Stream chloride concentrations ranged from 7 to 35 mg/L with a median of 12 mg/L. This range of values was well within the B.C. water quality guidelines for any use including drinking water; natural background levels of chloride in freshwater are 1-100 mg/L (Nagpal et al., 2003)[21] . The average standard deviation and coefficient of variation for replicate samples was 0.19 mg/L and 2.4%, respectively. Figure 6.1 shows the stream chloride concentrations in a downstream direction, distinguishing between the wet and dry seasons. In the Salmon River, the highest chloride concentrations are found in the headwaters (S7) during the dry season and at the sites nearest the river mouth (S1 and S2). Apart from at site S7, there was little distinction between chloride levels in the wet and dry seasons. Union Creek (site T1) had slightly higher chloride levels than the Salmon, which may account for the small increase in the Salmon chloride levels after Union Creek joins it. Davidson Creek (D1) had low chloride levels, comparable to those in the mid-Salmon (S4, S5). Coghlan Creek showed the greatest variation in chloride levels. For sites C2 and C3, the wet season chloride levels were higher than the dry season. The highest levels for each Coghlan site were measured in October 2006.

Orthophosphate-P

Orthophosphate-P concentrations in surface water samples ranged between 4 to 44 ppb PO_4^{-3}-P, with a median of 18 ppb (0.018 mg/L); these are very low levels and would not be of concern in terms of water quality. The average standard deviation and coefficient of variation for replicate samples was 0.5 ppb and 4.8%, respectively. Figure 6.2 shows the stream orthophosphate concentrations in a downstream direction, distinguishing between the wet and dry seasons. In the Salmon River, the spatial or

[21] Original citation for: Bright, D.A. and J. Addison. 2002. Derivation of matrix soil standards for salt under the British Columbia Contaminated Sites Regulation. Royal Roads University. Prepared for BC Ministry of Water, Land and Air Protection, BC Ministry of Transportation and Highways, BC Buildings Corp., and the Canadian Association of Petroleum Producers. Victoria, BC.

seasonal differences were not strong. For many of the sites, the October sampling occasion (classified as wet season) caused overlap between the seasons. In general, the Salmon headwater and downstream sites (S7, S6, S1) had higher phosphorus in the wet season, which would be expected because the cooler temperatures mean that less phosphorus is being removed by plants and algae. Wernick (1996) found that all stream sites had a greater orthophosphate concentration in the winter than in the summer; Cook (1994) did not find such a clear pattern for total P measurements.

The tributaries to the Salmon River showed an unexpected trend, with higher phosphorus levels in the dry season than the wet season, although levels were still very low (mostly under 0.03 mg/L). Coghlan sites C3 and C2 stood out from the others with higher dry season orthophosphate-P concentrations. Given the relatively low solubility of phosphorus it is generally expected that phosphate values are highest during the wet season when erosion and sediment transport is high. This was evident in the headwater section of the Salmon River, but not in the Coghlan and Davidson Creeks, probably due to groundwater influences. Given the heavy agricultural land use near sites C3 and C2, the higher P values in the dry season may be due to local inputs (e.g. animals walking through the water upstream).

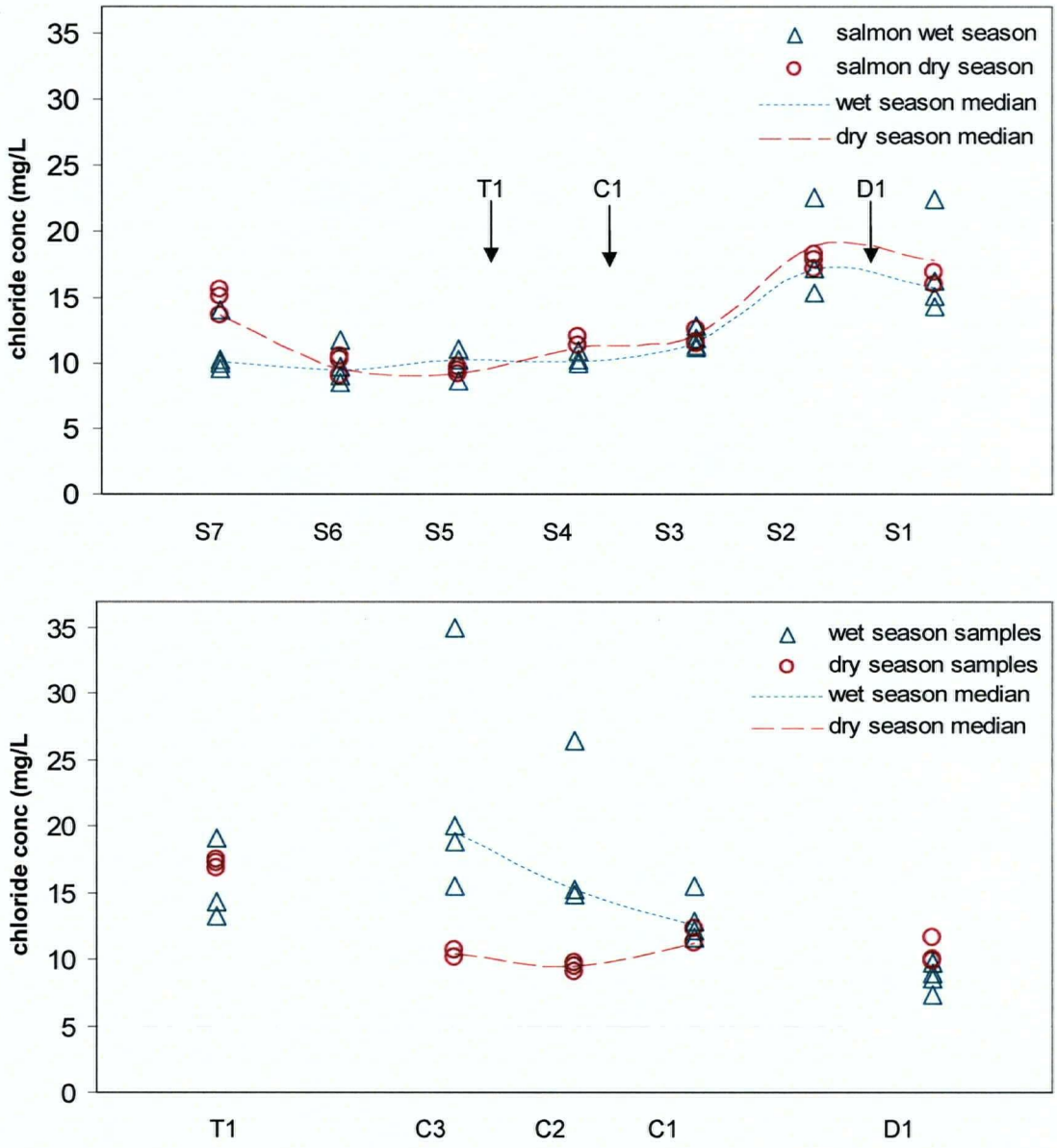

Figure 6.1. Stream chloride concentrations, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

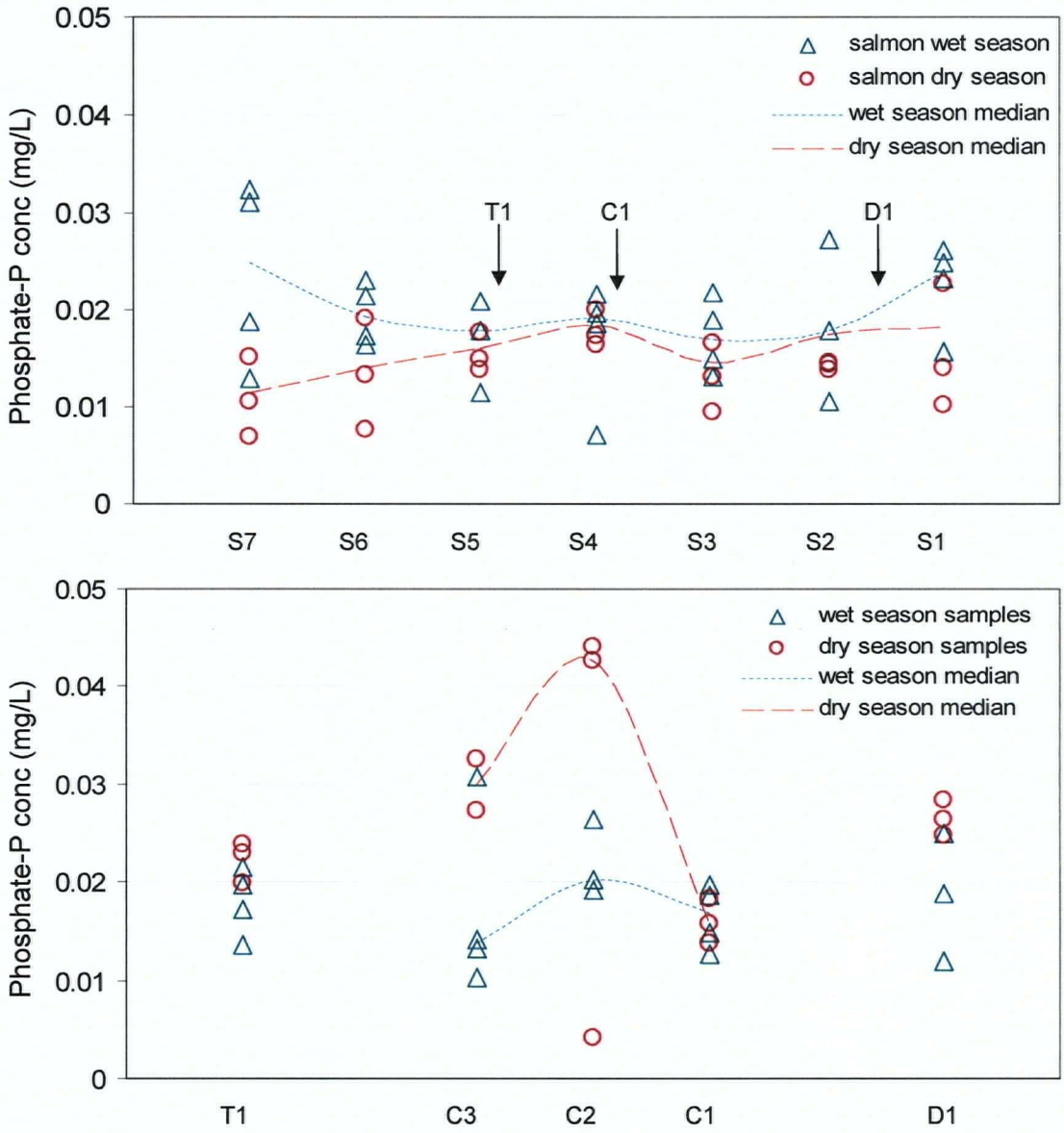

Figure 6.2. Stream orthophosphate concentrations, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

Ammonium-nitrogen

Concentrations of nitrogen as ammonium (NH_4^+-N) in surface water samples ranged between 0.03 and 0.68 mg N/L, with the median being 0.07 mg NH_4^+-N/L. These are very low levels and many of the samples were below the lowest standard used for analysis (0.1 mg/L), therefore interpretation of these results was limited. The average

standard deviation and coefficient of variation for replicate samples was 0.02 mg/L and 19.4%, respectively. Figure 6.3 shows the stream ammonia-N concentrations in a downstream direction, distinguishing between the wet and dry seasons. There were no clear seasonal or spatial trends. October 2006 (wet season) had higher than usual values at all sites. Higher concentrations during the wet season would be expected.

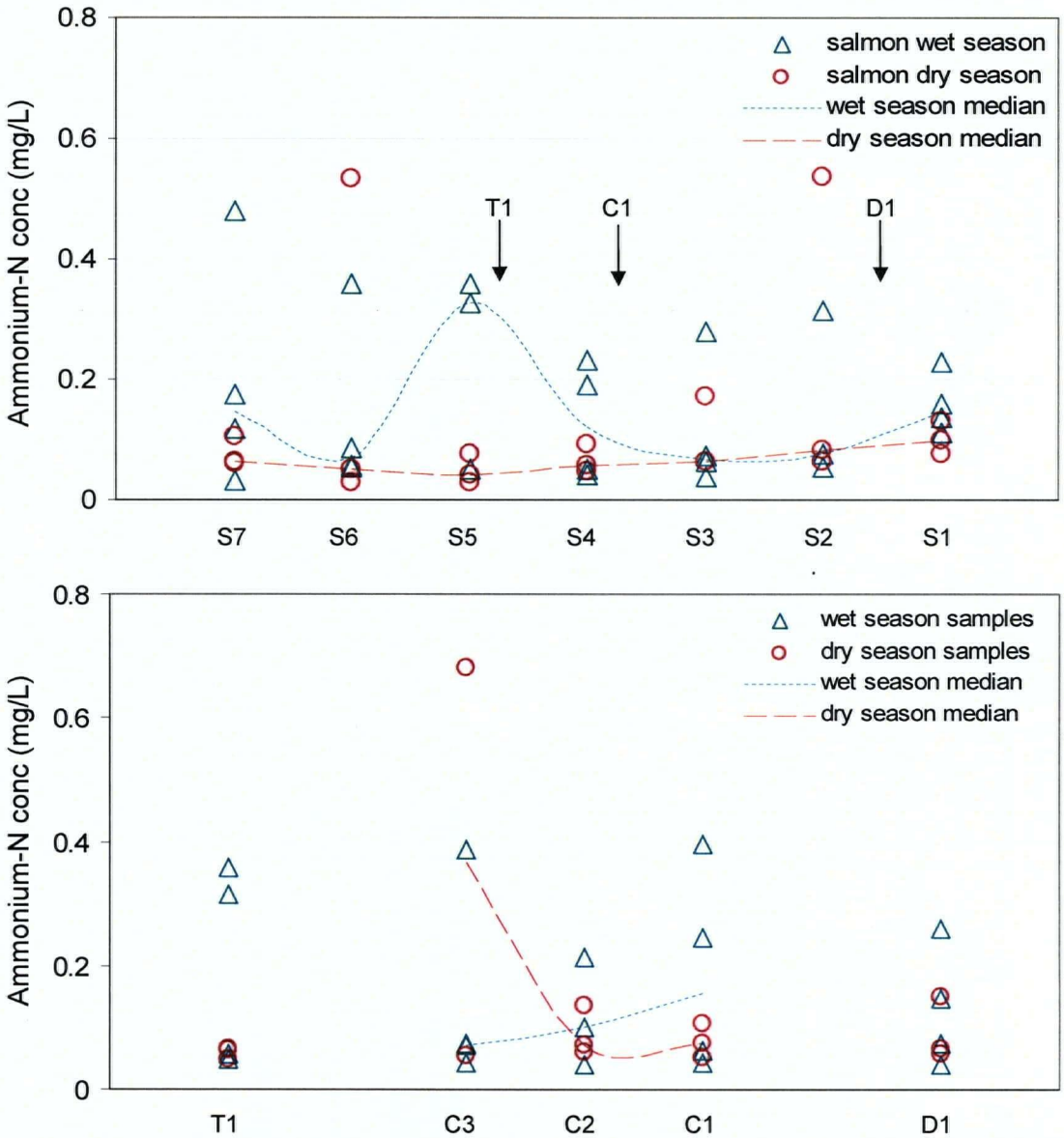

Figure 6.3. Stream ammonium concentrations as mg NH_4^+-N, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

6.3.2. Groundwater

Groundwater chloride concentrations ranged from < 6.0 mg/L (LRL) to 33 mg/L, with a median of 8 mg/L. Wells in the Hopington A and B aquifers had similar values, although A was more variable; Hopington C had lower chloride than A and B (see Figure 6.4). Values are low overall and within both the Canadian and BC drinking water quality guidelines.

Phosphate-P concentrations in groundwater ranged from < 0.02 mg/L (LRL) to 0.20 mg PO_4^{-3}–P /L, with a median value less than the lowest standard used (LRL). Hopington A and B had very low phosphate levels, but Hopington C phosphates were higher, distinguishing these wells from the other groundwater samples (see Figure 6.4). Ammonia-N levels were all below the lowest readable limit (0.1 mg/L) and thus no distinctions could be made between the aquifers or seasons.

6.3.3. Groundwater – surface water interaction

As Figure 6.5 shows, there were no significant differences between the stream water chloride, orthophosphate, or ammonia levels for different stream site "positions" relative to the Hopington AB aquifer. None of these parameters proved to be useful for looking at groundwater-surface water interactions.

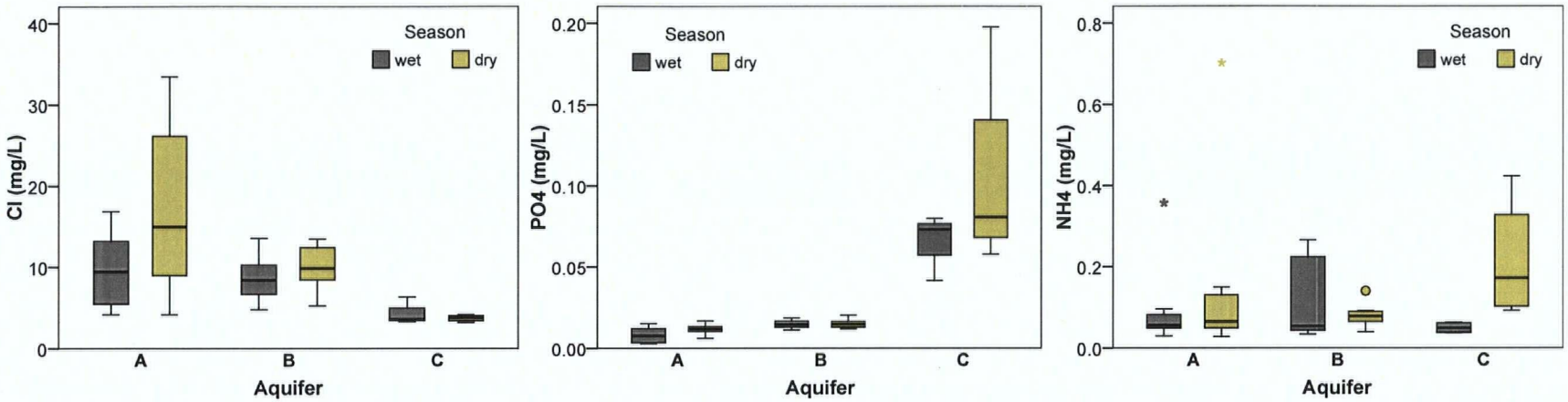

Figure 6.4. Boxplots of chloride, phosphate, and ammonium concentrations in well samples from Hopington A, B, and C aquifers. Boxplots show the median, interquartile range, 95% confidence intervals, outliers (O), extreme values (*).

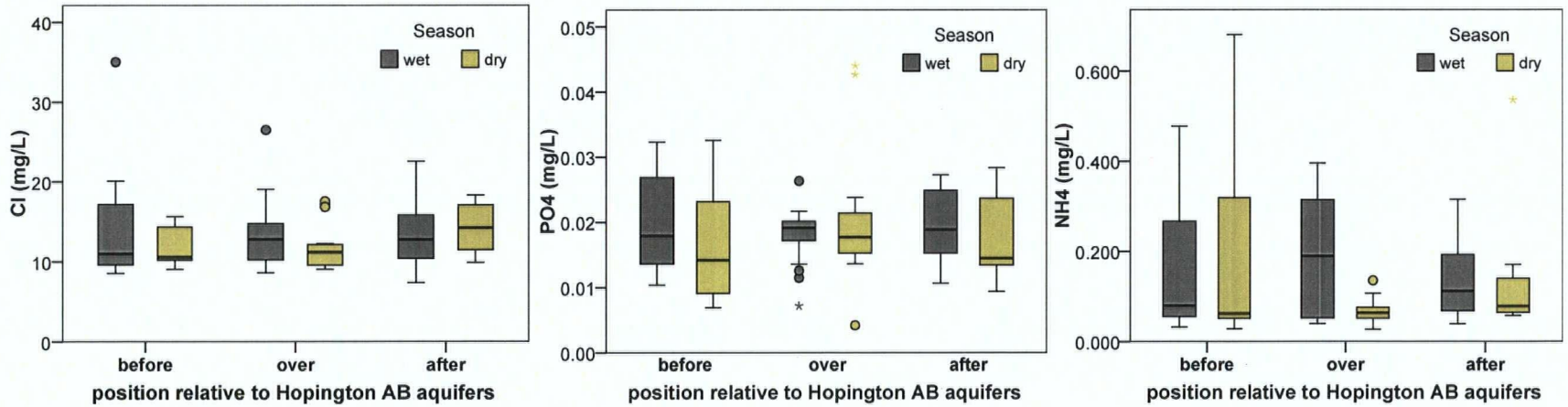

Figure 6.5. Boxplots of chloride, phosphate, and ammonium concentrations in surface water samples, grouped into position relative to Hopington AB aquifers. Boxplots show the median, interquartile range, 95% confidence intervals, outliers (O), extreme values (*).

6.3.4. **Possible sources and land use interactions**

There were no meaningful correlations between land use and chloride concentrations. The spatial trend in Coghlan Creek suggests a surface runoff source of chloride. Upstream of site C3, there was a zoo, a horse farm (and other farms), and there was also a beaver dam; all of these could be a source of chlorides. The decreasing trend in a downstream direction may indicate dilution of the original upstream source, with no significant new sources. There may have been a peak in levels in October because it was just the beginning of the wet season and thus there may have been a larger supply of chloride to be flushed into the stream. Sewage may have been one cause of increased chlorides downstream in the Salmon; Trinity Western University discharges sewage into the river between sampling sites S3 and S2. The marine sediments must also be considered as these could be a source of chloride, especially in the headwater and downstream regions.

The spatial and seasonal chloride trends for streamwater were similar to those observed in studies in the Salmon River watershed in the 1990s (Cook, 1994; Wernick, 1996), however, chloride levels were a bit higher overall, potentially indicating a greater anthropogenic influence.

The Coghlan stream sites C3 and C2 had higher dry season orthophosphate-P concentrations than the other sites. Site C3 is just downstream of a horse farm and between C3 and C2 there were are several farms with livestock quite close to the stream; perhaps there was a direct source of P from the animal waste during the summer months. These suggestions are speculative and hold little weight if only orthophosphate is being considered, especially given the low concentrations being measured.

Phosphate-P had several statistically significant correlations with land use and land cover, particularly for the wet season stream samples (Table 6.1). Overall, phosphate-P levels were positively correlated with some agricultural activities and negatively correlated with unused land and mature tree cover. It is reasonable that agricultural activities act as a source of P and that tree cover would reduce the P reaching the stream (Houlahan & Findlay, 2004).

Stream ammonia-N had a significant positive correlation with livestock agriculture during the dry season (Spearman rank correlation of 0.622 (p-value 0.031) for the 100 m stream buffer), however, given the low levels this may not be meaningful.

Table 6.1. Summary of significant correlations between land use and wet season stream PO_4^{-3}-P concentrations (n=12)

Land use (LU) / Land cover (LC) category	**Spearman rank correlation**	**Stream buffer (50 m, 100 m) or contributing area (CA)**
LU: All agriculture	0.867**	50 m
	0.867**	100 m
	0.538	CA
LU: Agriculture (crops/arable land)	0.769**	50 m
	0.762**	100 m
LU: Residential	-0.776**	100 m
LU: Unused/other	-0.923**	50 m
	-0.797**	100 m
	-0.559	CA
LC: Woody vegetation	-0.958**	50 m
	-0.818**	100 m

** Correlation is significant at 0.01 level (2-tailed).

6.4. Dissolved metals and trace elements

Analysis for dissolved elements was done in May and August 2006 for all sampling sites, giving a total of 43 samples for both occasions. One stream and one well site were sampled and analyzed in triplicate on each occasion for quality control. Table 6.2 gives an average variance for each element and the number of observations that were above detection limit. Due to a high number of observations being below detection limit, Al, B, and Zn will be discussed only in terms of the specific sites where they were above detection limit; for well sites, the majority of Ba and Mn levels were below readable limits and will therefore only be given brief comment.[22] Of the elements discussed in this section, the British Columbia and Canadian guidelines for drinking water quality include Al, Ba, B, Fe, Mn, Na, and Zn.

[22] As, Cd, Co, Cr, Cu, Mo, Ni, P, Pb, and Se were excluded from all analysis and discussion due to lack of observations above detection limits.

Table 6.2. Descriptive information for dissolved elements results.

		Sample concentration (mg/L)				
Element	LRL* (mg/L)	Max	Min	Median	Average std dev for replicates**	# obs. > LRL
Al	0.025	0.076	< LRL	< LRL	0.004	14
B	0.025	0.048	< LRL	< LRL	0.020	16
Ba	0.005	0.150	< LRL	0.008	0.001	29
Ca	0.05	36.81	5.98	16.70	0.13	43
Fe	0.025	1.00	< LRL	0.09	0.14	31
K	0.25	3.99	0.66	1.73	0.02	43
Mg	0.005	12.52	2.88	5.69	0.05	43
Mn	0.0025	0.219	< LRL	0.005	0.001	27
Na	0.12	13.90	3.49	6.36	0.08	43
Si	0.07	16.19	1.64	7.66	0.38	43
Sr	0.001	0.340	0.024	0.088	0.001	43
Zn	0.005	0.478	< LRL	< LRL	0.000	6

* These values are ½ the lowest readable limit (LRL) for the machine because samples were concentrated (see methods section for details)

6.4.1. Surface water - spatial and seasonal trends

For stream samples, no zinc values were above the detection limit. Figure 6.7 shows the spatial trend for aluminum and boron in May and August; quite a few observations were below detection limits, especially in August. In the Salmon River in May, both Al and B decreased as the stream cut through the Hopington aquifer. Boron levels were within the guidelines for any use and within typical range for surface water in British Columbia (Moss & Nagpal, 2003). Aluminum levels were within a reasonable range for rivers in British Columbia and levels were below the B.C. water quality guidelines for drinking water and other uses (Butcher, 1988).

In the Salmon River, dissolved Fe and K were highest in the headwaters and showed a decreasing trend downstream (see Figure 6.6), with May samples generally being higher than August samples. Dissolved iron ranged from 0.03-0.85 mg/L with a median of 0.16 mg/L. The majority of samples were above the Canadian drinking water guidelines aesthetic objective of 0.3 mg/L (FPT Committee on Drinking Water, 2006), but these levels do not pose any health concerns. These exceedances occurred at stream sites S7 (0.6 and 0.8 mg/L for August and May, respectively) and sites S6, S5, S1, and C3 in May (0.6, 0.3, 0.4, 0.5 mg/L, respectively).

Potassium levels were between 1.2 mg/L and 4.0 mg/L, with a median of 2.2 mg/L. Sodium levels decreased over the Hopington aquifer and increased again further downstream, with higher levels in May (see Figure 6.7). Groundwater was likely diluting the Na sources from upstream.

Dissolved elements showing an increasing downstream trend in the Salmon River included Mg, Si (see Figure 6.6), Ca (see Figure 6.7), and Sr (see Figure 6.8). Concentrations of these elements were higher in August than in May, except Sr which had slightly higher May values for the headwater and downstream sites. Site T1 had lower levels of Mg, Si, and Ca than the Salmon, where the two joined. There are no water quality guidelines for any of these elements. The range of calcium concentrations was 9.2-22.6 mg/L with a median of 14.3 mg/L. Magnesium concentrations were from 2.9 to 7.8 mg/L, with a median of 5.5 mg/L. Silicon concentrations were from 1.6 to 8.9 mg/L, median 5.9 mg/L. Strontium concentrations were 0.07 to 0.10mg/L, with median concentration of 0.08 mg/L.

Barium and manganese did not show a strong downstream trend (see Figure 6.8). Stream sample barium and manganese concentrations ranged from < LRL to 0.04 mg/L and 0.059 mg/L, respectively and with a median of 0.01 mg/L and 0.006 mg/L, respectively. Ba levels were well below the health-based guideline in the Canadian drinking water quality guidelines, the highest levels were measured at site T1. In May, S1 and S2 had Mn levels slightly above the aesthetic objective for drinking water (Canadian water quality guidelines). Manganese can be toxic to aquatic life and toxicity increases with water hardness, but levels measured in the Salmon River (~0.06 mg/L) were below levels of concern (Nagpal, 2001).

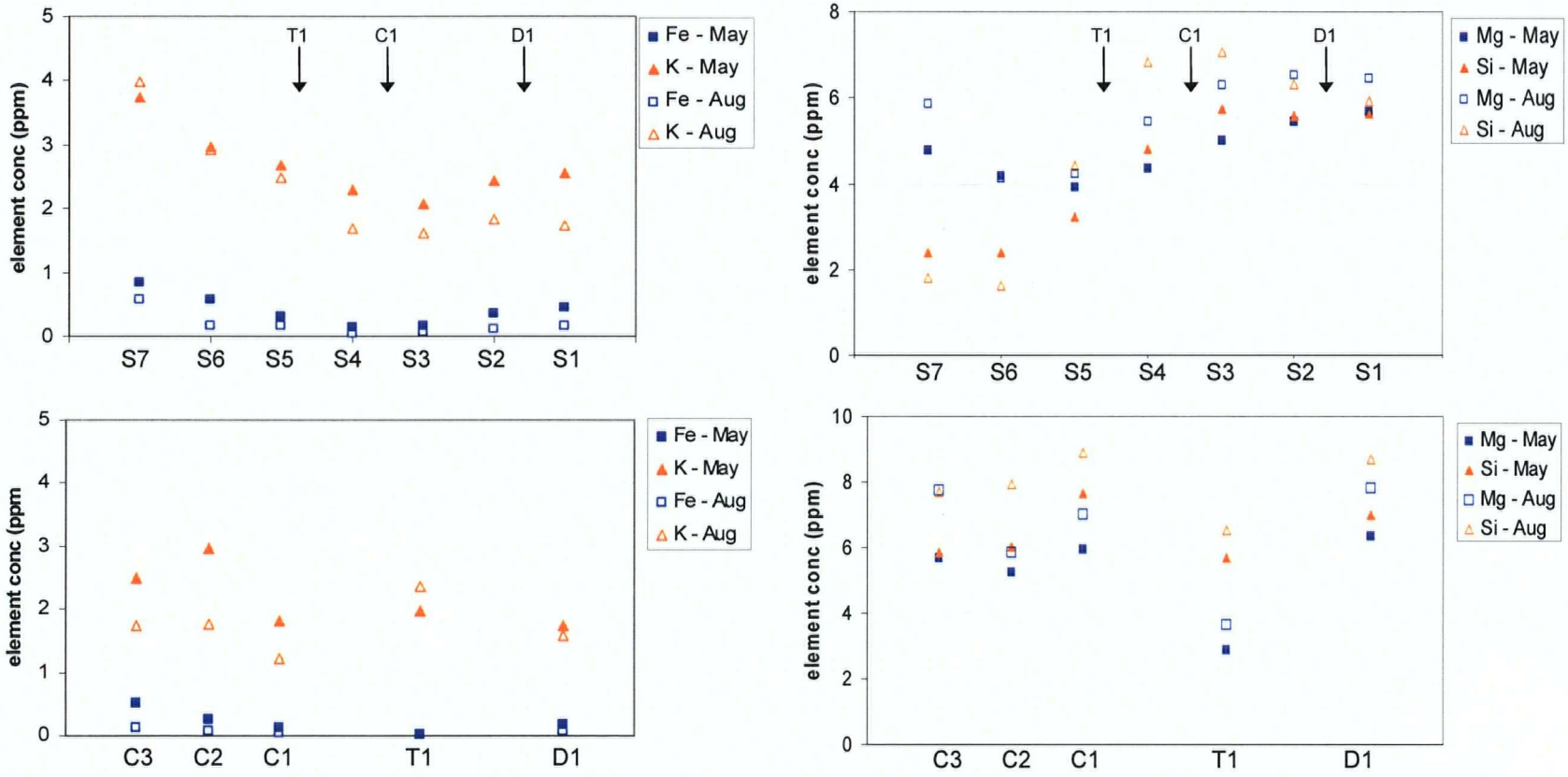

Figure 6.6. Graphs showing downstream trend for dissolved Fe, K, Mg, and Si. All samples are represented (May and August sampling for each site), see detail on QA/QC for measurement variability.

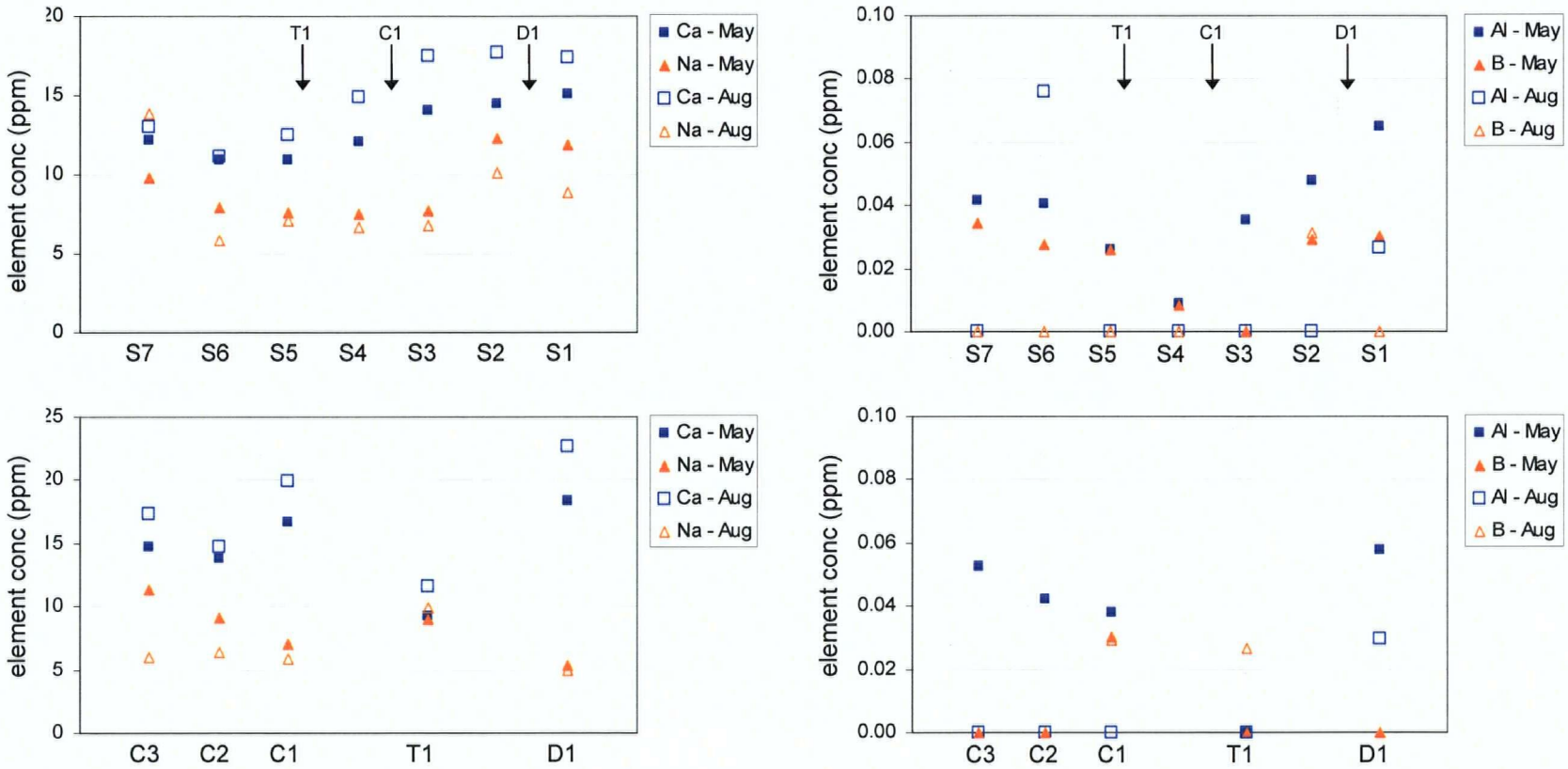

Figure 6.7. Graphs showing downstream trend for dissolved Ca, Na, Al, and B. All samples are represented (May and August sampling for each site), see detail on QA/QC for measurement variability.

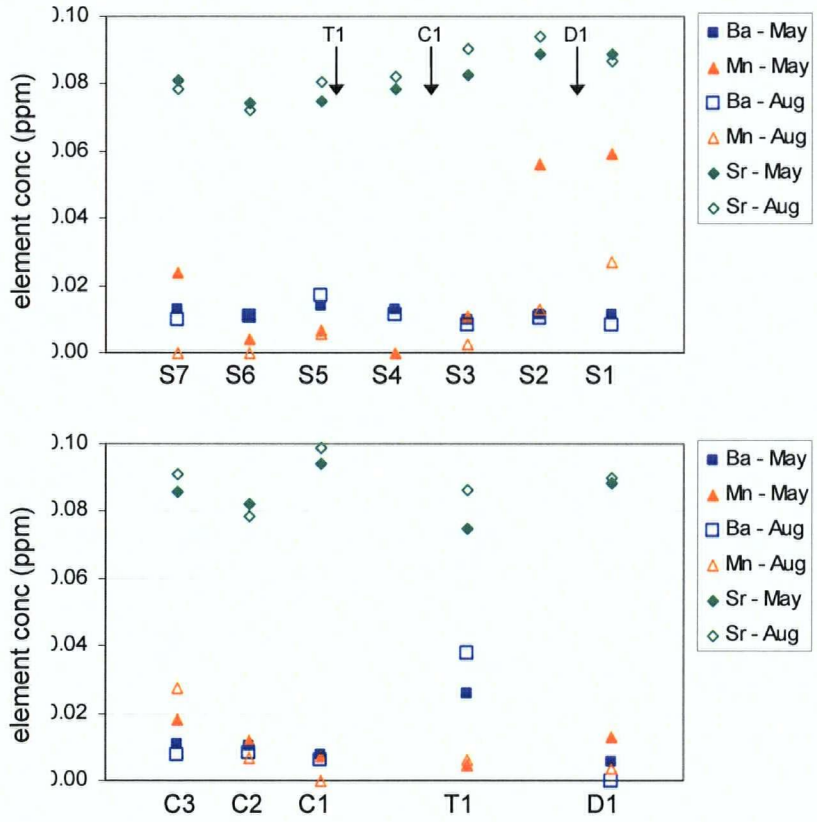

Figure 6.8. Graphs showing downstream trend for dissolved Ba, Mn, and Sr. All samples are represented (May and August sampling for each site), see detail on QA/QC for measurement variability.

6.4.2. **Groundwater – spatial and seasonal trends**

Elements with limited observations above LRL (Zn, B, Ba, Mn, Fe)

There were a limited number of well water samples that had concentrations of Al, B, Ba, Fe, Mn, and Zn above the LRL. Aluminum had no observations greater than the LRL of 0.05 mg/L. No well samples had notable iron concentrations, except observation well A2 had an iron concentration of about 1 ppm in August, which exceeded the guideline for Canadian drinking water quality (aesthetic objective). This site was only sampled once for dissolved elements and this result may have been an outlier.

There were 6 observations above the detection limit for zinc. Wells A3 and A4 had concentrations greater than the LRL for both the May and August sampling occasions; wells A1 and B3 had concentrations greater than the LRL in May and August, respectively. These sporadic occurrences may have been due to dissolution of Zn from pipes, especially as samples were taken from the taps and not directly from the well.

Only 4 wells had boron levels about the LRL: A3, X1, A2, and B4. A3 and B4 were "high" in both May and August, with slightly greater values in May. Well A4 had a barium concentration that stuck out from the others, which were all very low or below the LRL. The highest manganese level in the wells sampled was 0.22 mg/L (Well A2, August); well A1 (May) was also above the aesthetic objective (0.05 mg/L) in the Canadian drinking water quality guidelines (FPT Committee on Drinking Water, 2006).

Seasonal differences

All wells had similar values (Sr, Si, Na, Mg, Ca, K) for the May and August samples. Well A1 was an exception because it had higher levels of Ca, K, Mg, and Sr in August than in May.

Aquifer differences

Figure 6.9 summarizes the concentrations of dissolved elements for the Hopington A, B and C aquifers. Mg, Na, Ca, and Sr were lower in the well water samples from Hopington C than from Hopington A and B.

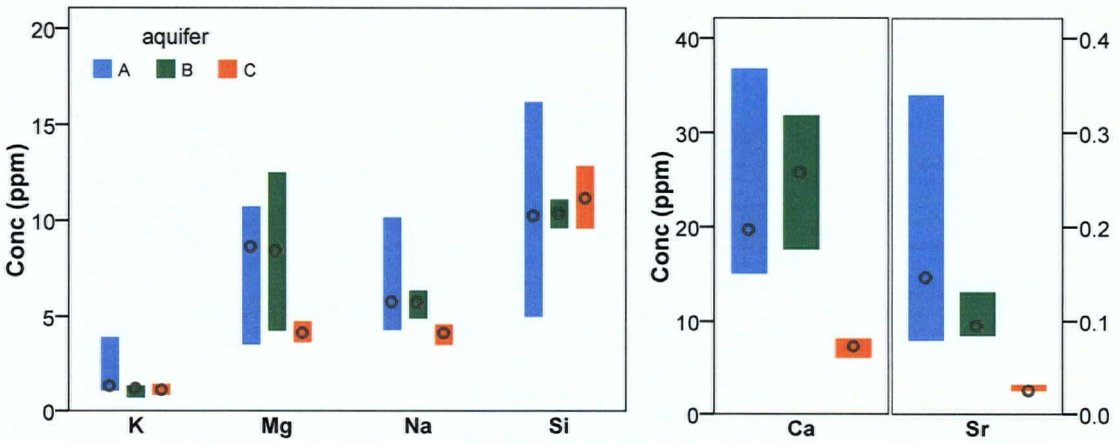

Figure 6.9. Dissolved elements in groundwater samples, displayed by aquifer group. Central points represent median value and bars represent the max-min spread. Number of samples for A, B, and C aquifers was 7, 8, and 4, respectively.

6.4.3. **Groundwater – surface water interaction**

The spatial trends for the streams suggested that groundwater inputs may be a source of Ca, Si, Sr, and Mg to the stream. These elements were in higher concentration in the groundwater than streamwater so this trend makes sense, especially since levels were higher in August when the groundwater input would be making up a larger proportion of the stream flow. Conversely, the streamwater spatial trends showed a downstream decrease in Fe, K and Na with lower levels in August, which would make sense if groundwater from Hopington A and B aquifers (Fe, K, and Na concentrations lower than the streamwater) was diluting the "surface sources" of these elements. Figure 6.10 shows dissolved element concentrations for streamwater grouped according to position. Fe still showed a decrease downstream from the headwaters, Si showed an increase after the "above" sites, and Ca was higher "after" the aquifer than "before". Sr also showed a small increase for the "after" sites. Mg had a decreased median concentration "over" the aquifer, but this may be lowered by the inclusion of site T1, which had low Mg levels. Grouping the sites (and grouping the two sampling occasions) obscured some of the trends that could be seen by visual inspection of spatial graphs.

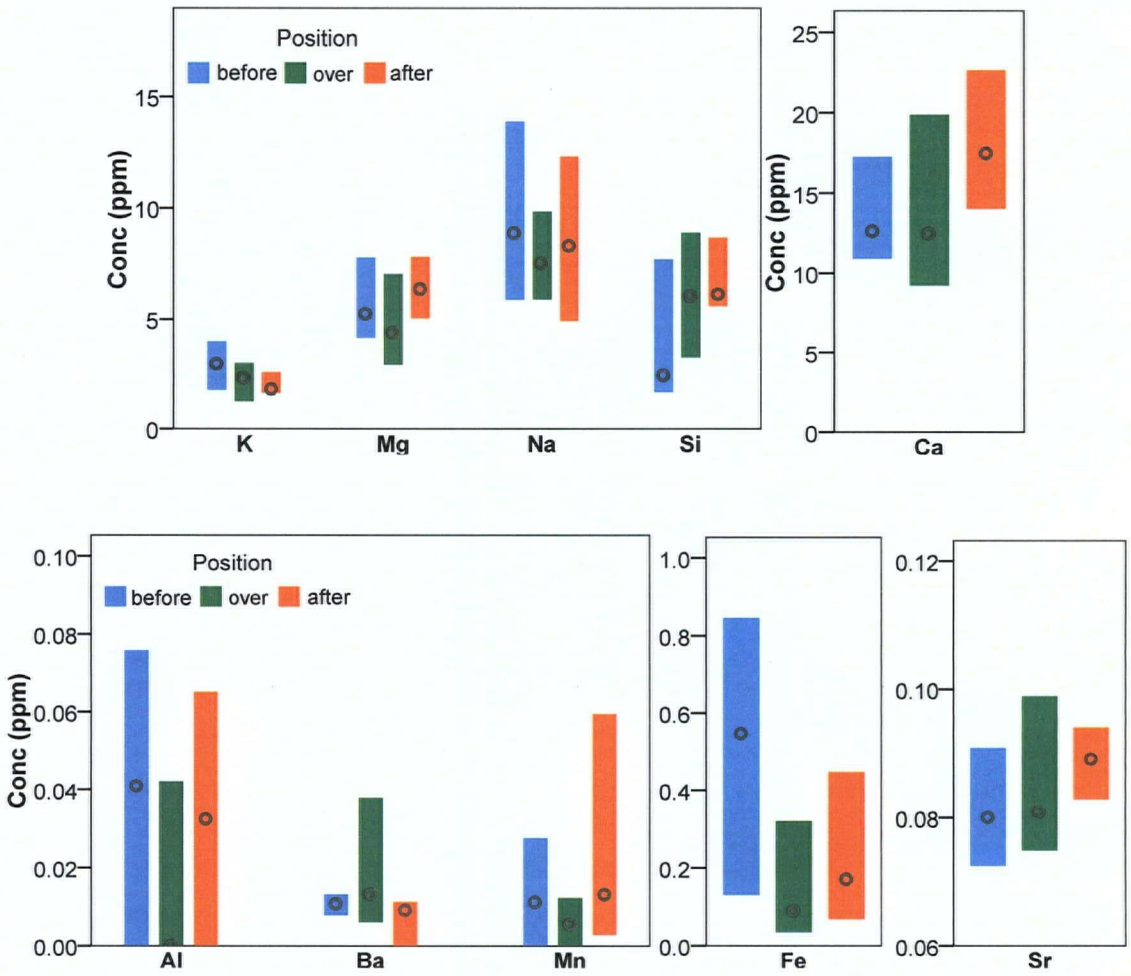

Figure 6.10. Dissolved elements in surface water samples, displayed by position relative to Hopington aquifer (before, over after). Central points represent median value and bars represent the max-min spread. n = 6, 12, and 8 for before, over, and after positions, respectively.

6.4.4. **Discussion of possible sources**

Boron is found in marine sediments and this may be the cause of the May trend in the Salmon River, with groundwater diluting the B levels in the mid-reach. Cleaning products, agrochemicals, and sewage sludge are also potential sources of B (Moss & Nagpal, 2003); B levels at site C1 in May and site T1 in August may be indicative of septic system leaching, or perhaps of historical agrochemical use, which has leached into the groundwater over time. Of the four wells with boron concentrations above the LRL, wells A3, B4 and A2 all had berry production operations nearby, thus agrochemicals are a potential source to consider.

Well A2 and A1 had high Mn. Well A1 was in a residential area and, speculatively, may have been impacted by septic leachate. Manganese levels were greater than the LRL at stream sites C3 (May and August), S1, S3, and S7 (May only). Mn can be associated with agricultural operations, as can Fe (Smith, 2004); some of the higher iron levels occurred at the same sites (S7, S1, C3, as well as S6). Over 50% of the contributing areas for S1 and S6 had agricultural land use. The contributing area for stream site S7 had a mix of land uses, however, there were several farms close to the stream and the Greater Vancouver Zoo is upstream. Stream site C3 had a mixed land use in the contributing area, but there was a farm with horses very close to the sampling point, as well as other agricultural operations upstream.

Correlations between land use and the dissolved elements gave significant results for surface water iron, aluminum and manganese (see Table 6.3). Fe was positively correlated with agriculture and arable/cropped land in the wet season; residential land use and Fe were negatively correlated. Dry season Fe correlations were very similar to those for the wet season, perhaps indicating a natural source of Fe. Aluminum was also positively correlated with agriculture, with stronger correlations in the wet season as many of the August samples were below detection limits. Stream manganese concentrations were positively correlated with agriculture in the wet season. In the wet season, there may be more erosion from agricultural lands, transporting Al, Fe, and Mn from soils to the surface water. Stream manganese was also positively correlated with transport/roads in the dry season. Methylcyclopentadienyl manganese tricarbonyl (MMT) is an additive to gasoline and might explain the positive correlation between Mn and transport related land use.

Table 6.3. Spearman rank correlations between land use and dissolved Fe, Al, Mn concentrations in stream water samples (n=12).

	Land use (LU) / Land cover (LC) category	**Spearman rank corr. wet/(dry) season**	**Stream buffer (50 m, 100 m) or contributing area (CA)**
Fe	LU: All agriculture	0.580* / (0.580*)	100 m
Fe	LU: Agriculture (crops/arable)	0.580*	50 m
		0.559	100 m
Fe	LU: Residential	-0.692* / (-0.622*)	100 m
		-0.664*	CA
Al	LU: All agriculture	0.727** / (0.606*)	50 m
		0.727** / (0.560)	100 m
		0.650* / (0.404)	CA
Al	LU: Agriculture (crops/arable)	0.706* / (0.587*)	50 m
		0.790* / (0.615*)	100 m
		0.664*	CA
Al	LU: Residential	-0.706* / (-0.615*)	100 m
		-0.601*	CA
Mn	LU: All agriculture	0.538*	50 m
		0.587*	100 m
Mn	LU: Transport / roads	0.622* / (0.626*)	50 m
		/ (0.573)	100 m
		/ (0.658*)	CA

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at 0.01 level (2-tailed).

6.5. Conclusions

Chloride, orthophosphate, Mg, Na, Ca, and Sr can be used to distinguish between waters from the different Hopington aquifers. Wells in the Hopington A and B aquifers had similar chloride and orthophosphate concentrations, but differed from the wells sampled in the Hopington C, which had lower chloride and higher orthophosphates. Mg, Na, Ca, and Sr were lower in the well water samples from Hopington C than from Hopington A and B.

Groundwater influence on the surface water was observed by increased Ca, Si, and Mg concentrations from groundwater input and decreased Fe and Na concentrations due to dilution by groundwater input. Chloride levels were higher in the Salmon River headwater sites and at the lower stations; Coghlan Creek also showed higher levels, especially in the wet season. These trends were most likely a function of input from sediments, fertilizer, manure, and septic waste.

Agricultural land use was influencing the streamwater quality, especially during the wet season. Orthophosphate-P was positively correlated to agricultural land use and negatively correlated with tree cover. The highest levels of manganese were at sites with a high proportion of agricultural land use. Concentrations of manganese, aluminum, and iron in surface water during the wet season were all positively correlated with agricultural land use. Manganese was also positively correlated with the percent land area in roads.

7. ABSORPTION AND FLUORESCENCE

7.1. Introduction

This chapter will explore the utility of absorption and fluorescence spectroscopy measurements of water samples with the aim of differentiating potential contaminants in groundwater and surface waters. Can spectral measurements be used as general water quality measures? Are they useful for source tracking of contaminants and understanding land use impacts? Spatial and seasonal trends for each measurement will be presented. Correlations between the spectral measures will be presented and relationships with other parameters measured will be discussed.

This chapter specifically addresses the following issues: (1) groundwater – surface water interactions in the Salmon River watershed as observed through spectral measurements. (2) The relationships between absorption and fluorescence spectral measurements and other measures of water quality. (3) Absorption and fluorescence spectroscopy as measures of water quality and tools for pollutant sourcing. (4) The potential of fluorescence spectroscopy to detect pollution events.

7.2. Methods

Laboratory methods for collection of spectral data were detailed in Chapter 3. From February 2006 onwards, all samples were analyzed for both absorption and fluorescence. Analysis was always done within 48 hours of sample collection. Samples were centrifuged (details in methods chapter) to remove particulate matter. As a trial, one set of samples was run "raw" with no centrifuging, but the suspended particulates caused a great deal of light that strains the instrument sensors. Output from both the absorption and fluorescence instruments was exported and further analyzed in Excel.

Absorption scans were from 200-700 nm. The absorption values at 220 nm, 254 nm, and 280 nm (A220, A254, and A280, respectively) were selected for more detailed

analysis. Fluorescence scans generated an excitation-emission matrix (EEM), with excitation and emission wavelengths 230-450 nm (5 nm increments) and 260-300 nm (2 nm increments), respectively. The EEM was generated through a series of scans, each scan measuring the range of emission wavelengths for a given excitation wavelength.

Specific regions/peaks of fluorescence were defined based on the literature. These "fluorescence regions" included two humic-like fluorescence regions (labeled as humic-like and humic-like 2) and two protein-like fluorescence regions (tyrosine-like and tryptophan-like); Table 7.1 gives the excitation and emission wavelengths associated with these regions. A mean value was calculated for each region and was used for further analysis.[23] Within this thesis, any reference to fluorescence intensity of a specific region or a specific fluorescence peak is referring to the calculated mean for that region. There are no units associated with absorption or fluorescence intensity (arbitrary units) and samples within this study were corrected for instrument fluctuations so that comparisons could be made across sampling dates.

Table 7.1. Regions of fluorescence used for analysis.

Fluorescence region / peak	**Excitation λ (nm)**	**Emission λ (nm)**
humic-like	230-250	400-440
humic-like2	315-340	400-435
Tyrosine-like	270-280	300-310
Tryptophan-like	270-280	340-360

There were other peaks on the fluorescence EEMs besides those listed in Table 7.1, but they were not considered in this thesis. This was a preliminary study on the application of these tools and a simplistic approach was selected for analyzing both the absorption and fluorescence data. The focus of this study was not a detailed examination of the dissolved organic matter composition of the sampled waters; discussion of DOM is simplified to differentiate between natural organic sources (humic and fulvic-like substances) and protein-like substances (tyrosine and tryptophan). The treatment of the

[23] Use of the maximum value within each "region" was also explored; the maximum and mean measures were highly correlated and it was decided to use the mean so that background noise due to the instruments would be averaged out.

data was in no way exhaustive and in a later section there will be some discussion on the potential for further analysis.

7.3. Range and variability of measurements

Groundwater samples had lower fluorescence intensity and lower absorption than stream water samples. Table 7.2 gives summary statistics for groundwater and stream water samples. Figure 7.1 shows some example EEMs, with scatter lines and fluorescence regions highlighted; the contrast between stream and groundwater fluorescence is obvious.

Table 7.2. Summary statistics for spectral measurements, stream and groundwater samples.

	Mean	Median	Minimum	Maximum	Std. Deviation
All samples (n=113)					
Humic-like	98.0	82.6	0.0	412.1	94.3
Humic-like 2	59.5	43.0	1.4	266.8	59.4
Tyrosine-like	5.8	5.2	0.0	24.9	4.2
Tryptophan-like	15.7	13.4	0.0	65.9	13.7
A220	1.60	0.95	0.02	10.00	2.02
A254	0.10	0.07	0.00	0.39	0.10
A280	0.07	0.05	0.00	0.28	0.07
Stream samples (n=70)					
Humic-like	151.3	143.6	38.3	412.1	81.9
Humic-like 2	92.0	84.4	24.5	266.8	53.6
Tyrosine-like	6.9	6.6	0.8	20.6	3.7
Tryptophan-like	23.3	22.0	5.7	65.9	12.1
A220	0.83	0.78	0.26	1.53	0.28
A254	0.15	0.14	0.04	0.39	0.08
A280	0.11	0.10	0.03	0.28	0.06
Groundwater samples (n=43)					
Humic-like	11.3	6.0	0.0	82.6	16.3
Humic-like 2	6.5	5.1	1.4	30.1	6.5
Tyrosine-like	4.0	2.7	0.0	24.9	4.5
Tryptophan-like	3.2	2.5	0.0	10.5	2.3
A220	2.86	2.42	0.02	10.00	2.84
A254	0.01	0.01	0.00	0.06	0.01
A280	0.01	0.01	0.00	0.05	0.01

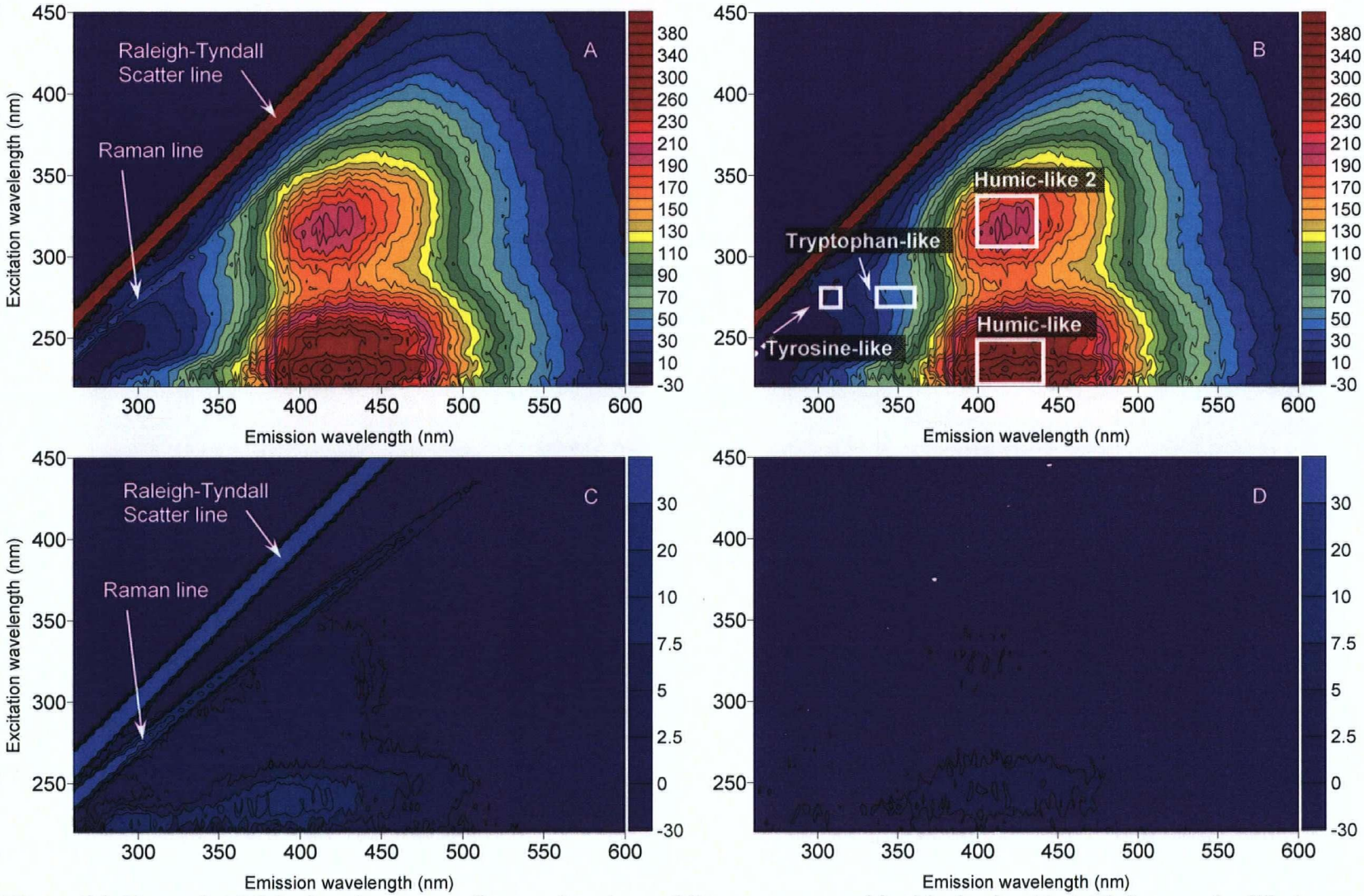

Figure 7.1. Example EEMs showing scatter lines and regions of fluorescence used in this thesis. (A & B) Stream site S7, August. (C & D) Well site A1, August. B and D have had a de-ionized water blank subtracted. Note that in A and B the contour interval is 10 units up to 240 after which it is 20 units.

In total there were 6 groundwater replicates and 6 stream water replicates (each measured in triplicate, except February 2006 samples, which were done in duplicate). Table 7.3 shows the average variability for the replicates. Due to the low fluorescence intensities, replicate groundwater samples had a higher coefficient of variation (CV) for fluorescence measurements (>10%). Stream sample replicates had an average CV <10% with the exception of tyrosine-like fluorescence, which had a median CV of 22% for the six replicate samples (mean CV was even higher). This high variation may be in part due to interference/overlapping with the Raman line of water and also due to the low intensity levels (tyrosine-like fluorescence intensity was generally <10). These levels of variation were not so extreme as to exclude any measures from further analysis, however the level of variability was kept in mind when interpreting results, particularly for protein-like fluorescence intensities.

Table 7.3. Summary of replicate sample variability for spectral measurements.

	all replicates (12)		*stream replicates (6)*		*well replicates (6)*	
	mean CV[1] (%)	mean st dev[2]	mean CV[1] (%)	mean st dev[2]	mean CV[1] (%)	mean st dev[2]
Humic-like	8.9	1.4	0.6	1.3	17.2	1.5
Humic-like 2	6.0	0.7	0.8	1.1	11.3	0.3
Tyrosine-like	45.4	2.7	38.0	1.9	52.8	3.4
Tryptophan-like	15.1	1.0	4.2	1.0	26.1	0.9
A220	5.3	0.274	0.5	0.003	10.1	0.544
A254	0	0.002	0.9	0.002	0	0.002
A280	0	0.002	1.0	0.002	0	0.002

[1] coefficient of variation
[2] standard deviation

7.4. Correlations between spectral measurements

Correlations between fluorescence regions are shown in Table 7.4. The two regions of humic-like fluorescence were significantly positively correlated and tryptophan-like fluorescence was significantly positively correlated with humic-like fluorescence. Tyrosine-like fluorescence was the least correlated to the other fluorescence regions, although the positive correlations were still significant. Correlations for the groundwater samples showed the same trend, but were weaker, probably due to low levels of fluorescence overall (groundwater fluorescence measures also had the highest

coefficient of variation). The humic and protein-like fluorescence regions seemed to be related, but were also representing some distinctive CDOM characteristics, which was expected.

Absorption measurements at 254 nm and 280 nm were highly correlated, having a Spearman's rank correlation of 0.996 for all samples pooled together (see Table 7.5); these wavelengths captured similar trends and differences discussed later in this chapter. For the stream samples and pooled samples, A254 and A280 had a strong positive correlation to the humic-like and tryptophan-like fluorescence. A220 had significant negative correlations with the other absorption wavelengths and fluorescence intensities; A220 was selected as a key wavelength for its relationship with nitrate, which will be discussed in a later section. Tyrosine-like fluorescence had the weakest correlations with absorption values and stood out from the other spectral measurements, capturing different aspects of the dissolved CDOM.

Table 7.4. Spearman rank correlations among the humic-like and protein-like fluorescence regions.

	correlation coefficient (Spearman's rho)			
	Humic	Humic2	Tyrosine	Tryptophan
All samples (n=113)				
Humic-like	1.000	.985**	.608**	.972**
Humic-like 2		1.000	.555**	.956**
Tyrosine-like			1.000	.681**
Tryptophan-like				1.000
Stream samples (n=70)				
Humic-like	1.000	.998**	.452**	.928**
Humic-like 2		1.000	.444**	.928**
Tyrosine-like			1.000	.581**
Tryptophan-like				1.000
Groundwater samples (n=43)				
Humic-like	1.000	.750**	.571**	.839**
Humic-like 2		1.000	0.197	.556**
Tyrosine-like			1.000	.783**
Tryptophan-like				1.000

* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

Table 7.5. Spearman rank correlations for A220, A254, and A280 with each other and with fluorescence regions.

	A220	A254	A280	Humic	Humic2	Tyrosine	Tryptophan
All samples (n=110)							
A220	1.000	-.498**	-.476**	-.598**	-.515**	-.378**	-.563**
A254		1.000	.996**	.954**	.976**	.528**	.935**
A280			1.000	.946**	.969**	.525**	.928**
Stream samples (n=68)							
A220	1.000	-.498**	-.476**	-.731**	-.712**	-0.196	-0.647**
A254		1.000	.996**	.953**	.964**	.428**	.904**
A280			1.000	.948**	.959**	.426**	.903**
Groundwater samples (n=42)							
A220	1.000	.344*	.446**	-0.191	0.247	-0.290	-0.166
A254		1.000	.936**	.386*	.730**	-0.151	0.291
A280			1.000	0.261	.630**	-0.186	0.176

* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

7.5. Stream water spatial and seasonal trends

Stream water humic-like fluorescence (both regions), tryptophan-like fluorescence, A254, and A280 all showed very similar spatial and seasonal trends, as might be expected given the correlations between these measures. As an example, Figure 7.2 shows the data for humic-like fluorescence. The highest absorption and fluorescence was in the Salmon headwaters (site S7), with a decreasing trend downstream. There was a slight upward trend for the lower three sites on the Salmon (S3-S1). Wet season values were higher for all sites except for S7, which was higher in the dry season. Ross (2006) also found that in the Salmon watershed A280 values peaked in the winter, with the exception of site S7, which peaked in August. Site S7 had heavy vegetative growth in the summer months and this plant material would contribute to the spike in dissolved organic matter and humic-like fluorescence. Higher values in the wet season could be attributed to increased overland flow and runoff, which would carry and move organic matter into the stream.

Both Coghlan Creek and the Salmon River showed a declining downstream trend for humic-like fluorescence and A254/A280. This might suggest groundwater influence that was diluting the higher upstream CDOM concentrations. Humic-like fluorescence

and A254/A280 were very low throughout the year at site T1 (Union Creek), indicating that there was either no source of CDOM (unlikely) or perhaps that stream flow was dominated by groundwater discharge. Union Creek is incised into the aquifer and it is reasonable to expect significant groundwater discharge to the creek, especially given groundwater flow is in a NW direction (see Chapter 4). Davidson Creek, which is influenced by groundwater, also showed fairly low humic-like fluorescence and A254/A280. Site D1 was after the creek has passed through the northern tip of the Hopington B, another region of groundwater discharge. The contributing area for D1, however, had a high proportion of agricultural land use, which may account for the values not being even lower.

A220 showed a spatial and seasonal trend opposite to that for A254/A280 and the humic-like fluorescence (see Figure 7.6). This trend was very similar to that of nitrate, as discussed in Chapter 5. Downstream increases were due to nitrate inputs from groundwater as the stream cuts through the Hopington A and B aquifers, and from tributaries (Union Creek and Coghlan Creek). A220 decreased again at the stations nearest the river mouth (S3-S1).

Tyrosine-like fluorescence showed a mixed trend (see Figure 7.4). Some of the variation and scatter could have been due to low levels and sample variability, as previously noted, however there seemed to be individual occasions of high protein-like fluorescence that were not attributable to analytical or sample variability. These anomalies will be explored further as potential indicators of contamination events. There was still a general declining trend from S7 down through site S5, perhaps because of a significant source in the contributing area of S7 (farms, zoo, beavers – all of which might be a source of protein-like CDOM). Further downstream, there was a slight increase again. Most of the higher values occurred in the wet season when sources can be more easily mobilized and transported to the stream. Overall, the protein-like fluorescence was not as useful for marking groundwater influence, but it may be helpful for pollutant sourcing and for indicating potential contamination events.

Figure 7.7 and Figure 7.8 show downstream trends for fluorescence using contour plots of the EEMs for the August 21, 2006 sampling date. There was an obvious downstream dilution of humic-like fluorescence and then an increase again at sites S2 and

S1. The similar dowsnstream dilution could be seen with the 3 Coghlan sites. Union Creek and Davidson Creek were both very low for all regions. The protein-like fluorescence, showing up as a shoulder to the left of the large humic-like peaks, could be seen most prominently at sites S7, S6, S2, S1, and C3 fluorescence (λ_{ex}= 270-280 nm, λ_{em} = 300-310, 340-360 nm).

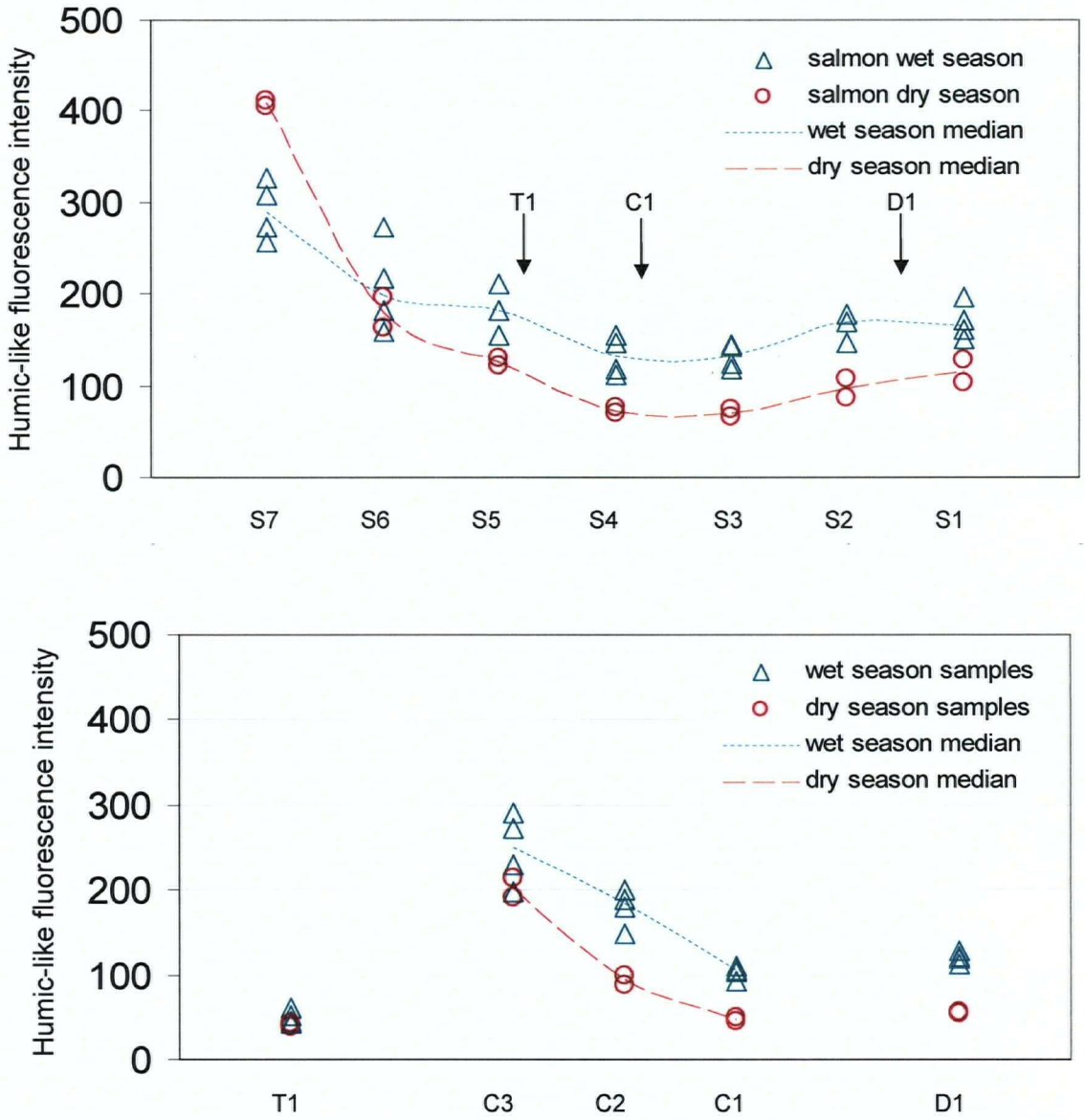

Figure 7.2. Stream sample humic-like fluorescence, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

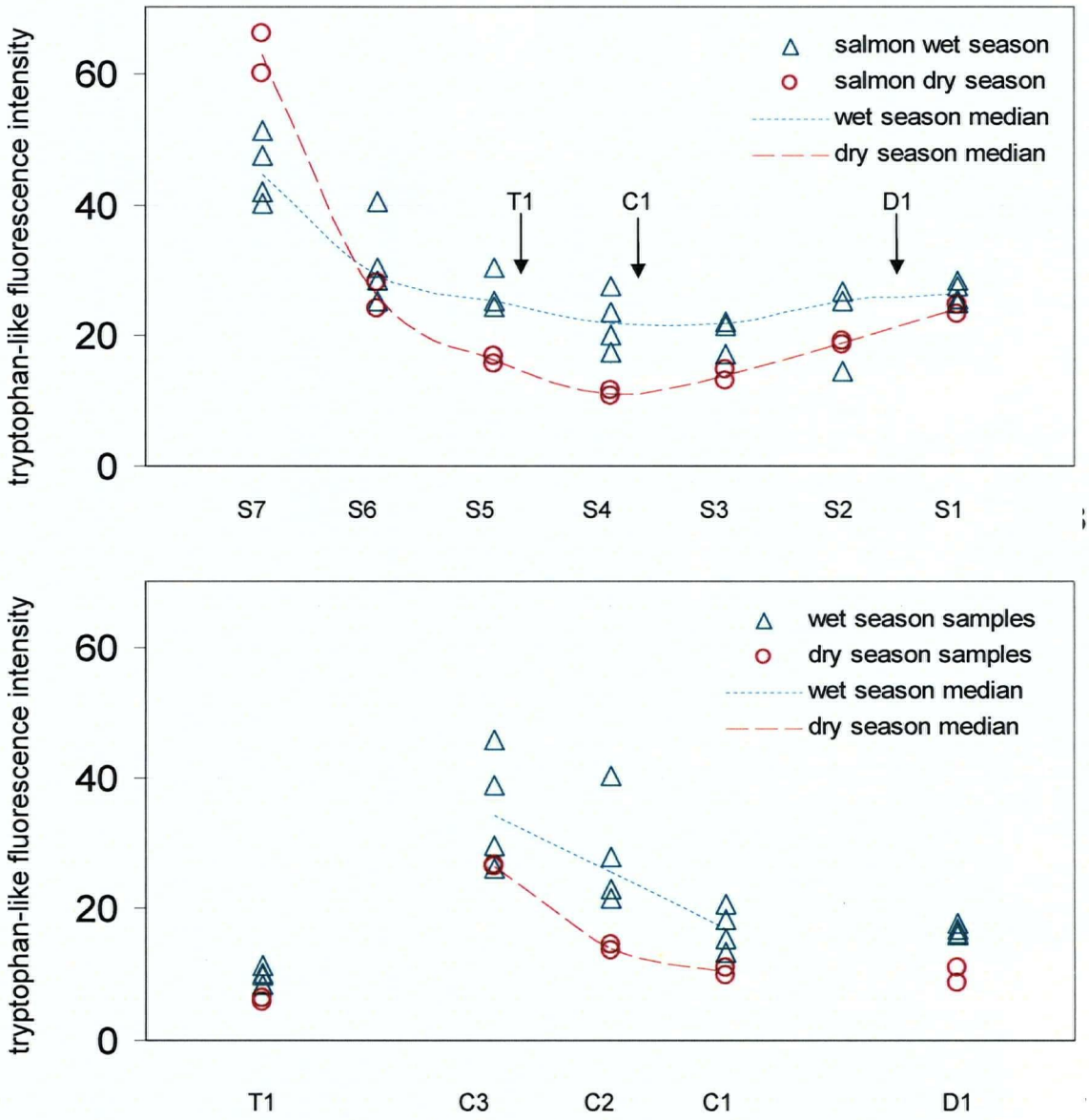

Figure 7.3. Stream sample tryptophan-like fluorescence, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

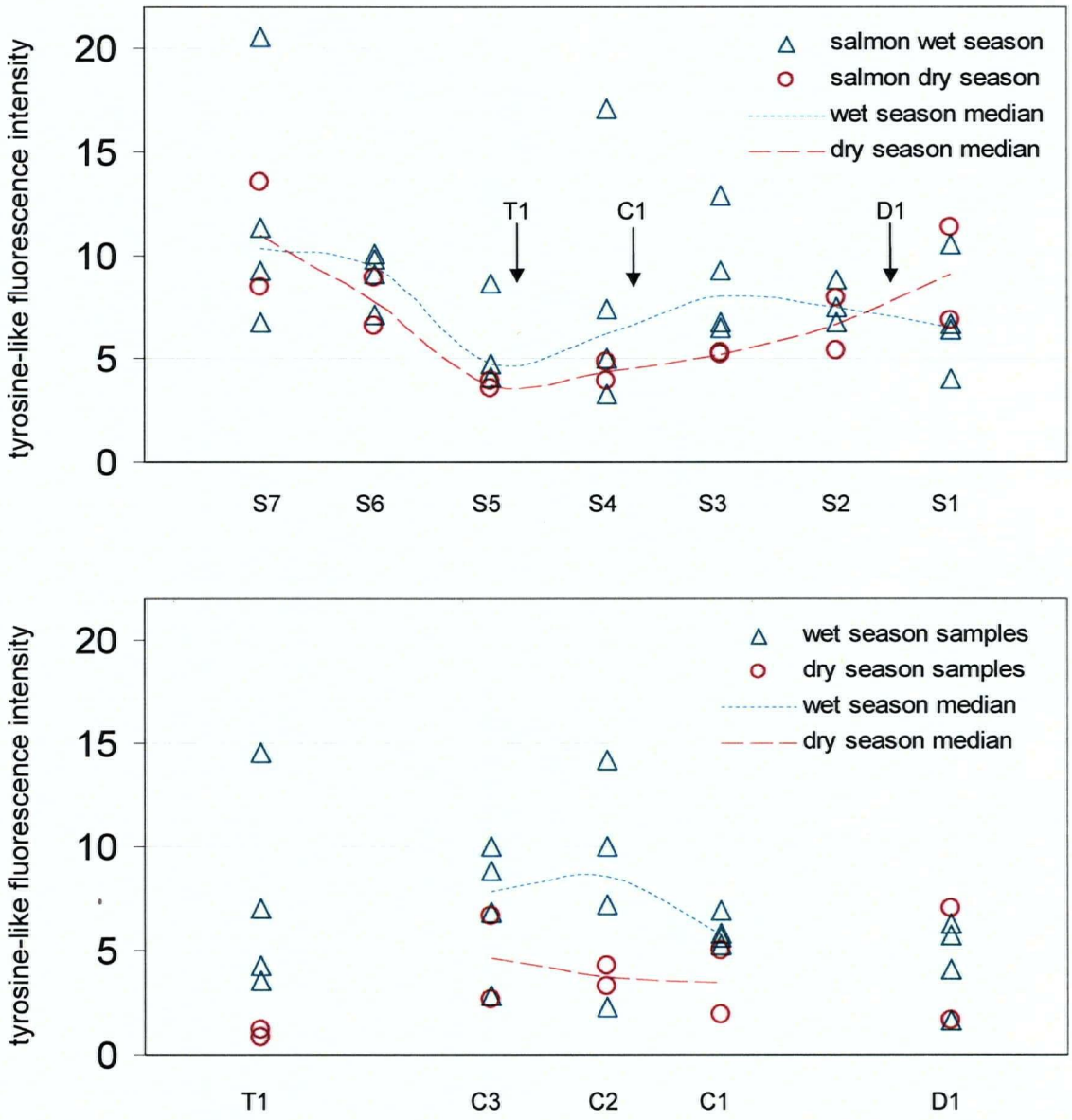

Figure 7.4. Stream sample tyrosine-like fluorescence, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

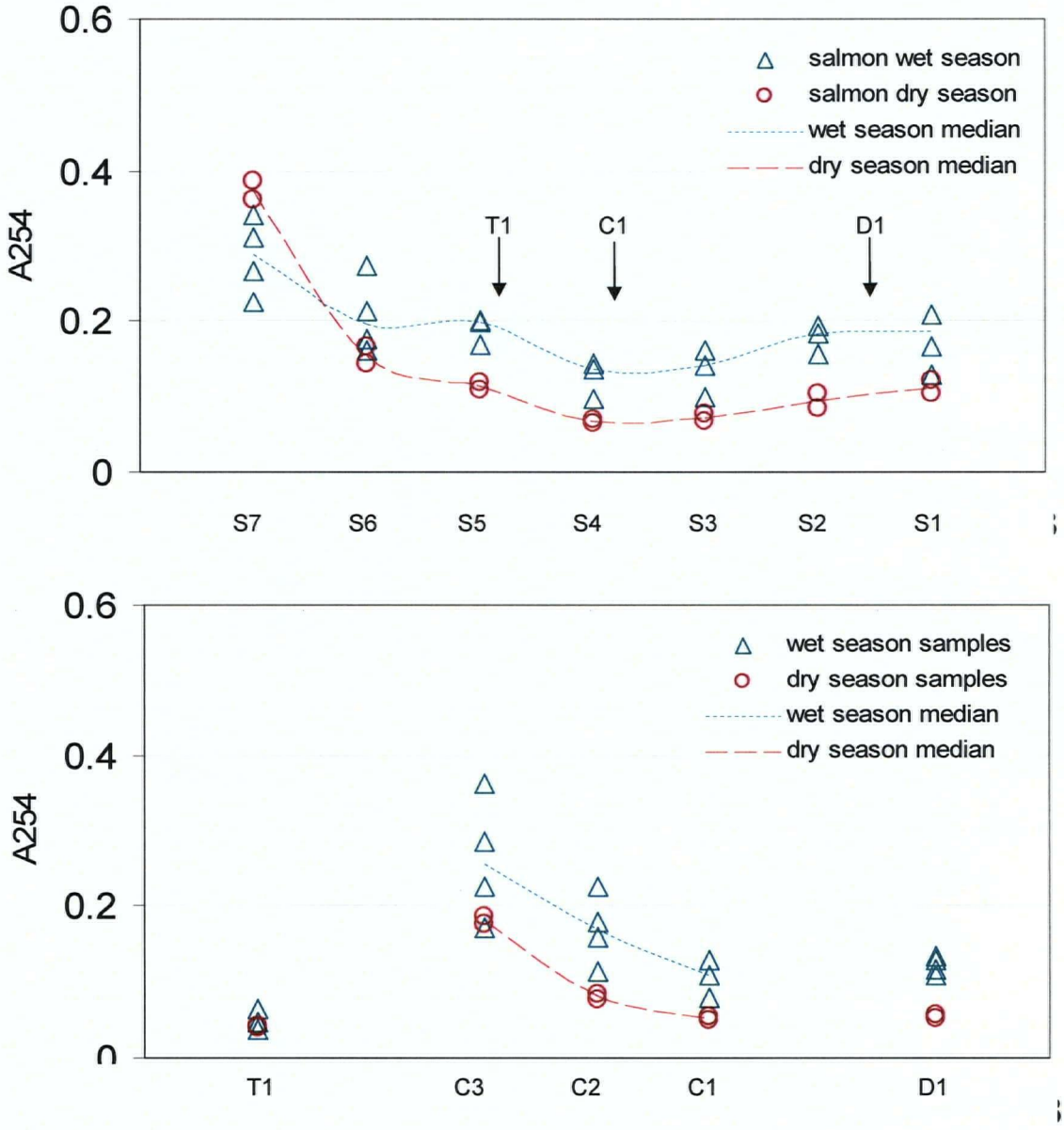

Figure 7.5. Stream sample absorbance at 254 nm, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

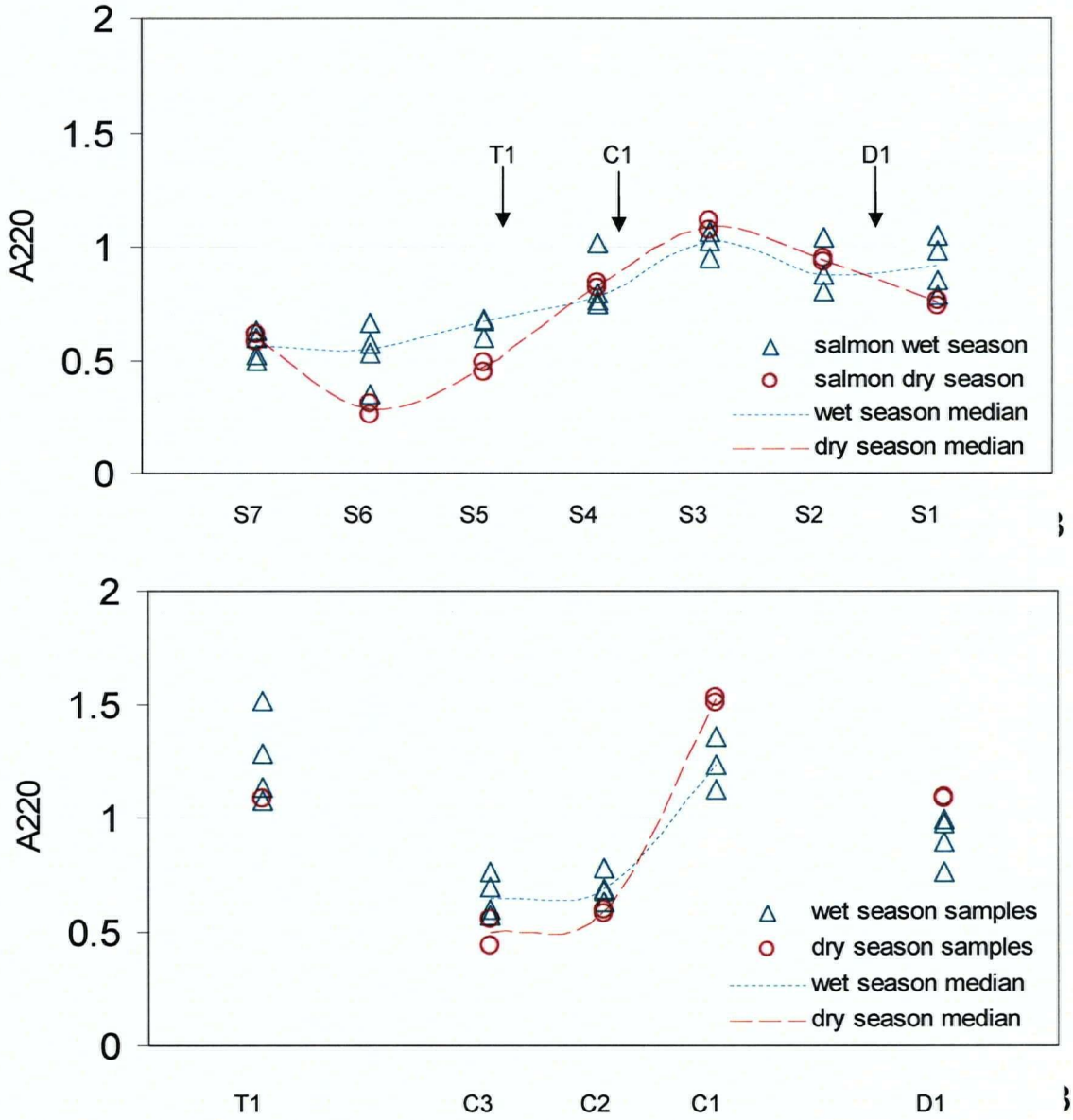

Figure 7.6. Stream sample absorbance at 220 nm, upstream to downstream sampling stations (left to right). All samples taken in both wet and dry seasons are represented; broken lines connect median values for that season. X-axis is not to scale and arrows in the top graph indicate where tributaries enter the Salmon mainstem.

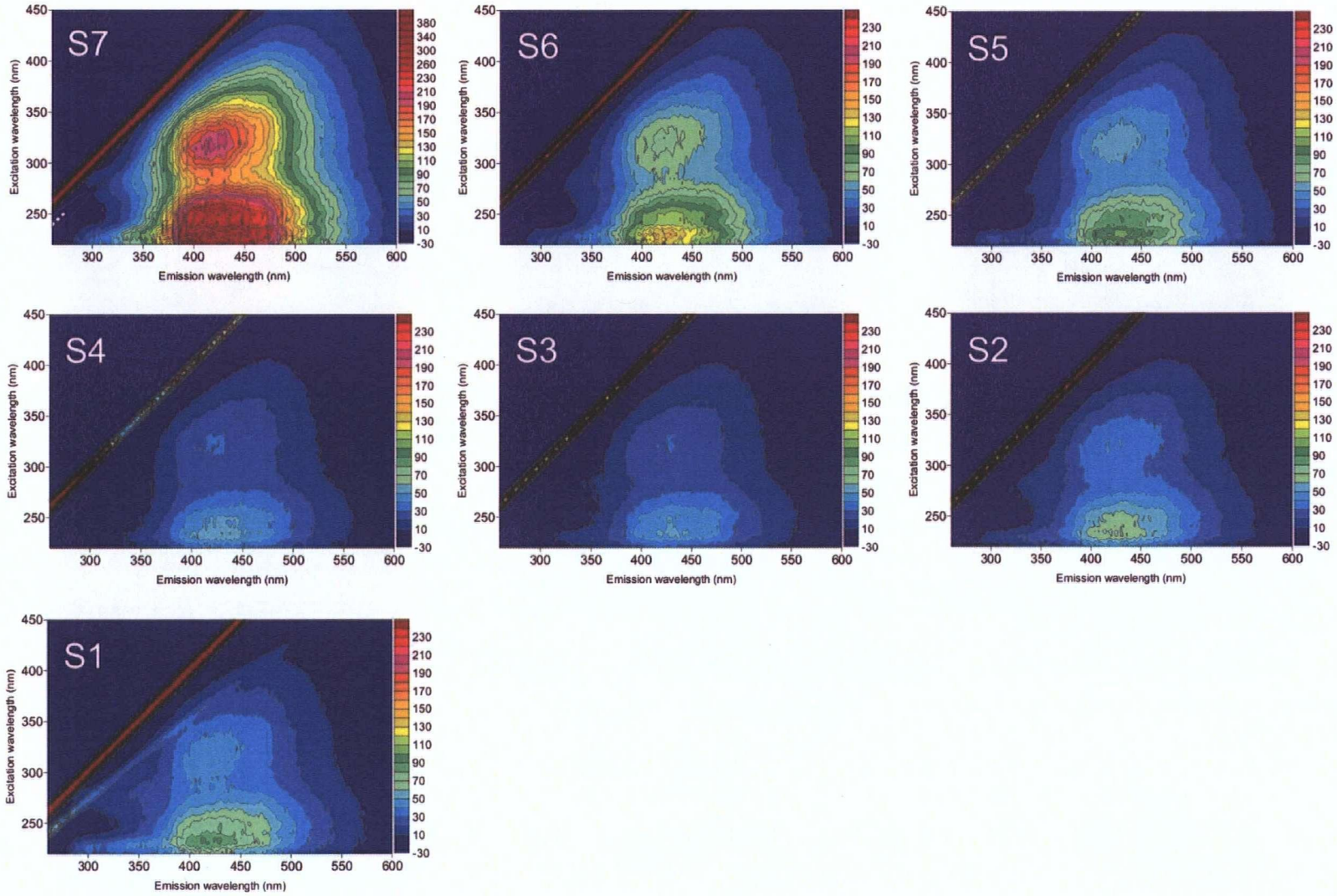

Figure 7.7. Contour plots of fluorescence EEMs for Salmon River sampling stations, upstream to downstream (S7 through S1). Samples from August 21, 2006. Contours are in increments of 10 intensity units (except S7 switches to 20 unit intervals after 240).

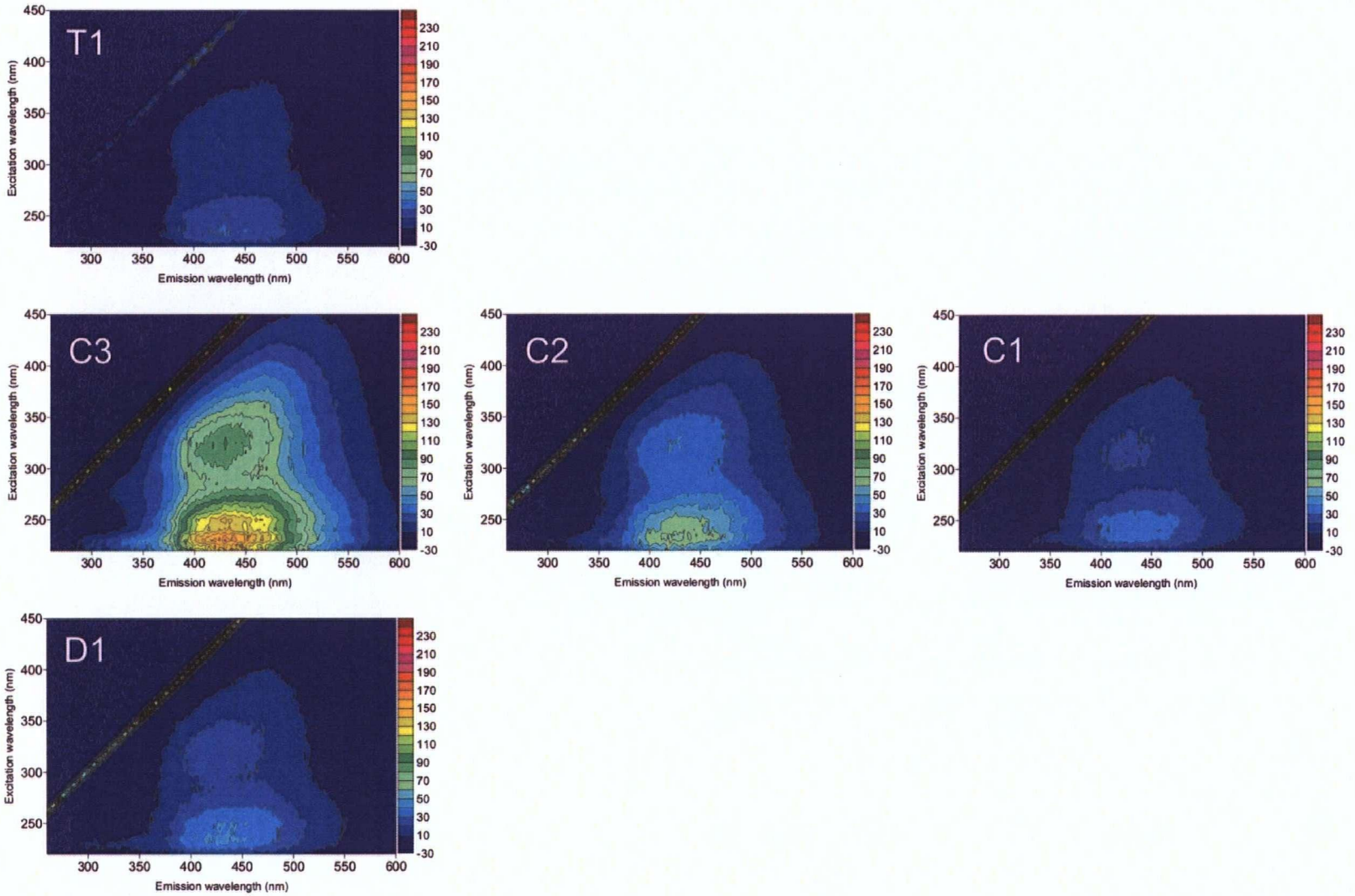

Figure 7.8. Contour plots of fluorescence EEMs for tributaries to the Salmon River (Union Creek, Coghlan Creek, Davidson Creek). All samples were from August 21, 2006. Contours are in increments of 10 intensity units.

7.6. Groundwater fluorescence

Compared to stream samples, wells generally had very low humic-like fluorescence (both regions) and tryptophan-like fluorescence. This made sense as lower CDOM levels are expected in groundwater. There were no significant differences between the Hopington A, B, and C aquifers for any of the spectral measurements. For the most part, humic-like2 fluorescence of groundwater samples was less than 10 units and tryptophan-like fluorescence <5 units. There were a few exceptions, however, which are shown in Table 7.6.

Table 7.6. Well samples with high fluorescence

Date	Site	Mean intensity of fluorescence region			
		Humic-like	Humic-like2	Tyrosine-like	Tryptophan-like
Humic-like2 fluorescence >10					
21 Aug 2006	Well X3	62.0	30.1	2.6	6.4
20 Feb 2006	Well A2	82.6	30.0	24.9	10.5
21 Aug 2006	Well A2	49.5	22.5	11.8	6.7
21 Aug 2006	Well X2	25.5	12.7	3.3	4.2
20 Feb 2006	Well X2	33.0	15.0	2.3	5.0
Tyrosine-like fluorescence >5					
20 Feb 2006	Well A2*	82.6	30.0	24.9	10.5
28 Mar 2006	Well B4	7.0	4.9	12.1	10.5
21 Aug 2006	Well A2*	49.5	22.5	11.8	6.7
30 May 2006	Well X1	5.0	1.8	9.9	2.5
22 Feb 2006	Well B3	12.5	8.8	8.0	4.0
22 Feb 2006	Well A1	10.7	4.4	6.8	3.9
30 May 2006	Well A1	10.4	5.4	6.6	7.0

* Repeated because have high humic-like and protein-like fluorescence.

The humic-like2 fluorescence peak exceeded 10 units for only 5 groundwater samples (3 wells). Compared to other wells, site X3 (Hopington C aquifer) had very high humic-like and humic-like2 fluorescence, 62 and 30 respectively. Protein-like fluorescence was not elevated. This well was sampled only once (August 2006) and so the unusual value was not confirmed and may be an outlier or contaminated sample.

Well X2, an observation well for the BC Ministry of Environment (and therefore sampled only twice in Feb and Aug) was a site with high fluorescence. The average of the

humic-like fluorescence regions for both sampling occasions was 29.2 and 13.8 for humic-like and humic-like2, respectively. Tryptophan-like fluorescence was not much higher than other wells and tyrosine-like fluorescence was low. Well A2, the other Ministry observation well, had fluorescence values approximately double that of well X2. Humic-like2 fluorescence was 30 and 22 for February and August, respectively. Tyrosine-like fluorescence was also high at this site.

There were seven groundwater samples with tyrosine-like fluorescence greater than 5 units (Table 7.6). The monitoring well A2 also had high protein-like fluorescence on both sampling occasions, particularly in February (24.9), which was one of the highest tyrosine-like fluorescence values for all sampling occasions and sites. August tyrosine-like fluorescence was moderately high (11.8). The high levels of CDOM indicated by these fluorescence levels is very unusual, particularly the high protein-like fluorescence. There was no visually evident turbidity when sampling, but perhaps the well is not properly sealed or is contaminated. There was some animal holding less than 300 m NW of the well and there is also berry production and greenhouses very nearby. The source of the CDOM can not, however, be determined with the current level of data.

Well B4 had high protein-like fluorescence only for the March sampling. It rained on this sampling day (3.9 mm for the whole day) and within 48 hours prior to sampling. Perhaps there was some sort of flush into the system due to the precipitation and conditions of this date. This well is located on a horse stadium grounds. The August sample had tyrosine-like fluorescence of 4.9, but the other 2 dates (May and July) were less than 2.5. In August there was a show happening at the time of sampling with a lot of animals on the premises.

Tyrosine-like fluorescence for well X1 was also elevated on only one occasion (May). There was some precipitation in the preceding days, but none on the day of sampling. February was the next highest at 6.0. Well B3 is a third site with a one-time high reading for tyrosine-like fluorescence (February); samples from all other occasions were under 4.

Well A1 had elevated tyrosine-like fluorescence in February and May (~7); March was next highest with 2.0 and the summer samples were very low. It is suspected that this well was impacted by surface water during the winter months. In March, when there was

more precipitation prior to sampling, this impact was diluted and less noticeable. Stream site S4 (closest stream site in a downstream direction) also had its highest Tyrosine-like fluorescence in February and May.

7.7. Groundwater – surface water interactions

Given the low fluorescence and absorption (A254 and A280) of groundwater, groundwater input to the stream would be observed by a decrease in absorption and fluorescence intensity. Once again, humic-like(2) fluorescence, tryptophan-like fluorescence, A254, and A280 showed a very similar trend. These measures were all highest in the headwater sites before the Hopington aquifer, decreased as the stream flowed through the Hopington aquifer and then stayed lower until the river mouth. Stream sites "before" the Hopington A and B aquifers had significantly higher humic-like(2) fluorescence, tryptophan-like fluorescence, A254, A280 (0.01 level of significance) and tyrosine-like fluorescence (0.05 level of significance) than stream sites over and after the aquifers.[24] See Figure 7.9 for an example of this trend (humic-like2; Figure 7.10 for A254).

A220 showed the groundwater (high nitrate) input over the Hopington aquifer. A220 was significantly higher over and after the aquifers than before (p-value=0.009 and 0.002, respectively); over and after were not significantly different.

Tyrosine-like fluorescence did not show the groundwater input as strongly (Figure 7.9). In the dry season, tyrosine-like fluorescence was significantly lower at the "over aquifer" stream sites than at sites before or after the aquifer (p-values < 0.03). During the dry season the groundwater contribution would make up a greater proportion of the stream flow and thus "dilution" of the upstream CDOM would be more pronounced; there may also have been less inputs from the surface (due to less precipitation). There were no differences for the wet season.

There was no difference between seasons for the "before" stream sites. For "over" aquifer stream sites, tyrosine-like fluorescence was greater in the wet season (p-value 0.009), and the same was true for humic-like(2) and tryptophan-like fluorescence (all had

[24] Site-season summary values were used for these tests; n=6, 10, and 8 for before, over, and after, respectively.

p-value = 0.076, N=5 for each season). Again, these differences reflected the increase in proportional contribution of groundwater during low-flow conditions. Humic-like and humic-like 2 fluorescence was higher in the wet season for the "after" aquifer stream sites (p-value = 0.021, N=4 for each season).

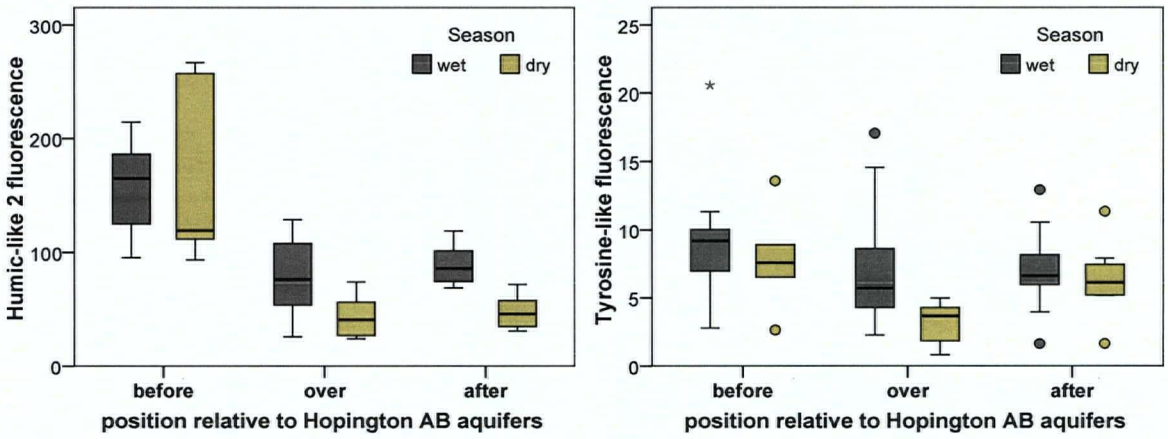

Figure 7.9. Fluorescence (humic-like2 and tyrosine-like) of stream water samples, boxplots by position relative to the Hopington AB aquifers. n=18, 28, and 23 for before, over, and after, respectively (including both seasons).

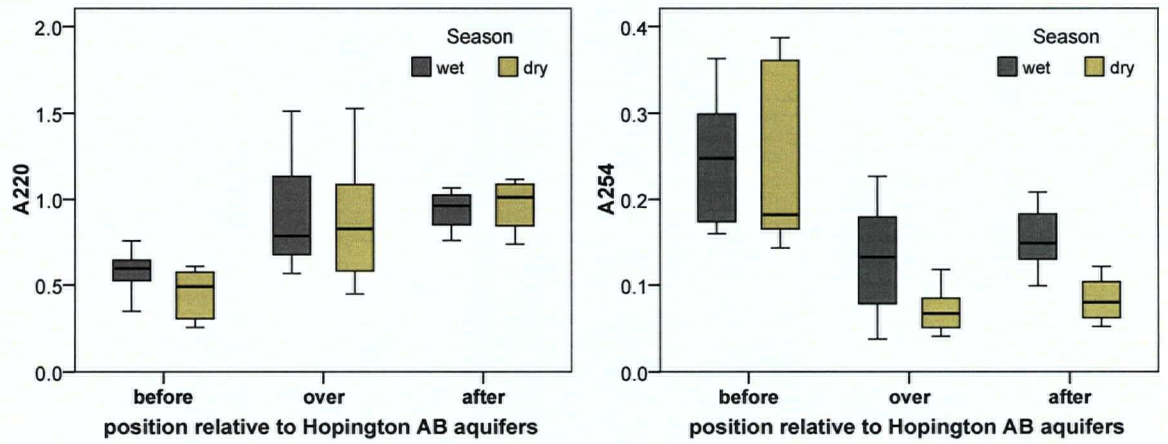

Figure 7.10. Absorption (A220, A254) of stream water samples, boxplots by position relative to the Hopington AB aquifers. n=18, 28, and 23 for before, over, and after, respectively (including both seasons).

7.8. Protein-like fluorescence as an indicator

Of the two protein-like fluorescence regions, tyrosine-like was more independent of the humic-like fluorescence, which is dominated by humic and fulvic compounds. The protein-like fluorescence (tyrosine-like) is potentially a good indicator of "fresh" DOM contamination (e.g. septic, manure, wildlife waste). As noted previously, groundwater samples generally had low protein-like fluorescence, with a few exceptions. Variability of the tyrosine-like intensity measurement makes comparisons for such low levels difficult. Some wells had higher values on sampling days with some precipitation in the preceding 96 hours (February, March, May), but this was not true for all sites. Individual occurrences of higher tyrosine-like fluorescence may indicate a contamination event. Well A1 (Feb.), B3 (Feb.), and X1 (May) are potentially in this category.

Plots of antecedent precipitation and tyrosine-like fluorescence (stream sites) showed no consistent trend between the different sites. Many of the higher tyrosine-like values were also associated with some precipitation in 24-96 hours preceding sampling, but this was not always the case. In July and August there was no precipitation the day of sampling or in the 96 hours preceding sampling, yet 5 stream sites had tyrosine-like fluorescence greater than 8 (July: S6, S7, T1; August: S1, S7). For Sites D1 and S1, the highest tyrosine-like fluorescence intensities were in August. It was also true that sampling occasions with preceding rainfall (e.g. March) did not necessarily have elevated tyrosine-like fluorescence; sites C3, S1, and S7 had very low values in March, while other stations (S3 and T1) had the highest values in March. These inconsistencies reflect the different circumstances at the sampling stations.

Transport and supply limitations both must be considered in understanding the links between antecedent precipitation and tyrosine-like fluorescence in the stream. The duration and intensity of the precipitation event, and antecedent soil moisture conditions will have an impact on how much runoff (subsurface and overland flow) will reach the stream. Runoff is the primary transport mechanism for OM to reach the stream. If there is no protein-related OM to transport or the supply has been exhausted (supply limitation) there will be no increase in the stream or the precipitation may simply be diluting the pre-existing stream concentration. Land use practices may mean that there is simply no source of protein-related CDOM (e.g. no septic leakage or animal waste) or the supply might be

exhausted if there have been recent precipitation events. For example, in March there had already been a lot of precipitation, which would have flushed and transported DOM so perhaps there was not much left to be transported at those sites that showed low fluorescence on this occasion. Sites that maintained a high value in March may have had a constant source (e.g. an animal operation nearby where manure production is independent of season).

The Salmon River downstream sites (S1, S2, and S3) had moderate levels of tyrosine-like fluorescence for most sampling occasions. These sites would have reflected the cumulative influence of upstream sources and possibly new sources post-aquifer influence. Site S3 had a higher peak in March, which may have reflected a specific contamination event (e.g. farm inputs, domestic or wild animal waste). Other sites (S4, T1, and C2) had a mix of high and low tyrosine-like fluorescence, which may reflect interplay between dilution of groundwater, supply and transport, and specific contamination events. Meanwhile, stream sites S5 and C1 had mostly low levels and sites C3 and D1 had moderate to low tyrosine-like fluorescence. Stream sites S7 and S6 had high tyrosine-like fluorescence on most sampling occasions. This likely reflects year-round inputs from upstream land use (zoo and lots of animal agriculture).

Thus the protein-like fluorescence can reflect overall water quality risks (e.g. Site C1 having low protein-related fluorescence, but site S7 having quality problems year-round). The protein-like fluorescence also has the potential to capture single or unusual contaminations events. If continuous monitoring was being done, a peak in tyrosine-like fluorescence could act as an indicator of quality problems that may potentially pose health-risks (if bacterial concentrations are associated with the protein-like DOM).

Returning salmon populations that spawn and then undergo death / decomposition would also be a source of tyrosine and tryptophan, increasing the protein-like fluorescence intensity of stream water samples. Given the recent low return rates for coho, as well as the sampling schedule of this study, it was felt that this was not a key factor. Significant salmon populations might also impact nitrogen concentrations and nitrogen-isotope values.

7.9. Relationships with other parameters

If fluorescence and absorption are to be used as indicators, it is important to know what the values are reflecting. While a detailed examination of the OM composition was not a part of this study, there were other parameters measured (nutrients, dissolved elements, total and dissolved organic carbon). Correlations between these other parameters and the fluorescence and absorption measurements can be found in Table 7.7 and Table 7.8, respectively.

There was a strong positive correlation with TOC/DOC[25] concentrations and humic-like(2) fluorescence, tryptophan-like fluorescence, A254, and A280. Correlations with tyrosine-like fluorescence were weaker overall, but also significant. Groundwater samples only had a significant correlation with humic-like 2 fluorescence. These relationships are not expected to be perfect because there is a variety of fluorescing compounds. Ross (2006) found similar relationships, with humic-like fluorescence being significantly positively correlated with DOC and log-transformed fecal coliform concentrations; tyrosine-like fluorescence had the weakest correlations with nutrients, but did have a strong positive correlation with log-transformed fecal coliform. For the Salmon River watershed specifically, humic-like fluorescence was positively correlated to ammonia concentration and protein-like fluorescence to fecal and total coliform (log-transformed) (Ross, 2006); this correlation with nutrients was not found with this study. For absorption, Ross found a significant positive correlation between A280 and fecal coliform concentration during a storm even in an agriculture-dominated catchment, but in the Salmon watershed the log of total coliform was negatively correlated with A280 (-0.339) (Ross, 2006).

The negative correlations with nitrate, calcium, and silica might be equated to a negative correlation with groundwater influence since groundwater discharge from the Hopington A and B aquifers seem to be a source of these chemical constituents (see previous chapters for evidence). Correlations with nitrate were also negative (except for A220). Tyrosine-like fluorescence had the weakest negative correlation with nitrate for the stream samples. If protein-like (tyrosine) fluorescence was associated with septic or

[25] There were 4 replicate samples for TOC/DOC (2 wells and 2 streams sampled in triplicate in May and August). The average CV of the replicates was 0.10 and 0.19 (TOC and DOC); the average standard deviation was 0.13 and 0.08 (TOC and DOC).

manure influences (which would also be a source of nitrate) then it makes sense for this correlation to be weakened and in the absence of high-nitrate groundwater inputs perhaps this would be a positive correlation.

Nitrate had a significant positive correlation with A220 (0.97, for all samples). Ross (2006) found that A220 explained 91% of the variance in stream water nitrate concentrations; for the Salmon River watershed specifically, the correlation between nitrate concentration and the 2nd derivative of absorbance at 224 nm was 0.969. The lack of correlation between A220 and humic-like(2) fluorescence and A254 suggests that nitrate and dissolved organic matter were not necessarily related. For example, Union Creek had high nitrate concentrations (A220), but very low humic-like fluorescence and low A254.

There was a significant negative correlation between pH and stream sample humic-like fluorescence. Correlations between pH and humic-like, humic-like2, and tryptophan like fluorescence were -0.327**, -0.315**, and -0.265*, respectively (stream water samples only)[26]. This was because changes in pH affect the DOC structure (Baker, 2002; Mobed, Hemmingsen, Autry, & McGown, 1996). There was no correlation for groundwater alone or when the groundwater and stream water samples were pooled together, probably due to the low groundwater DOC levels.

[26] N=70, **/* signifies the correlation was significant at 0.01/0.05 level

Table 7.7. Spearman's rank correlations for fluorescence regions and other parameters measured.

	correlation coefficient (Spearman's rho)									
	NO_3^-	TOC	DOC	A254	Ca	Fe	K	Na	Si	Mn
All samples	*n=112*	*n=43*	*n=43*	*n=110*	*n=43*	*n=43*	*n=43*	*n=43*	*n=43*	*n=43*
Humic-like	-.685**	.947**	.947**	.954**	-.500**	.844**	.751**	.597**	-.748**	.427**
Humic-like2	-.614**	.965**	.965**	.976**	-.459**	.809**	.774**	.623**	-.772**	.403**
Tyrosine-like	-.456**	.612**	.582**	.528**	-0.287	.670**	.468**	.385*	-.436**	.316*
Tryptophan-like	-.650**	.929**	.930**	.935**	-.449**	.807**	.747**	.606**	-.759**	.407**
Stream samples	*n=69*	*n=24*	*n=24*	*n=68*	*n=24*	*n=24*	*n=24*	*n=24*	*n=24*	*n=24*
Humic-like	-.877**	.982**	.993**	.953**	-0.363	.927**	.769**	0.403	-.658**	0.317
Humic-like2	-.866**	.983**	.993**	.964**	-0.361	.933**	.777**	.420**	-.657**	0.321
Tyrosine-like	-.296*	.708**	.693**	.428**	-0.051	.697**	.446*	.490*	-0.403	0.280
Tryptophan-like	-.800**	.910**	.939**	.904**	-0.264	.878**	.710**	0.403	-.596**	0.325
Groundwater samples	*n=43*	*n=19*	*n=19*	*n=42*	*n=19*	*n=19*	*n=19*	*n=19*	*n=19*	*n=19*
Humic-like	-0.263	.465*	0.446	.386*	-0.384	.649**	0.284	-0.044	-0.061	.738**
Humic-like2	0.148	.644**	.625**	.730**	-0.167	.523*	0.388	0.039	-0.091	.701**
Tyrosine-like	-.339*	0.011	-0.172	-0.151	-0.338	0.298	0.133	-0.091	0.025	0.317
Tryptophan-like	-0.239	0.377	0.332	0.291	-0.295	.581**	0.363	0.012	-0.111	.701**

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

Table 7.8. Spearman's rank correlations for absorption and other parameters measured.

	Correlation coefficient (Spearman's rho)								
	NO_3^-	TOC	DOC	Ca	Fe	K	Na	Si	Mn
All samples	*n=109*	*n=42*	*n=42*	*n=42*	*n=42*	*n=42*	*n=42*	*n=42*	*n=42*
A220	.975**	-.434**	-.460**	.728**	-.667**	-.306*	-0.003	0.214	-.312*
A254	-.610**	.959**	.982**	-.426**	.856**	.759**	.643**	-.738**	.438**
A280	-.589**	.955**	.980**	-.423**	.846**	.765**	.635**	-.735**	.426**
Stream samples	*n=67*	*n=23*	*n=23*	*n=23*	*n=23*	*n=23*	*n=23*	*n=23*	*n=23*
A220	.940**	-.623**	-.692**	.417*	-.536**	-.606**	0.005	.537**	-0.060
A254	-.834**	.986**	.987**	-0.295	.960**	.777**	.467*	-.658**	0.365
A280	-.828**	.986**	.987**	-0.295	.960**	.777**	.467*	-.658**	0.365
Groundwater samples	*n=42*	*n=19*	*n=19*	*n=19*	*n=19*	*n=19*	*n=19*	*n=19*	*n=19*
A220	.996**	0.019	0.015	.575*	-0.436	-0.009	.462*	-0.317	-0.190
A254	.344*	.612**	.865**	0.000	.704**	0.416	0.072	0.007	.783**
A280	.448**	.593**	.854**	0.012	.627**	0.437	0.026	0.030	.707**

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

7.9.1. **Fluorescence and nitrate-isotopes**

Streamwater fluorescence intensity and ^{15}N were inversely related (values were too low for groundwater). Figure 7.11 shows a similar trend for both humic-like and tyrosine-like fluorescence. Higher humic-like fluorescence would be indicative of natural OM, which has lower $\delta^{15}N_{NO3}$ than animal-derived nitrate; this relationship was reflected in the stream data. Dry season samples (August) had lower humic-like fluorescence and higher $\delta^{15}N_{NO3}$, when groundwater nitrate source was dominant.

Tyrosine-like fluorescence had a similar relationship (Figure 7.11, A), although the inverse might be expected since the "protein" signature would be associated with animal wastes, which would presumably have higher $\delta^{15}N_{NO3}$. For the sites that were sampled for nitrate isotopes, protein-like fluorescence (tyrosine-like) was higher in May, but $\delta^{15}N_{NO3}$ values were lower; the protein-related source would not necessarily have been accompanied by high $\delta^{15}N$ nitrates because the CDOM may not be related to nitrate (no significant correlation) and there could be source mixing that obscures the signal. Notably, the "after" aquifer stream sites (S1 and D1) were positioned differently in the graph with tyrosine-like fluorescence; nitrate source at these sites might have reflected "fresh" inputs from the land surface (livestock waste or septic impact), which also had higher tyrosine-like fluorescence. Well samples showed no clear trends, which may have been due to the small range of values.

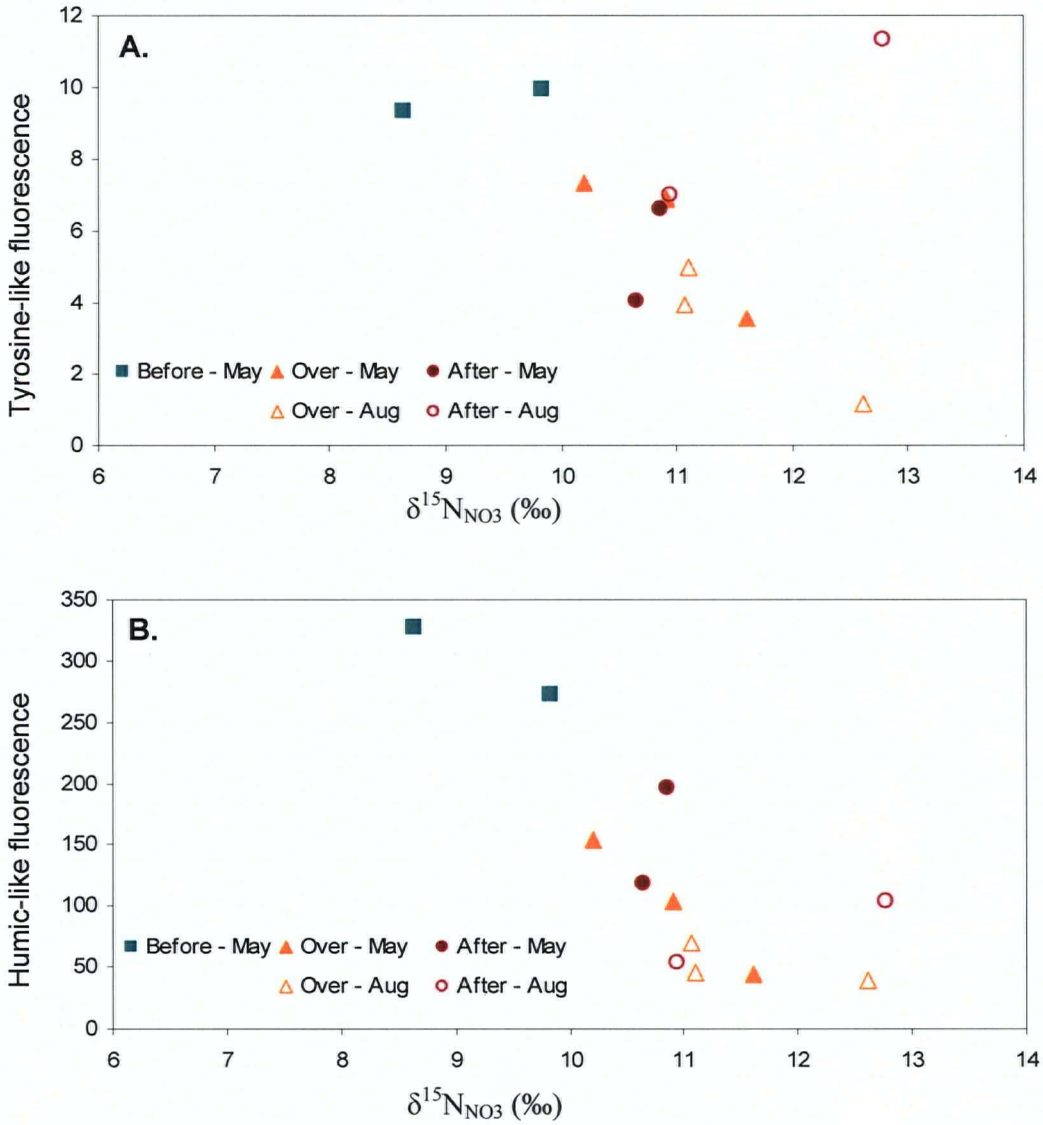

Figure 7.11. Tyrosine-like (A) and Humic-like (B) fluorescence vs. $\delta^{15}N_{NO3}$ for surface water samples.

7.10. Land Use

Significant correlations between land use and spectral measurements are shown in Table 7.9, Table 7.10, and Table 7.11. Positive correlations between tyrosine-like fluorescence and agriculture (for stream sites) suggest that agricultural activities were contributing protein-related DOM to the streams, but residential land use (associated with septic systems) were not a consistent contributor. The strongest of these correlations was

for tyrosine-like fluorescence and livestock activity in the wet season. For the Salmon watershed, tyrosine-like fluorescence may be a good indicator for agricultural influence. Ross (2006) found positive correlations between humic-like fluorescence and the percent agricultural activity in the cumulative contributing area. In the wet season, bare surfaces within 100 m of the stream channel were positively correlated to the humic-like fluorescence and A254 (Table 7.10). Soil organic matter was likely being flushed from these bare surfaces into the stream; covering bare surfaces, planting vegetation, or having buffers along the stream banks might help reduce this impact. Ross (2006) found positive correlations between A280 and total upstream area under agriculture and found that forested and mixed sites had lower A440 than agricultural sites. Land use within the 500 m buffers around wells showed a positive correlation between agriculture and humic-like fluorescence and A254. Note that the correlations for humic-like and humic-like 2 were very similar; correlations for A254 and A280 were identical.

Table 7.9. Significant correlations between spectral measurements for streams in the dry season and % land use / land cover (n=12).

Land use (LU) / Land cover (LC) category	Spearman rank correlation	Stream buffer (50 m, 100 m) or contributing area (CA)
Tyrosine-like fluorescence (streams, dry season)		
LU: All agriculture	0.601*	100 m
LU: Agriculture (crops/arable land)	0.580*	100 m
LU: Residential	-0.825**	100 m
	-0.706*	CA
LC: Constructed cover	-0.608*	CA

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at 0.01 level (2-tailed).

Table 7.10. Significant correlations between spectral measurements for streams in the wet season and % land use / land cover (n=12).

Land use (LU) / Land cover (LC) category	Spearman rank correlation	Stream buffer (50 m, 100 m) or contributing area (CA)
Humic-like fluorescence (streams, wet season)		
LU: Residential	-0.503	CA
LC: Bare surfaces	0.592*	100 m
Tyrosine-like fluorescence (streams, wet season)		
LU: Agriculture (livestock activities)	0.713**	100 m
LU: Residential	-0.594*	50 m
A254, Absorbance at 254 nm (streams, wet season)		
LC: Bare surfaces	0.623*	100 m

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at 0.01 level (2-tailed).

Table 7.11. Significant correlations between spectral measurements for wells and % land use / land cover (n=11).

Land use (LU) / Land cover (LC) category	Spearman rank correlation	Well buffer (100 m, 500 m)
Humic-like fluorescence (wells)		
LU: Agriculture (livestock activities)	0.536[1]	500 m
LU: Residential	-0.645*	500 m
A254, Absorbance at 254 nm (wells)		
LU: All agriculture	0.536[1]	500 m

* Correlation is significant at the 0.05 level (2-tailed).
[1] p-value = 0.089

7.11. Absorption and fluorescence tools for water quality monitoring

Both absorption and fluorescence spectroscopy have potential for qualitative assessment of water quality and for monitoring. One of the key limitations of both tools is overlapping or unresolved peaks that represent multiple compounds. This limitation may be a strength for some applications because it offers a more holistic measure than monitoring concentrations of individual compounds. Spectroscopy also has advantages in terms of sample processing time, the small sample size required, and the lack of reagent required. A "quick" (depending on the level of detail desired) scan can provide a wealth of information.

Both the absorption and fluorescence can provide distinction between groundwater and stream water. A220 can be used to measure nitrate concentrations; A220 has potential as a quantitative measure, although there can be interfering compounds that also absorb at 220 nm. Agricultural impact can be reflected in the A254 and by the presence of protein-like fluorescence (tyrosine-like in particular). It would be important, however, to calibrate these relationships for a particular study area or region because so many conditions can vary between sites (land use and vegetation, soil types). Tyrosine-like fluorescence also has potential for signaling contamination events (e.g. septic leakage, animal waste).

7.12. Further work / analysis of interest

The treatment of the data set collected for this thesis was not exhaustive. Further analysis may yield interesting results and further detail regarding source tracking and water quality assessment. Furthermore, with additional sampling and discharge measurements a more quantitative evaluation could be done. Absorbance data might be analyzed further by looking at the shape of the absorption curves and by taking derivatives of the curves (smaller wavelength intervals may be necessary) to try and resolve some of the overlapping peaks. A parallel factor analysis (PARAFAC) has been used for analysis of fluorescence EEMs in other studies (Holbrook et al., 2006; Stedmon & Markager, 2005; Stedmon et al., 2003) in order to break the scan down into more detailed regions that vary between samples. Simplifying the fluorescence scans to a synchronous scan (Galapate et al., 1998; Sierra et al., 2005) may also be an interesting avenue to explore as scans would

be faster and there is more potential for in-field measurement. Studies extending this preliminary work in the Salmon watershed might also look at the spectral characteristics of specific local sources (e.g. septic samples, agricultural wastes and manure, soil water) and include some analysis of storm events and runoff. One aspect of this work might include a protein analysis of different source materials and then tracking that fingerprint during a rainfall event as the material is mobilized and transported to a stream. Inclusion of bacterial analysis would also be advised in order to better consider the health risks associated with protein-like fluorescence.

7.13. Conclusions

(1) Spectral measurements supported the trends of groundwater – surface water interaction shown by other measures. Groundwater had much lower fluorescence (humic-like) and A254/A280 than the surface water samples. Groundwater input to the stream as it cuts through the aquifer was manifested by a drop in fluorescence intensities and A254. Increases in protein-like fluorescence in some wells suggested that stream or surface water was influencing some wells in the winter months.

(2) A254 and A280 were closely related to humic-like fluorescence. Protein-like fluorescence, particularly tyrosine-like fluorescence, was more independent of the other measures. A220 had a strong positive correlation with nitrate concentration. DOC/TOC had strong positive correlations with humic-like fluorescence and A254. Correlations with other dissolved elements (e.g. Ca, Si) reflected groundwater concentrations and the negative relationship between groundwater influence and intensity of absorption / fluorescence.

(3) Absorption and fluorescence spectroscopy offer a different means of looking at the dissolved organic matter in raw water samples and thereby assessing the water quality in this respect. Significant positive correlations between agricultural land use and fluorescence intensity suggested that agricultural activities were impacting water quality in the Salmon River watershed throughout the year.

(4) Increases in fluorescence intensity and in particular, protein-like fluorescence may be a good indicator of specific pollution events. For example, increases in tyrosine-like fluorescence may occur due to mobilization of diffuse agricultural sources or septic leachate during a precipitation event. Some point-source pollution occurrences might also be identified by this means.

8. INTEGRATED DISCUSSION AND CONCLUSIONS

The goal of this chapter is to summarize and integrate the results with respect to groundwater – surface water interactions, and relationships between pollutant sources and land use. Some comments regarding how the different results compliment and support each other are made. Finally, some recommendations and opportunities for future studies are also made.

8.1. Water quality

In general, stream water met the Canadian and BC guidelines; nitrate concentrations were quite high at some sites, but did not exceed the 10mg/L NO_3-N guideline. Five wells that were sampled exceeded the Canadian and B.C. drinking water guideline for nitrate-N on at least one occasion. Other water chemistry measures were within the guidelines for drinking water quality. The microbiological water quality will not be discussed due to insufficient data.

8.2. Water "fingerprints"

Groundwater samples from the Hopington A and B aquifers had very similar chemistry, but the Hopington C wells were quite different. In general, the groundwater samples from the Hopington C aquifer had higher phosphate, lower nitrate, lower chloride, and lower Mg, Na, Ca, and Sr concentrations when compared to Hopington A and B. Although values overlapped, Hopington B wells overall had higher $\delta^{15}N_{NO3}$ values than Hopington A and C. All groundwater samples were also characterized by low humic-like(2) and tryptophan-like fluorescence and low A254 / A280; stream water samples had higher fluorescence and absorption.

Compared to the Hopington A and B groundwater samples, the stream water had lower nitrate, Ca, Si and Mg; dissolved Fe, K, and Na were generally higher in the surface water than groundwater. Stream N isotope values for nitrate were more similar to

Hopington B values and overall were higher than the groundwater values. These differences between stream and groundwater enable the groundwater influence to be seen.

8.3. Groundwater – surface water interactions

Groundwater contribution to the Salmon River (and tributaries) can be seen by the change in water chemistry and character as the stream cuts through the Hopington A and B aquifers. Results from this study confirmed the spatial and seasonal trends of nitrate that were previously recorded. High nitrate groundwater from the Hopington A and B aquifers was being discharged to the streams and this is particularly pronounced in the dry season when groundwater inputs are making up a greater proportion of the stream flow. Stream sites "before" the aquifer (not groundwater influenced) had significantly lower nitrate concentrations than the over or after sites. This study was able to confirm groundwater influence using other measures besides nitrate (see Figure 8.1 for an overview of this system).

Groundwater discharge could be observed by increased Ca, Si, and Mg concentrations in the stream water. Groundwater inputs "diluted" the stream Fe and Na, decreasing the concentrations over the aquifer area. There were no significant differences between the stream water chloride, orthophosphate or ammonia levels for different stream sites relative to the Hopington A and B aquifers. Stream locations with expected groundwater influence also had lower water temperatures than the headwater and downstream sites. In this thesis, fluorescence spectroscopy was explored as a new measure for looking at groundwater influence. Given the low fluorescence and absorption of groundwater samples, groundwater inputs to the stream caused a decrease in the intensity of stream water fluorescence. Humic-like (2) fluorescence, tryptophan-like fluorescence, A254 and A280 all showed spatial and seasonal trends opposite to nitrate concentrations, with "before" aquifer sites having significantly higher values for these spectral measures. Tyrosine-like fluorescence did not show the groundwater input as strongly. Nitrate isotope results offered a further confirmation that groundwater was entering the stream, with wells and stream sites having similar values, which would suggest a similar nitrate source or combination of sources.

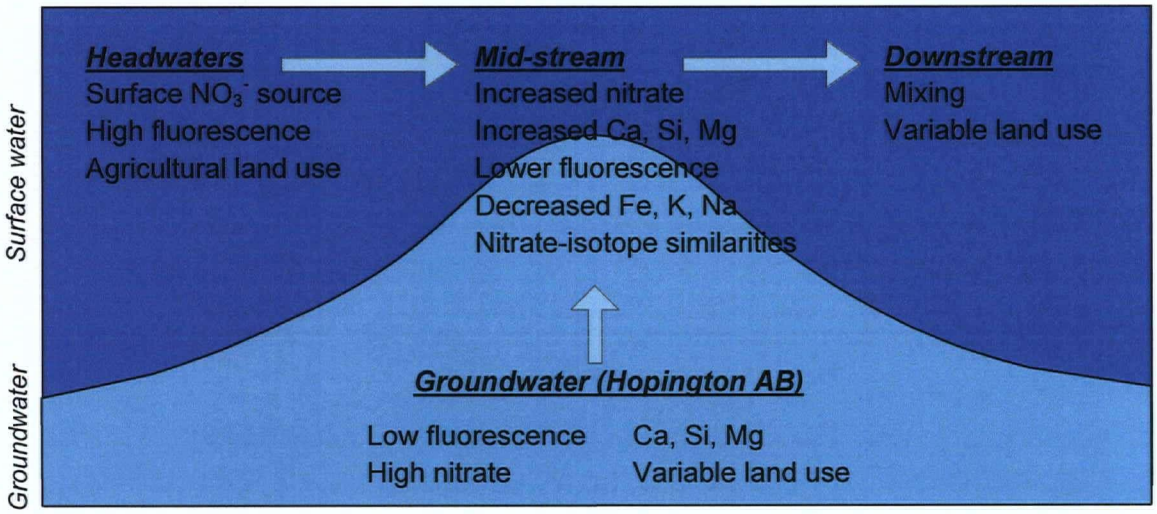

Figure 8.1. Schematic diagram representing the groundwater influence in the mid-section of the Salmon River watershed. The two colours represent a proportional influence from groundwater (light turquoise, bottom) and surface water (sky blue, top).

8.4. Nitrate sources and land use

The "before" aquifer sites (not groundwater influenced) had significantly higher nitrates in the wet season suggesting a surface nitrate source; nitrate concentrations "after" the aquifer were higher in the dry season because of groundwater inputs. As was mentioned in the previous section, nitrate-isotope results showed that the stream nitrate and groundwater nitrate were from the same source. Nitrate-isotope values indicated that manure and septic systems were the primary nitrate sources, supporting the assertions from previous work (Wernick et al., 1998); soil nitrogen may also be an important nitrate source for some sites, and for one well site inorganic fertilizers are of greater importance.

There were no significant correlations between land use and nitrate concentrations, but given that stream water nitrate was a combination of groundwater inputs and surface sources proximate land use would not be expected to have much explanatory power. Other parameters, however, were positively correlated with land use.

Overall, stream water phosphate-P had some positive correlations with agricultural activities. Agricultural land use was also positively correlated with fluorescence intensity, in particular tyrosine-like fluorescence; the strongest of these correlations was with livestock activity during the wet season. These correlations strongly suggest that

agricultural land use is impacting stream water quality in the Salmon River watershed throughout the year and particularly in the wet season. Residential land use does not seem to be impacting the water quality to any extent.

Land use relationships with well water quality were not as clear. It is worth noting, however, that the Hopington B aquifer had slightly higher $\delta^{15}N_{NO3}$ values and also had a higher percentage of land use under agriculture (compared to Hopington A, which had more than twice the residential land use (%)), perhaps indicating a more significant contribution from agricultural nitrate sources.

8.5. Comments on tool set

Measurements of nitrate and dissolved elements provided a basic framework for understanding spatial and seasonal trends in the surface water and for observing groundwater – surface water interactions. The dissolved elements were a good confirmation of nutrient trends. Addition of the nitrate isotope measurements provided more conclusive evidence that the nitrate in the groundwater was the same as that impacting stream water. Isotope measurements were also able to clarify that inorganic fertilizers were not the primary cause of elevated nitrate levels. Independently, $\delta^{15}N_{NO3}$ was not able to distinguish between septic and manure sources, but the positive correlations between agricultural land use and other measures suggested that agriculture was a key nitrate source. It was important to interpret the nitrate-isotope data in the context of other measurements and the dual isotope approach was helpful to confirm that no (or limited) denitrification was taking place in the system.

Fluorescence measurements supported the results from other tools. These spectral measurements proved useful in discerning groundwater influence on the stream and also have potential to be a good measure of general water quality. Protein-like fluorescence may be able to act as an indicator for pollution events and this potential could be further investigated and measurements calibrated for this particular watershed.

8.6. Recommendations and opportunities

In future studies some additional analyses might be helpful to clarify contaminant sources and better characterize the system. Microbiological measurements would be appropriate to see if fecal contamination is occurring. Analysis for selective pharmaceuticals or other anthropogenic compounds (e.g. caffeine) might help to better distinguish between the septic and agricultural impacts. Taking a closer look at historical land use may also be helpful for understanding potential groundwater nitrate sources and expansion of nitrate plumes.

Further exploration of the fluorescence data set may yield interesting insights. The understanding and application of water sample fluorescence scans continues to develop. If the spectral characteristics of the watershed were further characterized, fluorescence may be a very useful tool for managing and monitoring local water quality and risks.

Future sampling schemes should explore storm event dynamics and directly sample potential contaminant sources (e.g. storm runoff, septic tank material, local manure and fertilizer, and soil water). Having "sources" that are more clearly defined, combined with discharge measurements at the sampling sites would enable a more quantitative analysis. It might also be appropriate to take a more complex approach to the land use analysis and relationships, perhaps using distance-weighted buffers or altering the well buffers to reflect a cone of influence.

Agricultural land use is definitely impacting water quality in the Salmon River watershed. Given the vulnerability of the Hopington A and B aquifers, nutrient applications to the land surface should be carefully managed so as to prevent further increases in nitrate concentration, protecting both human and ecosystem health.

REFERENCES

Allan, J. D., Erickson, D. L., & Fay, J. (1997). The influence of catchment land use on stream integrity across multiple spatial scales. *Freshwater Biology, 37*(1), 149-161.

Aravena, R., Evans, M. L., & Cherry, J. A. (1993). Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. *Ground Water, 31*(2), 180-186.

Baker, A. (2001). Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. *Environmental Science & Technology, 35*(5), 948-953.

Baker, A. (2002). Fluorescence properties of some farm wastes: Implications for water quality monitoring. *Water Research, 36*(1), 189-195.

Baker, A. (2002). Spectrophotometric discrimination of river dissolved organic matter. *Hydrological Processes, 16*(16), 3203-3213.

Baker, A. (2005). Fluorescence tracing of diffuse landfill leachate contamination in rivers. *Water Air and Soil Pollution, 163*(1-4), 229-244.

Baker, A. (2005). Thermal fluorescence quenching properties of dissolved organic matter. *Water Research, 39*, 4405-4412.

Baker, A., & Curry, M. (2004). Fluorescence of leachates from three contrasting landfills. *Water Research, 38*(10), 2605-2613.

Baker, A., & Inverarity, R. (2004). Protein-like fluorescence intensity as a possible tool for determining river water quality. *Hydrological Processes, 18*(15), 2927-2945.

Baker, A., Inverarity, R., Charlton, M., & Richmond, S. (2003). Detecting river pollution using fluorescence spectrophotometry: Case studies from the Ouseburn, NE England. *Environmental Pollution, 124*(1), 57-70.

Baker, A., Inverarity, R., & Ward, D. (2005). Catchment-scale fluorescence water quality determination. *Water Science and Technology, 52*(9), 199-207.

Baker, A., & Spencer, R. G. M. (2004). Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy. *Science Of The Total Environment, 333*(1-3), 217-232.

Baker, A., Ward, D., Lieten, S. H., Periera, R., Simpson, E. C., & Slater, M. (2004). Measurement of protein-like fluorescence in river and waste water using a handheld spectrophotometer. *Water Research, 38*(12), 2934-2938.

BC Ministry of Water Land and Air Protection. (1999). *Ambient water quality guidelines for zinc, overview report.*

Beale, R. L. (1976). *Analysis of the effects of land use and soils on the water quality of the Salmon River watershed, Langley.* University of British Columbia, Vancouver.

Berardinucci, J., & Ronneseth, K. (2002). *Guide to using the BC aquifer classification maps for the protection and management of groundwater*: BC Ministry of Water, Land and Air Protection.

Berka, C., Schreier, H., & Hall, K. (2001). Linking water quality with agricultural intensification in a rural watershed. *Water Air and Soil Pollution, 127*(1-4), 389-401.

British Columbia Ministry of Environment. Aquifer classification database.

Burns, D. (2005). What do hydrologists mean when they use the term flushing? *Hydrological Processes, 19*(6), 1325-1327.

Butcher, G. A. (1988). *Water quality criteria for aluminum*: BC Ministry of Water Land and Air Protection.

Cantor, K. P., Shy, C. M., & Chilvers, C. (1996). Water pollution. In D. Schottenfeld & J. F. Fraumeni (Eds.), *Cancer epidemiology and prevention* (2 ed.). New York: Oxford University Press.

Carmichael, V., Wei, M., & Ringham, L. (1995). *Fraser Valley groundwater monitoring program final report*: Ministry of Environment Lands and Parks, and Ministry of Agriculture, Fisheries and Food.

Chambers, P. A., Guy, M., Roberts, E. S., Charlton, M. N., Kent, R., Gagnon, C., et al. (2001). Nutrients and their impact on the Canadian environment (pp. 241): Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada, and Natural Resources Canada.

Chang, C. C. Y., Kendall, C., Silva, S. R., Battaglin, W. A., & Campbell, D. H. (2002). Nitrate stable isotopes: Tools for determining nitrate sources among different land uses in the Mississippi River basin. *Canadian Journal of Fisheries and Aquatic Sciences, 59*(12), 1874-1885.

Clark, I., & Fritz, P. (1997). *Environmental isotopes in hydrogeology.* New York: Lewis Publishers.

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Marine Chemistry, 51*, 325-346.

Comly, H. H. (1945). Cyanosis in infants caused by nitrates in well water. *The Journal of the American Medical Association, 129*(2), 112-116.

Cook, K. E. (1994). *An evaluation of water quality and land use in the Salmon River watershed, Langley, BC, using GIS techniques.* University of British Columbia, Vancouver.

Coplen, T. B., Krouse, H. R., & Bohlke, J. K. (1992). Reporting of nitrogen-isotope abundances. *Pure & Applied Chemistry, 64*(6), 907-908.

Cuffney, T. F., Meador, M. R., Porter, S. D., & Gurtz, M. E. (2000). Responses of physical, chemical, and biological indicators of water quality to a gradient of agricultural land use in the Yakima River basin, Washington. *Environmental Monitoring and Assessment, 64*(1), 259-270.

Eaton, A., Clesceri, L., & Greenberg, A. (1995). *Standard methods for the examination of water and wastewater* (19th ed.). USA: American Public Health Association.

Environment Canada. (2003). Canadian water quality guidelines for the protection of aquatic life: Nitrate ion. Ecosystem health: Science-based solutions report no. 1-6. (pp. 115): National Guidelines and Standards Office, Water Policy and Coordination Directorate, Environment Canada.

FPT Committee on Drinking Water. (2006). Guidelines for Canadian drinking water quality, summary table: Health Canada.

FPT Committee on Drinking Water. (2007). Guidelines for Canadian drinking water quality, summary table: Health Canada.

Galapate, R. P., Baes, A. U., Ito, K., Mukai, T., Shoto, E., & Okada, M. (1998). Detection of domestic wastes in Kurose River using synchronous fluorescence spectroscopy. *Water Resources, 32*(7), 2232-2239.

Gartner Lee Limited. (2000). *Hopington aquifer water balance study; prepared for the Township of Langley* (No. GLL 99-718).

Godfrey, E., Woessner, W. W., & Benotti, M. J. (2007). Pharmaceuticals in on-site sewage effluent and ground water, western Montana. *Ground Water, 45*(3), 263-271.

Golder Associates. (2004). *Final report on comprehensive groundwater modeling assignment, Township of Langley* (No. 022-1826/5000): Golder Associates Ltd.

Golder Associates. (2005). *Report on groundwater vulnerability mapping, Township of Langley* (No. 04-1412-224): Golder Associates, Ltd.

Heaton, T. H. E. (1986). Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. *Chemical Geology (Isotope Geoscience Section), 59*, 87-102.

Holbrook, R. D., Yen, J. H., & Grizzard, T. J. (2006). Characterizing natural organic material from the Occoquan watershed (Northern Virginia, US) using fluorescence spectroscopy and parafac. *Science of the Total Environment, 361*(1-3), 249-266.

Houlahan, J. E., & Findlay, C. S. (2004). Estimating the 'critical' distance at which adjacent land-use degrades wetland water and sediment quality. *Landscape Ecology, 19*(6), 677-690.

Hunsaker, C. T., & Levine, D. A. (1995). Hierarchical approaches to the study of water-quality in rivers. *Bioscience, 45*(3), 193-203.

Hur, J., Williams, M. A., & Schlautman, M. A. (2006). Evaluating spectroscopic and chromatographic techniques to resolve dissolved organic matter via end member mixing analysis. *Chemosphere, 63*(3), 387-402.

Jin, Z. F., Chen, Y. X., Wang, F., & Ogura, N. (2004). Detection of nitrate sources in urban groundwater by isotopic and chemical indicators, Hangzhou City, China. *Environmental Geology, 45*(7), 1017-1024.

Johnson, L. B., & Gage, S. H. (1997). Landscape approaches to the analysis of aquatic ecosystems. *Freshwater Biology, 37*(1), 113-132.

Johnson, L. B., Richards, C., Host, G. E., & Arthur, J. W. (1997). Landscape influences on water chemistry in midwestern stream ecosystems. *Freshwater Biology, 37*(1), 193-&.

Katsuyama, M., & Ohte, N. (2002). Determining the sources of stormflow from the fluorescence properties of dissolved organic carbon in a forested headwater catchment. *Journal of Hydrology, 268*(1-4), 192-202.

Kellman, L. M., & Hillaire-Marcel, C. (2003). Evaluation of nitrogen isotopes as indicators of nitrate contamination sources in an agricultural watershed. *Agriculture Ecosystems & Environment, 95*(1), 87-102.

Kendall, C. (1998). Tracing nitrogen sources and cycling in catchments. In C. Kendall & J. J. McDonnell (Eds.), *Isotope tracers in catchment hydrology* (1 ed., pp. 519-576). Amsterdam: Elsevier Science.

King, R. S., Baker, M. E., Whigham, D. F., Weller, D. E., Jordan, T. E., Kazyak, P. F., et al. (2005). Spatial considerations for linking watershed land cover to ecological indicators in streams. *Ecological Applications, 15*(1), 137-153.

Leenheer, J. A., & Croue, J. P. (2003). Characterizing aquatic dissolved organic matter. *Environmental Science & Technology, 37*(1), 18a-26a.

Li, K., & Schreier, H. (2004). *Evaluating long-term groundwater monitoring data in the Lower Fraser Valley* (for the BC Ministry of Water Land and Air Protection): Institute for Resources and Environment, UBC.

Manassaram, D. M., Backer, L. C., & Moll, D. M. (2006). A review of nitrates in drinking water: Maternal exposure and adverse reproductive and developmental outcomes. *Environmental Health Perspectives, 114*(3), 320-327.

McFarland, A. M. S., & Hauck, L. M. (1999). Relating agricultural land uses to in-stream stormwater quality. *Journal of Environmental Quality, 28*(3), 836-844.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., & Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography, 46*(1), 38-48.

Mehnert, E., Hwang, H. H., Johnson, T. M., Sanford, R. A., Beaumont, W. C., & Holm, T. R. (2007). Denitrification in the shallow ground water of a tile-drained, agricultural watershed. *Journal of Environmental Quality, 36*(1), 80-90.

Mengis, M., Walther, U., Bernasconi, S. M., & Wehrli, B. (2001). Limitations of using d18O for the source identification of nitrate in agricultural soils. *Environmental Science & Technology, 35*(9), 1840-1844.

Minton, G. R. (2005). *Stormwater treatment: Biological, chemical, and engineering principles* (2nd ed.). Seattle: Sheridan Books.

Mitchell, R. J., Babcock, R. S., Gelinas, S., Nanus, L., & Stasney, D. E. (2003). Nitrate distributions and source identification in the Abbotsford-Sumas aquifer, northwestern Washington State. *Journal of Environmental Quality, 32*(3), 789-800.

Mobed, J. J., Hemmingsen, S. L., Autry, J. L., & McGown, L. B. (1996). Fluorescence characterization of IHSS humic substances: Total luminescence spectra with absorbance correction. *Environmental Science & Technology, 30*(10), 3061-3065.

Moss, S. A., & Nagpal, N. K. (2003). *Ambient water quality guidelines for boron: Overview [electronic resource]*: BC Ministry of Water Land and Air Protection.

Nagpal, N. K. (2001). *Ambient water quality guidelines for manganese: Overview report*: BC Ministry of Water Land and Air Protection.

Nagpal, N. K., Levy, D. A., & MacDonald, D. D. (2003). *Ambient water quality guidelines for chloride*: BC Ministry of Water Land and Air Protection.

Nomura, A. (1996). Stomach cancer. In D. Schottenfeld & J. F. Fraumeni (Eds.), *Cancer epidemiology and prevention* (2nd ed.). New York: Oxford University Press.

Nordin, R. N. (1985). *Water quality criteria for nutrients and algae, overview report*: BC Ministry of Water Land and Air Protection.

Nordin, R. N., & Pommen, L. W. (1986). *Water quality criteria for nitrogen (nitrate, nitrite, and ammonia)*:BC Ministry of Water Land and Air Protection.

Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environmental Science & Technology, 36*(4), 742-746.

Osborne, L. L., & Wiley, M. J. (1988). Empirical relationships between land-use cover and stream water-quality in an agricultural watershed. *Journal of Environmental Management, 26*(1), 9-27.

Panno, S. V., Hackley, K. C., Hwang, H. H., & Kelly, W. R. (2001). Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chemical Geology, 179*(1-4), 113-128.

Panno, S. V., Hackley, K. C., Kelly, W. R., & Hwang, H. H. (2006). Isotopic evidence of nitrate sources and denitrification in the Mississippi River, Illinois. *Journal Of Environmental Quality, 35*(2), 495-504.

Poor, C. J., & McDonnell, J. J. (2007). The effects of land use on stream nitrate dynamics. *Journal of Hydrology, 332*(1-2), 54-68.

Reynolds, D. M. (2003). Rapid and direct determination of tryptophan in water using synchronous fluorescence spectroscopy. *Water Research, 37*(13), 3055-3060.

Ritter, L., Solomon, K., Sibley, P., Hall, K., Keen, P., Mattu, G., et al. (2002). Sources, pathways, and relative risks of contaminants in surface water and groundwater: A perspective prepared for the Walkerton inquiry. *Journal of Toxicology and Environmental Health, Part A, 65*(1), 1-142.

Ross, J. (2006). *Influence of climate and land use on nutrient and bacterial dynamics in surface waters of the Lower Fraser Valley, British Columbia.* University of British Columbia, Vancouver.

Schindler, D. W., Dillon, P. J., & Schreier, H. (2006). A review of anthropogenic sources of nitrogen and their effects on Canadian aquatic ecosystems. *Biogeochemistry, 79*(1-2), 25-44.

Schoenholtz, S. H. (2004). Impacts of forest managment on water quality. In J. Burley, J. Evans & J. Youngquist (Eds.), *Encyclopedia of forest sciences* (pp. 377-388). Oxford, U.K.: Elsevier.

Seiler, R. L. (2005). Combined use of N-15 and O-18 of nitrate and B-11 to evaluate nitrate contamination in groundwater. *Applied Geochemistry, 20*(9), 1626-1636.

Sierra, M. M. D., Giovanela, M., Parlanti, E., & Soriano-Sierra, E. J. (2005). Fluorescence fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques. *Chemosphere, 58*(6), 715-733.

Silva, S. R., Ging, P. B., Lee, R. W., Ebbert, J. C., Tesoriero, A. J., & Inkpen, E. L. (2002). Forensic applications of nitrogen and oxygen isotopes in tracing nitrate sources in urban environments. *Environmental Forensics, 3*(2), 125-130.

Silva, S. R., Kendall, C., Wilkison, D. H., Ziegler, A. C., Chang, C. C. Y., & Avanzino, R. J. (2000). A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. *Journal of Hydrology, 228*(1-2), 22-36.

Singleton, H. J. (1987). Water quality criteria for copper: Technical appendix. In British Columbia Ministry of Environment and Parks (Ed.).

Sliva, L., & Williams, D. D. (2001). Buffer zone versus whole catchment approaches to studying land use impact on river water quality. *Water Research, 35*(14), 3462-3472.

Smith, I. M. (2004). *Cumulative effects of agricultural intensification on nutrient and trace metal pollution in the Sumas River watershed, Abbotsford, BC*, University of British Columbia.

Spencer, R. G. M., Baker, A., Ahad, J. M. E., Cowie, G. L., Ganeshram, R., Upstill-Goddard, R. C., et al. (2007). Discriminatory classification of natural and anthropogenic waters in two UK estuaries. *Science of the Total Environment, 373*(1), 305-323.

Stedmon, C. A., & Markager, S. (2005). Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using parafac analysis. *Limnology and Oceanography, 50*(2), 686-697.

Stedmon, C. A., & Markager, S. (2005). Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis. *Limnology and Oceanography, 50*(5), 1415-1426.

Stedmon, C. A., Markager, S., & Bro, R. (2003). Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry, 82*(3-4), 239-254.

Stjepovic, M. (2007). Environmental coordinator II, Township of Langley.

Townsend-Small, A., McCarthy, M. J., Brandes, J. A., Yang, L. Y., Zhang, L., & Gardner, W. S. (2007). Stable isotopic composition of nitrate in Lake Taihu, China, and major inflow rivers. *Hydrobiologia, 581*, 135-140.

Township of Langley.Water resources and environment: Stormwater, sewers and water supply. Retrieved 8 May, 2007, from http://www.tol.bc.ca

Tsihrintzis, V. A., Hamid, R., & Fuentes, H. R. (1996). Use of geographic information systems (GIS) in water resources: A review. *Water Resources Management, 10*, 251-277.

Verstraeten, I. M., Fetterman, G. S., Meyer, M. T., Bullen, T., & DSebree, S. K. (2005). Use of tracers and isotopes to evaluate vulnerability of water in domestic wells to septic waste. *Ground Water Monitoring & Remediation, 25*(2), 107-117.

Vitoria, L., Otero, N., Soler, A., & Canals, A. (2004). Fertilizer characterization: Isotopic data (N, S, O, C, and Sr). *Environmental Science & Technology, 38*(12), 3254-3262.

Wang, X. (2001). Integrating water-quality management and land-use planning in a watershed context. *Journal Of Environmental Management, 61*(1), 25-36.

Wassenaar, L. I. (1995). Evaluation of the origin and fate of nitrate in the Abbotsford aquifer using the isotopes of N-15 and O-18 in NO3-. *Applied Geochemistry, 10*(4), 391-405.

Wassenaar, L. I., Hendry, M. J., & Harrington, N. (2006). Decadal geochemical and isotopic trends for nitrate in a transboundary aquifer and implications for agricultural beneficial management practices. *Environmental Science & Technology, 40*(15), 4626-4632.

Watts, R. D. (1992). *A GIS evaluation of land use dynamics and fish habitat in the Salmon River watershed - Langley, BC*, University of British Columbia, Vancouver.

Wernick, B. G. (1996). *Land use and water quality dynamics on the urban-rural fringe: A GIS evaluation of the Salmon River watershed, Langley, BC.* University of British Columbia, Vancouver.

Wernick, B. G., Cook, K. E., & Schreier, H. (1998). Land use and streamwater nitrate-N dynamics in an urban-rural fringe watershed. *Journal of the American Water Resources Association, 34*(3), 639-650.

Westerhoff, P., Chen, W., & Esparza, M. (2001). Fluorescence analysis of a standard fulvic acid and tertiary treated wastewater. *Journal of Environmental Quality, 30*(6), 2037-2046.

World Health Organization. (2006). Chemical fact sheets. In *Guidelines for drinking-water quality: First addendum to third edition.* Geneva: WHO Press.

Yan, Y., Li, H., & Myrick, M. L. (2000). Fluorescence fingerprint of waters: Excitation-emission matrix spectroscopy as a tracking tool. *Applied Spectroscopy, 54*(10), 1539-1542.

APPENDICES

Appendix A: Record of field sampling activities

Table A1. Details of sampling dates, sites, and replicates

Site	06-Sep-05			22-Feb-06			28-Mar-06			30-May-06							26-Jul-06		21-Aug-06							17-Oct-06	
	nut	spec	18O	nut	spec	18O	nut	spec	18O	nut	spec	18O/D	DOC	NO3-iso	ICP		nut	spec	nut	spec	18O/D	DOC	NO3-iso	ICP		nut	spec
C1	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓✓✓	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
C2	✓		✓	✓	✓		✓	✓		✓	✓		✓		✓		✓	✓	✓	✓		✓		✓		✓	✓
C3				✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
D1	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
S1	✓			✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
S2	✓		✓				✓	✓		✓	✓	✓	✓		✓		✓	✓	✓	✓		✓		✓		✓	✓
S3	✓			✓	✓		✓	✓		✓	✓		✓		✓		✓	✓	✓	✓		✓		✓		✓✓✓	✓✓✓
S4	✓		✓	✓	✓	✓	✓✓✓	✓✓✓		✓✓✓	✓✓✓	✓✓✓	✓✓✓		✓✓✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
S5	✓						✓	✓		✓	✓	✓	✓		✓		✓	✓	✓✓✓	✓✓✓	✓	✓✓✓		✓✓✓		✓	✓
S6	✓		✓	✓	✓		✓	✓		✓	✓	✓	✓		✓		✓	✓	✓	✓	✓	✓		✓		✓	✓
S7	✓			✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓✓✓	✓✓✓	✓	✓	✓✓	✓		✓		✓	✓
T1	✓			✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
A1				✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓			
A2				✓	✓	✓													✓✓✓	✓✓✓	✓	✓✓✓		✓✓✓			
A3							✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓			
A4				✓✓	✓✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓✓✓	✓✓✓	✓	✓	✓	✓	✓	✓			
B1				✓	✓	✓	✓✓✓	✓✓✓		✓	✓	✓	✓		✓		✓	✓	✓	✓	✓	✓		✓			
B2				✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓			
B3				✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓			
B4	✓	✓	✓				✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓✓✓	✓					
X1				✓	✓	✓	✓	✓		✓✓✓	✓✓✓	✓	✓✓✓	✓	✓✓✓		✓	✓	✓	✓	✓	✓		✓			
X2				✓	✓	✓													✓	✓	✓	✓		✓			
X3																			✓	✓	✓	✓		✓			

* replicates indicated by multiple checkmarks for the same item.

Appendix B: Record of thermistor activities

Table B1. Summary of thermistor activities (deployment, collection, and problems).

Date	Sal 1	Sal 4	Sal 6	Cough 1	Dav 1
22-Feb-06	UD	Unable to find logger.	UD	Replaced logger*	Unable to find logger
28-Mar-06	UD		UD	UD	Found logger buried in sediment.
30-May-06	UD	Unable to find logger; Deployed a new one	UD	UD	
26-Jul-06	UD	UD	UD Relocated**	UD	
21-Aug-06	Relocated**				
17-Oct-06			All thermistors collected		

UD = Uploaded data.

* Logger would not read-out; the data were recovered.

** Due to low water levels, thermistors were not completely submerged and so were moved to a different area of the channel.

Appendix C: Lowest readable limits for ICP-AES

Table C1. Lowest readable limits for ICP-AES

Element	Lowest Readable Limits (ppm)
Al 167.019	0.05
As 188.980	0.2
B 249.678	0.05
Ba 493.408	0.01
Ca 317.933	0.1
Cd 226.502	0.025
Co 228.615	0.055
Cr 267.716	0.025
Cu 327.395	0.05
Fe 238.204	0.05
K 766.491	0.5
Mg 279.553	0.01
Mn 257.610	0.005
Mo 202.032	0.05
Na 589.592	0.25
Ni 231.604	0.1
P 213.618	0.2
Pb 220.353	0.2
Se 196.026	0.2
Si 288.158	0.15
Sr 407.771	0.002
Zn 213.857	0.01

Appendix D: Laboratory method for water stable isotopes

Stable isotope analytical techniques for measuring $\delta^{18}O$ and $\delta^{2}H$ in water*

PCIGR laboratory in the Department of Earth and Ocean Sciences, UBC
Instrument: Finnigan Delta XL Plus mass spectrometer in continuous flow mode.

Water samples are loaded into the autosampler tray in glass vials with a pierceable septum. The autosampler takes 1 microlitre and drops it into the furnace of the TC/EA (thermal combustion elemental analyser). The furnace runs at 1450°C, which pyrolyses the water. The component gases are carried in continuous flow mode in a helium stream to the mass spectrometer via a GC and Conflo III interface.

Both elements are analysed from the same aliquot, and the sample peaks are bracketed with H and CO reference gases of known isotopic composition. Five separate aliquots are analysed for each sample, and the mean is calculated. Isotopic fractionation is calculated from multiple analyses of UBC internal laboratory water standards that have been calibrated against international standards V-SLAP and V-SMOW.

The results are reported using the δ notation measured in ‰ relative to the V-SLAP and V-SMOW standards.

*Note that the above description is taken directly from documentation received from the PCIGR technician who ran the samples.

Appendix E: Stream temperature data

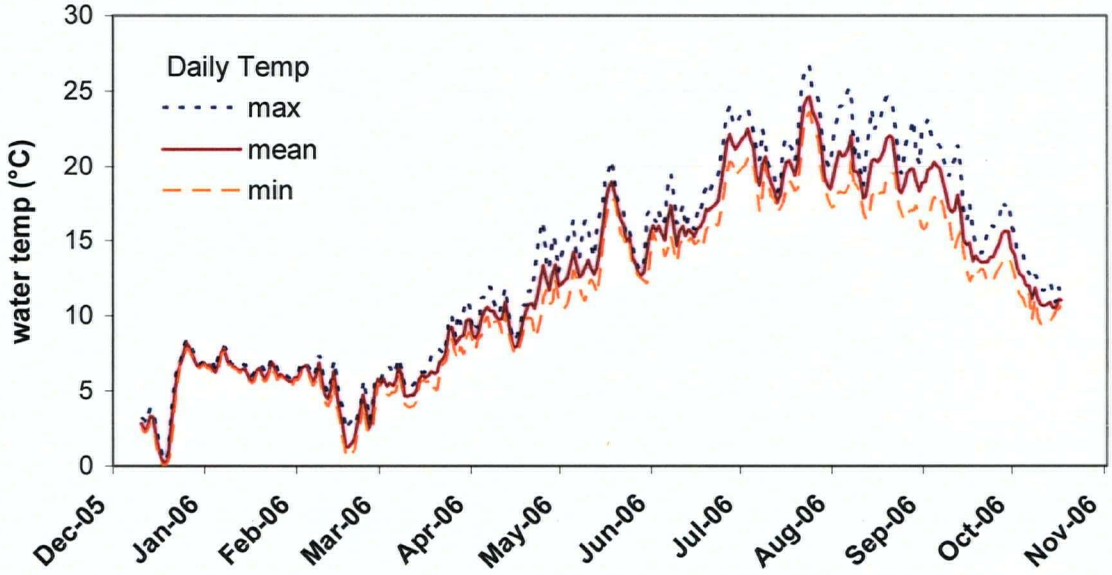

Figure E1. Daily water temperature for mouth of Salmon River (S1).

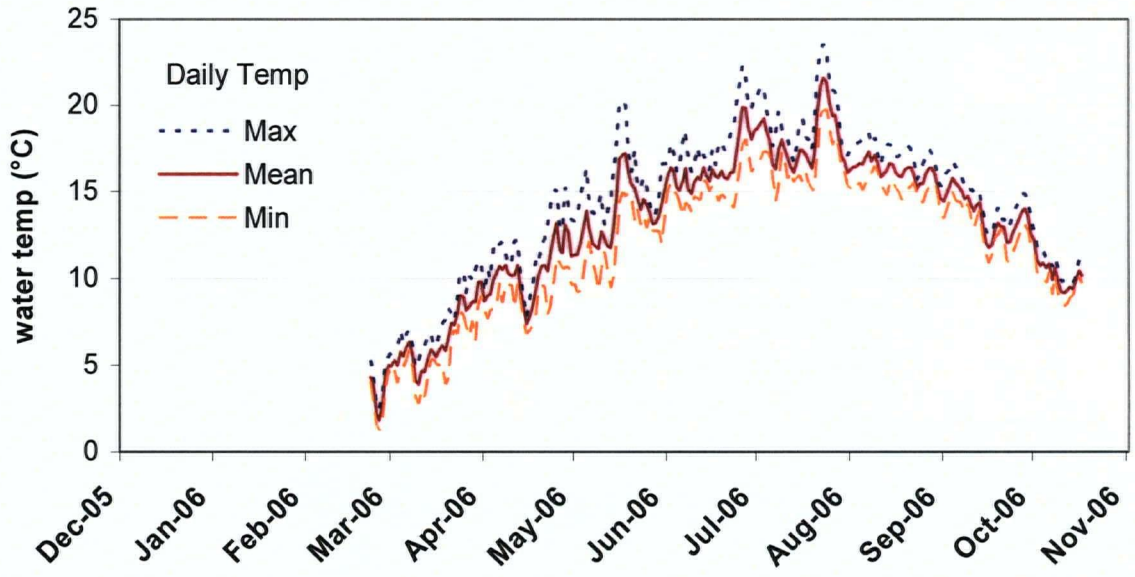

Figure E2. Daily water temperature for lower headwaters of Salmon River (S7).

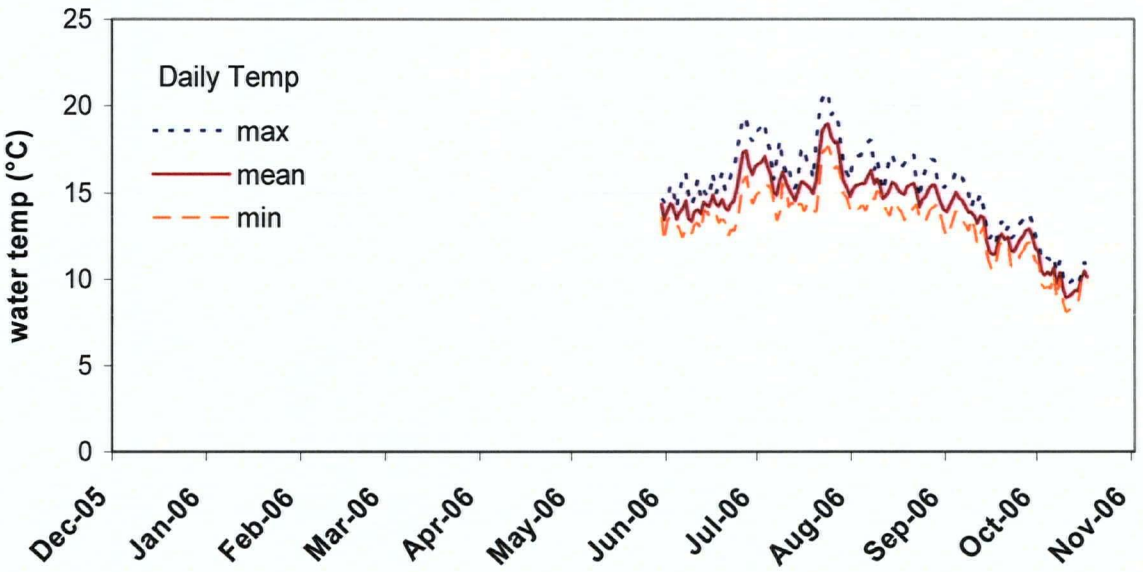

Figure E3. Daily water temperature for Salmon River at Williams Park (S4).

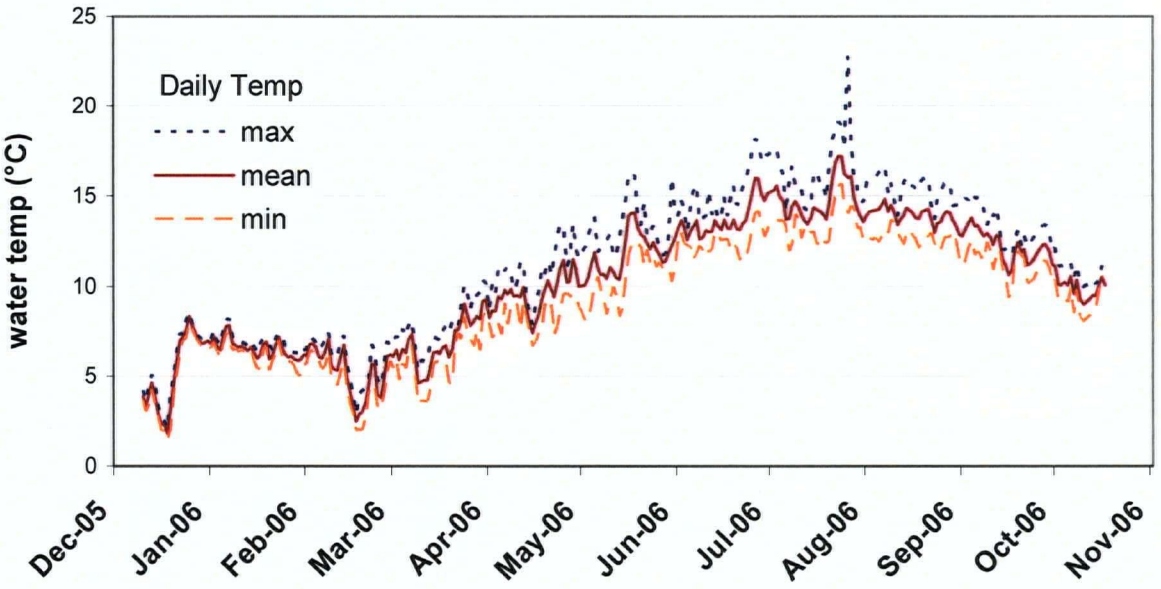

Figure E4. Daily water temperature for Coghlan Creek at Williams Park (C1).

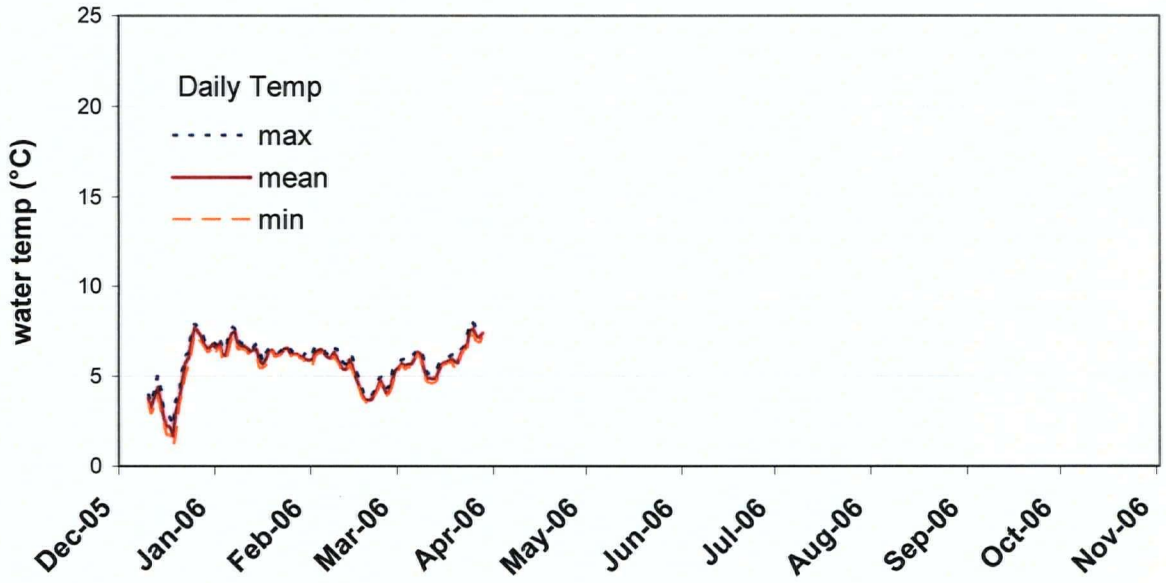

Figure E5. Daily water temperature for Davidson Creek (D1).

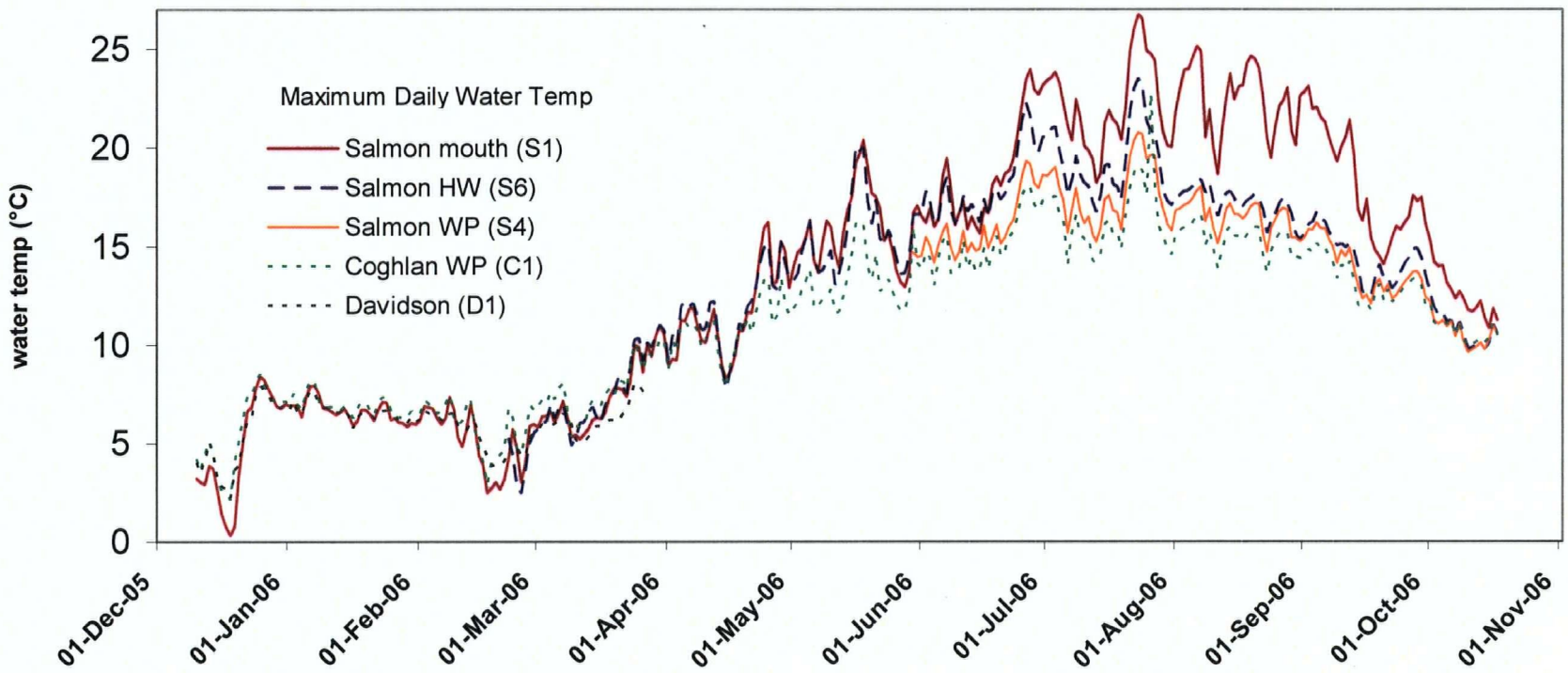

Figure E6. Daily maximum water temperature for selected sites in Salmon River Watershed

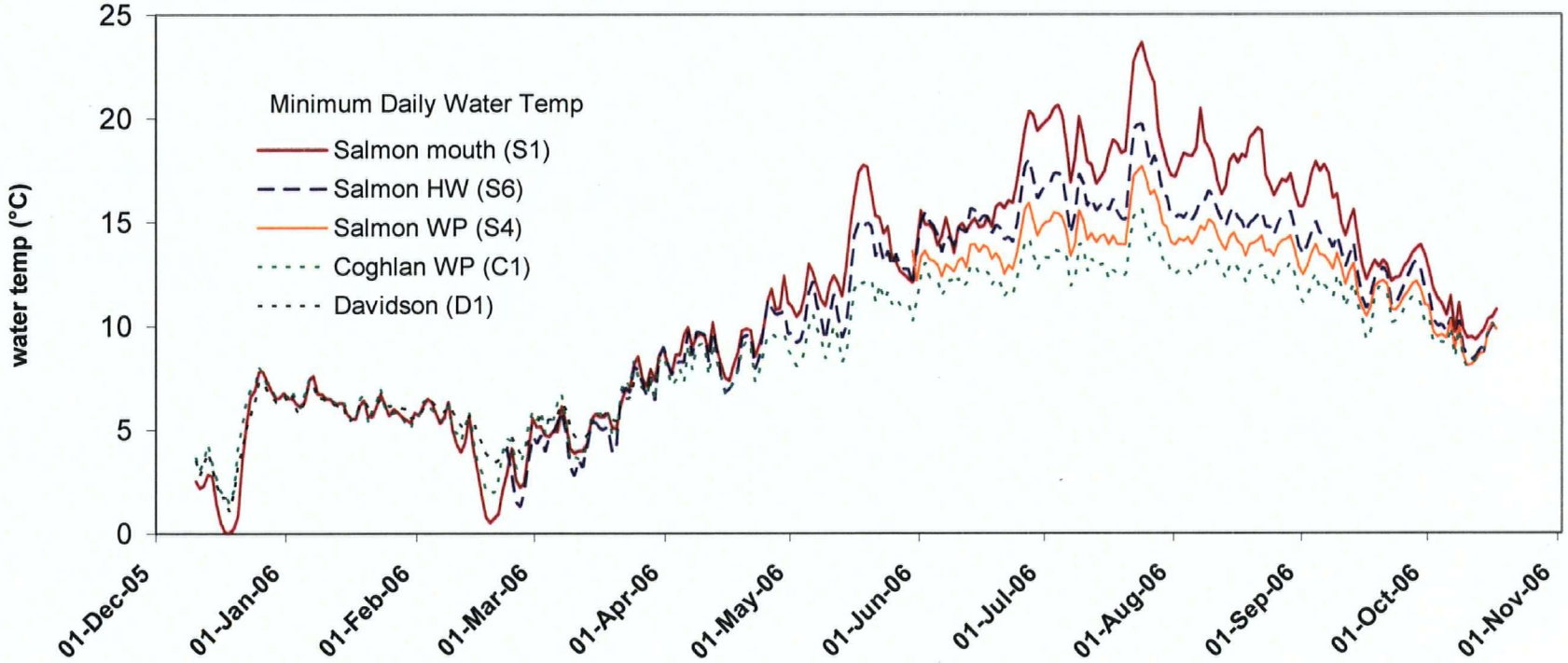

Figure E7. Daily minimum water temperature for selected sites in Salmon River Watershed

Appendix F: Land use summaries

Salmon River watershed, Hopington aquifers, CAs, 100 m stream buffers, and 100 m well buffers

Table F1. Summary of land use in the Salmon River watershed and above the Hopington aquifers.

	Land Use Category (% of total area)						Total Area
	agriculture	residential	com/ind/inst	transport	recreation	other	(km^2)
Salmon Watershed	49.6	15.6	4.0	7.0	3.3	20.5	73.56
Hopington A	37.5	29.1	5.7	7.2	1.8	18.7	16.39
Hopington B	50.6	13.9	2.6	7.1	2.2	23.6	7.06
Hopington C	58.3	14.0	2.8	4.0	0.3	20.6	16.46

Table F2. Summary of land use in 100 m buffer zone around well sampling sites

	Land Use Category, % of total buffer area (31400 m^2)					
	agriculture	residential	com/ind/inst	transport	recreation	other
WELL A1	24.5	42.9	0.0	4.3	0.0	28.3
WELL A2	53.8	11.9	0.0	0.7	33.6	0.0
WELL A3	53.5	23.7	0.0	8.8	0.0	14.1
WELL A4	48.1	39.3	0.0	12.5	0.0	0.0
WELL B1	0.0	56.4	0.0	13.0	0.0	30.6
WELL B2	8.5	81.3	0.5	9.7	0.0	0.0
WELL B3	33.4	49.5	0.0	16.6	0.0	0.5
WELL B4	98.4	1.6	0.0	0.0	0.0	0.0
WELL X1	34.4	38.2	0.0	9.0	0.0	18.4
WELL X2	54.0	32.0	0.0	12.6	0.0	1.4
WELL X3	28.1	32.5	0.0	0.0	0.0	39.4

Table F3. Summary of land use for contributing areas and 100 m buffer areas above streams sampling locations.

	Land Use Category (% of total area)						Total Area
	agriculture	residential	com/ind/inst	transport	recreation	other	(km^2)
Contributing Area							
Sal 1	56.5	13.0	0.6	8.4	5.3	16.2	8.81
Sal 2	48.2	15.4	3.4	9.0	1.0	22.9	13.24
Sal 3	62.4	10.8	0.7	6.2	3.1	16.8	3.86
Sal 4	12.0	38.1	0.9	7.5	9.8	31.7	2.19
Sal 5	34.9	32.8	0.6	7.1	1.0	23.6	5.35
Sal 6	53.5	8.6	7.5	4.3	4.3	21.7	8.45
Sal 7	37.1	3.6	25.2	2.9	9.4	21.9	4.75
Coug 1	42.8	22.7	2.8	7.8	0.1	23.8	4.56
Coug 2	67.8	15.7	1.7	6.5	0.0	8.4	5.72
Coug 3	45.3	10.9	2.5	12.4	0.3	28.6	3.69
Trib 1	36.7	40.3	2.8	8.8	1.4	10.0	1.67
Dav 1	63.8	6.1	1.3	3.5	0.0	25.3	5.92
100 m Buffer							
Sal 1	80.1	3.6	0.0	3.6	10.7	1.9	1.15
Sal 2	30.2	9.1	3.8	7.1	0.6	49.2	1.69
Sal 3	27.2	16.4	0.2	4.8	6.2	45.1	0.88
Sal 4	3.3	9.5	1.5	2.9	5.4	77.3	0.71
Sal 5	7.1	36.0	0.0	4.6	0.0	52.3	0.92
Sal 6	59.8	6.8	1.1	2.1	1.4	28.8	1.46
Sal 7	33.6	3.8	20.6	3.9	13.9	24.2	1.15
Cog 1	12.9	21.9	1.6	3.6	0.4	59.6	0.91
Cog 2	71.2	9.3	0.9	3.7	0.0	14.9	1.03
Cog 3	22.3	14.4	1.6	8.0	0.0	53.8	0.24
Trib 1	7.9	42.0	4.1	10.1	4.6	31.3	0.24
Dav 1	33.0	8.1	0.9	2.3	0.0	55.8	1.02

Table F4. Breakdown of agricultural land use component for Salmon River watershed and Hopington aquifers.

	Land Use Category (% of total area)							Total Area
	crops/arable	livestock	hort/grnhse	other ag	unused	unclass ag	Ag. Total	(km^2)
Salmon Watershed	35.2	6.7	2.1	0.6	2.5	2.3	49.6	73.56
Hopington A	22.8	5.6	4.2	0.7	2.4	1.7	37.5	16.39
Hopington B	36.9	6.5	2.8	1.3	1.7	1.5	50.6	7.06
Hopington C	41.6	9.7	1.8	0.4	1.4	3.4	58.3	16.46

Table F5. Breakdown of agricultural land use component for 100 m buffer zone around well sampling sites.

	Land Use Category, % of total buffer area (31400 m^2)						
	crops/arable	livestock	hort/grnhse	other ag	unused	unclass ag	Ag. Total
WELL A1	23.8	0.7	0.0	0.0	0.0	0.0	24.5
WELL A2	52.4	0.0	1.4	0.0	0.0	0.0	53.8
WELL A3	30.3	23.1	0.0	0.0	0.0	0.0	53.5
WELL A4	47.0	0.0	1.1	0.0	0.0	0.0	48.1
WELL B1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WELL B2	0.0	8.5	0.0	0.0	0.0	0.0	8.5
WELL B3	13.6	19.8	0.0	0.0	0.0	0.0	33.4
WELL B4	8.7	30.2	0.0	0.0	0.0	59.4	98.4
WELL X1	19.1	2.9	0.0	0.0	0.0	12.4	34.4
WELL X2	18.1	6.1	2.1	27.8	0.0	0.0	54.0
WELL X3	0.0	11.0	0.7	0.0	0.0	16.4	28.1

Table F6. Breakdown of agricultural land use component for contributing areas and 100 m buffer areas above stream sampling locations.

	Land Use Category (% of total area)							Total Area
	crops/arable	livestock	hort/grnhse	other ag	unused	unclass ag	Ag. Total	(km^2)
Contributing Area								
Sal 1	48.6	2.4	0.8	0.0	2.0	2.6	56.5	8.81
Sal 2	32.1	3.1	4.6	0.5	3.5	4.4	48.2	13.24
Sal 3	45.6	10.3	0.6	0.9	4.2	0.9	62.4	3.86
Sal 4	8.0	2.8	0.4	0.7	0.0	0.0	12.0	2.19
Sal 5	18.8	8.8	2.0	0.5	0.8	4.0	34.9	5.35
Sal 6	36.6	9.6	1.6	0.5	4.0	1.3	53.5	8.45
Sal 7	22.7	8.4	0.7	0.3	3.9	1.2	37.1	4.75
Coug 1	30.1	7.5	3.7	1.4	0.1	0.0	42.8	4.56
Coug 2	48.2	9.7	3.7	1.7	1.7	2.8	67.8	5.72
Coug 3	29.3	8.5	0.9	0.9	4.2	1.4	45.3	3.69
Trib 1	24.0	4.8	1.2	0.9	2.1	3.6	36.7	1.67
Dav 1	47.2	8.5	2.5	0.9	2.2	2.5	63.8	5.92
100 m Buffer								
Sal 1	78.3	0.0	0.0	0.1	0.0	1.7	80.1	1.15
Sal 2	21.7	1.9	1.2	0.4	2.3	2.6	30.2	1.69
Sal 3	17.5	7.7	0.0	0.0	1.2	0.8	27.2	0.88
Sal 4	1.0	0.9	0.1	0.2	0.0	1.0	3.3	0.71
Sal 5	4.3	0.9	1.6	0.3	0.0	0.0	7.1	0.92
Sal 6	50.9	7.3	0.1	0.2	0.8	0.5	59.8	1.46
Sal 7	21.0	10.0	0.0	0.0	1.5	1.1	33.6	1.15
Cog 1	6.6	2.6	3.6	0.0	0.0	0.1	12.9	0.91
Cog 2	58.3	4.3	1.6	2.3	1.0	3.7	71.2	1.03
Cog 3	10.4	7.2	0.0	0.0	0.2	4.5	22.3	0.24
Trib 1	0.0	4.8	0.0	0.0	1.2	1.9	7.9	0.24
Dav 1	27.0	1.9	1.3	0.0	1.6	1.3	33.0	1.02

Appendix G: Land cover summaries

Salmon River watershed, Hopington aquifers, CAs,
100m stream buffers, and 100 m well buffers

Table G1. Land cover summary for Salmon River watershed and for land areas above the Hopington aquifers.

	Land Cover Category (% of total area)					Total Area
	grass/veg	woody veg	bare	constructed	water	(km^2)
Salmon Watershed	52.1	29.4	3.8	14.4	0.3	73.56
Hopington A	42.6	33.0	2.8	20.4	1.1	16.39
Hopington B	47.7	36.8	3.8	11.1	0.6	7.06
Hopington C	55.0	25.5	7.4	11.8	0.2	16.46

Table G2. Land cover summary for 100 m buffer zone around well sampling sites.

	Land Cover Category*, % of total buffer area (31400 m^2)			
	grass/veg	woody veg	bare	constructed
WELL A1	43.8	28.3	0.0	27.9
WELL A2	62.8	35.0	0.0	2.1
WELL A3	23.0	38.4	5.0	33.7
WELL A4	86.3	1.2	0.0	12.5
WELL B1	43.4	43.6	0.0	13.0
WELL B2	60.5	12.1	0.5	26.9
WELL B3	82.7	0.7	0.0	16.6
WELL B4	35.2	37.2	22.2	5.3
WELL X1	64.5	8.5	18.0	9.0
WELL X2	84.7	1.4	0.0	13.9
WELL X3	55.8	39.4	4.0	0.7

* Note that the water and 'other' categories have not been included in this summary.

Table G3. Land cover summary for contributing areas and 100 m buffer areas above streams sampling locations.

	Land Cover Category* (% of total area)				Total Area
	grass/veg	woody veg	bare	constructed	(km^2)
Contributing Area					
Sal 1	61.1	20.5	4.7	13.1	8.81
Sal 2	52.6	27.1	4.1	15.8	13.24
Sal 3	63.8	25.1	0.9	10.0	3.86
Sal 4	35.3	38.5	0.2	26.0	2.19
Sal 5	49.1	29.6	4.2	16.6	5.35
Sal 6	49.0	36.9	2.7	11.4	8.45
Sal 7	60.1	30.5	3.4	5.8	4.75
Coug 1	35.2	44.0	4.5	15.4	4.56
Coug 2	51.1	31.0	3.1	14.5	5.72
Coug 3	50.8	29.8	6.1	13.1	3.69
Trib 1	48.3	18.6	4.4	28.5	1.67
Dav 1	50.2	36.9	3.8	9.1	5.92
100m Buffer					
Sal 1	88.7	8.1	0.1	2.3	1.15
Sal 2	39.9	47.4	0.6	10.0	1.69
Sal 3	41.8	51.2	0.3	6.3	0.88
Sal 4	8.3	85.3	0.0	6.4	0.71
Sal 5	24.1	64.8	0.5	10.7	0.92
Sal 6	51.0	39.3	2.4	7.2	1.46
Sal 7	61.0	32.1	0.6	6.1	1.15
Cog 1	14.7	77.5	0.2	5.8	0.91
Cog 2	48.0	43.5	1.6	7.0	1.03
Cog 3	31.7	54.0	6.8	7.5	0.24
Trib 1	33.1	33.8	0.0	33.2	0.24
Dav 1	29.6	63.7	2.1	4.2	1.02

Note that the water and 'other' categories have not been included in this summary.

Appendix H: Nitrate-isotopes, raw data

Table H1. Raw data from nitrate-isotope analysis.

Date	Site ID	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	aquifer	position	Comments
30-May-06	A1	9.9	-2.0	A		
30-May-06	A3	5.7	12.3	A		
30-May-06	A4	7.2	2.7	A		
30-May-06	B2	9.7	-2.2	B		
30-May-06	B3	14.8	-2.7	B		Stdev 0.24 (n=3)
30-May-06	B4	8.6	-0.5	B		
30-May-06	X1	7.0	2.2	C		
30-May-06	S1	10.9	1.0		after	
30-May-06	S4	10.2	1.6		over	
30-May-06	S7	8.6	-		before	no data
30-May-06	C1	10.9	-0.7		over	(triplicate sample)
30-May-06	C1	10.9	-0.4		over	(triplicate sample)
30-May-06	C1	11.0	-2.2		over	(triplicate sample)
30-May-06	C3	9.8	3.9		before	
30-May-06	D1	10.6	-0.8		after	
30-May-06	T1	11.6	*		over	* contaminated with $AgNO_3$ ppt

Date	Site ID	$\delta^{15}N_{NO3}$	$\delta^{18}O_{NO3}$	aquifer	position	Comments
21-Aug-06	A1	8.2	-3.4	A		
21-Aug-06	A3	6.1	10.9	A		
21-Aug-06	A4	6.7	-0.6	A		
21-Aug-06	B2	10.5	-2.2	B		
21-Aug-06	B3	14.4	-2.7	B		
21-Aug-06	B4	8.7	-1.2	B		(triplicate sample)
21-Aug-06	B4	8.7	-1.2	B		(triplicate sample)
21-Aug-06	B4	8.7	-0.5	B		(triplicate sample)
21-Aug-06	X1	7.0	1.7	C		
21-Aug-06	S1	12.8	-0.4		after	
21-Aug-06	S4	11.1	-0.3		over	
21-Aug-06	C1	11.1	-0.4		over	
21-Aug-06	D1	10.9	-0.7		after	
21-Aug-06	T1	12.6	2.1		over	Stdev 0.44 (n=3)

Appendix I: Water isotopes, raw data

Table I1. Raw data from water stable isotope analysis.

Date	Site ID	combined mean δ18O/16O	% std dev δ18O/16O	combined mean δ2H/1H	% std dev δ2H/1H
06-Sep-05	B4	-11.09	0.17	-	-
06-Sep-05	C1	-11.43	0.14	-	-
06-Sep-05	C2	-10.82	0.10	-	-
06-Sep-05	D1	-11.20	0.04	-	-
06-Sep-05	S4	-10.61	0.59	-	-
06-Sep-05	S6	-8.50	0.37	-	-
20-Feb-06	A2	-9.85	0.06	-79.50	1.02
20-Feb-06	X2	-10.47	0.08	-74.55	0.50
22-Feb-06	A1	-8.76	0.96	-	-
22-Feb-06	A4	-10.11	0.86	-	-
22-Feb-06	B1	-11.40	0.17	-	-
22-Feb-06	B2	-7.41	0.11	-	-
22-Feb-06	B3	-8.51	0.54	-	-
22-Feb-06	C1	-11.71	0.16	-	-
22-Feb-06	C3	-11.47	0.03	-	-
22-Feb-06	D1	-11.31	0.18	-	-
22-Feb-06	S1	-10.67	0.46	-	-
22-Feb-06	S4	-11.40	0.17	-	-
22-Feb-06	S7	-11.73	0.10	-	-
22-Feb-06	T1	-11.10	0.08	-	-
22-Feb-06	X1	-11.86	0.14	-	-
30-May-06	A1	-7.26	1.19	-80.15	7.42
30-May-06	A3	-9.22	0.37	-67.35	3.96
30-May-06	A4	-7.99	0.70	-71.89	4.57
30-May-06	B1	-8.29	1.30	-64.86	5.50
30-May-06	B2	-9.73	1.32	-74.14	2.44
30-May-06	B3	-10.13	0.37	-80.22	2.03
30-May-06	B4	-8.58	1.40	-67.42	3.25
30-May-06	C1	-9.85	1.08	-57.22	8.73
30-May-06	D1	-9.03	0.49	-79.52	9.72
30-May-06	S1	-7.01	2.99	-86.36	2.37
30-May-06	S2	-9.92	0.87	-82.81	6.50
30-May-06	S4	-8.03	1.51	-70.37	4.75
30-May-06	S5	-6.53	0.14	-70.32	4.05
30-May-06	S6	-6.18	0.48	-64.85	2.06
30-May-06	S7	-9.39	3.49	-64.44	0.87
30-May-06	T1	-8.94	1.90	-70.24	6.97
30-May-06	X1	-9.35	0.90	-67.61	4.98

Table I1 (continued). Raw data from water stable isotope analysis.

Date	Site ID	combined mean δ18O/16O	% std dev δ18O/16O	combined mean δ2H/1H	% std dev δ2H/1H
21-Aug-06	A1	-10.86	0.16	-99.42	6.01
21-Aug-06	A2	-10.23	0.14	-70.31	4.74
21-Aug-06	A3	-9.95	0.19	-70.34	5.17
21-Aug-06	A4	-10.04	0.25	-77.26	5.02
21-Aug-06	B1	-10.94	0.23	-72.37	2.98
21-Aug-06	B2	-10.74	0.51	-87.60	3.99
21-Aug-06	B3	-11.99	1.93	-96.23	10.38
21-Aug-06	B4	-10.59	0.07	-50.34	0.59
21-Aug-06	C1	-10.68	0.13	-53.45	7.55
21-Aug-06	C3	-9.84	0.11	-69.82	4.80
21-Aug-06	D1	-10.65	0.30	-112.75	7.29
21-Aug-06	S1	-10.84	0.45	-120.08	8.61
21-Aug-06	S2	-10.33	0.10	-82.21	4.69
21-Aug-06	S4	-10.63	0.28	-64.33	8.56
21-Aug-06	S5	-9.84	0.22	-97.66	4.01
21-Aug-06	S6	-8.44	0.24	-90.69	7.87
21-Aug-06	S7	-6.16	0.11	-71.75	4.83
21-Aug-06	T1	-10.53	0.11	-99.45	2.19
21-Aug-06	X1	-11.13	0.27	-87.67	10.29
21-Aug-06	X2	-11.51	0.05	-95.47	3.61
21-Aug-06	X3	-11.06	0.30	-84.53	6.21

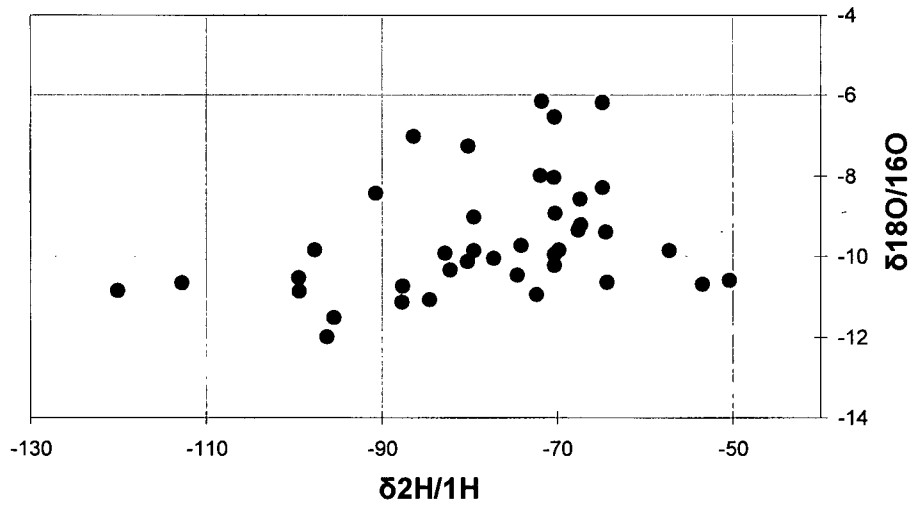

Figure I1. Plot of $\delta^{18}O_{H2O}$ vs $\delta^{2}H_{H2O}$, all stream and groundwater samples with both H and O measurements.

Note that distinguishing between date, stream position or aquifer did not offer any insight as to similar values or commonality of recharge sources for the aquifers.

Appendix J: Dilution tests for spectral measurements

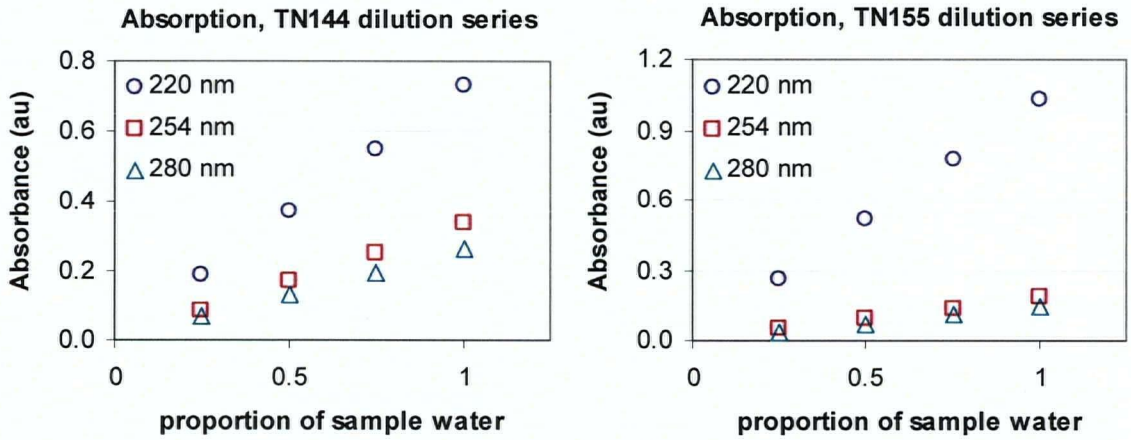

Figure J1. Absorption results for surface water dilution tests.
Samples were prepared using deionized water and stream sample water mixed in different proportions; after mixing, the samples were centrifuged as per normal protocol.

Note the linear relationship between concentration and absorption, especially in the TN144 dilution series where A_{254} is 0.34; $A_{254} > 0.3$ is sometimes considered an upper limit for samples not requiring an inner filtering correction for fluorescence measurements (Ohno, 2002). Linear regression for both dilution series and all wavelengths had an R^2 value greater than 0.999.

Humic-like and fulvic-like[27] regions of fluorescence have a strong linear relationship with the sample concentration ($R^2 \geq 0.98$ for linear regression), suggesting that inner-filtering is not a problem; interpretation of "raw" values for these regions of fluorescence were thus considered valid for all samples.

[27] In this appendix, "Fulvic-like" is equivalent to "humic-like2" used in the body of the thesis.

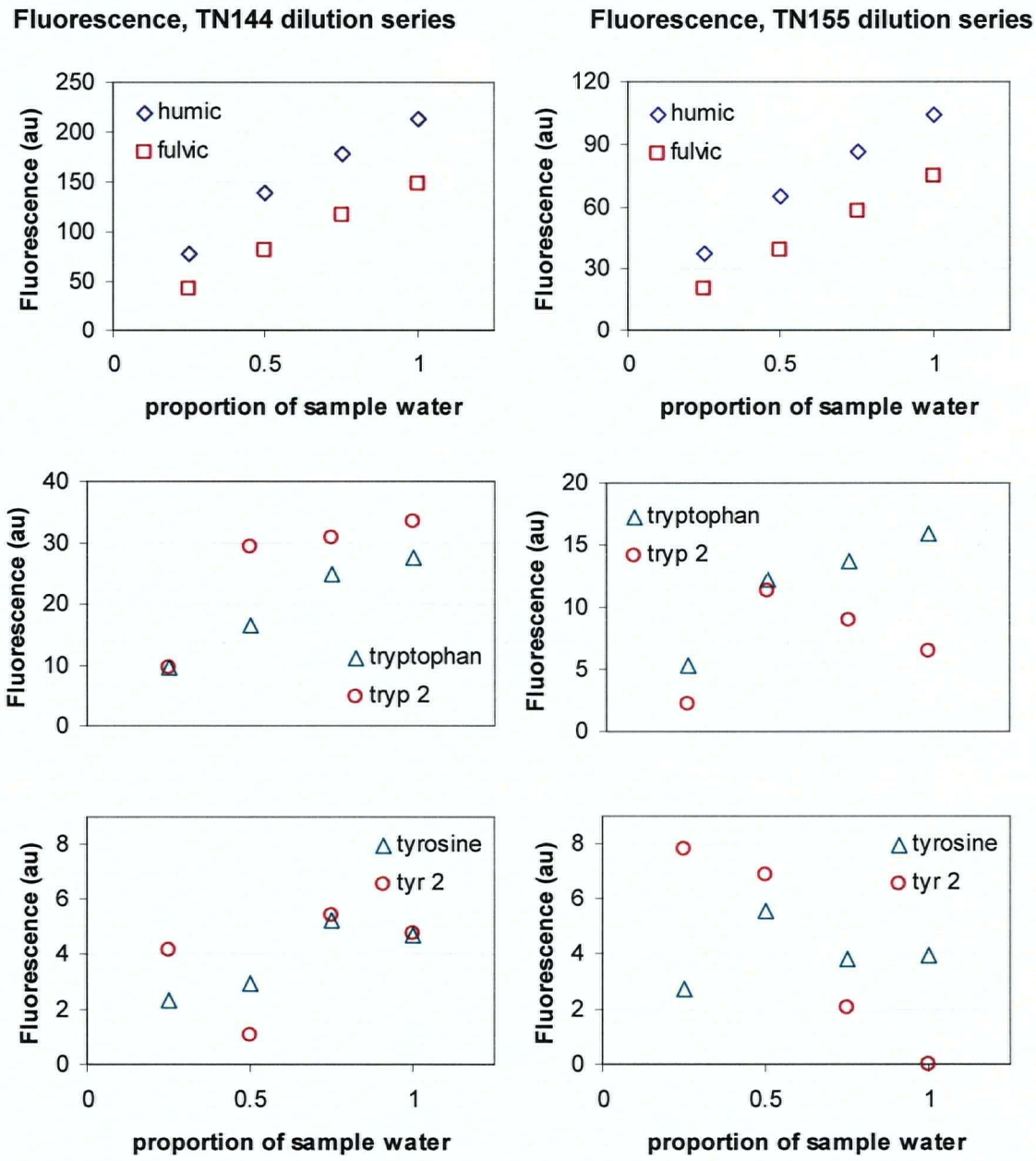

Figure J2. Fluorescence results for surface water dilution tests.
Fluorescence values are the "mean" for each region as defined in the body of this report.
Samples were prepared using deionized water and stream sample water mixed in different proportions; after mixing, the samples were centrifuged as per normal protocol.

The regions of protein-like fluorescence (tyrosine-like and tryptophan-like) show signs of inner-filtering; the relationship between fluorescence intensity and concentration (proportion of sample water) is weaker than for humic-like regions. The primary

tryptophan region is acceptable for direct interpretation with inner-filtering being minimal (R^2 of 0.96 and 0.88 for samples TN144 and 155, respectively). The second tryptophan-like region of fluorescence ("tryp 2" in the preceding figure) does not show a good correlation, and for TN155 has a negative correlation. This region of fluorescence was therefore not used for interpretation in the body of the thesis.

The main tyrosine region does show a positive relationship to concentration, but the fluorescence intensity levels off at higher concentration indicating possible inner-filtering. TN144 represents the higher range of values for DOC and absorption (A_{254} in particular); there were only five samples in the main data set with absorption values greater than 0.3. Keeping this in mind, it is reasonable to directly interpret values for the sample sets collected in this study. Caution should be used in interpreting results for those samples with particularly high absorption. The second tyrosine-like region ("tyr 2") shows confused results with the dilution series and is therefore not used in this study.

Table J1. Regions of fluorescence.

Fluorescence region / peak	**Excitation λ (nm)**	**Emission λ (nm)**
humic-like	230-250	400-440
Fulvic-like (humic-like2)	315-340	400-435
Tyrosine-like	270-280	300-310
Tyrosine-like2	220-225	300-310
Tryptophan-like	270-280	340-360
Tryptophan-like2	220	340-350

Appendix K: Ternary diagrams using Ca, Na, and Si concentrations

Figure K1 shows ternary diagrams using several dissolved elements that can help differentiate between groundwater sources and different sections of the Salmon River watershed. The Hopington A and B aquifers are very similar, but the Hopington C wells were in a different region of the graph because of lower calcium. Surface water samples generally had higher sodium and lower silica than the groundwater samples, which could be used to differentiate the two sources. Groundwater influence could be noted because the stream water sites that are strongly influenced by groundwater (over and after aquifer positions) plot closer to groundwater values.

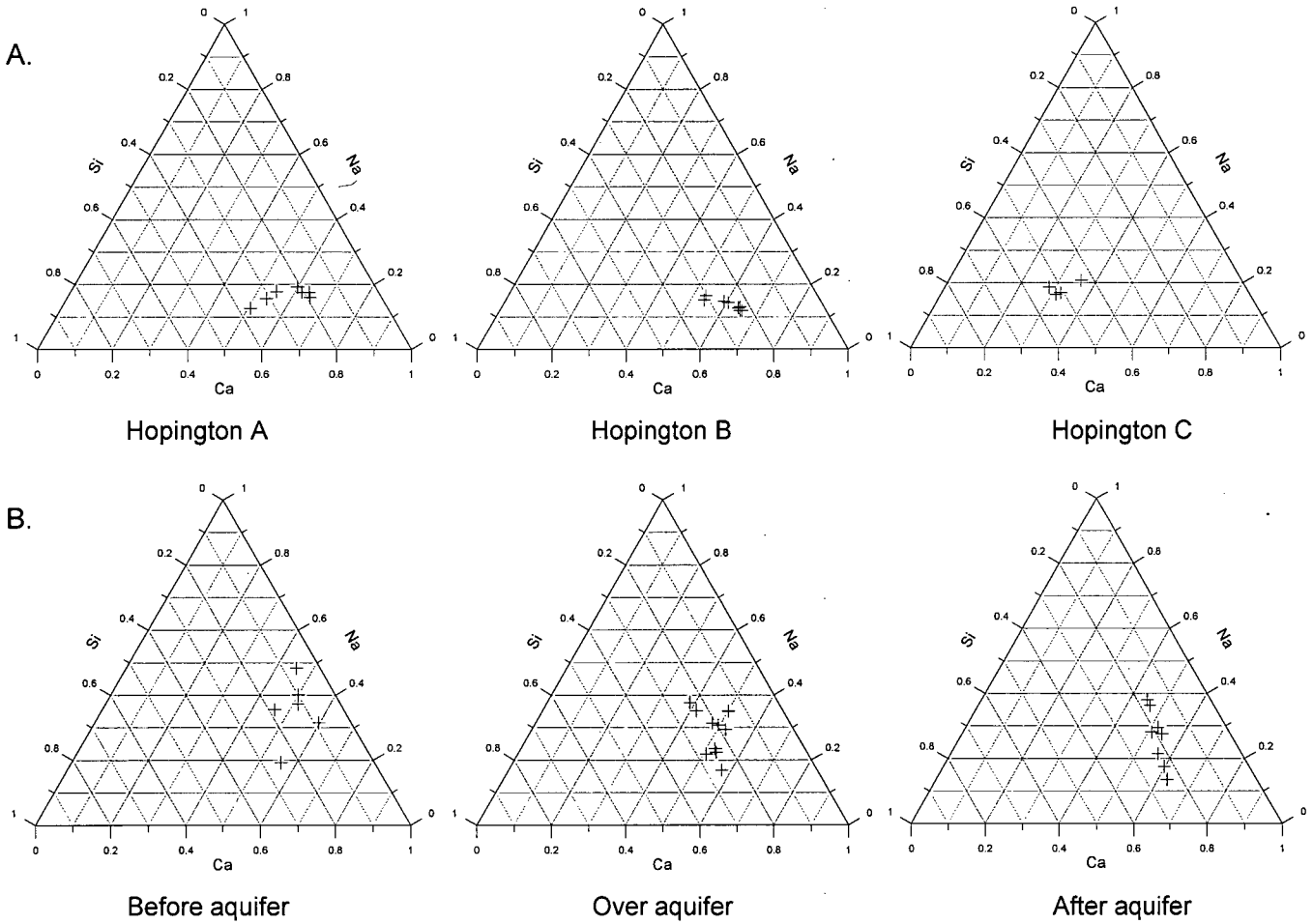

Figure K1. Ternary diagrams using Ca, Na, Si (x, y, z respectively) concentrations (A.) for the Hopington aquifers and (B.) for stream sites in different positions relative to the Hopington aquifers.

Appendix L Nitrate-nitrogen isotope and chloride ratios

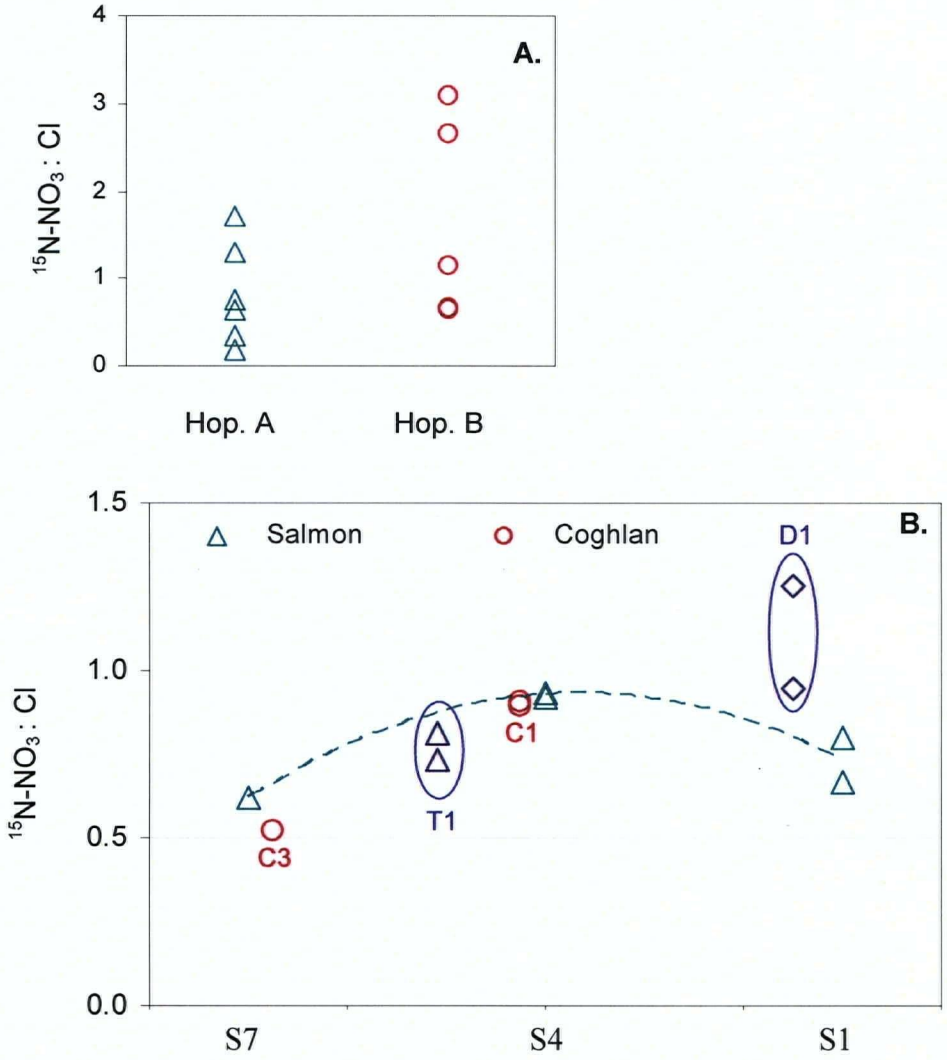

Figure L1. ^{15}N-NO$_3$: Cl ratios for (A.) Hopington A and B aquifer samples and (B.) stream samples.

Figure L1 suggests that the ratio of ^{15}N-nitrate values and the chloride concentration may provide another means of differentiating source waters. Ratios for Hopington B wells spanned higher values than for A and the values for groundwater were generally higher than for stream water. The downstream trend for surface waters showed a ratio increase from the groundwater influx. Davidson Creek was quite different from the other surface water sites, perhaps indicating an unusual or unique pollutant source in this area.

Appendix M: Nutrients and pH, raw data

Table M1. Raw data for nutrient analysis (NH_4^+, NO_3^-, PO_4^{-3}, Cl^-) and pH.

Date	Site	pH	NH_4^+-N (mg/L)	NO_3^--N (mg/L)	PO_4^{-3} (mg/L)	Cl^- (mg/L)
06-Sep-05	**B4**	-	0.04	11.30	0.01	13.47
06-Sep-05	**C1**	-	0.08	5.48	0.02	11.20
06-Sep-05	**C2**	-	0.07	1.95	0.00	9.70
06-Sep-05	**D1**	-	0.06	4.14	0.02	9.91
06-Sep-05	**S1**	-	0.10	2.65	0.01	16.04
06-Sep-05	**S2**	-	0.08	3.13	0.01	17.83
06-Sep-05	**S3**	-	0.06	3.82	0.01	11.55
06-Sep-05	**S4**	-	0.06	2.92	0.02	11.32
06-Sep-05	**S5**	-	0.03	1.30	0.01	9.37
06-Sep-05	**S6**	-	0.05	0.06	0.01	10.23
06-Sep-05	**S7**	-	0.06	0.01	0.01	15.11
06-Sep-05	**T1**	-	0.05	3.86	0.02	17.56
20-Feb-06	**A2**	6.82	0.08	0.00	0.00	15.25
20-Feb-06	**X2**	8.65	0.04	0.00	0.04	6.33
22-Feb-06	**A1**	6.83	0.05	2.86	0.01	8.38
22-Feb-06	**A4**	5.75	0.06	17.01	0.00	5.48
22-Feb-06	**B1**	7.41	0.05	6.73	0.01	10.45
22-Feb-06	**B2**	7.51	0.05	12.94	0.02	8.40
22-Feb-06	**B3**	6.86	0.04	12.44	0.01	5.16
22-Feb-06	**C1**	7.35	0.04	4.37	0.02	11.63
22-Feb-06	**C3**	7.30	0.07	1.28	0.01	15.46
22-Feb-06	**D1**	7.36	0.07	3.18	0.02	9.00
22-Feb-06	**S1**	7.19	0.14	3.10	0.02	14.28
22-Feb-06	**S3**	7.21	0.07	3.55	0.02	11.26
22-Feb-06	**S4**	7.21	0.04	3.38	0.02	9.91
22-Feb-06	**S6**	7.10	0.08	1.56	0.02	9.06
22-Feb-06	**S7**	6.89	0.17	1.00	0.03	9.56
22-Feb-06	**T1**	7.15	0.05	5.76	0.02	13.22
22-Feb-06	**X1**	7.35	0.06	0.68	0.07	3.61
28-Mar-06	**A1**	7.25	0.36	3.70	0.01	9.43
28-Mar-06	**A3**	6.15	0.07	22.60	0.02	10.36
28-Mar-06	**A4**	6.13	0.10	13.07	0.00	4.26
28-Mar-06	**B1**	7.23	0.26	6.55	0.01	9.88
28-Mar-06	**B2**	7.24	0.26	12.70	0.02	8.27
28-Mar-06	**B3**	6.88	0.27	11.94	0.01	4.78
28-Mar-06	**B4**	6.62	0.19	9.75	0.01	13.20
28-Mar-06	**C1**	7.01	0.25	3.77	0.01	12.83
28-Mar-06	**C2**	7.21	0.10	1.41	0.02	15.18
28-Mar-06	**C3**	7.21	0.07	0.82	0.01	20.09
28-Mar-06	**D1**	7.19	0.15	2.12	0.01	7.37

Table M1 (continued). Raw data for nutrients and pH.

Date	Site	pH	NH_4^+-N (mg/L)	NO_3^--N (mg/L)	PO_4^{-3} (mg/L)	Cl^- (mg/L)
28-Mar-06	**S1**	7.05	0.16	2.01	0.02	15.08
28-Mar-06	**S2**	7.15	0.05	2.12	0.01	15.34
28-Mar-06	**S3**	7.21	0.06	2.44	0.01	11.14
28-Mar-06	**S4**	7.29	0.19	2.06	0.01	9.96
28-Mar-06	**S5**	7.34	0.36	1.53	0.01	10.24
28-Mar-06	**S6**	7.00	0.05	0.69	0.02	9.66
28-Mar-06	**S7**	7.01	0.03	0.36	0.02	10.25
28-Mar-06	**T1**	7.31	0.31	4.68	0.01	13.28
28-Mar-06	**X1**	7.28	0.06	0.73	0.08	3.33
30-May-06	**A1**	7.05	0.04	3.41	0.01	13.19
30-May-06	**A3**	6.22	0.05	21.97	0.01	16.89
30-May-06	**A4**	5.75	0.03	13.99	0.01	4.18
30-May-06	**B1**	7.46	0.06	6.37	0.02	10.09
30-May-06	**B2**	7.52	0.03	12.66	0.02	8.44
30-May-06	**B3**	6.92	0.04	10.72	0.01	4.78
30-May-06	**B4**	6.54	0.03	9.51	0.01	13.58
30-May-06	**C1**	7.38	0.06	4.48	0.01	12.19
30-May-06	**C2**	7.44	0.04	1.49	0.02	14.76
30-May-06	**C3**	7.40	0.04	0.90	0.01	18.87
30-May-06	**D1**	7.44	0.04	2.68	0.02	8.50
30-May-06	**S1**	7.22	0.11	2.00	0.02	16.31
30-May-06	**S2**	7.28	0.08	2.24	0.02	17.22
30-May-06	**S3**	7.46	0.04	2.79	0.01	11.78
30-May-06	**S4**	7.49	0.05	2.08	0.02	10.92
30-May-06	**S5**	7.19	0.05	1.36	0.02	11.04
30-May-06	**S6**	6.88	0.06	0.50	0.02	11.69
30-May-06	**S7**	6.78	0.12	0.19	0.03	13.99
30-May-06	**T1**	7.02	0.06	4.15	0.02	14.24
30-May-06	**X1**	7.47	0.04	0.68	0.07	3.61
26-Jul-06	**A1**	6.73	0.06	4.68	0.01	14.11
26-Jul-06	**A3**	6.12	0.03	26.45	0.01	27.57
26-Jul-06	**A3**	6.13	0.04	26.61	0.01	24.73
26-Jul-06	**A4**	5.66	0.06	17.10	0.01	4.19
26-Jul-06	**B1**	7.29	0.04	6.34	0.01	9.89
26-Jul-06	**B2**	7.30	0.09	12.64	0.02	8.46
26-Jul-06	**B3**	6.96	0.06	9.27	0.01	5.26
26-Jul-06	**B4**	6.51	0.07	9.58	0.01	12.45
26-Jul-06	**C1**	7.24	0.05	5.72	0.01	11.17
26-Jul-06	**C2**	7.03	0.06	1.79	0.04	9.05
26-Jul-06	**C3**	7.15	0.05	1.00	0.03	10.15
26-Jul-06	**D1**	7.24	0.07	3.88	0.03	10.03
26-Jul-06	**S1**	7.35	0.07	2.15	0.01	16.91
26-Jul-06	**S2**	7.32	0.06	2.90	0.01	17.23
26-Jul-06	**S3**	7.58	0.06	3.67	0.01	11.41

Table M1 (continued). Raw data for nutrients and pH.

Date	Site	pH	NH_4^+-N (mg/L)	NO_3^--N (mg/L)	PO_4^{-3} (mg/L)	Cl^- (mg/L)
26-Jul-06	**S4**	7.20	0.05	2.82	0.02	11.28
26-Jul-06	**S5**	7.02	0.04	1.21	0.01	9.09
26-Jul-06	**S6**	6.96	0.03	0.15	0.01	9.06
26-Jul-06	**S7**	6.70	0.10	0.02	0.01	13.58
26-Jul-06	**T1**	7.00	0.06	4.03	0.02	16.85
26-Jul-06	**X1**	7.12	0.09	0.68	0.08	3.67
21-Aug-06	**A1**	7.06	0.07	3.89	0.01	12.85
21-Aug-06	**A2**	7.10	0.15	0.01	0.01	15.92
21-Aug-06	**A3**	7.03	0.11	20.83	0.02	33.46
21-Aug-06	**A4**	6.25	0.70	17.84	0.01	5.17
21-Aug-06	**B1**	6.96	0.08	6.47	0.02	10.56
21-Aug-06	**B2**	7.48	0.09	13.10	0.02	9.31
21-Aug-06	**B3**	7.01	0.09	8.91	0.01	5.41
21-Aug-06	**B4**	7.00	0.14	9.60	0.02	13.17
21-Aug-06	**C1**	7.41	0.11	5.77	0.02	12.27
21-Aug-06	**C2**	7.48	0.14	1.75	0.04	9.43
21-Aug-06	**C3**	7.56	0.68	0.62	0.03	10.65
21-Aug-06	**D1**	7.67	0.15	3.95	0.03	11.58
21-Aug-06	**S1**	7.58	0.13	2.38	0.02	15.99
21-Aug-06	**S2**	7.57	0.54	3.27	0.01	18.35
21-Aug-06	**S3**	7.56	0.17	3.99	0.02	12.51
21-Aug-06	**S4**	7.43	0.09	2.92	0.02	12.00
21-Aug-06	**S5**	7.31	0.08	1.06	0.02	9.73
21-Aug-06	**S6**	7.21	0.53	0.08	0.02	10.47
21-Aug-06	**S7**	7.23	0.06	0.00	0.02	15.65
21-Aug-06	**T1**	6.81	0.07	4.09	0.02	17.16
21-Aug-06	**X1**	7.41	0.23	0.69	0.08	4.19
21-Aug-06	**X2**	7.48	0.11	0.00	0.06	3.86
21-Aug-06	**X3**	7.40	0.42	0.01	0.20	3.20
17-Oct-06	**C1**	7.25	0.40	4.35	0.02	15.49
17-Oct-06	**C2**	7.39	0.21	1.16	0.03	26.50
17-Oct-06	**C3**	7.25	0.39	0.62	0.03	35.02
17-Oct-06	**D1**	7.40	0.26	2.93	0.02	9.72
17-Oct-06	**S1**	7.25	0.23	2.68	0.03	22.48
17-Oct-06	**S2**	7.15	0.32	2.70	0.03	22.58
17-Oct-06	**S3**	7.40	0.28	2.85	0.02	12.76
17-Oct-06	**S4**	7.38	0.23	2.05	0.02	10.17
17-Oct-06	**S5**	7.26	0.33	1.01	0.02	8.64
17-Oct-06	**S6**	7.28	0.36	0.26	0.02	8.54
17-Oct-06	**S7**	7.00	0.48	0.05	0.01	9.90
17-Oct-06	**T1**	7.31	0.36	3.76	0.02	19.06

Appendix N: Dissolved elements, raw data

Table N1. Raw data for ICP analysis for dissolved elements (mg/L).

Date	Site	Al	B	Ba	Ca	Fe	K	Mg	Mn	Na	Si	Sr	Zn
30-May-06	A1	0.000	0.000	0.000	19.67	0.171	1.03	9.456	0.150	6.37	9.74	0.095	0.048
30-May-06	A3	0.000	0.048	0.000	29.49	0.074	1.12	8.638	0.004	9.48	10.25	0.274	0.012
30-May-06	A4	0.000	0.000	0.113	15.03	0.000	3.40	3.505	0.023	4.29	4.99	0.147	0.008
30-May-06	B1	0.000	0.000	0.000	26.89	0.000	1.31	10.306	0.000	5.34	9.81	0.102	0.000
30-May-06	B2	0.000	0.000	0.000	31.36	0.000	1.07	12.515	0.000	6.38	11.10	0.131	0.000
30-May-06	B3	0.000	0.000	0.000	18.42	0.000	0.79	4.397	0.000	5.71	10.40	0.093	0.000
30-May-06	B4	0.000	0.043	0.000	23.87	0.000	1.29	6.188	0.000	5.98	10.58	0.092	0.000
30-May-06	C1	0.038	0.030	0.008	16.71	0.137	1.83	5.980	0.007	7.04	7.66	0.094	0.000
30-May-06	C2	0.042	0.000	0.011	13.78	0.260	2.97	5.269	0.012	9.07	6.03	0.082	0.000
30-May-06	C3	0.053	0.000	0.011	14.66	0.527	2.50	5.692	0.018	11.37	5.88	0.086	0.000
30-May-06	D1	0.058	0.000	0.006	18.38	0.195	1.73	6.373	0.013	5.40	7.01	0.089	0.000
30-May-06	S1	0.065	0.030	0.011	15.12	0.449	2.55	5.687	0.060	11.87	5.65	0.089	0.000
30-May-06	S2	0.048	0.029	0.011	14.52	0.359	2.45	5.464	0.056	12.33	5.59	0.089	0.000
30-May-06	S3	0.035	0.000	0.010	14.02	0.176	2.07	5.030	0.011	7.74	5.76	0.083	0.000
30-May-06	S4	0.009	0.008	0.013	12.10	0.154	2.31	4.385	0.000	7.52	4.82	0.079	0.000
30-May-06	S5	0.026	0.026	0.014	10.90	0.322	2.68	3.944	0.007	7.62	3.23	0.075	0.000
30-May-06	S6	0.040	0.028	0.011	10.92	0.568	2.97	4.206	0.004	7.93	2.42	0.074	0.000
30-May-06	S7	0.041	0.035	0.013	12.20	0.846	3.75	4.789	0.024	9.82	2.41	0.081	0.000
30-May-06	T1	0.000	0.000	0.026	9.22	0.035	1.97	2.883	0.005	9.03	5.70	0.075	0.000
30-May-06	X1	0.000	0.024	0.000	5.98	0.047	0.86	3.620	0.000	3.97	11.26	0.025	0.000
21-Aug-06	A1	0.000	0.000	0.000	19.69	0.000	1.08	8.641	0.000	5.78	11.43	0.095	0.000
21-Aug-06	A2	0.000	0.039	0.009	22.32	1.002	1.69	8.623	0.219	5.60	16.19	0.079	0.000
21-Aug-06	A3	0.000	0.042	0.000	36.81	0.075	1.30	10.727	0.006	10.17	10.72	0.340	0.021
21-Aug-06	A4	0.000	0.000	0.150	17.41	0.000	3.90	4.085	0.022	4.30	5.15	0.166	0.008
21-Aug-06	B1	0.000	0.000	0.005	26.69	0.000	1.31	10.293	0.000	4.90	9.60	0.096	0.000
21-Aug-06	B2	0.000	0.000	0.006	31.80	0.000	1.01	12.521	0.000	5.79	11.11	0.131	0.000
21-Aug-06	B3	0.000	0.000	0.000	17.56	0.000	0.66	4.251	0.000	4.98	10.26	0.084	0.012
21-Aug-06	B4	0.000	0.031	0.005	24.86	0.000	1.31	6.572	0.000	5.90	10.37	0.090	0.000
21-Aug-06	C1	0.000	0.029	0.006	19.88	0.063	1.22	7.032	0.000	5.88	8.91	0.099	0.000
21-Aug-06	C2	0.000	0.000	0.008	14.76	0.090	1.77	5.870	0.007	6.33	7.95	0.079	0.000
21-Aug-06	C3	0.000	0.000	0.008	17.28	0.130	1.74	7.776	0.028	5.98	7.72	0.091	0.000
21-Aug-06	D1	0.030	0.000	0.000	22.65	0.069	1.60	7.823	0.004	4.90	8.69	0.090	0.000
21-Aug-06	S1	0.027	0.000	0.008	17.42	0.167	1.74	6.466	0.027	8.87	5.92	0.087	0.000
21-Aug-06	S2	0.000	0.031	0.010	17.73	0.130	1.83	6.549	0.013	10.09	6.32	0.094	0.000
21-Aug-06	S3	0.000	0.000	0.009	17.54	0.080	1.61	6.317	0.003	6.72	7.07	0.091	0.000
21-Aug-06	S4	0.000	0.000	0.012	14.85	0.042	1.70	5.460	0.000	6.68	6.84	0.082	0.000
21-Aug-06	S5	0.000	0.000	0.017	12.48	0.160	2.50	4.245	0.005	7.04	4.42	0.081	0.000
21-Aug-06	S6	0.076	0.000	0.011	11.12	0.174	2.91	4.142	0.000	5.87	1.64	0.072	0.000
21-Aug-06	S7	0.000	0.000	0.010	13.06	0.576	3.99	5.887	0.000	13.90	1.81	0.079	0.000
21-Aug-06	T1	0.000	0.026	0.038	11.60	0.035	2.36	3.673	0.006	9.86	6.53	0.087	0.000
21-Aug-06	X1	0.000	0.000	0.000	6.59	0.000	0.82	3.883	0.000	3.49	11.08	0.025	0.000
21-Aug-06	X2	0.000	0.000	0.000	7.91	0.190	1.34	4.417	0.063	4.60	9.59	0.024	0.000
21-Aug-06	X3	0.000	0.000	0.000	8.16	0.218	1.42	4.761	0.042	4.30	12.88	0.032	0.000

Appendix O: Spectral analysis, raw data

Table O1. Raw data for spectral analyses; fluorescence intensity for specified regions on EEMs (Ex/Em, in nm) and absorption.

		Humic-like (230-250/400-440)		*Humic-like 2 (315-340/400-435)*		*Tyrosine-like (270-280/300-310)*		*Tryptophan-like (270-280/340-360)*		*Absorption*		
Date	**Site**	max Int	mean Int	max Int	mean Int	max Int	mean Int	max Int	mean Int	A220	A254	A280
20-Feb-06	**A2**	153.1	82.6	51.6	30.0	44.8	24.9	20.8	10.5			
20-Feb-06	**X2**	43.7	33.0	17.8	15.0	6.0	2.3	7.7	5.0	0.02	0.01	0.00
22-Feb-06	**A1**	15.8	10.8	6.8	4.4	9.7	6.8	4.9	3.9	0.73	0.01	0.00
22-Feb-06	**A4**	20.2	13.3	11.7	8.9	9.0	5.2	6.9	5.4	5.10	0.01	0.01
22-Feb-06	**B1**	11.3	8.1	5.6	4.0	8.8	6.0	6.2	5.1	1.72	0.01	0.00
22-Feb-06	**B2**	13.0	8.0	7.3	5.1	7.0	3.9	4.2	3.2	3.33	0.01	0.01
22-Feb-06	**B3**	18.3	12.5	12.5	8.8	6.6	8.0	5.0	4.0	3.21	0.01	0.01
22-Feb-06	**C1**	105.1	92.2	61.1	53.8	8.9	5.6	17.3	13.4	1.24	0.08	0.06
22-Feb-06	**C2**	173.8	147.8	93.2	84.7	15.0	10.0	27.4	21.5	0.78	0.11	0.09
22-Feb-06	**C3**	231.9	198.8	134.9	118.7	12.0	6.9	35.0	26.2	0.60	0.17	0.13
22-Feb-06	**D1**	140.9	122.3	82.1	72.7	9.2	5.7	22.2	17.6	0.99	0.11	0.08
22-Feb-06	**S1**	171.7	150.6	99.8	88.8	16.2	10.6	30.7	24.8	0.98	0.13	0.10
22-Feb-06	**S3**	136.1	117.7	77.6	68.7	12.7	9.2	22.2	17.1	1.07	0.10	0.08
22-Feb-06	**S4**	136.1	116.8	76.6	68.0	21.1	17.1	34.5	27.5	1.02	0.10	0.07
22-Feb-06	**S6**	212.0	181.7	117.8	106.9	13.4	9.0	33.0	25.3	0.66	0.16	0.12
22-Feb-06	**S7**	298.8	256.6	174.5	158.5	26.1	20.6	53.1	42.0	0.63	0.23	0.17
22-Feb-06	**T1**	53.9	46.0	32.7	28.1	10.5	7.0	11.7	9.9	1.51	0.04	0.03
22-Feb-06	**X1**	22.1	14.4	5.4	3.8	8.9	6.0	5.7	4.3	0.19	0.00	0.00
28-Mar-06	**A1**	14.1	8.2	4.9	3.3	5.8	2.0	3.6	2.1	0.94	0.01	0.00
28-Mar-06	**A3**	15.4	7.9	7.8	5.6	3.9	0.6	4.3	3.1	10.00	0.02	0.01
28-Mar-06	**A4**	11.7	7.5	8.6	6.6	2.1	0.3	3.8	1.9	3.82	0.01	0.01
28-Mar-06	**B1**	8.4	4.6	4.3	2.7	9.2	5.7	3.7	2.3	1.68	0.01	0.00
28-Mar-06	**B2**	8.3	4.4	5.7	3.8	4.9	3.1	2.8	1.8	3.31	0.01	0.01
28-Mar-06	**B3**	9.5	6.0	10.1	6.5	5.9	3.5	2.9	2.1	3.11	0.01	0.01
28-Mar-06	**B4**	10.9	7.0	6.6	4.9	15.6	12.1	12.8	10.5	2.51	0.01	0.01
28-Mar-06	**C1**	130.8	109.9	75.1	66.6	9.6	5.2	20.0	15.2	1.12	0.11	0.08
28-Mar-06	**C2**	209.0	179.1	120.9	108.1	7.9	2.3	31.0	23.0	0.57	0.22	0.17

Table O1 (continued). Raw spectral data.

		Humic-like		*Humic-like 2*		*Tyrosine-like*		*Tryptophan-like*				
		(230-250/400-440)		*(315-340/400-435)*		*(270-280/300-310)*		*(270-280/340-360)*		*Absorption*		
Date	**Site**	max Int	mean Int	max Int	mean Int	max Int	mean Int	max Int	mean Int	A220	A254	A280
28-Mar-06	**C3**	269.8	229.1	161.7	141.3	9.5	2.8	40.6	29.4	0.63	0.16	0.12
28-Mar-06	**D1**	156.8	128.9	86.5	76.1	6.1	1.7	23.0	16.9	0.76	0.13	0.10
28-Mar-06	**S1**	207.4	171.0	115.2	103.3	10.0	4.0	33.4	25.4	0.79	0.17	0.13
28-Mar-06	**S2**	192.7	168.8	113.4	101.1	14.2	7.5	33.5	26.7	0.80	0.16	0.12
28-Mar-06	**S3**	165.5	144.5	97.1	85.8	18.7	12.9	27.6	21.9			
28-Mar-06	**S4**	168.1	146.1	96.5	86.8	10.0	5.0	26.9	19.9	0.75	0.14	0.10
28-Mar-06	**S5**	211.6	181.0	119.5	108.3	10.0	4.1	33.8	25.3	0.67	0.17	0.13
28-Mar-06	**S6**	256.6	216.6	149.2	132.2	13.7	7.1	39.6	30.4	0.53	0.21	0.16
28-Mar-06	**S7**	314.6	272.2	189.9	171.7	15.5	6.8	52.7	40.2	0.52	0.27	0.20
28-Mar-06	**T1**	62.0	52.2	34.3	29.4	6.9	4.3	13.1	10.1	1.28	0.05	0.04
28-Mar-06	**X1**	10.4	5.4	3.3	2.1	5.5	2.2	3.7	2.4	0.19	0.00	0.00
30-May-06	**A1**	16.6	10.4	8.5	5.4	10.8	6.7	8.3	7.0	0.95	0.01	0.00
30-May-06	**A3**	12.1	6.5	8.0	5.8	3.9	2.0	3.9	2.6	10.00	0.01	0.01
30-May-06	**A4**	13.3	8.7	8.8	6.6	8.4	4.9	4.2	3.4	3.78	0.01	0.00
30-May-06	**B1**	6.5	4.1	4.2	2.4	4.6	2.4	2.9	1.8	1.65	0.00	0.00
30-May-06	**B2**	8.8	5.0	5.5	3.9	7.5	5.2	3.4	2.9	3.33	0.00	0.00
30-May-06	**B3**	10.5	6.7	8.6	6.4	4.9	1.8	2.7	1.5	2.79	0.00	0.00
30-May-06	**B4**	8.6	4.9	5.7	4.1	6.6	4.5	3.3	2.4	2.45	0.00	0.00
30-May-06	**C1**	114.4	103.8	68.7	62.0	10.2	6.9	24.1	18.3			
30-May-06	**C2**	217.9	189.4	126.5	115.8	12.2	7.2	36.7	27.9	0.68	0.18	0.14
30-May-06	**C3**	311.1	271.6	197.7	177.7	16.8	10.0	50.2	38.6	0.69	0.29	0.22
30-May-06	**D1**	137.2	118.4	77.1	68.8	6.9	4.1	21.2	16.1	0.89	0.12	0.09
30-May-06	**S1**	229.8	196.1	134.8	119.1	11.8	6.6	36.9	28.3	0.85	0.21	0.16
30-May-06	**S2**	204.0	178.3	120.4	107.2	14.0	8.8	35.5	14.5	0.88	0.18	0.14
30-May-06	**S3**	163.2	142.6	93.3	84.1	11.6	6.7	29.2	21.4	0.95	0.14	0.11
30-May-06	**S4**	177.7	154.2	102.2	91.2	11.3	7.3	31.2	23.3	0.76	0.14	0.10
30-May-06	**S5**	242.1	211.5	142.4	129.0	14.7	8.6	38.5	30.4	0.67	0.20	0.15

Table O1 (continued). Raw spectral data.

		Humic-like (230-250/400-440)		Humic-like 2 (315-340/400-435)		Tyrosine-like (270-280/300-310)		Tryptophan-like (270-280/340-360)		Absorption		
Date	Site	max Int	mean Int	max Int	mean Int	max Int	mean Int	max Int	mean Int	A220	A254	A280
30-May-06	**S6**	320.4	272.3	186.6	171.3	16.0	9.8	53.7	40.4	0.57	0.28	0.21
30-May-06	**S7**	389.4	327.2	234.7	214.6	18.0	9.3	64.1	47.3	0.59	0.34	0.26
30-May-06	**T1**	49.4	43.1	30.1	26.2	4.9	3.5	10.2	8.4	1.13	0.04	0.03
30-May-06	**X1**	8.7	5.0	2.9	1.8	20.9	9.9	3.5	2.5	0.18	0.00	0.00
26-Jul-06	**A1**	2.5	0.0	3.2	1.6	1.7	0.0	0.6	0.0	1.19	0.01	0.00
26-Jul-06	**A3**	7.9	2.7	7.9	5.6	1.8	0.0	2.2	1.0	10.00	0.02	0.02
26-Jul-06	**A4**	8.5	3.5	8.0	5.4	4.5	1.6	3.7	2.3	6.47	0.01	0.01
26-Jul-06	**B1**	4.4	1.5	3.7	2.1	2.4	0.6	1.7	0.7	1.63	0.01	0.01
26-Jul-06	**B2**	11.8	5.4	6.0	4.0	5.6	2.4	5.0	3.4	3.34	0.01	0.01
26-Jul-06	**B3**	10.2	5.5	9.5	6.0	3.1	0.1	2.7	1.7	2.42	0.01	0.01
26-Jul-06	**B4**	5.8	2.1	5.3	3.5	4.2	0.5	1.8	0.8	2.42	0.01	0.01
26-Jul-06	**C1**	60.5	49.6	35.3	29.8	4.8	1.9	11.7	9.7	1.51	0.06	0.04
26-Jul-06	**C2**	117.6	99.4	63.7	56.2	5.6	3.2	18.6	14.4	0.59	0.08	0.06
26-Jul-06	**C3**	254.9	213.2	142.3	125.5	8.2	2.7	36.4	26.2	0.55	0.19	0.14
26-Jul-06	**D1**	65.6	56.0	37.2	32.9	3.8	1.7	11.1	8.7	1.09	0.06	0.04
26-Jul-06	**S1**	150.9	129.1	83.0	71.9	11.4	6.9	28.4	23.2	0.74	0.12	0.09
26-Jul-06	**S2**	124.9	106.4	69.3	59.4	9.0	5.4	23.1	18.6	0.93	0.10	0.08
26-Jul-06	**S3**	96.1	74.9	50.1	43.0	8.4	5.2	17.5	14.7	1.07	0.08	0.06
26-Jul-06	**S4**	88.9	75.8	48.7	42.9	8.4	4.9	14.3	11.6	0.81	0.07	0.05
26-Jul-06	**S5**	156.5	130.4	83.5	74.3	7.4	3.9	22.3	16.7	0.49	0.12	0.09
26-Jul-06	**S6**	239.3	196.0	126.3	113.1	12.5	8.9	35.7	28.0	0.31	0.17	0.12
26-Jul-06	**S7**	483.7	412.1	295.6	266.8	18.0	8.5	81.9	59.9	0.61	0.39	0.28
26-Jul-06	**T1**	52.1	43.3	30.6	26.2	3.2	0.8	8.8	6.3	1.09	0.04	0.03
26-Jul-06	**X1**	5.5	2.5	2.6	1.4	6.8	4.1	4.3	2.5	0.18	0.00	0.00
21-Aug-06	**A1**	9.1	4.9	4.6	2.8	4.7	1.3	2.1	1.3	1.02	0.00	0.00
21-Aug-06	**A2**	74.8	49.5	28.4	22.5	20.1	11.8	17.9	6.7	0.08	0.06	0.05
21-Aug-06	**A3**	10.3	5.2	9.1	6.0	2.1	0.0	3.0	2.2	10.00	0.02	0.02

Table O1 (continued). Raw spectral data.

Date	Site	Humic-like (230-250/400-440) max Int	Humic-like (230-250/400-440) mean Int	Humic-like 2 (315-340/400-435) max Int	Humic-like 2 (315-340/400-435) mean Int	Tyrosine-like (270-280/300-310) max Int	Tyrosine-like (270-280/300-310) mean Int	Tryptophan-like (270-280/340-360) max Int	Tryptophan-like (270-280/340-360) mean Int	Absorption A220	Absorption A254	Absorption A280
21-Aug-06	**A4**	11.1	5.5	8.2	5.9	6.6	2.5	4.5	3.1	6.43	0.01	0.01
21-Aug-06	**B1**	5.2	1.6	3.4	2.2	2.5	0.6	2.0	0.9	1.65	0.01	0.00
21-Aug-06	**B2**	6.8	2.3	5.1	3.3	1.7	0.0	1.8	0.7	3.45	0.01	0.01
21-Aug-06	**B3**	16.4	9.7	9.7	6.8	7.0	3.6	4.9	3.8	2.28	0.01	0.01
21-Aug-06	**B4**	12.7	7.8	7.0	5.1	8.9	5.5	6.4	4.9	2.46	0.01	0.01
21-Aug-06	**C1**	55.1	45.7	31.3	27.1	7.6	5.0	13.2	11.0	1.53	0.05	0.04
21-Aug-06	**C2**	112.7	88.6	58.3	50.5	7.6	4.3	18.4	13.5	0.58	0.08	0.06
21-Aug-06	**C3**	233.8	192.4	124.6	111.8	12.7	6.7	30.3	26.7	0.43	0.18	0.13
21-Aug-06	**D1**	63.9	53.0	36.7	31.2	9.4	7.0	13.4	11.1	1.08	0.05	0.04
21-Aug-06	**S1**	122.4	103.8	66.5	56.1	14.8	11.4	27.3	24.7	0.76	0.10	0.08
21-Aug-06	**S2**	102.2	87.7	58.1	48.8	11.4	7.9	22.3	19.0	0.95	0.08	0.06
21-Aug-06	**S3**	77.1	65.3	44.4	37.3	8.7	5.2	16.4	13.1	1.12	0.07	0.05
21-Aug-06	**S4**	86.3	70.3	46.3	39.1	7.5	3.9	13.9	10.6	0.84	0.06	0.05
21-Aug-06	**S5**	145.1	122.6	79.3	70.2	7.7	3.5	21.2	15.5	0.45	0.11	0.08
21-Aug-06	**S6**	207.0	163.7	102.9	93.3	10.5	6.5	31.7	24.1	0.26	0.14	0.11
21-Aug-06	**S7**	477.1	405.1	285.0	256.9	23.5	13.6	86.8	65.9	0.57	0.36	0.26
21-Aug-06	**T1**	50.3	38.3	28.5	24.5	4.6	1.2	7.5	5.7	1.08	0.04	0.03
21-Aug-06	**X1**	6.5	2.9	2.8	1.5	8.1	1.4	1.8	1.1	0.19	0.00	0.00
21-Aug-06	**X2**	32.5	25.5	16.2	12.7	8.6	3.3	5.8	4.2	0.03	0.02	0.01
21-Aug-06	**X3**	79.2	62.0	36.7	30.1	6.0	2.7	8.6	6.4	0.07	0.04	0.03

Table O1 (continued). Raw spectral data.

		Humic-like (230-250/400-440)		Humic-like 2 (315-340/400-435)		Tyrosine-like (270-280/300-310)		Tryptophan-like (270-280/340-360)		Absorption		
Date	**Site**	max Int	mean Int	max Int	mean Int	max Int	mean Int	max Int	mean Int	A220	A254	A280
17-Oct-06	**C1**	119.5	105.7	74.4	65.7	10.0	5.8	24.0	20.4	1.36	0.13	0.10
17-Oct-06	**C2**	225.1	199.7	140.8	127.8	21.2	14.2	49.3	40.3	0.69	0.23	0.18
17-Oct-06	**C3**	334.2	291.4	220.0	203.4	17.0	8.8	59.8	45.7	0.76	0.36	0.28
17-Oct-06	**D1**	134.1	111.9	81.5	69.5	10.0	6.3	22.1	16.3	0.98	0.13	0.10
17-Oct-06	**S1**	181.0	161.3	112.8	102.2	12.5	6.4	33.2	27.4	1.05	0.21	0.16
17-Oct-06	**S2**	174.0	146.8	102.5	92.9	12.4	6.7	32.6	25.2	1.04	0.19	0.15
17-Oct-06	**S3**	143.7	123.4	87.2	77.0	10.7	6.4	27.4	22.1	1.03	0.16	0.13
17-Oct-06	**S4**	136.3	111.0	77.0	67.4	7.4	3.2	21.2	17.2	0.79	0.14	0.11
17-Oct-06	**S5**	179.9	154.7	108.3	96.6	11.3	4.7	31.3	24.4	0.59	0.20	0.15
17-Oct-06	**S6**	192.5	158.3	107.3	95.4	13.9	10.1	34.6	28.3	0.35	0.18	0.14
17-Oct-06	**S7**	372.0	307.6	215.5	195.0	18.2	11.3	64.9	51.1	0.50	0.31	0.23
17-Oct-06	**T1**	75.7	59.9	39.0	34.4	27.1	14.6	15.5	11.2	1.08	0.07	0.05

Appendix P: Total and dissolved organic carbon, raw data

Table P1. Raw data for TOC/DOC analysis.

Date	***Site***	*TOC*	*DOC*	*Date*	***Site***	*TOC*	*DOC*
		(mg C / L)				*(mg C / L)*	
30-May-06	**A1**	0.37	0.52	21-Aug-06	**A1**	0.12	0.47
				21-Aug-06	**A2**	0.63	0.78
30-May-06	**A3**	0.48	0.51	21-Aug-06	**A3**	0.41	0.62
30-May-06	**A4**	0.51	0.49	21-Aug-06	**A4**	0.39	0.56
30-May-06	**B1**	0.13	0.28	21-Aug-06	**B1**	1.05	0.30
30-May-06	**B2**	0.20	0.24	21-Aug-06	**B2**	0.10	0.82
30-May-06	**B3**	0.30	0.27	21-Aug-06	**B3**	0.33	0.38
30-May-06	**B4**	0.31	0.27	21-Aug-06	**B4**	0.08	0.29
30-May-06	**C1**	3.14	2.91	21-Aug-06	**C1**	1.33	1.48
30-May-06	**C2**	5.18	4.91	21-Aug-06	**C2**	1.83	2.36
30-May-06	**C3**	7.64	7.42	21-Aug-06	**C3**	4.21	4.85
30-May-06	**D1**	3.27	3.06	21-Aug-06	**D1**	1.59	1.44
30-May-06	**S1**	5.69	5.38	21-Aug-06	**S1**	2.51	3.07
30-May-06	**S2**	5.20	4.79	21-Aug-06	**S2**	2.48	2.11
30-May-06	**S3**	4.14	3.79	21-Aug-06	**S3**	1.91	1.96
30-May-06	**S4**	4.40	4.17	21-Aug-06	**S4**	1.95	1.91
30-May-06	**S5**	6.19	5.70	21-Aug-06	**S5**	3.09	3.39
30-May-06	**S6**	8.40	7.42	21-Aug-06	**S6**	4.34	3.96
30-May-06	**S7**	10.98	9.70	21-Aug-06	**S7**	12.20	10.18
30-May-06	**T1**	1.26	1.17	21-Aug-06	**T1**	1.12	1.43
30-May-06	**X1**	0.04	0.07	21-Aug-06	**X1**	0.05	0.17
				21-Aug-06	**X2**	0.47	0.64
				21-Aug-06	**X3**	0.53	0.79