Influence of climate and land use on nutrient and bacterial dynamics in surface waters of the Lower Fraser Valley, British Columbia

by

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ABSTRACT

It is understood that intensive agricultural activities can adversely impact surface-water quality resulting in risks to ecosystem and human health. What is less clear are the links between agricultural land use (type and intensity), environmental conditions and surface-water quality at varying spatial and temporal scales. There are also challenges with detecting agricultural influence on surface waters in a timely and accurate manner. This is of concern in the Lower Fraser Valley as this region has experienced significant agricultural intensification and population growth in recent years. This study examined influences of agricultural land use, climate and hydrology on water quality in three watersheds to identify land-use practices and environmental conditions producing the greatest risk of contamination. This was accomplished through an intensive surface-water sampling program to assess nutrient and bacterial dynamics in the Hatzic, Elk Creek and Salmon watersheds, combined with hydrometric and meteorological monitoring from 2002-2005. Spectroscopic techniques (absorption and fluorescence) were also evaluated as tools to detect and quantify agricultural influence.

Consistent correlations between agricultural land use and contamination (nutrient and bacterial concentrations) were observed across all watersheds. Seasonal trends were consistent, with nutrient concentrations peaking during winter months (illustrating strong hydrological control over mobilisation and transport) and bacterial concentrations peaking during summer months (illustrating the supply-constrained nature of bacterial stores). Contaminant concentrations correlated with measures of agricultural intensity. Livestock operations represented the highest-risk land use for contamination, with even small operations producing observable impacts on water quality. Temporally, the greatest risk of bacterial contamination was associated with storm events preceded by periods of dry weather during summer months.

Absorption and fluorescence were effective measures of agricultural influence as they quantify and characterize agriculturally-derived dissolved organic matter. Advantages of these techniques include rapid sample processing, minimal requirements for sample treatment and volume. Further, they provide qualitative information regarding water quality, water source and land use that is not available from nutrient or bacterial analyses alone. These techniques do not accurately detect contaminants in areas with minimal agricultural influence and therefore are limited as direct indicators of bacterial or nutrient concentrations.
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# LIST OF ABBREVIATIONS AND COMMON TERMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
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<tbody>
<tr>
<td>Aₙ</td>
<td>Absorbance at wavelength n</td>
</tr>
<tr>
<td>ALR</td>
<td>Agricultural land reserve</td>
</tr>
<tr>
<td>CDOM</td>
<td>Chromophoric dissolved organic matter</td>
</tr>
<tr>
<td>CFU</td>
<td>Colony-forming units</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>EMMA</td>
<td>End-member mixing analysis</td>
</tr>
<tr>
<td>Ex/Em</td>
<td>Excitation-emission wavelength pair</td>
</tr>
<tr>
<td>EA</td>
<td>Enumeration area</td>
</tr>
<tr>
<td>EEM</td>
<td>Excitation-emission matrix</td>
</tr>
<tr>
<td>FVRD</td>
<td>Fraser Valley Regional District</td>
</tr>
<tr>
<td>GVRD</td>
<td>Greater Vancouver Regional District</td>
</tr>
<tr>
<td>HACCP</td>
<td>Hazard analysis critical control points</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LFV</td>
<td>Lower Fraser Valley</td>
</tr>
<tr>
<td>MPN</td>
<td>Most probable number</td>
</tr>
<tr>
<td>NPS</td>
<td>Non-point source</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>PCA</td>
<td>Principle components analysis</td>
</tr>
<tr>
<td>rₛ</td>
<td>Spearman rank correlation coefficient</td>
</tr>
<tr>
<td>S</td>
<td>Spectral slope</td>
</tr>
<tr>
<td>STP</td>
<td>Sewage treatment plant</td>
</tr>
<tr>
<td>SUVA</td>
<td>Specific ultraviolet absorbance</td>
</tr>
<tr>
<td>Tₙ</td>
<td>Tryptophan fluorescence intensity at wavelength n</td>
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<tr>
<td>Tyrₙ</td>
<td>Tyrosine fluorescence intensity at excitation wavelength n</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
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encouragement, when it was needed most. I can’t thank you enough, and I look forward to the lifetime of
opportunities ahead of us.
1. **Introduction**

1.1. **Background**

Canada's agricultural sector has experienced significant growth in recent decades due to technological advances that have allowed increased crop and livestock production on a relatively stable agricultural land base. This sector has also grown substantially in British Columbia (BC), generating approximately $2.4 billion in revenue in 2004 (BC Ministry of Agriculture and Lands, 2006). Since 1971, crop production in BC has increased, while total area under field crops and vegetables has remained constant or has decreased. Similarly, livestock numbers have increased during this time. Between 1971-2001, cattle, poultry and swine numbers in the province increased by 43%, 140% and 111% respectively, again, with little change in total area under livestock. Such increases in agricultural intensity across Canada have generated concerns regarding the impact of farming activities on both ecosystem and human health (Coote and Gregorich, 2000; Chambers et al., 2001; Environment Canada, 2001). An increase in crop yields per unit area requires more intensive applications of mineral fertilizers and agrichemicals, resulting in the accumulation of nutrients and pesticides in the soil profile. This material is then available for transport to groundwater or nearby surface-water systems. Similarly, the growing productivity of livestock operations results in localized surpluses of animal manure which can act as significant sources of nutrients and pathogens\(^1\). In both cases, the assimilative capacity of the land base decreases as intensity increases.

The Lower Fraser Valley (LFV) in southwestern British Columbia is one of the most productive agricultural areas in Canada, and is the most intensively farmed region in BC. In recent years, the intensity of both livestock and crop agriculture in this region has increased substantially, with the most significant change observed in poultry numbers, which increased by more than 80% between 1991-2001 (Schreier et al., 2003). This has resulted in significant nutrient surpluses in watersheds in the region and impairment of surface water and groundwater resources as a result of nutrient and bacterial loading (Berka et al., 2001; Schreier et al., 2003; Hii, 2004). The Fraser Valley is also experiencing significant urban development and population growth. By 2031, the population of the Fraser Valley Regional District

\(^1\) In this document, the term "pathogen" is used to refer to organisms (bacteria, protozoa, viruses, etc.) that cause disease in their hosts (humans or animals). Where appropriate, a distinction is made between human and animal pathogens.
Chapter 1

is projected to increase by 82% (from 254,229 in 2003 to 462,666), with the greatest growth forecasted to
take place in Abbotsford, Mission and Chilliwack (82%, 92% and 84%, respectively) (Urban Futures,
2005).

As a result of this growth and agricultural intensification, drinking water supplies in the LFV are
under increasing pressure. Currently, there are approximately 494 public drinking water systems within
the boundaries of the Fraser Health Authority, which spans from Delta to Boston Bar (Zubel, 2005). At the
end of 2004, the Health Authority classified 116 of these systems as representing a potentially “high risk”
to human health, and 40 of the systems in this region were under boil water advisories. Nineteen of these
advisories were issued for systems with surface-water sources (Zubel, 2005).

1.2. Drinking water and public health in British Columbia

When compared to other regions across Canada, BC has historically had the highest incidence of
enteric (waterborne and foodborne) illness in Canada (BC Auditor General, 1999). In fact, between 1980-
2004, there were 29 recorded outbreaks of waterborne disease in the province (BC Provincial Health
Officer, 2001). The majority of these (93%) were associated with rural drinking-water systems deriving
water from streams, lakes or reservoirs. Such surface water sources supply approximately 76% of the
province's drinking water (BC Provincial Health Officer, 2001). The human health risks associated with
surface-water sources are generally considered higher than for groundwater due to the susceptibility of
the former to influence by local land-use activities and meteorological conditions. In particular, the impact
of agricultural activities on surface-water quality in BC has been noted (BC Auditor General, 1999; Coote
and Gregorich, 2000; Hooda et al., 2000; BC Provincial Health Officer, 2001).

Given BC’s dependence on surface sources for drinking water, there is a clear need for effective
protection of surface-water sources in BC. In 2003, there were roughly 340 boil-water advisories in place
at one time across the province, representing more than 10% of the province’s water systems
(Christensen, 2003). A report by the province’s Auditor General noted the importance of source-
watershed protection, and concluded that the Province was not adequately protecting drinking-water
sources from human activities (BC Auditor General, 1999). The need for improved source protection was
also noted by the Provincial Health Officer (BC Provincial Health Officer, 2001) and by an independent
drinking water review panel (Drinking Water Review Panel, 2003). As a result, new legislation and
regulations (the Drinking Water Protection Act and Regulation) were enacted in 2003. This legislation
recognizes the need for source-watershed protection and requires water suppliers to conduct "source-to-tap" assessments to identify contamination risks and to prepare mitigation plans to address these risks. The legislation also requires routine monitoring commensurate to the risk of contamination based on these assessments.

1.3. Research context

In the LFV, agricultural activities represent a significant threat to water quality. Several studies have assessed the influence of agricultural land use on surface-water quality (Schreier et al., 1999; Berka et al., 2001; Schreier et al., 2003; Schreier et al., 2004; Smith, 2004) and groundwater quality (Liebscher et al., 1992; Wassenaar, 1995; Zebarth et al., 1998; Hii, 2004) in this region. However, few have addressed the combined ecosystem and human health risks associated with agricultural intensification. In other words, there have been few studies to assess nutrient and bacterial contributions to surface waters over a range of spatial and temporal scales in this region. Further, little research has been conducted to assess the influence of agricultural intensity on the timing and degree of contaminant contributions to surface waters. As noted by Environment Canada (2001) in an assessment of threats to surface-water quality, there are several gaps in our current understanding of surface-water contamination by nutrients and waterborne pathogens. In terms of nutrients, these included: 1) availability of monitoring data and 2) the need for data regarding trends and processes at different spatial scales (i.e., from plot to region). In terms of waterborne pathogens, gaps included: 1) a need to identify baseline trends in surface-water pathogen concentrations to understand the impact of agricultural activities, 2) identification of contamination "hot spots" in agricultural watersheds to support targeted monitoring and 3) improved understanding of environmental influences on pathogen dynamics. Similar gaps with respect to pathogen loading were identified by the BC Provincial Health Officer in an assessment of drinking-water quality across the province (BC Provincial Health Officer, 2001).

Finally, Environment Canada (2001) noted several knowledge needs with respect to agricultural contamination of surface waters and groundwaters. Specific to agricultural watersheds, these included: 1) a better understanding of the influence of different agricultural activities on contaminant production and mobilization, 2) a better understanding of the links between hydrological conditions and agricultural contaminant dynamics over varying spatial and temporal scales, and 3) a more effective approach to water-quality risk assessment for point-source and non-point-source (NPS) contaminant loading, and for
cumulative effects. Similar gaps in terms of contamination processes and monitoring data have also been noted by the BC Auditor General (1999), Smith and McRae (2000), Chambers et al. (2001), the BC Provincial Health Officer (2001) and Krewski et al. (2002).

This thesis attempts to address many of the gaps described above by taking a multidisciplinary approach to the issue of surface-water contamination in agricultural watersheds. Recognizing the link between issues of environmental contamination and public health, a collaborative project was initiated with the Institute for Resources, Environment and Sustainability (IRES) and the BC Centre for Disease Control (BC CDC). The purpose of this collaboration was to improve understanding of the link between environmental variables, land-use activities and potential threats to human and ecosystem health. Another objective of the thesis was to assess novel monitoring techniques for the detection of agricultural influence to support rapid and accurate detection of agricultural contamination. In order to develop a regional picture of the influences of land-use on surface-water quality, research was conducted in three agricultural watersheds in the LFV. The multi-watershed approach was chosen in order to minimize the effects of site-specific variables on the trends and correlations observed and to identify consistent patterns and mechanisms of agricultural influence across several sites.

Specifically, this thesis aims to accomplish the following objectives:

1) Develop an improved understanding of the link between agricultural land-use practices and nutrient and bacterial dynamics in surface waters in agricultural watersheds by:
   a) Capturing baseline data for bacterial concentrations in surface waters in forested regions of agricultural watersheds in the Lower Fraser Valley
   b) Assessing bacterial contributions from agricultural activities through a comparison with baseline data
   c) Quantifying the link between nutrient and bacterial dynamics in surface waters
   d) Assessing the link between agricultural intensity and the degree of surface-water impairment
   e) Gaining an improved understanding of the role of agricultural activities in cumulative impacts to surface-water quality

2) Assess the influence of meteorological conditions on nutrient and bacterial dynamics in surface waters in agricultural watersheds, by:
   a) Assessing the link between meteorological and hydrometric parameters and surface-water quality at different temporal scales
   b) Identifying periods of high risk in terms of surface-water impairment by assessing seasonal trends in nutrient and bacterial cycling in surface waters
c) Assessing the consistency of these trends across several watersheds to determine if the results are scalable to the regional level

3) Assess spectroscopic techniques for the detection of agricultural influence on surface water quality in order to support a more proactive, risk-based approach to surface-water quality management by:
   a) Assessing the utility of absorbance and fluorescence spectroscopy for detecting agricultural contaminants (nutrients and bacteria)
   b) Assessing the potential for these techniques to provide additional information regarding contaminant sources and mechanisms of mobilization and transport to surface waters

Another objective of this project was to test field-based spectroscopic sensors as a mechanism for real-time monitoring of agricultural influence. However, as described in Appendix A, technological and logistical difficulties prevented this evaluation.

1.4. Thesis organization

The overall aim of this thesis to identify the land-use activities and environmental conditions which lead to the greatest risk of nutrient and bacterial contributions to surface waters, and to determine if these results are scalable to the LFV and other regions by assessing trends across multiple watersheds. Further, this thesis provides a preliminary assessment of spectroscopic techniques which have significant potential for rapid and sensitive monitoring of surface-water contamination, particularly in agricultural environments.

The remainder of this thesis is divided into 7 chapters. Chapter 2 provides the context for this work by summarizing the relevant literature. This includes a review of historical agricultural land-use trends in BC, a discussion of agricultural contaminants and their sources and mechanisms of transport, an overview of drinking-water quality issues in the province and a review of existing water-quality monitoring tools and technologies. This is followed by a description of laboratory and field methods in Chapter 3.

Chapters 4 and 5 describe the results of an intensive sampling program conducted in the Hatzic, Elk Creek and Salmon watersheds from 2002-2005. Chapter 4 focuses on the impact of moderate-intensity agriculture on surface-water quality in the Hatzic watershed, and describes the influence of meteorological and hydrological conditions on contaminant mobilization and transport. Chapter 5 compares surface-water impairment across three watersheds with varying levels of agricultural intensity.
to assess the implications of increasing agricultural production on a stable land base in terms of water quality.

Chapters 6 and 7 outline the results of the evaluation of absorbance and fluorescence spectroscopic techniques, respectively, for the detection of agricultural influence on surface waters. Chapter 6 describes the potential of absorbance spectroscopy as both a qualitative and quantitative tool that has several advantages over traditional monitoring technologies, including small sample size, minimal sample preparation and rapid analysis. Chapter 7 provides a similar assessment of fluorescence techniques. Finally, Chapter 8 provides an integrated discussion regarding the conclusions and implications of this work and areas for future research.
2. Literature review

2.1. Introduction

Farming activities in agriculturally dominated watersheds have the potential to introduce a variety of contaminants into local surface waters. These include nutrients from fertilizers (chemical or manure), animal and human pathogens from livestock wastes, metals, pesticides, herbicides and endocrine (hormone) disrupting substances. The potential for surface water impairment is a function of the type and intensity of agricultural activity, and is directly influenced by local geophysical, hydrological and meteorological conditions.

The purpose of this chapter is to review the current literature regarding surface water contamination in agricultural watersheds and the potential use of spectroscopic techniques to detect and quantify such contamination. This chapter begins with an overview of trends in agricultural activity in the Lower Fraser Valley and describes the vulnerability of water resources in the region to agricultural contaminants. The second section describes agricultural contaminants in greater detail and traces their fate from sources on the land surface, through mobilization and transport processes to their delivery to, and cycling within, surface waters. Current monitoring methodologies and techniques for these contaminants are also reviewed, and their strengths and weaknesses are discussed. The chapter concludes with a review of spectroscopic techniques as tools for water-quality assessments.

2.2. Agriculture in the Lower Fraser Valley

2.2.1. Overview

The Lower Fraser Valley (LFV, see Figure 2-1) contains the most productive and intensively farmed agricultural land in British Columbia. To understand the value of this region to the province's economy, and the dynamics of land use change in recent years, it is instructive to review statistical data collected through the Agricultural Census of Canada, conducted every 5 years (2001 being the most recent). The following review is based on data extracted from the Agricultural Census of Canada for the LFV from 1986-2001 by Schreier et al., (2003) for 13 municipalities (Langley, Richmond, Surrey, Chilliwack, Delta, Matsqui, Agassiz, Abbotsford, Mission, Maple Ridge, Pitt Meadows, Nicomen and Burnaby). These fall within the greater Fraser Valley which covers a total of 1.7 million ha, with
approximately 129,210 ha zoned as Agricultural Land Reserve (ALR).

Figure 2-1 - Map of the Lower Fraser Valley with census enumeration areas. Note that Richmond, Langley, Matsqui and Chilliwack include several enumeration areas (East and West Richmond, North, Central and South Langley, North, South and West Matsqui and East and West Chilliwack).

In 2001, the agricultural sector in British Columbia accounted for over 30,000 jobs\textsuperscript{2} and generated $2.22\textsuperscript{3} billion in gross farm receipts (GFR's; a measure of total revenue generated by agricultural holdings). Of this total, $1.42 billion (approximately 64\%) was generated in the LFV, a region that contains only 3.5\% of the total farmed area in BC. Farm land occupies 83,308 ha within this region, with approximately 39,700 ha in the Greater Vancouver Regional District (GVRD) and 48,700 ha in the Fraser Valley Regional District (FVRD). This is less than the area of the ALR, as much of the ALR is held for conservation, rural residential or recreational uses. Across the region, 62\% of farm land is under crops, while the remainder falls under other uses\textsuperscript{4} (17\%), unimproved pasture (14\%) and improved pasture (7\%).

Compared to the rest of the province, the LFV is unique in a number of ways. Average farm size is much smaller, at 16 ha compared to the provincial average of 128 ha [and a national average of 274 ha

\textsuperscript{2} Including 1,900 jobs in aquaculture.
\textsuperscript{3} For this analysis census data are provided for illustrative purposes and are rounded for clarity
\textsuperscript{4} Land under farm buildings, barnyards, lanes, home gardens, greenhouses, woodlots, sugarbush, bogs, marshes, etc.
The relatively high productivity and agricultural intensity of the region is illustrated by the GFR’s per hectare, which at nearly $16,200 are almost 20 times higher than the provincial average. Per-farm GFR’s average $259,293 and are more than twice the provincial average ($109,540). Finally, profitability in terms of return on operating expenses was approximately 50% greater for LFV farms (15.5% return) when compared to the provincial average (10.2%).

While it is important to note that these average values mask significant variability among municipalities in the LFV, the above data illustrate the high productivity, intensity and profitability of agricultural land in the LFV relative to the rest of the province.

2.2.2. Land-use change: 1986-2001

Between 1974-1975, the Agricultural Land Reserve (ALR) was established in British Columbia to preserve agricultural land for farming purposes and prevent encroachment by urban land uses (Agricultural Land Commission, 2004). As a result, the total amount of agriculturally zoned land has remained relatively constant at approximately 4.7 million ha (this has changed slightly as a result of applications for rezoning). However, the type and intensity of farming practices has evolved significantly in recent years.

Significant changes in the economic and competitive landscape in the agriculture sector have forced the industry to adapt in order to remain competitive and viable. Free trade agreements have opened new markets for Canadian products, but have also led to increased competition from international suppliers, resulting in significant downward pressure on prices in local markets, particularly for commodity products. This downward pressure, combined with increasing costs of production (labour, property, farm inputs, etc.), has resulted in the amalgamation and intensification of farming operations to ensure maximum yield per unit area (Artemis Agri-Strategy Group, 2001a). A similar trend in declining farm numbers and increasing productivity was observed in all Canadian provinces between 1996-2001 (Statistics Canada, 2001).

In the past 20 years, there have been significant changes in agricultural production in the LFV. The total number of farms in the region increased steadily from 1986 to 1996, with a rise in hobby farms (horses and ponies), field crops, greenhouses and tree fruit and berry operations. Between 1996 and 2001; however, there was a nearly 13% drop in the number of farms, accounted for mainly by lower
numbers of horse and pony, cattle and swine operations while the number of field crop, poultry, dairy and berry operations remained relatively constant. As the total amount of agricultural land has remained relatively stable, this indicates a trend towards amalgamation of farming operations in the region, primarily driven by a need to increase economies of scale to remain competitive in local and international markets (Artemis Agri-Strategy Group, 2001b).

There has also been a trend towards higher stocking densities (animals per farm) across the LFV. Between 1991-2001, the number of animals per farm in the LFV increased by approximately 25%, 50%, 70% and 75% for cattle, pigs, dairy cows and chickens, respectively (Schreier et al., 2003). This is partially explained by decreasing farm numbers, but is also attributable to growth in the total number of animals over this time (particularly chickens, as described below).

Gross farm receipts have increased from 1986-2001 by 146% (~$577 million to ~$1.42 billion), with total farm expenses keeping pace at 145% (~$500 million to ~$1.2 billion). Due to consolidation and increasing intensification, the average profit per farm in the LFV has increased markedly from $21,143 in 1986 to over $36,610 in 2001 (adjusted for inflation to 2001 dollars). There has been a commensurate increase in returns per hectare, with values growing from $1,341/ha in 1986 to $2,260/ha in 2001 (2001 dollars). Average return per farm and return per hectare in the LFV are 1.6 and 11.9 times the provincial averages, respectively.

The two most significant changes to the type of agricultural practices in the LFV in the past 20 years have been: 1) a major increase in total poultry numbers, and 2) a significant expansion in the total land under greenhouse operations. While the numbers of cattle, sheep and pigs in the region have generally decreased, and horses and dairy cows have shown moderate increases (10-20%), the number of chickens in the region has grown by 124% (from 6.8 million to 15.3 million). Poultry farm numbers during this time have remained relatively constant, resulting in average current stocking densities of 11,130 birds per farm vs. 4,870 per farm in 1986.

Greenhouse operations have also expanded significantly due to growth in year-round demand for greenhouse vegetables and flowers both domestically and in the United States. The total area under glass greenhouses has increased by almost 300% from 935 000 m² in 1986 to 3.6 million m² in 2001. The most significant growth took place between 1996 and 2001, and has been concentrated in Delta, Langley and Matsqui (which account for almost two thirds of total area under greenhouses in the LFV).
The changes in agricultural intensity and type described above have the potential to influence surface water and groundwater quality in the LFV (particularly due to the high nutrient concentrations of poultry manure, described below). Groundwater contamination is of particular concern due to the high susceptibility of local aquifers to non-point source contamination and the reliance by the local population on groundwater for drinking and residential uses (Liebscher et al., 1992; BC Provincial Health Officer, 2001; Hii, 2004). However, attention has more recently turned to surface water contamination for several reasons. Firstly, in many communities, local surface water sources are used as drinking-water supplies. Also, the surface water streams in the region provide approximately 65% of the habitat in the LFV for Fraser River Coho salmon, and 85% for chum salmon, generating concerns that water quality impairment arising from agricultural land uses may impact the health of these fish stocks (Fraser Basin Council, 2001). Finally, in many locations there is a strong coupling between surface water and groundwater sources, meaning that contaminants in surface waters can affect groundwater systems and vice versa (Berka et al., 2001).

The changes in land use described above have resulted in the development of significant nutrient surpluses in the LFV. Schreier et al. (2003) used nutrient budgets and land-management data from Statistics Canada's Census of Agriculture to assess trends in nutrient surpluses in the LFV over time (1991-2001). A comparison of agricultural inputs to calculated losses and removals illustrated that >65% of census enumeration areas in the LFV have nitrogen (N) surpluses of >100 kg·ha⁻¹·yr⁻¹, and a similar proportion had phosphorus (P) surpluses of >50 kg·ha⁻¹·yr⁻¹. Zebarth et al. (1998) constructed N budgets for typical poultry operations and raspberry fields, which are commonly the receiving environments for poultry wastes. It was noted that not only are the rates of waste production increasing (due to growing numbers of animals), but the inputs of nutrients to the region as a whole are also increasing. The latter issue is a result of the marked growth in the poultry industry. As chicken feed is not grown locally, significant volumes are imported annually. Because chicken manure is managed locally, this results in substantial net increase in nutrient stores in the LFV. This is in contrast to cattle feed, a large proportion of which is grown locally.

The impact of growing nutrient surpluses is exacerbated by changing cropping patterns. In regions of the LFV where chicken operations are common, there has also been a trend towards increasing small fruit (raspberries, strawberries, etc.) production. These crops generally require well-drained soils, are planted in wide rows, and have lower nutrient requirements than corn or grasses (Hii,
2004). As a result, the exposure of local groundwaters and surface waters to contamination by fertilizer and manure from these operations has increased.

2.3. Susceptibility of water resources to contamination in the LFV

This section describes the regional geophysical and meteorological characteristics of the LFV, as they play an important role in surface water and groundwater contamination.

2.3.1. Surficial geology and aquifer vulnerability

The LFV is underlain by a complex series of Quaternary deposits reaching depths of up to 300 m. Relatively impermeable tills, deposited during periods of glacial advance, are interspersed with more permeable glaciofluvial deposits from interglacial periods. Low-permeability marine and glaciomarine sediments are observed at depth and throughout the Quaternary sequence in low-lying areas near the coast, as a result of isostatic depression during glacial advances (Dakin, 1993).

Many aquifers in the region are found within thick sandy or gravelly glaciofluvial deposits that extend to the surface, and are thus susceptible to influence by agricultural activities. The BC Ministry of Water, Land and Air Protection developed a classification system that ranks aquifers based upon their susceptibility to contamination and the level of local development and demand (Kreye and Wei, 1994). Of the 6 high-demand aquifers in the region (those with > 20 domestic wells per square kilometre), 4 are classified as “highly vulnerable.”

Recent studies have documented the impairment of groundwater resources in this region. Wassenaar (1995) used an analysis of N and oxygen (O) isotopes to assess the sources, mechanisms and timing of groundwater contamination in the Abbotsford aquifer. In this study, nitrate (NO\(_3^-\)) values in domestic wells exceeded 150 mg·L\(^{-1}\); significantly higher than the 45 mg·L\(^{-1}\) NO\(_3^-\) drinking water quality guideline recommended by Health Canada.

In the same study, an analysis of tritium (a radioactive isotope of hydrogen) indicated that groundwater in the upper aquifer was less than 10 years old, indicating a rapid recharge rate. Using the distinctive isotopic signatures of poultry manure, chemical fertilizers and septic wastes, it was determined that poultry manure was the primary source of NO\(_3^-\)-N to the aquifer. An analysis of oxygen isotopes (δ\(^{18}\)O) also indicated that nitrification took place soon after the application of manure in the summer months, but that the subsequent transport of NO\(_3^-\) to the aquifer was accomplished during heavier
autumn rains (based on the $\delta^{18}$O signatures of summer vs. fall rains). This supports the hypothesis that there is a direct and rapid link between land management activities and groundwater quality in the region. Using similar techniques, Mitchell et al. (2003) attributed groundwater contamination in deep wells in northern Washington State to poultry operations in the LFV, while contamination of shallower wells was associated with local agricultural activities.

In another assessment of $\text{NO}_3^-$ contamination in the Abbotsford aquifer, Zebarth et al., (1998) monitored 35 piezometers and observed that $\text{NO}_3^-$ concentrations at 15 of these sites never dropped below the Health Canada guideline of 10 mg·L$^{-1}$ $\text{NO}_3^-$-N, while only 12 sites had more than half of the samples under the guideline. Hii et al. (2004) conducted a review of groundwater contamination in several LFV aquifers that serve approximately 120,000 residents (including Chilliwack, Abbotsford and Matsqui). They noted total N (nitrate + nitrite) levels of over 30 mg·L$^{-1}$, along with guideline exceedences for several metals and organic contaminants.

2.3.2. Climate

Regional precipitation patterns play a significant role in the dynamics of water quality, particularly for surface waters. Precipitation in the LFV is highly seasonal (Figure 2-2), with the majority falling during the late autumn and winter months. It is during this time that contaminants on the land surface are susceptible to mobilization and transport to surface streams and aquifers.
Many studies have noted the role of this seasonal climatic regime on water quality in the LFV (Hall et al., 1991; Schreier et al., 1999; e.g., Berka et al., 2001; Smith, 2004; Macdonald, 2005). Hall et al. (1991), in a review of water quality data throughout the Fraser River Basin, observed a dilution effect during winter months for major cations. However, Berka et al., (2001) and Smith (2004) noted that concentrations of $\text{NO}_3^-$ and orthophosphate ($\text{PO}_4^{3-}$) and bacteria (total and fecal coliform) during wet season sampling in the Sumas River watershed were consistently higher than dry season values. A similar trend was observed in the Elk Creek watershed by Schreier et al. (2004) for nutrients in surface waters, with peaks in concentration generally occurring in October or November, the time during which the first heavy rains of the season mobilize surface nutrient sources. Heavy rains throughout the winter months resulted in continued loading to surface waters; however, a seasonal hysteresis was evident as nutrient sources were depleted over time (local regulations prohibit application of manure to agricultural fields once heavy rains begin in autumn).

Shaw and Tuominen (1998) also described seasonal trends in surface water fecal coliform levels. During summer months, bacterial concentrations showed a marked decrease at several sites along the Fraser River from Mission to the Fraser River Estuary. This seasonal depression in coliform numbers was
attributed to lower rainfall and improved chlorination of effluent from sewage treatment plants. As
described below, the influence of rainfall on water quality depends largely on site-specific factors and
processes (contaminant type, sources, transport pathways, groundwater and surface water interactions,
etc.), and it is therefore difficult to describe this influence in general terms in the LFV.

2.4. Nutrients

This section provides an overview of nutrient sources in agricultural operations and describes the
processes governing their mobilization and transport to surface waters. This is followed by a discussion of
the ecological and human health risks associated with nutrients. The focus of this section is on N and P,
due to their relative abundance (arising from human inputs), and their impact on biological productivity
and human and ecosystem health.

2.4.1. Nutrient sources in agricultural watersheds

Nutrients are added to agricultural fields in the form of chemical fertilizer, manure, sewage sludge
and industrial waste products in order to replace elements essential for plant growth and ensure
maximum yield for a given crop. These elements include N, P, potassium (K), calcium (Ca), magnesium
(Mg) and sulphur (S) and some metals, including iron (Fe), manganese (Mn), zinc (Zn), boron (B),
chlorine (Cl), cobalt (Co) and copper (Cu). In agricultural areas, manure is also applied to fields as a
means of disposal in regions with high-intensity livestock operations. In the LFV, a moderate market
exists for selling these wastes as fertilizer to nearby regions that are in overall nutrient deficit. Since the
early 1990's, the Sustainable Poultry Farming Group has been transporting poultry manure to nutrient-
poor regions, initially to Merritt, and more recently to Delta (Schreier et al., 2003). However, this is not
feasible for all operators as the cost effectiveness of this option depends on manure type (nutrient
concentration per unit weight), operation size (and the potential for economies of scale), availability of
processing facilities and transport distance (Wohl, 1996).

In British Columbia, manure is commonly used as a component of the annual fertilization
process. For field crops, manure can account for up to 75% of a crop's total N requirements (BC Ministry
of Agriculture Food and Fisheries, 2004). The nutrient and moisture contents of different types of manure
are outlined in Table 2-1. While actual values vary depending on feeding strategies, storage techniques
and the age of the manure, the data illustrate two important characteristics of these materials: 1) their
high moisture content (which makes transport out of the region financially impractical) and 2) the substantially higher nutrient content of poultry manure relative to other livestock. This is particularly relevant in the LFV where poultry production has undergone significant expansion in recent years, as described above.

Table 2-1 - Typical moisture content and nutrient content of various manures on a wet-weight basis (modified from BC Ministry of Agriculture, Food and Forests, 2004)

<table>
<thead>
<tr>
<th>Manure</th>
<th>Moisture Content (%)</th>
<th>Total N Content (kg/t)</th>
<th>Total P₂O₅ Content (kg/t)</th>
<th>Total K₂O Content (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beef (solid)</td>
<td>68</td>
<td>4.2</td>
<td>4.8</td>
<td>8.2</td>
</tr>
<tr>
<td>Dairy (solid)</td>
<td>77</td>
<td>3.9</td>
<td>3.4</td>
<td>9.0</td>
</tr>
<tr>
<td>Dairy (liquid)</td>
<td>91</td>
<td>2.9</td>
<td>2.1</td>
<td>4.5</td>
</tr>
<tr>
<td>Swine (covered)</td>
<td>93</td>
<td>6.3</td>
<td>3.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Poultry (broiler)</td>
<td>25</td>
<td>31.6</td>
<td>22.8</td>
<td>12.2</td>
</tr>
<tr>
<td>Poultry (layer)</td>
<td>35</td>
<td>22.8</td>
<td>29.2</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Manure management practices vary by region in BC; however, provincial statistics provide a good indication of how they may contribute to surface water and groundwater contamination, particularly when considered in the context of other Canadian provinces. In BC, most livestock operations (79.7%) apply excess manure to local fields during the spring, just prior to the growing season, to ensure uptake rates are maximized (Beaulieu, 2004). However, nearly 25% of livestock farms apply manure during the late fall and winter, when rates of uptake are lowest and total precipitation and precipitation intensities are highest (Beaulieu, 2004). A review of manure storage practices across Canada (Statistics Canada, 2003) revealed that BC had the highest percentage of farms (43.2%) with no manure storage facilities (liquid or solid). This was 19% higher than the national average.

The timing of manure incorporation into soils also influences the degree to which nutrients (and pathogens) will be available for transport to nearby surface waters. In BC, 68.7% of farms (representing 55.4% of all manure produced in the province) delayed incorporation of manure into the soil for longer than 7 days, compared to the national average of 52.4% (Beaulieu, 2004). As demonstrated by Mueller et al. (1984), early incorporation can result in more than a 20-fold decrease in the amount of nutrients exported from agricultural fields.
Commercial fertilizers are also used to augment field nutrient levels over and above manure inputs. In 2001, 61.6% of BC field crop producers applied commercial fertilizers, compared to the national average of 74.5% (Korol, 2003). This lower value is likely explained by the fact that much of the province’s crop production is located in the LFV where the significant nutrient surplus from livestock operations reduces the need for commercial nutrient inputs.

Aerial deposition is also an important source of nutrient accumulation. While losses to the atmosphere do occur, atmospheric interactions result in a net increase of N in soils. Brisbin (1995) developed a nutrient balance model for the LFV and identified two components of atmospheric nitrogen input: 1) background deposition and 2) return flow, which was assumed to be 30% of the volatilized nitrogen (not including denitrification) resulting from manure management practices. In this model, atmospheric exchange of P and potassium (K) were considered negligible. Nitrogen returns as a result of atmospheric deposition in the LFV are considerable, as noted by Schreier et al. (1999), who estimated average wet and dry NH$_3$ deposition in the region of up to 9.5 kg N·ha$^{-1}$·yr$^{-1}$.

### 2.4.2. Transport processes

The mobilization and transport of nutrients from agricultural fields to surface waters and groundwaters are complex processes. This is because nutrients can occur in many chemical forms (e.g., nitrogen occurs as nitrate (NO$_3^-$), nitrite (NO$_2^-$), ammonia (NH$_3$) and ammonium (NH$_4^+$) among many others) and in different physical states (dissolved, adsorbed or in gaseous form). Each chemical form and physical state is governed by different mobilization and transport processes. Further, several transport pathways and mechanisms exist between agricultural fields and surface waters, with each controlled by site-specific geophysical factors and responding differently to environmental conditions. It should be noted that there is a significant body of literature in the field of landscape ecology that addresses the mechanisms through which land use influences surface-water quality (a comprehensive review is provided by Baker, 2005b). This section reviews many of these processes, with emphasis on the roles of land-management activities, hydrological variables and climate.

#### 2.4.2.1. Nitrogen

Before describing the details of N transport, it is necessary to briefly review the N cycle (Figure 2-3). From a functional perspective, the N cycle involves the transformation of unreactive N gas (N$_2$) to biologically accessible forms (through fixation, mineralization and nitrification) and then back to N$_2$. 
(Chambers et al., 2001). The literature on this topic is extensive, and for details regarding the entire N cycle, the reader is referred to Pierzynski et al. (1994) and Chambers et al. (2001).

![Nitrogen Cycle Diagram]

**Nitrogen is present in the environment in both organic and inorganic forms.** Organic N is defined as N that is bound to carbon (shown in Figure 2-3 as biomass N and soil organic N). It is derived from biological processes and can be found in both soluble and particulate forms. Particulate forms are comprised of living and dead organisms, while soluble organic N is derived from human and animal waste, or the breakdown of the particulate form. In its organic form, N must go through the process of mineralization (transformation to NH$_4^+$ or NO$_3^-$) before it can be assimilated by plants.

Inorganic N (sometimes referred to as mineral N) is derived from microbial processes that convert N$_2$ and organic N into several different forms which can be assimilated by plants. From a water-quality perspective, the inorganic forms of N of greatest interest are NO$_3^-$, NO$_2^-$, NH$_3$ and NH$_4^+$. Figure 2-3 illustrates the key chemical reactions involved in the conversion of N between these forms. In particular, NH$_4^+$ and NO$_3^-$ are of primary concern in surface waters and groundwaters due to their solubility and stability in solution. Nitrite is often converted to NO$_3^-$, and NH$_3$ is converted to ionized NH$_4^+$. Ammonium predominates at pH levels below approximately 8.75, while NH$_3$ is more common under more basic conditions (Pierzynski et al., 1994).

The application of N to agricultural fields in the form of chemical and organic fertilizers initially leads to a surplus in the upper soil profile once the nutrient requirements of crops are exceeded.
Ammonium and $\text{NO}_3^-$ are then available for transport either laterally via overland flow or throughflow, via artificial subsurface drainage networks, or downward through leaching into local aquifers. The mobility of these two species of N is governed by their specific chemical properties, local geophysical and meteorological parameters and by the type of land management activities employed.

Due to its positive charge, $\text{NH}_4^+$ has a higher propensity for retention in the upper soil profile through cation exchange mechanisms than $\text{NO}_3^-$ (Hooda et al., 2000). As a result, a large portion of N is lost through leaching and transported via subsurface flow as $\text{NO}_3^-$. Nitrogen that is present in excess of crop requirements is subject to biological denitrification (conversion to $N_2$ gas). The degree to which this occurs is a function of the organic carbon content in the soil, as this acts as an energy source for denitrifying bacteria (Chambers et al., 2001). As $\text{NO}_3^-$ migrates downward through the soil profile, ongoing biological dissimilation is possible; however, such processes are often restricted at depth due to a lack of organic carbon to act as an energy source. As a result, $\text{NO}_3^-$ accumulation in groundwater aquifers is common where a continuous source is available.

The permeability of the soil profile and underlying material determine the sub-surface mobility of $\text{NO}_3^-$. As would be expected, and has been demonstrated previously (e.g., Bergstrom and Johansson, 1991; e.g., Berka et al., 2001; Chae et al., 2004), well-drained soils favour N mobility, while fine-textured soils promote lateral flow to nearby surface waters. Bergstrom and Johansson (1991), in a controlled lysimeter study, noted a three-fold increase in N losses through leaching for sandy soils, as compared to clay-rich soils. It should be noted; however, that sandy soils rich in organic matter showed minimal losses to leaching due to denitrification.

Climate and hydrology strongly influence N movement in watersheds. A review of the literature reveals the complexity of the relationships between precipitation, watershed hydrology and N transport. Van Herpe and Troch (2000) outlined the role of seasonal hydrological conditions, precipitation and land use on stream water $\text{NO}_3^-$ concentrations for several sub-catchments in the Zwalm watershed in Belgium. In general, they noted a positive correlation between discharge and $\text{NO}_3^-$ concentration; however, this relationship was much stronger during the winter months (in summer, $\text{NO}_3^-$ peaks were more delayed). This was attributed to differing seasonal hydrological states, with the dry summer months resulting in hydrologically disconnected groundwater stores, in contrast to the wet winter months during which these sources were strongly coupled, leading to faster hydrological response. As a result, stream flow during summer storms was initially comprised of relatively $\text{NO}_3^-$-poor overland flow. Subsurface sources that
were richer in NO$_3^-$ responded more slowly, leading to a later peak in NO$_3^-$ concentrations when compared to winter storms. It should also be noted that N available for transport during summer months is generally lower due to greater biological uptake associated with the growing season.

Similarly, in catchments with well-drained soils, a negative relationship between precipitation and N concentrations may be observed (e.g., Schreier et al., 1999; Kemp and Dodds, 2001). In such situations, streams that are strongly linked to contaminated groundwater sources will show much higher NO$_3^-$ concentrations during baseflow conditions, with dilution by overland flow taking place during storm events (Smith, 2004).

The role of land-management activities in N leaching is also significant. In early studies of N dynamics on experimental plots, Rolston and Broadbent (1977), Rolston et al. (1978) and Rolston et al. (1979) [as reviewed by Sharpley et al. (1998)], developed winter and summer N budgets for experimental plots under three conditions: 1) manure application, 2) rye-grass cropping and 3) a control treatment (no crop or manure applied). During the summer, they demonstrated that manure additions resulted in the denitrification of 79% of total N (due to high biological productivity arising from ample organic carbon and warm temperatures), while plots under crops lost 66% to leaching. Uncropped control plots experienced the greatest loss to leaching (87%) due to a lack of uptake and denitrification. Winter data showed a marked difference, with manured fields losing 77% of total N (due to reduced microbial activity under cooler, wetter conditions). Losses to leaching in the winter months were lowest for the cropped plot (39%), as the cool-season grass that was planted thrived in the lower-temperatures, resulting in greater metabolism of available N. Under winter conditions, leaching in the uncropped plot was the dominant process, with a loss of 99% of total N. These early studies demonstrate the fundamental dynamics of N on agricultural fields and the influence of precipitation, temperature, organic matter content and active crops on the fate of available N. It is important to note; however, that field-based studies do not always show consistent results, due primarily to the strong influence of site-specific conditions on these processes (Chambers et al., 2001).

The species of N observed in surface waters vary depending upon the location of the sampling site and site-specific conditions. In a comprehensive study of nutrient fluxes in the UK, Russell et al. (1998) assessed the speciation of N at the outlet of four watersheds with varying degrees of cropped land and pasture over a complete water year. It was noted that only 8% of total exported N was in particulate form (the majority of which was particulate organic N). Total dissolved N formed the largest component of
total N loads (76-82%) with NO$_3^-$ and NO$_2^-$ dominating. Dissolved organic N comprised 13-16% of annual N exports, while NH$_4^+$-N made up only 0.3-1.2% of the total. This is in contrast to a study by Heathwaite and Johnes (1996) which noted that over 90% of surface runoff from pasture was in the form of NH$_4^+$. The observed differences are likely due to the scales represented by each study. Samples from the former study represent integrated catchment-scale N loading, and therefore include N inputs from several pathways, including overland flow, throughflow and contributions from groundwater. The latter study observed high NH$_4^+$ concentrations in overland flow draining directly from heavily grazed lands. Also, the timing of sampling relative to grazing or manure or fertilizer application can influence the relative proportion of N appearing as NH$_4^+$ vs. NO$_3^-$. This was illustrated by Pierson et al. (2001) and Smith et al. (2003) for chicken and cattle wastes, respectively. Both studies showed relatively high NH$_4^+$ concentrations immediately after application of NH$_4^+$-rich manure, as there had been little time for conversion to NO$_3^-$ via nitrification. Kurz et al. (2005) noted similar trends after the application of N fertilizer to three study sites in Ireland.

Yet another factor, subsurface drainage networks, may also strongly influence NO$_3^-$ mobility within a catchment. Randall and Mulla (2001) provide an overview of several studies assessing links between precipitation and NO$_3^-$ content in tile drainage. Because an artificial drainage network essentially acts as a direct link to nutrient stores within the soil profile, response to rainfall events is generally rapid, with concentration being a function of drainage volume and N availability.

The above examples illustrate a variety of processes involved in nutrient mobility and transport in agricultural watersheds. Further, they highlight the need to consider site-specific variables when identifying and quantifying nutrient sources and pathways in such watersheds and when making inferences regarding the mechanics of nutrient transport based on water-quality data.

2.4.2.2. Phosphorus

Figure 2-4 illustrates the soil P cycle, including primary P sources, interactions between inorganic and organic P, and routes by which P is lost from the soil profile. Although concentrations of P in surface waters and groundwaters tend to be lower than those of N, P is commonly considered a greater threat to water quality because it is often the limiting nutrient for aquatic biological activity in fresh waters (Wetzel, 1983; Bechmann et al., 2005). Like N, P is found in both particulate and dissolved phases. The particulate form includes plant and animal tissue, P precipitates and P adsorbed to sediments, while the
dissolved form includes inorganic P (or \( \text{PO}_4^{3-} \)) and organically bound phosphates. Operationally, most studies define particulate P as that which does not pass through a 0.45 μm filter.

![Simplified phosphorus cycle](image)

Figure 2-4 - Simplified phosphorus cycle, illustrating sources and pathways by which phosphorus is lost from the soil profile. Modified from Sutton (1997).

The processes governing P transport from agricultural soils to surface waters and groundwater differ from those associated with N. In contrast to N, P is strongly adsorbed in most soils, and thus has a strong tendency toward transport in particulate form. This suggests that groundwater and surface water contamination with soluble P is minimal; however, the amount of soluble P in a soil is inversely related to P sorption capacity and strength, both of which are variable. Sorption capacity and strength are a function of soil texture (finer grained material has a higher sorption capacity), soil chemistry (P is strongly bound to calcium, aluminum, iron and manganese) and current P saturation (which is strongly affected by the history of P application at a given site). These characteristics can change over time as a result of land management practices. For example, Laboski and Lamb (2004) observed a significant decrease in soil sorption capacity after manure applications in five of seven soil types in experimental plots. Further, a strong negative correlation between sorption strength and P saturation was observed, indicating that surplus P applications can increase soluble P availability by simultaneously reducing soil capacity and binding strength.

There are differing opinions in the literature regarding the dominant form of P transport from agricultural fields to surface waters. Hooda et al. (2000), in a review of research on water quality concerns related to agriculture, noted that P transport is dominated by the particulate fraction. Similarly, Hart et al. (2004) reviewed several studies of P runoff from agricultural land in New Zealand where this trend was observed, with particulate P accounting for 62-91% of total P loads. However, in the same
review, it was noted that numerous studies describe the opposite trend, with the dissolved form (primarily organically bound P) dominating P export. This difference was attributed to variations in site-specific factors that affect the availability and mobilization of different forms of P (described above), the scale of the monitoring programs (i.e., plot, sub-catchment or catchment scale) and the timing of water sampling relative to P additions and rainfall events (Hart et al., 2004; Haygarth et al., 2005).

The spatial scale of sampling is an important variable as the ratio of soluble to particulate P observed in a water sample is a function of the original ratio (as it is transported from the site), and the time between mobilization and sampling, as P adsorption can take place in transit. As an example, Cooke (1988, in Hart et al. (2004)) noted that soluble P dominated in surface runoff (comprising 63% of total P) from a 16 ha catchment in New Zealand, but more than 85% of P exported from the catchment via streams was in particulate form. In-stream processes play a major role in the balance between soluble and particulate P phases in surface waters, and under well-mixed conditions an equilibrium between the two forms may exist during baseflow (McDowell et al., 2003). The equilibrium P concentration (EPC) of sediments in suspension determines the mobility of P between the two fractions (with a high EPC relative to stream P concentrations leading to desorption, and vice versa). McDowell et al. (2003) noted a significant positive correlation between EPC and stream soluble P concentrations during baseflow conditions, but not during storm flow as this equilibrium cannot be maintained under conditions of rapid particulate and soluble P loading. Interestingly, in a study of the influence of stream sediments on in-stream P cycling in a watershed influenced by sewage treatment plant (STP) discharges, Jarvie et al. (2005) noted that bed sediments acted alternately as a net sink or source of P, depending on the soluble P concentration of stream waters. During periods of STP effluent discharge, the net flux of soluble P was from the water column to bed sediments. During periods of low effluent discharge, the opposite was true due to the reversal in the diffusion gradient at the sediment boundary layer.

The availability of soluble P in a saturated soil profile may also result in downward mobility of P with the potential to reach subsurface drainage networks and groundwater sources. The presence of artificial or natural subsurface drainage networks facilitates the delivery of soluble P to surface waters and groundwater due to shorter contact time between soluble P and soil particles (Sharpley et al., 1995; Hooda et al., 2000; Lazzarotto et al., 2005). Sims et al. (1998) conducted a comprehensive review of research into P leaching in agricultural drainage systems, and noted that under certain conditions, this
source, generally thought to be negligible, can actually result in significant P loss relative to overland transport.

These studies indicate the influence of antecedent soil conditions, spatial scale and transport pathways on P availability and transport. It is clear that the risk of P loading to surface waters and groundwaters is exacerbated by intensive agricultural activity due to the decreased sorption capacity of agricultural soils and the presence of sub-surface drainage networks which directly link P sources to receiving waters. The resulting impacts to ecosystem health can be significant, as described below.

2.4.3. Ecological and human health impacts

2.4.3.1. Ecological impacts

The ecological impacts associated with nutrient enrichment and eutrophication of surface waters have been reported extensively and thus will not be covered in detail here. The primary issues of concern are the promotion of excess algal and plant growth leading to decreased dissolved oxygen levels (resulting from decomposition), decreased photic zone depth in both rivers and lakes, impairment of spawning beds and reduction in aquatic species diversity (Chambers et al., 2001). Apart from ecological impacts, such impairment of water quality also limits the use of aquatic resources for drinking water, commercial and sport fishing and recreational purposes (Haygarth et al., 2005). For a comprehensive review of the mechanisms and ecological impacts related to eutrophication in aquatic environments, the reader is referred to Wetzel (1983). For a review of this issue from a Canadian perspective, Coote and Gregorich (2000) and Chambers et al. (2001) are recommended.

2.4.3.2. Human health impacts

Both N and P are essential elements for living organisms; however, in certain forms and in high concentrations both can be harmful to human health. Phosphorus, in forms commonly found in the environment, is not directly toxic (Chambers et al., 2001). However, excessive P in aquatic systems can lead to blooms of toxin-producing algae. For example, *Microcystis*, a blue-green algae, is known to produce hepatotoxins (which affect the liver), while two genera (*Anabaena* and *Aphanizomenon*) are known sources of neurotoxins which can cause significant neurological impairment or death in humans and animals (Chambers et al., 2001). In marine environments, *Pfiesteria piscicida* has been linked to large-scale fish kills (Burkholder et al., 1992). While blooms of these organisms are not controlled
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exclusively by P concentrations, P is often the limiting element for growth, and therefore strongly influences algal production (Wetzel, 1983).

Nitrogen also contributes indirectly to human and animal health effects by promoting algal production, but in contrast to P, there are several forms of N that are thought to be directly toxic to living organisms. The exact role of these forms of N in causing human illness is unclear. Historically, high NO$_3^-$ concentrations in drinking water have been associated with methemoglobinemia, or “blue-baby syndrome” (Coote and Gregorich, 2000; Knobeloch et al., 2000; Chambers et al., 2001; Environment Canada, 2001). Infants under 3 months of age have traditionally been considered at greatest risk for this condition which is traditionally thought to occur when NO$_3^-$ is converted to NO$_2^-$ by bacteria in the stomach. This conversion leads to oxidation of ferrous iron to ferric iron in hemoglobin and results in reduced oxygen carrying capacity in the blood. However, in a recent review, Fewtrell (2004) questioned the role of nitrates as a causative factor since a clear exposure-response relationship has not been identified. He went on to state that although nitrates may play a role in the onset of methemoglobinemia (along with other factors), attributing this condition to drinking-water NO$_3^-$ levels is inappropriate given the current level of evidence. A similar conclusion was reached by Avery (1999), who stated that several factors, such as diarrhea and gastrointestinal and urinary tract infections, can directly cause methemoglobinemia in infants without exposure to nitrates in drinking water.

A number of studies have investigated the possible causal link between high drinking-water NO$_3^-$ levels and various forms of cancer. This link is suspected because once ingested, NO$_3^-$ is reduced to NO$_2^-$, which can interact with compounds in the stomach to produce N-nitrosoamines and N-nitrosoamides, both of which are among the strongest known carcinogens (Cantor, 1997). This hypothesis is supported by experimental studies, but epidemiological evidence linking drinking-water NO$_3^-$ to cancer is mixed. Several authors report a link between nitrates and different types of cancer, including, for example, urothelial cancer (Volkmer et al., 2005), non-Hodgkin’s lymphoma (Ward et al., 1996), brain cancer (Ward et al., 2000), bladder cancer (Weyer et al., 2001) and gastric cancer (Xu et al., 1992). In contrast, there are several studies which report no relationship between the incidence of different forms of cancer and drinking-water nitrates (e.g., De Roos et al., 2003; Mensinga et al., 2003; Ward et al., 2003; Coss et al., 2004).

Nitrates in drinking water have been implicated in other conditions, including hyperthyroidism (Seffner, 1995) and insulin-dependent diabetes (Kostraba et al., 1992). In addition, the US Centers for
Disease Control and Prevention tentatively linked high NO$_3^-$ concentrations to spontaneous abortions in LaGrange County, Indiana (Centers for Disease Control and Prevention, 1996). Nitrates may also have a negative impact on animal health. A recent review of endocrine disruption in invertebrates suggests that nitrates may play a key role in this process in wildlife populations (Guillette and Edwards, 2005).

The inconsistent findings regarding the role of nitrates (and their derivatives) in human and animal illness make interpretation of cause-effect relationships difficult. Experimental data suggest that a link to disease does exist; however, the retrospective and/or ecological (i.e., population-based) design of many studies limits the ability to control for confounding factors and clearly establish that link (Cantor, 1997). The only way to reliably establish such a link would be through controlled dose-response experiments in animals in a laboratory setting.

2.5. Pathogens

This section provides an overview of waterborne human and animal pathogens of concern in North American agricultural watersheds. It first reviews various types of common pathogens (bacteria, protozoa and viruses), and then describes their sources, associated mobilization and transport processes and concludes with a discussion of the potential impacts of these organisms on human and ecosystem health.

2.5.1. Pathogens of concern

While a wide variety of bacteria, protozoa and viruses are shed from humans and domestic and wild animal populations, relatively few are known to cause waterborne disease outbreaks (Rosen, 2000). The organisms reviewed below are currently regarded as those posing a significant risk to human health in agricultural environments. Background on each type of organism is provided and is followed by descriptions of specific pathogens and their associated health impacts.

2.5.1.1. Bacteria

Bacteria are predominantly single-celled organisms of various shapes, including spherical (coccus), rod-shaped (bacillus), comma-shaped (vibrio), spiral (spirillum) or corkscrew-shaped (spirochete), and are generally 0.5 to 5.0 μm in size (Rosen, 2000). They are found in almost every environment on earth; however, those found in the intestinal systems of animals and humans (enterobacteria) are of primary concern. While there are numerous waterborne bacterial pathogens, those
of greatest interest in agricultural watersheds with livestock are enterohemorrhagic \textit{Escherichia coli}, \textit{Campylobacter}, \textit{Salmonella} and \textit{Yersinia} (Ferguson et al., 2003).

\textbf{\textit{E. coli} 0157:H7}

\textit{Escherichia coli} (\textit{E. coli}) is a member of the coliform group of bacteria and is commonly found in the intestines of animals and humans. There are over 100 strains of \textit{E. coli} (most of which are non-pathogenic and serve useful functions in the gastrointestinal tract), and it is often used as an indicator of fecal contamination in water. \textit{E. coli} 0157:H7 is an enterohaemorrhagic strain of \textit{E. coli} (intestinal bleeding is commonly associated with infection) and is highly infectious, with as few as 10 cells causing human illness (Rosen, 2000). The cells produce toxins (Verotoxin, Shiga-like toxin) that may impair kidney function (hemolytic uremic syndrome, or HUS), cause kidney failure and/or break down intestinal lining. These toxins pose the greatest risk to the young, elderly and immunocompromised (Szewzyk et al., 2000). As a result, the incidence of HUS associated with \textit{E. coli} outbreaks varies depending on the population involved (e.g., community outbreak vs. a nursing home outbreak), and can range from 0-15% (Food and Drug Administration, 2005). The mortality rate for HUS has been estimated at 3-5% (Boyce et al., 1995), but can be as high as 50% among the elderly when observed with fever and neurologic symptoms, a condition known as thrombocytopenic purpura (Food and Drug Administration, 2005).

\textit{E. coli} 0157:H7 was one of the primary pathogens involved in the Walkerton, Ontario outbreak in May, 2000, during which over 2,300 people fell seriously ill, and 7 people died as a result of contamination of a municipal water system with agricultural runoff (Hrudey et al., 2003).

\textbf{\textit{Campylobacter}}

Several species of \textit{Campylobacter} can cause illness in humans; however, \textit{Campylobacter jejuni} is the primary cause of all diagnosed cases (Rosen, 2000). The most common sources of \textit{Campylobacter} in agricultural watersheds include wild bird and poultry populations, cattle, pigs, dogs and cats. The organism can be spread via surface water and groundwater (Szewzyk et al., 2000), and can be foodborne or spread person-to-person. As few as 400-500 organisms may be sufficient to produce illness in humans, with onset of illness (campylobacteriosis) generally occurring 2-5 days after exposure (Food and Drug Administration, 2005). Complications from campylobacteriosis are rare and the fatality rate is low (0.1%, or 1 in 1,000 cases), but kidney failure, HUS, diarrhea (often bloody), reactive arthritis or
infections in any major organ are possible in susceptible populations (the immunocompromised or patients with a serious pre-existing condition) (Food and Drug Administration, 2005).

Livestock operations are reservoirs for *Campylobacter* and play a significant role in their dispersal in the environment (Stanley and Jones, 2003). *Campylobacter jejuni* is thought to have played a role in the Walkerton outbreak described above (Hrudey et al., 2003). Also, in European countries, it is considered a significant threat to drinking water quality, having been responsible for the majority of outbreaks in private water systems in England and Wales in the early-mid 1990’s (Szewzyk et al., 2000).

**Salmonella**

*Salmonella* species are a well recognized cause of enteric illness in humans, with up to 4 million infections occurring annually in the United States alone (Rosen, 2000). *Salmonella enteriditis* and *Salmonella typhi* (responsible for typhoid fever) are strains commonly observed to infect humans. The infective dose for *Salmonella* is relatively small, at 15-20 bacterial cells (Food and Drug Administration, 2005). The majority of *Salmonella*-related cases are the result of foodborne transmission from poultry, beef, pig and dairy products. However, the potential exists for waterborne transmission to humans from livestock sources. Hooda et al. (2000) cite several studies describing the longevity of *Salmonella* as ranging from days to several years after infected animal wastes have been spread on agricultural fields and incorporated into soils. Despite this potential, there are few documented outbreaks of waterborne illness attributed to *Salmonella spp.* (Angulo et al., 1997; Taylor et al., 2000) and there are no known cases linked directly to agriculture.

**Yersinia**

*Yersinia* has been implicated in both foodborne and waterborne outbreaks of enteric illness; however, few strains are pathogenic to humans (Szewzyk et al., 2000). *Yersinia enterocolitica* is the primary cause of human infections, which number approximately 3,000-20,000 per year in the United States (Rosen, 2000).

2.5.1.2. Protozoa

Protozoa are single-celled organisms (a subtype of parasite) with more complex structures and life cycles than bacteria (Rosen, 2000). The two protozoan parasites of primary concern with regard to agricultural watersheds are *Giardia* and *Cryptosporidium*, with size ranges of 8-15 μm, and 4-6 μm, respectively (Szewzyk et al., 2000). These organisms reproduce only within the gastrointestinal tract of
humans and animals (not in the environment) and are more resistant to environmental stressors and traditional water treatment techniques than most other pathogenic microorganisms (Health Canada, 2004b).

The lifecycle of these parasites is particularly well suited to dispersion and subsequent infection via contaminated drinking water. Infection occurs when the parasites either attach themselves to the intestinal lining (*Giardia*) or invade host cells (*Cryptosporidium*) where they thrive and reproduce. Prior to being shed by the host organism, they encase themselves in a protective cyst wall (*Giardia*) or oocyst wall (*Cryptosporidium*) that is highly resistant to environmental degradation and standard chemical disinfectants (Szewzyk et al., 2000). Once ingested, and if environmental conditions are favourable, the organism excysts and infects the new host.

**Giardia**

*Giardia lamblia* (also referred to as *Giardia intestinalis* or *Giardia duodenalis*) is a protozoan parasite found in the intestinal tracts of many different hosts, including humans, dogs, cats, bears, muskrats, cattle and pigs, and is capable of cross-species transmission (Olson et al., 1999; Rosen, 2000). When the feeding stage (trophozoite) of the organism detaches from the intestinal wall, it forms a cyst, divides within the protective casing and is shed to the environment with the feces (Health Canada, 2004b). Once ingested, excystation is triggered by stomach acids and enzymes. Two trophozoites emerge and infect the intestinal tract via asexual reproduction (Health Canada, 2004b).

*Giardia* is the most commonly reported intestinal parasite worldwide. In Canada, the prevalence (percent of population infected) in humans is approximately 1-5%, although this number may be much larger as many cases are thought to be asymptomatic (Health Canada, 2004b). Of the 29 documented waterborne disease outbreaks in BC between 1980-2002, 13 were attributed to *Giardia* (Christensen, 2003). Prevalence ranges from 10-100% in cattle and from 1-20% in pigs (Olson et al., 1999).

*Giardia lamblia* cysts can survive for extended periods in surface water and drinking water systems. Bingham et al. (1979) demonstrated that cysts could survive for up to 77 days in tap water at 8 °C, but that longevity decreased with increasing temperatures.

The infectious dose for *G. lamblia* is very low; in mice 1-10 organisms generate infection (giardiasis) (Stachan and Kunsty, 1983). Onset of illness is generally within one week of cyst ingestion, and may last 1 to 2 weeks; however, chronic cases lasting years have been reported (Food and Drug
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Administration, 2005). Symptoms of the acute phase of the illness may include nausea, diarrhea, malaise and sometimes low-grade fever or chills; however, this usually resolves spontaneously in healthy individuals (Health Canada, 2004b).

While it is believed that giardiasis is a zoonotic disease (transmitted from animals to humans), little evidence from controlled experiments is available to definitively link livestock sources to human illness via waterborne transmission (Health Canada, 2004b). However, given the very low infectious dose, high prevalence in livestock animals, longevity of cysts in the environment and number of known outbreaks of giardiasis in rural water systems in BC (and elsewhere), it is considered a significant human health risk when detected in water supplies.

 Cryptosporidium

 Cryptosporidium infects a wide range of hosts, including humans, cattle, goats, sheep, pigs, horses, dogs, cats, mice, voles and raccoons (Rosen, 2000). It has a relatively complex lifecycle (see Smith and Rose (1998) for a complete overview), but is similar to Giardia in that it infects the intestine. However, rather than affixing to the intestinal wall, Cryptosporidium invades cells that line the intestine (enterocytes). It then reproduces intracellularly, and is transmitted in an environmentally resistant casing (oocyst). Approximately 80% of oocysts produced in the intestine are “thick-walled” and are generally excreted from the body. These oocysts are much more resistant to environmental degradation than Giardia cysts (Olson et al., 1999). The remaining 20% of oocysts are “thin-walled” and readily rupture in the intestine, reinvade new enterocytes and continue to reproduce leading to autoinfection, thus prolonging the infection (Rosen, 2000). An infected person or animal can shed oocysts for several days over the course of the illness, with concentrations of up to 10 million oocysts per gram of feces. As with Giardia, the infectious dose for Cryptosporidium is very low. The infectious dose, as estimated by Health Canada (2004b), is 39 oocysts in humans and 10 in animals; however, one organism is thought to be enough to produce illness in a healthy individual (Food and Drug Administration, 2005). There is currently no known treatment for cryptosporidiosis. The infection is self-limiting in healthy individuals (lasting 2-4 days) but can be fatal for those with compromised immune systems (Food and Drug Administration, 2005).

 Cryptosporidium parvum is thought to be the species of primary concern in terms of human illness, and infections in cattle populations have been well documented (Casemore et al., 1997). Other
zoonotic sources have been identified, including deer (Ong et al., 2002), suggesting that multiple exposure paths exist in rural watersheds.

In BC, *Cryptosporidium* was the causative agent in three of the 29 waterborne disease outbreaks documented from 1980-2002. Two of these (one in Cranbrook and one in Kelowna, in 1996) were among the largest outbreaks during that time, and in two of the three outbreaks cattle were identified as the source (BC Provincial Health Officer, 2001). In the spring of 2001, an outbreak of cryptosporidiosis in North Battleford, Saskatchewan, resulted in 1,907 confirmed cases (5,800-7,100 estimated). The community derives its drinking water from the North Saskatchewan River, and while the source of the pathogen was not confirmed, it is thought that upstream sewage treatment plants may have played a role (Laing, 2002). *Cryptosporidium* was also the cause of the largest documented waterborne disease outbreak in North America, which took place in Milwaukee in 1993, and affected over 400,000 people (MacKenzie et al., 1994). Based on an analysis of death certificates for two years after the outbreak, cryptosporidiosis was listed as an underlying or contributing cause for 54 deaths in the Milwaukee area, compared to four deaths for the two years prior to the outbreak (Hoxie et al., 1997).

Other parasites

It should be noted that other protozoan parasites are capable of causing human illness. In BC, for example, the world's largest outbreak of waterborne toxoplasmosis (caused by the parasite *Toxoplasma gondii*) occurred in late 1994 and early 1995, infecting 100 people in the municipality of Victoria (Bowie et al., 1997). This outbreak was associated with peaks in local rainfall and turbidity in the municipal drinking water reservoir, and it is hypothesized that the parasite was derived from one or more infected wild or domestic cat(s).

2.5.1.3. Viruses

Viruses are one of the the smallest known pathogens (from 20-300 nm), consisting of a nucleic acid core (of RNA or DNA) encapsulated in a protein shell (Health Canada, 2004a). All viruses are inactive unless they are within living cells. Viruses reproduce by instructing a host cell to produce multiple copies of its genetic material (as well as the protective protein shell) using the cell's own processes, until it ruptures and the viruses are released and continue infecting other cells. Enteric viruses are those that reproduce only in the host's gastrointestinal tract (Rosen, 2000).
Like protozoan parasites, viruses are shed by infected hosts in high concentrations, reaching up to 1 billion viruses per gram of feces (Health Canada, 2004a). They are also resistant to environmental degradation in water, where they may remain infectious for months (Szewzyk et al., 2000), particularly at low temperatures and/or when adsorbed to sediments (Health Canada, 2004a).

Pathogenic viruses are regularly detected in surface waters. For example, Ehlers et al. (2005) detected viable enteroviruses in 28.5% of river water samples, and 26.7% of spring/dam surface water samples in selected sites across South Africa. Interestingly, this study also detected viruses in treated drinking water samples, all of which met current World Health Organization (WHO) drinking water guidelines for heterotrophic plate counts and fecal coliform counts. The most common source of viruses is human sewage derived from sewage treatment plants (e.g., Lodder and Husman, 2005), sewage leaks or septic systems (Rosen, 2000). In agricultural watersheds, viruses may also be derived from sewage sludge spread on agricultural fields (Health Canada, 2004a; Carter, 2005). While interspecies transmission of infectious viruses is documented, there have been no documented cases that would suggest a link between human illness and livestock sources of waterborne viruses (Rosen, 2000). However, Cliver and Fayer (2004) suggested that the potential for waterborne viral zoonoses does exist, particularly given the number of viruses produced in infected animals, their consistent detection in surface waters, and the significant potential for genetic mutation (leading to a change in host specificity) during the process of viral synthesis. They described several potential scenarios in which cross-species, waterborne transmission could take place, and note that there are several examples of interspecies viral infection (e.g., avian influenza, bovine spongiform encephalopathy) where waterborne transmission has not been documented, but cannot be ruled out.

2.5.2. Pathogen sources in agricultural watersheds

In agricultural watersheds, there are three primary sources of pathogenic organisms: 1) wildlife, 2) livestock (direct deposition into surface waters, transport from manure storage facilities or from agricultural fields receiving manure) and 3) humans (septic systems, sewage treatment plants or sewage sludge). The following describes pathogen levels in the wastes generated by each of these sources.

2.5.2.1. Wildlife

Wild animals are known reservoirs of pathogenic bacteria, protozoa and viruses (Daszak et al., 2000). In many cases, these pathogens are host-specific (they infect a limited range of host species), and
are not pathogenic in humans. Wildlife sources represent a risk to human health when: 1) they carry and/or are infected by microbial strains that are also pathogenic to humans or 2) wildlife-specific pathogens mutate so as to be able to infect humans.

*Cryptosporidium* is a good example of a pathogen that is highly infectious to human and animal hosts. In total, 15 species of *Cryptosporidium* are known to infect vertebrate hosts, seven of which are infectious to humans (Fayer, 2004). These species, *C. baileyi*, *C. canis*, *C. felis*, *C. meleagris*, *C. muris*, *C. hominis* and *C. parvum*, were originally thought to be specific to chickens, dogs, cats, turkeys, mice, humans and mice, respectively. However, each species has been found to infect humans, and *C. hominis* has also been shown to infect marine and land mammals (Fayer, 2004). *Cryptosporidium parvum* and *C. hominis* are considered the most infectious strains to healthy humans (Sturdee et al., 1999), and they have been identified in 155 species of mammals, including several species of sheep, deer, bear, felines and rodents. The other species are commonly found in immunocompromised individuals (Fayer, 2004). Recently, Ong et al. (2002) identified a cervine (deer) *C. parvum* genotype in humans in BC, illustrating the potential for the emergence of new wildlife sources of cryptosporidiosis.

Strains of *G. lamblia* are also infective in multiple species. Several different strains of this organism have been identified, and while they demonstrate similar morphological characteristics, they are genetically unique and therefore are infectious to different hosts. *Giardia* strains found in humans fall under two genetic groupings, known as Assemblage A and Assemblage B. Assemblage A organisms (thought to be the more infectious of the two assemblages) are commonly found in humans, cats, dogs, deer and beavers, while Assemblage B parasites have been observed in humans, chinchillas, beavers and rats (Trout et al., 2003; Thompson, 2004). Other wildlife species are known reservoirs for *Giardia*; however, research is needed to genetically characterize these *Giardia* strains to understand the role of wildlife in waterborne outbreaks of giardiasis in humans (Thompson, 2004). Importantly, while there are several wildlife reservoirs for *Giardia* strains that are pathogenic to humans, there is little direct evidence of a link between waterborne outbreaks of giardiasis and wildlife sources (Thompson, 2004).

Relatively little work has been done to determine the role of wildlife in the transmission of waterborne bacterial pathogens to humans. Several studies have noted the presence of pathogenic bacteria in wildlife species, however their role in human illness is not well understood. Wild deer have been shown to carry *E. coli* 0157:H7 (Sargeant et al., 1999); however, prevalence is generally low (< 3%) in populations studied (Sargeant et al., 1999; Fischer et al., 2001; Renter et al., 2001). The same
bacterium has also been observed in rats (Cizek et al., 1999) and various bird species in close proximity to farms (Nielsen et al., 2004) indicating that there is likely two-way transmission between farm and wild animals in agricultural environments.

2.5.2.2. Livestock

Pathogens derived from livestock enter surface waters via direct contact (i.e., livestock accessing streams or standing water bodies) or via transport from manured agricultural fields or manure storage piles. Table 2-2 provides a summary of pathogen levels in livestock manure from recent studies, and describes the prevalence of infection (% of animals infected) where available.

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Cattle</th>
<th>Pigs</th>
<th>Animal Host</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prevalence (%)</td>
<td>Conc. (cfu/g)</td>
<td>Prevalence (%)</td>
</tr>
<tr>
<td>E. coli 0157:H7</td>
<td>13.2</td>
<td>1200</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>(9.1)</td>
<td>(260)</td>
<td>(15.5)</td>
</tr>
<tr>
<td>Salmonella spp.</td>
<td>7.7</td>
<td>2100</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>(10)</td>
<td>(2500)</td>
<td>(5.2)</td>
</tr>
<tr>
<td>Campylobacter spp.</td>
<td>12.8</td>
<td>320</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>(9.8)</td>
<td>(530)</td>
<td>(10.3)</td>
</tr>
<tr>
<td>C. parvum</td>
<td>5.4</td>
<td>19</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>(2.8)</td>
<td>(10)</td>
<td>(5.2)</td>
</tr>
<tr>
<td>G. lamblia</td>
<td>100¹</td>
<td>2230¹</td>
<td>ND</td>
</tr>
</tbody>
</table>

¹ Ralston et al. (2003) in a 27 week study of G. lamblia and C. parvum prevalence in newborn calves
² Giangaspero et al. (2005)

Table 2-2 illustrates several important points regarding livestock as sources of waterborne pathogens. Firstly, pathogens were detected in considerable numbers in both stored and fresh manure for all animal types. While pathogen prevalence varies significantly from study to study, and over time (see below), it is clear that livestock are reservoirs for a range of zoonotic pathogens. Further, in most cases, storage of animal wastes for extended periods of time did not result in a substantial drop in the number of organisms detected, indicating that both fresh and stored wastes are important pathogen sources that must be properly managed.
Animal age also plays a role in prevalence. Hutchison et al. (2005a) demonstrated significantly higher levels of *E. coli* 0157:H7 and *Campylobacter spp.* in wastes from young calves, lambs and piglets (< 3 months of age), and observed a higher prevalence of these pathogens in wastes derived from animal populations containing young stock. Similar trends have been observed elsewhere (e.g., Garber et al., 1995; Ralston et al., 2003), and in a review of several studies, Olson et al. (2004) noted that the average age for peak shedding of (oo)cysts (cysts and oocysts) from cattle is approximately five weeks and one-two weeks, respectively. This indicates that the season during which livestock animals are born is a period of increased risk of surface water contamination from these sources.

The survival of pathogenic organisms in manure and soil is a function of several factors, including initial pathogen concentrations, length of storage period, type of storage and environmental variables (temperature, moisture, pH, UV exposure, nutrient availability). Pathogenic bacteria, for example, show increased longevity in soils with high soil moisture content (Rosen, 2000; Duffy, 2003; Guan and Holley, 2003). Mubiru et al. (2000), in a controlled laboratory study, observed pathogenic *E. coli* survival in two soil types, and noted that culturable bacteria were still present after 8 weeks, with higher concentrations in finer-grained, moister soils.

Temperature also plays a significant role in pathogen survival, although the impact varies by pathogen type. In general, as temperatures increase (above 4 °C), longevity decreases. However, freezing temperatures also increase pathogen mortality. In a 12-week study, Olson et al. (1999) assessed (oo)cyst survival in water, cattle manure and soil at -4, 4 and 25 °C. After one week in soil, water and feces, *Giardia* cysts were no longer viable at -4 °C and 25 °C. Cysts kept at 4 °C were infective for 11 weeks in water, seven weeks in soil and one week in feces. *Cryptosporidium* oocysts were much more resistant and survived the entire 12 weeks in water and soil, when kept at -4 and 4 °C. Higher temperatures also appear to adversely impact the survival rates of viruses and bacteria. Himathongkham et al. (1999) examined survival rates of *E. coli* 0157:H7 and *Salmonella typhimurium* in manure and manure slurry at 4, 20 and 37 °C and noted that bacteria survived more than seven times longer at 4 °C than at 37 °C. In a review of several studies on pathogen survival, Guan et al. (2003) noted that most pathogens can survive for at least 30 days in cold (4-6 °C) soil, and that *Cryptosporidium* shows the greatest resilience to freezing temperatures, while *E. coli* and *Salmonella* are the most resilient in warmer soils (20-30 °C).
Survival rates in manure tend to decrease after manure is applied to agricultural fields. Bolton et al. (1999) assessed the survival of *E. coli* 0157:H7 in samples of inoculated cattle manure under different environmental conditions (stored in plastic at 10 °C, stored in plastic outside and spread on grazing land), and observed culturable bacteria after 99 days in both containers and after 50 days in the surrounding soils of the grazing land. Hutchison et al. (2005b) applied livestock wastes that had been inoculated with *E. coli* 0157:H7, *C. jejuni*, *Salmonella* and *C. parvum* to grass pasture and monitored their concentrations over time. Pathogen concentrations showed a marked decline within 24 hours of application. The average time required for a 1-Log reduction was 1.94 days for bacteria and ranged from 8-31 days for oocysts (with little or no decrease in viability over that time).

### 2.5.2.3. Humans

Pathogens associated with human sewage reach surface waters via sewage treatment plant (STP) effluent to streams, application of sewage sludge to agricultural lands and through leaching from septic systems. It is suggested that human-infective strains of certain pathogens (such as *G. lamblia*) were first introduced to current wildlife hosts through contact with water contaminated by human fecal matter (Thompson, 2004). Consequently, these hosts now serve to amplify and spread these pathogens in natural systems.

Sewage treatment plant effluent represents a significant point source of enteric pathogens to surface waters. Payment et al. (2001) assessed the removal of indicator bacteria and specific pathogenic viruses and protozoa by a primary STP (that does not employ chlorination) discharging to the St. Lawrence river at Montreal. Removal rates of *C. parvum*, *G. lamblia*, *E. coli* and viruses were 27%, 76%, 12% and 0%, respectively, resulting in significant inputs of pathogens to the river at this point, and a potential health impact on recreational users and biota downstream. Charles et al. (2003a) conducted a review of pathogen loads from STP's discharging effluent into drinking water catchments in Sydney, Australia, and noted that 76% of effluent samples contained *Cryptosporidium* oocysts and 17% were positive for enteric viruses. Sewage treatment plants that chlorinate effluent prior to discharge have also been observed to release significant quantities of pathogens to the environment. While bacterial reduction does take place, removal and/or inactivation of protozoan parasites is often incomplete, due to the resistance provided by the protective casings of (oo)cysts (e.g., Briancesco and Bonadonna, 2005).
The use of biosolids (the isolated portion of sewage sludge remaining after treatment) as an amendment to agricultural soils can also contribute significantly to the concentrations of human pathogens, heavy metals and, potentially, endocrine disrupting substances in soil (Coote and Gregorich, 2000). While treatment of biosolids is required prior to application to agricultural fields in Canada (Chambers et al., 2001), total inactivation of microbes is often not achieved (Rose et al., 1996). As noted in a review by Gerba and Smith (2005), the pathogenic organisms found in sewage sludge are similar to those in animal manure, but also include human viruses. As described above, and as noted by Gerba and Smith (2005), these organisms can persist in the soil for months to years and can act as a reservoir for contamination of crops and nearby surface waters.

Household septic systems, common in agricultural watersheds, can be hydrologically linked to surface water and groundwater networks and contribute to loading of waterborne pathogens. The degree to which such contamination takes place is a function of the septic system maintenance record, its proximity to surface waters and groundwaters and the texture of surrounding soils, with finer-grained materials reducing the potential for pathogen transport (Charles et al., 2003b). Harwood et al. (2000) used the antibiotic resistance patterns of fecal coliform and fecal streptococci to identify sources of bacterial contamination of surface waters in Florida, and identified septic systems as a primary source of contamination. Groundwater contamination with septic tank effluent is also common (Scandura and Sobsey, 1997; DeBorde et al., 1998; Bopp et al., 2003; Charles et al., 2003a; Charles et al., 2003b), and has been implicated in waterborne disease outbreaks (e.g., Bopp et al., 2003).

2.5.3. Transport processes

In a review of transport mechanisms for waterborne pathogens, Ferguson et al. (2003) noted that transport to surface waters is governed by three groups of processes: 1) those that influence adsorption to and desorption from particulate matter, 2) hydrological/meteorological processes and 3) mechanical and biological processes that influence transport pathways. Simply put, these define the availability of free organisms for transport, the existence of a transport force and medium and the availability of a pathway for transport, respectively. A similar framework is used in the following discussion.

2.5.3.1. Adsorption and desorption processes

Adsorption and desorption processes are controlled by the physical characteristics of the microbial pathogens involved (hydrophobic and hydrophilic properties, size and morphology), the nature
Chapter 2

of the soil solution and by the soil texture, chemical composition, electrostatic potential and bulk characteristics (Ferguson et al., 2003). Hydrophobic organisms preferentially adsorb to soil particles, a process that is enhanced as the ionic strength of the soil solution increases (Jewett et al., 1995). Further, for viruses, variations in surface charge associated with protein coats on different viruses (or strains of the same virus) influence adsorptive behaviour (Sobsey et al., 1995). In a soil column experiment, Sobsey et al. (1995) also noted the roles of temperature, soil texture and soil solution on virus transport. Due to the availability of fewer adsorption sites, coarser-grained, sandy soils resulted in decreased retention of viruses relative to sandy loam and clayey soils. The addition of organic-rich water to the soil column reduced virus retention in all soil types due to competition for binding sites by organic compounds. Finally, higher temperatures (25 °C compared to 5 °C) resulted in fewer viruses being released from soil columns for all soil types due to a decrease in virus survival and increased adsorption rates.

Similar influences on bacterial adsorption have also been observed. Heise and Gust (1999) utilized a controlled flow experiment over a sandy substrate to compare the distribution of nourished bacteria, starved bacteria and inert microspheres to determine the relative influence of biological and physical parameters on cell movement. The distribution of inert particles and starved bacteria correlated with flow patterns. In contrast, nourished bacteria were more equally dispersed across the sediment-water interface, indicating that they exert some control over their transport (such as active movement and adsorption) that is independent of flow. These results suggest that prediction of bacterial transport using particulate (soil) transport models, while useful in providing order-of-magnitude estimates, may not accurately reflect processes at the cellular or soil particle level (Heise and Gust, 1999; Tyrrel and Quinton, 2003). Further, mitigation strategies aimed at limiting soil (and therefore microbial) transport may not have the desired effect (Jamieson et al., 2004). It should be noted; however, that the impact force associated with simulated rainfall has been observed to detach and transport bacterial cells individually (Muirhead et al., 2005), as described in more detail below.

Oocysts and cysts also have an affinity for adsorption. While few studies have experimentally assessed (oo)cyst attachment (Ferguson et al., 2003), two have provided some insight into the processes involved. In a controlled experiment, Dai and Boll (2003) used flow cytometry and confocal microscopy to investigate the degree to which (oo)cysts attach to soil particles relative to positively and negatively charged beads. They quantified the negative surface charges on soil particles, negatively charged beads and (oo)cysts, and noted that neither cysts nor oocysts attached to beads or soil particles of like charge.
Attachment to positively charged beads; however, was observed. This is in contrast to studies which demonstrated attachment of (oo)cysts to organic matter in sewage and to sediments (Medema et al., 1998; Searcy et al., 2005, respectively). The discrepancy observed for organic matter is attributed to differing charge characteristics and adsorption behaviour for soil vs. biological aggregates found in sewage effluent (Dai and Boll, 2003). The discrepancy in the latter study (Searcy et al., 2005), is credited to the use of higher suspended sediment concentrations as part of the experimental protocol.

2.5.3.2. Hydrological and meteorological processes

Water is the primary transport medium linking pathogens to surface waters and thus, it is not surprising that many studies have observed correlations between rainfall events and waterborne disease outbreaks. Curriero et al. (2001) compared the incidence of waterborne disease outbreaks in the United States to precipitation levels between 1948 and 1994. A total of 68% of all outbreaks were preceded (in the same month) by rainfall events above the 80th percentile for their region. Kovatz et al. (2005), in an international study of the seasonality of laboratory-confirmed cases of campylobacter infection, also suggested a link between climate and incidence of infection. Further, extreme precipitation has been implicated as a causative factor in several outbreaks [e.g., Milwaukee, Wisconsin (Mackenzie, 1994), Walkerton, Ontario (Hrudey et al., 2003) and numerous outbreaks in Finland (Miettinen et al., 2001)].

These observations are supported by plot and watershed-scale studies linking rainfall to increased pathogen concentrations in surface waters. Schijven et al. (2004) identified the importance of rainfall impact force in (oo)cysts mobilization by applying the same volume of precipitation in mist and drop form to different types of manure in a laboratory environment. Release of oocysts and cysts was four and nine times higher, respectively, as a result of drip application. This was attributed to increased release efficiencies resulting from the impact forces of water droplets. In addition, cumulative release values were greater for oocysts than cysts, suggesting that release efficiencies are higher for smaller parasitic pathogens.

Muirhead et al. (2005) assessed the effects of rainfall on E. coli mobilization from cowpats after grazing using simulated rainfall. Transported cells were partitioned into attached (to particles) and unattached fractions. They observed that E. coli concentrations in surface runoff were strongly correlated to those in cowpats, and that cowpats served as a viable bacteria source for more than 30 days. Further, the majority of transported cells were not only unattached to soil or organic particles, but were also
transported as single cells, rather than in cell clumps. This is in contrast to studies which have noted cell clumping in surface waters (e.g., Kiorboe et al., 2002), and is thought to represent the initial transport phase of these cells (associated with mobilization by rainfall impact forces) prior to aggregating in surface waters. These results suggest that bacterial transport modeling, which has often equated bacterial transport with particulate (sediment) transport, needs to account for different bacterial mobilization and transport thresholds due to differences in mass and density when compared to sediment.

Several researchers have examined the relationship between rainfall and stream water quality in an effort to quantify the water-quality risk associated with storm events (Hansen and Ongerth, 1991; Atherholt et al., 1998; Kistemann et al., 2002). Kistemann et al. (2002) investigated the influence of rainfall on pathogen concentrations in tributaries of three German drinking water reservoirs, two of which had significant pathogen sources (agriculture or sewage treatment plants), while the third was almost entirely forested. Significantly higher bacterial concentrations were observed in surface waters of all three watersheds during rainfall events. Parasite concentrations were only observed to increase significantly in the non-forested watersheds where significant parasite sources were known to exist. A similar trend was documented by Atherholt et al. (1998). In an attempt to correlate (oo)cyst concentrations with more easily measured water quality parameters, they noted significant correlations between rainfall and parasite numbers in the Delaware River, and attributed the observed trend to increased overland transport as well as resuspension of stream-bottom sediment.

While pathogen concentrations generally show positive correlations with rainfall, microbe loading per unit of precipitation appears to follow a seasonal pattern that is controlled by source availability and rainfall frequency, thus complicating the development of a quantitative relationship between these two variables. Hunter and McDonald (1991) observed significantly higher fecal coliform concentrations in surface waters during summer months, and associated these values with higher concentrations in overland flow from agricultural fields at this time. The decrease in concentrations observed during the winter months was attributed to seasonal changes in the land store of enteric bacteria resulting from reduced application of manure and continual flushing by winter rains. Similar seasonal trends have been observed elsewhere (e.g., Hunter et al., 1999; e.g., Rodgers et al., 2003).

In-stream processes are also important in pathogen mobilization as streambed sediments can serve as a significant store of viruses, bacteria and protozoa. Pathogen concentration in sediments may be up to 1000 times those in the water column (Buckley et al., 1998). This has been attributed to
continual sedimentation of organisms adsorbed to sediments, stream access by livestock (Nagels et al., 2002) and prolonged survival of bacteria when associated with sediments (Sherer et al., 1992). To illustrate the importance of in-stream bacterial stores, Muirhead et al. (2004) created artificial floods downstream of a water reservoir during dry conditions. By eliminating bacterial transfer from the land surface via overland flow, they were able to assess bacterial loading from the streambed alone. For three successive flushing events of equal magnitude, turbidity and E. coli concentrations showed characteristic hysteretic responses, with peaks at the onset of maximum flow, followed by rapid declines for both parameters. Bacterial concentrations during the first storm event increased by more than two orders of magnitude. Subsequent floods over the next two days resulted in similar, but successively smaller peaks for both parameters, suggesting source exhaustion over time. A similar study (Nagels et al., 2002) documented the impact of a natural and an artificial flood on the same river. The natural event resulted in an increase in stream E. coli concentrations to a maximum of approximately 40,000 MPN/100 mL (most probable number per 100 mL), an increase of over two orders of magnitude from background levels. The artificial flood produced a peak concentration of over 12,000 MPN/100 mL, demonstrating the significance of the in-stream store to event-related bacterial concentrations in surface waters. Interestingly, the peak bacterial concentration for the natural storm was observed prior to peak flow, while the artificial flood generated maximum concentrations after peak flow was reached, due to the relative steepness of the artificial flood front.

Relatively little work has been done to assess the role of stream-bed sediments on (oo)cyst and virus concentrations in overlying waters. Work in the marine environment indicates that concentrations of viruses in sediment can exceed those in overlying seawater (Labelle et al., 1980), that bacterial concentrations in suspended flocs can exceed those in the sediment and water column (Schendel et al., 2004) and that sediments can increase survival time of viruses significantly (Labelle and Gerba, 1980). Further, the work of Medema et al. (1998) suggests (oo)cysts can settle out of suspension when significant amounts of organic matter are present. These studies indicate that stream sediments must be considered a potentially significant source for all pathogen types.

2.5.3.3. Mechanical and biological processes

Overland transport is often considered the primary pathway for pathogen movement (Jamieson et al., 2004). However, subsurface flow must be considered when assessing pathogen transport and
mitigation strategies, particularly where field drainage systems are present as they can represent a direct, subsurface link to surface waters. Ogden et al. (2001) assessed bacterial leaching to drainage systems after slurry applications in a plot-scale experiment. Between 0.2 and 10% leaching of *E. coli* bacteria to subsurface drainage systems was observed as result of rainfall, with the highest concentrations observed within a week of slurry application. Hunter et al. (1992) conducted a study to assess the relative contribution of overland flow, matrix throughflow and macropore flow to surface water bacterial cycling in an upland watershed in northern England. Each pathway was observed to transport fecal bacteria to surface waters, with macropore and overland flow contributing most to stream bacterial loading. For all pathways, loading was positively correlated with stream gauge height, illustrating the role of rainfall in surface and subsurface transport. It should be noted that rainfall is not required to initiate downward transport of pathogens. The application of liquid manure can lead to an almost instantaneous response in bacterial water quality in sub-surface soils and drains (Dean and Foran, 1992).

The presence of macropores in a soil profile allows transport of larger volumes of water and particulates down the soil profile than would be possible through the soil matrix, thus encouraging downward mobility of pathogens (Jamieson et al., 2002). Physical soil characteristics, biological activity and land management practices are the primary drivers of macropore development in a soil profile.

Soil texture has been observed to influence the development of macropores and the degree to which non-matrix (macropore) flow takes place. Flury et al. (1994) assessed the development of preferential flow pathways in soils of different texture and noted that structured, clay-rich soils are highly prone to macropore development when compared to poorly-structured, sandy soils.

Natsch et al. (1996) observed the influence of root growth and soil biological activity on downward movement of bacteria in two inoculated soils (one planted with wheat and regularly ploughed, the other a grassland that had not been tilled in several years). Downward migration in the grassland plot occurred to greater depths due to extensive earthworm activity, a well-developed, deep root network and the lack of an impermeable plough pan that had developed in the wheat field as a result of regular tillage. Regular tilling of the soil not only results in a plough pan, it also continually destroys macropore networks, and greatly decreases downward mobility of pathogens. Davies et al. (2004) observed a similar trend for oocyst transport and noted that overland flow was five times higher for unvegetated plots than vegetated plots. This resulted in significantly higher numbers of transported oocysts in overland flow.
2.5.4. Ecological and human health impacts

2.5.4.1. Ecological impacts

Emerging infectious diseases often arise from wild, domestic or livestock animal populations and are generally considered in light of their potential impacts to human health (Daszak et al., 2000). Indeed, in a review of the risk factors associated with emerging infectious diseases, Taylor et al. (2001) illustrated that 75% are caused by zoonotic pathogens. Recent work suggests; however, that emerging pathogens (those that have a sudden increase in range, have moved from one species to another, increased in severity, undergone a change in pathogenesis or are the result of recently evolved pathogens) can also significantly impact wildlife populations (Daszak et al., 2000; Environment Canada, 2001; Daszak et al., 2004). Daszak et al. (2000) referred to the transmission of emerging pathogens amongst populations in the same geographic region (often between livestock and local wildlife) as spill-over, and noted that spill-back, the re-transmission of a similar or more virulent form back to the original population, can have devastating effects on livestock.

One of the most dramatic examples of this is the well-documented global decline in amphibian populations observed in natural environments over the past several decades (Houlahan et al., 2000). Numerous potential causes were proposed, including habitat loss, increased UV radiation, pollution and climate change. Berger et al. (1998) proposed that the observed declines in Central America and Australia were actually the result of a fungal pathogen (phylum Chytridiomycota) that attacked epidermal cells of host organisms. Since then, this pathogen, which is thought to have emerged from humans, has been implicated in declines of several other amphibian populations globally (Daszak et al., 2004).

While water plays a role in transmission of wildlife pathogens (e.g., avian botulism, commonly observed in and around shallow lakes), limited conclusive evidence exists for waterborne transmission of emerging infectious diseases from livestock or humans to wildlife populations. Given the potential for emergence in wildlife populations as a result of genetic mutation and geographic expansion, and the subsequent threat posed to humans and livestock by spill-back, it has been recommended that a more proactive approach to wildlife infection be adopted (Daszak et al., 2000).
2.5.4.2. Human health impacts

The illnesses caused by some common waterborne pathogens were described previously (Section 2.5.1). This section describes health impacts at the population level by reviewing the incidence of waterborne outbreaks in BC, across Canada and internationally.

Waterborne disease in British Columbia

Recently, reviews were conducted of waterborne disease outbreaks in BC since 1980 (BC Provincial Health Officer, 2001; Christensen, 2003) and of drinking water infrastructure and drinking water sources in the province (BC Auditor General, 1999). Table 2-3 provides a summary of the 29 outbreaks to take place over this time period. This list illustrates some important points about waterborne illness in BC in terms of incidence, common pathogens, pathogen sources and mechanisms of infection.
Table 2-3 - Waterborne disease outbreaks in BC from 1980-2004. Modified from (BC Auditor General, 1999; Peck, 2004)

<table>
<thead>
<tr>
<th>Year</th>
<th>Location</th>
<th>Pathogen</th>
<th>Number of cases</th>
<th>Water Source</th>
<th>Suspected Pathogen Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980</td>
<td>Nakusp</td>
<td>Campylobacter</td>
<td>12 / 800</td>
<td>Surface</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1981</td>
<td>100 Mile House</td>
<td>Giardia</td>
<td>69</td>
<td>Surface</td>
<td>Beaver</td>
</tr>
<tr>
<td>1982</td>
<td>Kimberly</td>
<td>Giardia</td>
<td>82</td>
<td>Surface</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1984</td>
<td>Chilliwack</td>
<td>Salmonella</td>
<td>72</td>
<td>Surface</td>
<td>Beaver</td>
</tr>
<tr>
<td>1985</td>
<td>Creston</td>
<td>Giardia</td>
<td>109 / 3,125</td>
<td>Surface and groundwater</td>
<td>Beaver</td>
</tr>
<tr>
<td>1987</td>
<td>Black Mountain</td>
<td>Giardia</td>
<td>28</td>
<td>Surface</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1988</td>
<td>Kamloops</td>
<td>Campylobacter</td>
<td>50</td>
<td>Surface (spring fed)</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1990</td>
<td>Kitimat</td>
<td>Giardia</td>
<td>130</td>
<td>Surface</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1990</td>
<td>Creston</td>
<td>Giardia</td>
<td>25</td>
<td>Surface (spring fed)</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1990</td>
<td>Fernie</td>
<td>Giardia</td>
<td>146</td>
<td>Groundwater</td>
<td>Human (sewage break)</td>
</tr>
<tr>
<td>1990</td>
<td>West Trail/Rossland</td>
<td>Giardia</td>
<td>29 / 2,097</td>
<td>Surface</td>
<td>Beaver/wildlife</td>
</tr>
<tr>
<td>1991</td>
<td>Matsqui</td>
<td>Unknown</td>
<td>60</td>
<td>Surface</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1992</td>
<td>Kaslo</td>
<td>Campylobacter</td>
<td>10</td>
<td>Surface</td>
<td>Wildlife</td>
</tr>
<tr>
<td>1993</td>
<td>Fernie</td>
<td>Campylobacter</td>
<td>110 / 3,000</td>
<td>Surface</td>
<td>Cats/cougar</td>
</tr>
<tr>
<td>1995</td>
<td>Victoria</td>
<td>Cryptosporidum</td>
<td>71</td>
<td>Surface</td>
<td>Beaver/wildlife</td>
</tr>
<tr>
<td>1996</td>
<td>Cranbrook</td>
<td>Cryptosporidum</td>
<td>177 / 10,000</td>
<td>Surface</td>
<td>Calves</td>
</tr>
<tr>
<td>1996</td>
<td>Kelowna</td>
<td>Campylobacter</td>
<td>146</td>
<td>Groundwater</td>
<td>Human</td>
</tr>
<tr>
<td>1997</td>
<td>Princeton</td>
<td>Giardia</td>
<td>19</td>
<td>Surface and groundwater</td>
<td>Cattle</td>
</tr>
<tr>
<td>1998</td>
<td>Camp Malibu</td>
<td>Campylobacter</td>
<td>26</td>
<td>Surface</td>
<td>Wildlife</td>
</tr>
</tbody>
</table>
Table 2-3 emphasizes several key points regarding waterborne illness in the province: 1) waterborne illness has impacted thousands of people in British Columbia over the past 25 years, 2) the majority of outbreaks (97%) took place in systems with surface-water or mixed surfacewater and groundwater sources, 3) 59% of outbreaks were due to protozoan parasites, and 4) most outbreaks were associated with small water systems. As a result of the 29 outbreaks, there were 1,734 laboratory-confirmed illnesses. The true impact; however, was likely much greater as the number of unreported cases in such outbreaks can range from 10 to 1000 times those that are reported (Environment Canada, 2001). Of the total number of people affected by an outbreak, only a small percentage will see a physician, and only a percentage of those visits will involve a full microbiological workup (Krewski et al., 2002; Medema et al., 2003). As a result, it is likely that entire outbreaks go unreported, and that the number of confirmed cases in observed outbreaks significantly underestimates the true impact on public health (Medema et al., 2003). From 1986-1998, BC had the highest incidence of enteric disease rates in Canada, with rates ranging from approximately 140 to 210 cases per 100,000 individuals. This is 30-300% higher than incidence rates in other Canadian provinces (BC Provincial Health Officer, 2001).

Of the 29 water systems involved in the BC outbreaks, 28 derived their water from surface water sources (or, in some cases, a combination of surface and groundwater). Approximately 76% of the province's drinking water is derived from surface-water sources, as illustrated in Figure 2-5 (a disproportionately high percentage compared to the rest of Canada). There are currently over 3,300 water systems in British Columbia, 96 of which are large municipal systems that serve 90% of the province's population. The remaining 10% are served by smaller private and public systems which are much more difficult to monitor, inspect and regulate. In 2003 there were as many as 340 boil-water advisories in place at one time, indicating that there was sufficient concern regarding water quality to require users of these smaller systems to disinfect their water prior to consumption.
Protozoan parasites, particularly *Giardia*, were responsible for the majority of BC outbreaks over the past 25 years. In most cases, it is believed that contamination was derived from wildlife sources; however, several cases of livestock contamination were also observed. This is not surprising given many of these small water systems are in rural communities. Further, most of the systems are supplied with surface water, which is much more likely than groundwater to become infected by protozoan pathogens.

Most of the 29 outbreaks took place in small water systems. Many of these systems (30%) did not utilize any form of water treatment or disinfection (no filtration or chemical additives). In several others, chemical disinfection was accomplished with chlorine or chloramines which were ineffective against protozoan parasites (Christensen, 2003).

National and international burden of waterborne disease

In Canada, waterborne disease outbreaks have been recorded by Health Canada since 1974, and from that time until 1996 over 200 outbreaks were identified. These outbreaks resulted in 8,000 confirmed cases of illness (Todd and Chapman, 1974-1996 in Environment Canada, 2001); however, for the reasons described above this is likely a significant underestimate. Further, this number does not include the impact of the Walkerton, Ontario, and North Battleford, Saskatchewan, outbreaks.

In the United States, several researchers have attempted to estimate the incidence of waterborne disease in humans. Rose et al. (1999) cited an estimate (from the US CDC) of up to 900,000 cases of
illness and up to 900 deaths resulting from waterborne infections each year. Morris and Levine (1995 in Medema et al., 2003), in an assessment of the waterborne disease burden in the US, estimated that 560,000 people may suffer from moderate to severe symptoms, and that 7.1 million people suffer from mild to moderate infection as a result of waterborne disease. Considering the many similarities between drinking water systems in Canada and the US, it is not unreasonable to estimate that the incidence of waterborne disease in Canada could be 10% of that in the US, on the basis of relative population size (Environment Canada, 2001). This suggests that such illness affects between 50,000 and 100,000 people annually in Canada.

Globally, assessing the burden of waterborne disease is more complicated. The WHO estimates that 1.1 billion people worldwide do not have access to clean water (World Health Organization, 2000). While the impact of this in terms of disease burden is not known, an extrapolation of data for the United States and Canada, two highly industrialized countries, indicates that it is severe. Pruss et al. (2002) estimate the impact of disease arising from water, sanitation and hygiene issues to be approximately 4% of all deaths and 5.7% of the global disease burden.

While the above are estimates of the impact of waterborne illness, they indicate the magnitude of the waterborne disease burden at the local, national and international level. Pruss et al. (2002) suggest that much of the disease burden attributed to water, sanitation and hygiene is preventable. As described below, considerable effort is now focused on the development of innovative monitoring technologies and risk-management frameworks in order to address this issue.

### 2.6. Water-quality monitoring

Given the strong dependence in BC on surface water as a drinking water source, and the significant potential for contamination of these waters with chemical or biological agents, it is clear that water quality monitoring is critical to ensuring the safety of drinking water supplies. This section describes the common techniques and tools used for detecting and quantifying the contaminants described above, and includes a review of their effectiveness, advantages and disadvantages. This is followed by a discussion of recently-developed frameworks that have been recommended to ensure drinking water quality. The purpose of this section is to illustrate the strengths and weaknesses of current monitoring methodologies, and is not intended as a comprehensive review and description of each available method. For such details, the reader is referred to the American Public Health Association’s *Standard Methods for
the Examination of Water and Wastewater (American Public Health Association, 1999), hereafter referred to as "Standard Methods."

2.6.1. Detection methods

Table 2-4 summarizes the common methods used to detect different contaminant types (nutrients, bacteria, protozoa and viruses) in water. Issues of importance for a given monitoring technique include timeliness, detection limit and accuracy. These are addressed in greater detail below.
Table 2-4 - Common detection techniques for various water-quality parameters.

<table>
<thead>
<tr>
<th>Variable/Organism</th>
<th>Method Name</th>
<th>Method Description</th>
<th>Water volume required</th>
<th>Field/ Laboratory</th>
<th>Turnaround Time</th>
<th>Detection Limit</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical/Chemical Variables</td>
<td>Conductivity</td>
<td>NA</td>
<td>Field sensor</td>
<td>Measured in situ</td>
<td>Field/laboratory</td>
<td>Instant</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>NA</td>
<td>Field sensor</td>
<td>Measured in situ</td>
<td>Field/laboratory</td>
<td>Instant</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>NA</td>
<td>Field sensor</td>
<td>Measured in situ</td>
<td>Field/laboratory</td>
<td>Instant</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Dissolved oxygen</td>
<td>NA</td>
<td>Field sensor</td>
<td>Measured in situ</td>
<td>Field/laboratory</td>
<td>Instant</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Chloride</td>
<td>Standard Methods - Method 4130</td>
<td>Flow injection analysis</td>
<td>&lt; 1 ml</td>
<td>Laboratory</td>
<td>4-6 hours</td>
<td>Variable</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Reagents, specialized equipment and trained technicians required</td>
</tr>
<tr>
<td>Nutrients</td>
<td>Phosphorus</td>
<td>Standard Methods - Method 4130</td>
<td>Flow injection analysis</td>
<td>&lt; 1 ml</td>
<td>Laboratory</td>
<td>4-6 hours</td>
<td>.02 mg·L⁻¹</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>Standard Methods - Method 4130</td>
<td>Flow injection analysis</td>
<td>&lt; 1 ml</td>
<td>Laboratory</td>
<td>4-6 hours</td>
<td>.05 mg·L⁻¹</td>
</tr>
<tr>
<td></td>
<td>Nitrite</td>
<td>Standard Methods - Method 4130</td>
<td>Flow injection analysis</td>
<td>&lt; 1 ml</td>
<td>Laboratory</td>
<td>4-6 hours</td>
<td>.1 mg·L⁻¹</td>
</tr>
<tr>
<td></td>
<td>Ammonium</td>
<td>Standard Methods - Method 4130</td>
<td>Flow injection analysis</td>
<td>&lt; 1 ml</td>
<td>Laboratory</td>
<td>4-6 hours</td>
<td>6 mg·L⁻¹</td>
</tr>
<tr>
<td>Protozoa</td>
<td>Giardia</td>
<td>EPA 1623</td>
<td>Filtration, immunomagnetic separation, immunofluorescence assay</td>
<td>10-100 L</td>
<td>Laboratory</td>
<td>36 hours</td>
<td>Variable</td>
</tr>
<tr>
<td></td>
<td>Cryptosporidium</td>
<td>EPA 1623</td>
<td>Filtration, immunomagnetic separation, immunofluorescence assay</td>
<td>10-100 L</td>
<td>Laboratory</td>
<td>36 hours</td>
<td>Variable</td>
</tr>
<tr>
<td>Bacteria</td>
<td>Total Coliform</td>
<td>Standard Methods - Method 9222</td>
<td>Membrane filter technique for members of the coliform group</td>
<td>100 L</td>
<td>Laboratory</td>
<td>48 hours</td>
<td>Variable</td>
</tr>
<tr>
<td></td>
<td>Fecal Coliform</td>
<td>Standard Methods - Method 9222</td>
<td>Membrane filter technique for members of the coliform group</td>
<td>100 L</td>
<td>Laboratory</td>
<td>48 hours</td>
<td>Variable</td>
</tr>
<tr>
<td>Viruses</td>
<td>Enteric Viruses</td>
<td>Standard Methods - Method 9510</td>
<td>Virus concentration and enumeration</td>
<td>2-200 L</td>
<td>Laboratory</td>
<td>48-72 hours</td>
<td>Variable</td>
</tr>
</tbody>
</table>
2.6.2. Parameters

2.6.2.1. Physical and chemical variables

Temperature, dissolved oxygen, specific conductance or conductivity (a measure of total dissolved solids), and pH are commonly measured in the field using hand-held sensors. Assessing these parameters in the field is advantageous as they are quickly measured and can be used to gain preliminary insight into contaminant sources and flow pathways. Water from different stores in a watershed (groundwater, surface runoff) often has characteristic values for these parameters due to the different physical and chemical characteristics and processes associated with each. For example, groundwater, due to prolonged contact time with bedrock or surficial materials, often carries a greater dissolved load than surface runoff, and therefore has a higher conductivity (and often a consistently different temperature). Further, surface-runoff sources can be discerned based on these variables with agricultural sites often having higher conductivity than forested sources (Dow and Zampella, 2000). When monitoring for agricultural contamination, these parameters are valuable proxies for water impairment, but they do not provide a direct measure of contamination or potential risk.

2.6.2.2. Nutrients

Nutrient concentrations are often measured using colourimetric techniques that require filtered samples, specialized laboratory equipment, reagents and trained operators. The time required for analysis is generally several hours, when sample and reagent preparation are included.

Monitoring of surface-water nutrient concentrations is a means to detect and quantify the influence of agricultural land use on surface water quality. Natural, or background, levels of NO$_3^-$, P and NH$_4^+$ tend to be around 0.1 mg·L$^{-1}$, 0.005-0.02 mg·L$^{-1}$ and 0.1-3.0 mg·L$^{-1}$, respectively in mesotrophic systems. Thus, values above these ranges are often an indication of agricultural contamination (Chapman and Kimstach, 1992). Aside from the direct impact of nutrient loading on water quality, nutrients can also serve as a surrogate for potential pathogen loading from agricultural operations.

2.6.2.3. Bacteria

Compared to viruses and protozoa, detection and quantification of coliform bacteria in water is relatively easy. Broadly defined, coliforms are a group of rod-shaped, gram-negative bacteria that include the genera *Escherichia*, *Enterobacteria*, *Klebsiella*, *Citrobacter* and many others. This group, also referred
to as “total coliforms”, is often used as an indicator of fecal contamination because many of its members are found in the intestinal tract of warm-blooded organisms. However, many bacteria in the total coliform group are non-fecal (thriving in the environment), and, therefore, have limited use as indicators of contamination, due to the potential for false positives (i.e., they may be present when fecal contamination has not occurred). Instead, the non-fecal bacteria are used to assess bacterial growth in drinking-water treatment and distribution systems. The fecal (or thermotolerant) coliforms are better indicators of fecal contamination because they are almost always derived from the gut of warm-blooded organisms. While these coliforms may also arise from non-fecal sources (e.g., industrial wastes) they are a more specific indicator than the total coliform group and are the most commonly used indicator of bacterial pollution (Rosen, 2000; Jamieson et al., 2004). Escherichia coli, a member of the fecal coliform group, are specific to the intestinal tract and are the best indicators of fecal contamination among coliforms. While some strains are pathogenic (e.g., E. coli O157:H7, described in Section 2.5.1.1), the majority are not.

The most common technique for enumeration of coliform bacteria from water samples is Method 9222 (membrane filter technique for members of the coliform group) outlined in Standard Methods (American Public Health Association, 1999). The technique involves filtering between 100-1000 mL of water onto a membrane filter, placing the filter into a nutrient-rich growth medium and incubating it at 35 °C or 44.5 °C for 22-24 hours. The two temperatures are used to differentiate between total coliforms and E. coli (35 °C) and fecal coliforms (44.5 °C), and for each temperature a different culture medium is used. After incubation, colonies that have grown on the filter are identified and enumerated and the concentration is given in colony forming units (cfu) per 100 mL.

Recent work has focused on the validity of these bacteria as indicator organisms. While fecal coliforms and E. coli are accepted indicators of fecal contamination, they do not always correlate well with viral and protozoan concentrations in water (Krewski et al., 2002). This is primarily due to: 1) differences in susceptibility to environmental stressors, 2) differing methods of reproduction (neither viruses nor protozoa can reproduce outside of a host), 3) different mobilization and transport patterns and, 4) in treated water, differing levels of resistance to traditional methods of disinfection (Heise and Gust, 1999; Krewski et al., 2002). While many studies report a significant correlation between indicator bacteria and viral or protozoan pathogens in untreated source waters (e.g., Lechevallier et al., 1991), several report poor or no correlation with these pathogens (Grabow, 1996; Ehlers et al., 2005) or with waterborne illness (Craun et al., 1997).
2.6.2.4. Protozoa

Detection methods for Giardia and Cryptosporidium are significantly more expensive, complex and time consuming than for bacteria, as protozoa cannot be cultured. The most common method for enumeration of these organisms involves three steps: 1) filtration, 2) elution and separation and 3) enumeration. Because (oo)cysts tend to be present in relatively low concentrations, and because recovery of (oo)cysts is not always complete, this method requires the filtration of large volumes of water (commonly 10-100 L). All material on the filter is then eluted and centrifuged. The supernatant fluid is then removed and magnetic beads are used to separate the (oo)cysts from the remaining detritus. The magnetic beads selectively attach to the (oo)cysts as they are bound with Giardia- and Cryptosporidium-specific antibodies (a process referred to as immunomagnetic separation). The (oo)cysts are then extracted using a magnet, stained with fluorescently labeled antibodies and enumerated using fluorescence and differential interference contrast microscopy (US EPA, 2001). This analysis requires approximately 1.5 days (S. Shay, personal communication).

Although this method is currently the standard, it has several constraints which limit its widespread use. These include the significant costs associated with the equipment and materials involved, as well as the person hours required to process each sample (the enumeration step can take several hours). Further, recovery of (oo)cysts is often incomplete, meaning that false negatives are possible.

Molecular techniques such as polymerase chain reaction (PCR) are also used to detect (oo)cysts and identify live and dead oocysts (Mahbubani et al., 1991). Molecular techniques also allow for the identification of specific protozoan genotypes which assists in identifying contaminant sources (Ong et al., 2002).

2.6.2.5. Viruses

Regular screening for viruses in surface waters is not currently done, primarily because existing methods are evolving rapidly (American Public Health Association, 1999). Further, many outbreaks attributed to waterborne enteric viruses have been associated with significant contamination events involving human sewage, and as a result, can be detected using traditional indicator bacteria. However, because viruses are more resistant to environmental degradation and disinfection than bacteria (Health Canada, 2004a) and because they are increasingly observed in surface waters (Ehlers et al., 2005) and
treated drinking water supplies that have met current standards for bacterial water quality (Vivier et al., 2004), methods for detection and enumeration are continually being refined.

Standard methods for the enumeration of viruses in water involve collection of a sample of appropriate volume (2-200 L, depending on source), the concentration of viruses from that sample and the culturing of these viruses (in primate cells or living organisms, such as mice) to enable identification and enumeration. The details of this procedure are beyond the scope of this section, and the reader is referred to American Public Health Association (1999) for a complete description. There are several limitations and/or challenges associated with the detection of viruses in water samples, including: 1) the small size of virus particles, 2) low virus concentrations in water, and significant variation in concentrations, 3) the inherent instability of viruses, 4) interference from dissolved and suspended materials and 5) limitations in current estimation and quantification techniques.

Currently, the processes described in Standard Methods require several days to complete. Therefore, they have limited use as a preventative monitoring tool. However, recent progress in detection techniques has been made using a combination of viral culture and PCR. This has allowed more rapid identification and enumeration of waterborne viruses (Abbaszadegan et al., 1999; Vivier et al., 2004). These techniques have yet to be incorporated into Standard Methods.

It should be noted that bacteriophages (viruses that infect bacteria) have also been proposed as indicators of fecal pollution. They are useful indicators as they often survive longer than bacteria, are specific to their hosts and, in groundwater, can travel farther than larger pathogens (Abbaszadegan et al., 1999; Health Canada, 2004a). To date, efficacy studies of these organisms as indicators have yielded inconsistent results due to the many variables that affect bacteriophage survival in water, as well as a lack of standardization of detection and enumeration techniques (Ashbolt et al., 2001; Health Canada, 2004a). As a result, they have not gained widespread acceptance as effective indicators.

2.6.3. Monitoring frameworks

The approach used to monitor surface water quality in a given watershed is determined by the objectives of the monitoring program. If the objective is to gain insight into specific physical, chemical or biological processes, a focused program may be implemented to test a defined research hypothesis. Such programs are often designed to capture spatial and/or temporal variations in water-quality
parameters at the scales of interest, and over a specified time period, and are therefore unique to each project.

Where drinking water is derived from surface-water sources, the objective of a monitoring program is first to assess the suitability of the source. Once the source is chosen, the objective is to detect potential contamination events and support necessary interventions to minimize the risks of human health impacts. While such programs may also illustrate cause-effect relationships between activities of human and/or animal populations and water quality, the primary goal is the protection of human health. As a result, such monitoring programs are often more robust and more rigorous than those designed solely for research purposes.

This section provides a review of two methodologies designed to monitor drinking-water quality that are based on the principles of risk management. The Multi-barrier Approach and the Hazard Analysis and Critical Control Point framework, are two methodologies that have been applied to drinking-water systems in response to several waterborne outbreaks (Krewski et al., 2002; Hrudey et al., 2003). These frameworks demonstrate the importance of source watershed protection and provide the context for the following section (2.7 Spectroscopy and water quality), which describes spectrophotometry as a tool for water quality monitoring.

2.6.3.1. The Multi-barrier Approach

The premise behind the multi-barrier approach is that redundancy minimizes the risk associated with the failure of any one point in a drinking water system. In other words, no process will have a 0% risk of failure, and therefore, multiple processes with low failure rates, working in serial, offer the greatest chance of protection against a failure in any one process (Anonymous, 2002; Krewski et al., 2002; O'Connor, 2002).

In the context of drinking water, this approach is applied from "source-to-tap," meaning that multiple barriers are implemented between the source watershed and the end user, as illustrated in Table 2-5. This framework requires that each barrier have unique modes of failure (i.e., a failure in one will not result in a failure in any of the others), and that no barrier be relied upon at the expense of the others, as this could result in a failure of the overall system.
The multi-barrier approach has been adopted in principal as a framework for drinking water quality protection at the Federal level in both Canada and the United States, and forms the foundation for guidelines and legislation related to drinking water systems. In both countries, guidance documents have been developed to assist municipal and provincial/state governments in the implementation of the multi-barrier framework (US EPA, 2003; Federal-Provincial-Territorial Committee on Drinking Water and CCME Water Quality Task Group, 2004).

A review of the multi-barrier approach would not be complete without mentioning recent advances in the application of more advanced risk management methodologies to drinking-water protection. The Hazard Assessment and Critical Control Point (HACCP) framework is a commonly employed risk assessment and management tool. This approach, initially developed by NASA and the Pillsbury Company to ensure the safety of food consumed by astronauts, is based on the principle of controlling key "risk points" within a system to limit the potential for contamination, and it has been successfully adapted to water systems within the multi-barrier framework. The process begins with a full drinking-water system assessment in order to identify key hazards or risks for contamination. Critical control points within this system are then identified so that controls can be implemented to eliminate or reduce the identified risks. Each control point is closely monitored to ensure that quality parameters are maintained below pre-
Chapter 2

defined thresholds. Further, plans for corrective action are defined in advance to ensure proactive response if thresholds are exceeded, and continual improvement is ensured through a series of performance measurement processes and reviews (Federal-Provincial-Territorial Committee on Drinking Water and CCME Water Quality Task Group, 2004). The HACCP approach is similar to other “quality management systems” such as ISO 9000 and ISO 14000 in that it is designed to minimize risk by identifying all potential hazards, implementing processes to control them and ensuring continual improvement through ongoing review and revision. The integration of these strategies into national water-quality management strategies is already taking place in several countries. Australia’s Drinking Water Guidelines are often cited as a good example of a comprehensive, national water quality management system (Anonymous, 2002).

Of particular relevance to this study is the emphasis placed by these frameworks on source protection, the first in a series of protective barriers from source to tap. Both frameworks stress a thorough source-watershed review, an assessment of potential risks (based on potential contaminants and water resource vulnerability) and continual monitoring in order to minimize the risk of contamination and to support a proactive approach to water quality management. This is represented graphically in Figure 2-6, which illustrates the components of source protection as outlined in Canadian guidance documents.
Figure 2-6 - A framework for source protection as part of the multi-barrier approach (modified from Federal-Provincial-Territorial Committee on Drinking Water and CCME Water Quality Task Group, 2004)

Water-quality monitoring in source watersheds is integral to the multi-barrier approach. A comprehensive monitoring program provides the information necessary to: 1) identify and quantify contamination risk, 2) determine the vulnerability of source waters, 3) quantify spatial and temporal trends in contaminant loading in order to target remediation and risk mitigation activities and 4) provide information to stakeholders (end users, water system managers, etc.) for decision-making purposes (Federal-Provincial-Territorial Committee on Drinking Water and CCME Water Quality Task Group, 2004).

As outlined above, monitoring for all potential hazards associated with agricultural activities is not feasible due to the costs, time required and limitations of many tests in terms of contaminant detection. It is therefore necessary to utilize a few key indicators that provide a realistic approximation of water quality risk. In agricultural watersheds, the greatest potential risks are likely to be associated with farming operations (unless large wildlife populations are also present). Thus, monitoring for agricultural influence on surface water quality is essential. The following section describes how fluorescence and absorbance properties of surface waters may be used to accomplish this.
2.7. Spectroscopy and water quality

In recent years there has been significant focus on the potential for spectroscopic properties of water to act as water-quality indicators and to assist with source and flow-path identification. This section provides an overview of the theory and principles of spectroscopy as related to water analysis. It then reviews the recent literature concerning the use of this technology to assess water quality and makes inferences regarding contaminant loading and transport processes in marine and freshwater environments.

2.7.1. Theoretical background

Spectroscopy is the study of the absorption or emission of electromagnetic energy by atoms or molecules in order to quantitatively or qualitatively study elements and compounds. It is based on the principle that elements or compounds absorb and emit energy at characteristic wavelengths when irradiated with energy at a known wavelength (or wavelengths). This review focuses on the use of absorbance and emission (fluorescence) spectroscopy as a tool for assessing water quality using light energy in the ultraviolet (UV), visible (Vis) and infrared (IR) range (between 200 and 900 nm, see Figure 2-7).

![Figure 2-7 - UV-visible-near infrared spectrum with wavelengths in nm.](image)

When a substance is irradiated with light energy, the incoming energy is converted into internal energy through absorption. This energy is then dissipated in the form of fluorescence. These processes are illustrated schematically using a Jablonski diagram (Figure 2-8). Absorption results in the excitation of a molecule to a higher-energy state. The absorbed energy is translated into rotational, vibrational modes or it can elevate the molecule to an excited state, depending on the wavelength of incoming light.
Because vibrational and rotational energy levels are relatively close together (vibrational levels fall between the rotational levels shown in Figure 2-8), long-wave radiation (i.e., in the infrared range) often results in excitation to these levels. Higher-energy visible or UV radiation results in a transition to a higher electronic state (S1, S2, etc.), when its wavelength, multiplied by Planck's constant, equals the energy difference between the ground state and the excited state (Sharma and Schulman, 1999). When this occurs, energy is almost immediately dissipated through a process called internal conversion or vibrational relaxation (a radiationless transition to lower energy levels), until the molecule reaches the lowest vibrational level of the first excited state. The molecule then returns to any of the vibrational levels of the ground state. This process results in the emission of light energy in the form of fluorescence (Lakowicz, 1999).

![Jablonski Diagram](image)

Figure 2-8 - Jablonski diagram illustrating the processes of absorption, internal conversion and fluorescence. Times associated with each process are also provided (modified from Lakowicz, 1999).

Due to energy loss during this process (through heat, collisions or vibration), energy is emitted at a longer wavelength (lower energy level) than that of the excitation energy. The difference between excitation and emission wavelengths is termed the Stokes shift. While the entire process takes only a
fraction of a second, the time required for each step (absorption, internal conversion and fluorescence) varies by orders of magnitude as illustrated in Figure 2-8.

### 2.7.2. Absorbance spectroscopy

Absorbance spectroscopy is the qualitative and quantitative study of absorption patterns of compounds, generally in solution. Substances in solution are identified qualitatively according to unique absorption patterns (i.e., the wavelengths at which absorption occurs). The concentration of a solute can also be determined using absorbance spectroscopy as the amount of energy absorbed by a substance in solution is directly related to its concentration, as determined by the Beer-Lambert Law, described below (Lakowicz, 1999). Absorbance is a dimensionless variable that is calculated as:

\[
A = \log_{10}\left(\frac{P_0}{P}\right)
\]

where:
- \(P_0\) = radiant power of incident radiation at a given wavelength
- \(P\) = radiant power of outgoing light

The Beer-Lambert law describes how absorbance varies as a function of the concentration of a substance in solution:

\[
A = \varepsilon bc
\]

where:
- \(\varepsilon\) = molar absorptivity of the substance (wavelength dependent)
- \(b\) = pathlength of the sample container (absorbance increases with pathlength)
- \(c\) = concentration of the substance in solution

It should be noted that there is some confusion in the literature regarding the nomenclature related to absorption spectroscopy, particularly the terms “absorbance” and “absorption coefficient” (Hu et al., 2002). Throughout this document, the terms absorbance and absorption refer to the dimensionless parameter defined by the equation: \(A = \log_{10}(P_0/P)\).

The instrument used in UV-Vis absorbance spectroscopy (also referred to as UV-Vis-NIR spectroscopy, for near-infra-red) is an absorbance spectrophotometer, illustrated schematically in Figure 54.
2-9. A variety of lamps are employed as light sources for absorbance spectroscopy, including tungsten, deuterium and xenon. An important characteristic of the lamp is the spectral range of the emitted light. Both tungsten and deuterium lamps are often used; however, their spectral ranges are 340-1000 nm and 180-400 nm, respectively, meaning that two light sources are required to span the full UV-IR spectrum. Xenon lamps emit light across the full spectral range (180-1100 nm) and are therefore more versatile and more commonly used (Boeker and van Grondelle, 2001). The wavelength of light reaching the sample is controlled by a monochromater, or filter, which selects the specific wavelength for analysis, or adjusts to scan across a range of wavelengths. The sample, commonly in liquid form, is held in a cuvette, ideally made of quartz to allow transmission of UV radiation (plastic cuvettes are not UV-transparent).

![Schematic representation of an absorbance spectrophotometer.](image)

An absorbance spectrum is a plot of absorbance as a function of wavelength (Figure 2-10). The shape of the absorbance spectrum is used to qualitatively identify one or several compounds in solution, based on the location of absorbance peaks. When several absorbing compounds are present in solution, their absorbance peaks may overlap, thus making it difficult to resolve individual maxima and to detect individual compounds. This issue is addressed using derivative spectroscopy, whereby the derivative (first, second, nth) of the absorbance values is plotted against wavelength (described in Section 2.7.5.3). Note also that the emission spectrum is commonly a mirror image of the absorbance spectrum as the same energy transitions are favoured for both absorbance and emission (Lakowicz, 1999). However, this is not observed if there are compounds in solution that do not fluoresce (Coble, 1996).
2.7.3. Fluorescence spectroscopy

Fluorescence or emission spectroscopy deals with the release of energy from a molecule or atom that has been irradiated with a high-energy light source. As with absorbance, compounds in solution have characteristic fluorescence signatures which provide both qualitative and quantitative information. The location of fluorescence peaks are often given as excitation-emission pairs, with the first number representing the excitation wavelength, and the second the emission wavelength at which the peak appears. The intensity of a fluorescence peak is measured in fluorescence units which are dimensionless, and calculated as:

\[ F = \phi I_0 (1 - e^{\varepsilon bc}) \]

where:

- \( F \) = fluorescence intensity
- \( \phi \) = quantum efficiency (number of photons emitted as a percentage of those absorbed, with a maximum value of one)
- \( I_0 \) = radiant power (amount of energy associated with incoming radiation)
- \( \varepsilon \) = molar absorptivity of the substance (wavelength dependent)
- \( b \) = pathlength of the sample container
- \( c \) = concentration of the substance in solution
A fluorescence spectrophotometer is schematically similar to an absorbance spectrophotometer. Similar light sources are used (with xenon lamps being most common), a monochromater is employed to control the wavelength of radiation directed at the sample and the sample is contained in a quartz cuvette. A second monochromater is used between the sample and the detector to detect fluorescence at specific wavelengths.

Several methods are employed to analyse and represent fluorescence data. Excitation spectra are generated by measuring the intensity of emission at one wavelength, while varying the excitation wavelength. Emission spectra, on the other hand, are obtained by measuring the variation in emission or fluorescence intensity across a range of wavelengths, while maintaining a fixed excitation wavelength (Figure 2-11). The type of spectra recorded depends on the purpose of the analysis.

![Figure 2-11](image)

**Figure 2-11** - Emission spectra for river water (at three excitation wavelengths) illustrating several features: 1) Rayleigh-Tyndall scattering, 2) Raman scattering and 3) variations in fluorescence intensity based on excitation and emission wavelengths (see text for explanation).

Figure 2-11 illustrates several important features of emission spectra that are relevant when analysing fluorophores in water. When incident light reaches the water sample in the cuvette, it is either absorbed or transmitted, as described above. However, it can also be scattered by molecules and
particles in suspension, resulting in detection of a strong energy signal at the same wavelength as the incoming radiation. Rayleigh and Tyndall scattering are terms used to describe scattering that arises from molecules and particles, respectively. A second type of scatter, Raman scattering, is similar but involves some loss of energy to the molecules in solution. This occurs when a small portion of the energy of incoming photons is lost to rotational or vibrational processes within a molecule (but it does not result in a transition of the molecule to a higher excited state). These photons, having lost some energy, are then scattered and detected at a slightly longer wavelength (Lakowicz, 1999). Because Raman scattering involves only a small proportion of incoming radiation, it is weaker than Rayleigh Tyndall scattering, and usually weaker than the fluorescence arising from the sample (both types of scatter are also illustrated in Figure 2-12). These forms of scatter are relevant as they can interfere with the analysis of fluorophores in solution, particularly if fluorescent peaks are found near the excitation wavelength. This is addressed either by subtracting the emission spectra of a de-ionized water “blank” or through the application of algorithms to remove scatter peaks and subsequent interpolation of the remaining data (Zepp et al., 2004).

To fully characterize a water sample using fluorescence spectroscopy, emission spectra must be obtained over a range of excitation wavelengths. A useful way to represent and analyse these data is to create a matrix of resulting fluorescence intensities (referred to as an excitation-emission matrix, or EEM) and plot a surface of these values, in either two or three dimensions (Figure 2-12). This type of plot clearly illustrates the Rayleigh-Tyndall line (occurring along the line where excitation equals emission), Raman scattering and three fluorescence peaks commonly observed in surface waters (associated with humic material, fulvic material and tyrosine, explained in greater detail below). It is also very useful for an initial, qualitative assessment of compounds in a water sample, as they will have peaks in known regions on the EEM plot (i.e., known excitation-emission pairs). A quantitative assessment of concentration can be obtained by measuring fluorescence intensity in these peak regions. Collection of fluorescence information in this format at the time of analysis is also advantageous as it allows for the data to be analyzed in many different ways after collection. This includes EEM’s, excitation spectra, emission spectra or synchronous-scan spectra (obtained when a sample is irradiated across a range of excitation wavelengths, and fluorescence is detected at Ex+n, where Ex=excitation wavelength and n is a constant integer) (Coble, 1996).
2.7.4. Advantages and limitations of spectroscopic techniques

The use of spectroscopic techniques for the assessment of water quality has become increasingly common in recent years. This is due to recent technological improvements that have improved the capabilities and performance of fluorescence and absorbance spectroscopy equipment. Spectroscopic techniques offer several advantages over traditional water-quality monitoring approaches, including 1) rapid analysis, 2) low sample volumes, 3) high sensitivity, 4) minimal sample preparation (filtering), 5) no requirements for reagents, 6) non-destructive analysis and 7) the potential for real-time monitoring using automated sensors (Reynolds and Ahmad, 1997; Ahmad and Reynolds, 1999; Baker and Curry, 2004).

Absorbance scans require very little time after water samples have been filtered, with one scan from 200-900 nm lasting approximately one minute (depending on the scan rate). Absorbance spectrophotometers can also be equipped with multi-sample trays allowing automated throughput of several samples in series. Fluorescence scans require minutes to several hours, depending on the range.
of excitation and emission wavelengths used, and on the desired signal to noise ratio, or SNR (a lower SNR requires longer data collection times at each excitation-emission pair).

Very little sample is required for absorbance and fluorescence scans. Most standard cuvettes hold 3-4 mL of sample, with only 2 mL required for standard analysis. Smaller cuvettes can also be used, requiring only 80-90 µL of sample. As a result, the majority of the original sample is available for other analyses.

Both fluorescence and absorbance scans are highly sensitive. Depending on the fluorophore, fluorescence scans detect in the range of parts per million (ppm) or parts per billion (ppb). Measures of absorbance can also be used to detect in these ranges; however, fluorescence tends to be more sensitive due to the relatively lower background signal. In other words, when measuring absorbance, the detector is comparing the difference between two relatively strong signals of the same wavelength, while a fluorescence system is detecting a relatively weak emission signal against very low background levels (Lakowicz, 1999).

Spectroscopic techniques require minimal sample treatment. Filtering is necessary to remove particulates that could affect light transmission; however, no other treatment is necessary. As many optically active components of interest are dissolved (see below), filtering does not adversely affect the analysis. Neither fluorescence nor absorbance techniques require the addition of reagents, further simplifying the analysis process. Further, both types of scan are non-destructive, meaning that the sample is available for further analyses if required.

While both techniques offer significant advantages over traditional approaches to water-quality assessment, they do have limitations. These limitations must be accounted for in order to ensure proper interpretation of results. Firstly, fluorescence is sensitive to several environmental variables, including pH and temperature. Changes in pH can result in a shift in the wavelength of fluorescence peaks or the elimination or creation of fluorescence due to chemical alterations associated with the presence of an acid or base (Sharma and Schulman, 1999). Temperature also strongly influences fluorescence as it directly controls sample viscosity. A higher-viscosity sample results in more molecular collisions, thus increasing energy loss in forms other than fluorescence emission (i.e., heat). Generally, higher temperatures result in decreased fluorescence. Many fluorescence spectrophotometers are equipped with temperature-stabilizing cuvette holders to address this problem.
Quenching is a process by which quantum efficiency of a fluorophore is reduced, through one of several mechanisms. Collisional quenching involves loss of excitation energy from an excited molecule as heat (rather than fluorescence) as a result of contact with other molecules. Static quenching occurs when a fluorophore forms a non-fluorescent compound as a result of interactions with another substance in solution. Resonance energy transfer is another form of quenching whereby an excited molecule transfers energy via electronic coupling to another molecule in a ground state, without a collision actually taking place (Lakowicz, 1999). Inner-filtering is another type of quenching arising from the presence of other absorbing compounds in solution (or high concentrations of the compound of interest). This can result in attenuation of incoming or emitted radiation, thus altering the fluorescence intensity measured at the detector. The absorbance of excitation energy and emitted radiation are referred to as primary inner-filtering and secondary inner-filtering, respectively. These processes result in a non-linear relationship between concentration and fluorescence (i.e., very high fluorophore concentrations could actually produce very low fluorescence intensity) and thus, must be corrected for when significant absorbance is measured in a given sample. Ohno (2002) suggests a threshold of 0.3 absorbance units at 254 nm as the level beyond which correction for inner-filtering is required.

The primary limitation associated with absorbance spectroscopy is the potential for overlapping or adjacent absorbance peaks associated with several compounds in solution. This overlap results in compound peaks that are broader and higher than those for individual compounds, and reduces the specificity of the scan unless mathematical techniques are applied to the data.

2.7.5. Applications of spectroscopy in environmental research

Fluorescence and absorbance spectroscopy have been increasingly applied to environmental research in marine, freshwater and wastewater systems. This section provides an overview of the applications of fluorescence and absorbance spectroscopy in environmental research. Of particular relevance to this study are the unique absorbance and fluorescence characteristics of dissolved organic matter (DOM). This section begins with an overview of these characteristics. This is followed by a review of the relevant literature. As much of the recent work involving these techniques has been conducted in marine and freshwater environments, this review is divided broadly under these two headings.
2.7.5.1. Spectroscopic properties of DOM

Dissolved organic matter is defined as organic material that passes through a 0.45 μm filter (McDonald et al., 2004), and is produced from the degradation of terrestrial and aquatic plant material. It is released through the chemical, biological or physical breakdown of these materials and can be produced either autochthonously (i.e., in a water body through microbial metabolism) or allochthonously (i.e., on the land surface) and transported to surface waters during storm events. DOM is difficult to characterize chemically because it represents a broad range of compounds with varying molecular weights. As a result, traditional analytical techniques are complex and require large sample volumes (Leenheer and Croue, 2003).

A significant proportion (30-60%) of DOM in surface waters is comprised of humic substances (Figure 2-13), defined as non-volatile, coloured, polyelectrolytic acids that range in molecular weight from 500 to 5000 (Thurman, 1985). The primary constituents of humic matter are humic and fulvic acids which are chemically similar; however, fulvic acids have lower molecular weights (500-2000) and are soluble in water at any pH. Humic acids are soluble in water only under alkaline conditions and are larger (molecular weights greater than 2000). Due to their solubility, fulvic acids are generally more mobile than humic acids and tend to be found commonly in surface waters, while humic acids occur most commonly in the solid phase in soils (Tipping, 2002). As illustrated in Figure 2-13, DOM also contains amino acids and proteins, which have unique fluorescence properties, and are thought to produce protein-like fluorescence commonly observed in natural waters.
Figure 2-13- Average composition of dissolved organic matter in river water with 5 mg·L⁻¹ dissolved organic carbon. Modified from Thurman (1985).

Absorbance is an effective indicator of chromophoric (light absorbing) DOM concentration in natural waters (Green, 1992; Del Castillo et al., 1999; Kowalczyk et al., 2003; McDonald et al., 2004). Chromophoric DOM (CDOM) refers to that portion of the DOM pool that absorbs light in the UV-A, UV-B and visible wavelength ranges (Blough and Del Vecchio, 2002). Although detection of individual compounds in solution using absorbance can be difficult due to broad and overlapping absorbance peaks, the slope of the absorbance curve (referred to as spectral slope, or S) can be used to characterize the composition and source of CDOM in natural water samples (Carder et al., 1989; Twardowski and Donaghay, 2001; Blough and Del Vecchio, 2002; Kowalczyk et al., 2003; Twardowski et al., 2004). This slope is often used as a proxy for the proportion of CDOM comprised of fulvic vs. humic acids as fulvic acids exhibit higher absorptivities at shorter wavelengths (~280 nm) than humic acids which absorb in the blue range of the spectrum (~440 nm) (Thurman, 1985). As described by Carder (1989) and Blough and Del Vecchio (2002), slopes of ~0.02 or greater reflect dominance of low-molecular-weight fulvic material. Lower slopes (~0.010) represent CDOM dominated by humic acids.

Analysis of fluorescence properties of CDOM are also common due to greater sensitivity of fluorescence techniques (Blough and Del Vecchio, 2002). Two distinct classes of fluorophores are commonly found in CDOM in natural waters: humic-like and protein-like materials (Leenheer and Croue, 2003). The fluorophores are referred to as “humic-like” and “protein-like” because fluorescence for the former occurs at the same excitation/emission pairs as fluorescence for isolated humic and fulvic
materials. Fluorescence for the latter occurs at the same excitation/emission wavelengths as the known aromatic amino acids tyrosine and tryptophan. The optically active components of DOM, therefore, are a potentially useful indicator of agricultural influence as they are present in all natural waters, but their composition and concentration vary depending on source, dominant vegetation type, soil type, land use and microbial activity (Kirk, 1994; Leenheer and Croue, 2003).

2.7.5.2. Spectroscopy in marine research

One of the first applications of modern, high-sensitivity spectroscopic techniques in marine research was conducted by Coble et al. (1990), who used fluorescence spectroscopy to analyse CDOM extracted from seawater samples collected at depths ranging from the surface to 375 m. They noted three fluorescence maxima in EEM's from these samples, referring to them as regions A (Ex/Em$^5 = 260/435$), B (Ex/Em = 285/335-345) and C (Ex/Em = 345/445-450). These maxima were attributed to fluorophores in CDOM associated with different sources (river, marine, and soil) and their relative intensities were observed to vary with depth, suggesting that this technique could be used to distinguish CDOM sources, transport pathways and marine mixing processes. In a continuation of this work, Coble (1996) assessed fluorescence from seawater and riverine samples, and illustrated a progressive change in the location of humic-like fluorescence peaks as freshwater became mixed with estuarine waters. This transition was attributed to a change in source of humic material from terrestrial to marine, particularly in eutrophic waters.

Del Castillo et al. (1999) used absorbance and fluorescence spectroscopy to determine the nature and extent of the contribution of the Orinoco River plume to high concentrations of dissolved organic carbon (DOC) and CDOM in the Caribbean Sea. Both techniques were used to characterize freshwater organic matter, which comprised a significant proportion of that observed in marine samples. The identification and quantification of CDOM was of particular importance due to its influence on the location of the photic zone, and this was accomplished using absorbance at 300 nm ($A_{300}$) as an index of CDOM concentrations. Fluorescence was also used to identify changes in CDOM composition with increased mixing between the marine and riverine endmembers by assessing the location of fluorescence peaks for different humic materials. Constituents of terrestrial (riverine) CDOM changed very little below salinities of approximately 30, but shifts in emission maxima were observed above this threshold (higher

$^5$Ex/Em = Excitation/Emission wavelength at which fluorescence is observed, and is given in nm.
salinities indicate dominance of marine water), suggesting significant mixing and a change in the dominant source of CDOM from terrestrial to aquatic. Similar results were observed at or near this threshold by Guéguen et al. (2005) in the Western Arctic Ocean and by Jaffe et al. (2004) in a study assessing CDOM sources and mixing processes in an estuary in southwestern Florida. In the latter study, a fluorescence index of Em. 450/Em. 500 at an excitation of 370 nm (first used by Mcknight et al. (2001)) was also successfully used to differentiate terrestrial vs. marine CDOM, with higher values being indicative of marine production. Also, because terrestrially-derived CDOM underwent conservative mixing in the estuary, it was used to determine the degree to which marine and fresh water mixing occurred in geomorphologically compartmentalized sub-regions.

Chen and Gardner (2004) used a similar approach to assess CDOM cycling and physical mixing processes in the Gulf of Mexico using a submersible pump linked directly to a shipboard laboratory. This allowed for analysis of spectroscopic variables along multiple transects and profiles to quantify changes in CDOM concentration and source both spatially and with depth. Their analysis indicated that coastal CDOM was dominated by terrestrial material from the Mississippi and Atchafalaya Rivers, that end-members from a given river can vary over time due to seasonal effects and that plumes from each river could be identified and traced based on their unique spectroscopic properties (the Atchafalaya River has significant wetland influence compared to the Mississippi). This technique has also been useful for identifying significant marine CDOM sources at depth that are associated with bacterial breakdown of organic detritus at the pycnocline (Chen et al., 2004).

Given the extensive information contained within EEM plots (potentially several thousand data points), and the numerous optically active compounds found within CDOM, multivariate statistical procedures are popular for EEM interpretation and analysis. Person and Wedborg (2001) applied principal component analysis (PCA) to EEM’s to identify structural differences related to varying CDOM sources in the Baltic Sea. By first normalizing all scans to the same fluorescence intensity at one excitation/emission wavelength pair, it was possible to remove concentration effects from the data sets and isolate structural differences. Plotting the resulting PCA scores against the first and second principal components resulted in clustering of sample sites according to dominant humic source (terrestrial vs. aquatic). This technique allowed the authors to make inferences regarding mass mixing processes between the Baltic Sea (dominated by terrestrial humic materials from large riverine sources) and the Atlantic Ocean (with relatively little terrestrial humic input) due to their characteristic EEM structures. A
similar approach was used by Boehme et al. (2004) on a large data set of over 600 samples to identify CDOM end-members and mixing patterns in the Gulf of Mexico. It is worth noting that several authors have suggested that a three-dimensional multivariate model called Parallel Factor Analysis (PARAFAC) is more appropriate for analysis of EEM's, as PCA is essentially a two-dimensional technique with limitations in terms of data treatment and identification of underlying spectra of fluorophores in solution (Jiji et al., 1999; Stedmon et al., 2003; Fulton et al., 2004). This approach allows the extraction of peaks associated with individual CDOM components that might otherwise be masked by overlapping peak fluorescence wavelengths.

2.7.5.3. Freshwater systems

Recently, fluorescence and absorbance properties of organic matter in freshwater environments have been investigated as tools to assess: 1) paleoenvironmental trends, 2) hydrological flowpaths and mixing processes and 3) contaminant loading and source tracking. Baker et al. (1993) identified annual, luminescent bands in speleothems (stalactites and stalagmites), and noted that luminescence, from humic and fulvic acids derived from overlying soils, could provide an accurate proxy of paleoprecipitation. This approach has been applied elsewhere with similar results (Baker et al., 1999; Proctor et al., 2002). Wolfe et al. (2002) applied the fluorescence index of McKnight et al. (2001) to humic materials extracted from sediment cores from lakes in the Colorado Front Range (core sub-samples were subjected to two wet chemical extraction techniques in order to isolate humic materials). Using this technique, it was possible to trace changes in CDOM sourcing (terrestrial vs. aquatic) over time and thereby reconstruct a pattern of eutrophication resulting from anthropogenic nutrient loading in the latter half of the 20th century. These observations were validated by comparing this index to other accepted measures of eutrophication (diatom assemblages and C:N ratios), thus indicating the potential of this index as a proxy for paleoenvironmental change.

As demonstrated in the marine studies described above, CDOM has the potential to serve as a conservative tracer, which, in freshwater systems is useful for assessing flowpaths and the contributions of different water sources to stormflow. Newson et al. (2001) identified distinct source areas in a watershed in northern England and assessed their contributions to catchment flow based on the luminescence properties of unique organic components of different soils. Baker and Spencer (2004) used absorbance and fluorescence to characterize changes in CDOM along the entire profile of the River Tyne.
in a large (~3000 km$^2$) catchment. Dissolved organic matter contributions from three main tributaries were identifiable and quantifiable based on unique organic matter signatures associated with a peat-dominated source area, a relatively undeveloped upland catchment and a developed catchment with treated sewage discharges. Due to the colour associated with peaty soils, absorption at 340 nm and DOC concentrations were used to identify water from the first source area. Protein-like fluorescence, which was low in undeveloped catchments, showed significant increases associated with sewage treatment discharge, and served as a useful signature of water from the third source area. Further, these characteristics could be used to distinguish between CDOM sources in estuarine samples at the outlet of the watershed, indicating the value of this approach in source apportionment and studies of large-scale CDOM cycling. Katsuyama and Ohte (2002) used fluorescence intensity (in conjunction with dissolved organic carbon and SiO$_2$) as a tracer to quantify the relative input of saturated throughflow, non-saturated throughflow and rainfall to stormflow in a forested headwater catchment in Japan. Using end-member mixing analysis (EMMA) (Hooper et al., 1990), they demonstrated that non-saturated throughflow dominated stormflow and that there were minimal interactions between this zone and the saturated zone during storm events.

Contaminant detection and source identification are areas where spectroscopy offers significant advantages over other techniques for reasons mentioned above. Recent research has focused on refining these techniques to aid in detection of several types of contaminants, including hydrocarbons, pesticides, bacteria, industrial outflows, landfill leachate and agricultural effluent. Jiji et al. (1999), in a laboratory experiment, demonstrated that fluorescence spectroscopy combined with parallel factor analysis could be used to detect and quantify pesticides and polycyclic aromatic hydrocarbons (PAH's) in solution with detection limits of 1.1-13 ppb and 0.2 ppb, respectively. Giana et al. (2003) used fluorescence spectroscopy to identify bacteria in suspension and correctly classified organisms to one of three species by applying PCA to EEM data. Other studies have also demonstrated that fluorescence techniques can be used to detect the influence of landfill leachate (Baker and Curry, 2004; Baker, 2005a) and industrial effluent (Baker, 2002a) on surface water quality.

Research in the area of sewage contamination indicates that absorbance and fluorescence spectroscopy can be applied to process control in sewage treatment plants and environmental monitoring. Reynolds and Ahmad (1997) described the correlation of absorbance at 254 nm to biochemical oxygen demand (BOD) in treated and untreated sewage, and several studies have utilized this measure to identify sewage treatment plant discharge to surface waters (Baker, 2001; Baker and Spencer, 2004).
Similarly, Ahmad and Reynolds (1999) noted that fluorescence at Ex/Em = 248/350 is strongly correlated to BOD, and proposed this as a measure for on-line process control in STP's. Galapate et al. (1998) used synchronous-scan fluorescence spectroscopy to identify a characteristic fluorescence peak for sewage between 512 nm and 531 nm in the laboratory, and used these peaks to detect sewage effluent in Kurose River (Japan) downstream from a STP (no peaks were observed in samples taken upstream of the STP). A fluorescence ratio (tryptophan-like to fulvic-like fluorescence intensity) was used by Baker (2001) to identify sewage contamination in rivers influenced by STP discharge, and by Baker et al. (2003) to identify sewage and grey-water contamination in surface waters of an urbanized catchment in northeastern England.

Of relevance to this thesis is the use of spectroscopy in the identification of agricultural influence on water quality. Fluorescence and absorbance have proven to be useful indicators of agricultural influence on surface waters and groundwaters. Baker (2002b) first examined fluorescence properties of farm wastes by analyzing samples of silage liquor (effluent from stored, wet grasses that have fermented), pig and cattle slurry (liquid manure) and sheep barn wastes. Each waste type had high tryptophan concentrations and was discernible by its tryptophan:fulvic-like fluorescence intensity ratio, with silage effluent having a value >20 and the slurries and sheep barn wastes having lower values (~2-5 and ~0.5-4.0, respectively). As these values are higher than those observed in natural river waters (generally <1.0) this illustrates the potential of this index as an indicator of agricultural contamination. Recent work has been conducted to assess the link between protein-like fluorescence observed in natural waters and bacterial concentrations (Elliott et al., 2006b; Elliott et al., 2006a). These studies illustrated that both tyrosine-like and tryptophan-like fluorescence are found in isolated bacterial cultures. Thus, bacterial concentrations contribute at least partially to protein-like fluorescence observed in natural waters.

Recent studies have also been aimed at discerning CDOM derived from forested vs. agricultural sub-catchments in agricultural watersheds. Stedmon et al. (2003), collected surface water samples from several sub-catchments in the Horsens watershed in Denmark to determine if distinctive fluorescence patterns could be detected for forested, agricultural and estuarine water. Using PARAFAC analysis, they extracted five components that correlated with fluorescence peaks for terrestrial humic-like material and tryptophan-like material. The extraction of five components for these two broad categories of CDOM suggests that each is comprised of multiple organic components that are controlled by different
processes. Using these components, Stedmon et al. (2003) developed a fingerprint for source areas based on their relative abundance. A follow up to this study (Stedmon and Markager, 2005) involved a more extensive data set (1,200 samples), allowed further refinement of the PARAFAC model and resulted in the extraction of eight components (four terrestrial, two anthropogenic/agricultural and two protein-like). Again, CDOM sources could be identified by the relative intensities of each component. Forested sites tended to be characterized by the highest fluorescence intensities, and relative peaks in emission for humic-like materials. Agricultural sites showed lower fluorescence intensities (likely due to UV and microbial degradation of CDOM), but relatively higher intensities for fulvic-like and tryptophan-like materials. Co-variability between the components was analysed by plotting each against the other, and five groupings were observed in the plotted data (sites dominated by forest, >50% agriculture, >75% agriculture, estuarine sites, and lakes). These plots also illustrated which CDOM components were likely controlled by similar physical, chemical and biological processes, as they showed strong linear correlations.

Finally, recent work by Ohno et al. (2006) represents one of the first rigorous assessments of the properties of CDOM isolated from plant residues and agricultural amendments (beef, dairy, poultry and pig manures), and provides further support for the observed strong correlation between spectroscopic properties and agricultural influence. This assessment, which compared plant- and manure-derived CDOM, noted that CDOM derived from beef and poultry manures was characterised by significantly higher molecular weights than that derived from plant residue. It was also observed that CDOM derived from beef and poultry manure had the highest molar absorptivities (at 280 nm) when compared to plant-derived CDOM. These studies indicate that CDOM source tracking in agricultural watershed is possible, and that agricultural influence on surface waters can be detected.

Absorbance spectroscopy has significant potential as a tool to detect agricultural influence given its effectiveness in quickly and accurately determining NO$_3^-$ concentrations (the NO$_3^-$ ion absorbs strongly in the 210-220 nm range). One of the challenges associated with this technique is that readings can be confounded by interferences from other compounds in solution (metals, dissolved organic matter, etc.) that also absorb in this wavelength range. This results in broad absorbance bands as a result of overlapping peaks (Crumpton et al., 1992; Twardowski et al., 2004). This issue can be addressed either by processing water samples to remove interfering compounds or by correcting the data for the interference. Rennie et al. (1979) accomplished the former for raw water, treated water and wastewater
samples by adding sodium hydroxide (to increase pH), and passing them through a carbon filter to remove CDOM and dissolved iron and manganese. Measurements of absorbance at 210 nm for these processed samples resulted in NO$_3^-$ concentrations that did not differ significantly from established methods. The latter method, involving a mathematical correction for absorbing substances, has traditionally been used in organic-rich waters. Absorbance at another wavelength where NO$_3^-$ absorbance is negligible (several have been used) is measured as a proxy for CDOM concentration. This value is then subtracted from absorbance at 210 nm to determine NO$_3^-$ concentration (e.g., Thompson and Blankley, 1984).

A third method for addressing interferences from other compounds involves the calculation of derivatives of the original absorbance spectra. The first derivative defines the rates of change at each wavelength along the original spectrum, and in so doing minimizes broad featureless peaks. The second derivative calculates rates of change of the first-derivative curve, thus emphasizing sharper peaks in the original absorbance spectrum. As illustrated in Figure 2-14, the second derivative of the original absorbance spectrum produces a peak at ~224 nm, allowing the extraction of the NO$_3^-$ signal (Cahill, 1979; Suzuki and Kuroda, 1987).

![Figure 2-14 - Absorbance spectrum for EC-4 collected on December 20, 2004 (dashed) and second-derivative of the same spectrum (solid). Note second-derivative peak at 224 nm.](image)
Several authors have used this technique to quantify NO$_3^-$ concentrations in water samples. Crumpton et al. (1992) demonstrated that this approach could be used to determine NO$_3^-$ content in surface-water samples without treatment (i.e., without extraction or digestion). Ferree and Shannon (2001) found that absorbance spectroscopy could accurately assess NO$_3^-$ concentrations in wastewater using NO$_3^-$ spiked samples and comparison with ion chromatography. Karlsson et al. (1995) observed similar results when analyzing unfiltered wastewater samples for NO$_3^-$ concentrations ranging from 0.5-13.7 mg·L$^{-1}$, illustrating the potential for real-time process control in STP's.

2.8. Current gaps and opportunities

Due to increased awareness regarding the risks associated with waterborne disease, and several highly-publicized waterborne outbreaks, substantial resources have been directed at improving our understanding of issues related to water contamination, water-quality monitoring and risk management.

Significant progress has been made in each of these areas; however, several gaps still exist. Environment Canada (2001) described several “knowledge needs” related to waterborne pathogens, including a need to improve the timeliness and effectiveness of pathogen detection techniques, and to identify contamination “hotspots” in source watersheds through improved monitoring techniques. The same report also described the need for improved monitoring of nutrient contributions to surface waters and groundwaters.

The BC Provincial Health Officer’s annual report on drinking-water quality made several recommendations to improve the province’s ability to manage water related health risks. These recommendations included rigorous testing and analysis of new surface-water sources, improved monitoring of existing systems and improved contaminant source identification. Further, Krewski et al. (2002) stressed the need for water-quality monitoring programs to detect contamination events in a timely fashion so interventions can be implemented to minimize public health risk.

Given the observed increase in agricultural intensity in the LFV and a growing demand for drinking water arising from regional population growth, an improved understanding of the links between agricultural land use and surface-water quality is critical. This thesis attempts to address the above gaps by identifying the links between climate, hydrology, land use and water quality in watersheds with differing types and intensities of agriculture. The primary objective is to identify the land use activities and meteorological/hydrological conditions leading to the greatest risk of water contamination in order to
support a more proactive approach to water-quality risk management. Further, this thesis attempts to address the current gaps related to monitoring technologies (timeliness, sensitivity, etc.) by assessing the utility of spectroscopic tools for monitoring agricultural influence on water quality.
3. Site descriptions and methods

3.1. Introduction

This chapter describes the research approach used in this thesis, the field methods employed for collection of meteorological, hydrometric and water-quality data, and laboratory methods employed for microbiological, chemical and spectroscopic analysis of water samples.

3.2. Site selection and overview

Research for this thesis was conducted in three catchments in the LFV, the Hatzic, Elk Creek and Salmon watersheds (Figure 3-1). The criteria for evaluating and selecting these watersheds were designed to ensure the field sites would meet the objectives of the research, and were as follows: 1) land use in the watersheds must be dominated by agricultural activities, 2) both crop and livestock agriculture must be present, 3) the watersheds must represent differing intensities of agricultural activity and 4) they must be close enough to Vancouver to enable frequent sampling and equipment maintenance. The three watersheds met these criteria, with the Elk Creek watershed representing the higher-intensity agricultural site. The Salmon watershed was added later in the study to augment the evaluation of spectroscopic techniques. The watershed is dominated by agriculture, but unlike the Hatzic and Elk Creek watersheds, it offered the opportunity to evaluate fluorescence and absorbance characteristics of nitrate-rich groundwaters.
Figure 3-1 - Lower Fraser Valley with locations of three study watersheds.

The climate of the LFV is highly seasonal, with the majority of annual rainfall occurring between October and April (Figure 3-2). During the wet season, the region is dominated by low-pressure, maritime systems delivered by prevailing westerly winds (during these months the Westerlies shift southwards to an average latitude of 45° N). Upon landfall, these relatively warm, moisture-rich air masses are driven to higher elevations by coastal mountains, resulting in the observed peak in precipitation during this time. Occasionally, colder, northern air masses meet these maritime systems and produce snowfall. However, on average, snow accounts for only 4% of annual precipitation. Prolonged precipitation during these months results in elevation of the water table, which frequently leads to drainage problems and flooding on agricultural land (Bertrand et al., 1991).

During summer months, the Westerlies shift north to an average latitude of 55° N, resulting in warmer, drier conditions across the region. A precipitation gradient is observed across the LFV, with mean values increasing from southwest to northeast. A similar trend occurs for mean temperatures as the moderating maritime influence decreases inland (Bertrand et al., 1991).
Figure 3-2 - Mean monthly precipitation and mean daily temperatures (minimum, maximum and average) at Chilliwack (near the Elk Creek watershed) from 1971 – 2000 (Environment Canada, 2005).

Table 3-1 provides a comparison of the Hatzic, Elk Creek and Salmon watersheds in terms of area, land use, livestock densities and nutrient surpluses. It should be noted that the animal numbers are for the Census of Agriculture Enumeration Areas (EA’s) within which the watersheds fall. In each case, there is agricultural land in the EA that falls outside the bounds of the watershed. However, these numbers provide an indication of total animal numbers and density. Agricultural intensity, and the potential for impairment of surface waters and groundwaters is also illustrated using nutrient surplus calculations from Schreier et al. (2003).
Table 3-1 - Comparison of the Hatzic, Elk Creek and Salmon watersheds in terms of size, land use and stocking densities (modified from Schreier et al., 2003). "X" denotes no data available.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Hatzic</th>
<th>Elk Creek</th>
<th>Salmon</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area (km²)</td>
<td>84</td>
<td>33</td>
<td>80</td>
</tr>
<tr>
<td>Forest (%)</td>
<td>68</td>
<td>71</td>
<td>5</td>
</tr>
<tr>
<td>Agriculture (%)</td>
<td>14</td>
<td>21</td>
<td>45</td>
</tr>
<tr>
<td>Urban/residential (%)</td>
<td>11</td>
<td>2</td>
<td>36</td>
</tr>
<tr>
<td>Other</td>
<td>7</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>Livestock¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chickens (#)</td>
<td>X</td>
<td>1,156,486</td>
<td>942,708</td>
</tr>
<tr>
<td>Cattle (#)</td>
<td>7,841</td>
<td>23,766</td>
<td>5,221</td>
</tr>
<tr>
<td>Pigs (#)</td>
<td>X</td>
<td>22,835</td>
<td>4,409</td>
</tr>
<tr>
<td>Sheep (#)</td>
<td>568</td>
<td>1,351</td>
<td>1,209</td>
</tr>
<tr>
<td>Horses (#)</td>
<td>210</td>
<td>499</td>
<td>1,739</td>
</tr>
<tr>
<td>Stocking density (AUE/ha)²</td>
<td>1.25</td>
<td>11.04</td>
<td>3.9</td>
</tr>
<tr>
<td>Nutrient surpluses (kg/cropped ha)</td>
<td>16</td>
<td>65</td>
<td>30</td>
</tr>
</tbody>
</table>

¹ - Livestock data based on Census of Agriculture enumeration areas, which include agricultural land outside of watershed boundaries. These values are provided to illustrate animal density only.
² - AUE = Animal Unit Equivalent, a value based on manure production potential (1 beef cow = 1 AUE). The area value used in the calculation was derived by subtracting agricultural area under crops from total agricultural area for the enumeration area.

3.2.1. The Hatzic watershed

The Hatzic watershed (Figure 3-3) is located east of the city of Mission, on the north side of the Fraser River. It is dominated by low-mid intensity agriculture consisting primarily of livestock farms (mainly dairy and beef cattle) and fruit and greenhouse operations. The watershed covers approximately 83 km² and is bordered to the east, west, and north by steep mountain slopes. Low-lying areas are predominantly agricultural with some residential developments and numerous recreational properties (on Hatzic Lake). The watershed is drained by Pattison Creek and Lagace Creek, both of which flow into Hatzic Slough on the valley floor. Several other agricultural sloughs also flow into Hatzic Slough before it reaches the lake.
Figure 3-3 - Map of the Hatzic Valley watershed showing topography, major streams, sampling sites and hydrometric and climate stations.

The watershed drains into the Fraser River through four floodboxes and a pump station located near the outlet of Hatzic Lake. During heavy rains and the spring freshet, these floodboxes remain closed and drainage is controlled by the pump station. The pump capacity is often exceeded and several major
floods in low-lying agricultural and residential areas have occurred over the past 50 years (Associated Engineering, 1992). The problem is exacerbated in upstream (northern) areas of the watershed where channel avulsions resulting from stream aggradation are common. This often leads to flooding of agricultural land. Several large, active landslides in the headwaters have been estimated to supply 5,000 – 10,000 m$^3$ of sediment per year to these streams (Associated Engineering, 1992), and as a result, a long-term channel dredging initiative has been undertaken to mitigate flood risk. Such flooding is of concern in agricultural watersheds as it directly links streams with manure and fertilizer sources on agricultural fields.

3.2.2. The Elk Creek watershed

The Elk Creek watershed is located near the city of Chilliwack on the south side of the Fraser River. The area of the watershed is approximately 33 km$^2$, and the southeastern portion is dominated by the steep slopes of Elk Mountain (1,429 m) and Mt. Thurston (1,626 m). Much of the cropland in the watershed is under corn, and livestock farming is dominated by cattle and chicken operations. Chicken numbers in the East Chilliwack EA (of which the Elk Creek watershed is a part), have increased drastically in the past 20 years from approximately 402,000 in 1986 to over 1.1 million in 2001 (Schreier et al., 2003). Expansion of urban and recreational land uses is also taking place, primarily on the upland slopes located in the southern half of the watershed. From 1905 to 1998, the Elk Creek served as a primary water supply to the City of Chilliwack, but was decommissioned after Giardia and Cryptosporidium were detected in surface water samples (water treatment to that time was limited to chlorination).
3.2.3. The Salmon River watershed

The Salmon River watershed is located northeast of Langley, along the southern shores of the Fraser River and is approximately 80 km² in area. It is topographically less rugged than the Elk Creek and Hatzic watersheds, with a maximum elevation of approximately 140 m. As a result, much of the watershed is developed and there is very little contiguous forest present. There are more than 550 farms
in the area, with a larger proportion of hobby farms than in the other two watersheds (predominantly horse farms on marginal soils). Crop agriculture is dominated by cranberry operations, and there are significant cattle and chicken populations in the watershed. More than 13,000 people live in the area, and, as of 1997, the population was served by over 4,000 septic systems (Schreier et al., 1999).

The watershed is underlain by the Hoppington aquifer which contributes significantly to streamflow during summer months. This cold water source, combined with gravel-bed streams, produces excellent spawning habitat for salmon. However, this aquifer is unconfined and nitrate contamination from septic systems and agricultural operations has been documented, with concentrations regularly exceeding the Health Canada guideline of 10 mg/L (Schreier et al., 1999).
3.3. Field methods

3.3.1. Meteorological monitoring

The purpose of the meteorological monitoring program was to gain an understanding of the influence of precipitation and temperature on surface-water quality at a range of scales (i.e., from storm-event to seasonal). Of particular importance to this thesis was the collection of high-resolution rainfall data in order to assess the impact of rainfall events on contaminant mobilization and transport.

In the Hatzic valley, meteorological data were collected between November, 2002, and August, 2005, at a station established in the northeastern region of the watershed, on a small promontory where Pattison Creek reaches the valley floor (Figure 3-3). This site was located on a private woodlot (with permission of the landowner), and was chosen for two reasons. Firstly, it is near the headwaters of Pattison Creek, which is the largest tributary feeding into the mainstem river of the watershed. Secondly, it is located approximately 280 m above the valley floor, thereby providing a more realistic assessment of rainfall in the higher-elevation headwaters of the watershed.

Scaffolding was used to elevate all sensors approximately 4 m in order to avoid interception losses from nearby trees and to prevent snow burial during winter months (as this site was located on private property, falling of the trees to completely eliminate interference was not possible). The station included components from Forest Technology Systems (FTS), namely a RG-T model tipping-bucket raingauge (resolution: 0.254 mm; accuracy: ± 2% at 50 mm/hr), a THS-1 air temperature thermistor (resolution: 0.1 °C; range: -51→+60 °C; accuracy: 0.2 °C) and a PG-4 precipitation column (capacity: 1410 mm), all of which were connected to an FWS-12S data logger. Data were collected for each sensor at 15-minute intervals and downloaded to a laptop on a regular basis (every 1-3 months).
Figure 3-6 - a) meteorological station located in the Hatzic watershed, b) data logger, power supply and field laptop used to download data.

For the Elk Creek watershed, rainfall data were obtained from the City of Chilliwack for a tipping-bucket raingauge located on Marble Hill (Figure 3-4).

### 3.3.2. Hydrometric monitoring

Hydrometric data were collected in the Hatzic and Elk Creek watersheds to investigate the relationships between rainfall and stream hydrology and the influence that both variables have on surface-water quality. In the Hatzic watershed, two hydrometric stations were established on the mainstem river in July and December, 2002 and remained operational until August, 2005. Each station was equipped with 4 sensors: 1) an Analite 195 turbidity probe (equipped with an automated, anti-fouling wiper), with a range of 1-1000 NTU (nepholometric turbidity units), 2) a Unidata four electrode, temperature-compensated conductivity sensor, with a range of 0-200,000 μS·cm⁻¹, 3) a Unidata hydrostatic water depth probe (Model 6508), with a range of 0 – 2 m and 4) a temperature sensor (part of the hydrostatic probe). All sensors were connected to a Unidata “Display Starlogger” data logger (model 6004-2) which was downloaded on a regular basis (every 1-3 months). Sensors were cleaned during every visit and calibrated at least once every 6 months.

The criteria for selecting both sites were as follows: 1) that they allow a comparison of “headwater” and “downstream” hydrologic conditions (i.e., a comparison of hydrometric variables under...
forested, un-influenced conditions vs. agricultural conditions), 2) that they be located in morphologically appropriate reaches of the stream (straight banks, single channel, minimal turbulence), 3) that the upper station be located far enough downstream from the headwaters to limit potential damage by debris transported from 2 slope failures in the upper catchment and 4) that they both be located on private property in order to minimize the potential for vandalism. Based on these criteria, the sites were established on upper Lagace Creek and the Lower Hatzic Slough (Figure 3-3).

Each site was similarly constructed (Figure 3-7). The data loggers were housed in sealable, hard plastic cases, which were in turn stored inside locked wooden cabinets. Leading from the cabinet was a 3.8 cm ABS pipe that housed the sensor cables. This pipe fed into a section of 7.6 cm pipe using a "reducing Y-joint", with one 3.8 cm branch and two 7.6 cm branches; one that screwed onto the main pipe, and the other with a removable cap. The sensors were mounted on a rod and rested at the bottom of the 7.6 cm pipe, which was perforated (to allow free movement of water around sensors) and capped. The rod could be pulled out when the cap at the top of the main pipe was removed allowing the sensors to be cleaned, calibrated and re-inserted into the pipe to the exact same depth. To ensure that the pressure transducers remained at the same depth over the course of the study, the 7.6 cm pipe was anchored to fixed points in the stream or on the shore.
Discharge was measured at the upper hydrometric station using a Swoffer Model 2100 Current Velocity Meter, and a top-set wading rod following standard procedures (Ministry of Environment Lands and Parks, 1998). Velocity measurements were obtained at 0.6 of the depth at 50 cm intervals across the channel. Stage was collected from the automated sensor prior to, and just after, velocity measurements, and averaged if there was any change over the measurement time. Unfortunately, over the course of the study, several severe weather events resulted in transport of significant quantities of gravel to the region upstream of this station. This material was subsequently excavated on three separate occasions. As a result, the morphology of the channel changed significantly during the three years the station was in operation and it was not possible to establish a reliable rating curve for this site.

In the Elk Creek watershed, hydrometric data for six stations were obtained from the City of Chilliwack from July, 2002 to May, 2005. Each station consisted of an Isco 4150 Area Velocity Meter (AVM) and an Isco data logger that recorded flow at 5-minute intervals. Due to maintenance issues, complete records are not available for any station; however, a comparison with rainfall data allows an assessment of streamflow response to storm events. Due to limitations associated with these hydrometric
Chapter 3

data, the influence of storm events on water quality will be assessed primarily using rainfall data from the Marble Hill raingauge.

3.3.3. Water quality monitoring

The water-quality monitoring program in each watershed was designed to: 1) determine baseline values for nutrient and bacterial concentrations from forested sub-catchments, 2) assess the influence of agricultural activities on surface water quality and 3) to determine spatial and temporal trends in contamination in order to identify time periods and land use activities associated with the greatest risk in terms of water contamination. To accomplish this, water samples were obtained from stations representing various land use types (forested, agricultural and urban) and different hydrological conditions (tributaries, mainstem river and sloughs) and sampled under a range of meteorological and hydrological conditions (dry season vs. wet season and during storm events).

The locations of sampling stations in each of the three watersheds are illustrated above (Figure 3-3, Figure 3-4 and Figure 3-5). The dominant land uses associated with each station in the three watersheds are provided in Table 3-2. Land-use categories were assigned to each station based on activities in their respective contributing area. Sub-catchments with less than 1% disturbance were categorized as "forested". Those with between 1-10% agricultural activity were assigned to the "mixed-use" category, while sites with greater than 10% agricultural land use were assigned to the "agricultural" category. Sites with no agricultural influence but greater than 1% of total contributing area under residential development were categorized as "urban".
### Table 3-2 - Land-use categories for the three watersheds based on contributing area.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Station</th>
<th>Land use category</th>
<th>Area (ha)</th>
<th>Forest (%)</th>
<th>Agriculture (%)</th>
<th>Urban/Rural Residential (%)</th>
<th>Other (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatzic</td>
<td>HV-1</td>
<td>Agricultural</td>
<td>961.5</td>
<td>80.9</td>
<td>15.8</td>
<td>3.3</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>HV-2</td>
<td>Forested</td>
<td>152.5</td>
<td>99.0</td>
<td>0.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>HV-4</td>
<td>Forested</td>
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<td>0.0</td>
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</tr>
<tr>
<td></td>
<td>HV-5</td>
<td>Mixed</td>
<td>227.9</td>
<td>97.1</td>
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<td>1.8</td>
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</tr>
<tr>
<td></td>
<td>HV-6</td>
<td>Forested</td>
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<td>99.8</td>
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<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>HV-8</td>
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<td>86.3</td>
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<td>9.4</td>
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<tr>
<td></td>
<td>HV-9</td>
<td>Agricultural</td>
<td>45.0</td>
<td>69.7</td>
<td>29.4</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>HV-10</td>
<td>Mixed</td>
<td>206.8</td>
<td>92.3</td>
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<td>5.9</td>
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</tr>
<tr>
<td></td>
<td>HV-11</td>
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</tr>
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<td>Agricultural</td>
<td>3128.8</td>
<td>72.9</td>
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<td>5.9</td>
</tr>
<tr>
<td></td>
<td>EC-2</td>
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<td>1.6</td>
<td>5.9</td>
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<tr>
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<tr>
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<tr>
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<td>EC-7</td>
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<td>Forested</td>
<td>1313.1</td>
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</tr>
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<td>Forested</td>
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<tr>
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<td>Urban</td>
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<td></td>
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<tr>
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<td></td>
<td>SA-9</td>
<td>Agricultural</td>
<td>577.7</td>
<td>12.4</td>
<td>62.4</td>
<td>17.4</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>SA-14</td>
<td>Agricultural</td>
<td>475.3</td>
<td>5.3</td>
<td>38.6</td>
<td>12.5</td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>SA-19</td>
<td>Agricultural</td>
<td>581.9</td>
<td>2.6</td>
<td>56.2</td>
<td>32.1</td>
<td>9.1</td>
</tr>
</tbody>
</table>

1 - EC-14 was assigned to the category of "Mixed" as it was determined after site selection that significant logging activities had occurred upstream.

2 - SA-17 was defined as "Agricultural" as the majority of "other" was cleared, but undeveloped Crown land.
In the Hatzic watershed, 20 sampling sites were initially selected. Two of these, HV-3 and HV-7, were eliminated from the sampling program as both were ephemeral, only flowing during the wettest months of the winter season. In the Elk Creek watershed, 15 stations were selected to represent a range of forested and agricultural conditions, while in the Salmon watershed, 11 sites were chosen to represent agricultural conditions, and to include streams under the influence of \( \text{NO}_3^- \) -rich groundwater. Due to a limited range in elevation across the Salmon watershed, delineation of contributing areas is approximate. Further, unlike the Hatzic and Elk Creek catchments, there is significant rural residential (low density, hobby farms or similar) land use in the watershed. As agriculture was the dominant land use in each of the subcatchments, and residential development was relatively low-density, each of the subcatchments was categorized as "agricultural."

Sampling was timed to capture seasonal conditions throughout the water year and was most frequent during the wet season (October-April) as this was the most hydrologically active and variable time of the year. Sampling during summer months was also conducted to capture low-flow conditions and to determine the influence of storm events on water quality after prolonged dry periods.

All samples for chemical analysis were collected in acid-washed 250 ml or 500 ml low-density polyethylene (LDPE) bottles. Samples were stored on ice in a cooler during sampling and refrigerated within 4-6 hours of collection. All samples were analysed within 48 hours, and usually within 24 hours. While analysis within 24 hours is recommended, analysis after 48 hours with refrigeration has been shown to produce comparable results (Kotlash and Chessman, 1998). At each site, depth integrated samples were collected by hand by opening the bottle near the stream bed and drawing it towards the surface as it filled with water.

Samples for microbiological analysis were collected in sterile, factory-sealed bottles, which were also stored on ice in a cooler during sampling. All microbiological samples were returned to the BC Centre for Disease Control (BC CDC) for analysis within 4-6 hours of sampling where they were subsequently analysed within 24 hours.
3.4. **Laboratory methods**

3.4.1. **Nutrient analysis**

Analyses for nutrients (NO$_3^-$, NH$_4^+$ and PO$_4^{3-}$) were conducted at the University of British Columbia Soil Chemistry Laboratory using a Lachat Instruments QuikChem FIA+ 8000. The methods used to detect and quantify these compounds were QuikChem 12-107-04-1-B, QuikChem 10-107-06-2-A and QuikChem 10-115-01-1-A, respectively (Lachat Instruments). For NO$_3^-$ analysis, method 12-107-04-1-B involves reducing NO$_3^-$ to NO$_2^-$ by passing the sample through a column containing copper coated cadmium. Nitrate concentration was then determined by diazotizing with sulphanilamide dihydrochloride and measuring absorption of the resulting magenta dye at 520 nm. Values were expressed as NO$_3^-$-N with a minimum detection limit is 0.025 mg·L$^{-1}$. For NH$_4^+$ analysis, method 10-107-06-2-A involved heating samples with salicylate and hypochlorite in an alkaline phosphate buffer, resulting in the production of an emerald green dye that is in proportion to NH$_4^+$ concentration. The colour was then intensified by the addition of sodium nitroprusside. Results were expressed as NH$_4^+$-N. The detection limit for this method is 0.1 mg·L$^{-1}$. Analysis for PO$_4^{3-}$ involved digestion in the presence of sulphuric acid and persulphate to hydrolize polyphosphates and organic P to PO$_4^{3-}$. The PO$_4^{3-}$ ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to produce ascorbic acid which absorbs at 880 nm. Absorption at this wavelength is measured to determine concentration of PO$_4^{3-}$-P, with a detection limit of 0.02 mg·L$^{-1}$.

Analysis for chloride (Cl$^-$) was conducted using QuikChem method 10-117-07-1-A. This method involves measuring the absorption of ferric thiocyanate at 480 nm. This compound is produced as a result of the liberation of thiocyanate from mercuric thiocyanate through the formation of soluble mercuric chloride. Absorption at 480 nm is proportional to Cl$^-$ concentration. The detection limit for this method is 6 mg·L$^{-1}$.

Dissolved organic carbon (DOC) was analyzed in the UBC Civil Environmental Engineering Laboratory using a Shimadzu (TOC-500) Total Organic Carbon Analyzer. Concentrations of DOC were determined by subtracting dissolved inorganic carbon from total dissolved carbon, and were expressed as mg·L$^{-1}$.

Prior to analysis, all samples were filtered using Whatman #41 filter paper. Quality control was ensured through the analysis of standards after every 10 samples.
3.4.2. Microbiological analysis

All microbiological analyses for total and fecal coliforms were carried out in the Environmental Microbiology Laboratory at the BC CDC following Method 9222 of Standard Methods (American Public Health Association, 1999). Values were reported as colony forming units per 100 ml (cfu/100 ml). When excessive growth on the filter prevented enumeration, the result was reported as "overgrowth" or "OG".

3.4.3. Spectrophotometric analysis

Prior to spectrophotometric analysis, all samples were filtered through 2.5 μm pre-ashed Whatman 42 filters to remove particulate matter that could interact with light during absorbance or fluorescence scans. Absorbance spectra were collected using a Cary 4000 UV-Vis absorbance spectrophotometer. Samples were placed in quartz cuvettes with a 1-cm pathlength, and absorbance was measured between 200-800 nm at 1 nm intervals, using a scan rate of 600 nm/min. For each scan, baseline correction was applied, whereby the absorbance spectrum for a Milli-Q de-ionized water sample was subtracted from that of the field sample in order to measure absorbance only for dissolved materials in the sample. Post-processing of absorbance scans (to obtain second derivative curves) was accomplished using the "Maths" function within the Cary Scan software (version 3.0(182)). Duplicate scans were collected once for every 20 samples.

Fluorescence readings were acquired using a Varian Cary Eclipse fluorescence spectrophotometer. Emission scans were acquired for several excitation wavelengths (between 220-450 nm at 5 nm increments). Emission was measured between 230-600 nm at 2 nm increments for each excitation wavelength (producing a total of 47 emission spectra for each sample). Excitation and emission slits (which control the resolution of the emission spectrum) were set to 5 nm. Corrected spectra (provided by Varian, Inc.) were used to account for variations in emission that arise from the instrument itself (primarily a result of the changing intensity of the excitation source with wavelength). The excitation filter, used to select the excitation wavelength of interest, was set to automatic. The emission filter was also set to automatic in order to eliminate residual excitation light.

Prior to each sample run, a blank of de-ionized water was scanned at Ex/Em: 350/395 (the Raman peak for water) for two minutes to assess system stability (Baker, 2001). De-ionized blanks were scanned once every 20 samples. Emission at 395 nm averaged 18.3 ± 0.60 over the course of the study.
Chapter 3

with no drift observed. All EEM scans were normalized to a Raman peak of 20.0 to eliminate concentration effects and allow comparisons of DOM components across sites. Duplicate scans were also collected during each sample run. Duplicate scans were subtracted from the original and the percent difference was calculated for all 47 emission spectra for each duplicate water sample (8742 data points). The difference between original and duplicate scans was consistently less than 5% for more than 99.5% of all data points.

Several authors note the need to apply corrections to fluorescence data to account for the inner-filtering effect associated with high DOM concentrations in the sample (Mobed et al., 1996; Lakowicz, 1999; Ohno, 2002). Correction for inner-filtering was not applied to samples in this study for two reasons. Firstly, absorbance at 254 nm in most samples (93%) was below 0.3, indicating that DOM concentrations were not sufficient to produce a significant inner-filtering effect (Ohno, 2002). Secondly, a primary objective of this study was to assess fluorescence spectroscopy as a rapid and simple technique for water-quality determination with minimal data-processing requirements. It was therefore decided to conduct the assessment using the raw fluorescence data.

3.5. Data analysis and representation

A significant challenge in the analysis of environmental data involves the use of inferential statistics on data that are not independent either in time or in space. A critical assumption of statistical tests is that all data points, or replicates, are independent. In environmental monitoring, due to repeated sampling at individual sites over time, or sampling of sites that are not geographically dispersed, the assumption of independence is not often satisfied. The use of inferential statistics to test for differences in such data was termed pseudoreplication by Hurlbert (1984). Using inferential tests for samples collected from the same site over time (and counting them as replicates) is termed temporal pseudoreplication, while spatial pseudoreplication results from analysis of data collected from locations that are not sufficiently geographically distant. The result of such analyses is to artificially inflate the degrees of freedom, thereby increasing the potential for a Type 1 error (detecting a significant difference when one does not exist).

To address this issue, when conducting comparisons of water-quality data between land uses or seasons, all data for each variable were averaged for each site to produce one value per site, per variable. In contrast to pseudoreplication, this results in a substantial decrease in sample size (in some
cases up to an order of magnitude). This reduces the statistical power of the analysis (and the ability to detect real differences), but was preferred over the interpretation of invalid results that would arise by using the entire data set inappropriately. For Chapters 6 and 7, where correlations between spectroscopic variables and water quality parameters were assessed, analyses were conducted on pooled data and on data from individual sampling dates to see if there was any influence of autocorrelation. Results for both were consistent, and so pooled data are presented.

All statistical analyses were conducted using SPSS (13.0 and 14.0). Prior to analysis, all water-quality variables were assessed for normality through visual inspection of histograms and Q-Q plots and by using the Kolmogorov-Smirnov test (with Lilliefors significance correction). None of the variables met the criteria for normal distribution. Therefore, a conservative approach was used for comparison tests. The non-parametric Mann-Whitney test was used for inter-group comparisons (i.e., those comparing water-quality variables across land uses or seasons) and the Bonferroni correction was applied to multiple group comparisons to account for the increased probability of Type 1 errors. Spearman rank order correlations were used to test for associations between variables.

Boxplots produced in SPSS were used in this thesis as a tool for data analysis and visual representation. In these plots, each box displays the median value (horizontal line within the box) and the 25th and 75th percentiles (the lower and upper bounds of the box). The minimum and maximum values that are not outliers are represented by the upper and lower horizontal lines outside the box. Outliers (more than 1.5 box lengths away from the box edge) are represented by circles and extreme values (more than three box lengths from the edge of the box) are represented by asterisks. All other 2-dimensional graphs were produced using Grapher 6.0 (Golden Software), and all contour and surface plots were produced using SigmaPlot 9.0 and 10.0 (Systat). All maps were produced using ArcMap, within ArcGIS Desktop 9.0 (ESRI).
4. Influence of land use, climate and hydrological conditions on nutrient and bacterial cycling in an agricultural watershed.

4.1. Introduction

This chapter describes the results of a multi-year (May, 2002 – August, 2005) assessment of surface-water quality in the Hatzic watershed. The objectives of this study were to: 1) determine "baseline" nutrient and bacterial levels in surface waters draining forested, undeveloped sub-catchments, 2) quantify the impact of agricultural land use on surface-water quality, including cumulative impacts associated with increased agricultural influence and 3) assess spatial and temporal trends in nutrient and bacterial cycling in order to identify high-risk conditions for contamination. To date, few multi-year studies have addressed the combined influence of climate and agricultural land use on bacterial and nutrient cycling in surface waters in the LFV. This study assesses baseline conditions in undeveloped subcatchments, and the mechanisms of nutrient and bacterial transfer from agricultural fields to surface waters at a range of temporal and spatial scales.

The chapter begins with an overview of the hydrological and meteorological conditions observed during the study. This is followed by a discussion of spatial trends in surface-water quality in terms of nutrients and bacteria (with particular emphasis on the role of differing land uses). Temporal trends from storm-event to annual scales are then described, and are followed by conclusions.

4.2. Methods

Methods used for the collection and analysis of data described in this chapter are described in detail in Chapter 3. Data presented in this chapter include variables measured at two hydrometric stations (temperature, specific conductance, water level and turbidity), one meteorological station (air temperature and rainfall) in the Hatzic watershed. This chapter also describes results from chemical and microbiological analyses conducted on grab samples (specific conductance, NO₃⁻, NH₄⁺ and PO₄³⁻ concentrations and fecal coliform, total coliform and E. coli concentrations). Note that, for simplicity, the term "conductivity" is used to refer to specific conductance.
4.3. Results

4.3.1. Hydrology and climate of the Hatzic watershed

4.3.1.1. Hydrometric parameters

Figure 4-1 provides an overview of hydrological and climatological conditions in the Hatzic watershed during the study. The strong seasonality of rainfall and streamflow is evident in this graph. Based on historical data (1959-2000) for the Hatzic watershed, wet season rainfall (October – April) averages 220 mm·month$^{-1}$, compared to 89 mm·month$^{-1}$ during the dry season (Environment Canada, 2005). Stream response to rainfall events was rapid at the upper station with peak flow arriving within hours of peak rainfall. Onset of maximum flow at the downstream station was generally delayed by several hours and the peak was broader and receded more slowly due to the integration of flow from approximately half of the watershed (44 ha) and the influence of Hatzic Lake, located approximately 1 km downstream. A broad peak in water level was visible during each summer season at the lower station. These peaks are due to the deliberate elevation of lake water levels (flow is controlled at the flood boxes) for recreational uses during this time.
Figure 4-1 - 24-hour rainfall, water level and specific conductance for the upper and lower hydrometric stations in the Hatzic watershed. Black horizontal lines denote missing data as a result of logger failure. Three major storm events are also noted (see text for details).
Specific conductance showed a marked difference between the upper and lower stations, with mean values of 51.9 $\mu$S·cm$^{-1}$ and 80.1 $\mu$S·cm$^{-1}$, respectively. This difference is attributed to the higher total contributing area under agriculture for the lower monitoring station (883 ha vs. 28 ha for the upper site), and is supported by the fact that mean conductivity in surface-water samples from agricultural sites was significantly higher than in samples from forested sites (93.8 $\mu$S·cm$^{-1}$ vs. 29.1 $\mu$S·cm$^{-1}$, respectively, $P < 0.001$). This link between agricultural land use and elevated surface-water conductivity values has been observed in previous studies (e.g., Dow and Zampella, 2000; Chen et al., 2006) and is attributed to higher inputs of ions such as NO$_3^-$ and Cl$^-$ derived from agricultural activities (tillage and applications of organic and chemical fertilizers). These data indicate that the two stations were situated appropriately to represent forested and agricultural influence on hydrometrics parameters.

It should also be noted that an earlier study of groundwater quality in the watershed (Magwood, 2004) revealed elevated conductivity levels in groundwater samples, with values ranging from 17 – 3,290 $\mu$S·cm$^{-1}$. This influence on surface-water conductivity can be seen at both hydrometric stations during summer months (Figure 4-1), as values showed a continual increase in the absence of contributions from rainfall. During the wet seasons, conductivity at both stations showed a rapid downward response to storm events. Pre-storm levels were quickly re-established as the relative contribution of rainfall to streamflow decreased on the falling limb of the storm hydrograph.

Water temperature varied similarly for both stations over the period of record (Figure 4-2). Minimum values of 0.4 °C and 1.4 °C were observed during January, 2004 for the upper and lower stations, respectively. Maximum values at the upper and lower station were 23.3 °C and 19.3 °C, respectively (in July, 2004 for the upper station and July, 2003 for the lower station). The shallower cross-sectional profile at the upper station resulted in the lower minima and higher maxima that were observed at this site, as well as the greater diurnal fluctuations observed.
Figure 4.2 - Water temperature for the period of record for the upper and lower hydrometric stations.
Chapter 4

The water level data for both upper and lower stations contain a unique daily cycle in water depth that is easily observed during periods of low flow. To assess this relationship without the influence of precipitation, a set of 4400 data points was extracted from the time series (July 22 – September 5, 2003) during a low-flow period with no recorded rainfall. These data suggest that there is a relationship between stage and water temperature; however, the nature of this relationship is different between the two stations. At the upper station, there was a strong and significant negative correlation ($r_s = -0.833$, $P < 0.001$) between diurnal water temperature and water depth. A similar pattern was observed by Bond et al. (2002), and was attributed to daily evapotranspiration losses in forested catchments. This may explain the results of the present study, as the contributing area to this station was 91% forested. The observed trend may also have been due to an inadequately vented air tube. The venting tube is designed to allow the sensor to compensate for changes in atmospheric pressure, and in these stations, ran from the sensor to the data logger box. Inadequate venting of the data logger box may have caused the sensor to calibrate for pressure changes associated with warm, expanding air in the case, resulting in the observed inverse relationship.

The relationship at the lower site was also significant ($r_s = 0.440$) but was positive and slightly weaker. The daily peaks at this station contained secondary maxima, suggesting that tidal changes in the Fraser River (which can be in excess of 1.0 m) may be influencing Hatzic Lake and Hatzic Slough levels (it is unknown what role, if any, the flood boxes at the outlet of the watershed may play in mitigating this effect). These patterns are observed through the hydrometric record; however, because the amplitude of the cycle is generally small (4-6 cm) in comparison to storm-induced depth increases, it does not obscure the rainfall-water level relationship.

Turbidity was monitored at both hydrometric stations over the course of the study. During the first wet season (2002-2003), rainfall amounts were moderate and turbidity probes recorded elevated concentrations of suspended particulates associated with storm events (Figure 4-3). During the second and third wet seasons (2003-2004 and 2004-2005), several extreme storm events (described below) delivered large quantities of clastic material to the mainstem river (from active landslide scars located in the headwaters). Both sensors were overwhelmed during these events (turbidity exceeded the upper limit of both probes), likely due to sediment accumulation in the sensor housing. Despite continual maintenance, both sensors repeatedly recorded maximum values due to fouling over the latter two wet seasons. As a result, useful turbidity data are only available on a periodic basis.
Figure 4-3 - Rainfall, water level and turbidity data illustrating: a) clear correlation between the three variables at the lower hydrometric station during the moderate wet season of 2002-2003, and b) an example of fouling of the turbidity sensor at the upper station after heavy rains.
4.3.1.2. Meteorological parameters

Three wet seasons were monitored during this study (a portion of 2002-2003 and all of 2003-2004 and 2004-2005). During the latter two seasons, the three largest storm events caused extensive flooding in the Hatzic watershed (Figure 4-1). The first, in October 2003, resulted from the arrival of several moist, Pacific sub-tropical air masses that stalled in a low pressure system over the GVRD and LFV for several days (October 15 – 22). Record 24- and 48-hour rainfall totals were recorded at several meteorological stations on Vancouver Island and the mainland. The return period for the storm was calculated at 100 years in many locations (Northwest Hydraulic Consultants and Scott Resources Services, 2005). An analysis of rainfall data (Table 4-1) from several stations in the LFV indicated that rainfall was particularly heavy in the Hatzic watershed (although higher rainfall values are due in part to the higher elevation of the Hatzic climate station). Peak rainfall intensity reached 19.3 mm-hr$^{-1}$, and remained high for several days, resulting in a maximum 48-hour total of 257.3 mm (October 16-17).

Table 4-1 - Daily rainfall at four weather stations in the Lower Fraser Valley for the major storm event in October, 2003 (Environment Canada, 2005). Numbers in brackets represent station elevation.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbotsford Airport</td>
<td>12.4</td>
<td>93.8</td>
<td>73.6</td>
<td>T</td>
<td>11.8</td>
<td>50.6</td>
<td>25.0</td>
<td>23.0</td>
<td>290.2</td>
</tr>
<tr>
<td>(57.9 m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chilliwack</td>
<td>22.6</td>
<td>100.3</td>
<td>28.2</td>
<td>8.9</td>
<td>20.5</td>
<td>73.8</td>
<td>0</td>
<td>23.0</td>
<td>277.3</td>
</tr>
<tr>
<td>(11.0 m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mission, West Abbey</td>
<td>32.2</td>
<td>123.2</td>
<td>62.0</td>
<td>15.4</td>
<td>17.0</td>
<td>66.8</td>
<td>1.8</td>
<td>27.8</td>
<td>346.2</td>
</tr>
<tr>
<td>(221 m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hatzic Climate Station</td>
<td>11.4</td>
<td>136.4</td>
<td>120.9</td>
<td>1.3</td>
<td>32.5</td>
<td>64.3</td>
<td>24.9</td>
<td>35.1</td>
<td>426.7</td>
</tr>
<tr>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

Significant flooding was observed throughout the watershed (Figure 4-4), with the majority of lowland agricultural fields being completely submerged. Water levels at the lower hydrometric station increased from 0.27 m to a peak of 2.0 m (the upper limit of the hydrostatic depth probe), and Hatzic Slough breached its banks in several locations. Conductance at the lower hydrometric station initially declined, but as water levels peaked, it subsequently increased to a maximum of 213 $\mu$S·cm$^{-1}$ (the highest value observed during the study) and remained high during the recession of the storm peak. As a prolonged peak was not observed at the upper hydrometric station at the same time, this is attributed to
an increase in dissolved solids derived from nearby agricultural fields that had been submerged for more than 11 days.

Figure 4-4 - a) Lower hydrometric station from the west, illustrating low-flow conditions typical of a dry period during winter, and b) looking south at the same hydrometric station from the bank during the October, 2003 event (note data logger and submerged dock railing for reference).

The second largest event took place from November 21-27, 2004. Rainfall for the first three days was moderate (24-hour maxima from 5.3-16.5 mm), but was followed by 137.2 mm on November 24th, with peak rainfall intensities of 10.2 mm-hr⁻¹. Again, excessive flooding occurred in low-lying areas, but was shorter in duration (less than 2 days) when compared to the 2003 event and total rainfall volumes were much lower (186.2 mm). The third notable event (January 16–23, 2005) produced total rainfall of 340 mm, a 48-hour maximum of 209 mm, and again resulted in significant flooding throughout the watershed, with agricultural fields submerged for nearly 5 days. It is notable that, while agricultural fields were submerged for several days during these latter floods, neither event produced a peak in conductivity at the lower hydrometric station as was observed in October, 2003. This is attributed to differing antecedent conditions and the longer duration of the 2003 flood. The 2003 event was preceded by several months of dry weather allowing accumulation of animal wastes in storage areas and on pasture fields, as well as the accumulation of organic matter and agrichemicals on crop fields. Further,
conductivity only exceeded pre-storm levels during the 2003 event after agricultural fields had been submerged for nearly five days, and peak values were not observed until nearly 11 days after flooding began.

4.3.2. Spatial trends in surface water quality

Spatial trends in nutrient and bacterial concentrations were assessed in order to determine the impacts of agricultural land-use practices on surface water quality and to identify significant point sources of agricultural contamination.

4.3.2.1. Nutrients

4.3.2.1.1. Site-to-site variability

Nutrient concentrations in surface waters throughout the Hatzic watershed were low (Table 4-2), reflecting the relatively low intensity of agricultural activities. The percentage of samples with concentrations below detection limits for NO$_3^-$, NH$_4^+$ and PO$_4^{3-}$ were 4.3%, 39% and 44%, respectively. These samples were assigned a concentration of 50% of the detection limit. Mean NO$_3^-$ values were highest at stations HV-13 and HV-20 (1.0 mg·L$^{-1}$ and 0.67 mg·L$^{-1}$, respectively), and lowest at stations HV-6 and HV-1 (0.23 mg·L$^{-1}$ for both). In contrast, the highest mean NH$_4^+$ concentrations were observed at station HV-18 at 0.34 mg·L$^{-1}$, with stations HV-1, HV-8, HV-10 and HV-16 having similar mean concentrations of 0.24, 0.21, 0.19 and 0.22 mg·L$^{-1}$, respectively. Mean NH$_4^+$ was lowest at HV-20, at 0.09 mg·L$^{-1}$. Maximum mean PO$_4^{3-}$ concentrations were also observed at HV-18 (0.10 mg·L$^{-1}$), and the second highest mean value was observed at HV-9 (0.08 mg·L$^{-1}$). The two lowest average PO$_4^{3-}$ concentrations were observed in forested subcatchments at HV-2 and HV-12 (0.04 mg·L$^{-1}$ for both).

4.3.2.1.2. Land-use influence

A comparison of results stratified by land-use using the Kruskal-Wallis test revealed significant differences for NO$_3^-$ between land-use categories ($P = 0.03, n = 18$). As described in Chapter 3, all statistical comparisons were conducted using mean values from each station in order to avoid pseudoreplication. This significantly reduced the sample size for each test as only one value was used for each station. When post-hoc analysis was conducted using Mann-Whitney tests (with Bonferroni correction to account for multiple comparisons), the resulting significance values were above $P = 0.05$. As a result, the following describes qualitative differences for these parameters by land use.
As illustrated in Table 4-2, maximum mean NO\textsubscript{3}\textsuperscript{-} concentrations were observed at the urban site (HV-20). It is important to note that, because the urban site was not replicated, it is not possible to draw conclusions regarding the impacts of urban land use in general. Mean NH\textsubscript{4}\textsuperscript{+} and PO\textsubscript{4}\textsuperscript{3-} concentrations were highest at agricultural sites. Interestingly, mean NO\textsubscript{3}\textsuperscript{-} concentrations were higher at mixed sites than at agricultural sites. At each mixed site, agricultural operations were located just upstream of the sampling location. The difference observed likely reflects direct NO\textsubscript{3}\textsuperscript{-} inputs from these farms. Finally, NO\textsubscript{3}\textsuperscript{-} concentrations at agricultural sites were higher than those measured in forested subcatchments.

Table 4-2 - Descriptive statistics for ammonia, nitrate and orthophosphate (2002–2005). Note that concentrations below detection limits were assigned a value of 0.5 x detection limit.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Land Use</th>
<th>N</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>Median</th>
<th>SD\textsuperscript{1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+}</td>
<td>Combined</td>
<td>317</td>
<td>0.05</td>
<td>1.22</td>
<td>0.16</td>
<td>0.11</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Forested</td>
<td>77</td>
<td>0.05</td>
<td>0.48</td>
<td>0.14</td>
<td>0.05</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>137</td>
<td>0.05</td>
<td>1.22</td>
<td>0.19</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Mixed use</td>
<td>87</td>
<td>0.05</td>
<td>0.68</td>
<td>0.16</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>16</td>
<td>0.05</td>
<td>0.31</td>
<td>0.09</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-}</td>
<td>Combined</td>
<td>317</td>
<td>0.01</td>
<td>2.51</td>
<td>0.44</td>
<td>0.37</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>Forested</td>
<td>77</td>
<td>0.01</td>
<td>1.25</td>
<td>0.30</td>
<td>0.26</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>137</td>
<td>0.01</td>
<td>1.76</td>
<td>0.41</td>
<td>0.34</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>Mixed use</td>
<td>87</td>
<td>0.20</td>
<td>2.51</td>
<td>0.57</td>
<td>0.46</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>16</td>
<td>0.39</td>
<td>1.17</td>
<td>0.67</td>
<td>0.59</td>
<td>0.27</td>
</tr>
<tr>
<td>PO\textsubscript{4}\textsuperscript{3-}</td>
<td>Combined</td>
<td>291</td>
<td>0.01</td>
<td>0.40</td>
<td>0.06</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Forested</td>
<td>71</td>
<td>0.01</td>
<td>0.28</td>
<td>0.04</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>126</td>
<td>0.01</td>
<td>0.40</td>
<td>0.07</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Mixed use</td>
<td>80</td>
<td>0.01</td>
<td>0.35</td>
<td>0.06</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>14</td>
<td>0.01</td>
<td>0.34</td>
<td>0.06</td>
<td>0.02</td>
<td>0.09</td>
</tr>
</tbody>
</table>

\textsuperscript{1} - Standard Deviation

Agricultural sites generally produced elevated nutrient levels; however, the three nutrients did not vary similarly. An analysis of Spearman rank correlations between these variables for agricultural sites revealed significant correlations between NH\textsubscript{4}\textsuperscript{+} and PO\textsubscript{4}\textsuperscript{3-} (\(r_s = 0.255, P = 0.004, n = 126\)). A similar correlation was observed for mixed sites (\(r_s = 0.235, P = 0.036, n = 80\)).

In forested subcatchments, mean nutrient concentrations were consistently lower than for all other land uses. Peak values were typically observed during the wet season, reflecting the mobilization of natural degradation byproducts in forest litter.
4.3.2.2. Bacteria

4.3.2.2.1. Site-to-site variability

Bacterial concentrations were highly variable throughout the watershed (Table 4-3). The ranges for total and fecal coliforms were $10 - 29,400 \text{ cfu}\cdot100 \text{ ml}^{-1}$ and $0 - 10,400 \text{ cfu}\cdot100 \text{ ml}^{-1}$, respectively. When all samples were considered ($N = 192$), the two variables were strongly correlated ($r_s = 0.736$).

Fecal coliform bacteria were detected in all but 7 samples, 6 of which were collected from forested sites. Maximum values for fecal coliforms were recorded at HV-18, a slow-moving agricultural slough that flows through several cattle and horse farms. Large numbers of waterfowl (>100 ducks and geese) were also frequently observed upstream of HV-18 during winter months. The next highest maximum values were observed at HV-5, HV-17, HV-13 and HV-19.
Table 4-3 - Descriptive statistics for total and fecal coliform by station (2003-2005).

<table>
<thead>
<tr>
<th>Station</th>
<th>N</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>Median</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Coliform</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HV-1</td>
<td>12</td>
<td>110</td>
<td>5,300</td>
<td>1,152</td>
<td>475</td>
<td>1,620</td>
</tr>
<tr>
<td>HV-2</td>
<td>11</td>
<td>23</td>
<td>1,250</td>
<td>269</td>
<td>150</td>
<td>362</td>
</tr>
<tr>
<td>HV-4</td>
<td>10</td>
<td>24</td>
<td>2,900</td>
<td>478</td>
<td>167</td>
<td>877</td>
</tr>
<tr>
<td>HV-5</td>
<td>11</td>
<td>100</td>
<td>14,700</td>
<td>2,923</td>
<td>800</td>
<td>4,872</td>
</tr>
<tr>
<td>HV-6</td>
<td>12</td>
<td>12</td>
<td>320</td>
<td>100</td>
<td>76</td>
<td>95</td>
</tr>
<tr>
<td>HV-8</td>
<td>10</td>
<td>100</td>
<td>4,200</td>
<td>1,618</td>
<td>1,090</td>
<td>1,578</td>
</tr>
<tr>
<td>HV-9</td>
<td>10</td>
<td>100</td>
<td>7,800</td>
<td>2,513</td>
<td>1,700</td>
<td>2,513</td>
</tr>
<tr>
<td>HV-10</td>
<td>10</td>
<td>130</td>
<td>4,200</td>
<td>1,593</td>
<td>1,150</td>
<td>1,492</td>
</tr>
<tr>
<td>HV-11</td>
<td>11</td>
<td>30</td>
<td>2,100</td>
<td>641</td>
<td>360</td>
<td>713</td>
</tr>
<tr>
<td>HV-12</td>
<td>10</td>
<td>44</td>
<td>5,000</td>
<td>821</td>
<td>305</td>
<td>1,501</td>
</tr>
<tr>
<td>HV-13</td>
<td>10</td>
<td>300</td>
<td>6,300</td>
<td>3,017</td>
<td>2,500</td>
<td>2,543</td>
</tr>
<tr>
<td>HV-14</td>
<td>10</td>
<td>390</td>
<td>6,020</td>
<td>2,304</td>
<td>1,900</td>
<td>1,674</td>
</tr>
<tr>
<td>HV-15</td>
<td>10</td>
<td>780</td>
<td>4,800</td>
<td>2,018</td>
<td>1,550</td>
<td>1,332</td>
</tr>
<tr>
<td>HV-16</td>
<td>11</td>
<td>350</td>
<td>8,500</td>
<td>2,505</td>
<td>2,300</td>
<td>2,159</td>
</tr>
<tr>
<td>HV-17</td>
<td>11</td>
<td>340</td>
<td>6,700</td>
<td>2,381</td>
<td>1,670</td>
<td>2,099</td>
</tr>
<tr>
<td>HV-18</td>
<td>10</td>
<td>110</td>
<td>29,400</td>
<td>5,525</td>
<td>2,435</td>
<td>8,745</td>
</tr>
<tr>
<td>HV-19</td>
<td>10</td>
<td>460</td>
<td>4,400</td>
<td>2,095</td>
<td>2,510</td>
<td>1,383</td>
</tr>
<tr>
<td>HV-20</td>
<td>10</td>
<td>470</td>
<td>7,400</td>
<td>3,203</td>
<td>2,950</td>
<td>2,473</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fecal Coliform</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HV-1</td>
<td>12</td>
<td>0</td>
<td>410</td>
<td>70</td>
<td>24</td>
<td>114</td>
</tr>
<tr>
<td>HV-2</td>
<td>12</td>
<td>0</td>
<td>40</td>
<td>10</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>HV-4</td>
<td>10</td>
<td>0</td>
<td>710</td>
<td>76</td>
<td>10</td>
<td>223</td>
</tr>
<tr>
<td>HV-5</td>
<td>11</td>
<td>2</td>
<td>7,400</td>
<td>1,027</td>
<td>50</td>
<td>2,218</td>
</tr>
<tr>
<td>HV-6</td>
<td>12</td>
<td>0</td>
<td>20</td>
<td>6</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>HV-8</td>
<td>10</td>
<td>1</td>
<td>240</td>
<td>91</td>
<td>63</td>
<td>88</td>
</tr>
<tr>
<td>HV-9</td>
<td>10</td>
<td>7</td>
<td>370</td>
<td>100</td>
<td>72</td>
<td>107</td>
</tr>
<tr>
<td>HV-10</td>
<td>10</td>
<td>2</td>
<td>710</td>
<td>152</td>
<td>39</td>
<td>252</td>
</tr>
<tr>
<td>HV-11</td>
<td>11</td>
<td>2</td>
<td>76</td>
<td>23</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>HV-12</td>
<td>10</td>
<td>0</td>
<td>180</td>
<td>27</td>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td>HV-13</td>
<td>11</td>
<td>4</td>
<td>2,400</td>
<td>335</td>
<td>30</td>
<td>733</td>
</tr>
<tr>
<td>HV-14</td>
<td>10</td>
<td>10</td>
<td>910</td>
<td>128</td>
<td>49</td>
<td>276</td>
</tr>
<tr>
<td>HV-15</td>
<td>10</td>
<td>10</td>
<td>170</td>
<td>50</td>
<td>30</td>
<td>51</td>
</tr>
<tr>
<td>HV-16</td>
<td>11</td>
<td>10</td>
<td>140</td>
<td>56</td>
<td>51</td>
<td>48</td>
</tr>
<tr>
<td>HV-17</td>
<td>11</td>
<td>1</td>
<td>2,900</td>
<td>390</td>
<td>76</td>
<td>858</td>
</tr>
<tr>
<td>HV-18</td>
<td>12</td>
<td>2</td>
<td>10,400</td>
<td>1,395</td>
<td>395</td>
<td>2,900</td>
</tr>
<tr>
<td>HV-19</td>
<td>11</td>
<td>10</td>
<td>2,120</td>
<td>311</td>
<td>108</td>
<td>611</td>
</tr>
<tr>
<td>HV-20</td>
<td>10</td>
<td>1</td>
<td>1,410</td>
<td>333</td>
<td>111</td>
<td>481</td>
</tr>
</tbody>
</table>

1 – Standard deviation

A consistent increase in bacterial concentrations was observed along the mainstem from the forested headwaters (HV-6) to the final sampling site above Hatzic Lake (HV-19), reflecting the cumulative influence of moderate-intensity agricultural land use on surface-water quality (Figure 4-5). This coincides with an increase in the percentage of total land use accounted for by agriculture in the contributing area of each station, and also reflects contributions from tributaries with high bacterial concentrations derived from livestock operations (described below).
On two occasions (March 12 and May 1, 2003) samples were analysed for *E. coli* as part of an experiment at the BC Centre for Disease Control to assess a new *E. coli* culturing technique. This also provided an opportunity to determine the relationship between fecal coliform bacteria, which are known to have non-fecal origins, and *E. coli* which is derived solely from the intestinal tracts of animals and humans. On March 12, the highest *E. coli* concentrations were observed at HV-1 and HV-19 (exact counts could not be obtained as excessive *E. coli* colony growth prohibited enumeration, returning a result of “too numerous to count”). The next five highest values (ranging from 100-160 cfu·100 ml⁻¹) were observed at HV-5, HV-8, HV-9, HV-15, and HV-18, all of which are agricultural sites, except for HV-5 (mixed use).

On May 1, the highest count was observed at HV-20 (1080 cfu·100 ml⁻¹) on Draper Creek. This is substantially higher than the Health Canada guideline for recreational water quality (200 cfu·100 ml⁻¹), and represents a potential health risk as Draper Creek flows into Hatzic Lake near the beach at Neilson Park, a popular summer recreation site. The next highest value observed was at HV-19 (75 cfu·100 ml⁻¹). All other sites had concentrations below 30 cfu·100 ml⁻¹.

For the two days on which both fecal coliform and *E. coli* data were collected, a significant positive correlation between the variables was observed ($r_s = 0.728, P < 0.001, n = 35$). This is illustrated graphically in Figure 4-6, as is the influence of land use, demonstrated by the grouping of samples according to land-use category. This analysis suggests the fecal coliform data collected during this study...
provide a valid indication of true fecal contamination. While it is recognized that the small sample size ($n = 35$) and relatively low bacterial counts on these two days prevent the extrapolation of this relationship to the entire data set, this is a useful means of confirming the value of fecal coliform bacteria as indicators of fecal contamination in this instance.

![Graph showing correlation between concentrations of fecal coliform and E. coli](image)

Figure 4-6 - Log10 Fecal coliform vs. Log10 E. coli for March 23 and May 1, 2003 showing strong positive correlation between concentrations of the two bacteria in stream samples. Symbols also illustrate concentrations by land-use category.

4.3.2.2.2. Land-use influence

The highest median total and fecal coliform concentrations in the watershed were observed at the urban site (HV-20). Median values were used as an estimate of centrality due to the large standard deviations observed with coliform data (Table 4-3). The second and third highest median values were observed at agricultural and mixed use sites, respectively, and the lowest concentrations were consistently found at forested sites (Table 4-4). Median total and fecal coliform results from forested sites were significantly lower than for agricultural sites when all data were averaged for each station ($P = 0.002, n = 13$ for both). There were no significant differences between agricultural and urban sites for either type of bacteria, or between mixed use and urban sites for fecal coliform.
Table 4-4 - Descriptive statistics for total and fecal coliform data by land use (2003-2005).

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>Land Use</th>
<th>N</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>Median</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total coliform</td>
<td>Combined</td>
<td>192</td>
<td>10</td>
<td>29,400</td>
<td>1,901</td>
<td>885</td>
<td>2,956</td>
</tr>
<tr>
<td></td>
<td>Forested</td>
<td>45</td>
<td>10</td>
<td>5,000</td>
<td>383</td>
<td>114</td>
<td>852</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>85</td>
<td>100</td>
<td>29,400</td>
<td>2,520</td>
<td>1,780</td>
<td>3,524</td>
</tr>
<tr>
<td></td>
<td>Mixed use</td>
<td>52</td>
<td>30</td>
<td>14,700</td>
<td>1,951</td>
<td>850</td>
<td>2,751</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>10</td>
<td>470</td>
<td>7,400</td>
<td>3,203</td>
<td>2,950</td>
<td>2,473</td>
</tr>
<tr>
<td>Fecal coliform</td>
<td>Combined</td>
<td>196</td>
<td>0</td>
<td>10,400</td>
<td>260</td>
<td>29</td>
<td>986</td>
</tr>
<tr>
<td></td>
<td>Forested</td>
<td>46</td>
<td>0</td>
<td>710</td>
<td>27</td>
<td>9</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>87</td>
<td>0</td>
<td>10,400</td>
<td>330</td>
<td>64</td>
<td>1,189</td>
</tr>
<tr>
<td></td>
<td>Mixed use</td>
<td>53</td>
<td>2</td>
<td>7,400</td>
<td>333</td>
<td>40</td>
<td>1,096</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>10</td>
<td>2</td>
<td>1,410</td>
<td>333</td>
<td>111</td>
<td>481</td>
</tr>
</tbody>
</table>

Of particular interest is the substantial impact of cattle and horse operations on surface water bacterial concentrations throughout the watershed. Of the five highest fecal coliform values recorded during the study, three were at agricultural sites that either drained cattle and horse operations directly (HV-17 and HV-18) or were near the outlet of the mainstem river below several cattle operations (HV-19). The remaining two maxima were observed at mixed-use sites (HV-5 and HV-13) where the only influence in each forested subcatchment was one cattle operation (Figure 4-7). While it is not possible to relate animal densities to stream coliform levels at this scale (agricultural census data are only provided at an aggregate level for the Census Enumeration Area), it is clear that individual livestock operations act as point sources for indicator bacteria, and therefore, potentially pathogenic microorganisms. These data also indicate that "total area under agriculture" is not an effective indicator of water-quality risk. In studies on the influence of urban land use on water quality, several authors have noted a threshold of approximately 10% impervious area to generate a detectable change in water quality (e.g., Arnold and Gibbons, 1996; e.g., Hall et al., 1999). For mixed sites in this study, it is apparent that the threshold is much lower, and that one farm can have a significant impact on the microbiological quality of surface waters.
Figure 4-7 - Map of the Hatzic watershed illustrating locations of horse and dairy and beef cattle operations and stream sampling sites with the highest observed fecal coliform concentrations (black arrows).

Bacterial concentrations in forested regions of the watershed were significantly lower than in agricultural subcatchments; however, in contrast to nutrient levels, they were observed to exceed Canadian guidelines for both recreational water quality and drinking water quality (Table 4-3). Recreational guidelines require that mean fecal coliform or \( E. \ coli \) concentrations (from at least 5 samples taken over less than 30 days) not exceed 200 cfu·100 ml\(^{-1} \) (Federal-Provincial Working Group on Recreational Water Quality, 1992) and drinking water guidelines require that no fecal coliforms be detected (Federal-Provincial-Territorial Committee on Drinking Water, 2006). While consecutive samples were not collected within the 30 days required, the recreational limit of 200 cfu·100 ml\(^{-1} \) was exceeded at forested sites on one occasion at HV-4 (780 cfu·100 ml\(^{-1} \)), and nearly exceeded at HV-12 (180 cfu·100 ml\(^{-1} \)). Further, fecal coliforms were detected in 87% samples from forested sites. Maximum
concentrations were observed after prolonged dry periods during summer months suggesting the accumulation of fecal materials from wildlife sources during this time. Further, *E. coli* were detected in all samples from forested sites (concentrations ranged from 1-37 cfu·100 ml⁻¹). These results suggest the presence of active wildlife sources of fecal material in the watershed, which are adversely affecting water draining forested subcatchments. While bacterial concentrations tend to be low, significant spikes were observed indicating the potential for non-bacterial pathogens in these waters (i.e., parasites and viruses). As several residents obtain drinking water from surface sources draining forested subcatchments in the watershed, regular testing for pathogens should be conducted to ensure adequate treatment.

4.3.3. **Temporal trends in surface water quality**

Temporal trends at different scales (storm, seasonal, annual) were assessed to gain insight regarding the time periods of greatest contributions of agricultural runoff to surface waters.

4.3.3.1. **Nutrients**

Figure 4-8 is a plot of nutrient levels for the entire period of record, along with water levels at the upper hydrometric station (this station is used as it was not influenced by the artificial elevation of summer water levels associated with recreational use of Hatzic Lake). It is immediately apparent when looking at the aggregate record that $\text{NO}_3^-$ and $\text{PO}_4^{3-}$ levels were highest during the wet season of 2002-2003. A comparison of data for the three wet seasons on record revealed that mean concentrations for $\text{NO}_3^-$ were higher in the first wet season than in the second or third (0.64 mg·L⁻¹ vs. 0.46 mg·L⁻¹ and 0.42 mg·L⁻¹). A similar trend was observed for $\text{PO}_4^{3-}$ (0.11 mg·L⁻¹ vs 0.02 mg·L⁻¹ and 0.01 mg·L⁻¹). Mean $\text{NH}_4^+$ concentrations were higher in the first wet season than in the third (0.20 mg·L⁻¹ vs. 0.13 mg·L⁻¹) but lower than in the second (0.30 mg·L⁻¹).
Figure 4-8 - Nutrient concentrations vs. water level (upper hydrometric station) for the period of record. Note higher concentrations in first wet season. Red bars denote mean concentrations for day of sampling.
The observed difference is attributed to the extraordinary rainfall events observed in the watershed in the second and third wet seasons (the two largest events were each greater than one-third of the total rainfall observed from December to April in the first season). All wet-season sampling for the latter two seasons was conducted after these events (both occurred in the autumn). It is likely that these events resulted in basin-scale flushing of nutrient stores, with all subsequent events of smaller magnitude producing lower nutrient concentrations in surface waters than would be expected under more typical rainfall conditions.

A distinct seasonal trend is also visible in Figure 4-8. Mean wet-season NO$_3^-$ concentrations were higher than those observed during the dry season for all three years of study. Although N additions to agricultural soils (in the form of fertilizer and manure) are highest during spring and summer months, increased uptake on the land surface and in streams (due to plant and microbial metabolism) reduces the amount of N available for transport. Further, higher flows during the wet season result in greater mobilization of surface and subsurface sources than occurs in drier, summer months. A weak positive correlation is in fact observed between water depth at the upper hydrometric station and stream NO$_3^-$ concentrations when all stations are considered simultaneously. Stratifying the correlation by land use reveals differences in this relationship at the site level. Agricultural sites show a significant positive correlation between NO$_3^-$ and water depth ($r_s = 0.622$, $P < 0.001$, $n = 98$). This is expected as agricultural sites have greater NO$_3^-$ stores which are progressively accessed as water levels increase during a storm event (e.g., Moreau et al., 1998; e.g., Moog and Whiting, 2002). This correlation increases to $r_s = 0.727$ ($P < 0.001$, $n = 36$) when only mainstem stations are considered as the cumulative upstream agricultural influence is greatest at these sites.

At forested sites, the relationship between depth and NO$_3^-$ is negative and weaker ($r_s = -0.320$, $P = 0.020$, $n = 53$). There are two factors that likely contributed to this observed trend. Firstly, NO$_3^-$ stores in forested subcatchments are limited relative to agricultural sites and rapidly depleted as flow increases. As a result, NO$_3^-$ concentrations at times of increased discharge are consistently lower. Secondly, these forested streams drain steep slopes and respond to rainfall more quickly than the upper hydrometric station. As a result, water depth at that station may be a lagging indicator of depth at these sites.

Mixed-use sites fall between forested and agricultural stations, with a weak positive correlation ($r_s = 0.276$, $n = 62$) between water depth and nitrate. This reflects the influence of a smaller agricultural land base (in terms of percentage area) when compared to sites classified as “agricultural.”
Ammonia concentrations also varied seasonally, with higher concentrations during the wet season. Unlike NO$_3^-$, a correlation between water levels and NH$_4^+$ was not observed at any site, suggesting that different processes control the mobilization and transport of these two N species (cf. Kemp and Dodds, 2001). No consistent seasonal trend was observed for PO$_4^{3-}$. This is likely due to the low PO$_4^{3-}$ additions associated with moderate agricultural intensity. Also, because P is commonly a limiting nutrient (Wetzel, 1983) any excess P is likely either adsorbed in the soil profile or metabolized by plants or aquatic biota in streams draining agricultural fields.

### 4.3.3.2. Bacteria

A seasonal difference was observed (Table 4-5) for bacteria, with median fecal coliform concentrations being significantly higher during summer months when all sites and all seasons are considered ($P = 0.030, n = 38$). Median concentrations were also higher for total coliforms during summer months, although this difference was not significant. This pattern is in contrast to seasonal trends for nutrients, which had consistently higher concentrations in samples collected during winter months. This difference in both seasonal and inter-annual trends is due to the unique processes controlling the availability of bacterial vs. chemical contaminants for mobilization and transport. With continual addition of animal wastes and fertilizers to agricultural soils, both N and P accumulate in the soil profile and underlying groundwaters over time (as described in Chapter 2). In the absence of rainfall, plant and microbial metabolism (and, to a lesser extent, atmospheric losses) are the primary processes acting to reduce these stores. However, as demonstrated by Schreier et al. (2003), the application of nutrients in excess of the amounts lost to these processes is common. The resulting surplus nutrients are therefore available for transport during storm events (thus the positive correlation between stream flow and NO$_3^-$ concentrations described above).
Bacterial concentrations in agricultural soils, on the other hand, are controlled to a great extent by the dynamics of bacterial decay, which prevent the accumulation of significant stores over time (Beaudeau et al., 2001; Jamieson et al., 2004). While manure application rates are highest during spring and autumn, the combination of bacterial inactivation, depletion by early wet season rains and prohibitions on manure spreading in late autumn and winter months results in consistently lower bacterial concentrations in surface waters during the wet season. It should be noted that lower bacterial concentrations do not necessarily indicate a lower risk of contamination of surface waters with waterborne pathogens, as more resilient organisms (viruses and parasites) are not subject to in-situ decay at the same rates.

The highest median concentrations for both fecal and total coliforms in the watershed were observed on September 16, 2003. This is notable as sampling on this day coincided with a relatively small rainfall event (16.5 mm on September 16, and a total of 31.7 mm from the 14th-16th), which was preceded by two months of dry weather (total rainfall over the previous 60 days was 33.3 mm). Maximum fecal coliform concentrations for 10 sites were recorded on this day, and four samples had concentrations \( \geq 2,000 \text{ cfu-100 ml}^{-1} \). Two of these were at mixed sites located downstream of cattle operations (HV-5 and HV-13, with values of 2,000 and 2,400 cfu-100 ml\(^{-1}\), respectively). The two others were at HV-17 and HV-19, the lowermost stations on Hatzic Slough (2,900 and 2,120 cfu-100 ml\(^{-1}\), respectively). These are
substantially higher than the median values for these stations over the course of the study, which ranged from 30-108 cfu·100 ml⁻¹.

Two factors contributed to the higher concentrations observed on this day. Firstly, dry antecedent conditions allowed the accumulation of bacterial stores on the land surface and in stream sediments, as has been noted in other studies (e.g., Wilkinson et al., 1995). While data regarding the exact timing of manure applications to agricultural fields during this time are not available, manure spreading during summer months was observed on several occasions during the study. Resident livestock populations were also continually grazing during this period. Both activities contributed to the development of surface bacterial stores in the absence of any appreciable rainfall in the previous 60 days. Further, background levels of total and fecal coliform bacteria (at forested sites) were also elevated, suggesting accumulation of bacteria from active wildlife fecal sources (or potentially non-fecal sources) during this warm, dry period.

Secondly, samples were collected during the rising limb of the storm hydrograph. As surface and in-stream bacterial sources are accessed during the rising limb, bacterial mobilization and transport is greatest, and tends to increase until the onset of the recession limb (Nagels et al., 2002; Rodgers et al., 2003; Muirhead et al., 2004). It is therefore likely that samples collected during the rising limb on other dates would have produced similarly elevated values. The importance of antecedent conditions is demonstrated when comparing this event to another in March, 2005. During storm-based sampling from March 17-21, 2005 (described below) peak fecal coliform concentrations were again observed during the rising limb of the hydrograph; however, they did not surpass those observed during the September 16th event, which was less than one-third the size of the March, 2005 event. Although the latter event was larger (75.3 mm), and had similar peak intensities (approximately 5 mm·hr⁻¹), it took place near the end of the 2004-2005 wet season, and it was preceded by several storms of greater magnitude, which likely depleted surface and in-stream fecal bacterial stores.

4.3.4. Storm-event dynamics

Storm-event sampling was conducted at the lower hydrometric station on one occasion to assess event-scale relationships between rainfall, streamflow and water quality. Samples were collected every 3 hours beginning at 09:00 on March 18, 2005 and ending at 07:15 on March 21 using an ISCO 3700 automated water sampler placed at the lower hydrometric station. Total rainfall during this time was 75.4
mm; with three distinct events totalling 23.6 mm, 15.5 mm and 35.3 mm between March 19-21 (approximately 1 mm fell on the first day of sampling). Because these events took place in rapid succession, each resulted in successively higher water levels, thus providing the opportunity to assess the response of water-quality variables to a stepped hydrograph with three sequentially higher flow regimes. Figure 4-9 illustrates the response of hydrometric and water-quality variables to these precipitation events. The initial increase in water level was observed approximately 5.5 hours after the first event began on March 19. Conductivity and temperature (not shown) decreased at the onset of the first event as a result of dilution, with similar responses during the subsequent two events. Chloride also showed a marked decrease with rainfall, as described below. Turbidity values at the lower station were not included in this analysis due to sensor fouling. However, data from the upper station are provided for reference. While they should be interpreted with caution, they provide an indication of suspended sediment levels in the mainstem river over the course of the three events.
Figure 4-9 - a) rainfall, stage and chloride and nutrient concentrations, and b) rainfall, stage, turbidity and coliform concentrations measured every three hours from March 18-21, 2005 at the lower hydrometric station (turbidity measured at upper station).
4.3.4.1. Nutrients

Of the three nutrient species studied, only NO$_3^-$ showed an appreciable and consistent response to rainfall and elevated streamflow. Of all variables measured during these events, streamflow (expressed as stage) and NO$_3^-$ were most strongly correlated ($r_s = 0.875$, $n = 24$). For each event, peak NO$_3^-$ concentrations were observed early on the rising limb, and subsequently decreased at peak flow, suggesting either source exhaustion or dilution with NO$_3^-$ poor rainwater. Interestingly, as flow receded and water levels decreased, NO$_3^-$ increased slightly prior to the next event. This could represent the contribution of subsurface sources to stream N loads. Earlier sampling of shallow wells (<10 m) in the watershed revealed NO$_3^-$ levels as high as 12 mg·L$^{-1}$, with 12 wells having concentrations greater than 3 mg·L$^{-1}$ (Magwood, 2004), suggesting that groundwater could contribute significantly to stream NO$_3^-$. Further, leaching of soil NO$_3^-$ via throughflow may also contribute to the observed increase.

Chloride values and conductivity can be used as a proxy for the relative contribution of pre-event water to total flow (Laudon and Slaymaker, 1997; Peters and Ratcliffe, 1998). Over the three rainfall events, Cl$^-$ was significantly positively correlated with conductivity ($r_s = 0.708$, $n = 24$). Before the onset of the first event, Cl$^-$ concentrations were relatively consistent, with an average of 9.3 mg·L$^{-1}$. During peak flows, concentrations reached local minima (between 6.5-8.1 mg·L$^{-1}$). On the falling limb of the hydrograph, Cl$^-$ concentrations were rapidly restored to pre-event levels until dilution by the next event began. During the third storm event (the largest of the three), the greatest dilution took place and Cl$^-$ values dropped to a minimum of 6.5 mg·L$^{-1}$. Nitrate values were negatively correlated with both Cl$^-$ and conductivity ($r_s = -0.617$ and -0.800, respectively; $n = 24$), as increases in both variables represent the greater relative contribution of NO$_3^-$-poor rainfall to streamflow. It is likely that NO$_3^-$ loads to the stream at this time represent a combination of contributions from event water (transporting NO$_3^-$ from the land surface and soil profile in overland flow and throughflow, respectively), and pre-event water; however, the relative contribution of each source is not known.

The continual increase in NO$_3^-$ concentrations with higher water levels suggests ample N stores in the watershed, both in the soil profile and in dissolved form in shallow groundwater sources. It was not possible to investigate hysteresis effects for these events as the autosampler reached capacity as rainfall ceased during the final event.
Storm-event and seasonal dynamics of NO$_3^-$ concentrations in surface waters suggest that, despite relatively low nutrient surpluses (Schreier et al., 2003) N accumulation in agricultural soils and groundwater does take place during summer months, and that mobilization of these stores is a function of rainfall and streamflow. Consistent increases in NO$_3^-$ concentrations with river stage, while small in absolute terms, suggest that these stores are geographically extensive and susceptible to transport as they become hydrologically connected to the drainage network. These event-scale observations indicate that throughflow and groundwater do contribute to total stream NO$_3^-$ during these events. When combined with the results described previously (Section 4.3.3.1), these data suggest that the wet seasons, during which N stores are hydrologically linked to surface waters, are periods of peak N input.

4.3.4.2. Bacteria

Total and fecal coliforms were detected in all samples, including pre-event samples, suggesting the presence of active in-stream stores. Both types of bacteria responded similarly across all three storm events, although concentrations differed by more than an order of magnitude. Maxima for total and fecal coliforms reached 25,000 and 1,400 cfu·100 ml$^{-1}$, respectively. During the first event, peaks in total and fecal coliform concentrations occurred 30 minutes after peak flow. With the passing of the flood peak, concentrations for both types of bacteria decreased, but remained above pre-event levels. Concentrations for the first sample collected on the next rising limb remained low as depth had barely surpassed the previous peak (by 1 cm) and new bacterial stores had not been accessed. The large increase observed in the next sample (during the second event) indicates that streamflow had increased sufficiently to mobilize new bacterial sources. Total coliforms and fecal coliforms reached local maxima just prior to the peak in flow and near the end of the storm peak, respectively.

The third and largest event produced the highest fecal coliform concentrations and the third highest total coliform counts observed over the three days. Both peaked on the rising limb, approximately four hours before maximum flow, and decreased steadily over the next six hours until sampling concluded. It is worth noting that the minima observed at the conclusion of the third event were nearly an order of magnitude higher than pre-event levels. This indicates that, while sources accessed by increased flow were being depleted, they were still actively contributing to significantly elevated bacterial concentrations even on the receding limb.
A comparison with Cl⁻ data indicates that elevated bacterial concentrations were often associated with Cl⁻ minima. Chloride concentrations were negatively correlated with total coliform ($r_s = 0.505$, $P = 0.012$, $n = 24$) and fecal coliform ($r_s = 0.678$, $P < 0.001$, $n = 24$). During these minima, relative contributions to streamflow by rainfall were highest, suggesting that overland transport was a dominant transfer mechanism for bacteria from the land surface. However, the fact that this relationship is not stronger suggests that a portion of the bacterial load is derived from in-stream sources. As pre-storm Cl⁻ concentrations are re-established in the time between rainfall events, bacterial concentrations appear to stabilize or decrease, but remain above pre-event levels. This reflects the ongoing contribution of in-stream sources as overland flow decreases.

Turbidity data from the upper hydrometric station provide an indication of the timing of sediment transport to the mainstem over the course of the three events. As there was a slight delay in the response of the lower station to rainfall (as described in Section 4.3.1.1) the turbidity data are likely two-three hours ahead of the data described above. As illustrated in Figure 4-9, when this time difference is accounted for, peaks in turbidity coincide with the rising limb of each event and with peaks for total and fecal coliforms. This would be expected as these turbidity peaks represent sediment contributions from overland flow and resuspension of in-stream sources, both of which would contribute to elevated bacterial concentrations.

### 4.4. Conclusions

The impacts of land use on surface water quality are of growing concern, particularly in the LFV due to increasing intensification of agricultural activities, population growth and a dependence upon local water supplies, many of which utilize surface sources. While agricultural land use in the Hatzic watershed is not as intense as elsewhere in the LFV, its influence on water quality is apparent. Based on this assessment of surface-water quality over 2.5 years, the following conclusions can be drawn:

1) **Moderate agricultural intensity results in minor nutrient contributions to surface waters**

The influence of agricultural activities on surface waters was observed throughout the Hatzic watershed with consistently higher nutrient concentrations observed for agricultural and mixed sites. However, nutrient delivery to surface waters was relatively limited and comparable to contributions from the urban site. This reflects the moderate intensity of farming activities in the watershed [N concentrations were consistently below Canadian Environmental Quality Guidelines for the protection of aquatic life (13-]
16 mg L⁻¹) and P concentrations were below detection limits in 44% of samples. These values place surface waters in the oligotrophic-mesotrophic range (Wetzel, 1983), and are considerably lower than surface water concentrations in other agriculturally-dominated watersheds in the LFV (Schreier et al., 1999; Berka et al., 2001; Schreier et al., 2004).

2) **Moderate agricultural intensity produces significant bacterial contributions to surface waters**

In terms of risk, results from the present study suggest that fecal contamination from livestock and wildlife represent the greatest water-quality hazard in the Hatzic watershed. Fecal coliforms were detected in 98% of samples collected (N = 87) in agricultural subcatchments, indicating the presence of robust sources of fecal contamination. Of particular interest was the fact that individual livestock operations acted as significant point sources of fecal contamination at mixed sites. Some groups have found strong positive correlations between different indices of agricultural intensity and water-quality variables (e.g., Berka et al., 2001), while others have found weak correlation, or no relationship (e.g., Hunter et al., 1999). Consistent increases in bacterial concentrations were observed in a downstream direction (a result of increasing contributing area under agriculture). However, the data for mixed sites illustrate that this is a poor predictor of water-quality risk as individual agricultural operations can act as significant point sources of contaminants.

3) **Mid-summer or early wet season rainfall events represent high-risk periods for bacterial contamination of surface waters**

Antecedent conditions were observed to play a strong role in determining the risk of bacterial contamination of surface waters. Thus, the highest bacterial concentrations were observed during a relatively small storm event, after a prolonged dry period during which bacterial accumulation in surface soils of both forested and agricultural sites took place. As a result, fecal coliform concentrations in sites draining both types of subcatchments exceeded Health Canada recreational water quality guidelines at 11 out of 18 sampling sites, in many cases by more than an order of magnitude.

The summer months appear to be times of peak bacterial concentrations in surface waters in forested and agricultural catchments, particularly after prolonged periods of dry weather during which fecal matter accumulates on the land surface. This would suggest that, in BC, mid-summer rainfall events
and the onset of wet season rains represent times of significant risk in terms of pathogen contributions to surface waters.

4) **Active wildlife sources of fecal contamination are present in undeveloped subcatchments**

Background nutrient concentrations in forested subcatchments were consistently low and appeared to represent little risk in terms of human or ecosystem health. However, bacterial concentrations (including *E. coli* and total and fecal coliforms) were relatively high in some undeveloped subcatchments. This suggests that fecal inputs to surface waters from wildlife sources was taking place, and could represent a risk to human health where these streams are used as sources of drinking water. Several residents obtain drinking water from surface sources draining forested subcatchments. Where this occurs, regular testing for pathogens is recommended in order to assess the risk associated with these water sources.

The observation of fecal bacteria in undeveloped subcatchments has implications for the numerous drinking-water systems in BC that rely on surface-water sources. The consistency in patterns of bacterial concentrations in these subcatchments suggest they are representative of those in undisturbed catchments used as drinking-water sources elsewhere in the province (e.g., GVRD, Capital Regional District, etc.). As stated above, the period of greatest risk for contamination of these water sources appears to be during mid-summer or early wet-season rainfall events.

5) **Extreme rainfall events impact catchment-scale nutrient stores and nutrient contributions to surface waters**

Inter-annual variation in nutrient concentrations was observed and revealed the role of extreme events in depleting catchment-scale nutrient stores. This trend is particularly evident in the Hatzic watershed due to relatively moderate nutrient additions which result in slower recovery of these stores over time. Bacterial concentrations did not exhibit a similar response, reflecting the more transient nature of bacterial stores (they do not persist from season to season), and the relative speed with which they are replenished on an annual basis.
5. The effect of agricultural intensity on surface-water quality in the Lower Fraser Valley

5.1. Introduction

In Chapter 4 it was demonstrated that moderate agricultural intensity can result in measurable impairment of surface waters, particularly in terms of bacterial concentrations. Land-use intensity in the LFV varies significantly across watersheds; however, little work has been done to evaluate the link between agricultural intensity and surface-water quality in this region. This chapter aims to do so by assessing surface-water quality across three watersheds of varying agricultural intensity (the Hatzic, Elk Creek and Salmon watersheds).

In particular, the objectives of this chapter are to: 1) determine if spatial and temporal trends in background levels of nutrient and bacterial concentrations are similar in undeveloped catchments across watersheds, 2) determine if the effect of land-use intensity on nutrient and bacterial concentrations can be detected through a comparison of spatial and temporal trends across the three watersheds and 3) assess if agricultural intensity influences watershed-scale patterns of nutrient and bacterial mobilization, transport and inputs to surface waters.

5.2. Methods

Methods used for the collection of field samples and for laboratory analysis are described in detail in Chapter 3. Sample collection in the three watersheds was timed to occur on the same days to ensure similar environmental conditions across all sites. Statistical methods used in this chapter for analysis of correlations and comparisons of means are also outlined in Chapter 3.

5.3. Agricultural intensity

5.3.1. Quantifying agricultural intensity

In order to assess agricultural land-use intensity for the Hatzic, Elk Creek and Salmon watersheds it is necessary to quantify the intensity of crop and livestock operations, as both contribute to the impairment of water quality through manure and fertilizer applications. An effective way to determine agricultural intensity is through the use of nutrient budgets to calculate surpluses or deficits based on total...
nutrient inputs (fertilizer, manure, atmospheric deposition) and outputs (crop growth, atmospheric losses) for a given agricultural area. Any surplus represents the potential nutrient loss to surface waters and groundwater (Oborn et al., 2003). Schreier et al. (2003) calculated nutrient surpluses by EA in the LFV based on data from the Canadian Census of Agriculture (1986-2001) conducted by Statistics Canada. These data are used here to determine the potential for nutrient enrichment of surface waters based upon the availability of surplus N and P.

Animal density is also an effective index of the intensity of livestock operations. To measure density in areas with multiple livestock types, a method is required to convert all animals to equivalent units. This can be accomplished using feed requirements or waste production characteristics and results in a value of “animal unit equivalents” or AUE’s (Beaulieu et al., 2001). As waste production is the primary concern in this study, the latter method will be used. Conversion factors for AUE’s have been developed by several provincial agricultural ministries, but in a recent assessment of livestock density across Canada, Beaulieu et al. (2001) developed a common set of coefficients to be applied nationally (Table 5-1). Once livestock numbers are converted to AUE’s, this value is divided by the total area under agriculture to determine a measure of density (AUE-ha\(^{-1}\)) (Beaulieu et al., 2001).

<table>
<thead>
<tr>
<th>Livestock Type</th>
<th>Animal Type</th>
<th>AUE Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poultry</td>
<td>Broilers</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Layers</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Pullets</td>
<td>300</td>
</tr>
<tr>
<td>Cattle</td>
<td>Dairy cow</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Dairy bull</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Beef cow</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Heifer</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Steers</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>Calves</td>
<td>3.8</td>
</tr>
<tr>
<td>Pigs</td>
<td>Boars/sows</td>
<td>5</td>
</tr>
<tr>
<td>Sheep</td>
<td>Rams</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Ewes</td>
<td>5</td>
</tr>
<tr>
<td>Others</td>
<td>Horses</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Goats</td>
<td>7</td>
</tr>
</tbody>
</table>

\(^{1}\) – number of animals that equal 1 AUE.

5.3.2. Hatzic, Elk Creek and Salmon watersheds

5.3.2.1. Nutrient Surpluses

Based on an assessment of manure production, fertilizer applications, uptake by crops and atmospheric interactions, Schreier et al. (2003) calculated nutrient budgets for the Nicomen, East
Chilliwack and North Langley EA's (Table 5-2). These EA's contain the Hatzic, Elk Creek and Salmon watersheds, respectively. Surpluses or deficits were expressed in kg·ha$^{-1}$ for 2001. For the Nicomen EA, small N and P surpluses of 13 kg·ha$^{-1}$ and 16 kg·ha$^{-1}$, respectively, were observed. As agricultural intensity in the Hatzic watershed is lower than that throughout the rest of the Nicomen EA (based on field observations, and as illustrated by nutrient concentrations in surface waters described in Chapter 4), this is likely an overestimate of surplus nutrients in the Hatzic watershed.

Table 5-2 - Land-use distributions and nutrient surpluses for the Hatzic, Elk Creek and Salmon watersheds (note that nutrient surpluses are calculated based on the EA's within which these watersheds are located)

<table>
<thead>
<tr>
<th></th>
<th>Hatzic</th>
<th>Elk Creek</th>
<th>Salmon</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td>8400</td>
<td>3300</td>
<td>8000</td>
</tr>
<tr>
<td>Forest (ha / %)</td>
<td>5712 / 68</td>
<td>2343 / 71</td>
<td>400 / 5</td>
</tr>
<tr>
<td>Agriculture (ha / %)</td>
<td>1140 / 14</td>
<td>693 / 21</td>
<td>3600 / 45</td>
</tr>
<tr>
<td>Urban/residential (ha / %)</td>
<td>924 / 11</td>
<td>66 / 2</td>
<td>2880 / 36</td>
</tr>
<tr>
<td>Other (ha / %)</td>
<td>588 / 7</td>
<td>198 / 6</td>
<td>1120 / 14</td>
</tr>
<tr>
<td>Nutrient surpluses</td>
<td>Nitrogen (kg/cropped ha)</td>
<td>13</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>Phosphorus (kg/cropped ha)</td>
<td>16</td>
<td>65</td>
</tr>
</tbody>
</table>

1 – note that N surpluses within the Salmon watershed were found to be significantly higher than for the EA as a whole, as described by Schreier et al. (1999).

In the North Langley EA, N and P surpluses of 18 kg·ha$^{-1}$ and 30 kg·ha$^{-1}$, respectively, were observed. This estimate masks significantly higher N applications in some parts of the Salmon watershed. A detailed analysis of nutrient surpluses in the Salmon watershed (Schreier et al., 1999) revealed that localized NO$_3^-$ surpluses were in excess of 100 kg·ha$^{-1}$. Schreier et al. (1999) also estimated surplus N applications over the highly-vulnerable Hopington aquifer, which underlies the middle section of the watershed. Using a model that accounted for N derived from commercial agriculture (fertilizers), hobby farms (manure), septic systems and atmospheric inputs, N surpluses ranging from 9-268 kg·ha$^{-1}$ were calculated, with an average of 68 kg·ha$^{-1}$ in the area over the aquifer.

Nitrogen and P surpluses of 159 kg·ha$^{-1}$ and 65 kg·ha$^{-1}$, respectively, were calculated for East Chilliwack. Using Census of Agriculture data, Macdonald (2000) used residual, or surplus N as an indicator of agricultural production intensity across Canada. Regions were assigned to one of four classes based on total surplus N as follows: Class 1 = ≤ 20 kg·ha$^{-1}$, Class 2 = 21-40 kg·ha$^{-1}$, Class 3 = 41-60
kg·ha	extsuperscript{-1} and Class 4 = > 60 kg·ha	extsuperscript{-1}. Much of the LFV was assigned to Class 4, which was described as having significant potential for N losses to surface water and groundwater.

5.3.2.2. Animal Densities

Animal densities in the Hatzic watershed were low, and were estimated based on the number of dairy, beef, sheep and horse operations identified during land-use surveys conducted by the Fraser Valley Regional District, in conjunction with the BC Ministry of Agriculture (Graham Daneluz, personal communication). Because census data on animal numbers are only available for the Nicomen EA, assumptions were made regarding the number of animals per farm in the watershed (Table 5-3), as agricultural intensity is not consistent across the EA. These values were based on a review of census data and on animal numbers observed during field work and farm visits. Based on these visits and observations of pasture fields over several years of fieldwork, the mid-range estimate is taken to be the most accurate, providing a stocking density for the watershed of 1.25 AUE·ha	extsuperscript{-1}.

Table 5-3 - Estimates of livestock populations in the Hatzic watershed

<table>
<thead>
<tr>
<th></th>
<th>Dairy</th>
<th>Beef</th>
<th>Horse</th>
<th>Sheep</th>
<th>AUE</th>
<th>AUE·ha	extsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td># of farms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Animals / farm</td>
<td>11</td>
<td>15</td>
<td>33</td>
<td>3</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>(low estimate)</td>
<td>20</td>
<td>20</td>
<td>2</td>
<td>20</td>
<td>692</td>
<td>0.61</td>
</tr>
<tr>
<td>Animals / farm</td>
<td>40</td>
<td>40</td>
<td>5</td>
<td>40</td>
<td>1424</td>
<td>1.25</td>
</tr>
<tr>
<td>Mid-range estimate</td>
<td>60</td>
<td>60</td>
<td>8</td>
<td>60</td>
<td>2158</td>
<td>1.89</td>
</tr>
<tr>
<td>Animals / farm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High estimate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 - Low values are used for horses as the total number of horses in the entire EA was only 210 (Schreier et al., 2003)

2 - An average conversion factor of 6.0 was used for sheep (rams = 7 and ewes = 5)

Stocking densities in the Elk Creek watershed were significantly higher than in the Hatzic watershed, based on calculations for the EA as a whole (agricultural intensity is more consistent in the East Chilliwack EA than in the Nicomen EA). Values for cattle, poultry, horses, goats and sheep were used to calculate a total of 35,445 AUE's in the EA, which has a total area under non-crop agriculture of 3,204 ha (out of a total of 9,867 ha of agricultural land). This results in a stocking density of 11.04 AUE·ha	extsuperscript{-1} for land under livestock. While the animal numbers used for this calculation apply to the EA as a whole, observations of several large poultry and cattle operations (at least four large poultry farms and 15 large cattle operations) within the watershed boundary during field work suggest that 11.04 AUE·ha	extsuperscript{-1} is a reasonable estimate for the Elk Creek catchment.
Chapter 5

For the Salmon watershed, livestock populations are dominated by chickens, with far fewer cattle and pigs than in the East Chilliwack EA. The total number of AUE's in the EA is 15,098, leading to a stocking density of 3.9 AUE·ha⁻¹ for 3,878 ha of non-crop agricultural land (out of a total of 6,507 ha of agricultural land).

The above data indicate that agricultural intensity, based on animal numbers, is lowest in the Hatzic watershed and highest in the Elk Creek watershed, with the Salmon watershed falling in between (Table 5-4). Stocking densities in the Salmon watershed are far below those in the Elk Creek catchment, based on calculations for their respective EA's. However, it should be noted that the value of 3.9 AUE·ha⁻¹ in the Salmon watershed is above 2.8 AUE·ha⁻¹, identified by Breaden and Lovejoy (1990) as the level beyond which contamination of water resources becomes critical.

Table 5-4 - Animal stocking densities for the Hatzic, Elk Creek and Salmon watersheds (see text for sources).

<table>
<thead>
<tr>
<th>Watershed</th>
<th>AUE's</th>
<th>Area under livestock (ha)</th>
<th>AUE·ha⁻¹ (area under livestock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatzic</td>
<td>1,424</td>
<td>1,130</td>
<td>1.25</td>
</tr>
<tr>
<td>Elk Creek</td>
<td>35,445</td>
<td>3,204</td>
<td>11.04</td>
</tr>
<tr>
<td>Salmon</td>
<td>15,098</td>
<td>3,878</td>
<td>3.9</td>
</tr>
</tbody>
</table>

It must be acknowledged that the above calculations for nutrient surpluses and stocking densities are subject to error given the nature of the available data and assumptions related to nutrient modeling and animal unit equivalency. However, they do illustrate a substantial gradient in agricultural intensity between the three watersheds that is sufficient to support an analysis of its influence on water quality.

5.4. Results and discussion

5.4.1. Comparison of land-use types

Surface-water quality was compared across similar land-use types in the three watersheds to assess the influence of land-use intensity on nutrient and bacterial concentrations (Table 5-5). This analysis also provides an opportunity to compare background levels of nutrients and bacteria at forested sites across watersheds. Note that there were no forested or mixed sites in the Salmon watershed, and therefore only data from the Hatzic and Elk Creek watersheds are compared for these land-use categories.
Table 5-5 - Water-quality data by land use and watershed (Salmon data include groundwater).

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Land-use</th>
<th>Parameter (mg·L⁻¹ / cfu·100 ml⁻¹)</th>
<th>N</th>
<th>Min.</th>
<th>Mean</th>
<th>Median</th>
<th>Max.</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
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<td>Hatzic</td>
<td>Forested</td>
<td>NO₃⁻</td>
<td>77</td>
<td>0.03</td>
<td>0.3</td>
<td>0.26</td>
<td>1.25</td>
<td>0.18</td>
</tr>
<tr>
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<td>NH₄⁺</td>
<td>77</td>
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<td>0.1</td>
<td>0.48</td>
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</tr>
<tr>
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<td>PO₄³⁻</td>
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<td>0.04</td>
<td>0.04</td>
<td>0.28</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fecal coliform</td>
<td>46</td>
<td>0</td>
<td>27</td>
<td>9</td>
<td>710</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total coliform</td>
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<td>10</td>
<td>383</td>
<td>114</td>
<td>5,000</td>
<td>852</td>
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<tr>
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<td>0.57</td>
<td>0.46</td>
<td>2.51</td>
<td>0.39</td>
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<td>0.17</td>
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<td>0.03</td>
<td>0.34</td>
<td>0.09</td>
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<td>0.15</td>
<td>0.13</td>
<td>0.30</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
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<td>0.02</td>
<td>0.01</td>
<td>0.12</td>
<td>0.04</td>
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<td>100</td>
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<td>0.38</td>
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</tr>
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<td></td>
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<td>PO₄³⁻</td>
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<td>0.03</td>
<td>0.01</td>
<td>0.18</td>
<td>0.05</td>
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<td>0.28</td>
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<td>20,500</td>
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<td>NH₄⁺</td>
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<td>0.13</td>
<td>0.12</td>
<td>0.27</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄³⁻</td>
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<td>0.24</td>
<td>0.07</td>
</tr>
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<td>0.08</td>
<td>0.07</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄³⁻</td>
<td>34</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.10</td>
<td>0.02</td>
</tr>
<tr>
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<td>Fecal coliform</td>
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<td>672</td>
</tr>
<tr>
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<td></td>
<td>Total coliform</td>
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<td>1,936</td>
<td>860</td>
<td>7,700</td>
<td>2280</td>
</tr>
</tbody>
</table>
5.4.1.1. Forested sites

Median fecal coliform concentrations at forested sites were 9 cfu·100 ml\(^{-1}\) and 10 cfu·100 ml\(^{-1}\) for the Hatzic and Elk Creek catchments, respectively (see Table 5-5 and Figure 5-1). Median total coliform concentrations were higher in forested sites of the Elk Creek watershed (170 cfu·100 ml\(^{-1}\) vs. 114 cfu·100 ml\(^{-1}\) in the Hatzic watershed), but this difference was not statistically significant. Total and fecal coliform concentrations were positively correlated in the Hatzic watershed \(r_s = 0.799, n = 39\) and Elk Creek watershed \(r_s = 0.732, n = 15\) suggesting that concentrations of both are controlled by similar processes.

![Graph](image)

Figure 5-1 – a) Median fecal and total coliform concentrations, and b) mean nutrient concentrations at forested sites in the Hatzic and Elk Creek watersheds. Error bars represent 95% confidence intervals.

Across all forested sites, fecal coliform concentrations (when averaged for each site over the period of record) were significantly higher during summer months \(P = 0.038, n = 14\). No significant difference was observed for total coliform. During winter months, total and fecal coliform concentrations in forested sub-catchments of both watersheds were low. Fecal coliform concentrations at all sites were at, or below, 10 cfu·100 ml\(^{-1}\) on all days (except for one sample at EC-8 collected on December 13, 2004, when a concentration of 25 cfu·100 ml\(^{-1}\) was observed). During summer months, variability across sites was greater and the maximum values for all forested sites were observed. The two highest concentrations recorded at forested sites (710 cfu·100 ml\(^{-1}\) and 180 cfu·100 ml\(^{-1}\) at HV-4 and HV-12, respectively) were observed on September 16, 2003. These samples were collected during a minor
rainfall event that took place after 60 days with minimal precipitation (33.3 mm), and represent the highest fecal coliform concentrations observed at forested sites during the present study.

Elevated coliform concentrations during summer months are expected, as several factors contribute to increased availability of fecal bacteria during this time. Wildlife activity (waterfowl, rodents, etc.) in and around waterways would be expected to increase during summer months, thus leading to greater potential for direct fecal loading to surface waters. Further, during summer months, warmer air temperatures are more conducive to the survival of thermotolerant bacteria such as fecal coliforms in the environment. Growth of indicator bacteria colonies in forest soils has been demonstrated in sub-tropical watersheds (Hardina and Fujioka, 1991; Byappanahalli and Fujioka, 1998; Solo-Gabriele et al., 2000) and temperate environments (Byappanahalli et al., 2003), suggesting that elevated levels in summer months may represent a combination of increased fecal loading from wildlife and increased in situ reproduction.

These data suggest that persistent sources of fecal bacteria exist in forested catchments of both watersheds. While concentrations were generally low, small rainfall events produced significantly elevated bacterial concentrations in undisturbed subcatchments, particularly after prolonged dry periods (e.g., on September 16, 2003). Such conditions should be considered as high risk for drinking-water systems utilizing surface-water sources, even in areas not influenced by agricultural or urban land uses.

At forested sites, $\text{NH}_4^+$ concentrations also showed a significant seasonal trend, with concentrations being higher in winter ($P = 0.002, n = 14$). No other seasonal differences were observed. Further, within forested sites, there were no significant differences for $\text{NO}_3^-$, $\text{NH}_4^+$ or $\text{PO}_4^{3-}$ between watersheds. However, mean concentrations for $\text{NO}_3^-$ were slightly higher in Elk Creek sites and, $\text{PO}_4^{3-}$ levels were elevated slightly in the Hatzic watershed (Figure 5-1b).

5.4.1.2. Mixed sites

Mixed sites in the Hatzic and Elk Creek catchments contained agricultural, urban and recreational land uses in subcatchments that were otherwise dominated by forest. The influence of these land uses was evident in both watersheds (Table 5-5). Mean $\text{NO}_3^-$ concentrations at mixed-use sites were 0.57 mg$\text{L}^{-1}$ and 0.90 mg$\text{L}^{-1}$ in the Hatzic and Elk Creek catchments, respectively, and were significantly higher than at forested sites in the Hatzic watershed ($P = 0.016, n = 10$). Median total coliform concentrations at mixed sites were 850 cfu·100 ml$^{-1}$ and 1200 cfu·100 ml$^{-1}$ for Hatzic and Elk Creek,
respectively. In the Hatzic watershed, the median fecal coliform concentration was 40 cfu·100 ml\(^{-1}\), compared to 45 cfu·100 ml\(^{-1}\) in the Elk Creek catchment.

A comparison of mixed sites between the two watersheds revealed significant differences only for PO\(_4\)\(^3-\) (P = 0.008, n = 10). Mean NO\(_3\)\(^-\) concentrations were higher in Elk Creek, due primarily to elevated values at EC-13 and EC-14 (1.23 mg·L\(^{-1}\) and 1.35 mg·L\(^{-1}\), respectively), but this difference was not significant when all data for each site were averaged. At EC-13, this was due to agricultural influence from a dairy farm located directly adjacent to the sampling site. Site EC-14 is not subject to agricultural influence, but recent timber harvesting activities in the headwaters of this subcatchment likely resulted in increased mobilization of soil nutrients (cf. Briggs et al., 2000), leading to higher-than-expected values at this site. Mean values for PO\(_4\)\(^3-\) at EC-14 were also higher than would be expected from a predominantly forested subcatchment (fifth highest mean concentration in the watershed), and were likely also due to post-harvest losses.

For all variables other than PO\(_4\)\(^3-\), no significant difference was observed between the two watersheds at mixed sites. As the land-use activities upstream of mixed-use sites vary significantly from site to site and from watershed to watershed (cattle operations, urban development, golf course, etc.) this was not necessarily expected. A review of standard deviations indicated substantial variability in these outcomes within this land-use category, but there was no significant difference when all mixed sites were grouped.

Seasonally, NH\(_4\)\(^+\) and NO\(_3\)\(^-\) concentrations were significantly higher at mixed-use sites in winter when all mixed sites were considered (P = 0.011 and P = 0.043, respectively, n = 20). Similarly, total and fecal coliform concentrations were significantly higher in summer (P = 0.019 and 0.005, respectively, n = 20). No statistically significant differences were observed for other variables between seasons.

### 5.4.1.3. Agricultural sites

**Hatzic**

The maximum bacterial concentrations observed at agricultural sites in the Hatzic watershed were observed at HV-18. The maximum total coliform concentration observed was 29,400 cfu·100 ml\(^{-1}\) while the peak fecal coliform value was 10,400 cfu·100 ml\(^{-1}\). Fecal and total coliform concentrations were not consistently high, as illustrated by far lower median values of 64 cfu·100 ml\(^{-1}\) and 1,780 cfu·100 ml\(^{-1}\),
respectively. Maximum nutrient concentrations for NO$_3^-$, NH$_4^+$ and PO$_4^{3-}$ were 1.76 mg·L$^{-1}$, 1.22 mg·L$^{-1}$ and 0.40 mg·L$^{-1}$ and were observed at HV-16, HV-18 and HV-9, respectively.

Based on a seasonal comparison of concentrations NO$_3^-$ and NH$_4^+$ concentrations were highest during winter months (P < 0.001 and P = 0.007, respectively, n = 16). Total and fecal coliform concentrations were highest in summer months (P = 0.028 and P = 0.038, respectively, n = 16).

**Elk Creek**

In the Elk Creek catchment, peak bacterial concentrations were regularly observed in two regions of the watershed: 1) at EC-4, EC-5 and EC-6, the three sites with contributing areas containing 100% agriculture, located in the low-lying, northeastern portion of the watershed, and 2) at the urban sites EC-11 and EC-12 in the southwest corner of the watershed (described below). Maximum total and fecal coliform concentrations were observed at EC-4 (52,200 cfu·100 ml$^{-1}$ and 20,500 cfu·100 ml$^{-1}$, respectively). Median concentrations at this site were more than an order of magnitude higher than at any other site during this study. These values can be attributed to a high-density dairy cattle farm located directly east of the sampling site, adjacent to the ditch where EC-4 samples were collected. Numerous cattle (50-100) were consistently observed grazing at this site, and bacterial concentrations suggest that fecal sources are closely linked to surface waters at this location.

The highest observed nutrient concentrations in the Elk Creek watershed were also recorded at EC-4, EC-5 and EC-6. The peak NO$_3^-$ value (4.25 mg·L$^{-1}$) and the peak PO$_4^{3-}$ value (0.28 mg·L$^{-1}$) were both observed at EC-6. The maximum NH$_4^+$ concentration (3.58 mg·L$^{-1}$, almost three times higher than the next highest value) was recorded at EC-4 providing further evidence of a direct link between nearby high-density cattle operations and water quality in this region. As in the Hatzic watershed, NO$_3^-$ concentrations were significantly higher in summer months (P = 0.002, n = 12). Total coliform concentrations were highest in summer months (P = 0.041, n = 12).

**Salmon**

In the Salmon watershed, a maximum fecal coliform concentration of 3,700 cfu·100 ml$^{-1}$ was observed at SA-1, near the outlet of the watershed. This reflects the cumulative impact of upstream agricultural contributions. The highest NO$_3^-$ value recorded at any surface-water station during this study (4.44 mg·L$^{-1}$) was observed at SA-5; however, elevated values were also observed at SA-14 and SA-19, (3.6 and 2.79 mg·L$^{-1}$, respectively). These elevated values are attributed to 50 large commercial farms and > 100 horse farms in the central portion of the watershed [as note by Schreier et al. (1999)], which
are directly adjacent to surface waters at, or upstream of, these sites. These operations are also underlain by the unconfined Hopington aquifer, which is heavily contaminated with nitrates and contributes significantly to NO$_3^-$ contributions to surface waters at SA-5 and SA-7. The highest NH$_4^+$ values in the watershed (0.17 mg·L$^{-1}$) were observed at SA-19 and are also attributed to the relatively intensive agriculture in this region of the watershed. A maximum PO$_4^{3-}$ concentration of 0.10 mg·L$^{-1}$ was found at SA-17.

Similar to the Hatzic and Elk Creek watersheds, fecal and total coliform concentrations were highest in summer months ($P < 0.001$ for both, $n = 24$). No significant seasonal difference was observed for NO$_3^-$, NH$_4^+$ or PO$_4^{3-}$. This was due to nutrient contributions from the Hopington aquifer during the drier summer months (described in greater detail below).

**Inter-watershed comparison**

A comparison of bacterial concentrations across the three watersheds revealed that land-use intensity exerts strong control over surface water quality. Based on Mann-Whitney tests (with significance values adjusted using Bonferroni correction), fecal coliform concentrations were significantly higher at agricultural sites in the Elk Creek watershed than in the Hatzic ($P = 0.024$, $n = 14$) and Salmon ($P = 0.009$, $n = 18$) watersheds (Figure 5-2). No significant difference was observed between the Salmon and Hatzic watersheds for either variable (likely due to the high maximum values at HV-18).
Figure 5-2 - Median total and fecal coliform concentrations for agricultural sites in the Hatzic, Elk Creek and Salmon watersheds. Total coliform and fecal coliform values were higher in the Elk Creek watershed than in the Hatzic watershed (P < 0.001 and P = 0.018, respectively) and Salmon watershed (P = 0.030 and P = 0.048, respectively). Error bars represent 95% confidence intervals.

The trend for nutrients was not as consistent (Figure 5-3). Ammonium concentrations were significantly higher in the Elk Creek watershed than in the Salmon watershed (P < 0.001, n = 18). Mean NH$_4^+$ concentrations in the Elk Creek watershed were also higher than in agricultural sites in the Hatzic watershed, but this difference was not significant. The elevated values in the Elk Creek catchment are attributable to substantial NH$_4^+$ inputs at EC-4 arising from runoff from intensive cattle operations located nearby. Elevated NH$_4^+$ concentrations in surface waters are thought to result from direct application of manure from cattle (Eghball et al., 1997), chickens (Pierson et al., 2001) and hogs (Gangbazo et al., 1995; Gangbazo et al., 1999), and levels above 0.02 mg·L$^{-1}$ may be toxic to fish and aquatic biota (Cooper, 1993). In this instance, direct contributions of fecal material into the slough from cattle were responsible for the high concentrations observed. This is supported by the fact that the highest fecal coliform concentrations observed during the study were also observed at this site. It is worth noting that the next highest NH$_4^+$ concentrations were observed at HV-18, also a site under significant influence from cattle operations.
Significantly higher $\text{NO}_3^-$ concentrations were observed in the Salmon watershed than in the Elk Creek ($P = 0.006, n = 18$) or Hatzic systems ($P < 0.001, n = 20$). Given the nutrient surpluses described in Section 5.3.2, this difference is not surprising. Elevated $\text{NO}_3^-$ values observed in the Salmon watershed in both the dry and wet seasons are attributed to two sources. Firstly, due to significant localized $N$ surpluses, on the land surface and in the upper soil profile, $\text{NO}_3^-$ contributions to surface waters are significant during the wet season, as described for the Hatzic watershed in Chapter 4.

The second source contributing to high surface-water $\text{NO}_3^-$ concentrations is the Hopington aquifer. This unconfined aquifer underlies the central portion of the watershed and contributes significantly to streamflow during baseflow conditions in late summer. Long-term $N$ surpluses in the watershed have led to significant $\text{NO}_3^-$ accumulation in the Hopington aquifer. Schreier et al. (1999), in a study of groundwater $\text{NO}_3^-$ levels in the watershed, noted that $\text{NO}_3^-$ levels in 13% of wells sampled ($n=70$) exceeded the 10 mg-L$^{-1}$ limit contained within the Canadian Drinking Water Guidelines. During the present study, samples collected from a deep (48 m) groundwater well (SA-1G) drawn from the Hopington aquifer, had mean $\text{NO}_3^-$ concentrations of 11.95 mg-L$^{-1}$. During baseflow conditions,
contributions from NO₃⁻-rich groundwater result in elevated surface-water NO₃⁻ concentrations during the dry season. As a result, the significant seasonal differences observed in other watersheds were not present in this catchment (it should be noted that seasonal differences were observed at SA-17 where influence from the aquifer is minimal). Groundwater contributions are likely also significant during the wet season, when they are combined with contributions from the land surface and upper soil profile.

High groundwater NO₃⁻ levels may also be influenced by the presence of over 4000 septic systems in the watershed (Schreier et al., 1999). Septic systems only retain an average of 20-55% of total N from sewage (Coote and Gregorich, 2000), and therefore likely add to the elevated surface water concentrations observed, particularly during the wet season when the local water table is elevated.

These data indicate that significant soil NO₃⁻ stores have accumulated within the watershed due to long-term surplus N applications and significant growth in the number of septic systems in recent years (Schreier et al., 1999). The data also indicate that there is considerable interaction between the surface water and groundwater systems. This has significant implications for aquatic ecosystem health due to the high potential for eutrophic conditions in these waters, particularly when NO₃⁻ loading occurs during summer months. There is also a potential threat to human health associated with elevated NO₃⁻ levels, as described in Chapter 2.

Orthophosphate concentrations were significantly higher in the Hatzic watershed than in the Salmon (P < 0.001, n = 20) and Elk Creek (P = 0.003, n = 18) catchments; however, values were low in all three watersheds. There are two factors that most likely contribute to the low values across watersheds. Firstly, PO₄³⁻ is strongly adsorbed to soil particles, thus limiting its mobility in dissolved form. Secondly, P is often a limiting nutrient in aquatic and terrestrial systems and excess P is rapidly assimilated through metabolic activity (Wetzel, 1983). These data suggest that the intensity of livestock operations in the three watersheds was not sufficient to generate the surpluses needed to produce significantly higher PO₄³⁻ levels in surface waters. It should be noted; however, that the highest mean PO₄³⁻ levels in the Hatzic and Elk Creek watersheds were associated with intensive cattle operations. This trend that has been observed in several other watersheds in Canada and the United States (e.g., Schepers and Francis, 1982; Coote and Gregorich, 2000). It is attributed to decreased P adsorption capacity in soils after prolonged surpluses associated with manure application and direct contributions from grazing animals.
5.4.1.4. Urban sites

At a watershed scale, percentage area under urban influence is minimal in the Hatzic and Elk catchments (11% and 2%, respectively). For individual sampling sites, the maximum percentages of total contributing area under urban land uses were 11.1% and 37% for sites EC-11 and HV-20, respectively. Despite the relatively small percentage of total area under urban development, urban sites in both watersheds had concentrations of nutrients and bacteria that exceeded those observed at several agricultural sampling stations.

In the Elk Creek watershed the greatest urban influence in terms of contributing area was at site EC-11, with 11.1% under residential development. Samples collected from EC-11 had the 4th and 6th highest median fecal and total coliform concentrations observed in the watershed, respectively. This influence extended downstream to EC-12 where the 7th and 5th highest median values for these variables were observed. Mean concentrations for NH$_4^+$ at urban sites were significantly lower than for agricultural sites, but no significant differences were observed between the two groups for NO$_3^-$-N or PO$_4^{3-}$-P.

At 37%, the percentage of contributing area under residential development for HV-20 in the Hatzic watershed was the highest observed in both watersheds. No significant difference in concentrations for any of the variables was observed between the two watersheds or between seasons (this is likely a result of the low sample size when all values are averaged at the site level).

Impairment of surface-water quality as a result of urban development has been documented in several studies and contaminant levels often show strong agreement with the total impervious area within a catchment (Arnold and Gibbons, 1996; Hall et al., 1999; Mallin et al., 2001). Arnold and Gibbons (1996) suggested that 10% impervious area was the threshold above which deleterious effects in receiving waters could be detected. A similar threshold was observed by Mallin et al. (2001) in two watersheds in North Carolina where population and percentage impervious area were strongly correlated to fecal coliform concentrations in tidal creeks. Increased fecal bacterial concentrations in streams influenced by urban development has been attributed to several sources including storm sewer overflows and direct deposition of feces by house pets, rodents and other small mammals (e.g., raccoons) on paved surfaces and lawns (Young and Thackston, 1999; Mallin et al., 2001). This material is then easily mobilized during storm events and rapidly conveyed to surface waters. In the Elk Creek watershed, samples from EC-11 and EC-12 exceeded the Canadian guideline for recreational water quality (200 cfu·100 ml$^{-1}$) for four out
of seven samples, while at HV-20 four out of 10 samples exceeded this value. The guideline requires that the mean of five samples collected within 30 days not exceed this number, and while insufficient samples were collected to determine if the guidelines were officially exceeded, the trend described above suggests that this is likely.

5.4.2. Cumulative downstream impacts

5.4.2.1. Nutrients

A comparison of cumulative downstream impacts on water quality revealed differing patterns across the three watersheds for nutrients. Downstream trends are described below with reference to NO$_3^-$ concentrations as they showed the greatest spatial variation in response to land use. In both the Hatzic and Elk Creek watersheds, a discernible longitudinal trend was observed for NO$_3^-$ on the mainstem river. Concentrations increased as the percentage of total contributing area under agriculture increased from 0% in the forested headwaters to approximately 12% and 20% near the outlet of the Hatzic and Elk Creek watersheds, respectively (Figure 5-4a and Figure 5-4b). Along the mainstem river, NO$_3^-$ concentrations were significantly correlated with contributing area under agriculture in the Hatzic watershed ($r_s = 0.427$, $P < 0.001$, $n = 85$) and Elk Creek watershed ($r_s = 0.369$, $P = 0.023$, $n = 38$).
Figure 5-4 - Downstream trends in NO$_3^-$ in the mainstem river of a) the Hatzic and b) the Elk Creek watersheds and for tributaries to the mainstem in c) the Hatzic and d) the Elk Creek watersheds. Percentages represent the proportion of total contributing area under agriculture.
When tributaries to the mainstem were considered, this same cumulative trend was often not observed due to significant contributions from agricultural operations. In these cases, the relationship between NO$_3^-$ and contributing area under agriculture did not hold, as demonstrated at HV-13 where 1.2% agricultural land use in an otherwise forested subcatchment produced median NO$_3^-$ levels that exceeded those observed in areas under greater agricultural influence (Figure 5-4c). This influence decreased downstream as the tributary reached the mainstem. A similar trend was observed in the Elk Creek watershed (Figure 5-4d). Contributions were derived from sites under 100% agricultural influence (EC-4, EC-5 and EC-6), that were located along agricultural sloughs found entirely within the agriculturally-dominated northeast region of the watershed.

In both watersheds, NO$_3^-$ concentrations decreased downstream of point sources. This was likely a result of both dilution of NO$_3^-$ concentrations by mainstem flow, and of in-stream metabolism of excess NO$_3^-$ (Mulholland and Hill, 1997). These data reflect the influence of scale on nutrient concentrations and longitudinal trends in surface waters. As noted by Buck et al. (2004), at the watershed scale, total upstream area under agriculture is often a strong predictor of surface-water nutrient concentrations. At smaller scales; however, local land-use activities have a greater influence upon water quality as the impact of dilution by upland and groundwater flows is lower (see also Wood et al., 2005).

Different trends were observed along the mainstem in the Salmon watershed for NO$_3^-$ concentrations, due to the strong interaction between surface water and groundwater (Figure 5-5). Nitrate loading to surface waters increases substantially downstream of SA-9 due to intensive agriculture in the central portion of the watershed. This trend is similar to that observed by Schreier et al. (1999), and illustrates the significant interaction between groundwater and surface water systems in this watershed, particularly during baseflow conditions in summer months. As a result, the strongly seasonal patterns seen in the Hatzic and Elk Creek catchments were not observed in the Salmon watershed. The influence of NO$_3^-$ contributions from the Hopington aquifer extends downstream beyond the boundary of the aquifer itself, and represents the indirect influence of intensive agricultural practices located above this unconfined aquifer in the central portion of the watershed.
Figure 5-5 – Downstream trends in NO₃⁻ concentrations in the Salmon watershed, for a) the Salmon river and b) Coghlan Creek above and below its confluence with the Salmon river. Note the significant influence of the Hopington aquifer on surface-water nutrient levels.
5.4.2.2. Bacteria

In the Hatzic and Elk Creek watersheds, bacterial concentrations showed similar downstream trends to those observed for nutrients. Along the mainstem, fecal coliform concentrations showed a significant positive correlation with contributing area under agriculture for the Hatzic watershed \( r_s = 0.676, P < 0.001, n = 54 \) and for the Elk Creek watershed \( r_s = 0.654, P < 0.001, n = 37 \). As with nutrients, trends observed in tributaries were not as consistent. In both watersheds, elevated bacterial concentrations were generally observed in proximity to livestock operations. In the Hatzic watershed, median fecal coliform levels continued to increase downstream; however, concentrations near livestock operations (e.g., site HV-13) were highly variable, and often exceeded those observed downstream (Figure 5-6c). In the Elk Creek catchment, due to the significant bacterial inputs associated with sites EC-4, EC-5 and EC-6 a decreasing downstream trend was observed (e.g., Figure 5-6d).
Figure 5-6 - Downstream trends in log fecal coliform concentrations in the mainstem river of a) the Hatzic and b) the Elk Creek watersheds and for tributaries to the mainstem in c) the Hatzic and d) the Elk Creek watersheds.
The influence of groundwater contributions was again evident in the Salmon watershed. Unlike the Elk Creek and Hatzic watersheds, a consistent downstream increase in bacterial concentrations was not observed (Figure 5-7a and Figure 5-7b). This is attributable to dilution of bacterial concentrations by groundwater. This influence of groundwater contributions was lower at SA-1, likely as a result of inputs from Davidson creek which had consistently higher bacterial concentrations than sites over, or downstream of, the aquifer (as measured at SA-14).

Figure 5-7 - Downstream trends in fecal coliform concentrations in the Salmon watershed for a) the Salmon River and b) Coghlan Creek above and below its confluence with the Salmon River.
Differing patterns and intensities in agricultural activity across watersheds did not result in differing downstream trends in agricultural contaminants along mainstem river systems in the Hatzic and Elk Creek watersheds. In both watersheds, intensive livestock operations located in upstream locations contributed significantly to local bacterial and nutrient concentrations in tributaries. Upon entering the mainstem river in both watersheds, these contributions were diluted and values from sites along the mainstem represented a more integrated signal of land-use influence.

The unique cumulative downstream impacts in the Salmon watershed were due to the strong interactions between groundwater and surface water in this catchment. The unconfined Hopington aquifer provides a mechanism for increased N retention within the watershed. As a result of strong linkages between these two systems, lateral and longitudinal nutrient fluxes were different in both spatial and temporal extent when compared to the Hatzic and Elk Creek watersheds. The Hopington aquifer provides a direct link between the intensive agricultural activity in the central portion of the watershed and surface waters throughout the lower half of the catchment, resulting in spatial trends that are not necessarily attributable to upstream land-use type or intensity. Temporally, the accumulation of substantial N stores within the aquifer results in year-round N inputs to the surface-water network. The risk of eutrophication is therefore far greater within the Salmon watershed, as N loading during productive summer months is relatively high.

5.5. Conclusions

The varying intensity of agricultural activities in watersheds throughout the LFV (described in Chapter 2) necessitates an understanding of the implications of land-use intensity for surface-water quality and human health. This study, which represents the first multi-year assessment of water quality across these three watersheds, addressed this question through an analysis of nutrient and bacterial dynamics as affected by agricultural intensity, and supports the following conclusions.

1) Bacterial concentrations in forested subcatchments are consistent across watersheds in the LFV in terms of intensity and timing

Background concentrations of bacteria in forested subcatchments of the Elk Creek watershed were not significantly different from that observed in the Hatzic watershed. The consistency from year-to-
year and between these two watersheds suggests that the values and trends in bacterial concentrations observed provide a reasonable indication of baseline levels for these parameters in this region.

In both watersheds, bacterial concentrations in forested subcatchments were low, but peaked during summer months, reflecting increased wildlife activity and in situ survival and reproduction at this time (as compared to winter months). As noted in Chapter 4, small rainfall events during summer months can increase in-stream bacterial concentrations significantly, and therefore represent a time of increased water-quality risk.

2) A positive correlation exists between agricultural intensity and surface-water impairment from fecal sources

Agricultural intensity (in terms of nutrient surpluses and animal densities) was highest in the Elk Creek watershed, with the contributing areas for three sites in this catchment under 100% agricultural land use. This intensity was reflected in indicators of fecal loading as both fecal coliform and NH₄⁺ concentrations were higher at these sites than at any other in the three watersheds. A similar trend was observed within each watershed, with the sites under the greatest agricultural influence showing consistently elevated contaminant levels. The strong influence of land-use intensity is also visible in the cumulative downstream impacts observed in each watershed. This trend suggests that agricultural intensity represents a useful indicator for identifying peak nutrient and bacterial inputs to surface waters. It also indicates that further intensification of agricultural operations on the fixed land base within the ALR in this region will lead to increased risk of fecal contamination of surface waters and associated risks to human and ecosystem health.

3) Seasonal trends in surface-water nutrient and bacterial concentrations are similar across land use types

Seasonal patterns of nutrient and bacterial concentrations were similar across all land use types for the three watersheds. Nutrient concentrations were consistently higher in winter (reflecting the hydrological controls on mobilization and transport), whereas bacterial concentrations were higher in summer (reflecting the seasonality of fecal sources and in situ reproduction).

In the Salmon watershed, seasonal differences for NO₃⁻ concentrations were not statistically significant, due to the substantial inputs from the Hopington aquifer. The presence of a robust subsurface
NO₃⁻ store within the watershed extends the influence of intensive agriculture in the central portion of the watershed both spatially and temporally. Spatially, the high nutrient surplus focused over the aquifer is distributed beyond its borders as a result of strong interactions with the surface-water system. Temporally, unlike the Hatzic and Elk Creek watersheds, NO₃⁻ contributions to surface waters occur year-round, resulting in a greatly increased risk for eutrophication during summer months when in-stream productivity is highest.

4) **Cumulative, downstream impacts are controlled by both land use and hydrological dynamics and are scale dependent**

   As demonstrated in each watershed, cumulative trends in nutrient and bacterial concentrations were influenced by total area under agricultural land use. In the mainstem of the three watersheds, bacterial concentrations consistently increased in the downstream direction, and values were positively correlated with total upstream area under agriculture. The same pattern was observed in the Hatzic and Elk Creek mainstems for nutrient concentrations. In the Salmon watershed, the unconfined Hopington aquifer serves as a long-term store for surplus N arising from intensive agricultural activity in the central portion of the catchment, and extends the influence of these activities downstream through substantial inputs to the Salmon River.

   The influence of scale in nutrient and bacterial fluxes was evident, particularly in agricultural tributaries where nutrient and bacterial concentrations often decreased in the downstream direction. At the catchment scale, total area under agriculture was positively correlated with nutrient and bacterial concentrations. In smaller-order streams, this relationship was not observed due to significant inputs associated with animal access and/or manure applications. This highlights a significant limitation with the use of "area under agriculture" as an indicator of surface-water contamination at all scales, and the need to target monitoring programs and management options at both the plot and catchment scale in order to address surface water impairment in agricultural catchments.
6. Absorbance spectroscopy as a tool to detect agricultural influence on water quality

6.1. Introduction

As demonstrated previously, agricultural land-use activities can act as significant point and non-point sources of contaminants such as nutrients and waterborne pathogens. The detection of such influence on surface-water quality is difficult. While concentrations of these and other agriculturally-derived contaminants in surface waters are often correlated, these correlations are not consistent. As a result, multiple detection methods are required in order to identify agricultural influence.

Detection methods for these contaminants are often time-consuming and expensive and can require large water volumes, specialized equipment and training. When monitoring the quality of surface water used for drinking or recreation in agricultural watersheds, the ability to characterize agricultural influence with a rapid, sensitive technique would allow a more proactive approach to the protection of human and ecosystem health. While one detection method may not provide sufficient information regarding the presence or concentration of all potential agricultural contaminants, rapid qualitative and/or quantitative detection of agricultural influence qualitatively and/or quantitatively could provide the necessary information to initiate precautions or corrective actions while more detailed analyses are conducted.

A useful indicator of agricultural influence on surface waters must either directly reflect the presence of contaminants, or represent a unique attribute of agricultural vs. non-agricultural runoff. As described in Chapter 2 (Section 2.7.5.3), absorbance spectroscopy is a potentially useful tool to detect such influence for several reasons. Firstly, absorbance in the UV has been shown to vary proportionately with NO$_3^-$ concentrations in wastewater systems (Ferree and Shannon, 2001) and in surface waters (Crumpton et al., 1992). Secondly, absorbance in the UV-visible range has been used to characterize chromophoric DOM (CDOM) in freshwater and marine environments and to identify source areas based on geophysical characteristics and land use. Finally, absorbance spectroscopy offers several advantages over traditional detection techniques in terms of sample volume, preparation time and analysis time.

The purpose of this chapter is to assess the utility of absorbance spectroscopy as a tool to rapidly and accurately detect agricultural influence in bulk surface-water and groundwater samples. This
represents the first multi-watershed assessment of absorbance parameters (absorbance, second-derivative absorbance and spectral slope) as qualitative and quantitative indicators of nutrient and bacterial concentrations at different spatial and temporal scales. To accomplish this, water samples were collected from three watersheds (Hatzic watershed, Elk Creek watershed and Salmon watershed), each of which is dominated by agricultural activities of varying type and intensity, as described in Chapter 3.

The objectives of this assessment were to: 1) determine if UV-Vis absorbance spectroscopy could be used as a qualitative and/or quantitative technique for the detection of agricultural contamination of surface waters, and 2) determine the degree to which absorbance spectroscopy could be used to discriminate between water sources and transport pathways to better understand flow routing and contamination dynamics in agricultural watersheds.

6.2. Methods

6.2.1. Sample collection

Samples were collected and analysed following the techniques described in Chapter 3. On three separate dates, samples were collected from 11-19 surface-water and groundwater monitoring sites (see Chapter 3 for site locations) in each watershed under dry and wet conditions (Table 6-1). A series of samples was also collected over the course of a rainfall event in the Hatzic watershed to determine if the absorbance properties of water samples reflected event-scale agricultural influence on surface waters.
Table 6-1 – Sample collection dates (*) and rainfall (mm) for the previous 5 days for the Hatzic, Elk Creek and Salmon watersheds.

<table>
<thead>
<tr>
<th>Date</th>
<th>Hatzic</th>
<th>Elk Creek</th>
<th>Salmon</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 27, 2004</td>
<td>5.84</td>
<td>1.4</td>
<td>0</td>
</tr>
<tr>
<td>August 28, 2004</td>
<td>14.48</td>
<td>4.8</td>
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<td>August 29, 2004</td>
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</tr>
<tr>
<td>August 30, 2004</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>August 31, 2004*</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5-Day Total</td>
<td>20.32</td>
<td>6.2</td>
<td>2.8</td>
</tr>
<tr>
<td>December 9, 2004</td>
<td>12.19</td>
<td>4.4</td>
<td>11.6</td>
</tr>
<tr>
<td>December 10, 2004</td>
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<td>77.4</td>
<td>56.7</td>
</tr>
<tr>
<td>December 11, 2004</td>
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<td>3.4</td>
<td>1.8</td>
</tr>
<tr>
<td>December 12, 2004</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>December 13, 2004*</td>
<td>9.14</td>
<td>7.4</td>
<td>5.2</td>
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<tr>
<td>5-Day Total</td>
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<td>92.6</td>
<td>75.3</td>
</tr>
<tr>
<td>February 11, 2005</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>February 12, 2005</td>
<td>14.48</td>
<td>13.8</td>
<td>8.4</td>
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<td>20.2</td>
<td>3.8</td>
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<tr>
<td>February 15, 2005*</td>
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<td>5-Day Total</td>
<td>20.57</td>
<td>40</td>
<td>23</td>
</tr>
</tbody>
</table>

6.2.2. Spectroscopic analysis

Water samples were analyzed following the techniques described in Chapter 3, with complete absorbance spectra collected from 200-800 nm. The shape and features of these spectra were first assessed qualitatively to determine if samples collected from different sources displayed characteristic patterns. Quantitative analyses were then conducted using absorbance data for specific wavelengths in order to assess spatial and temporal patterns and to evaluate correlations with nutrient and bacterial concentrations in water samples. The wavelengths used in this study are listed in Table 6-2, along with common water-quality parameters for which they are used as proxies.
### Table 6-2 – Absorbance wavelengths used as proxies for common water-quality parameters.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;220&lt;/sub&gt;</td>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>(Dress et al., 1998)</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; derivative @ 224 nm</td>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>(Cahill, 1979; Crumpton et al., 1992; Ferree and Shannon, 2001)</td>
</tr>
<tr>
<td>A&lt;sub&gt;254&lt;/sub&gt;</td>
<td>BOD</td>
<td>(Reynolds and Ahmad, 1997)</td>
</tr>
<tr>
<td>A&lt;sub&gt;280&lt;/sub&gt;</td>
<td>Aromaticity; BOD</td>
<td>(Chin et al., 1994; Brookman, 1997)</td>
</tr>
<tr>
<td>A&lt;sub&gt;300&lt;/sub&gt;</td>
<td>CDOM concentration</td>
<td>(Green, 1992; Del Castillo et al., 1999)</td>
</tr>
<tr>
<td>A&lt;sub&gt;350&lt;/sub&gt;</td>
<td>CDOM concentration</td>
<td>(Kowalczyk et al., 2003)</td>
</tr>
<tr>
<td>A&lt;sub&gt;440&lt;/sub&gt;</td>
<td>Colour/concentration of humic substances, DOC vs. fulvic content</td>
<td>(Cuthbert and Delgiorgio, 1992; Yacobi et al., 2003; McDonald et al., 2004)</td>
</tr>
<tr>
<td>Spectral slope</td>
<td>DOM composition, humic vs. fulvic content</td>
<td>(Carder et al., 1989; Blough and Del Vecchio, 2002)</td>
</tr>
</tbody>
</table>

* A<sub>220</sub> = absorbance at 220 nm

#### 6.2.3. Spectral slope

Spectral slope (S), defined in Chapter 2 (Section 2.7.5.1), was calculated as the slope of a least-squares regression line through log-transformed absorbance data (Green and Blough, 1994; Yacobi et al., 2003; Zanardi-Lamardo et al., 2004) as shown in Figure 6-1. Absorbance spectra were log-transformed to generate a near-linear plot to which a least-squares line could be fit in order to obtain an approximation of S. It has been noted that the use of a linear fit (as opposed to a non-linear fit to the raw spectrum) can enhance the relative weighting of low absorbance values at longer wavelengths where absorbance readings can be near detection limits, thus overestimating S (Twardowski et al., 2004). This can be particularly pronounced in transformed spectra for samples with low CDOM concentrations as they display significant variation from linearity at longer wavelengths. To account for this, the calculation of spectral slope was limited to 290-450 nm, as this wavelength range showed minimal departures from linearity. As outlined by Blough and Del Vecchio (2002), this is a commonly-used technique that produces S values with a strong linear correlation to those calculated through non-linear fitting techniques.

Due to the characteristic shape of absorbance spectra, slope values for least-squares fit lines are negative. In the literature, S is consistently reported as a positive integer, and therefore, following this convention, all S values here are reported as positive numbers.
6.3. Results and discussion

This section describes the results of absorbance analysis by first providing an overview of the shapes and features of complete absorbance spectra, and then by describing quantitative characteristics for specific absorbance wavelength ranges. Quantitative analysis was focused on three regions of the spectra, as each provided information regarding different aspects of water quality. These regions were: 1) the far-UV (190-200 nm), 2) the UV-C range (220-290 nm) and 3) the visible range, with emphasis on absorbance at 440 nm. Event-scale absorbance trends for the March, 2005 storm event in the Hatzic watershed are then described. This is followed by a discussion regarding the value of absorbance as a qualitative and quantitative tool in the analysis of water quality.

6.3.1. Absorbance spectra (200-800 nm)

Absorbance spectra for all samples displayed a similar pattern of near-exponential decline with increasing wavelength. A visual inspection of spectra from differing land uses and from surface water and groundwater sites revealed consistent structural differences reflecting the varying composition of CDOM in these samples (Figure 6-2). Agricultural sites displayed higher absorbance values across the entire wavelength range and relatively featureless spectra, both of which reflect relatively high concentrations and more heterogeneous CDOM compared to surface waters without significant agricultural influence.
Absorbance values were lower for samples collected from forested and mixed-use sites in the Hatzic and Elk Creek watersheds. Many spectra from forested and mixed sites showed minimal increases in absorbance with decreasing wavelengths until reaching a shoulder at approximately 280 nm. Absorbance subsequently increased sharply between 280–200 nm. This shoulder at 280 nm was most pronounced in those samples collected in August.
Figure 6-2- a) absorbance spectra for samples collected in the Hatzic watershed on August 31, 2004, plotted by land use; b) absorbance spectra for samples collected in the Salmon watershed at: 1) SA-1G (dashed, right axis), a deep well with significant NO$_3^-$ contamination (~11 mg·L$^{-1}$) as illustrated by the peak at ~220 nm and 2) SA-3G (left axis), a municipal well with NO$_3^-$ concentrations below detection limits. The sharp drop at 350 nm is an analytical artifact. Note the different scales for the two Y-axes.
Spectra for samples collected from groundwater sources (SA-1G and SA-3G) showed the lowest absorbance values across most of the wavelength range, reflecting low CDOM concentrations common for groundwaters (Figure 6-2b). Nitrate contamination in these samples was easily detected through visual inspection. Samples high in NO$_3^-$ produced peaks in the absorbance spectra at ~220 nm (for reasons described in Section 6.3.2), as illustrated for station SA-1G in Figure 6-2b.

6.3.2. Far UV (190-220 nm)

As described in Chapter 3, absorbance at 220 nm ($A_{220}$) is a good indicator of NO$_3^-$ concentration due to the strong absorbance of the NO$_3^-$ ion in the 210-220 nm range. Figure 6-3 illustrates the range in $A_{220}$ values by land use for all three watersheds combined. As expected, values were highest where peak NO$_3^-$ concentrations were observed across all three watersheds (agricultural sites, and, particularly, groundwater site SA-1G in the Salmon watershed).

![Figure 6-3 - Absorbance at 220 nm vs. land use for the Hatzic, Salmon and Elk Creek watersheds combined.](image)

Linear regression was used to determine how well $A_{220}$ predicted actual NO$_3^-$ concentrations measured using a Lachat Instruments QuikChem FIA+ 8000. As illustrated in Figure 6-4a, $A_{220}$ explains 91% of the variance in measured NO$_3^-$ values ($n = 134$). For many agricultural sites, absorbance values
overestimate NO$_3^-$ concentrations. This is most prevalent in slow-moving agricultural sloughs (e.g., HV-1, HV-15, HV-18, EC-4, EC-5, and EC-6) where CDOM concentrations are high due to autochthonous production, most notably for samples collected during the summer (August). An abundance of CDOM in these samples resulted in increased absorbance in the range of 220 nm, leading to the overestimation observed.

Conducting the same analysis using second-derivative absorbance at 224 nm (Figure 6-4b), produced a stronger relationship, with absorbance explaining 99.8% of the variance in NO$_3^-$ concentrations ($n = 124$). Note that this relationship remains strong with the three highest NO$_3^-$ values removed ($r^2 = 0.996$, $n = 121$). Further, the relationship is stable across a range of NO$_3^-$ concentrations (from detection limit – 12.0 mg·L$^{-1}$). These results are in accordance with other studies that have compared the results of second-derivative spectroscopy to traditional ion chromatography. Crumpton et al. (1992) found no significant difference between this method and the automated cadmium reduction method for the analysis of surface waters. Similarly, Ferree and Shannon (2001), in an analysis of wastewater samples, observed excellent correlation between the second derivative technique and ion chromatography. This method represents a significant time savings over the traditional QuikChem method as each sample can be analysed in less than 60 seconds, and requires only that the sample be filtered to remove particulate matter in order to avoid light scattering during the absorption scan. Another advantage, as illustrated in Figure 6-2, is that absorbance spectra also provide greater qualitative information than nutrient analysis alone, as it is possible to visually differentiate water source (e.g., surface-water vs. groundwater source).
Figure 6-4 - a) linear regression of absorbance at 220 nm vs. nitrate concentrations measured using the Lachat QuikChem method, with $r^2 = 0.91$ ($r^2 = 0.85$ with three highest nitrate values removed); b) linear regression of second-derivative absorbance at 224 nm vs. nitrate, with $r^2 = 0.99$ ($r^2 = 0.99$ with three highest nitrate values removed).
6.3.3. UV-C (220-290 nm)

The UV-C range of the absorbance spectrum is an area of interest as it encompasses the range in which $\pi-\pi^*$ electron transitions occur for phenolic substances, aniline derivatives, benzoic acids and polycyclic aromatic hydrocarbons (Chin et al., 1994; Peuravuori and Pihlaja, 1997; Khorassani et al., 1998; Duarte et al., 2003). This transition represents the elevation of an electron from a $\pi$ bonding orbital to a $\pi$ antibonding orbital, and is the most commonly observed (Lakowicz, 1999). These substances are common precursors to (or components of) humic substances, particularly those derived from terrestrial sources. As a result they have the potential to provide insight regarding CDOM source and transportation (Chin et al., 1994).

As described in Section 6.3.1, many absorbance spectra collected in August, 2004, showed a pronounced shoulder at approximately 280 nm. Figure 6-5 and Figure 6-6 show spectra plotted by land use for each day of sampling for the Hatzic and Elk Creek watersheds (the Salmon watershed is not included as it contained no completely forested subcatchments). The shoulder at 280 nm was observed primarily in samples collected in forested and mixed-use subcatchments. Spectra collected in agricultural subcatchments showed less definition in this area. This likely reflects higher total organic matter concentrations and a greater variety of organic matter sources (allochthonous as well as autochthonous sources such as algae and rooted macrophytes that were commonly observed in agricultural sloughs), rather than a lack of absorbance at 280 nm. The one exception to this trend was at HV-18, where a peak at 280 nm was observed for samples collected in December and February.
Figure 6-5 – Absorbance spectra for all sites in the Hatzic watershed over the three days of sampling. Note the consistent presence of a shoulder at 280 nm at forested and mixed sites on August 31, 2004. Grouping of spectra by land use is still observed but the distinction is not as obvious as for the Elk Creek due to the lower intensity of land use in this catchment.
Figure 6-6 - Absorbance spectra for all sites in the Elk Creek watershed over the three days of sampling. Note the consistent presence of a shoulder at 280 nm at forested and mixed sites on August 31, 2004. Note also the consistent distinction between land-use types and the consistently high absorbance values for the sites under the greatest degree of agricultural influence (EC-4, EC-5 and EC-6).
Absorbance at 280 nm was positively correlated with total upstream area under agriculture ($r_s = 0.669$, $P < 0.001$, $n = 92$). Values were higher at agricultural sites than at forested and mixed sites in all watersheds (Table 6-3); however, these values were not significant when averaged for each site and significance levels were adjusted using Bonferroni correction for multiple comparisons. For agricultural sites, mean $A_{280}$ values appear to correspond well with agricultural intensity (Table 6-3). While differences between watersheds were not statistically significant using the above approach, this trend appears to reflect differences in land-use intensity described in Chapter 5.

Table 6-3 - Absorbance at 280 nm by land use for the Hatzic, Elk Creek and Salmon watersheds.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Land use</th>
<th>N</th>
<th>Minimum</th>
<th>Mean</th>
<th>Maximum</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatzic</td>
<td>Forested</td>
<td>12</td>
<td>.021</td>
<td>.050</td>
<td>.084</td>
<td>.020</td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>15</td>
<td>.025</td>
<td>.041</td>
<td>.074</td>
<td>.013</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>24</td>
<td>.042</td>
<td>.121</td>
<td>.348</td>
<td>.075</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>3</td>
<td>.105</td>
<td>.133</td>
<td>.182</td>
<td>.043</td>
</tr>
<tr>
<td>Elk Creek</td>
<td>Forested</td>
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<td>.036</td>
<td>.042</td>
<td>.048</td>
<td>.004</td>
</tr>
<tr>
<td></td>
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<td>.023</td>
<td>.047</td>
<td>.096</td>
<td>.025</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
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</tr>
<tr>
<td></td>
<td>Urban</td>
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<td>.041</td>
<td>.047</td>
<td>.007</td>
</tr>
<tr>
<td>Salmon</td>
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<td>35</td>
<td>.011</td>
<td>.141</td>
<td>.451</td>
<td>.078</td>
</tr>
</tbody>
</table>

1 - Standard Deviation

In the Hatzic watershed, peak $A_{280}$ values at each station were observed during the August sampling (Figure 6-7a), with the only exceptions being HV-2, HV-4, HV-8 and HV-11, all of which are forested except HV-8 (mixed). Samples collected in the slowest-moving agricultural sloughs (HV-1, HV-15, HV-16 and HV-18) and in the urban subcatchment (HV-20) showed the highest $A_{280}$ values over the three days of sampling. Data collected from the Elk Creek watershed did not show a similarly consistent pattern. Samples collected at some stations showed maxima in August, while others peaked in December (Figure 6-7b). It was noted; however, that samples collected in close proximity and along the same watercourse displayed similar patterns in terms of timing for maximum values. In the Salmon watershed, peak $A_{280}$ values were observed at all stations for samples collected in December, except for SA-17 (Figure 6-7c). Peak values for $A_{280}$ were not observed at any station in the three catchments for samples collected in February, likely reflecting a dilution effect after several months of winter precipitation.
Figure 6-7 - Absorbance at 280 nm by station for the: a) Hatzic, b) Elk and c) Salmon watersheds.
6.3.4. Visible (440 nm)

A relationship between land use and mean $A_{440}$ values was observed (Table 6-4). When all sites were considered, forested and mixed sites consistently had significantly lower $A_{440}$ values than agricultural sites ($P < 0.001$ for both, $n = 32$ and $n = 36$, for forested and mixed site comparisons, respectively). In the Hatzic watershed, mean $A_{440}$ absorbance at the one urban site (HV-20) was lower than that observed at agricultural sites. In the Elk Creek watershed, mean values at urban sites were lower than at agricultural sites (Table 6-4), but not significantly so. Across all watersheds, $A_{440}$ was also positively correlated with total upstream area under agriculture ($r_s = 0.635$, $P < 0.001$, $n = 92$). Between watersheds, when considering mean values for all sites, no significant differences between mean absorbance were observed between the Hatzic and Elk Creek catchments.

Table 6-4 - Absorbance at 440 nm by land use for the Hatzic, Elk Creek and Salmon watersheds.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Land use</th>
<th>N</th>
<th>Minimum</th>
<th>Mean</th>
<th>Maximum</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatzic</td>
<td>Forested</td>
<td>12</td>
<td>.000</td>
<td>.006</td>
<td>.020</td>
<td>.005</td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>15</td>
<td>.000</td>
<td>.005</td>
<td>.013</td>
<td>.004</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>24</td>
<td>.006</td>
<td>.016</td>
<td>.044</td>
<td>.010</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>3</td>
<td>.014</td>
<td>.015</td>
<td>.017</td>
<td>.002</td>
</tr>
<tr>
<td>Elk Creek</td>
<td>Forested</td>
<td>5</td>
<td>.001</td>
<td>.004</td>
<td>.007</td>
<td>.003</td>
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<tr>
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<td>.000</td>
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<tr>
<td></td>
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<td>.019</td>
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<tr>
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<td>5</td>
<td>.004</td>
<td>.007</td>
<td>.008</td>
<td>.002</td>
</tr>
<tr>
<td>Salmon</td>
<td>Agricultural</td>
<td>31</td>
<td>.004</td>
<td>.019</td>
<td>.067</td>
<td>.013</td>
</tr>
</tbody>
</table>

1 - Standard Deviation

6.3.5. Spectral slope

Table 6-5 contains mean spectral slope ($S$) values according to land use and watershed for the three days of sampling. The greatest variability was observed in the Hatzic and Elk Creek watersheds, with maximum values observed at forested sites in August. A comparison of $S$ values between the two watersheds by land use category revealed no significant differences. Mean $S$ values in the Salmon watershed were relatively consistent over the three days of sampling, reflecting the comparatively homogenous agricultural land-use in the catchment.
Table 6-5 - Mean S values by land use and watershed for the three days of sample collection.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatzic</td>
<td>Forested</td>
<td>0.021</td>
<td>0.011</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>0.019</td>
<td>0.010</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>0.014</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>0.016</td>
<td>0.013</td>
<td>0.012</td>
</tr>
<tr>
<td>Elk Creek</td>
<td>Forested</td>
<td>0.022</td>
<td>0.014</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>0.017</td>
<td>0.012</td>
<td>0.012</td>
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<tr>
<td></td>
<td>Agricultural</td>
<td>0.016</td>
<td>0.014</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>0.013</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>Salmon</td>
<td>Agricultural</td>
<td>0.014</td>
<td>0.013</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Plotting S against A_{440} provides valuable insight into the composition of CDOM in surface water samples as it provides an indication of CDOM concentration (A_{440}) and the relative concentration of high-molecular-weight humic substances vs. lower-weight fulvic materials (S). As illustrated in Figure 6-8 when plotted against these two variables, stations tend to separate into one of two groups. The first are those sites that show minimal variation in CDOM concentration but noticeable variability in CDOM composition as illustrated by a range of values for S over the three days of sampling. These sites are predominantly found in forested and mixed-use sub-catchments. The second grouping contains those stations with CDOM concentrations that varied over the three days of sampling, but have consistently low S values. For all three watersheds, this group was consistently comprised of agricultural sites.
Figure 6-8 - Absorbance at 440 nm vs. spectral slope for the Hatzic, Elk Creek and Salmon watersheds. Note clustering of samples by land use.
Forested and mixed-use sites in the Hatzic and Elk Creek catchments showed the greatest variation in spectral slope, with the highest $S$ values observed during the August sampling period. Samples collected from these sites during or immediately after larger rainfall events in December and February showed much lower $S$ values that were comparable to, or lower than, those observed in agricultural sites. For forested sites in the Hatzic watershed (the only watershed where continuous water-level data were collected), $S$ showed a strong negative correlation with stage ($r_s = -0.887$, $P < 0.001$, $n = 12$). This trend was also observed for mixed-use sites ($r_s = -0.756$, $P = 0.001$, $n = 15$) and agricultural sites ($r_s = -0.767$, $P < 0.001$, $n = 24$); however, no correlation existed for urban site HV-20.

As noted by Blough and Del Vecchio (2002) $S$ is larger for fulvic acids and is inversely correlated with molecular weight. Lower $S$ values therefore suggest a greater proportion of the CDOM load is comprised of fulvic acids. As fulvic acids are more soluble than humic acids, this would be expected in undisturbed subcatchments during dry weather. During winter months when increased rainfall results in greater allochthonous CDOM inputs (Thurman, 1985), it is likely that lower $S$ values reflect an increase in the proportion of CDOM comprised of less-soluble humic acids (due to higher rainfall and decomposition of autumn leaf litter).

Agricultural sites showed minimal variation in $S$, with values ranging from 0.010 – 0.020. The low $S$ values at these sites reflect the relatively greater proportion of higher molecular weight humic materials associated with agricultural amendments, as noted by Ohno et al. (2006). These sites did, however, display a broader range of $A_{440}$ values, reflecting variations in CDOM concentration. Maximum $A_{440}$ values were consistently observed in agricultural sloughs in the Elk Creek and Hatzic watersheds. Higher CDOM concentrations and lower spectral slopes at these sites likely reflect the presence of higher-molecular-weight organic matter as a result of both greater autochthonous (in situ) production and greater contributions from the adjacent land surface during rainfall events (Ohno et al., 2006). Urban sites in both the Hatzic and Elk Creek catchments displayed similar properties.

6.3.6. Storm event dynamics

In order to assess the change in CDOM concentration and composition over the course of a storm event, samples were collected every three hours over the 36-hour event in the Hatzic watershed from March 18-21, 2005 (Figure 6-9). The storm was comprised of three rainfall events with rainfall of 23.6 mm, 15.5 mm and 35.3 mm. Absorbance at 220 nm reflects NO$_3^-$ concentration and therefore
showed a strong positive relationship with river stage. Values for $A_{254}$, $A_{280}$, $A_{300}$, $A_{340}$ and $A_{440}$ showed a large increase during the second rainfall event, which had the lowest total rainfall of the three events. For both the first and second events these values peaked just prior to the water-level maximum.
Figure 6-9 – Water level, 1-hour rainfall and spectral properties of samples collected at the lower hydrometric station in the Hatzic Slough during a storm event, March 18-21, 2004. Note increase in $A_{440}$ during second storm peak.
Although the third event was the largest in terms of total rainfall and the subsequent response of stream stage, it did not generate an equally large response in absorbance values. Absorbance at 220 nm increased with stream stage during this event. A similar trend was observed for absorbance in other UV wavelengths ($A_{254}$, $A_{280}$ and $A_{300}$), with maximum values as high as, or higher than those observed during the second event. Absorbance values at longer wavelengths in the visible range ($A_{440}$, $A_{465}$ and $A_{665}$) did not show the same positive correlation with stream stage ($A_{465}$ and $A_{665}$ not shown). These values peaked during the second event, and while they did respond to the third event, values did not approach those observed during the second event. These data suggest that the second event resulted in the transport of easily accessible organic matter that was rich in humic material, possibly reflecting mobilization of near-stream stores in agricultural regions of the watershed. The lack of a response in absorbance at longer wavelengths during the third event indicates that easily-accessible CDOM stores had been depleted by this time. It also likely reflects an increase in the relative contribution of rainfall to streamflow during this time. This is supported by the fact that both conductivity and chloride values reached absolute minima during this event as well.

Over the three events, absorbance parameters correlated strongly with bacterial and nutrient concentrations. Absorbance at 280 nm showed the strongest correlation with fecal coliform concentrations ($r_s = 0.732$, $P < 0.001$) and $A_{220}$ showed a similar relationship with NO$_3^-$ ($r_s = 0.832$, $P < 0.001$). While correlations with fecal coliforms were strong, maximum absorbance values did not correspond to peak bacterial concentrations during the third event, highlighting different mobilization and transport mechanisms for CDOM and bacteria.

These trends in absorbance in the UV and visible ranges were reflected in the spectral slope values during the storm. Minima in $S$ were consistently observed on the rising limb of each rainfall event, and the lowest values were observed during the second storm peak. Values reached a minimum just prior to the increase in stream stage during this event, and remained low for 9 hours while absorbance at longer wavelengths ($A_{440}$ and $A_{665}$) reached maximum values. After the second event, $S$ briefly reached pre-storm levels, and then fluctuated moderately during the third event but did not reach the minimum values observed in the first and second events.

As illustrated in Figure 6-10, each event was characterized by a slightly different organic-matter signature. The first event was short lived, with only one peak in $A_{440}$ and a concurrent decrease in $S$. The second event, captured by samples 16, 17 and 18, reflects the contributions of humic-rich organic matter,
and was characterized by high CDOM concentrations and the lowest spectral slopes observed in any of the watersheds over the three days of sampling. Chloride values were depressed during this time; however, to a lesser extent than observed during the third event. This suggests that streamflow during the second event, while diluted by rainfall, was comprised of pre-event water. Data for the third event suggest an exhaustion of stores of easily transported organic matter, a reduction in the relative content of humic acids and a greater proportion of streamflow comprised of rainfall, as indicated by lower Cl⁻ concentrations (Figure 6-10).

Figure 6-10 - Spectral slope vs. $A_{440}$ for the storm event in the Hatzic watershed. Chloride concentrations are represented by bubble size. Numbers refer to the consecutively numbered samples which were collected every 3 hours, from 09:00 on March 18 to 09:00 on March 21, 2005.

6.3.7. Absorbance spectroscopy as a qualitative tool

Several authors have demonstrated the value of absorbance spectra in the qualitative assessment of water in marine and freshwater environments (Khorassani et al., 1998; Vaillant et al.,
2002; Langergraber et al., 2004). Such analysis includes assessment of the location and intensity of individual absorbance peaks and shoulders and of spectral slope. In the present study, qualitative variations in spectra observed between land-use types and water sources (i.e., groundwater vs. surface water) supported rapid determination of: 1) relative NO$_3^-$ concentrations, 2) relative CDOM concentrations and 3) relative CDOM composition. These three characteristics provide an indication of water source (i.e., surface water vs. groundwater), land-use type (forested vs. agricultural) and land-use intensity.

For example, in the Salmon watershed, where samples were collected from surface water and groundwater sites, water source could easily be distinguished based on a visual comparison of absorbance values between 245-800 nm, a range that encompasses the wavelengths for absorbance by humic substances. Values for groundwater samples from SA-1G and SA-3G were at, or near, zero throughout this range, while absorbance for all surface-water sites was consistently higher, particularly between 200-400 nm (Figure 6-2b). These data suggest minimal CDOM content in these deep groundwater samples (the depths of the wells at SA-1G and SA-3G are 48 m and 74 m, respectively). This is consistent with the generally low concentrations of organic matter in deep groundwaters. Organic materials initially derived from the litter layer are rarely transported to significant depth as they are either consumed by heterotrophic microbes or adsorbed onto the surface of soil particles during downward transport (Thurman, 1985). Relative NO$_3^-$ concentrations for both groundwater sources were also easily discerned through visual inspection in the 220-225 nm range (Figure 6-2b).

As illustrated in Figure 6-5 and Figure 6-6 for each of the three sampling dates, an inspection of spectra consistently allowed visual differentiation by land-use type. Further, sites observed to be under the greatest degree of agricultural influence in both watersheds (as indicated by consistently higher average nutrient and bacterial concentrations throughout the present study), consistently displayed the highest absorbance values across the entire wavelength range. For the Elk Creek catchment, there was an obvious visual distinction between agricultural and mixed sites for samples collected on December 20, 2004 and February 16, 2005. For samples collected on August 31, 2004, there was some overlap of spectra for mixed sites and agricultural sites (not including EC-4, EC-5 and EC-6, which could be easily differentiated for each day of sampling). This was likely due to relatively dry conditions resulting in minimal transport of agriculturally-derived CDOM to surface waters. This was not the case for EC-4, EC-5 and EC-6 as each of these sites is located in a slow-moving agricultural slough with limited riparian vegetation and located in close proximity to cattle operations. These conditions favour in-stream
biological productivity and the resulting spectra likely reflect the combined influence of agriculturally-derived CDOM and autochthonous CDOM production.

Similar trends were observed in the Hatzic watershed; however, the distinction between spectra representing different land uses was not as clear. This reflects the general trend of lower-intensity agriculture in this watershed (see Chapter 5). As observed in the Elk Creek catchment, the site with the highest nutrient and bacterial concentrations (HV-18) consistently displayed the highest absorbance values across the entire wavelength range. This is also a slow-moving agricultural slough draining a region with active cattle operations bordering the stream. It appears, therefore, that qualitative assessment of entire spectra is a useful comparative tool to assess relative agricultural land-use intensity at different sites.

Visual inspection of spectra can also provide insight regarding CDOM composition. As described above (Section 6.3.2), spectra for samples collected from forested and mixed sites in August showed a distinctive shoulder at ~280 nm. Thurman (1985) noted that humic acids, due to their darker colour, absorb in the visible range, while fulvic acids absorb at wavelengths near 280 nm (thus the value of spectral slope as an indicator of humic vs. fulvic acid content). This shoulder appears to reflect the presence of lower molecular weight fulvic acids and a relative lack of humic materials which tend to obscure the peak at 280 nm at agriculturally-dominated sites. This would be expected in relatively “clear,” headwater streams in forested sites as fulvic acids are more easily dissolved from surrounding soils (Tipping, 2002). This peak is not observed under wet, winter conditions indicating either a flushing of fulvic acids from these sites, or an increase in the relative abundance of terrestrially-derived humic acids transported during rainfall events (or, more likely, a combination of the two). Spectra with low absorbance values and a visible absorbance peak at 280 nm therefore appear to indicate dominance of CDOM by fulvic acids under dry-weather conditions.

Qualitative analysis is also useful to assess relative changes in water quality at one site over time. This is illustrated in Figure 6-11 and Figure 6-12 which show contour and surface plots of absorbance spectra and log-transformed absorbance spectra collected during the storm event in the Hatzic watershed. The surface in Figure 6-11 clearly illustrates increasing absorption in two regions over the course of the storm event. The first region, from 200-225 nm, reflects increasing NO$_3^-$ concentrations associated with the peaks in stream stage. The second, in the visible region, shows the greatest response during the second event and reflects the peak CDOM contributions described above. The input
of CDOM during the second event is more clearly illustrated in Figure 6-12 which clearly shows the
decrease in $S$ at that time. In both cases, it can be seen that samples collected prior to the first event
provided a baseline against which future samples could be compared. Further, qualitative analyses of
these surfaces provide a rapid means of assessing relative CDOM concentration and composition
throughout the event.
Figure 6-11 - Time series of absorbance spectra for storm event in Hatzic watershed. Samples were collected every 3 hours starting at 09:00 on March 18 (Y-axis lines align with discrete spectra for each sample and correlate with the data points on Figure 6).
Figure 6-12 - In-transformed spectra for the storm event captured in the Hatzic watershed. Note the clear decrease in spectral slope associated with the second peak in river stage, suggesting a shift to increased high-molecular-weight compounds in transported DOM.
The above illustrates that qualitative analysis of absorbance spectra provides useful information regarding water source, land-use type and land-use intensity beyond that which can be obtained from nutrient or bacterial analysis alone. As demonstrated during the storm event in the Hatzic watershed, the utility of this technique improves when baseline data are available. While it is clear that further sampling is required to fully elucidate the potential of this technique, data collected from the three watersheds in this study suggest that it is a useful tool for rapid assessment of water source and water quality.

6.3.8. Absorbance spectroscopy as a quantitative tool

As illustrated above, absorption in the UV-C range shows excellent correlation with \( \text{NO}_3^- \) concentration. This relationship is improved when the second derivative is used to minimize the influence of other absorbing species in solution. Based on the observed relationship, second-derivative absorption spectroscopy offers an effective, rapid, simple and accurate technique for the determination of \( \text{NO}_3^- \) in surface waters. The linear relationship between \( \text{NO}_3^- \) and second-derivative absorbance has been observed to deteriorate at concentrations approaching 40 mg·L\(^{-1}\) (Suzuki and Kuroda, 1987). While this may represent a challenge when directly monitoring effluent from wastewater treatment plants, it is not likely to limit the application of this technique in the majority of agricultural watersheds.

For samples collected in August, analysis for dissolved organic carbon (DOC) was conducted to assess the correlation with absorbance parameters (Table 6-6). A significant positive correlation between DOC and absorbance at several wavelengths was observed, however the strongest relationship was found between \( A_{440} \) and DOC \( (r_s = 0.782, P = 0.001, n = 15) \), suggesting that this wavelength is a suitable indicator for dissolved organic material. The variability in the relationship is due to the fact that light-absorbing DOM represents only a portion of total DOC. Interferences from other absorbing compounds may also impact this relationship.
Table 6-6 - Mean DOC concentration by land use and watershed for samples collected on August 31, 2005

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Land use</th>
<th>N</th>
<th>Mean DOC Concentration (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatzic</td>
<td>Forested</td>
<td>1</td>
<td>7.87</td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>1</td>
<td>6.47</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>2</td>
<td>10.16</td>
</tr>
<tr>
<td>Elk Creek</td>
<td>Forested</td>
<td>1</td>
<td>9.60</td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>2</td>
<td>8.43</td>
</tr>
<tr>
<td></td>
<td>Agricultural</td>
<td>3</td>
<td>11.15</td>
</tr>
<tr>
<td></td>
<td>Urban</td>
<td>1</td>
<td>13.32</td>
</tr>
<tr>
<td>Salmon</td>
<td>Agricultural</td>
<td>4</td>
<td>8.74</td>
</tr>
</tbody>
</table>

Absorbance at other wavelengths correlates well with traditional indicators of contamination, including DOC, PO₄³⁻, NH₄⁺ and fecal coliform; however, these correlations were not consistent from site-to-site or between watersheds. Table 6-7 illustrates the absorbance wavelengths with the strongest correlations to traditional indicators of contamination for all watersheds. Significant, positive correlations are found for each water-quality variable when all watersheds are considered concurrently, and A₂₈₀ shows the strongest correlation with all indicators (other than NO₃⁻). As described above (Section 6.3.3), absorption in this range is attributed to the π-π* electron transition in substances which are commonly precursors to, or components of, humic materials. Absorbance at this wavelength, particularly when normalized to DOC concentration, has been used extensively as an indicator of the aromaticity and molecular weight of humic substances (Chin et al., 1994; Westerhoff and Anning, 2000; Chen et al., 2003; Volk et al., 2005). This normalized value is referred to as specific UV absorbance or (SUVA). As CDOM released by agricultural amendments (plant residue, manure, etc.) has consistently higher molecular weight than soil-derived CDOM, (Ohno et al., 2006) SUVA at 280 nm (SUVA₂₈₀) has the potential to serve as an effective indicator of agricultural influence. In the present study, A₂₈₀ and SUVA₂₈₀ were strongly correlated (rₛ = 0.964, P < 0.001, n = 15), suggesting that A₂₈₀ is also a good indicator of aromatic C content and molecular weight in the absence of DOC measurements.
Table 6-7 - Correlations between nutrient and bacterial indicators and absorbance at specific wavelengths.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Variable</th>
<th>Absorbance Indicator</th>
<th>n</th>
<th>Correlation ($r_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>Ammonium</td>
<td>$A_{280}$</td>
<td>146</td>
<td>0.322 **</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>$A_{224}$</td>
<td>115</td>
<td>0.999 **</td>
</tr>
<tr>
<td></td>
<td>Orthophosphate</td>
<td>$A_{280}$</td>
<td>144</td>
<td>0.572 **</td>
</tr>
<tr>
<td></td>
<td>FC (log)</td>
<td>$A_{280}$</td>
<td>108</td>
<td>0.412 *</td>
</tr>
<tr>
<td></td>
<td>TC (log)</td>
<td>$A_{280}$</td>
<td>117</td>
<td>0.214 **</td>
</tr>
<tr>
<td>Elk Creek</td>
<td>Ammonium</td>
<td>$A_{280}$</td>
<td>37</td>
<td>0.795 **</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>$A_{224}$</td>
<td>37</td>
<td>0.994 **</td>
</tr>
<tr>
<td></td>
<td>Orthophosphate</td>
<td>$A_{280}$</td>
<td>38</td>
<td>0.576 **</td>
</tr>
<tr>
<td></td>
<td>FC (log)</td>
<td>$A_{280}$</td>
<td>37</td>
<td>0.518 **</td>
</tr>
<tr>
<td></td>
<td>TC (log)</td>
<td>$A_{224}$</td>
<td>37</td>
<td>0.492 **</td>
</tr>
<tr>
<td>Hatzic</td>
<td>Ammonium</td>
<td>$A_{280}$</td>
<td>78</td>
<td>0.342 **</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>$A_{224}$</td>
<td>50</td>
<td>0.945 **</td>
</tr>
<tr>
<td></td>
<td>Orthophosphate</td>
<td>$A_{280}$</td>
<td>78</td>
<td>0.247 *</td>
</tr>
<tr>
<td></td>
<td>FC (log)</td>
<td>$A_{280}$</td>
<td>48</td>
<td>0.610 **</td>
</tr>
<tr>
<td></td>
<td>TC (log)</td>
<td>$A_{220}$</td>
<td>52</td>
<td>0.668 **</td>
</tr>
<tr>
<td>Salmon</td>
<td>Ammonium</td>
<td>$A_{280}$</td>
<td>31</td>
<td>0.606 **</td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>$A_{224}$</td>
<td>28</td>
<td>0.969 **</td>
</tr>
<tr>
<td></td>
<td>Orthophosphate</td>
<td>$A_{224}$</td>
<td>28</td>
<td>-0.525 **</td>
</tr>
<tr>
<td></td>
<td>FC (log)</td>
<td>$A_{224}$</td>
<td>23</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>TC (log)</td>
<td>$A_{280}$</td>
<td>28</td>
<td>-0.339</td>
</tr>
</tbody>
</table>

$A_{224}$ - 2nd derivative absorbance at 224 nm

* - $P < 0.05$
** - $P < 0.01$

The correlations between $A_{280}$ and nutrient and fecal coliform concentrations described above suggest that $A_{280}$ is in fact a good indicator for relative agricultural influence as it detects contributions of higher molecular weight CDOM. It is possible that the inconsistencies in the relationships described in the above table would be at least partially addressed through the use of SUVA$_{280}$ as it accounts for the bias introduced by higher DOC concentrations. Table 6-7 also illustrates that there is variability in the correlations between $A_{280}$ and nutrient and bacterial concentrations across watersheds, despite significant correlations within watersheds. As illustrated graphically in Figure 6-13, when considered on a watershed scale, the only consistent correlation is between 2nd-derivative absorbance at 224 nm and NO$_3^-$. 

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Figure 6-13 - Absorbance values vs. a) nitrate, b) ammonium and c) fecal coliform concentrations for all three watersheds. Note the strong, consistent correlation between 2nd derivative absorbance at 224 nm compared to correlations for NH$_4^+$ and fecal coliform, which vary by watershed.
The variance in the degree and consistency of correlations between absorbance values and NH$_4^+$, PO$_4^{3-}$ and bacterial concentrations is likely due to the fact that absorbance can result from several compounds in solution, thus complicating the relationship between absorbance values and the parameters of interest (Stumwohrer et al., 2003). The concentration of interfering compounds is dependent upon site-specific variables (land-use type, soil type, local vegetation, etc.), and as a result, so is the impact they have on these relationships. This explains the considerable variability in correlations from different sites and watersheds. However, as observed by Brookman (1997) once a relationship between absorbance values and parameters of interest are obtained for a given site, this rapid technique serves as a useful indicator of significant changes in water quality. Indeed, Langergraber et al. (2004) demonstrated an absorption system for rapid detection of surface water contamination events based on this principle. The system required a “learning period” during which site-specific calibration or baseline absorbance spectra could be collected. Once baselines were established, alarm levels were then defined based on the degree of variation from baseline levels, and the probability of variance as determined during the learning period. The author is currently unaware of any instances where such systems have been utilized to track agricultural influence on water quality.

6.4. Conclusions

The objectives of this chapter were to: 1) determine if absorbance spectroscopy could serve as a useful technique for the quantitative and/or qualitative assessment of agricultural influence on water quality, and 2) determine if this technique could also provide insight regarding water source and flowpaths. Based on the results described above, the following conclusions can be drawn.

1) Absorbance spectroscopy is a rapid and accurate technique for determining NO$_3^-$ concentrations in filtered, bulk water samples

It was demonstrated above that second-derivative spectroscopy could be used to accurately and rapidly determine NO$_3^-$ concentrations in bulk surface water and groundwater samples. This technique offers several advantages over the Quikchem methods used for NO$_3^-$ quantification in the present study. Firstly, absorbance techniques require minimal sample treatment (filtering) and no additional reagents. Secondly, analyses are rapid (< 1 minute) and require less than 5 ml of sample. Finally, absorbance
spectra provide a great deal of information regarding water source and CDOM composition which can be used for both qualitative and quantitative analyses of land-use influence.

2) **Absorbance values, particularly $A_{280}$, are an effective indicator of relative agricultural influence on water quality**

Absorbance at 280 nm and SUVA$_{280}$ provide an indication of molecular weight of CDOM in water samples. These parameters therefore have significant potential as indicators of agricultural influence as CDOM derived from manure and plant residues is generally of higher molecular weight than soil-derived CDOM. This is supported in the present study by observation of consistent, significant correlations between $A_{280}$ and nutrient and bacterial concentrations. Once baseline data were available, absorbance values provided a useful indicator of relative agricultural influence on water quality in each watershed.

3) **Absorbance spectra from filtered, bulk water samples provide useful qualitative information regarding water-quality and water source**

Visual inspection of absorbance spectra provided a rapid technique for the determination of water source (groundwater vs. headwater stream vs. agricultural slough), and relative organic matter concentration and composition. This supported the assessment of spatial trends in CDOM and agricultural influence, as well as the detection of changes in water quality and contributions to streamflow over the course of a storm event in the Hatzic watershed.
Chapter 7

7. Fluorescence spectroscopy as a tool to detect agricultural influence on water quality

7.1. Introduction

As described in Chapter 6, the absorbance properties of CDOM provide an indication of their concentration, as well as a preliminary indication of the relative amounts of fulvic vs. humic acids, both of which are useful in detecting agricultural influence. However, due to the overlap of absorption peaks arising from several chromophores in solution, it can be difficult to identify and/or quantify individual CDOM components, particularly at relatively low concentrations. Fluorescence spectroscopy may be used to address this challenge as many components of CDOM are fluorophores (compounds that re-emit absorbed radiation) which can be used to further characterize the concentration and composition of the CDOM load of surface waters and groundwaters.

As described in Chapter 2, there are two primary groups of fluorophores in CDOM, referred to as "protein-like" and "humic-like". Protein-like fluorescence refers to fluorescence peaks observed when samples are excited in the ultraviolet range (excitation/emission pairs 220/305 nm and 220/350 nm). These peaks are similar to those observed for the aromatic amino acids tyrosine (220/305) and tryptophan (220/350), and are therefore referred to as tyrosine-like and tryptophan-like fluorescence (Lakowicz, 1999; Blough and Del Vecchio, 2002). Humic-like fluorescence is attributed to aromatic organic compounds associated with humic and fulvic materials (Blough and Del Vecchio, 2002), and is therefore commonly referred to as humic-like and fulvic-like fluorescence.

Fluorescence spectroscopy offers many of the same advantages over traditional water quality assessment techniques as absorbance spectroscopy. Fluorescence techniques require small sample volumes (< 5 ml), are relatively rapid (1-20 minutes per sample, depending on the resolution of the scan, although longer scans are possible) and are non-destructive. Further, because individual fluorophores have unique excitation and emission wavelengths, fluorescence spectroscopy allows the detection of individual CDOM compounds in solution. Finally, fluorescence techniques are far more sensitive than absorption, thus allowing detection of CDOM compounds at low concentrations (Lakowicz, 1999).

As outlined in Chapter 2, several studies have utilized fluorescence spectroscopy to assess organic-matter dynamics in marine (e.g., Coble, 1996; e.g., Boehme et al., 2004), nearshore (e.g., Chen
and Gardner, 2004; Jaffe et al., 2004), wastewater (e.g., Reynolds and Ahmad, 1997; Westerhoff et al., 2001) and freshwater (e.g., Baker, 2002c; Katsuyama and Ohte, 2002) environments. Of particular relevance to the present study, Baker (2002b) examined the fluorescence properties of several types of isolated farm wastes (pig and cattle slurries, silage liquor and sheep barn wastes). However, this study represents the first aimed specifically at assessing the link between CDOM fluorescence and nutrient and bacterial concentrations in surface waters across multiple watersheds and land uses, in order to determine the potential of fluorescence spectroscopy as a tool to detect agricultural runoff. The purpose of this chapter is to conduct a preliminary assessment of the utility of fluorescence spectroscopy to further characterize agriculturally-derived organic matter in filtered, bulk water samples. Specifically, this chapter aims to: 1) evaluate relationships between land use and the type and concentration of fluorophores in surface waters, 2) assess the potential for fluorescence spectroscopy as a tool to detect agricultural effluent in surface waters and 3) assess the relationships between fluorescence parameters and nutrient and bacterial concentrations to evaluate the potential of fluorescence spectroscopy as a proxy for contaminants of concern.

7.2. Methods

Fluorescence data were collected following the laboratory methods outlined in Chapter 3. Analyses were conducted on a subset of the same samples for which absorbance data were collected (N = 67), including those representing the storm event in the Hatzic watershed (see Chapter 6 for collection dates, and associated meteorological conditions).

The duration of fluorescence scans ranges from less than one minute to several hours, depending on the desired signal to noise ratio (to reduce the noise in a scan, the averaging time at each excitation/emission pair is increased). As the objective of this study was to conduct a preliminary assessment of the technology as a tool to detect potentially minute differences in fluorescence signals, a scan time of approximately 20 minutes was chosen to ensure a reasonable signal to noise ratio while still permitting the analysis of numerous samples per day. As a result, analyses were conducted only on selected stations in the Hatzic, Elk Creek and Salmon watersheds.

Results are presented either as fluorescence intensity values or as excitation-emission matrices (EEM's). Each EEM is a collection of emission scans collected every 5 nm at successively longer excitation wavelengths between 220-450 nm. The resulting plot represents an interpolated surface for 47
separate emission scans, with fluorescence measured every 2 nm (between 230-600 nm), and contains 8,742 data points. As with absorbance, fluorescence intensity is given in arbitrary units as no calibration to a standard was conducted.

Six fluorescence peaks were initially considered in this analysis (Table 7-1). Humic-like fluorescence has previously been measured at two excitation wavelengths. The first, in the UV (220-260 nm), and the second, in the visible range (340-360 nm), have been referred to previously as “Peak A” and “Peak C”, respectively (Coble, 1996). For this study, only the latter was used to reflect humic-like fluorescence, as less work has been done to characterize the former in freshwater environments (Baker and Spencer, 2004).

Table 7-1 - Wavelengths for fluorescence peaks assessed in this study.

<table>
<thead>
<tr>
<th>Fluorescence Peak</th>
<th>Excitation/Emission Pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic-like</td>
<td>370-390/460-480</td>
</tr>
<tr>
<td>Fulvic-like</td>
<td>320-340/410-430</td>
</tr>
<tr>
<td>Tryptophan 1 (T&lt;sub&gt;220&lt;/sub&gt;)</td>
<td>220/340-350</td>
</tr>
<tr>
<td>Tryptophan 2 (T&lt;sub&gt;280&lt;/sub&gt;)</td>
<td>275-280/340-350</td>
</tr>
<tr>
<td>Tyrosine 1 (Tyr&lt;sub&gt;220&lt;/sub&gt;)</td>
<td>220-225/300-310</td>
</tr>
<tr>
<td>Tyrosine 2 (Tyr&lt;sub&gt;280&lt;/sub&gt;)</td>
<td>270-280/300-310</td>
</tr>
</tbody>
</table>

Protein-like fluorescence (tryptophan-like and tyrosine-like) was also measured as a potential indicator of agricultural influence, as it has been demonstrated to be a good proxy for wastewater effluent (Petrenko et al., 1997; Baker, 2001) and livestock waste (Baker, 2002b). Both amino acids were initially measured at 220 nm (T<sub>220</sub> and Tyr<sub>220</sub>) and 280 nm (T<sub>280</sub> and Tyr<sub>280</sub>) excitation. A comparison of fluorescence intensities of the two tryptophan peaks indicated that T<sub>220</sub> and T<sub>280</sub> were significantly positively correlated (r<sub>s</sub> = 0.860, P < 0.001, n = 42). The correlation between Tyr<sub>220</sub> and Tyr<sub>280</sub> was also significant, but not as strong (r<sub>s</sub> = 0.594, P < 0.001, n = 42). This is a result of interference caused by the Raman peak for water in the same wavelength range as Tyr<sub>280</sub>. Because of this interference, only Tyr<sub>220</sub> was considered in this study.

7.3. Results and discussion

7.3.1. EEM features

Figure 7-1 shows a typical contour plot for an EEM from HV-18, a site under significant agricultural influence in the Hatzic watershed. This plot illustrates fluorescence centres typically observed
in samples collected from agriculturally-influenced sites, as well as the excitation/emission ranges used for determining fluorescence intensity for humic-like and protein-like fluorophores. Maxima were observed in the range of fulvic-like material in the majority of samples analysed. Humic-like peaks were also visible in most samples, primarily as an extension of the fulvic-like peak. Protein fluorescence was observed less frequently, and was most common in samples from agricultural sites. Tryptophan-like fluorescence appeared as noticeable shoulders of the fulvic-like peaks at Ex/Em = 220/350 and 280/350. Tyrosine-like fluorescence peaks, when present, were observed at both Ex/Em = 220/305 and 280/305.

Figure 7-1 - EEM illustrating typical agricultural fluorescence patterns as well as regions used for extraction of fluorescence peaks (T=tryptophan and Tyr=tyrosine).

7.3.2. Site-to-site variability

Significant inter-site variability in fluorescence patterns and intensities was observed, as illustrated by EEMs for samples collected in the Hatzic watershed (Figure 7-2) and in the Elk Creek and Salmon watersheds (Figure 7-3). Agricultural sites showed consistently broader and higher fluorescence
peaks for humic-like and fulvic-like material, reflecting greater concentration and diversity of CDOM. Further, samples collected from agricultural sites were the only ones where protein-like fluorescence was observed. In the Hatzic watershed, humic-like and fulvic-like fluorescence were also observed at the urban site (HV-20). Fluorescence peaks at forested and mixed sites were lower than for other land uses and did not show significant variation between the two land-use types.
Figure 7-2 - EEM's for: a) HV-2, b) HV-5, c) HV-9, d) HV-14, e) HV-18 and f) HV-20 in the Hatzic watershed (Aug. 13, 2004) illustrating variability in fluorescence patterns by land use. Note the increase in humic-like and protein-like fluorescence intensity at agricultural sites and the lack of protein fluorescence at the urban site.
Figure 7-3 - EEM's for: a) EC-9, b) EC-14, c) EC-1, d) EC-4, e) SA-19 and f) SA-5 in the Elk Creek and Salmon watersheds (August 13, 2004). The impact of point-source agricultural contamination on fluorescence intensity can be seen at EC-4 (note the difference in scale). Similar fluorescence patterns were observed at SA-19 and SA-5; however, the influence of dilution by groundwater can be observed at SA-5.
Figure 7-4 shows mean fluorescence intensities for all fluorophores by station for the three days of sampling. Maximum mean fluorescence intensities for humic-like and fulvic-like material were observed at HV-18 and EC-4. These sites were located in slow-moving agricultural sloughs that were identified in previous chapters as having the highest concentrations of NH$_4^+$, PO$_4^{3-}$ and fecal coliform in their respective watersheds. The lowest values were observed at the two groundwater sites in the Salmon watershed. This is not surprising as CDOM concentrations in groundwaters are generally low due to microbial metabolism and minimal organic-matter inputs (Thurman, 1985).
Figure 7-4 - Mean fluorescence intensity for: a) protein-like fluorescence and b) humic-like and fulvic-like material at each station over the three days of sampling (GW = groundwater).
Maximum protein-like fluorescence was also observed at sites HV-18 and EC-4. Mean $T_{220}$ and $T_{280}$ fluorescence were 105.56 and 242.71, respectively at HV-18 and 95.74 and 174.04 at EC-4. The next highest values were observed at SA-19 ($T_{280} = 51.61$ and $T_{220} = 93.75$). Tyrosine-like fluorescence also peaked at these stations; however, the highest value by far was observed at HV-18 on December 13, 2004 (838.57), compared to a value of 83.84 at EC-4 on the same day.

Minimum $T_{220}$ and $T_{280}$ values (14.79 and 40.57) were observed at HV-13, a mixed-use site in the Hatzic watershed, while minimum Tyr$_{220}$ values were found at SA-1G, a deep groundwater site in the Salmon watershed. Interestingly, at the second groundwater site (SA-3G, a drinking-water source for Langley) tryptophan-like fluorescence was similar to that observed at forested sites and at SA-1G; however, mean Tyr$_{220}$ fluorescence was the third highest of all stations sampled. As this is a groundwater source with presumably little CDOM this would suggest a potential link to the surface-water system; however, the cause of this fluorescence could not be determined.

The role of groundwater in dilution of surface-water CDOM concentrations was observed in the Salmon watershed at SA-5. Although this station is downstream from SA-19, fluorescence intensities were consistently lower due to contributions from the Hopington aquifer (Figure 7-3 and Figure 7-4).

### 7.3.3. Land use and fluorescence intensity

An analysis of spatial variability revealed a strong influence of land use on the fluorescence intensity measured in surface waters (Table 7-2). For surface-water sites, mean fluorescence values were consistently lowest for samples collected from mixed and forested subcatchments; however, the difference was not significant when Bonferroni correction was applied to data aggregated to the site level. This is again likely a result of the small sample size resulting from the aggregation of data. Although a significant difference for these parameters was not observed, the data in Table 7-2 suggest a consistent trend of higher fluorescence intensities for all variables at agricultural sites.
Table 7-2 - Mean fluorescence intensities by land use for the Hatzic, Elk Creek and Salmon watersheds.

<table>
<thead>
<tr>
<th></th>
<th>Elk Creek</th>
<th></th>
<th>Hatzic</th>
<th></th>
<th>Salmon</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Forested</td>
<td>Mixed</td>
<td>Agricultural</td>
<td>Forested</td>
<td>Mixed</td>
<td>Agricultural</td>
</tr>
<tr>
<td>T220</td>
<td>46.62</td>
<td>49.60</td>
<td>131.58</td>
<td>44.51</td>
<td>133.47</td>
<td>69.61</td>
</tr>
<tr>
<td>T280</td>
<td>17.95</td>
<td>20.13</td>
<td>69.36</td>
<td>17.07</td>
<td>54.24</td>
<td>30.52</td>
</tr>
<tr>
<td>Ty220</td>
<td>62.38</td>
<td>62.26</td>
<td>112.62</td>
<td>63.66</td>
<td>217.59</td>
<td>63.44</td>
</tr>
<tr>
<td>Humic-like</td>
<td>21.56</td>
<td>15.59</td>
<td>123.00</td>
<td>22.22</td>
<td>55.90</td>
<td>67.86</td>
</tr>
<tr>
<td>Fulvic-like</td>
<td>50.53</td>
<td>39.49</td>
<td>206.56</td>
<td>54.19</td>
<td>103.41</td>
<td>110.46</td>
</tr>
</tbody>
</table>

The influence of land use was also observed when comparing total contributing area under agriculture to fluorescence intensity. Figure 7-5a illustrates the increase in fulvic-like fluorescence intensity associated with increasing area under agricultural land use. A similar trend was observed for humic-like materials (not shown), and both were significantly correlated to percentage area under agriculture ($r_s = 0.578$ and 0.523 for fulvic-like and humic-like fluorescence, respectively; $n = 29$). Increases in soil organic matter have been linked to agricultural management practices, including application of manure (Larson and Bott, 1980; Jenkinson, 1990; Gregorich et al., 1998; Rochette and Gregorich, 1998; Coote and Gregorich, 2000) and intensive tillage practices (Royer and David, 2005; Quinton et al., 2006). The correlation between humic-like and fulvic-like fluorescence and percentage area under agriculture reflects this trend, and suggests that these two parameters provide a good indication of agricultural influence and intensity.
Figure 7-5 - Percentage of contributing area under agriculture vs. a) fulvic-like fluorescence, b) $T_{280}$ and c) $Tyr_{220}$. Note the increased protein-like fluorescence associated with HV-18.
A similar relationship was observed between protein-like fluorescence and percentage area under agriculture (Figure 7-5b and Figure 7-5c) with significant correlations observed for both Tyr_{220} and T_{280} (r_s = 0.515 and r_s = 0.572, respectively, n = 29). As illustrated in Figure 7-4, the values for protein-like fluorescence at HV-18 could represent outliers. The strength of these relationships decreased slightly when these were removed (r_s = 0.452 and r_s = 0.421 for T_{280} and Tyr_{220}, respectively, n = 26), but both were still significant. Baker (2002b) noted elevated tyrosine-like and tryptophan-like fluorescence in pig and cattle slurries and characterized the unique spectroscopic signature of these materials using a ratio of tryptophan-to-fulvic-like fluorescence. This ratio was used to eliminate the influence of CDOM concentration on fluorescence intensities, and instead identify different contaminant sources based on the relative concentration of protein-like vs. humic-like fluorophores. This ratio ranged from approximately 2-5 for cattle and pig slurries. While the ratio observed at HV-18 did not exceed 1.5, the strong protein-like fluorescence signal observed suggests that there may be a direct link between manure storage sites from nearby cattle operations and surface water at this site. It is unclear what caused such elevated protein fluorescence at HV-18, as direct fecal loading was observed at several other sites where these values were much lower. Similar values have been observed in the UK near burial sites for cattle culled following the hoof-and-mouth disease outbreak in 2001 (Baker, personal communication). It is unknown whether there was a dead animal upstream of the sampling site on the day these values were observed. Further research is required to determine if this would produce the elevated values observed.

A comparison of mean fluorescence intensities for similar land uses across watersheds showed no significant differences between catchments. For agricultural sites, humic-like and fulvic-like intensities were consistently higher in the Elk Creek watershed (although not significantly so), likely reflecting the higher-intensity agricultural land use in the latter watershed (see Chapter 5). Protein-like fluorescence was comparable for agricultural sites between all three watersheds, except at HV-18 where, as described above, values were higher than at any other site.

7.3.4. Temporal trends

An analysis of temporal patterns in fluorescence intensities revealed no significant differences between the three days of sampling despite variations in antecedent rainfall. Relative changes in fluorescence from day to day were observed, but were not consistent across stations representing similar land use types. It is likely that this is a result of the small sample size and the number of days for which
data are available, as fluorescence intensities show strong, significant correlations with other variables that do show consistent trends over time (described in Section 7.3.5).

Samples collected over the course of the storm event in the Hatzic watershed indicated a strong link between water depth and some fluorescence parameters. As illustrated in Figure 7-6, both humic-like and fulvic-like fluorescence increased with water depth over the three rainfall events. Both variables were strongly correlated with depth ($r_s = 0.926$ and $r_s = 0.875$, respectively, $P < 0.001$, $n = 17$), and with NO$_3^-$ ($r_s = 0.917$ and $r_s = 0.826$, respectively, $P < 0.001$, $n = 17$), and both reached maxima just after the storm peak for the first two rainfall events. The highest fulvic-like fluorescence intensity was observed just after maximum stage during the second event. Fulvic-like fluorescence fluctuated thereafter, but did not exceed the maximum reached during the second event. In contrast, the humic-like fluorescence maximum coincided with peak stage during the third event.
Figure 7.6 - Fluorescence intensities for samples collected during the Hazc watershed storm event from March 18-21, 2005.

- Tryptophan Fluorescence Intensity
- Humic and Fulvic Fluorescence Intensity
Unlike humic-like and fulvic-like fluorescence, protein-like fluorescence showed an initial peak prior to the first rainfall event and then decreased until reaching a second peak on the rising limb of this event (as illustrated by $T_{280}$ in Figure 7-6). This may represent an initial dilution, followed by increased CDOM inputs as contributions from the land surface increased (as represented by an increase in stage). Intensity values for $T_{280}$ peaked on the rising limb of each of the three storm events and subsequently decreased at maximum stage, likely reflecting dilution by rainfall. The minimal peaks observed for protein fluorescence suggest limited availability of protein-rich CDOM sources upstream of the sampling site (note that HV-18, the site with maximum protein-like fluorescence, is downstream of the storm sampling site). As demonstrated above, protein-like fluorescence is generally only observed in highly-contaminated agricultural sloughs. As such sites are limited in the Hatzic watershed, any contributions of CDOM rich in protein-like fluorophores was likely diluted with increasing rainfall.

7.3.5. Relationships with other indicators

Statistically significant relationships were observed between fluorescence parameters and nutrient and bacterial concentrations when samples from all watersheds were pooled (Table 7-3). Humic-like and fulvic-like fluorescence were significantly positively correlated with DOC, NO$_3^-$, PO$_4^{3-}$, NH$_4^+$ and log-transformed fecal coliform concentrations (correlations were strongest for the latter three variables). Fluorescence intensities for both tryptophan-like peaks were strongly correlated with NH$_4^+$, PO$_4^{3-}$ and log-transformed fecal coliform. Only $T_{280}$ showed a weak correlation with NO$_3^-$ (the poor correlation with $T_{220}$ is likely a result of the strong absorbance of the NO$_3^-$ ion near 220 nm). Tyrosine-like fluorescence intensity showed the weakest correlations with nutrient concentrations (but still significant at $P < 0.05$); however, a strong positive relationship was observed with log-transformed fecal coliform.
Table 7-3 – Spearman rank correlations between fluorescence intensity and nutrient and bacteria concentrations for all samples from the three watersheds (numbers in brackets represent sample size).

<table>
<thead>
<tr>
<th></th>
<th>NO₃</th>
<th>NH₄⁺</th>
<th>PO₄³⁻</th>
<th>Log Fecal Coliform</th>
<th>Log Total Coliform</th>
<th>Dissolved Organic Carbon</th>
<th>A₂₅₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₂₂₀</td>
<td>.024</td>
<td>.579*</td>
<td>.583**</td>
<td>.615**</td>
<td>.337*</td>
<td>.432</td>
<td>.766**</td>
</tr>
<tr>
<td></td>
<td>(47)</td>
<td>(46)</td>
<td>(47)</td>
<td>(44)</td>
<td>(43)</td>
<td>(18)</td>
<td>(50)</td>
</tr>
<tr>
<td>T₂₈₀</td>
<td>.340*</td>
<td>.679**</td>
<td>.707**</td>
<td>.734**</td>
<td>.391*</td>
<td>.412</td>
<td>.865**</td>
</tr>
<tr>
<td></td>
<td>(47)</td>
<td>(46)</td>
<td>(47)</td>
<td>(44)</td>
<td>(43)</td>
<td>(18)</td>
<td>(50)</td>
</tr>
<tr>
<td>Tyr₂₂₀</td>
<td>-.301*</td>
<td>.391*</td>
<td>.384*</td>
<td>.513**</td>
<td>.332*</td>
<td>.406</td>
<td>-0.020</td>
</tr>
<tr>
<td></td>
<td>(47)</td>
<td>(46)</td>
<td>(47)</td>
<td>(44)</td>
<td>(43)</td>
<td>(18)</td>
<td>(50)</td>
</tr>
<tr>
<td>Humic-like</td>
<td>.365*</td>
<td>.676**</td>
<td>.646**</td>
<td>.630**</td>
<td>.271</td>
<td>.564*</td>
<td>.948**</td>
</tr>
<tr>
<td></td>
<td>(47)</td>
<td>(46)</td>
<td>(47)</td>
<td>(44)</td>
<td>(43)</td>
<td>(18)</td>
<td>(50)</td>
</tr>
<tr>
<td>Fulvic-like</td>
<td>.377*</td>
<td>.657**</td>
<td>.683**</td>
<td>.643**</td>
<td>.278</td>
<td>.581*</td>
<td>.938**</td>
</tr>
<tr>
<td></td>
<td>(47)</td>
<td>(46)</td>
<td>(47)</td>
<td>(44)</td>
<td>(43)</td>
<td>(18)</td>
<td>(50)</td>
</tr>
</tbody>
</table>

*P < 0.05; **P < 0.01

Fluorescence parameters also showed strong positive correlations with absorbance values, with the strongest relationship observed with A₂₅₄ (Table 7-3). Significant positive correlations were observed at longer absorbance wavelengths; however, the strength of the relationship decreased with increasing wavelength. This reflects the greater quantum yield (ratio of photons emitted to those absorbed) at lower excitation wavelengths, as illustrated by strong fluorescence in this region in the EEM's in Figure 7-2 and Figure 7-3.

Humic-like and fulvic-like fluorescence were also significantly correlated with DOC (Table 7-3), a trend that has been observed in a number of other studies (as described in Blough and Del Vecchio, 2002). The lack of a stronger correlation reflects the fact that humic and fulvic materials make up only approximately 50% of total DOC (Thurman, 1985).

When stratified by watershed, the correlations between fluorescence and nutrient and bacterial concentrations remain relatively consistent, with some minor variations (Table 7-4). In all three watersheds, significant relationships between log-transformed fecal coliform data and T₂₈₀ were observed. This relationship was strongest in the Elk Creek watershed where humic-like and fulvic-like fluorescence were also strongly correlated to fecal coliform concentrations. In the Hatzic and Salmon catchments no significant relationship between these variables was observed. In these two watersheds, protein-like fluorescence (tryptophan and tyrosine) was significantly correlated with NH₄⁺; however, a significant correlation was not observed in the Salmon watershed. In contrast, there was a significant relationship between humic-like and fulvic-like fluorescence and NH₄⁺ in the Elk Creek and Salmon watersheds but not in the Hatzic catchment. No significant correlations were observed between fluorescence parameters
and NO$_3^-$ in any of the watersheds. This is in contrast to results reported by Baker and Inverarity (2004) and Baker et al. (2005) where significant positive correlations with nitrate were consistently observed.

Table 7-4 – Spearman rank correlations between fluorescence parameters and water-quality indicators, by watershed (numbers in brackets represent sample size).

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Fluorescence Indicator</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>PO$_4^{3-}$</th>
<th>Log Fecal Coliform</th>
<th>Log Total Coliform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatzic</td>
<td>$T_{220}$</td>
<td>.038</td>
<td>.633**</td>
<td>.207</td>
<td>.353</td>
<td>.112</td>
</tr>
<tr>
<td></td>
<td>(18)</td>
<td>(18)</td>
<td>(18)</td>
<td>(16)</td>
<td>(16)</td>
<td>(16)</td>
</tr>
<tr>
<td></td>
<td>$T_{280}$</td>
<td>.102</td>
<td>.612**</td>
<td>.296</td>
<td>.602*</td>
<td>.389</td>
</tr>
<tr>
<td></td>
<td>(18)</td>
<td>(18)</td>
<td>(18)</td>
<td>(16)</td>
<td>(16)</td>
<td>(16)</td>
</tr>
<tr>
<td></td>
<td>Ty$_{220}$</td>
<td>-.294</td>
<td>.622**</td>
<td>.422</td>
<td>.469</td>
<td>.181</td>
</tr>
<tr>
<td></td>
<td>(18)</td>
<td>(18)</td>
<td>(18)</td>
<td>(16)</td>
<td>(16)</td>
<td>(16)</td>
</tr>
<tr>
<td></td>
<td>Humic-like</td>
<td>.195</td>
<td>.282</td>
<td>.214</td>
<td>.580*</td>
<td>.394</td>
</tr>
<tr>
<td></td>
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<td>(18)</td>
<td>(16)</td>
<td>(16)</td>
<td>(16)</td>
</tr>
<tr>
<td></td>
<td>Fulvic-like</td>
<td>.123</td>
<td>.330</td>
<td>.233</td>
<td>.560*</td>
<td>.384</td>
</tr>
<tr>
<td></td>
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<td>(18)</td>
<td>(18)</td>
<td>(16)</td>
<td>(16)</td>
<td>(16)</td>
</tr>
<tr>
<td>Elk Creek</td>
<td>$T_{220}$</td>
<td>-.100</td>
<td>.758*</td>
<td>.727*</td>
<td>.845**</td>
<td>.300</td>
</tr>
<tr>
<td></td>
<td>$T_{280}$</td>
<td>.145</td>
<td>.794**</td>
<td>.809**</td>
<td>.821**</td>
<td>.109</td>
</tr>
<tr>
<td></td>
<td>Ty$_{220}$</td>
<td>-.109</td>
<td>.648*</td>
<td>.591</td>
<td>.766**</td>
<td>.227</td>
</tr>
<tr>
<td></td>
<td>Humic-like</td>
<td>.091</td>
<td>.891**</td>
<td>.845**</td>
<td>.833**</td>
<td>.182</td>
</tr>
<tr>
<td></td>
<td>Fulvic-like</td>
<td>.165</td>
<td>.755*</td>
<td>.853**</td>
<td>.732*</td>
<td>-.009</td>
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<tr>
<td>Salmon</td>
<td>$T_{220}$</td>
<td>-.236</td>
<td>.273</td>
<td>.091</td>
<td>.571</td>
<td>.633</td>
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<tr>
<td></td>
<td>$T_{280}$</td>
<td>-.103</td>
<td>.175</td>
<td>-.006</td>
<td>.632*</td>
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<td></td>
<td>Ty$_{220}$</td>
<td>-.285</td>
<td>-.115</td>
<td>-.115</td>
<td>.693*</td>
<td>.883**</td>
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<td>(10)</td>
</tr>
<tr>
<td></td>
<td>Humic-like</td>
<td>-.055</td>
<td>.636*</td>
<td>.491</td>
<td>-.231</td>
<td>-.233</td>
</tr>
<tr>
<td></td>
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<td>(10)</td>
<td>(10)</td>
<td>(10)</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>Fulvic-like</td>
<td>-.188</td>
<td>.636*</td>
<td>.491</td>
<td>-.122</td>
<td>-.117</td>
</tr>
<tr>
<td></td>
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<td>(10)</td>
<td>(10)</td>
<td>(10)</td>
</tr>
</tbody>
</table>

*P < 0.05; **P < 0.01

The variability observed in these correlations is explained by the fact that fluorescence measurements detect agriculturally-derived CDOM. The strong correlation with nutrient and bacterial concentrations is a result of their association with agricultural runoff. The link between CDOM transported in agricultural runoff and nutrient and bacterial concentrations is site specific, and is a function of natural factors (including local soil and vegetation type) and anthropogenic influence (land-use type and intensity). As a result, the correlations, while consistently positive, are variable when compared from watershed to watershed. Despite this variability, it appears that within a given watershed, fluorescence parameters such as $T_{220}$, $T_{280}$ and humic-like and fulvic-like fluorescence are effective indicators of agricultural influence (as was demonstrated for absorbance in Chapter 6).
When stratified by land use, significant correlations between fluorescence parameters and nutrient and bacterial concentrations were only observed at agricultural sites (Table 7-5). Among these sites, an interesting pattern of associations was observed. Fecal coliform bacteria were most closely related to protein-like fluorescence, while nutrients ($NH_4^+$ and $PO_4^{3-}$) showed the strongest correlations with fulvic-like and humic-like fluorescence intensity and $T_{280}$.

Table 7-5 - Spearman rank correlations between fluorescence intensities and bacterial and nutrient concentrations for agricultural sites in the Hatzic, Elk Creek and Salmon watersheds (numbers in brackets represent sample size)

<table>
<thead>
<tr>
<th></th>
<th>NO$_3$</th>
<th>NH$_4^+$</th>
<th>PO$_4^{3-}$</th>
<th>Log Fecal Coliform</th>
<th>Log Total Coliform</th>
<th>Dissolved organic carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{220}$</td>
<td>-.277</td>
<td>.574**</td>
<td>.451*</td>
<td>.735**</td>
<td>2.33</td>
<td>.524</td>
</tr>
<tr>
<td></td>
<td>(24)</td>
<td>(23)</td>
<td>(24)</td>
<td>(23)</td>
<td>(21)</td>
<td>(8)</td>
</tr>
<tr>
<td>$T_{280}$</td>
<td>.113</td>
<td>.588**</td>
<td>.681**</td>
<td>.818**</td>
<td>.196</td>
<td>.619</td>
</tr>
<tr>
<td></td>
<td>(24)</td>
<td>(23)</td>
<td>(24)</td>
<td>(23)</td>
<td>(21)</td>
<td>(8)</td>
</tr>
<tr>
<td>Tyr$_{220}$</td>
<td>-.577**</td>
<td>.237</td>
<td>.229</td>
<td>.601**</td>
<td>.494*</td>
<td>.571</td>
</tr>
<tr>
<td></td>
<td>(24)</td>
<td>(23)</td>
<td>(24)</td>
<td>(23)</td>
<td>(21)</td>
<td>(8)</td>
</tr>
<tr>
<td>Humic-like</td>
<td>.312</td>
<td>.613**</td>
<td>.621**</td>
<td>.411*</td>
<td>-.133</td>
<td>.500</td>
</tr>
<tr>
<td></td>
<td>(24)</td>
<td>(23)</td>
<td>(24)</td>
<td>(23)</td>
<td>(21)</td>
<td>(8)</td>
</tr>
<tr>
<td>Fulvic-like</td>
<td>.299</td>
<td>.608**</td>
<td>.626**</td>
<td>.427*</td>
<td>-.112</td>
<td>.500</td>
</tr>
<tr>
<td></td>
<td>(24)</td>
<td>(23)</td>
<td>(24)</td>
<td>(23)</td>
<td>(21)</td>
<td>(8)</td>
</tr>
</tbody>
</table>

*P < 0.05; **P < 0.01

A link between protein-like fluorescence and microbial activity has been proposed in both freshwater and marine environments. Tryptophan-like fluorescence has been detected in marine bacterial cultures by Yamashita and Tanoue (2003) and has also been linked to bacterial degradation of organic matter in the marine water column (Del Castillo et al., 1999; Moran et al., 2000). In a study of the fluorescence properties of marine bacteria and phytoplankton, Determann (1998) noted strong correlations between tryptophan-like fluorescence and bacterial concentrations for several species. While correlations were not consistent across cultures, a clear link between bacterial numbers and fluorescence (attributed to intracellular tryptophan) was observed. More recently, Elliot et al. (2006a) measured fluorescence of *Psuedomonas aeruginosa* under laboratory conditions in an effort to establish the link between protein-like fluorescence observed in freshwaters and the presence of bacteria. In this study, tyrosine-like and tryptophan-like fluorescence were observed in laboratory-cultured bacteria collected from an urban river source in Birmingham, UK. Fluorescence was also assessed over a range of temperatures from 11 °C to 37 °C. Significantly lower fluorescence intensities were observed at 11 °C, and were attributed to a lower number of viable cells and the decreased metabolic rate that would be expected at colder temperatures. Finally, in relation to land use, Baker (2001; 2002c) and Baker et al.
(2005) noted a positive correlation between protein fluorescence and anthropogenic inputs to surface waters from sewage treatment plants and agricultural activities (through correlations between fluorescence parameters and nutrient concentrations).

The strong correlations between T_{220}, T_{280} and Tyr_{220} and log-fecal coliform concentrations at agricultural sites in the present study indicate a similar link between anthropogenic inputs and fluorescence intensity. However, correlations with total coliform concentrations were weak suggesting that fluorescence intensity in this case may not be attributed directly to microbial activity. These data suggest that the observed fluorescence patterns are linked to agriculturally-derived CDOM, and not to bacterial concentrations or in-situ aquatic microbial metabolism as has been observed in several studies in marine environments (e.g., Coble, 1996; e.g., Del Castillo et al., 1999). Rather than acting as a direct measure of bacterial concentrations, these signals may be due to protein-like fluorophores associated with agricultural runoff as observed by Baker (2002b), particularly at heavily contaminated sites (HV-18 and EC-4). If this is the case, the observed correlations with fecal coliform concentrations reflect the strong link between agricultural effluent and bacterial contamination, but are not actually a result of bacterially-derived proteins. This is supported by the fact that only a minimal increase in tryptophan-like fluorescence is observed at mixed sites, where fecal coliform concentrations approach those of sites under much more intense agricultural activity (Figure 7-7). It appears that, at mixed sites where agricultural activities comprise a small percentage of total contributing area, agriculturally-derived CDOM is diluted by non-agricultural inputs, resulting in decreased fluorescence intensity even in the presence of significant bacterial concentrations. These results suggest that, while fluorescence appears to be an effective indicator of agricultural influence on surface waters, it does not accurately reflect the potential risk to human health associated with limited direct contributions of bacterial contamination.
The same appears to be true for humic-like and fulvic-like fluorescence, which show strong correlations with nutrient concentrations. Fluorescence in the humic-like and fulvic-like regions is attributed to agricultural runoff that is rich in CDOM derived from decaying plant matter and agricultural amendments (Ohno et al., 2006). The correlation with nutrient concentrations is therefore also indirect, as the fluorescence signals observed are linked to organic inputs, which also result in increased dissolved nutrient concentrations.

7.4. Conclusions

This study represents an initial evaluation of the potential of fluorescence spectroscopy as a tool to detect contamination in surface waters subjected to various land-use types and intensities. The results described above yield the following conclusions:
1) **Fluorescence patterns and intensity values provide an indication of the relative degree of agricultural influence on surface waters**

Surface waters under agricultural influence were consistently characterized by higher protein-like and humic-like fluorescence intensities than were observed in undisturbed or minimally-disturbed (mixed) subcatchments. Although this difference was not significant for aggregated data, the data illustrate a trend of increasing fluorescence associated with agriculture. Qualitatively, EEMs generated for samples collected in agricultural subcatchments were easily distinguished from other land uses due to the presence of broader humic-like and fulvic-like fluorescence peaks, and the presence of protein-like fluorescence. Further, a significant, positive correlation was observed between percentage area under agricultural influence and humic-like, fulvic-like and protein-like fluorescence. These observations are in agreement with those for absorbance data (described in Chapter 6) and suggest that the two techniques provide complementary information regarding land-use influence on surface-water quality.

2) **Fluorescence spectroscopy provides an indirect measure of nutrient and bacterial concentrations through the detection of agriculturally-derived CDOM in surface waters.**

In the present study, when results were stratified by land use, significant correlations between fluorescence parameters and nutrient and bacterial concentrations were only observed in agricultural subcatchments. This suggests that these elevated values are a result of soluble proteins and organic acids derived from agricultural amendments and decaying plant matter (Baker, 2002b; Ohno et al., 2006), and do not directly reflect bacterially-derived organic materials. While others have noted a direct link between protein fluorescence and bacterial concentrations under laboratory conditions (Elliott et al., 2006a), under field conditions, CDOM-related fluorescence likely masks the fluorescence signal associated with bacterially-derived proteins.

These data suggest that fluorescence spectroscopy would be a useful tool to proactively manage water-quality risk in areas where agricultural contamination is a concern (particularly if monitored in real time). This would be particularly useful for agriculturally-derived pathogens such as protozoa or viruses. Detection methods for these organisms are currently time consuming, expensive and/or limited in terms of accuracy. Further, there are few reliable proxies for these organisms in surface waters (Grabow, 1996). Further research is required to assess the utility of this technique for this purpose.
It is important to note, however, that fluorescence has significant limitations as an absolute indicator of drinking-water quality risk in forested and mixed subcatchments. In fact, significant bacterial contamination at mixed sites produced minimal responses in fluorescence intensity, likely as a result of the dilution of agriculturally-derived CDOM. The ability to detect contamination events in such environments may be improved through adjustments to sensor sensitivity. This represents another avenue of potential further research for this technique.

3) **Protein-like fluorescence is a useful indicator of significant point sources of agricultural effluent**

As illustrated at HV-18 and EC-4, maximum protein-like fluorescence values are associated with sites under the greatest agricultural influence as determined by nutrient and bacterial concentrations and agricultural land use within their contributing areas. Peaks in protein-like fluorescence at these sites likely reflect direct inputs of manure from animals or storage areas upstream. This concurs with the work of Baker (2002b), who observed tryptophan-like fluorescence in farm wastes under laboratory conditions. This suggests that protein-like fluorescence could be used to detect significant contamination of surface waters by sewage or animal wastes.
Chapter 8

8. Integrated Discussion and Conclusions

8.1. Introduction

This study represents a multi-year, multi-watershed research effort aimed at assessing the links between agricultural land use (type and intensity), environmental factors (climate, hydrology, etc) and the risk of surface-water impairment in rural watersheds in the LFV. It incorporated a multidisciplinary approach to address the issues of human and ecosystem health risks arising from agricultural activities, and was designed to span several watersheds in order to identify consistent trends in water-quality response to these activities. The need for such a study arose from knowledge gaps in the literature (identified in Chapter 1), the intensification of agricultural operations in the province (particularly in the LFV), the strong dependence in BC on surface water as a source for rural drinking-water systems and the lack of comprehensive, long-term data linking agricultural land use to nutrient and bacterial inputs to surface waters at varying spatial and temporal scales. While the study was focused on catchments in the LFV, the consistent trends observed across watersheds provide insight regarding the regional implications of agricultural intensification which are likely applicable elsewhere.

The objectives of this study (outlined in Chapter 1) were developed to identify those land-use practices and environmental conditions that present the greatest risk to surface-water quality, and therefore, to human and ecosystem health, in order to support a risk-based approach to water-quality management. Recognizing the limitations of current water-quality monitoring techniques (timeliness, expense, quantity of sample required, etc.), absorbance and fluorescence spectroscopic techniques were also evaluated to determine their utility as rapid and accurate tools for detection of agricultural influence. This chapter integrates the results of the four major components of this study (Chapters 4-7) with reference to the original objectives of this thesis outlined in Chapter 1. The focus is on cross-cutting themes which link the results of each chapter in support of these objectives.

8.2. Integrated discussion

Several authors have studied the issue of agricultural influence on surface-water quality in rural watersheds in the LFV (Schreier et al., 1999; Berka et al., 2001; Magwood, 2004; Smith, 2004; Macdonald, 2005). This study built on these earlier efforts by increasing the spatial and temporal resolution of water-quality, hydrometric and meteorological monitoring in order to better characterize the
interactions between agricultural activities, environmental conditions, hydrological variables and water quality. In doing so, several important themes were identified, as described under each study objective below.

8.2.1. The link between agricultural land use type and intensity and nutrient and bacterial contributions to surface waters in agricultural watersheds

Water quality in undisturbed subcatchments

Anthropogenic activity was consistently observed to produce nutrient and bacterial concentrations elevated above those observed in forested subcatchments. Analysis of samples from forested subcatchments throughout this study indicated that nutrient stores are limited and rapidly depleted in undisturbed areas, as would be expected in the absence of human influence. However, the influence of wildlife on stream bacterial concentrations was apparent, and was observed to increase substantially during summer months. While fecal coliform and E. coli concentrations were generally low at forested sites (below 10 cfu·100 ml⁻¹), high concentrations were observed, particularly after prolonged dry periods that allowed the development of bacterial stores on the land surface.

These results illustrate the importance of conducting wildlife inventories in drinking-water source watersheds or subcatchments in order to evaluate potential risks of fecal contamination. Further, the variable bacterial concentrations observed during the study highlights the need for continual monitoring in order effectively assess wildlife contamination risk, as bacterial loading events are infrequent, but can be significant.

The importance of spatial scale

In the three watersheds studied, the importance of spatial scale in assessing the link between land use and water quality was evident. This was due to the scale-specificity of contaminant mobilization, transport and storage processes. At the plot scale, where samples were collected in tributary streams, relationships between contributing area under agriculture and water-quality variables were poor due to the significant influence of local point-source contamination. Further, spectroscopic indicators of agricultural influence were of limited utility in tributaries where the CDOM signal was diluted by non-agricultural inputs. This was observed in both agricultural and mixed subcatchments. Conversely, at the watershed scale, the cumulative impact of increasing area under agriculture produced a strong positive
correlation between land use and water-quality variables, including fluorescence and absorbance. Sites located along the mainstem or near the outlet of each watershed provided an integrated signal of land-use influence at the catchment scale, and showed a consistent trend of greater impairment associated with increasing land-use intensity. These integrated signals masked localized “hot spots” within each watershed, highlighting the need for risk-assessment and mitigation strategies to address land-use activities and processes at both the plot and watershed scale.

At a regional scale (i.e., across watersheds) water quality impairment trends were consistent across watersheds, with increasing area under agriculture producing higher concentrations of agricultural contaminants (except where significant groundwater contributions were noted). The timing of nutrient and bacterial cycling was also consistent across watersheds with peak nutrient concentrations observed in winter and peak bacterial concentrations observed in summer. This suggests that current and future agricultural development will ultimately contribute to regional water-quality impacts that are measurable beyond watershed boundaries. However, an assessment of water quality in the Fraser River by Shaw and Tuominen (1998) revealed different seasonal patterns in bacterial concentrations when compared to each of the watersheds (peaks observed during winter rather than summer months). This is attributed to lower rainfall and reduced stormwater flows during summer months, and lack of chlorination of sewage treatment plant discharge during winter months. At the regional scale, therefore, the influence of agriculture on water quality is apparently masked by impacts from other anthropogenic activities and upstream land uses. Impacts from agricultural intensification do not appear to be the dominant influence on water quality at this level.

The role of livestock operations

Agricultural activities in the watersheds studied included field crop production, tree farms, greenhouses, dairy and beef cattle farms and chicken operations. Across the three watersheds, livestock operations (particularly cattle) were associated with the greatest concentrations of nutrients and bacteria to surface waters. The direct link between livestock and water quality was also inferred from the unique protein-like fluorescence signals observed at highly-contaminated sites. Sites in areas of intensive agricultural activity (e.g., HV-18 and EC-4) consistently produced the highest nutrient and bacterial concentrations (and protein fluorescence intensities) under winter and summer conditions, indicating the resilience of contaminant stores at these locations.
Interestingly, in areas of less intensive agriculture (i.e., mixed sites) cattle operations were still observed to act as consistent sources of nutrients and bacteria. Research into the impacts of urban development on water quality has noted strong relationships between impervious area and surface-water quality (Hall et al., 1999). A threshold of 10-20% upstream impervious area has been observed as the point beyond which urban land use exerts noticeable influence on surface-water quality (Arnold and Gibbons, 1996). In the present study, elevated nutrient and bacterial concentrations in mixed subcatchments (where agricultural land use was less than 10%) suggest that the same threshold in agriculturally-dominated watersheds is lower. This is particularly true for bacterial contamination. While spectroscopic measurements indicated that agricultural effluent comprised a small proportion of total flow at mixed sites, local inputs produced bacterial concentrations that were as high as those observed at sites under more intensive agricultural influence. While this is due partly to the smaller scale of tributary streams where mixed land uses were observed, it indicates the importance of individual livestock operations as potential contaminant sources.

**Agricultural intensity and water quality**

At the watershed scale, increased agricultural intensity (as measured by nutrient surpluses and animal density) was linked to greater impairment of surface-water quality. Subcatchments under 100% agricultural land use in the Elk Creek watershed were observed to produce the highest levels of bacterial and nutrient concentrations in the three watersheds. While this finding is not surprising, it demonstrates the implications of ongoing agricultural intensification in the LFV. In Chapter 5, the cumulative, downstream impacts of intensive agricultural activities were described for each watershed. What is not yet clear is how these systems will respond to further intensification and increased land-use pressure associated with ongoing residential development. Further work is required to determine if there is a land-use intensity threshold beyond which a non-linear response in surface-water quality is likely to occur.
8.2.2. The influence of meteorological conditions on nutrient and bacterial dynamics in surface waters in agricultural watersheds

The dynamics of nutrient and bacterial stores at a watershed scale

Trends in nutrient and bacterial concentrations varied when compared temporally. At a watershed scale, nutrient and bacterial stores are governed by different processes of supply, storage and transport. These result in very different seasonal trends in inputs to surface waters, with bacterial concentrations peaking during summer months and maximum nutrient concentrations observed during winter. Watershed-scale bacterial stores are not as resilient as nutrient stores because bacteria are subject to biological processes of decay, and are far more susceptible to environmental stressors. As a result, bacterial dynamics in winter months are supply-constrained and therefore do not show the same seasonal trend as nutrients.

The availability of nutrients is also a function of supply; however, nutrient stores are not as easily depleted as those for living organisms. As observed in the Hatzic watershed; however, major storm events appeared to deplete catchment-scale nutrient stores, the results of which could be detected over several seasons. The recovery of these stores is likely to be prolonged due to the moderate nutrient surpluses characteristic of this watershed (Schreier et al., 2003). Nutrient stores in the Salmon watershed were far more resilient due to the storage capacity of the unconfined Hopington aquifer and greater nutrient surpluses within the watershed. This resulted in more consistent contributions of NO₃⁻ to surface waters over the entire year, particularly in summer months when NO₃⁻ concentrations in surface waters in the Elk Creek and Hatzic watersheds were consistently lower. This has significant implications for eutrophication in the Salmon watershed as biological productivity is far greater during summer months.

The importance of temporal scale

As stated above, seasonal trends in bacterial and nutrient concentrations were consistent across watersheds for similar land-use types. At an annual scale, nutrient concentrations correlated positively with stream stage, reflecting increased inputs during winter months, while bacterial concentrations were negatively correlated with stage. However, at the storm-event scale, both bacterial and nutrient concentrations were positively correlated with depth, reflecting the differing scale of mobilization and
transport processes. When determining periods of maximum water-quality risk, therefore, it is necessary to do so at multiple temporal scales.

Seasonally, the greatest risk with respect to human health from a bacterial perspective was observed in summer. This risk was exacerbated after prolonged dry weather which allowed accumulation of fecal material on the land surface. Rainfall events after prolonged dry summer weather produced the greatest bacterial concentrations per unit rainfall. However, even during winter months, stream fecal coliform concentrations were observed to increase by several orders of magnitude over background levels during peak flow at agricultural sites.

The importance of antecedent conditions

As noted above, antecedent conditions play a significant role in contaminant availability at a watershed scale. At a seasonal level, it was observed that major storm events could deplete watershed-scale nutrient stores in the Hatzic watershed, thus resulting in reduced mean nutrient concentrations in surface waters in subsequent years. Conversely, extended periods of dry weather, particularly during summer months, allowed development of surface stores of bacteria arising from manure applications and increased livestock and wildlife activity. As a result, minor storm events in late summer and early autumn can result in disproportionate surface-water bacterial concentrations, as was observed in the Hatzic watershed on September 16, 2003.

8.2.3. The potential of spectroscopic techniques to detect agricultural influence

The assessment of spectroscopic techniques in this study was conducted for two reasons. The first was to determine if these techniques could provide a faster and less labour intensive process for detecting agricultural influence in bulk water samples. The second was to determine what additional information regarding contaminant sources, transport processes and flow pathways could be derived from CDOM signals. Key findings are described below.

Procedural advantages associated with spectroscopic techniques

From a procedural perspective, absorption and fluorescence spectroscopy offered several advantages over traditional water-quality monitoring techniques. These included rapid analysis, small
sample size, minimal requirements for sample treatment (filtering), no requirement for reagents and minimal training required for the operation of spectroscopic equipment. Further, absorbance data, with minimal post-processing (calculation of second derivatives) provide a rapid and accurate technique for the detection of NO$_3^-$ in bulk water samples.

**Additional information derived from spectroscopic techniques**

In order to justify further use of, and research into, spectroscopic techniques in water-quality monitoring, these techniques must provide unique information not available from existing methods or they must offer significant procedural efficiencies while providing similar, reliable and accurate information (as described above). In the case of both absorbance and fluorescence, the data derived from bulk water scans provided additional information regarding water source, flow paths and land use that cannot be derived from nutrient or bacterial analysis alone.

The utility of spectroscopic techniques in water-quality monitoring is based on the fluorescence and absorption properties of CDOM. The composition and concentration of CDOM is strongly influenced by land-use activities, among other factors (Leenheer and Croue, 2003; Ohno et al., 2006), and therefore these techniques provide insight into anthropogenic influences on water quality. Qualitatively, visual inspection of absorbance scans provides an indication regarding DOC concentrations, thus allowing simple visual distinction of surface-water and groundwater samples. Further, NO$_3^-$ contamination is easily determined by the presence of an absorbance peak at ~220 nm. Absorbance values also reflect DOC concentrations in surface waters and can therefore provide a relative indication of anthropogenic influence. It is important to note; however, that agricultural activities are not the only cause of increased DOC. Effluent from wetlands is also high in dissolved organics and can therefore produce significantly elevated absorbance values.

Further, the potential for spectral slope to represent CDOM composition could provide additional insights into CDOM provenance and therefore land-use influence on water quality. In the present study, spectral slope showed consistent results by land use, with higher values in forested and mixed catchments during dry conditions. A larger number of samples, collected over a range of meteorological and hydrological conditions is required to validate the utility of this technique in such environments.

As with absorbance, fluorescence scans provided additional information regarding anthropogenic processes governing water quality. Each EEM collected in this study contained a substantial amount of
information (8,742 data points). Initial reviews of EEMs provided an indication of the presence of agricultural influence (due to elevated fluorescence values). Elevated humic-like and fulvic-like fluorescence were consistently associated with agricultural and urban influence, while protein-like fluorescence was observed only in cases of intensive agricultural influence.

Ultimately, the benefit of absorbance and fluorescence parameters is that they are responsive to agriculturally-derived CDOM. As a result, they appear to represent effective proxy indicators for contaminants derived from agricultural activities.

**Dissolved organic matter: the link to process and land use**

As noted by Ohno et al. (2006), little work has been done to characterize the DOM derived from agricultural amendments in terms of molecular weight. This recent work, however, noted characteristic properties of agriculturally-derived CDOM that are in agreement with the results described in Chapter 6 and Chapter 7. The increased molecular weight associated with CDOM derived from manure and decaying crop residues produced elevated fluorescence and absorbance values in agricultural subcatchments across the three watersheds. Further, these values increased with agricultural intensification, indicating that absorbance (particularly SUVA$_{280}$ and A$_{280}$) and fluorescence (humic-like and protein-like) are useful indicators of agricultural influence on surface waters.

Due to the unique spectroscopic signatures associated with different land uses and water sources, measurements of both absorbance and fluorescence over finer temporal scales (i.e., storm events) have the potential to provide insight into flow routing, source areas, watershed-scale DOM dynamics and mechanisms of contaminant loading and transport. The patterns of absorbance and fluorescence observed over the storm event in the Hatzic watershed indicated that CDOM inputs were strongly linked to flow, but that concentrations of individual CDOM components varied over time, potentially as a function of availability. Further work is required to evaluate the potential of these techniques to provide greater insight into these processes.

**Limitations associated with absorbance and fluorescence**

Ultimately, in order to be effective, absorbance or fluorescence parameters must improve the ability to manage the risks associated with surface-water contamination. The advantages described above suggest that this may be possible. However, a significant limitation to these technologies exists.
Where contributions of agriculturally-derived CDOM to surface waters are limited, neither fluorescence nor absorbance provided a reliable indication of water-quality risk. Elevated bacterial and nutrient concentrations did not produce a commensurate response in fluorescence or absorbance values. As a result, it appears the utility of these techniques is lower in areas with limited anthropogenic influence. However, even in undisturbed watersheds, the processes associated with surface-water contamination with wildlife-derived fecal material may also produce unique CDOM signals. There is an opportunity for further research to assess the potential of these techniques to act as proxies for such processes (much as turbidity is currently used for the majority of municipal water systems deriving water from surface sources).

Another limitation of these techniques is that they are predominantly laboratory-based, thus limiting the potential for real-time monitoring. However, Baker et al. (2004) demonstrated the potential of handheld spectrophotometers to provide similar data in the field in near-real time, thus indicating that field-based spectrophotometric monitoring is feasible. The next significant hurdle will be the implementation of field-based systems which collect and transmit real-time monitoring data. The system produced by Joule Microsystems was initially included in this study to assess the utility of real-time spectrophotometric data; however, as described in Appendix A, logistical and mechanical complications prevented further evaluation.

8.3. Limitations and opportunities for future work

This research has contributed to the existing body of knowledge regarding agricultural impacts on surface waters in rural catchments. It is important; however, to acknowledge challenges and limitations associated with the study, as well as opportunities for future research.

Challenges associated with field-based monitoring programs

The rationale and benefits of a multi-watershed study are clear when assessing geophysical and hydrological processes at a range of scales. Ideally, each watershed would have sufficient monitoring equipment in place to continually record hydrometric and meteorological data. In this study, such equipment was installed in the Hatzic watershed. For the Elk Creek and Salmon watershed, municipal monitoring stations were used. Due to maintenance and vandalism issues; however, much of the data
collected could not be used with confidence. This imposed limitations on the ability to evaluate contaminant cycling processes at similar temporal scales across all watersheds.

As noted in Appendix A, vandalism also resulted in the destruction, and ultimately, the removal of field-based spectrophotometers which represented a significant opportunity to further test the utility of absorbance and fluorescence for real-time contaminant detection. As a result of this the decision was made to focus on laboratory-based techniques.

**Sample size for spectrophotometric analysis**

While the results above suggest that absorbance and fluorescence techniques are promising tools for water-quality monitoring in agricultural watersheds, it is recognized that there are limitations associated with sample size. While sampling for spectroscopic analysis encompassed a broad range of land uses, samples were only collected on three occasions, thus limiting the range of meteorological and hydrological conditions represented. Samples collected over an entire water year would provide the range of conditions necessary to gain an improved understanding of the links between agriculturally-derived CDOM and agricultural contamination of surface waters. Further, while the trends and correlations observed for fluorescence and absorbance data were consistent and significant, it is acknowledged that a larger sample size would add further support to the conclusions described above.

**Challenges associated with statistical analysis**

As noted in Chapter 3 (Methods), a common challenge in the analysis of environmental data is the proper use of inferential statistics when data points are either spatially or temporally related or dependent. This violates a critical assumption of standard inferential tests, which require that replicates be independent. The result, referred to by Hurlbert (1984) as pseudoreplication, results in an increased likelihood of Type 1 error, (erroneously rejecting the null hypothesis). In this study, the issue of temporal pseudoreplication was addressed by aggregating all data to the site level for comparisons between land-use types, watersheds or seasons. This resulted in a substantial decrease in sample size (by up to an order of magnitude), and therefore, in statistical power. Thus, the discussions and conclusions presented above represent a conservative interpretation of the data. It is likely that these analyses contain Type 2 errors; however, it was decided that a conservative approach to interpretation was more appropriate than drawing conclusions from invalid results.
A potentially effective approach to addressing the issue of pseudoreplication is the use of linear mixed models, which do not require that observations be independent. Such models have been used extensively in the social sciences, and where data are hierarchical (i.e., data points are clustered within nested groups), a variation on the model (hierarchical linear models) has proven very effective (see Raudenbush and Bryk, 2002). A useful analogy can be found in the assessment of academic performance in a school setting where students are grouped into classes, which are in turn grouped into schools and districts. In a similar way, the environmental data described above are grouped at the site, land-use category and watershed levels. A significant opportunity exists to assess the appropriateness of hierarchical linear models for this type of data in order to increase statistical power and, therefore, the ability to more accurately detect the impacts of land use on water quality and spectroscopic variables.

**Opportunities for future research**

There are several recommended areas of focus for future research into spectrophotometric techniques. Firstly, it is important to further characterize the sources of fluorescence in agricultural runoff in order to gain a better understanding of the utility of this technique as a tool for detecting contamination events. This could be accomplished through the analysis of individual components of agricultural runoff, including undiluted effluent from manure storage facilities, DOC extracted from agricultural soil samples and laboratory-cultured coliform bacteria [building on the work of Baker (2002b) and Elliott et al. (2006a)]. It is also important to assess the influence of meteorological conditions on fluorescence parameters, and to determine if the correlations described above remain consistent over time. This could be accomplished through the collection of fluorescence data over an entire water year, and further storm-based sampling. The degree to which urban/residential effluent contributes to stream CDOM should also be assessed in order to determine the potential of this technique to further discriminate between CDOM sources. This would be best accomplished through the direct analysis of urban storm-water runoff and of septic tank effluent.

While it appears that the potential to detect contaminants in undisturbed or minimally-disturbed watersheds is limited, it would be useful to determine if fluorescence and/or absorbance offer any advantages over turbidity as an indicator of water-quality risk. These techniques may address the limited specificity of turbidity as an indicator if there are links between CDOM and pathogen transport in undeveloped watersheds.
Based on the characteristic absorbance and fluorescence properties of agricultural runoff, there is an opportunity to assess the potential of these parameters to act as proxies for human and animal pathogens that are more difficult to detect and enumerate, such as viruses and protozoa. Other commonly-used proxies (indicator bacteria and nutrients) do not show consistent correlations with these pathogens due to differences in decay rates, production rates, susceptibility to environmental stressors and in mechanisms of mobilization and transport. Assuming there would be a link between agriculturally-derived CDOM and protozoan and viral transport, spectroscopic parameters could offer significant advantages over existing monitoring techniques. This could be assessed through concurrent sampling and analysis for viral and protozoan concentrations and absorbance and fluorescence parameters in areas with intensive livestock operations.

Finally, one of the biggest opportunities associated with this technology is the ability to detect changes in water quality in real time through the use of field-deployed absorption spectrophotometers. This would provide a leading indicator of water contamination and support a more proactive approach to water-quality management in a "source-to-tap" model. Unfortunately, due to vandalism and technical challenges, this was not possible as part of this study. However, further work to address the difficulties is recommended as this represents a significant step towards real-time risk management for drinking-water sources. Such real-time data could provide an early indication of contamination and support immediate interventions that would minimize the impact on downstream populations.

In conclusion, this study has addressed several of the research gaps identified by numerous authors regarding agricultural influence on water quality (BC Auditor General, 1999; BC Provincial Health Officer, 2001; Chambers et al., 2001; Environment Canada, 2001; Krewski et al., 2002) and summarized in Chapter 1. It has built on the existing literature and contributed to improved understanding in these areas by providing: 1) an improved understanding of trends and processes involved in agricultural contaminant cycling at different spatial and temporal scales, 2) a record of patterns of pathogen indicator dynamics (in terms of timing and intensity) in undisturbed sub-catchments and 3) a clearer understanding of the relative influence of contamination "hot spots" vs. watershed-scale agricultural land-use patterns on surface-water quality. It has also addressed the question of agricultural intensity, and its impact on surface-water quality at the plot and watershed scale, and provided greater insight into the behaviour of watershed-scale nutrient and bacterial stores. Finally, to address challenges associated with current monitoring technologies, it has contributed to the existing literature on environmental applications of
spectroscopy by focusing specifically the links to nutrient and bacterial contamination in freshwater, agricultural environments. This assessment indicated that these techniques provide additional insight into surface-water quality, mechanisms of contaminant mobilization and transport and water routing. They also indicate that these tools have the potential to improve understanding of the processes of agricultural influence on surface waters and to address the need for a more effective assessment of water-quality risk assessment from point and non-point sources in agricultural watersheds.
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Appendix A - Real-time, field-based spectroscopic sensors

An initial objective of the present study was to assess the potential to develop and install a real-time, field-based spectroscopic sensor. Such a sensor, providing real-time data regarding the absorbance and fluorescence characteristics of surface water, could support more proactive management of water-quality risk, particularly in drinking-water source watersheds.

A partnership was established with Joule Microsystems, Inc., a company based in Delta, BC to pursue this objective. Joule Microsystems, Inc. developed real-time spectroscopic sensors known as Water Risk Control Points (WRCP) that utilized advanced algorithms to process and transmit water-quality data in near-real-time (i.e., data are transmitted in packets representing several minutes or hours). These sensors were equipped with cellular technology that supported transmission of spectroscopic data to an internet-accessible database. These systems were designed to be used in drinking-water distribution systems as a means to detect minute changes in drinking-water quality that may represent contamination or the need for infrastructure maintenance. A project was initiated to make adaptations to this technology to support: 1) analysis of raw surface water (and thus extend the reach of the sensor network to the water source) and 2) wireless transmission of spectroscopic data from remote field locations (the Elk Creek and Salmon watersheds).

A system was initially installed in the headwaters of the Elk Creek watershed. This site was chosen as there was a small building with a dedicated power supply located nearby, that could be used to house and power the sensor. A submersible pump (with a filter) was anchored to large boulders in the headwaters of the Elk Creek and a 3.8 cm flexible pipe was used to connect the pump to the sensor (Figure A1). Water was pumped approximately 35 m from the creek to the sensor where data were collected. The water then flowed out of the building and into a large storage tank that eventually drained back into the creek. A spin-down filter was installed in the pipe just prior to the sensor in order to remove particulate matter that may interfere with measurements or result in sensor fouling.
Figure A1 - a) submersible pump with power cable and pipe leading to spectrophotometer, b) secure building and trench leading from pump to sensor, c) Joule Microsystems, Inc. Water Risk Control Point sensor with automated anti-fouling system and cellular modem.
Unfortunately, after installation, this system was vandalized beyond repair before it became fully operational, and no usable data were collected. A second system was installed in the Salmon watershed near Langley. A tipping-bucket raingauge was also connected to the WRCP to support real-time transmission of rainfall and spectroscopic data. Initially, communications issues were encountered at the second system; however, these were addressed by Joule Microsystems, Inc., and rainfall data and spectroscopic data were transmitted successfully. However, analysis of spectroscopic data suggested significant sensor fouling was taking place due to high organic-matter and sediment loads during storm events. This was confirmed through subsequent site visits. Adaptations to the system were planned to address these issues; however, due to time constraints, it was not possible to include further testing as part of this study.