Developing Novel Techniques for Measuring In Situ Groundwater Nitrate Concentrations, Vertical Geochemical Profiling, and Real-time Remote Groundwater Quality Monitoring

by

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ABSTRACT

DEVELOPING NOVEL TECHNIQUES FOR MEASURING IN SITU GROUNDWATER NITRATE CONCENTRATIONS, VERTICAL GEOCHEMICAL PROFILING, AND REAL-TIME REMOTE GROUNDWATER QUALITY MONITORING

Graeme Daniel MacDonald
University of Guelph, 2015

Advances in field measurement techniques are required to improve our understanding of nitrate fate and transport in groundwater. This study applied innovative sensor equipment to develop novel techniques for in situ groundwater quality monitoring. Three unique methods were developed: modified flow cell testing, vertical geochemical profiling, and real-time remote monitoring (RTRM). While nitrate was the contaminant of focus, additional parameters including temperature, pH, EC, DO, turbidity, and groundwater levels were also monitored. Testing was conducted in different hydrogeological systems ranging from unconfined sandy aquifers (Norfolk County, Ontario, Canada) to fractured Silurian bedrock aquifers (Guelph, Ontario). Nitrate sensor readings were strongly correlated ($R^2=0.994$) to laboratory measurements obtained using traditional purging methods. RTRM techniques allowed for hourly groundwater quality monitoring over several months. The high temporal resolution datasets obtained will support future nitrate transport modeling initiatives and complement field projects in which detailed in situ nitrate measurements are desired.
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<td>ACF</td>
<td>Autocorrelation function</td>
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<tr>
<td>BAFF</td>
<td>Bedrock Aquifer Field Facility</td>
</tr>
<tr>
<td>BGS</td>
<td>Below ground surface</td>
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<tr>
<td>BMP</td>
<td>Best management practices</td>
</tr>
<tr>
<td>CCF</td>
<td>Cross-correlation function</td>
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<tr>
<td>DIW</td>
<td>Deionized water</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
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<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
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<tr>
<td>EC</td>
<td>Electroconductivity</td>
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<td>EXO</td>
<td>YSI field parameter sensor</td>
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<td>GMWL</td>
<td>Global Meteoric Water Line</td>
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<td>LPT3</td>
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<tr>
<td>OMAFRA</td>
<td>Ontario Ministry of Agriculture, Food and Rural Affairs</td>
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<tr>
<td>ORP</td>
<td>Oxidation-reduction potential</td>
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<td>ROW</td>
<td>Region of Waterloo</td>
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<td>SUNA</td>
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1 Introduction

1.1 Background

In Ontario alone, almost 30% - or 3.6 million citizens - depend on groundwater for their water supply (Government of Canada, 2013). These important groundwater resources must be protected from contamination. It is well known that groundwater is vulnerable to contamination due to anthropogenic activities at the surface (e.g. Almasri & Kaluarachchi, 2007; Burkart & Stoner, 2002; Gillham, 1991; Goss et al., 1998; Hallberg, 1989; Levison & Novakowski, 2009; Spalding & Exner, 1993). Contaminants associated with these activities can leach into the subsurface and impact groundwater quality. It is important to study these contaminants and their fate and transport within the subsurface in order to develop well-informed water supply management strategies.

The study of groundwater contaminants is particularly important in rural areas, which depend almost entirely on private wells (Goss et al., 1998; Levison & Novakowski, 2009). Approximately nine million Canadian citizens are reliant upon groundwater for domestic use; two thirds of which live in rural areas (Government of Canada, 2013). It is well documented that agriculture can impact groundwater quality (e.g. Bouwer, 1989; Goss et al., 1998; Levison & Novakowski, 2009) in different regions across Canada. Contaminants of concern include pesticides, pathogenic microorganisms and fertilizers. Nitrate contamination in groundwater is essentially ubiquitous in rural areas in southern Ontario (Gillham, 1991). Goss et al. (1998) conducted an extensive groundwater quality monitoring study in rural Ontario wells, and determined that approximately 15% of wells had elevated nitrate concentrations above the Ontario Drinking Water Quality Standard (10 mg/L NO$_3^-$ as N). A follow-up investigation was conducted in November 2010 at three of the same wells sampled by Goss et al. (1998), and noted that the wells were still vulnerable to nitrate contamination (Nottawasaga Valley Conservation Authority, 2011). Ingestion of nitrate in drinking water has important human health impacts, and has been linked to diseases including methemoglobinemia or “blue baby syndrome,” nervous system birth defects, non-Hodgkin’s lymphoma and stomach cancers (Almasri & Kaluarachchi, 2007; Kerr-Upal et al., 1999; Spalding & Exner, 1993). It is critical to understand the processes that influence nitrate contamination due to its widespread occurrence, persistence and potential human health impacts.
The hydrogeologic conditions which govern many of Canada’s aquifers render them particularly vulnerable to nitrate contamination. For example, agricultural regions situated upon coarse-grained overburden aquifers have proven vulnerable to nitrate contamination in several studies (e.g. Best et al., 2015; Burton, 2007; Egboka, 1984; Gillham, 1991; Hollingham, 2011; Kerr-Upal et al., 1999; Robertson, Cherry & Sudicky, 1991). Similarly, it has been established that fractured bedrock aquifers can be vulnerable to nitrate contamination in locations in Ontario (e.g. Best et al., 2015; Green et al., 1998; Levison & Novakowski, 2009; Opazo, 2012) and Prince Edward Island (e.g. Jiang et al., 2015; Zebarth et al., 2015). It is therefore prudent to monitor nitrate concentrations in groundwater across different physical settings to better understand the relationships between hydrogeologic conditions and nitrate contamination.

Nitrate transport and fate is influenced by many factors, including soil type and chemistry, climate, topography and land use (Goss et al., 1998; Benson et al., 2006; Bouwer, 1989; Rivett et al., 2008). It involves complex processes that are highly variable both spatially and temporally (Benson et al.; Fraters et al., 1998; Levison, 2009; McLay et al., 2001; Rivett et al., 2008). This variability can make monitoring initiatives for nitrate contamination in groundwater quite challenging. Traditional sampling is conducted by purging a well(s) and extracting water samples to be analyzed ex-situ in a laboratory setting (Brassington, 1998; Nielsen & Nielsen, 2007). These discrete samples represent the conditions present within a specific window of time, and therefore may be insufficient at capturing the spatial and temporal variability of nitrate concentrations (Levison & Novakowski, 2009), as well as vertically stratified nitrate concentrations along the well column (WESA Inc., 2012). Ontario’s Safe Drinking Water Act (2002) dictates that nitrate sampling in public supply wells should be conducted at least once every three months (Government of Ontario, 2014). In some cases, it is possible that discrete sampling at this interval will not sufficiently capture variations in nitrate concentrations in space and time, with potential implications on human health (Levison & Novakowski, 2009).

As groundwater monitoring and source water protection initiatives continue to be refined, there exists a need for the development of novel groundwater nitrate monitoring techniques. Traditional field sampling methods have been limited spatially and temporally, with more potential for data quality issues due to extended holding times and recording issues (Glasgow et al., 2004). It is evident that continuous and in situ monitoring initiatives would be useful to further evaluate nitrate fate and transport in groundwater. Continuous monitoring methods could better capture temporal variability and trends while improving understanding of nitrate transport and
attenuation processes, which are controlled by heterogeneity of aquifer properties as well as the dynamic nature of nitrogen inputs and reactions. In situ measurement methods can complement traditional purging techniques by better capturing the dynamic nature of nitrate transport and attenuation. Thus, the goal of this research study was to develop and evaluate innovative, continuous and in situ measurement methods for nitrate in groundwater.

1.2 Objectives and Approach

This research investigated the application of innovative groundwater monitoring equipment to develop techniques for in situ nitrate concentration measurements, vertical geochemical profiling, and continuous, real-time remote monitoring. While nitrate was the parameter of interest, other standard field parameters (temperature, pH, EC, DO and turbidity) were also monitored to provide additional insight and complement the nitrate data. Three main research locations (Norfolk County, Guelph and Waterloo, Ontario, Canada) were investigated to examine a range of hydrogeological settings, from shallow, unconfined sandy aquifers to fractured bedrock aquifers. Two sensors were used in this research project: the Submersible Ultraviolet Nitrate Analyzer (SUNA™) by Satlantic (Satlantic Inc., Halifax, NS, Canada), and EXO™ Water Quality Sonde by YSI (Yellow Springs Inc., Yellow Springs, OH, United States), along with an integrated telemetry system (Hoskin Scientific Ltd., Burlington, ON, Canada). The sensor equipment and their associated techniques will be discussed in the subsequent sections of this thesis.

Specific objectives for this research were as follows: 1) develop a protocol to evaluate and test techniques for groundwater nitrate measurements in the field, and demonstrate the precision and accuracy of sensor equipment; 2) determine spatial variability of well geochemistry, which is typically purged and sampled as a composite (single value) for nitrate and hydrochemistry; 3) determine temporal variability of well geochemistry using continuous, real-time remote monitoring methods; 4) assess spatial relationships and temporal trends regarding geochemical variability, particularly with respect to recharge events, and; 5) obtain high resolution geochemical datasets to complement future modeling initiatives.

1.3 Thesis Outline

Chapter Two of this thesis presents findings from a literature review conducted prior to commencing the field research. Nitrate contamination in groundwater, groundwater quality monitoring, and applications of the monitoring equipment used in the study are covered. Chapter Three describes the research sites, including climate, land use and surficial geology, as
well as any previous nitrate studies conducted nearby. Research sites were selected to expose
the monitoring equipment to a range of hydrogeological conditions while acknowledging
logistical constraints associated with the equipment. Chapter Four discusses the methodology
and method development processes, including a detailed description of the monitoring
equipment, field techniques, and data extraction/analysis upon completion of monitoring.
Chapter Five presents and discusses the results in context of the project objectives, and
Chapter Six provides conclusions and recommendations for further study.
2 Literature Review

2.1 Nitrogen Cycle

The nitrogen cycle is a complex system, as shown in Figure 2.1. In hydrogeological systems, important compounds within the nitrogen cycle include nitrate (NO$_3^-$), nitrite (NO$_2^-$), ammonium (NH$_4^+$), aqueous nitrogen (N$_2$), organic nitrogen (N) and nitrous oxide (N$_2$O). Key processes include mineralization, nitrification, denitrification and leaching.

![Figure 2.1: Nitrogen cycle, adopted from Rivett et al. (2008). Particular attention should be paid to mineralization, nitrification, denitrification and leaching in groundwater environments](image)

The first process that occurs after nitrogen loading at the surface is mineralization, in which ammonium is released through the decomposition of organic compounds in the soil (Rivett et al., 2008). Microbial activity then transforms ammonium into nitrite and then nitrate through nitrification processes. Nitrate is a highly mobile form of dissolved nitrogen and therefore leaches into the groundwater system with infiltration processes (Pacheco et al., 2001; McKague, Reid & Simpson, 2005). Once nitrate leaching occurs, it is subject to advection-dispersion processes in conjunction with groundwater flow (Almasri & Kaluarachchi, 2007).
Nitrate concentrations can be decreased during infiltration through the vadose zone and saturated zone by several physical processes: dilution through recharge-induced fluxes, dispersion and diffusion resulting in blending of the well water within the screened interval, and by microbial-mediated reactions that are dependent on several hydrogeochemical parameters in the aquifer (Rivett et al., 2008). Denitrification is the dominant nitrate-reducing process in groundwater, where nitrate and/or nitrite are reduced to nitrous oxide and eventually nitrogen gas ($N_2$) (Burkart & Stoner, 2002; Gillham, 1991; Rivett et al., 2008). Denitrification processes have three general requirements: presence of an electron donor(s), anaerobic conditions and denitrifying bacteria (Rivett et al., 2008; Robertson, Russell & Cherry, 1996). The denitrifying bacteria that are required for denitrification processes are obligate anaerobic. Thus, anaerobic conditions are required, as the bacteria would use free oxygen before oxygen from nitrate for cellular respiration (Rivett et al., 2008). Denitrification reactions in the presence of an electron donor can be expressed with the following general half reaction, which illustrates the reducing role of the electron donor but is not specific to the donor compound itself:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$$

Organic carbon, reduced iron and sulphur compounds (e.g. pyrite) typically act as electron donors for denitrification reactions (Opazo, 2012; Robertson et al., 1996; Rudolph, Devlin, & Bekeris, 2015). These compounds are naturally present within sediments and bedrock, although it has been shown that denitrification rates are more closely related to dissolved organic carbon (DOC) in porewater or groundwater rather than the geologic substrate (Rivett et al., 2008). Some substrates are able to more easily supply electron donors and promote denitrification (Trudell, Gillham, & Cherry, 1986). Finer-grained silty and clayey sediments often possess more sulphur compounds or organic carbon, both of which consume oxygen, resulting in a reducing environment with negative ORP which is likely favourable for denitrification reactions (Robertson et al., 1996). Reduced iron may act as an electron donor in the absence of organic carbon or sulphur and is typically located within the geologic substrate (Best et al., 2015; Rivett et al., 2008). Studies in bedrock aquifers have indicated that ferrous compounds and sulfide minerals such as pyrite can act as primary electron donors even in the presence of organic matter (Opazo, 2012).
2.2 Nitrate Contamination in Groundwater

2.2.1 Nitrogen Sources

Nitrate is the most prevalent groundwater contaminant, and concentrations are creeping upwards worldwide (Spalding & Exner, 1993; Gillham, 1991; Rivett et al., 2008). Nitrate sources are derived from nitrogen and can be both point or non-point in nature, originating from fertilizers, animal manure storage facilities, septic systems, exercise yards, feed lots, and organic nitrogen and ammonium in the unsaturated zone (Aravena, Evans, & Cherry, 1993; Goss et al., 1998; Rivett et al., 2008; Trudell et al., 1986). Nitrate originating from manure and organic fertilizers is easiest to evaluate and compare (Burkart & Stoner, 2002). When conducting such evaluations, it is important to differentiate between natural (i.e. “background”) and anthropogenic (i.e. human induced) sources of nitrate. Oxidation of organic nitrogen and ammonium produces background nitrate concentrations that do not reflect the influence of anthropogenic activities. While these background concentrations may range from 0.2 mg L⁻¹ to 20 mg L⁻¹, a generally accepted threshold is approximately 2 mg L⁻¹, such that the presence of concentrations exceeding this threshold typically suggests the influence of anthropogenic-induced sources such as animal manures, septic plumes or fertilizers (Burkart & Stoner, 2002).

Nitrate sources can be identified through isotopic fingerprinting. Stable isotope ratios for nitrogen (¹⁵N/¹⁴N) and oxygen (¹⁸O/¹⁶O) are compared to standards to calculate δ¹⁵N and δ¹⁸O, which are expressed as percentages. Plotting δ¹⁵N and δ¹⁸O can aid in evaluating whether nitrate is sourced from soil organic (i.e. background) nitrogen, or nitrogen sourced from anthropogenic activities (i.e. septic or manure inputs or ammonia-based fertilizers), as shown in Figure 2.2 (Aravena et al., 1993; Hollingham, 2011; Mariotti, Landreau, & Beatrice, 1988; Opazo, 2012; Savard et al., 2010). It has been demonstrated that ¹⁸O and ¹⁵N are useful for identifying septic plumes and nitrate derived from human waste; however, it can be more difficult to isolate sources from fertilizers or organic soil nitrogen (Aravena et al., 1993). Hollingham (2011) recently applied a new technique for sourcing septic-based nitrate, where artificial sweeteners (acesulfame, saccharin, cyclamate and sucralose) were used as tracers, as these compounds are essentially nonreactive in the natural environment.
Figure 2.2: Isotopic composition ($\delta^{15}$N and $\delta^{18}$O) for various sources of nitrogen, adopted from Motzer (2006). Plotting $\delta^{15}$N and $\delta^{18}$O can also aid in evaluating whether or not denitrification is occurring.

2.2.2 Contributing Factors

Nitrate distribution in groundwater is largely a function of source characteristics along with site specific hydrogeological conditions (Burkart & Stoner, 2002). Source characteristics refer to the rate and concentration of nitrate leaching (Burkart & Stoner, 2002; Spalding & Exner, 1993; Kerr-Upal et al., 1999). Hydrogeological characteristics include climate (precipitation and recharge rates and distribution, average annual temperature and evapotranspiration, length and intensity of each season, snowpack/snowmelt), soil or bedrock type, aquifer heterogeneity, saturated thickness and dispersion (Kerr-Upal et al., 1999). As previously discussed, there are also geochemical factors to consider, such as dissolved oxygen concentrations and electron donor availability, which govern nitrate attenuation processes (Aravena et al., 1993; Spalding & Exner, 1993).

2.2.2.1 Groundwater Extraction

Groundwater nitrate concentrations are influenced by human activities. For example, pumping regimes can affect nitrate fate and transport in the subsurface (Knapp, 2005). However, the complexity of hydrogeological systems results in uncertainty at any given location as to whether
altering the pumping rates will increase or decrease groundwater nitrate concentrations. An assessment conducted in Waterloo Region showed that at one location, from 1998-2011, lower pumping rates resulted in increased nitrate concentrations. In the same study, evidence suggested that pumping wells can act as a conduit for flow between different screened aquifer units, resulting in mixing of the groundwater geochemistry (WESA Inc., 2012). Another study conducted at the Thornton Wellfield in Oxford County, Ontario, suggest that increasing pumping rates can increase observed nitrate concentrations, particularly when considering an up-gradient contaminant plume (Haslauer, 2005; Koch, 2009). There is evidence from five wells in the Thornton well field that pumping rates affect nitrate concentrations. Another study demonstrated that high capacity wells tend to have lower nitrate concentrations, as they pump from a longer vertical interval and are therefore able to dilute concentrations (Spalding & Exner, 1993). It is likely that more detailed analyses would help improve understanding between groundwater extraction and nitrate transport.

2.2.2.2 Irrigation

Irrigation can impact groundwater nitrate concentrations, since it increases the vertical transport of nitrate into the groundwater system (Spalding & Exner, 1993). It can promote nitrate leaching by increasing groundwater recharge. Since irrigation is often used for crops with high nitrogen fertilizer demand, such as corn, wheat and soybeans, it can exacerbate the nitrate leaching effect (Burkart & Stoner, 2002). Leaching rates can be reduced through drip delivery of both water and nutrients. A study conducted in Norfolk County using drip irrigation instead of traditional overhead methods reduced nitrate leaching rates beneath cucumber by 10 kg ha\(^{-1}\) after three years (Bruin et al., 2010). Schepers, Varvel and Watts (1995) conducted a similar study beneath maize crops in Nebraska, and found that using surge flow and fertigation methods reduced nitrate leaching by 168 kg ha\(^{-1}\) and 105 kg ha\(^{-1}\) in consecutive years.

2.2.2.3 Land Use

Several studies have examined different land use categories and the diffuse nitrate sources that they introduce into groundwater. Some research has suggested that no specific land use results in significantly more groundwater nitrate contamination (e.g. Gillham, Blackport, & Cherry, 1978; Goss et al., 1998). However, it has been noted that natural wooded areas appear to have some assimilative capacity for groundwater nitrate. McLay et al. (2001) observed that groundwater nitrate concentrations in New Zealand were generally not related to land use, except in market garden areas, where average concentrations were slightly higher. Burkart and Stoner (2002) consolidated data from more than 10,000 wells and noticed that nitrate concentrations were
significantly larger beneath three different agricultural operations: cattle and grains; corn, soybean and hogs; and small grains. Another study conducted in Korea suggested that nitrate samples from 12 wells exceeded the 10 mg L\(^{-1}\) national standard 0, 23, 43 and 67% of the time beneath natural areas, cropping areas, cropping and livestock areas, and residential areas, respectively (Choi et al., 2007). The higher concentrations in residential areas were attributed to the presence of septic plumes. However, while septic plumes can certainly increase groundwater nitrate concentrations, it is unlikely that point-source septic plumes will always be intercepted by drinking water wells, as many wells have relatively small areas of influence (Spalding & Exner, 1993). Therefore, it may be more prudent to emphasize non-point sources when considering nitrate contamination of groundwater.

2.2.2.4 Legacy Effect

Groundwater nitrate concentrations are often subjected to legacy effects from previous activities that result in nitrogen loading in the unsaturated zone (Baily et al., 2011). This mass of nitrogen is the by-product of many years of nitrogen application at the surface (Best et al., 2015; Haslauer, 2005). It must be flushed from the unsaturated zone through infiltration before the effects of any land use changes can be observed (Bekeris, 2007). This can make it difficult to implement remediation or best management practices (BMPs), as there is often a lag time between reduction of nitrogen application at the surface and reduction of groundwater nitrate (Jiang et al., 2015; Baily et al., 2011; Burkart & Stoner, 2002; Koch, 2009; Zebarth et al., 2015). This lag time is influenced by geology, attenuation, recharge and flow rates, among other factors (Stotler, Frape & Labelle, 2014). A study conducted in France beneath an agricultural site determined that approximately 12-15% of fertilizer nitrogen persisted in the unsaturated zone 25 years after surface application (Sebilo et al., 2013). Another study at the Thornton well field in Woodstock, Ontario predicted a 6-17% decrease in groundwater nitrate over a 15 year period following BMP implementation (Haslauer, 2005). Response times and magnitudes can differ depending on hydrogeologic conditions. For example, groundwater responses to BMPs are often observed sooner in shallow systems where the soil is well-drained, as travel times are much faster (Rudolph et al., 2015; Fraters et al., 1998). Similar rapid responses can be observed in bedrock aquifers due to rapid flow through fractures, and because mass storage in the low permeability matrix is minimal (Levison & Novakowski, 2009). Since many important production wells are situated in deeper aquifers, they are more susceptible to legacy effects. Therefore, any nitrate management strategies must consider these legacy effects while recognizing that nitrate could persist in the subsurface for many years (Sebilo et al., 2013).
2.2.3 Aquifer Vulnerability

Site specific hydrogeological conditions are often more influential than the surrounding land use in contributing to aquifer vulnerability to nitrate contamination (McLay et al., 2001). In temperate climates similar to those in southern Ontario, nitrate is most readily available for leaching into groundwater outside of the growing season, with recharge events occurring in the spring and fall along with reduced plant N-uptake. Since this often coincides with periods of high fertilizer application rates, many aquifers are vulnerable to contamination (Burkart & Stoner, 2002; Sebilo et al., 2013).

Aquifer vulnerability to nitrate contamination is a function of the aforementioned source and site specific hydrogeological characteristics. Thus, some aquifers have been identified as being generally more vulnerable to contamination than others. Shallow unconfined aquifers are likely the most vulnerable to nitrate contamination, since they are closer to the source and typically have rapid recharge (Baker et al., 1989; Best et al., 2015; Burkart & Stoner, 2002). Unconsolidated sediments and permeable soils are also associated with high vulnerabilities. Goss, Barry and Rudolph (1998) suggest that permeable sands and gravels are most susceptible to nitrate contamination, and clayey sediments are least susceptible. Coarse grained materials have reduced travel times and therefore can promote rapid nitrate leaching (Best et al., 2015), and are more likely to have oxidizing conditions, as discussed in section 2.1.

Bedrock aquifers present moderate risk to nitrate contamination (Opazo, 2012), as they are often subject to varying degrees of protection by overburden aquifers (Burkart & Stoner, 2002) but can have large groundwater velocities and rapid response times (Levison & Novakowski, 2009; Pacheco et al., 2001). It is important to consider the processes controlling flow and transport in bedrock aquifers. While flow can be governed by matrix porosity in the bedrock portions of the vadose zone in numerous rock types, fracture networks present within the bedrock can dominate flow processes, such that nitrate is transported rapidly through the saturated zone (Zebarth et al., 2015).

2.2.4 Nitrate Attenuation

Vulnerability to nitrate contamination is also largely affected by the aquifer’s ability to naturally attenuate nitrate. As discussed in section 2.1, nitrate attenuation in groundwater typically occurs through microbial-induced denitrification processes in the presence of an electron donor(s) (Robertson & Cherry, 1995). Other processes such as advection and dispersion/diffusion
processes are ineffective at attenuating nitrate plumes *in situ* (Robertson et al., 1991), although they can dilute concentrations by transporting them through a larger aquifer volume. When subsurface conditions favour denitrification processes, nitrate concentrations can be reduced, even to non-detect levels; in contrast, unfavourable conditions for denitrification can result in high nitrate concentrations that are persistent (Egboka, 1984). Important contributing factors for denitrification include depth below surface, dissolved oxygen concentrations and redox conditions, aquifer thickness, position of overlying hydrogeologic units and sediment composition. Rates of denitrification will typically increase with respect to depth, as evidenced by decreasing nitrate concentrations with depth (Best et al., 2015; Goss et al., 1998; Hallberg, 1989) having a corresponding decrease in DO and transition to reducing conditions (Best et al., 2015; Egboka, 1983; Opazo, 2012; Trudell et al., 1986).

Denitrification processes have been shown to occur along discrete boundaries in the subsurface. Trudell et al. (1986) identified a specific zone of denitrification where nitrate concentrations decreased along a gradient from oxidizing to reducing conditions. This *redoxcline* was located at the boundary between weathered and unweathered sediments, suggesting similar boundaries could occur along intervals of only 1 m thickness (Robertson, Russell, & Cherry, 1996; Rivett et al., 2008). Opazo (2012) noticed a similar discrete boundary in the dolostone aquifer around Guelph, where nitrate did not persist below the Eramosa Formation due to reducing conditions and presence of pyrite acting as a suitable electron donor. Other studies have demonstrated that denitrification rates are temporally variable (e.g. Robertson and Cherry, 1995). Denitrification mechanisms also appear to be spatially variable depending on which electron donor species are present. In some cases, both dissolved organic carbon and sulfide compounds can act as electron donors (Aravena & Robertson, 1998; Levison, 2009).

Site-specific hydrogeological data is gathered to provide evidence for denitrification. The general approach used is to collect redox, DO and DOC measurements and complement them with ion and isotropic analyses (Aravena et al., 1993). Fingerprinting for $\delta^{15}$N and $\delta^{18}$O can identify reducing zones, as fractionation during denitrification process causes these isotope levels to increase (Aravena et al., 1993; Hollingham, 2011; Mariotti et al., 1988; Opazo, 2012; Savard, et al., 2010). Redox (ORP/Eh), DO and DOC measurements can help confirm that anoxic conditions in the presence of a suitable electron donor(s) are evident, suggesting that
denitrification is favourable. Sampling for ferric and sulphur compounds is also conducted if it is likely that they are acting as electron donors rather than DOC.

Recent studies have demonstrated the potential for artificially inducing denitrification processes using a unique remediation technique. The cross-injection system (CIS) uses a network of wells located both up- and down gradient of the contaminated site. Acetate is injected up gradient and drawn across the site by pumping the down gradient well(s). Pumping is then halted and the acetate pulse is able to travel across the site, stimulating denitrification. Acetate is added in separate pulses depending on the nature of the site and its degree of contamination. The CIS is particularly useful for sites subject to large legacy effects, as it can be used to decrease nitrate concentrations while waiting for changes to occur due to the implementation of BMPs (Critchley et al., 2014; Gierczak, Devlin & Rudolph, 2014; Rudolph et al., 2015).

2.2.5 Vertical Trends

Several studies have evaluated vertical trends of nitrate concentrations in groundwater. It is clear that in most cases, nitrate concentrations decrease with depth (Best et al., 2015; Burkart & Stoner, 2002; Egboka, 1984; McLay et al., 2001; Opazo, 2012; Goss et al., 1998; Robertson, Russell et al., 1996; Spalding & Exner, 1993; Trudell et al., 1986). It is also evident that nitrate is often vertically stratified in the subsurface due to the presence of redoxclines. For example, Egboka (1984) observed vertical nitrate stratification at sites in southern Ontario, with concentrations ranging from 105.5 mg L\(^{-1}\) in the upper aquifer at some locations, to <1.0 mg L\(^{-1}\) in the lower aquifer. Robertson et al. (1996) observed nitrate concentrations between 5 to 50 mg L\(^{-1}\) in the upper 3 to 5 m of shallow groundwater, with a rapid decrease upon approach of the redoxcline. Best et al. (2015) observed similar stratification within the upper 3 to 5 m, with decreases in nitrate concentrations from approximately 3 to 6 mg L\(^{-1}\) to <1.0 mg L\(^{-1}\). However, analysis at one bedrock borehole showed an increase in nitrate concentration with depth, which may be attributed to the variability of flowpaths (position of recharge to inputs and times of travel) in groundwater flow systems (Best et al., 2015). It is important to consider the location and construction of boreholes within the 3-D groundwater flow system when assessing vertical trends in groundwater nitrate. Sometimes, the design of the well, including screen size and extent of the seal can affect water quality by altering the vertical stratification characteristics of nitrate in the subsurface (WESA Inc., 2012).
2.2.6 Temporal Trends

Temporal trends of groundwater nitrate have also been evaluated in several studies. Nitrate concentrations at some locations in New Zealand were found to be highly temporally variable between two sampling dates, with larger values in fall than spring. Concentrations at one site ranged from approximately 7 mg L\textsuperscript{-1} in March 1995 to 22 mg L\textsuperscript{-1} in September 1995 (McLay et al., 2001). Pacheco et al. (2001) sampled monthly for nitrate at 12 different supply wells for one year in Mexico (1992 to 1993) and noted that concentrations typically decreased during the wet season due to dilution effects.

In agricultural regions in Canada, it is well established that nitrate contamination is most likely to occur in the spring and fall, when higher soil nitrate concentrations typically corresponding to nutrient applications are present in conjunction with recharge events. However, leaching may also occur during the growing season resulting from large rainfall events (Zebarth et al., 2015). Levison and Novakowski (2009) observed similar seasonal trends within a crystalline aquifer with thin overburden (less than two metres thick) near Perth, Ontario, where nitrate concentrations in two monitoring wells peaked around October, which suggests the higher concentrations might be correlated to autumnal recharge or nutrient source availability at the surface. However, Rudolph et al. (1998) evaluated the temporal variability in nitrate concentrations across Ontario by sampling two times per year (one winter and one summer sample), and suggested that there are no apparent temporal trends. Much uncertainty exists with sparse sampling frequencies. Thus, such studies may be complemented by new techniques that would allow for many samples to be measured over a longer time period.

2.2.7 Preferential Pathways

Since nitrate is transported mainly with groundwater advection, it is governed by the same preferential pathways that affect groundwater flow. Evidence suggests that preferential pathways occur in both the unsaturated and saturated zones and are influenced by the layering and heterogeneity of hydrogeologic units (Best et al., 2015). These pathways can induce rapid transport and increase nitrate concentrations, especially when correlated with recharge events (Levison & Novakowski, 2009; Opazo, 2012; Zebarth, et al., 2015). Nitrate and other surficial contaminants can be quickly transported with recharge through desiccation cracks in soil (Spalding & Exner, 1993) and fractures in bedrock (Levison & Novakowski, 2009), reducing the residence time and therefore the natural attenuation capacity within the aquifer.
It is clear that preferential flow pathways are prevalent across many hydrogeological settings and can influence nitrate transport and fate. Roberston et al. (1996) observed near-vertical fractures in silty sediment core samples taken from five different sampling sites in southern Ontario. They suggested that preferential pathways also exist through aquitards, limiting their ability to attenuate nitrate. Similar pathways have been observed in the fractures located throughout bedrock aquifers in Ontario. Best et al. (2015) observed higher nitrate concentrations at a larger depth from surface at one location near the Guelph area, suggesting the presence of preferential flow through fractures. Levison and Novakowski (2009) observed rapid peaking of nitrate and pathogen concentrations after recharge events, suggesting rapid transport through fracture flow in the subsurface. While preferential flow has been observed in the overburden above these bedrock aquifers in many cases, the overburden can also act as an inhibitor for rapid contamination within the deeper bedrock units (Burkart & Stoner, 2002; Levison & Novakowski, 2009).

2.3 Turbidity and Groundwater Field Parameters

Standard field parameters that are measured in geochemistry include temperature, pH, ORP, DO, EC and alkalinity (Brassington, 1998; Francy, Helsel & Nally, 2000; Nielsen & Nielsen, 2007). Laboratory analyses often include major ions (Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, and many others), minor ions, organic parameters (TOC, COD, BOD, hydrocarbons, etc.), pesticides and bacteria, including fecal coliforms (Brassington, 1998). Each of these parameters can be measured at different depths when possible, using technologies such as those discussed in Section 2.4, and vertical geochemical profiles can be created. Temperature, pH and conductivity profiles are useful for analyzing flow conditions within a borehole, and can aid in detecting changes in groundwater chemistry in different formations (Brassington, 1998). DO and Eh profiles are useful for analyzing the presence of redox conditions within the aquifer, which can help characterize denitrification processes as discussed in Section 2.2.4. However, DO and Eh are more difficult to measure and are often suspect, and should be measured in situ whenever possible. EC, pH and temperature are more easily measured, but should still be sampled quickly at the surface, as they will drift towards ambient conditions (Brassington, 1998).

More recently, turbidity has been included as a field parameter in hydrogeological studies. Turbidity is an expression of the property of light to be scattered and adsorbed to suspended particles in a water sample rather than transmitted through it (Environmental Protection Agency (EPA), 1999), and provides a general estimate of water quality. It is caused by suspended and
colloidal materials, such as clay, silt, and various organic and inorganic matter (Allen, Brecher, Copes, Hrudey, & Payment, 2008). Generally, better water quality is associated with lower turbidity values (Weipeng & Nan, 2012). While turbidity is less of an issue in properly screened and constructed wells, some ambient turbidity can be present in groundwater, up to and exceeding 10 NTU (Nielsen & Nielsen, 2007). Turbidity is a useful indicator of groundwater quality, as it can fluctuate during recharge events and can help identify groundwater under direct influence (GUDI) of surface water wells (Allen et al., 2008).

The effects of purging on groundwater field parameters including turbidity was studied by Gibs et al. (2000) in an unconfined sandy aquifer located in New Jersey. Three boreholes with depths ranging from 10 to 35 metres were evaluated. Turbidity was monitored continuously during purging, with samples taken every minute using a turbidimeter. It was determined that turbidity varied by an order of magnitude or more during the first 10 to 15 minutes of purging, with steady states reached after approximately 30 to 90 minutes of purging. EC, pH, temperature and DO did not appear to be as variable during purging compared to turbidity (Gibs et al., 2000).

Many studies have investigated trends in general groundwater field parameters, but few studies have attempted to monitor for several parameters continuously. Turbidity has been evaluated in karst aquifers and water treatment systems, but less frequently compared to other field parameters. Pronk, Goldscheider and Zopfi (2009) sampled a karst system in Switzerland continuously for discharge, temperature, EC, organic carbon and turbidity, with additional analyses conducted for nitrate and coliforms. They found that turbidity had primary and secondary responses in groundwater, with an initial peak immediately following recharge events, and a second peak (30 to 40 NTU) approximately seven days later, corresponding to groundwater that has infiltrated and is moving through the aquifer. Similar peaks in nitrate (80 mg L$^{-1}$), DOC (1.6 mg L$^{-1}$) and coliforms were observed during the secondary response, with simultaneous decreases in EC and temperature (Goldscheider, Pronk, & Zopfi, 2010). In a similar study at the same location in Switzerland, it was noted that while turbidity is easy to measure continuously, it is not a valuable indicator for groundwater microbial contamination (Pronk, Goldscheider, & Zopfi, 2009).

Fournier et al. (2007) studied a karst aquifer system in Pays de Caux, France, with three monitoring points located in a sink, swallow hole and well. Turbidity, EC and depth were sampled continuously at 15 minute intervals using YSI 6820$^{TM}$ multiparameter sondes, and
discrete samples were taken for water quality and major ions following rainfall events. A total of 31 samples were taken from the well after three distinct events: 9 in December 1999, 8 in April 2000 and 14 in November 2000. Some temporal variation was observed in pH (7.6 to 8.1), EC (543 to 558 μS cm⁻¹), turbidity (0.4 to 4.3 NTU) and nitrate (20.5 to 25.1 mg L⁻¹) within the well, with larger variations observed in the spring and sink. Turbidity peaks were readily observed during storm events. Decreases in nitrate were observed in the spring, likely resulting from dilution due to storm events. It was also suggested that EC can act as a valuable indicator of surface water in karstic systems, due to the variance in conductivity values between surface and groundwater (Fournier, et al., 2007).

2.4 Groundwater Chemistry Sampling/Monitoring

Groundwater quality monitoring has been subject to rapid advancements in recent years due to the development of innovative sensors and technologies. Although groundwater nitrate monitoring was conducted in the 1950s (Johnston, 1955), larger scale assessment and monitoring activities were not initiated until the 1980s. Traditional sampling techniques relied upon discrete samples taken up-hole from wells to provide spatial distribution data of contaminants. However, starting in the late 1980s, researchers determined that conventional monitoring techniques may fail to capture the true vertical distribution of contaminants in the subsurface (Einarson, 2006). As a result, multilevel sampling methods were developed, which allowed for depth-discrete sampling to be conducted.

More recent monitoring studies have relied upon sampling methods using a combination of traditional techniques and multilevel sampling, using piezometer nests, well clusters and multilevel wells (Goss et al., 1998; Egboka, 1984; Robertson & Cherry, 1995; Robertson et al., 1996). Groundwater samples are extracted from the well(s) and then analyzed in a laboratory. An advantage of these methods is that an extracted sample can be analyzed for a range of water quality parameters, such as nitrate, DO, EC, Eh and pH, as well as isotopes, pathogens, organic and inorganic compounds (Best, 2012; Egboka, 1984; Robertson et al., 1996). A disadvantage is that the sampling results are discrete; they offer a “snapshot in time” of the geochemical conditions, even in multi-year studies similar to those conducted by Goss et al. (1998). Since water quality parameters have been demonstrated to be temporally variable, these discrete samples may fail to capture temporal changes, particularly in settings with rapid transport, such as the crystalline bedrock aquifer studied by Levison and Novakowski (2009). There is a need for real-time, continuous monitoring in water and groundwater systems, to
improve response times in the event of a water quality emergency and therefore better protect human health (Storey, van der Gaag & Burns, 2011).

2.4.1 Piezometer Nests and Well Clusters

Sampling from piezometer nests and well clusters allows for representative samples of water quality parameters at different depths within the subsurface to be obtained (Gillham et al., 1978). The wells in a nest or cluster (e.g. shown Figure 2.3) are located in close proximity to one another, but are designed to prevent cross-contamination between groundwater at different depths (Robertson et al., 1996). Samples are extracted up-hole from each well/piezometer, typically using a pump, which allows for depth profiles to be constructed for each cluster. Vertical trends for nitrate and other water quality parameters can then be analyzed. Combining the results from several clusters provides spatial analysis of the geochemical conditions, which is useful for mapping the extent of a contaminant plume.

Figure 2.3: A typical cluster of monitoring wells located in Norfolk County. Each well is screened at a different depth to allow for depth-discrete sampling without the effects of cross-contamination between units.

Groundwater samples are extracted after purging a known volume of water from the well, typically using a peristaltic or submersible pump (Aravena et al., 1993; Best et al., 2015; Egboka, 1984; Fraters et al., 1998; Hollingham, 2011; Robertson et al., 1996). Wells are considered adequately purged after at least three borehole volumes are removed and standard field parameters are stabilized, whereupon it is assumed that the sample obtained is
representative of the surrounding aquifer conditions (Aravena et al., 1993; Francy, Helsel, & Nally, 2000; Nielsen & Nielsen, 2007). When conducting geochemical analyses, groundwater samples are usually filtered using a 45 μM filter and then chemically analyzed in a laboratory using techniques such as ultraviolet spectrophotometry, ion chromatography, automated cadmium reduction or a Nitrachek Reflectometer (Fraters et al., 1998; McLay et al., 2001; Robertson, Russell, & Cherry, 1996; Trudell, Gillham, & Cherry, 1986). Many other water quality parameters can be measured either in the field or laboratory. For example, DO can be measured in lab using the azide modification of the Winkler method, or in the field using various probes (Egboka, 1984; Trudell et al., 1986).

Alternative methods are sometimes used to extract samples from wells and piezometers. In some studies, particularly those involving public supply wells or private rural wells, samples are instead obtained from a tap located near the well. Purging is conducted by running the tap for several minutes before a sample is extracted (Allen, 2011; Goss et al., 1998; Savard, et al., 2010). McLay et al. (2001) collected samples by lowering a lead-weighted bottle into the well, opening the bottle to collect a sample, then removing the sample using rope. Haslauer (2005) sampled from a well using a Grundfos submersible pump at 1 ft intervals along the well screen to obtain a depth-discrete nitrate profile. The pump was lowered into the well and pumped to extract samples from the desired depth. It is noteworthy that in Haslauer (2005), nitrate concentrations remained uniform with respect to depth, at a concentration of approximately 6.3 mg L⁻¹ along the screened interval. It is likely that mixing within the pump made it difficult to obtain representative samples from different depths within the screen.

### 2.4.2 Multilevel Sampling Systems

Multilevel systems (MLS) are very useful for geochemical sampling because they allow for isolated discrete samples to be extracted from different depths at the same spatial location (Einarson, 2006). Depth-discrete samples allow for the analysis of specific hydrogeologic zones or even specific fractures in bedrock aquifers (Levison, 2009). MLS can also be used to differentiate between point and non-point contaminant sources, which are typically vertically stratified within an aquifer (Rudolph et al., 1998). Multilevel sampling can evaluate temporal variations of geochemical properties, hydraulic head profiles and assess groundwater age, source and movement (Best et al., 2015; Levison, 2009; Opazo, 2012). The robust datasets collected with multilevel sampling aid in constructing detailed geochemical profiles in the subsurface.
Preliminary MLS designs mirrored the well nest shown in Figure 2.4, using several lengths of polyethylene or PVC tubing that is screened and terminated at different depths, and encased within the borehole. A sand pack is located along the screened interval of each tube, with a bentonite seal placed above the sand pack and ground surface (Egboka, 1984; Rudolph et al., 1998; Trudell et al., 1986). Newer multilevel well systems have been developed in recent years for commercial use. For example, Continuous Multichannel Tubing (CMT) multilevel wells, which are marketed by Solinst Canada (Solinst Canada Ltd., Georgetown, ON, Canada), consist of extruded polyethylene tubing with channelized sampling ports that are screened and terminated at different depths (Best et al., 2015; Koch, 2009). CMT wells function in a very similar manner to preliminary multilevel designs, but do so using a single tube rather than several individual tubes grouped together. The Schlumberger Westbay MP is another multilevel system used in groundwater monitoring. Westbay systems use a sampling cannister which connects with valved couplings along specialized monitoring ports that connect directly into the adjacent formation (Einarson, 2006). Other commonly used multilevel systems include the Waterloo system (Solinst Canada Ltd.) and the FLUTE system (Flexible Liner Underground Technologies, LLC, Alcade, NM, United States).

Figure 2.4: Conceptual diagram demonstrating the differences in design between well clusters, well nests and multilevel sampling systems for depth-discrete groundwater monitoring applications (Solinst Canada Ltd., 2014).
2.4.3 Down-hole Sampling Techniques

Down-hole sampling methods are common in groundwater systems and involve deploying equipment directly into the well, rather than extracting samples up-hole. This can be advantageous because the parameters are obtained in situ, which can reduce the effects of mixing and turbulence compared to traditional purge methods. Purging techniques have been demonstrated to disturb the aquifer and are labourious (Britt, Parker & Cherry, 2010). Depending on the equipment, samples can also be obtained more frequently using down-hole methods. More frequent sampling means that the temporal variability present at a site can be better captured (Levison & Novakowski, 2009).

An interesting down-hole sampling method that was recently developed is the Snap Sampler (ProHydro Inc., United States), a patented double-opening bottle that can be deployed and triggered to collect groundwater samples with no purging required. The Snap Sampler performed excellently when sampling groundwater contaminated with VOCs, and is ideal in situations where large volumes of contaminated waste water would otherwise be generated (Britt, Parker, & Cherry, 2010). Other advancements in sensor technology have allowed for more groundwater parameters to be monitored down-hole. They are very useful for providing an early warning of groundwater quality changes (Brassington, 1998). However, there has been some reluctance on the part of both regulators and practitioners in adopting these in situ techniques (Nielsen & Nielsen, 2007).

Many geophysical techniques are performed using down-hole methods. For example, Pehme et al. (2010) used down-hole gamma logging and temperature profiling in fractured bedrock boreholes sealed using FLUTE™ liners to identify hydraulically active fractures at different contaminated sites in southern Ontario. Other down-hole techniques used at the same locations included straddle packer testing, acoustic televiewer (ATV) logging and heat pulse flowmeter testing. Munn (2012) utilized a down-hole video camera along with continuous coring and ATV logging to provide high resolution fracture mapping at three different boreholes in the Guelph area.

Some studies have evaluated the applicability of down-hole sampling methods compared to traditional methods. Down-hole methods are starting to gain acceptance as reliable means of sampling in which aquifer disturbance and errors due to sample handling are minimized (Britt et al., 2010), but have not been thoroughly investigated in the context of groundwater nitrate.
Down-hole methods are promising in fractured bedrock applications, where purge sampling can draw water from a large portion of the formation, therefore resulting in a non-representative sample being obtained (Nielsen & Nielsen, 2007). It is critical when conducting down-hole sampling to ensure that samples are representative of the ambient groundwater conditions. It is known that water located inside the well casing and along the borehole column cannot interact with formation water, except in screened intervals or open bedrock boreholes, and is therefore deemed stagnant. However, recent studies have demonstrated the screened interval has high hydraulic conductivity (Nielsen & Nielsen, 2007), is connected to the formation, and is therefore subject to natural flow conditions that are representative of ambient conditions (Britt et al., 2010).

It is important to consider the effects of vertical flow and cross-connection between different units when conducting down-hole sampling. In overburden wells with a long screen, it has been hypothesized that the screened interval within the overburden supply well can act as a conduit for flow between deep and shallow aquifer units, resulting in changes in geochemistry (WESA Inc., 2012). This has also been observed in open boreholes drilled through bedrock, which can introduce short circuiting between fractures, resulting in vertical flow and mixing within the borehole (Pehme et al., 2007). It is critical to consider and possibly mitigate these mixing effects when conducting down-hole geochemical sampling. Recent studies using the aforementioned FLUTE™ liners are conducted to seal the borehole and prevent cross-contamination, such that down-hole measurements are more indicative of the ambient groundwater conditions (Munn, 2012; Pehme et al., 2010; Pehme et al., 2007). It is largely unknown as to what effect these cross-contamination processes have on nitrate concentrations in boreholes. At the time of this study and to the best of the authors’ knowledge, no down-hole technique for obtaining nitrate concentrations had been developed. Such a technique would complement traditional groundwater quality sampling methods, which do not allow for the detailed vertical characterization of nitrate concentrations along the entire well profile (WESA Inc., 2012). Down-hole techniques would be useful for characterizing well conditions, as well as evaluating temporal trends through long-term equipment deployment. Thus, this research investigated the aforementioned submersible ultraviolet nitrate analyzer (SUNA) sensor and its applicability for down-hole nitrate measurements.
3 Research Sites

Research sites selected for this study were located throughout southern Ontario, in Norfolk County, Guelph and the Region of Waterloo (Figure 3.1). The sites were selected to target different hydrogeological settings and surficial land uses to evaluate the effectiveness of the research equipment. Hydrogeological settings included a shallow unconfined overburden aquifer (Norfolk County) and deeper confined/semi-confined overburden aquifer (Region of Waterloo), as well as shallow bedrock and deep bedrock aquifers (Guelph). Land uses included a forested tract (Norfolk County), conventional agriculture (Region of Waterloo), golf course (Guelph) and urbanized/natural areas (Region of Waterloo). Each of the specific research sites will be covered in detail in the subsequent sections of this report.

Figure 3.1: Locations of field sites (shown as orange stars) for this study, with Toronto shown for reference. Note that Norfolk County is denoted by Simcoe, the largest municipality and county seat for Norfolk. County boundaries extend beyond Simcoe. Map created using ESRI ArcMap Version 10.0, with province of Ontario basemap from Ontario Ministry of Natural Resources (2003)
3.1 Norfolk County

3.1.1 Site Descriptions

Norfolk County has a population of approximately 100,000, with approximately 15,000 residing in Simcoe and fewer than 1,000 residing in Port Rowan. It is located in the Long Point Region of the Lake Erie Source Protection Region (Matrix Solutions Inc., 2013). Other communities located near the study site include Delhi, Tillsonburg and Waterford. Land use in the area is predominantly agricultural. Approximately 78% of the total land area throughout Norfolk County is actively farmed. Livestock operations and agricultural crops are prevalent throughout Norfolk County. Commonly grown crops include soybean, corn, grains, ginseng and tobacco (LPRCA, 2008). Approximately 75% of the 60,000 residents on municipal water supply in Norfolk County are reliant on groundwater, with an additional 40,000 residents reliant on private groundwater wells. Simcoe, Waterford and Tillsonburg are entirely reliant on groundwater for their drinking water (Matrix Solutions Inc., 2013).

Two areas in Norfolk County were used for groundwater monitoring for this research. One location, hereby referred to as the “Long Point Tier 3,” or “LPT3” area, encompasses a network of 26 monitoring wells near Simcoe, Ontario (shown in Figure 3.2) that were developed by the Grand River Conservation Authority and Norfolk County. The other site, hereby referred to as the “Port Rowan site” comprises a proposed municipal water supply well field located approximately 10 km north of Port Rowan, a small community on the shore of the Long Point Inner Bay. The approximate location of the Port Rowan site is shown in Figure 3.3, along with the 11 monitoring wells and four production wells on site.
Figure 3.2: a) Field locations at the Long Point Tier 3 site with b) selected wells from LP-MW-18-10 and c) LP-MW-04-10. Shallow, intermediate and deep monitoring wells are located at both sites. Map created using ESRI ArcMap Version 10.0, with Ontario basemap from Ontario Ministry of Natural Resources (2003) and satellite imagery from SWOOP (2006).
Figure 3.3: a) Field locations at the Port Rowan site with production wells shown in yellow and monitoring wells shown in blue; b) production well PR8 and c) monitoring well MW4. Map created using ESRI ArcMap Version 10.0, with Ontario basemap from Ontario Ministry of Natural Resources (2003) and satellite imagery from SWOOP (2006)
The LPT3 wells were drilled in support of the Lake Erie Source Water Protection Committee’s Tier 3 water budget (Matrix Solutions Inc., 2013). Of the 26 monitoring wells, 9 were selected for analysis in this study, which was paired with an OMAFRA New Directions project research project conducted at the same locations (Mistry et al., 2014). The chosen wells are located adjacent to agricultural fields northwest of Simcoe. One location contains a single well, and the other four locations contain multiple wells (usually 2-3) screened at different depths. Well construction details from selected wells can be found in the Appendices.

The Port Rowan site is located just east of Walsingham and is part of an ongoing water supply investigation. The town of Port Rowan relies upon surface water from Lake Erie for its water supply. However, there are concerns about the sustainability of the supply due to silt and sediment accumulation near the supply pipeline intake, located near the mouth of Big Creek in Long Point Bay (LPRCA, 2008). As such, Norfolk County conducted a Municipal Water Supply Environmental Assessment to locate a groundwater source to supply Port Rowan with drinking water. A groundwater exploration program was initiated in 2010 at the Port Rowan site, located in a forested tract encompassing an area of approximately 43 hectares, as shown in Figure 3.3. Three production wells and seven monitoring wells were installed at the site by October 2012 (Banks, 2013). Well construction details can be found in the Appendices. The initial groundwater investigation concluded that the site could support a safe perennial yield of 2,200 m$^3$ day$^{-1}$ (Banks, 2013). However, groundwater quality analyses indicated the presence of nitrate at elevated levels (i.e. over 8 mg L$^{-1}$ as shown in Figure 3.8) in some areas on site, so it has not yet been established as a municipal water supply source. Norfolk County is continuing to investigate the suitability of the Port Rowan site in terms of water quality.

3.1.2 Geology and Climate

Quaternary Geology in Norfolk County is comprised of coarse glacial overburden sediments underlain by Upper Silurian to Middle Devonian bedrock, consisting mainly of limestones, dolostones and shales. Two physiographic regions dominate the Norfolk County area: the Norfolk Sand Plain and Haldimand Clay Plain, as shown in Figure 3.4. The Norfolk Sand Plain consists of low relief, silty sand and gravelly sediments that were deposited during Wisconsinan glacial period, and range from 1 m to 25 m in thickness (LPRCA, 2008). It is characterized by low runoff (i.e. < 100 mm year$^{-1}$ in some locations) and high groundwater recharge that exceeds 300 mm year$^{-1}$ in many locations (Matrix Solutions Inc., 2013). East of Simcoe is the Haldimand...
Clay Plain, which consists of fine-grained clay deposits formed by glaciolacustrine processes. The clayey sediments restrict drainage processes, resulting in high runoff (i.e. >300 mm year\(^{-1}\)) and low recharge (i.e. <100 mm year\(^{-1}\)), although localized tills are present throughout the area (LPRCA, 2008; Matrix Solutions Inc., 2013).

Figure 3.4: Quaternary geology within the Norfolk County area. The Port Rowan and LPT3 research sites are situated in the Norfolk Sand Plain. Map created using ESRI ArcMap Version 10.0, with Ontario basemap from Ontario Ministry of Natural Resources (2003) and geologic data from the Ontario Geological Survey (2003).
Both bedrock and overburden aquifers are used for water supply in Norfolk County. Overburden aquifers dominate to the west, since the coarse grained sands from the Norfolk Sand Plain typically provide excellent groundwater yields (LPRCA, 2008; Matrix Solutions Inc., 2013). Two overburden aquifers are present within the Norfolk Sand Plain. The upper aquifer is shallow and unconfined, and is associated with the coarse glacial deposits consistent with the Sand Plain. A layer of low permeability clayey material generally separates the upper and lower aquifer units. The lower aquifer is confined to semi-confined, and consists of medium- to fine-grained sands, but pinches out east of Simcoe as it encounters the Haldimand Clay Plain (LPRCA, 2008). The clayey deposits associated with the Haldimand Clay Plain do not provide sufficient yields for drinking water supply. Groundwater resources are instead extracted from the bedrock aquifer, typically within the first 10 to 30 metres of the Dundee Formation, which consists of highly permeable karstic limestone approximately 35 to 45 metres thick (Matrix Solutions Inc., 2013). All production and monitoring wells at the Port Rowan site are drilled into the upper overburden aquifer in the Norfolk Sand Plain, extending approximately 10 to 15 metres below surface until contact with the clayey material separating the upper and lower overburden aquifers (see Figure 3.5).
Figure 3.5: a) Port Rowan site showing production and monitoring wells along transect A-A’ and b) Lithology along transect as interpreted from well logs obtained from the Ontario Water Well Information System (WWIS) (Ontario Ministry of the Environment and Climate Change, 2014). Map created using ESRI ArcMap Version 10.0 and satellite imagery from SWOOP (2006), with well locations provided by Banks (2013)
The average monthly precipitation and temperature values taken from the Delhi research station, which is located approximately 20 kilometres north from the Port Rowan site, are shown in Figure 3.6. Norfolk County has a moderate temperate climate, with warm summers, winters below freezing, and relatively constant precipitation throughout the year. The proximity to Lake Erie, particularly at the Port Rowan site, provides a moderating effect for temperatures throughout the year. The average annual temperature (1981-2010) was approximately 7.5 to 8.0°C. The average annual precipitation ranged from approximately 975 to 1075 mm per year from 1980 to 2010 (LPRCA, 2008).

![Figure 3.6: Average monthly precipitation and rainfall from 1981-2010 in Norfolk County, obtained using values from the Delhi Climate Station (located approximately 20 km NW of the Port Rowan and LPT3 sites).](image)

Groundwater levels have been monitored hourly at well MW3 on the Port Rowan site since January 2013, and typically fluctuate between ranges of approximately 1 metre throughout each year. Daily averaged readings were plotted with daily and monthly precipitation data (shown in Figure 3.7) to show climate and recharge events preceding and complementing water quality datasets obtained during this project. A barometric logger located on site was used to correct groundwater readings, and daily climate data was obtained from the University of Guelph’s Simcoe research station, located approximately 20 kilometres northeast of the Port Rowan site. Analyzing the groundwater elevation patterns shown in Figure 3.7, it is evident that there are significant temporal differences in recharge in the 2013, 2014 and 2015 calendar years. There were significant recharge events beginning in early January 2013 and 2014, which likely coincided with snowmelt events; however, the extremely cold winter of 2015 meant that
Recharge did not occur until late March or early April. There was also less recharge in winter-spring 2015 compared to 2014 and 2013, as indicated by groundwater elevations in April – June 2015. However, June and July 2015 contained large amounts of rainfall, and likely contributed to further recharge during those periods, but this could not be verified at the time of this publication as groundwater elevation data was not retrieved. Water levels decreased to their lowest recorded value (approximately 211.0 masl) in October 2013, largely due to the lower than average recorded rainfall in July and August that year. Fall 2013 recharge appears to have initiated from two or three large rainfall events, whereas fall 2014 recharge shows 5 or six smaller peaks resulting from smaller, more frequent recharge events. The groundwater levels in fall 2014 and spring 2015 appear to have a more direct response to rainfall events, while no recharge seems to have occurred from January to March 2015 due to a period of extreme cold. These observations are important to consider for the interpretation of monitoring data collected at the Port Rowan site over the duration of this project.
Figure 3.7: Daily averaged groundwater levels plotted with daily and monthly precipitation at well MW3 on the Port Rowan site. Climate data was obtained from the University of Guelph’s Simcoe Research Station (1283 Blueline Rd., Simcoe, Ontario). Water level readings were obtained from monitoring program by Banks (2012).
3.1.3 Nitrate Issues and Previous Studies

Elevated nitrate (as NO$_3$-N) concentrations have been observed across the LPT3 and Port Rowan sites. Previous studies have investigated groundwater nitrate at various locations in the sandy aquifer around the LPT3 wells. Hollingham (2011) surveyed approximately 25 wells at various depths within the overburden in July 2010, and observed nitrate concentrations ranging from non-detectable to 23.1 mg L$^{-1}$. Isotope and chemical analyses confirmed that the majority of nitrate was sourced from fertilizer-derived ammonium, with inputs at one location from a residential septic system. The GRCA surveyed 91 private wells in Norfolk County in 2006 and analyzed samples for geochemistry. Many locations exhibited elevated nitrate concentrations ranging from 3.5 mg L$^{-1}$ to 15 mg L$^{-1}$, suggesting the influence of surface water on groundwater quality (LPRCA, 2008). Egboka (1984) sampled the shallow unconfined aquifer in the Venison Creek watershed near Delhi, Ontario. Nitrate concentrations ranged from 0.5 to 7.1 mg L$^{-1}$.

Nitrate concentrations observed at the Port Rowan site are shown in Table 3.1 and Figure 3.8. Concentrations approached half the MAC (5 mg L$^{-1}$) at PR11 and approached the MAC in several of the monitoring wells, with a maximum observed concentration of 8.04 mg L$^{-1}$ as NO$_3$-N at MW1 (Banks, 2013). Discrete nitrate samples were obtained for the production wells during aquifer testing in November 2012 and for the monitoring wells in January 2013. It is difficult to identify any temporal trends at the Port Rowan site since these discrete nitrate samples were taken within a three month period. A study conducted in Venison Creek in Norfolk County observed that nitrate concentrations appeared to be highest in glaciolacustrine sands overlying silt clay tills (Gillham et al., 1978). The Port Rowan site is comprised of similar hydrostratigraphic units, which is likely a contributing factor for nitrate contamination at the site. The hydraulic conductivity of the clay tills is likely 3 to 4 times lower than that of the sandy material, so significant time is required for nitrate to be transported into the till unit, (Gillham et al., 1978). Although capture zones have not been modelled for the Port Rowan site, initial flow direction interpretations from Figure 3.8 suggest that groundwater flows from the northeast to southwest across the site. There is a corn farm located up–gradient of the flow direction; however, it has not been confirmed as the nitrate source (Banks, 2013).
Table 3.1: Nitrate concentrations measured using purged samples from wells across the Port Rowan site. The concentrations in 2012 and 2013 were measured by Banks (2013), and were used to construct Figure 3.8.

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<td>PR8</td>
<td>0.491</td>
<td>-</td>
<td>0.91</td>
<td>0.84</td>
<td>1.00</td>
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<td>-</td>
<td>0.10</td>
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<td>PR9</td>
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<td>0.06</td>
<td>0.08</td>
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<tr>
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<td>-</td>
<td>8.04</td>
<td>8.70</td>
<td>9.08</td>
<td>10.80</td>
<td>-</td>
<td>-</td>
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<tr>
<td>MW2</td>
<td>-</td>
<td>3.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>0.556</td>
<td>0.80</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>MW4</td>
<td>-</td>
<td>3.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>0.169</td>
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Figure 3.8: Port Rowan site with well locations, contoured groundwater elevations and nitrate concentrations sampled by Banks (2013) from November 2012 to January 2013. Map created using ESRI ArcMap Version 10.0, with satellite imagery from SWOOP (2006)
Denitrification processes have been observed throughout the shallow aquifer in the Norfolk Sand Plain. Hollingham (2011) observed decreases in nitrate concentrations with depth and confirmed the presence of denitrification processes with $\delta^{15}$N and $\delta^{18}$O signatures. Egboke observed similar decreases in concentration with depth; however, sharp decreases were not observed, suggesting the lack of a redoxcline. Aravena and Robertson (1998) observed reducing conditions in the shallow sandy aquifer in Long Point Provincial Park. Nitrate concentrations from a septic plume decreased from 50 mg L$^{-1}$ in the upper aquifer to approximately 10 mg L$^{-1}$ at a 3 m depth below the water table, corresponding to a similar decrease in DO with depth, from 0.2 mg L$^{-1}$ at surface to non-detectable at 3 m depth. They estimated a rate of denitrification on the order of 1 mg L$^{-1}$ day considering zero order decay, or a half-life of one month considering first order decay. This rate of denitrification is higher than typical values for shallow groundwater (Aravena & Robertson, 1998). Other studies in the Norfolk Sand Plain have identified regions in which denitrification is not favoured. Gillham et al., (1978) suggested that due to the large thickness of the unsaturated zone, organic matter may be oxidized before the water table is reached, reducing DOC concentrations and its role as an electron donor.

### 3.2 Guelph

#### 3.2.1 Site Descriptions

The City of Guelph has a population of approximately 120,000, and is one of the largest communities in Canada that is almost entirely reliant on groundwater for its water supply. Average daily water demand is approximately 50,000 m$^3$ day$^{-1}$, which is supplied by a network of 23 groundwater wells dispersed throughout the city (Lake Erie Region Source Protection Committee, 2012). The majority of the wells in Guelph extract water from deeper bedrock locations, as the overburden does not provide sufficient yields. Land use within the city of Guelph is heavily urbanized, but the surrounding area is predominantly agricultural. There are areas of mixed land use nearby the study areas, including golf courses and naturalized areas, as shown in Figure 3.9 and Figure 3.10.

Two research sites were selected in the City of Guelph, to examine nitrate transport in different bedrock settings. The first research location, hereby referred to as the “BAFF” site, is located at the Bedrock Aquifer Field Facility (BAFF) in the Arboretum at the University of Guelph. A cluster of seven boreholes are located at the BAFF, which is shown in Figure 3.9. One specific borehole (GDC-10) was examined in this study. The second research location, hereby referred
to as the “Stone Well” site, is also shown in Figure 3.9 and is located within the Torrance Creek subwatershed near the Eramosa River, approximately 5 km southwest of the University of Guelph. The Stone Well, also referred to as PW1/62, was a former City of Guelph supply well that was decommissioned in 1972. Well construction details for GDC-10 and the Stone Well are provided in the Appendices.
Figure 3.9: a) Aerial imagery of Guelph showing b) selected wells at the BAFF and c) Stone Well sites. Map created using ESRI ArcMap Version 10.0, with satellite imagery from SWOOP (2006)
Figure 3.10: Land use classification in the Guelph area, with the locations of the BAFF and Stone Well sites. Both sites are situated in close proximity to golf courses. Map created using ESRI ArcMap Version 10.0, with Ontario basemap from Ontario Ministry of Natural Resources (2003) and land use imagery from the Grand River Conservation Authority (1999).
3.2.2 Geology and Climate

Surficial geology in the Guelph area is characterized by two distinct physiographic formations: the Guelph Drumlin Field and Horseshoe Moraines, as shown in Figure 3.11. The Guelph Drumlin Field consists of approximately 300 drumlins, oriented northwest-southeast, bordered by gravel terraces and separated by swampy valleys. Sediment types include sandy tills and gravel outwash coinciding with the aforementioned terraces (Lake Erie Region Source Protection Committee, 2012). To the southeast of Guelph are the Paris and Galt Moraines, which dominate the Horseshoe Moraines region. These moraines are characterized by loose, bouldery loams with large sandy and gravelly deposits (Lake Erie Region Source Protection Committee, 2012).

Geology underlying the overburden deposits around the Guelph area consists of multiple formations of Silurian bedrock. The uppermost layer is the Guelph Formation, a brown or tan dolostone that serves as an unconfined supply aquifer for several municipal wells. Underlying the Guelph Formation in locations towards Rockwood is the Eramosa Formation, a marine carbonate unit which can be up to 20 m thick and is characterized by low permeability (Lake Erie Region Source Protection Committee, 2012). The Eramosa Formation overlies the Gasport Formation, a unit ranging in thickness from 10 to 45 m which is comprised of fractured blue-grey dolostone. The Gasport Formation is confined to semi-confined, is characterized by high porosity and permeability, and serves as an important groundwater supply source that provides significant yields for the City of Guelph (Brunton, 2009). Hydraulic conductivity estimates for the Gasport Formation in the southeast quadrant of Guelph ranged from 4.4 to 1,478 m day$^{-1}$, with most estimates on the order of 50 to 100 m day$^{-1}$ (Jagger Hims Ltd., 1998). The geologic units present within the Guelph area are shown in Figure 3.12. A lithological cross section was constructed using wells located near the Stone Well and is shown in Figure 3.13.
Figure 3.11: Quaternary geology within the Guelph area. The BAFF and Stone Well sites are situated amongst the Guelph drumlin field to the North and Horseshoe Moraine regions to the south. Map created using ESRI ArcMap Version 10.0, with Ontario basemap from Ontario Ministry of Natural Resources (2003) and geologic data from the Ontario Geological Survey (2003)
Figure 3.12: Revised hydrostratigraphic sequence for Silurian bedrock formations in the Guelph area, adopted from Brunton (2009)
Figure 3.13: Stone Well site, showing production and monitoring wells along transect A-A' and b) Lithology along transect as interpreted from well logs. The Stone Well is located just north of the golf course, NW of well 7195101. Map created using ESRI ArcMap Version 10.0, with satellite imagery from SWOOP (2006). Well records selected from the Ontario Water Well Information System (WWIS) (Ontario Ministry of the Environment and Climate Change, 2014)
Research sites in the City of Guelph were chosen for this study to evaluate nitrate transport within fractured bedrock aquifers. Boreholes studied are drilled into either the shallow Guelph Formation, or deeper Gasport Formation. The wells located within the cluster at the BAFF site are drilled into the Gasport formation at approximate depths of 70 to 80 m BGS, with the exception of one shallow overburden well at a depth of 14.2 m BGS. The Stone Well (PW1/62) was drilled to a depth of 19.8 m BGS into what is likely the Guelph Formation. The overburden around the Stone Well is approximately 8 metres thick, with groundwater springs (shown in Figure 3.14) and artesian flow in some monitoring wells.

![Groundwater spring](image)

Figure 3.14: Capped groundwater upwelling/spring located approximately 100 m north of the Stone Well site in Guelph. An RTRM station was commissioned at this location. The spring discharges into a small creek which flows to the northeast, seen at the top of this photo.

Average monthly precipitation and temperature values for the City of Guelph are shown in Figure 3.15. The climate in Guelph is semihumid with four seasons and fairly consistent precipitation. It is located within the Huron and South Slopes climate region. Average annual temperature is approximately 6 to 7°C, with fairly distinctive seasons and unpredictable transition periods (Lake Erie Region Source Protection Committee, 2012). Annual precipitation ranges from approximately 800 to 1000 mm per year, with an average of 923 mm (Lake Erie Region Source Protection Committee, 2012).
3.2.3 Nitrate Issues and Previous Studies

Studies have examined the persistence of nitrate within the bedrock aquifer around Guelph. Nitrate issues around the Carter wells in Guelph are well documented. The wells are classified as Groundwater Under Direct Influence of surface water (GUDI) wells and are located near Torrance Creek. Since they draw water from the shallower Guelph Formation, they are more susceptible to contamination compared to wells that draw from the confined Gasport Formation (AquaResource Inc., 2010). Concentrations regularly exceed the MAC and persist at approximately 8 to 12 mg L\(^{-1}\). However, the City of Guelph mixes water from the Carter wells with water from the Arkell Springs before it is pumped, to ensure the drinking quality is excellent before distribution (AquaResource Inc., 2010; Lake Erie Region Source Protection Committee, 2012). Nitrate contamination does not appear to be a concern at other City of Guelph production wells (AquaResource Inc., 2010), as it does not persist in the Gasport Formation.

Best et al. (2015) conducted nitrate sampling at three sites around Guelph: Turfgrass Institute, Arkell Research Station and Vance Tract, to evaluate nitrate fate in different glacial settings and land uses. Nitrate concentrations consistently exceeded the MAC at the Arkell Research Station, ranging from 13 to 18 mg L\(^{-1}\). Oxidizing conditions suggest that denitrification is likely not occurring at the site. Nitrate concentrations at the Turfgrass Institute ranged from 0.4 to 1.7
mg L$^{-1}$ and increased with depth to 3.9 to 5.4 mg L$^{-1}$, before complete removal was observed with a further increase in depth. The higher concentrations with initial depth increase were attributed to a legacy effect due to different historical land use practices, and may be influenced by preferential flow paths in the overburden and in bedrock fractures, similar in nature to those hypothesized a crystalline bedrock aquifer site in eastern Ontario (Levison and Novakowski, 2009). Decreasing DO concentrations and the presence of reducing conditions suggests that denitrification is providing natural nitrate attenuation deeper into the aquifer. At the Vance Tract site, no nitrate contamination was detected. This suggests that land use practices did not contribute significant nitrate loading into the subsurface, and the presence of reducing conditions suggests that natural attenuation is likely occurring within the localized aquifer as well.

Opazo (2012) evaluated the nitrate attenuation mechanisms within the Silurian bedrock aquifer in the Guelph area. Groundwater samples were extracted from at the Arkell Research Station and private rural wells located down-gradient. Nitrate results were spatially variable and ranged from non-detectable to 19 mg L$^{-1}$, correlating to redox conditions that were also very spatially variable. Isotopic analyses suggested that nitrate attenuation is likely occurring in bedrock units through denitrification by pyrite oxidation. Vertical nitrate profiling was conducted through pore water extraction and suggested that nitrate contamination is largely restricted to the Guelph Formation due to strong reducing conditions in the underlying Eramosa Formation. Opazo (2012) suggested that nitrate distribution with depth in a bedrock aquifer is a function of rock transmissivity and denitrification processes.

### 3.3 Region of Waterloo

#### 3.3.1 Site Descriptions

The Region of Waterloo has a population of approximately 550,000, and operates a total of 24 drinking water supply systems (Lake Erie Region Source Protection Committee, 2012; Meyer et al., 2014; Stotler et al., 2014). It is one of the largest users of groundwater resources in Canada. Cities in Waterloo Region include Cambridge, Kitchener, Waterloo, Elmira, New Hamburg and St. Jacobs, along with many smaller rural communities. Groundwater for municipal supply is extracted from 122 wells throughout the Region, along with one surface water supply intake from the Grand River in Kitchener (Meyer et al., 2014). The wells can supply up to 269,000 m$^3$ of water per day (Lake Erie Region Source Protection Committee, 2012). Land use is similar to the Guelph area, with heavy urbanization and mixed land use surrounded by agricultural
regions, as shown in Figure 3.17. Region of Waterloo wells extract water from a series of overburden aquifers in a complex hydrogeological system, with a few additional deep bedrock wells in Cambridge (Lake Erie Region Source Protection Committee, 2012).

Two research locations were selected in the Region of Waterloo to examine nitrate transport in deeper overburden aquifers, as shown in Figure 3.16. The first site, hereby referred to as the “Test Well 1” site, is located at a municipal production well just west of Kitchener. The second site, hereby referred to as the “Test Well 2” site, is located at another municipal production well approximately 6 km west from the Test Well 1 site. Test wells were drilled in February and May 2013 at each of these locations to act as potential back-up supply sources to the Test Well 1 and Test Well 2 production wells. Field work for this study was conducted at both test wells. Well construction details for the test wells can be found in Appendix E.
Figure 3.16: a) Aerial imagery of Region of Waterloo with b) selected sites at Test Well 1 and c) Test Well 2. Map created using ESRI ArcMap Version 10.0, with satellite imagery from SWOOP (2006)
Land use around the sites contains a mix of residential, row crops and bare agricultural fields. Map created using ESRI ArcMap Version 10.0, with Ontario basemap from Ontario Ministry of Natural Resources (2003) and land use imagery from the Grand River Conservation Authority (GRCA) (1999).
3.3.2 Geology and Climate

Surficial geology in Waterloo Region is largely composed of the Waterloo Hills, which are characterized by well-drained soils, sand hills and hummocky terrain, gravel terraces and swampy valleys, as shown in Figure 3.19 (Kerr-Upal et al., 1999; Lake Erie Region Source Protection Committee, 2012). Many wells in Waterloo Region are located in the Waterloo Moraine, a glacial landform deposited during the Wisconsinan era. The Waterloo Moraine (shown in Figure 3.18) is a complex system, consisting of coarse grained sand and gravel deposits with interbedded tills, silt and clay materials that often exceeds 40 m in thickness (Blackport et al., 2014; Meyer et al., 2014; Kerr-Upal et al., 1999). It is characterized by its high permeability and extensive infiltration and recharge (Lake Erie Region Source Protection Committee, 2012), although recharge has been estimated to range from 50 to 450 mm/year across the Moraine (Blackport et al., 2014).

Figure 3.18: Updated conceptual hydrogeological model of the Waterloo Moraine, adopted from (Blackport et al., 2014)

The Waterloo Moraine consists of very spatially variable layered hydrostratigraphy, with three major overburden aquifers separated by three major aquitard units (Blackport et al., 2014; Kerr-Upal et al., 1999; Lake Erie Region Source Protection Committee, 2012; Martin & Frind, 1998; WESA Inc., 2012). There is limited data available on the Aquitard 4 and Aquifer 4 units (Blackport et al., 2014). The Port Stanley/Tavistock, Maryhill and Catfish Creek Till units comprise the three aquitard units, which overly Aquifer 1, Aquifer 2 and Aquifer 3 as shown in Figure 3.18. Aquifer 1 is the uppermost aquifer and is the most productive and regionally continuous of the three units, while Aquifers 2 and 3 are locally productive. Discontinuities have been observed in Aquifers 2 and 3, as well as Aquitard 3 (Martin & Frind, 1998). Recharge into the deeper aquifer units is governed by erosional windows in the aquitard units, which allows for
connectivity between different aquifer units in isolated areas (Blackport et al., 2014; Stotler et al., 2014). Hydraulic conductivity is very heterogeneous through the system, with estimated recharge rates between 15 and 25 cm per year (Martin & Frind, 1998).

The test wells at the Test Well 1 and Test Well 2 sites are located in the Upper Waterloo Moraine Aquifers, and are both screened within Aquifer 1 (Blackport et al., 2014). A lithological cross section using the same conceptual model from Figure 3.18 was constructed along a transect from Test Well 1 to Test Well 2 (see Figure 3.20). Well logs suggest the presence of a perched aquifer at Test Well 1, with a much thinner or possibly discontinuous Aquitard 1 unit. However, at Test Well 2, the perched aquifer is absent and Aquitard 1 is much thicker. The Aquifer 1 unit pinches out to the West towards New Hamburg, and is more extensive in the East towards Mannheim (WESA Inc., 2012). Groundwater was inferred to flow from north to south at both locations (Kerr-Upal et al., 1999; WESA Inc., 2012). Recharge in the Upper Waterloo Moraine aquifers ranges from 200 to 450 mm/year (Blackport et al., 2014).
Figure 3.19: Quaternary geology within Waterloo Region. Both the Test Well 1 and 2 research sites are located within the Waterloo Moraine, a highly heterogeneous area of stratified glaciofluvial and till deposits. Map created using ESRI ArcMap Version 10.0, with Ontario basemap from Ontario Ministry of Natural Resources (2003) and geologic data from the Ontario Geological Survey (2003).
Figure 3.20: Region of Waterloo site, showing a) Test Well 1 and Test Well 2, selected wells along transect A-A’ and b) Lithology along transect as interpreted from well logs. Map created using ESRI ArcMap Version 10.0, with satellite imagery from SWOOP (2006). Well records were selected from the Ontario Water Well Information System (WWIS) (Ontario Ministry of the Environment and Climate Change, 2014)
Average monthly precipitation and temperature values for the Region of Waterloo are shown in Figure 3.21. Climate in Waterloo Region is semihumid with four seasons and fairly consistent precipitation, similar to the City of Guelph. It is located within the Huron and South Slopes climate region. Average annual temperature is approximately 6 to 7°C, with fairly distinctive seasons and unpredictable transition periods (Lake Erie Region Source Protection Committee, 2012). Average annual precipitation ranges from approximately 800 to 1000 mm per year (Lake Erie Region Source Protection Committee, 2012; Martin & Frind, 1998).

![Figure 3.21: Average monthly precipitation and rainfall from 1981-2010 for the Region of Waterloo, obtained using values from the Roseville Climate Station (located <5 km from BAFF and Stone Well sites)](image)

### 3.3.3 Nitrate Issues and Previous Studies

Permeable soils and high fertilizer application rates have led to increased vulnerability to nitrate contamination Region of Waterloo aquifers (Kerr-Upal et al., 1999). High groundwater recharge throughout the Waterloo Moraine can transport surficial nitrogen sources into the subsurface. In the study vicinity, the lack of a surficial aquitard around the Upper Waterloo Moraine aquifer decreases vertical travel times through the unsaturated zone, which renders the area more vulnerable to surficial contamination from sources such as nitrate (Blackport et al., 2014; Stotler et al., 2014). Some wells located near Test Well 1 have shown elevated and increasing nitrate concentrations since 1985, typically ranging from 4 to 8 mg/L (Blackport et al., 2014).

Nitrate concentrations at two of the production wells in the Wilmot well field have increased since 1999, to a maximum of 6.20 mg L⁻¹ in 2010 and 4.5 to 5.0 mg/L in 2012. Sampling
conducted at a monitoring nest approximately 200 m east of the Wilmot well field consistently identified elevated nitrate concentrations of 10 to 16 mg/L (Lake Erie Region Source Protection Committee, 2012). Other sampling conducted by WESA Inc. (2012) at Wilmot Center observed similar concentrations ranging from 10 to 15 mg/L at depths of 46.9 m BGS and 31.4 m BGS, and concentrations ranging from 3.18 to 7.85 mg/L in the localized perched aquifer. Average concentrations at the top of Aquifer 1 ranged from not detectable to 9.84 mg/L, and from not detectable to 7.08 mg/L at the bottom of Aquifer 1. It is evident that nitrate is highly spatially variable and vertically stratified within the Moraine aquifers. It is suggested that at the Wilmot Center well field, well K50 has higher nitrate concentrations than well K51 because K50 has a higher production rate (Lake Erie Region Source Protection Committee, 2012). However, it was also observed that lower pumping rates at K50 resulted in higher nitrate concentrations (WESA Inc., 2012). Further research is required to evaluate the effects of pumping on nitrate transport at the Wilmot Center well field.

Nitrate concentrations must be reduced through the application of Beneficial Management Plans (BMPs), such as delayed fall plowing of forages, crop rotation and cover crops, which are aimed at reducing surficial nitrogen inputs (Jiang et al., 2015; Critchley et al., 2014; Lake Erie Region Source Protection Committee, 2012; Rudolph et al., 2015). Management practices for non-point sources of groundwater nitrate have been implemented across the Region of Waterloo, including around the study area. Nitrogen use in agriculture has been reduced from 50 kg N ha\(^{-1}\) to 30 kg N ha\(^{-1}\) over approximately the past 20 years (Stotler et al., 2014). Several wells near Test Well 1 have experienced a reduction in nitrate concentrations, indicating that BMPs may be effectively reducing the concentrations (Lake Erie Region Source Protection Committee, 2012).

Monitoring activities suggest that some attenuation might be occurring around Wilmot. Enriched \(^{15}\)N and \(^{18}\)O were observed, along with reduced oxygen conditions and enriched sulphate compounds (Stotler et al., 2014), which likely acts as an electron donor. It was estimated that denitrification is likely occurring in 25% of wells sampled for geochemistry across the region (Stotler et al., 2011). Decreasing concentrations with depth in Aquifer 1 suggest that natural attenuation or dilution effects may influence nitrate distribution (WESA Inc., 2012). Previous studies within Waterloo Region have identified that natural nitrate attenuation through autotrophic denitrification can occur in aquitard sediments using sulphur compounds as an electron donor (Robertson et al., 1996).
4 Methodology

4.1 Instrumentation

This study involved the application of two water quality sensors: the Satlantic SUNA V2 (Satlantic Inc., Halifax, NS) and YSI EXO (YSI Inc., Yellow Springs, OH) water quality sonde, as well as an integrated telemetry system. The SUNA measures dissolved nitrate concentrations, while the EXO sondes can measure multiple field parameters, including pH, temperature, EC, DO and turbidity. The sondes were integrated with a Sutron XLite 9210 datalogger (Sutron Corp., Sterling, VA), Sixnet Modem (Red Lion Controls Inc., York, PA) and radio antenna for in situ monitoring. At the time of this study and to the best of the author’s knowledge, no telemetry system had been developed or tested by other parties for down-hole remote monitoring of groundwater quality parameters; only groundwater levels were measured (e.g. Cunningham, 2014; Government of Ontario, 2014). Therefore, a major objective of this research was to develop and test methods for real-time remote groundwater quality monitoring and evaluate the feasibility of using similar systems in groundwater resources management.

4.1.1 SUNA and In Situ Ultraviolet Spectrophotometry (ISUS)

The SUNA (shown in Figure 4.1) is a smaller freshwater version of the In Situ Ultraviolet Spectrophotometer (ISUS), which was developed by Johnson and Coletti (2002) at the Monterey Bay Aquarium Research Institute. It is an optical sensor that measures nitrate concentrations in the field, eliminating the need for chemicals and laboratory analyses. Specifications and accuracy for the SUNA are summarized in Figure 4.2 (Satlantic, 2014). At wavelengths less than 240 nm, UV absorption is governed by dissolved nitrate ions. The SUNA uses a UV light source and quartz sampling chamber to measure absorbance. A curve-fitting algorithm is then used to back-calculate dissolved nitrate concentrations (MacIntyre et al., n.d.).
Research investigations using the SUNA have mainly been limited to marine environments. Deployments in freshwater environments have been more challenging due to interfering species and bio-fouling. Interfering species such as fine silt and sediment can alter light absorbance, which compromises the SUNA’s nitrate-fitting algorithm. While new curve-fitting algorithms have been developed, they have not yet been tested in challenging field conditions, such as a highly turbid freshwater environment (MacIntyre et al., n.d.). Bio-fouling presents an issue for almost all environmental sampling equipment, particularly in long-term deployments. The SUNA is impacted by bio-fouling on optical windows and sensing surfaces, which can affect data quality (Adornato et al., 2009). However, recent advancements in bio-fouling guards, such as automatic wipers and copper guards, have been developed, and show promise in reducing the effects of bio-fouling (MacIntyre et al., n.d.).

ISUS technology has been used to obtain accurate nitrate concentrations in marine environments. Johnson and Coletti (2002) observed that the ISUS can successfully obtain high resolution nitrate data for deployments greater than 3 months, operating at a scale of 50 cm and
a frequency of 1 s\(^{-1}\). They were also able to obtain vertical nitrate profiles by lowering the ISUS to a 400 m depth at a rate of 30 m min\(^{-1}\). The ISUS data was compared to discrete samples, and the datasets were excellently correlated. The SUNA was initially deployed in Halifax Harbour for approximately three months (MacIntyre et al., n.d.), and was coupled with additional equipment to obtain hourly measurements of nitrate concentration and other parameters such as salinity, temperature, DO and chlorophyll fluorescence. It was able to accurately capture nitrate trends, particularly those associated with run-off events.

Deployments of ISUS/SUNA technology in freshwater environments have been limited thus far. Sackmann (2011) sampled nitrate and other water quality parameters from a stream in Washington State from October 2009 to November 2010. Nitrate concentrations were obtained every 15 minutes using the SUNA, which were compared to discrete samples obtained three times per month. Although the results were impacted by lamp degradation and interfering nitrite species, SUNA measurements displayed excellent linearity. Nitrate concentrations were demonstrated to have a strong inverse relationship with flow due to dilution effects. It was evident that the SUNA can provide high-resolution time series datasets in surface water environments, which are very useful for analysis when compared to the coarser traditional sampling methods (Sackmann, 2011). Similar relationships may be observed using the SUNA in groundwater investigations.

### 4.1.2 EXO Water Quality Sondes

The EXO1 (Figure 4.2) is a rugged multiparameter sonde that can collect detailed water quality datasets with ports that house up to four sensors and an integral pressure transducer for measuring depth (YSI Inc., 2013). The EXO2 is the more recent iteration of the design, with the ports that can house up to six sensors. Two EXO1 sondes and one EXO2 sonde were used for water quality monitoring in this study. Parameters measured by each sonde include temperature, pH, EC, DO and turbidity. Preliminary field testing used ORP instead of turbidity, but the turbidity sensor was used for the majority of the study. Specifications and accuracy for the EXO sonde and its accompanying sensors are provided in Figure 4.2.

A range of field cable lengths are available for both the SUNA and EXO which can be customized upon ordering. Cable lengths ranged from 20-60 metres for this study, and were selected based on the monitoring needs for the study. Note that cable lengths can limit
measurement depths, particularly for profiling deeper boreholes, so the user should have an idea of where the equipment will be deployed before considering cable lengths.

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Resolution</th>
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<td>0.001°C</td>
</tr>
<tr>
<td>pH</td>
<td>± 0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>± 0.001 μS/cm</td>
<td>0.0001-0.01 μS/cm</td>
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<tr>
<td>DO (mg/L)</td>
<td>± 0.1 mg/L</td>
<td>0.01 mg/L</td>
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<tr>
<td>Turbidity (FNU)</td>
<td>± 0.3 FNU</td>
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</tr>
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Figure 4.2: YSI EXO1™ and specifications, obtained from YSI website and EXO product user manual (YSI Inc., 2013). More detailed specifications can be found in the user manual (http://www.ysi.com/productsdetail.php?EXO1-Water-Quality-Sonde-89)

The EXO sensors have internal wipers and an external sonde guard to mitigate the effects of biofouling. Each of the sensors is serviced and calibrated separately. Detailed information regarding sensor design is available in the EXO User Manual (YSI Inc., 2013). The temperature sensor uses a stable thermistor which converts changes in resistance to temperature. The pH sensor consists of two glass electrodes, one of which acts as a reference while the other contains the water sample. The difference in \( H^+ \) ions is measured between the electrodes and converted to a pH reading. The conductivity sensor uses four nickel electrodes; two of which are current driven and two which measure voltage drop. The voltage drop is converted to conductivity using a known nickel cell constant. The DO sensor uses a photodiode to measure the luminescence of a chemical dye, which is quenched by the presence of dissolved oxygen. The lifetime of luminescence is inversely proportional to the DO concentration; therefore, the longer the luminescence signal, the lower the DO concentration is (YSI Inc., 2013).
YSI multi-parameter sensors have been used in many groundwater applications (e.g. Best et al., 2015; Del Rosario et al., 2014; Humphrey Jr. et al., 2010; Schmidt & Clark, 2012). However, published applications of the EXO sonde in environmental monitoring studies have been limited. Ganju, Miselis and Aretxabaleta (2014) deployed the EXO in a marine estuary on the New Jersey coast and monitored for temperature, turbidity, salinity, fluorescence, fDOM, pH and depth. Hillier (2014) used the EXO sonde to monitor for temperature, pH, EC, DO and turbidity during a 60-day pumping test, with observations recorded every 5 minutes from August-October 2013. Other studies have used similar YSI water quality probes for groundwater applications. For example, Zimmerman (2010) applied the YSI 600QS to obtain vertical profile measurements of pH, temperature, EC and DO. Measurements were taken at depth intervals of approximately 1 meter, with the probe being held at each depth until concentrations stabilized. While YSI handheld sensors have been successfully applied in many groundwater studies, the EXO sensors might be more useful in some studies because of their robustness for \textit{in situ} monitoring. EXO technology was developed with internal logging abilities and has a longer battery life, and is therefore promising for \textit{in situ} monitoring applications. At the time of this study and to the best of the author’s knowledge, the YSI EXO probes had not been used for down-hole groundwater quality monitoring applications.

4.1.3 \textit{Integrated Telemetry Equipment}

A suite of telemetry equipment was integrated with the SUNA and EXO sensors to conduct real-time remote water quality monitoring. Remote monitoring systems transmit input signals over the desired network so that data can be downloaded and viewed by the end user. This can streamline data collection processes, improve data quality and quantity, reduce complexity and costs associated with data collection, all while improving the spatial and temporal resolution of the data collected (Glasgow et al., 2004). Remote monitoring is useful in reducing trips to the field because the end user can receive and interpret data continuously, while making it easier to identify any problems or damage to the equipment.

The telemetry system used for this study (shown in Figure 4.3) was developed and tested by Hoskin Scientific (Hoskin Scientific Ltd., Burlington, ON) and consists of a Sutron XLite 9210B datalogger, Sixnet BT6901 HSPA modem and antenna. The system is powered by a Stark Energy lithium ion deep cycle battery (Conergy Canada Inc., Toronto, ON) which is recharged using a solar array coupled with a 4 Amp solar regulator. The datalogger is connected to the SUNA and EXO sensors through DIN rail terminals. The sensors are operated in SDI-12 mode,
which allows the logger to communicate with the sensors directly. Using specified commands, the logger powers the sensors, measures and then records parameters at the desired interval. The recorded data is transmitted to the modem and is broadcast over the HSPA network using the antenna. Data can then be periodically and remotely downloaded using specialized Autopoll software that is compatible with the Sutron datalogger’s XTerm software (Sutron Corp., Sterling, VA).

Figure 4.3: The integrated telemetry system developed by Hoskin Scientific Ltd. prior to field deployment

Groundwater monitoring using telemetry is an emerging technique, with few applications at the time of this study. Perhaps the most locally extensive of these applications is Ontario’s Provincial Groundwater Monitoring Network (PGMN), a network of 474 wells operated by the Ontario Ministry of Environment and Climate Change (MOECC) that have monitored groundwater levels on an hourly basis from year 2000 to the present day. Of these 474 wells, approximately 350 are fitted with telemetry systems, which transmit hourly water level readings to a centralized information system (Government of Ontario, 2014). Additional telemetry networks are used to monitor groundwater levels in at least 584 wells in Florida, Pennsylvania, Texas, North Carolina, Kansas and Missouri (Cunningham, 2014). Other telemetry systems have been developed for estuarine monitoring, fish behaviour monitoring, oceanography and
surface water monitoring (Glasgow et al., 2004). The GRCA uses real-time streamflow gauges for flood forecasting, where measured data is telemetered to reservoirs or flood control centres using dedicated phone lines (Boyd, Smith & Veale, 2000). Other systems such as Supervisory Control and Data Acquisition (SCADA) systems have been implemented throughout municipalities in Ontario to provide water operators with remote access to water utility equipment, allowing for automatic control of operations and data logging in pump stations, well fields, sewers and water treatment plants (Nasby & Phillips, 2011). Remote monitoring systems are invaluable in providing early warning information for water system operators (Glasgow et al., 2004). While these systems have been beneficial for water resources managers, much work is required to continue refining and improving them.

4.2 Developed Field Methods

The SUNA, EXO and telemetry described in section 4.1 was applied in the development of three unique measurement methods for this study. The methods developed were: (1) Modified flow cell testing, for obtaining up-hole field nitrate measurements; (2) Vertical profiling, to evaluate geochemical stratification within a borehole water column, and; (3) Real-time remote monitoring, to provide a method for obtaining continuous, in situ groundwater quality measurements. Each of the field methods will be described in subsequent sections. The methods were tested in different hydrogeological settings to evaluate their effectiveness. Testing was located in Norfolk County, Guelph and Waterloo, Ontario, Canada, with hydrogeology ranging from shallow overburden aquifers to deep fractured Silurian dolostone bedrock aquifers. A summary of testing locations, dates, hydrogeology and land use can be found in Table 4.1.
4.2.1 Modified Flow Cell Testing

Modified flow cell testing was the first method tested within this study. Since the SUNA had not been previously evaluated in groundwater environments, and was used only sparingly in non-saline environments (i.e. Sackmann, 2011), flow cell testing was conducted to verify the SUNA’s accuracy in obtaining groundwater nitrate measurements. The objective was to compare SUNA nitrate concentrations to laboratory concentrations obtained using traditional purge sampling methods. Testing was conducted over four periods occurring approximately every two months (July 29 – August 1, October 2, November 25, 2014, and February 13, 2015) at nine monitoring wells located in Norfolk County that were drilled to complement the Lake Erie Source Protection Region’s Tier 3 Water Budget (Matrix Solutions Inc., 2013). The wells were being sampled concurrently at the time of this project in conjunction with an Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) New Directions project at the University of Guelph titled “Changing Agricultural Landscapes and Groundwater Quality in Sensitive Aquifers” (Mistry et al., 2014).

4.2.1.1 Field Methods

A conceptual diagram of the flow cell testing method is provided in Figure 4.4. The method is based upon traditional purge sampling methods as described in section 2.4. To initiate testing, a Grundfos submersible pump (Grundfos Inc., Oakville, ON) was lowered to a depth just above the well screen using a Geotech Reel E-Z Pumping System (Geotech Environmental Equipment...
Inc., Denver, CO). The well was then purged of at least three borehole volumes. Field parameters were monitored throughout purging using a YSI 556 handheld multiprobe system (YSI Inc., Yellow Springs, OH). The pump discharge was directed into a bucket (shown in Figure 4.5), which was allowed to overflow until three borehole volumes were purged and standard field parameters (temperature, pH, EC, DO, ORP) stabilized. The YSI 556 and SUNA were placed at the base of the bucket and sampled continuously during purging. The SUNA was connected to a 12V battery and field laptop to communicate with and power the device. Nitrate samples were obtained at a high frequency (1 sample s⁻¹) and were logged using the SUNA’s internal logging capabilities. The SUNA was calibrated using deionized water (DIW) as a baseline solution before each testing period using refrigerated DI water at temperatures of approximately 10-12 °C, which is representative of average groundwater temperatures in Norfolk County. Three different SUNA devices were tested to validate the accuracy of each sensor prior to long-term deployment.
Figure 4.4: Flow cell testing conceptual diagram (not to scale), including SUNA and Grundfos submersible pump

Figure 4.5: a) Field set-up for flow cell testing, showing Grundfos pump, E-Z reel, flow cell bucket with SUNA sensor, field laptop and battery supply; b) Close-up of flow cell bucket with pump discharge hose and SUNA submersed at bottom
Upon completion of purging, plastic sampling bottles were rinsed twice with sample water from the flow cell bucket and then filled to avoid any contamination, while ensuring that air bubbles were not contained within the bottle. Sample bottles were placed in a cooler and stored at 4°C. The samples were then submitted to the Agriculture and Food Laboratory (AFL) at the University of Guelph. When possible, samples were submitted on the same day as they were collected; otherwise, they were submitted the following day. Samples were analyzed at the AFL for nitrate using cadmium reduction to nitrite followed by spectrophotometric measurement at 520 nm using the Seal AQ2, in accordance with Methods for Chemical Analyses of Waters and Wastes 600/4-79-020: Method 354.1 (Rand, Greenberg & Taras, 1976).

4.2.1.2 Data Analysis

SUNA nitrate concentrations were compared to laboratory nitrate concentrations obtained from the University of Guelph’s AFL using extracted bottle samples. SUNA time series measurements were post-processed using specialized SUNACom software (Satlantic Inc., Halifax, NS). The standard deviation and sample mean were calculated for the entire time of purging for each trial to determine variation in concentrations throughout purging. Nitrate concentrations from the final 50 samples (i.e. approximately the last one minute) of time series measurements during purging were averaged for comparison to AFL readings, since they were deemed representative of the sample water obtained for purged samples (after purging the typical three well volumes). Four total testing periods were conducted, resulting in a total of 32 trials. Nine wells were sampled during each testing period, with the exception of February 2015, where only five wells were purged due to weather and site access issues.

The residual (error) between the Lab and average SUNA measurement was calculated for each trial. The average error, average absolute error, mean squared error (MSE), root-mean squared error (RMSE), normalized root-mean squared error (NRMSE), linear correlation coefficient (r), and coefficient of determination ($R^2$) were also calculated for each testing period. The precision of the SUNA nitrate measurements relative to lab nitrate measurements was quantified using those values, particularly $R^2$, average error and average absolute error. The $r$ value is a measure of the linearity of a relationship between two variables; the closer it is to -1.0 or 1.0, the more strongly associated the variables are with a linear relationship. The $R^2$ value is the square of $r$ and represents the percentage of variation in the dependent variable (i.e. lab nitrate concentration) that is accounted for by variation in the independent variable (i.e. SUNA nitrate concentration) (Taylor, 1990).
The SUNA and lab nitrate datasets from all 32 trials were plotted and then fitted with a simple linear regression model. A well fitted model would theoretically allow for accurate predictions of lab nitrate concentration given a SUNA field nitrate measurement. The linear regression model relies on parametric tests and is therefore based upon four assumptions: 1) the relationship between the two datasets is approximately linear; 2) the mean of the least squares residuals is zero; 3) the residuals are uncorrelated (i.e. independent trials); and 4) the residuals are normally distributed (Montgomery, Peck & Vining, 2012). Upper and lower confidence and prediction bands (95%, α=0.05) were calculated for the least squares approximation line. Confidence bands consider the accuracy of the line of best fit, while prediction bands consider the accuracy of model predictions for a specific data point (Heskes, 1996). In other words, at α=0.05, the model suggests at 95% confidence that the least squares regression line (i.e. the line of best fit) falls somewhere between the confidence bands; and, given a single measured value for the independent variable (SUNA concentration) and the equation of the regression line, the model suggests at 95% confidence that the predicted value (lab concentration) falls somewhere between the prediction bands.

The four assumptions required for the linear regression model were tested. The first assumption (linearity) was validated after examining the correlation coefficients between the SUNA and lab datasets, as shown in Table 5.1. The second assumption was validated because the least squares approximation line was applied such that the residual mean was zero. The third assumption was validated by analyzing the field methodology; it is reasonable to assume that samples were obtained using independent trials. The fourth assumption (normality) required further analysis. Since the 95% confidence and prediction bands are dependent upon the normality assumption, normality was assessed by constructing a histogram and Q-Q probability plot of the residuals. The histogram was analyzed to determine if the residuals were bell shaped and approximated by the normal distribution (Ghasemi & Zahediasl, 2012). The Q-Q plot (see Appendix A) was analyzed to determine if the observed vs. expected cumulative probability scores fall approximately on a straight line, which indicates that the data probably approximates a normal distribution (Montgomery, Peck & Vining, 2012).

4.2.2 Vertical Geochemical Profiling

Vertical profiling methods were developed in July and August 2014, following completion of the first flow cell testing period. There were two specific objectives for vertical profiling: 1) to develop
down-hole methods that could be easily applied to observe changes in geochemistry along the water column within a borehole; and 2) to suggest ideal locations for locating sensors within the borehole for continuous, real-time remote monitoring. Testing occurred over two distinct periods approximately one month apart (specific dates are provided in Table 4.1), with previous intermittent testing to develop methods and evaluate equipment performance. Both the EXO and SUNA sensors were used in vertical profiling methods, such that nitrate, temperature, pH, EC, DO and turbidity were measured and correlated to specific depths within the borehole. ORP was also available for profiling runs in June and July 2014. Profiling was focused on the Port Rowan, Region of Waterloo, BAFF and Stone Well sites due to equipment constraints and site logistics.

4.2.2.1 Field Methods

![Vertical profiling conceptual diagram](image)
A conceptual diagram for the vertical profiling method is provided in Figure 4.6. Depth to water was first measured so that logged data could be referenced relative to the top of casing. Profiling at each borehole was conducted with the SUNA first, followed by the EXO. Each sensor was attached to a wireline, lowered down the borehole at a specified rate and then retrieved, with measurements recorded at desired and pre-defined frequencies. Data from downward logging was generally used, as it was deemed more accurate than data from upward logs due to mixing caused by the sensor as it passed through the water column. Attempts were made to connect the two sensors in series such that a single profiling run could be completed, but this limited the spatial resolution which could be measured, especially in wells having short screened intervals.

Both the EXO and SUNA were calibrated prior to each profiling period to ensure accuracy. Profiling methods with the EXO were more straightforward to develop compared to the SUNA. The internal power supply, internal logging and integral depth sensor present within the EXO simplified data analysis, because measurements were easily recorded and plotted as a function of depth. Two parameters were monitored during profiling: logging rate and measurement rate. Logging rate refers to the speed at which the sensor is lowered and retrieved, while measurement rate refers to the frequency at which the device is recording measurements. A range of logging rates and measurement rates were initially tested at the BAFF. Subsequent trials at the Port Rowan, Region of Waterloo and Stone Well sites were generally conducted using logging rates of approximately 1 metre per minute, and EXO measurement rates of 1 reading per 5 seconds. The SUNA sampled at 1 reading per minute for all trials. Specific testing parameters used for each trial are provided in Table 4.2. Note that calculated logging rates are approximate because the sensors could not be controlled using an automated winch or pulley system, which is further explained below.
Table 4.2: Testing dates, measurement and logging rates used for EXO vertical profiling methods. Logging rates are approximate values calculated by dividing depth of water column by time to finish profiling.

<table>
<thead>
<tr>
<th>Site</th>
<th>Well</th>
<th>2014 Testing Dates</th>
<th>Sensors</th>
<th>Measurement Rate (s⁻¹)</th>
<th>Logging Rate (m⁻¹)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Port</td>
<td>Rowan</td>
<td>31-Jul, 28-Aug, 11-Oct</td>
<td>SUNA, EXO</td>
<td>1-5</td>
<td>0.5-1</td>
<td>Different logging, measurement rates tested on 31-Jul, with multiple runs in succession to evaluate borehole mixing from sensor movements</td>
</tr>
<tr>
<td>ROW</td>
<td>ROW1</td>
<td>04-Sept, 15-Oct</td>
<td>SUNA, EXO</td>
<td>5-10</td>
<td>1-3</td>
<td></td>
</tr>
<tr>
<td>ROW</td>
<td>ROW2</td>
<td>04-Sept, 15-Oct</td>
<td>SUNA, EXO</td>
<td>1-10</td>
<td>1-2</td>
<td>EXO not used at Stone Well on 16-Oct. GDC-10 used for initial testing of equipment</td>
</tr>
<tr>
<td>Guelph</td>
<td>GDC-10</td>
<td>10-Jul, 15-Jul</td>
<td>EXO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stone</td>
<td>04-Sept, 16-Oct</td>
<td>SUNA, EXO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Well 9</td>
<td>17-Sept</td>
<td>EXO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Well 10</td>
<td>17-Sept</td>
<td>EXO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.7: a) SUNA field cable and stainless cable, taped together and clamped to casing as the sensor is lowered down-hole; b) Stainless cable reel, laptop, Sutron logger and external power supply, which power and communicate with the sensor

The SUNA required physical modifications for vertical profiling, as it was not necessarily designed for use in groundwater environments. The SUNA does not possess internal power supply, so it requires constant communication with a power supply at the surface using a field cable. The device has significant weight (~2.5 kg) that cannot be supported by the field cable alone, so the body of the SUNA was fitted with a wireline cable that was securely fastened to the sensor using hose clamps. The sensor was lowered down-hole using the wireline cable, which was attached to the field cable approximately every one metre, as shown in Figure 4.6. A Sutron 9210B datalogger, which was powered by an external 12V battery at the surface, defined measurement intervals and provided power to the SUNA. Unlike some geophysical methods such as ATV logging, power supply and communication for the SUNA are not delivered through
a single wireline, and no winch or pulley system is available. This renders cable management and profiling rate control more challenging, as the user cannot automate retrieval speeds using a winch. However, careful field operation of the equipment ensured that logging rates were kept fairly consistent. It is also noteworthy that the SUNA does not contain an integral depth sensor, meaning that it cannot correlate measurements to depth in the water column. A Schlumberger Diver (Schlumberger Canada Ltd., Waterloo, ON) was attached to the base of the SUNA to measure depths of the device. Due to size constraints associated with the SUNA, it was determined that profiling methods would be difficult to apply in wells having diameters smaller than four inches. Therefore, profiling with the SUNA was not conducted at the BAFF site, which has HQ diameter boreholes (3.78"). EXO profiling during the second testing period at the Stone Well (October 16, 2014) could not be completed due to equipment failure.

4.2.2.2 Data Analysis

Profiling data obtained using the EXO was downloaded directly from the sonde using YSI’s KOR software. The sonde’s depth results were post-processed to compensate for barometric pressure and the position of the sonde’s depth sensor relative to its geochemical sensors. The SUNA and Diver data was then integrated with EXO data and separated into downward vs. upward profiling logs. In trials where multiple successive profiling runs in the same borehole were conducted, data was also separated for each profiling run. Geochemical profiles were plotted for each well relative to measured depth within the water column. Well construction details and hydrostratigraphic formations were plotted on the same axes. Changes in geochemistry were analyzed with respect to changes in formations or well construction. Profiling data from different testing periods was plotted on the same figure for each borehole to analyze any temporal variation in profile characteristics.

4.2.3 Real-time Remote Monitoring

Real-time remote monitoring (RTRM) techniques were developed in October to November 2014 following the completion of the second round of vertical profiling. The objective was to evaluate the technique for continuous, down-hole groundwater quality monitoring. Testing was initiated in one borehole (PR11/12) at the Port Rowan site in Norfolk County on November 7, 2014 with a second borehole instrumented at PR8/12 on January 9, 2015. A third site, located in Guelph approximately 150 metres north of the Stone Well, in a groundwater spring capped with a concrete structure (see Figure 3.14), was instrumented in May 2015. It could not be instrumented earlier due to a lack of winter access at the site. The Stone Well itself was not instrumented due to a lack of available sunlight near the well building, which is required to
power the monitoring system. Upon installation, all three monitoring sites were able to run continuously through June 2015.

4.2.3.1 Field Methods

![Diagram of remote monitoring system](image)

Figure 4.8: Real-time remote monitoring conceptual diagram (not drawn to scale), including EXO and SUNA, Diver, modified well cap, telemetry and battery enclosures and tripod stand, as well as solar array. Wireline and field cables were connected with PVC tape (shown in green).

A conceptual diagram for the real-time remote monitoring system is provided in Figure 4.8. Both the EXO and SUNA were deployed down-hole simultaneously, with their measurement depths located at the midpoint of the screened interval, as chemistry was hypothesized to represent average values for the screened interval at the midpoint. This was noted during vertical profiling and will be discussed in the results section. Each sensor was fitted with a communication cable and wireline cable, and the sensors were deployed one after the other to avoid any tangling. The EXO and SUNA sensors were suspended within the borehole at constant depths and were
attached to a modified well cap using threaded stainless steel carabiners. The well cap (shown in Figure 4.8) has two holes for accommodating field cables, a stainless steel eye bolt protruding from its bottom side for attaching equipment, and a rubber packer/seal that is tightened using bolts on its top surface. Field cables were threaded through the cap, which was then tightened to seal the borehole. The annular spaces around the holes in the well cap were sealed using conduit putty to ensure vermin-proofing of the well. A small hole was created in a vent tapping through the cap so that it was vented to atmospheric pressure.

A Schlumberger Diver was attached to the bottom of the SUNA at PR11 and recorded water levels hourly. An additional Diver was installed in MW3 to monitor groundwater levels in PR8. Since MW3 and PR8 are less than 20 m apart, and are screened in the same depth interval, it is reasonable to assume that groundwater levels in MW3 are the same as those in PR8. A third Diver was installed in MW3 to record hourly barometric pressure and correct water level readings across the site for atmospheric pressure. Precipitation and air temperature data for the Port Rowan site was obtained from the University of Guelph’s Simcoe Research Station, which is located about 20 km east of the RTRM stations (1283 Blueline Rd. Box 587, Simcoe, Ontario, Canada). Daily precipitation and temperature data was available for the duration of the monitoring period, but hourly data was only available beginning January 1, 2015. No Divers were installed at the Stone Well site, but a rooftop weather station operated by the School of Engineering at the University of Guelph (50 Stone Road East, Guelph, Ontario, Canada) was used to obtain hourly precipitation data for the duration of monitoring activities.

As described in the instrumentation section, field cables were connected to the Sutron datalogger through conduits in the telemetry enclosure. Small ferrules from the tail end of both field cables were connected to DIN rail terminals (shown in Figure 4.9) using an electronics screwdriver. Upon connection, a fused power terminal was switched on to initiate monitoring, and the telemetry and battery enclosures were locked to secure the equipment. Field documentation for the station implemented at PR11 is provided in Figure 4.9. It is important to note that while site and equipment security may present an issue at some locations, no challenges were encountered at the field sites for this project. No digging or site landscaping was required to secure the monitoring stations, which can be readily adjusted to accommodate site gradients and terrain. Each station sampled on hourly intervals and transmitted data remotely and wirelessly over the HSPA network.
Figure 4.9: Field set-up for real-time remote monitoring at the Port Rowan site; a) Modified well cap showing eye bolt and threaded carabiners from which sensors were suspended in the borehole; b) Top view of sealed well cap, with conduit putty used in annular spaces; c) View of tripod-mounted system as it operated at PR11/12 after installation; d) Close-up of telemetry enclosure showing datalogger, DIN rail terminals, modem, antenna, solar charge regulator and sensor input field cables; e) Close-up of battery enclosure, which housed a deep cycle lithium ion battery, as well as spare EXO field cable; f) SUNA field cable management and guy wire attachment to secure tripod to ground
Sensors at each field station were retrieved approximately every three weeks to one month, as shown in Table 4.3, to check for instrument drift. The SUNA was evaluated for two types of instrument drift that can occur in optical sensors: optical drift, which is caused by biofouling, particularly on the sampling window, and spectral drift, which is caused by actual changes in the absorbance spectra of the device relative to the deionized water (DIW) baseline. After retrieval from the borehole, SUNA measurements were taken using DIW and compared to pre-deployment readings. One measurement was first taken without cleaning the sensor, to account for optical drift. The sensor was then cleaned using warm water and isopropyl alcohol, and a second DIW reading was taken to account for spectral drift. The EXO was evaluated for instrument drift by taking measurements with the device in both DIW and tap water and comparing the readings to pre-deployment values. It was more difficult to measure exact drift readings for the EXO because some parameters (i.e. conductivity) are temperature dependent, and it is difficult to keep temperatures constant in the field. It was also challenging to maintain cleanliness on the device and its calibration environment. Exposing the standard solutions to the EXO after field deployment can contaminate the solutions, which require further use in future calibrations. After potential drift was evaluated and each sensor was re-calibrated, they were deployed down-hole to resume RTRM.

Table 4.3: Site visit dates for RTRM stations. Sensors were evaluated for drift and recalibrated if necessary.

<table>
<thead>
<tr>
<th></th>
<th>PR11</th>
<th>PR8</th>
<th>Stone Well</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR8</td>
<td>November 29, 2014</td>
<td>January 31, 2015</td>
<td>June 1, 2015</td>
</tr>
<tr>
<td>PR8</td>
<td>January 9, 2015</td>
<td>February 14, 2015</td>
<td></td>
</tr>
<tr>
<td>PR8</td>
<td>January 31, 2015</td>
<td>March 6, 2015</td>
<td></td>
</tr>
<tr>
<td>PR8</td>
<td>February 14, 2015</td>
<td>April 28, 2015</td>
<td></td>
</tr>
<tr>
<td>PR8</td>
<td>March 6, 2015</td>
<td>May 13, 2015</td>
<td></td>
</tr>
<tr>
<td>PR8</td>
<td>April 28, 2015</td>
<td>June 11, 2015</td>
<td></td>
</tr>
<tr>
<td>PR8</td>
<td>May 13, 2015</td>
<td>June 11, 2015</td>
<td></td>
</tr>
<tr>
<td>PR8</td>
<td>June 11, 2015</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SUNA readings from PR8 were compared to grab samples from the same location obtained using purge methods. Monitoring well MW3, which is located adjacent to PR8, was purged and nitrate concentrations were measured at the surface using the flow cell method developed in section 4.2.1. Purged samples were obtained on March 27, April 22 and May 13, 2015. Sampling was attempted earlier but could not be completed due to issues with site access and extensive snowfall during the 2014-2015 winter. Sampling also could not be conducted at PR11 because the adjacent monitoring well MW4 was subject to deformation, likely due to expansion.
of ice within the annular space between the PVC pipe and steel casing surrounding it, such that a submersible pump could not be lowered into the well.

Purge samples were also obtained from well MW1 on March 27 and submitted for isotope and chemical analyses. Nitrogen-15 ($^{15}$N) and Oxygen-18 ($^{18}$O) analyses were undertaken to provide evidence for denitrification and additional insight regarding potential nitrate sources as discussed in section 2.2.1. Dissolved organic carbon (DOC) and nitrite ($\text{NO}_2^-$) were also measured to provide evidence for denitrification. DOC can serve as an electron donor for denitrification, and elevated nitrite concentrations can suggest that nitrate is being reduced to nitrite and eventually nitrogen gas (Rivett et al., 2008). Deuterium ($^2$H) and $^{18}$O concentrations were measured relative to Vienna Standard Mean Ocean Water (VSMOW) to assess groundwater source. The isotope ratios $\delta^2$H and $\delta^{18}$O should be linearly correlated (i.e. they would lie on a straight line when plotted) if sourced from precipitation (Clark & Fritz, 1997). Tritium ($^3$H) concentrations were measured to estimate “ball park” values of groundwater age, applying a decay rate to known atmospheric tritium concentrations following nuclear bomb testing in the 1950s (Clark & Fritz, 1997). Tritium values ranging from 5 to 15 tritium units (T.U.) indicates the presence of modern groundwater (i.e. <5 to 10 years) (Clark & Fritz, 1997).

Isotope and chemical analyses were conducted using a range of standardized methods. EC and DO are required for isotope testing and were measured on site using the YSI 556 handheld multi-parameter sonde. Nitrite was measured using the colorimetric method (SM 4500 B), and DOC was measured using the high-temperature combustion method (SM 5310 B). Isotopic analysis for $^{15}$N was measured using a VG Micromass spectrometer following a sequence of precipitation and combustion reactions following the methods described by Silva et al. (2000). Analysis for $^{18}$O and $^2$H was conducted using a LGS Water-Vapor Isotope Analyzer (Los Gatos Research, Mountain View, CA, United States). Tritium ($^3$H) was analyzed by liquid scintillation counting after enrichment by a factor of 15 (A.E. Lalonde AMS Laboratory, n.d.). Duplicate samples were measured for all isotope analyses. Values for $^{15}$N, $^{18}$O and $^2$H were reported using $\delta$ notation relative to atmospheric $\text{N}_2$ (AIR) and VSMOW, respectively, while $^3$H results were reported using T.U.

4.2.3.2 Data Analysis

Raw and filtered data for all RTRM stations was plotted, while data from the PR11 and PR8 monitoring stations was further analyzed statistically. No correlations were calculated for the
Stone Well site. Statistical analyses were performed using SPSS (22.0) software. The objective of the analysis was to explore correlations and infer relationships between the measured parameters. It was hypothesized that one or several parameters including nitrate, EC, temperature, DO, pH or turbidity may serve as viable indicators for groundwater recharge, and may therefore be correlated to measured groundwater levels or precipitation. Furthermore, if strong correlations existed between any of the variables, it could be possible to develop linear regression models which would predict groundwater chemistry values given groundwater levels or precipitation readings. A secondary objective was to evaluate the spatial relationships between the two stations. It was expected that since PR11 and PR8 are located in the same aquifer unit and less than 500 metres from one another, their observed datasets should be *spatially correlated*; that is, if a parameter changes in one well, a similar change should be observed in the other. Thus, evaluating the correlations between datasets from each station provided a means of evaluating the efficacy of the RTRM monitoring methods.

Statistical Theory
Correlations between datasets obtained from PR11 and PR8 were evaluated using the cross-correlation function (CCF). Since the data is measured in time series, it is not certain that changes in one variable would immediately affect another, as there may be time-offsets or lags between the predictor and response variables. Simple bivariate linear correlation methods are inappropriate in these cases, which are more suited to cross-correlation techniques (Box & Jenkins, 1976). The CCF is essentially the Pearson product-moment correlation between two datasets that is calculated at different time lags, so it accounts for potential time-offsets between the two datasets (Meko, 2015). Consider two different time series: $x$ and $y$, each having $N$ observations with averages $\bar{x}$ and $\bar{y}$ that are measured at identical, equally spaced time intervals. The CCF is then given by equation 1:

$$r_{xy}(k) = \frac{c_{xy}(k)}{\sqrt{c_{xx}(0)c_{yy}(0)}}$$

(1)

Where $r_{xy}$ is the cross-correlation between $x$ and $y$ at the specified lag $k$, and $c_{xy}$ is the cross-covariance function (CCVF) between $x$ and $y$, which is given by equation 2:

$$c_{xy}(k) = \frac{1}{N} \sum_{t=1}^{N-k} (x_t - \bar{x})(y_{t+k} - \bar{y})$$

(2)
Thus, the CCF is the CCVF normalized by the sample variances of x and y (Meko, 2015). The CCF is calculated at different lags, both negative and positive, and correlations range between -1.0 and 1.0, which would imply perfect negative (i.e. one variable decreases linearly in response to an increase in the other) or positive (i.e. one variable increases linearly in response to an increase in the other) correlation, respectively (Fiorillo & Doglioni, 2010). High correlations at negative or positive lags indicates that one variable is either lagging or leading the other, which can aid in identifying which variable is the predictor and which is the response variable, if the relationship is unknown (Meko, 2015).

The CCF is typically plotted showing all cross-correlations at each time lag, along with 95% confidence intervals (CIs) for testing significance of the calculated cross-correlations. The confidence intervals were calculated assuming that 1) the processes generating x and y are uncorrelated and not autocorrelated; 2) the populations are normally distributed; and 3) the populations have a large sample size (Meko, 2015). These assumptions result in a CCF with mean zero and a variance $1/N$, such that any cross-correlation exceeding the confidence interval, either in the positive or negative direction, results in the null hypothesis that the CCF is zero is rejected (Meko, 2015). While not a required assumption for the CCF, it is also ideal if the relationship between x and y is linear, since the cross-correlation measures the strength of the linear association between them.

Autocorrelation or serial correlation refers to the dependence that a dataset has with itself over time (Montgomery et al., 1987). Autocorrelation is similar to cross-correlation in that it calculates Pearson’s product-moment correlations at different time lags, with the difference being that it is univariate; rather than correlating two different time series datasets, it correlates a single dataset with another version of itself that is shifted at different time lags. For the same time series dataset x measured at equal intervals, the autocorrelation function (ACF) is given by equation 3:

$$r_x(k) = \frac{\sum_{i=1}^{N-k} (x_i - \bar{x})(x_{i+k} - \bar{x})}{\sum_{i=1}^{N} (x_i - \bar{x})^2}$$  \hspace{1cm} (3)$$

where $r_x$ is the autocorrelation coefficient at lag $k$ (Box & Jenkins, 1976). The ACF is calculated at different time lags and then plotted, with coefficients ranging from -1.0 to 1.0, similar to the CCF (Meko, 2015).
Groundwater data, including the RTRM data obtained in this project, is frequently subject to autocorrelation. It is critical that autocorrelation is investigated because it can result in violation of the assumptions of independence (Montgomery et al., 1987) and stationarity (Horvatic et al., 2011), which are required for many time series applications including CCFs. A stationary dataset in time series analysis is defined as one whose statistical properties do not change over time (Nason, 2006); thus, the ACF of a stationary time series should exist as “white noise” clustered around an average correlation of zero across all lags. When evaluating confidence intervals for the CCF, a significant correlation is one that leads to rejection of the null hypothesis that the time series datasets are stationary. If the datasets are autocorrelated, the trends in data will tend to persist in the CCF, which can result in spurious correlations and conclusions to be postulated (Granger & Newbold, 1974). In such instances, it is recommended that any underlying trends be removed from the data prior to calculating the CCF. There are numerous de-trending methods available, such as linear regression, seasonal decomposition and differencing, and the reliability of each is dependent on the nature of the data (Yaffee & McGee, 2000). First differencing is a simple method which subtracts the value of the dataset one time lag before the present value (i.e. \( X_t - X_{t-1} \)), which is usually sufficient for removing stochastic, linear trends (Yaffee & McGee, 2000) and ensuring that the dataset is approximately stationary (Granger & Newbold, 1974; Nason, 2006). If complex trends exist within the data, first differencing may not completely alleviate the issue of autocorrelation, but it should render the CCF interpretations more accurate (Granger & Newbold, 1974).

Normality of the data is commonly investigated to support any conclusions associated with parametric testing. It is important to note that in this study, the normality assumption was tested largely for interpreting the confidence intervals of the CCF rather than the correlation values themselves. It has been demonstrated that Pearson’s \( r \) is robust in dealing with violations of normality, especially when dealing with large sample sizes (Norman, 2010). Having normally distributed data is therefore likely to be more useful for ensuring confidence in identifying significant or “outlying” correlations from the CCF. Normality can be assessed visually using histograms. Skewness and kurtosis of the distribution can also be analyzed and should approach zero and three for a normal distribution (Kim, 2013). If the distribution is normal, histograms should have data that is approximately bell shaped (Ghasemi & Zahediasl, 2012). There are additional normality tests, including the Shapiro-Wilks and Kolmogorov-Smirnov (K-S) tests. However, these methods are less reliable when dealing with large sample sizes, as they are sensitive to outliers (Ghasemi & Zahediasl, 2012; Kim, 2013). It is recommended that these
tests only be performed on datasets having $N \leq 50$, which is much smaller than any of the sample sizes in this study. In the case of clear departures from normality, one can attempt to approach normality by transforming the data using techniques such as the log transformation (Yaffee & McGee, 2000).

**Statistical Methods**

Figure 4.10: Simplified framework applied to Port Rowan RTRM data for statistical analysis

The framework used for statistical analyses of the monitoring data is shown in Figure 4.10. Hourly monitoring data from the RTRM stations was integrated with groundwater elevation and precipitation data in a centralized database. The data was initially pre-processed before any statistical analyses could be performed. Upon examination, it was noted that measurements tended to “stabilize” or revert to ambient conditions approximately 18-23 hours following a recalibration of the sensors, due to mixing within the water column. Thus, measurements within the first 24 hours following recalibration were carefully discarded, although the original data was retained for comparison purposes. Outliers were carefully discarded for each parameter using Tukey’s Hinge method, which calculates outliers using the expressions $>Q3 + (1.5 \times IQR)$ or $<Q1 – (1.5 \times IQR)$, where $Q3$ is the 3rd quadrant (i.e. the 75th percentile), $Q1$ is the first quadrant (i.e. the 25th percentile), and IQR is the interquartile range $Q3-Q1$ (Tukey, 1977).

Due to several issues that will be further discussed in the results section, the nitrate datasets contained several missing values. Missing value analyses were undertaken to determine a suitable process for imputing missing data. Little’s MCAR test returned a significant result ($p<0.05$), meaning that the null hypothesis that the data is missing completely at random (i.e. there are no observable patterns regarding the missing data) was rejected, and missing values
could not be imputed using listwise, pairwise, or regression methods. Robust imputation methods including expectation-maximization (EM) and multiple imputations were investigated, but the nature of the data distributions and patterns within the missing data made it difficult to find reasonable solutions. Missing values were therefore imputed using linear interpolation, with the exception of precipitation data, which was imputed using the series mean. The datasets were further consolidated into daily averages and standard deviations to smoothen any large aberrations within the hourly data, and were plotted to examine more generalized trends. First differences were taken to remove trends and ensure that the data was stationary.

Histograms were constructed for both pre- and post-differenced data to visually inspect the data for normality. Transformations were applied when necessary using Tukey’s ladder of transformations (Tukey, 1977), but it was determined that no transformations rendered the data more normal. This will be discussed further in the results section. ACFs were constructed for pre- and post-differenced data to ensure that the differenced data was approximately stationary. Two CCFs were first calculated using daily groundwater level and precipitation data collected from well MW3 on the Port Rowan site beginning in January 2013. Data from April through October, representing the general time period in which recharge can occur, was isolated for both 2013 and 2014. CCFs were then plotted for each year to determine if groundwater levels responded at a consistent lag time with respect to precipitation. This lag time, if such consistency existed between years, could then provide some guidance as to how many days/lags that water quality CCFs should be calculated for. For example, if a lag time of 5 days was observed in the CCF between precipitation and groundwater elevation for both 2013 and 2014, it follows that changes in groundwater quality due to recharge should occur sometime around 5 days, as this may represent the aquifer response time to precipitation events.

CCFs were then calculated by crossing each of the water quality parameters (nitrate, temperature, EC, pH, DO and turbidity) with groundwater levels and then precipitation. As mentioned, the number of specified lags was based on the initial precipitation-groundwater level CCFs with some additional lags added as a “safety factor”. CCFs were calculated using daily averaged data for two different time periods: once for all available data at each station, and again using data only from March 9th and onwards. This approximates when average temperatures exceeding zero degrees persisted in 2015, so recharge was more likely to occur following that date. It was hypothesized that perhaps the correlations from the CCFs would be stronger after isolating for potential recharge periods. CCFs were calculated using hourly data.
as well, but there was too much noise to identify correlations. Significant correlations (i.e. those exceeding the CIs) were identified for each CCF and then evaluated to examine linkages between the measured parameters. The results and implications are discussed in the following section, while all histograms and ACFs can be found in the Appendices.

5 Results

5.1 Flow Cell Testing

As described in the methodology, nitrate concentrations were measured using the SUNA flow cell method for samples from nine wells and over four testing periods, resulting in 32 independent trials. The SUNA measured nitrate concentrations continuously within the flow cell during purging, with one measurement recorded approximately every second. It was advantageous to have many hundreds of measurements for each trial, as personnel were able to ensure that nitrate concentrations stabilized before extracting a bottle sample. The measurements obtained were therefore more representative of the aquifer, and the residuals were minimized for each trial.

Nitrate time series graphs were generated for each testing period to evaluate concentration trends during purging. A sample of time series concentrations from five locations are provided in Figure 5.1. Note that nitrate concentrations were not obtained immediately upon purging (i.e. where time = 0), as the flow cell had to be filled to a height exceeding that of the SUNA’s optical sampling window. There are gaps in the measured data for some trials, such as those for wells 14-S and 07-S in Figure 5.1, as the flow cell was emptied and refilled due to the presence of sandy/silty interfering species.
Figure 5.1: Nitrate time series graphs for five LPT3 wells, obtained during the first flow cell testing period from July 29 to August 1, 2014. Trials from the four additional T3 wells from the same testing period were excluded because concentrations persisted at or around 0 mg L\(^{-1}\) throughout purging.

Concentrations were generally consistent throughout purging for most trials, with only slight increasing or decreasing trends (i.e. on the order of 0.2 to 0.3 mg L\(^{-1}\)), as demonstrated by wells 04-S, 18-S and 18-I in Figure 5.1. This stability in concentrations can be largely attributed to mixing of the purged water within the submersible pump and flow cell. Other trials displayed significant differences in concentrations from the start to finish of purging. Flow cell measurements from well 14-S increased throughout purging by almost 1.5 mg L\(^{-1}\), from approximately 7.69 mg L\(^{-1}\) to 9.08 mg L\(^{-1}\). Lower initial concentrations may have been caused by mixing of stagnant water located higher within the water column. Concentrations would theoretically increase as more representative groundwater having higher nitrate concentrations is discharged into the flow cell. It is also possible that concentrations increased as groundwater from the aquifer entered the flow cell after the water from the well column and sand pack was purged. It has been shown that water in the sand pack can have significantly different concentrations compared to water in the aquifer (Martin-Hayden, Robbins & Bristol, 1991).

Some time series displayed an initially damped or oscillating response, with nitrate samples having more deviation. This occurred at 07-S during the first testing period, and may have been caused by the presence of interfering sandy/silty species in the highly turbid purged water during the onset of pumping. The oscillating response that was observed indicates that SUNA performance may be affected by extremely turbid environments. The response may have been caused by mixing of purged water having lower nitrate concentrations that was present in the
pump tubing from previous trials. However, extra care was taken in running the pump for one to two minutes before discharging into the flow cell, to reduce any mixing effects within the pump tubing.

The mean concentration and standard deviation throughout purging was calculated for each flow cell trial, with results provided in Figure 5.2. Observed NO\textsubscript{3}⁻-N concentrations ranged from 0 to 15.81 mg L\textsuperscript{-1}, which was ideal for testing the SUNA’s performance, because those values span what may be considered a reasonable or “expected” range for groundwater environments, particularly in southern Ontario. Standard deviations were quite small, with the largest value being 0.45 mg L\textsuperscript{-1} and many being equal to or less than 0.10 mg L\textsuperscript{-1}. No single well appears to be more prone to variability in observed concentrations during purging. It is likely that in trials having larger standard deviations, variability may have been caused by sandy/silty interfering materials as previously discussed. Evaluation of the time series mean concentrations as well as standard deviations from Figure 5.2 suggests there is not much variability in nitrate concentrations in these wells throughout purging. Therefore, while it is generally good practice to purge at least three borehole volumes before extracting a sample for laboratory analysis, samples obtained earlier will likely suffice if nitrate is the desired parameter, especially if project or equipment constraints make extensive purging difficult. In many cases, the SUNA flow cell method would simplify the data collection process and make it easier to obtain more samples. It reduces the amount of equipment required, and may be more desirable if the user wishes to minimize sample handling, reduce trips to a laboratory and obtain samples directly in the field.
Figure 5.2: Average nitrate concentrations (NO₃⁻-N) and standard deviations for each flow cell testing trial, ordered by location and time. Concentrations generally appeared to decrease across the LPT3 site over winter 2015.

Although not a specific objective of this research, the results from Figure 5.2 can be analyzed for any temporal patterns in the observed nitrate concentrations. It appears that nitrate concentrations decreased over the winter at most locations. Wells 07-S and 04-S experienced increases by February 2015, although concentrations continued to decrease in the other wells. It was expected that nitrate concentrations should increase for most if not all wells after fertilizer application in early spring, and again after harvest in late fall, since nitrogen leaching is more likely to occur after the crop has been removed (OMAFRA, 2006). However, increases in concentrations were only observed in wells 14-S and 07-S in October 2014, and again in 04-S in November 2014. This might be explained by differences in travel times from surface to aquifer at the different locations, but it is hard to determine that nitrate concentrations increased due to fall recharge. Further testing during the spring may help to provide insight regarding recharge and its effect on nitrate concentrations within the aquifer as a function of contaminant travel times. However, caution must be exercised in analyzing the results from Figure 5.2. With gaps of approximately two months between each testing period, it is difficult to infer conclusions.
regarding concentrations between each testing period. In similar studies with data obtained using traditional sampling techniques, nitrate time series are linearly interpolated between sampling periods, which can be speculative in nature and may be insufficient in conclusions that are grounded in the temporal variability of the data. Having the ability to obtain nitrate concentrations at a finer temporal resolution would help to address this challenge. This underlines the value of developing real-time remote monitoring techniques as discussed in section 4.2.3.

The simple linear regression model fitting nitrate concentrations from laboratory samples with respect to nitrate concentrations from SUNA flow cell measurements is shown in Figure 5.3. Summary statistics regarding the errors and correlation between the Lab and field results are provided in Table 5.1. As discussed in section 4.2.1, it is important to examine the normality of residuals, which is a critical assumption when constructing linear regression models. A histogram and normal probability (or Q-Q) plot was constructed for the residuals and is shown in Figure A-3 in Appendix A. The residuals are reasonably normally distributed, so the linear regression model has a good fit and the constructed 95% confidence and prediction intervals can be used (Montgomery et al., 2012). The regression model does not necessarily require a preceding data transformation. However, it was determined that by log transforming the data, the linear regression model achieves a better fit, as the data is closer to normal, especially upon examining the Q-Q plot in Figure A-3 d). It is not necessary for this research to optimize the fit of the model, as it is really only used to evaluate the correlation between laboratory and SUNA nitrate-N concentrations, and pearson’s r (and therefore R²) is robust against departures from normality (Norman, 2010). Therefore, the linear regression model using log transformed nitrate-N data was not included or analyzed for this research, but if the user wishes to improve the accuracy of confidence and prediction intervals in the model (with no real expected changes to R²), it would be useful to first apply a log transformation to the data.
Figure 5.3: Simple linear regression model, with upper and lower 95% confidence and prediction bands for laboratory nitrate measurements as predicted by SUNA field nitrate measurements. Precision for each method is shown with error bars. A total of 32 independent trials from flow cell testing periods in Norfolk County were used.

Table 5.1: Mean squared error (MSE), root mean squared error (RMSE), normalized root mean squared error (NRMSE), linear correlation coefficient (r) and coefficient of determination ($R^2$) from flow cell testing period

<table>
<thead>
<tr>
<th>Testing Period</th>
<th>SUNA Device</th>
<th>n</th>
<th>MSE</th>
<th>RMSE</th>
<th>NRMSE (%)</th>
<th>r</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unit 1</td>
<td>9</td>
<td>0.02</td>
<td>0.13</td>
<td>1.19</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
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<td>Unit 2</td>
<td>9</td>
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<td>0.45</td>
<td>4.19</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>3</td>
<td>Unit 3</td>
<td>9</td>
<td>0.02</td>
<td>0.13</td>
<td>0.83</td>
<td>0.999</td>
<td>0.998</td>
</tr>
<tr>
<td>4</td>
<td>Unit 1</td>
<td>5</td>
<td>0.50</td>
<td>0.71</td>
<td>4.36</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Average Error: -0.25 mg L$^{-1}$  
Average Absolute Error: 0.28 mg L$^{-1}$

The regression model results from Figure 5.3 indicate that the SUNA performed tremendously well in groundwater environments, as evidenced by the high coefficient of determination ($R^2$=0.994) in comparison to laboratory values. The small average error (-0.25 mg L$^{-1}$) and
average absolute error (0.28 mg L$^{-1}$) suggest that the SUNA is precise in obtaining measurements that are consistently similar to laboratory analysis, and the sensor is not prone to having significant outlying errors relative to lab results. It should be noted that the results of the regression model do not imply causation, as lab concentrations are not a truly dependent variable; that is, SUNA concentrations do not directly affect lab concentrations. Rather, 99.4% of the variance in measured lab concentrations can be explained by corresponding variances in measured SUNA concentrations. At 95% confidence, the true slope of the regression line falls within the range of 1.07 ± 2.05. High coefficients of determination on the order of 0.98 to 1.0 were observed during all testing periods, with mean squared errors ranging from 0.02 to 0.20 mg L$^{-1}$. Therefore, each of the three individual SUNA units used throughout this project was shown to accurately measure groundwater nitrate concentrations. This suggests that the SUNA measurements obtained in groundwater environments can be reported with confidence.

The regression model, and by extension the SUNA, is especially accurate in measuring nitrate-N concentrations ranging from approximately 0 to 8 mg L$^{-1}$. The data within that range falls very close to the least squares regression line, which is contained by tightly spaced confidence bands. There is some divergence of the confidence bands starting at approximately 10 mg L$^{-1}$, but this is expected in linear regression models, since the standard error of the regression line is larger towards the edges of the model domain. The accuracy for the SUNA and Lab measurements are ± 8% and ± 10%, respectively. Thus, the larger the nitrate concentration is, the higher the absolute value of its uncertainty, as seen in Figure 5.3. In most cases, the extents of the uncertainties do not exceed those of the prediction interval bands, except at the largest observed concentrations at the edge of the model domain. While the model residuals are larger when nitrate concentrations exceed 10 mg L$^{-1}$, the SUNA still performs within what would be considered acceptable accuracy limits. Conducting more trials, especially in which concentrations exceed approximately 13 mg L$^{-1}$, would help further verify the accuracy of both the SUNA and the model.

After the SUNA’s accuracy was validated, the flow cell testing method was applied to the LPT3 monitoring well network, encompassing many of the same wells used when the flow cell method was first developed. The purpose was to apply the flow cell method to a case study to demonstrate its value in future applications. Testing was conducted on April 29th and 30th, 2015. A total of 23 wells were purged and nitrate concentrations were measured using the SUNA. The results were plotted with groundwater elevation contours as shown in Figure 5.4. The value in
using the SUNA flow cell method was clearly demonstrated. It was possible to characterize nitrate concentrations at a regional scale within a very short time frame, with field work and interpretation of the results requiring only three days. This greatly reduced processing time and potential sources of error due to sample handling that are typically associated with traditional methods. The analysis of results could even be completed in the field if desired. The flow cell method would be particularly valuable for municipalities, conservation authorities or other water supply managers that require regular nitrate sampling at the regional scale. For some parties, it may be more convenient to have the means of obtaining nitrate measurements in-house, and the flow cell method could provide a means of doing so. It could also be useful for screening purposes; one could use the SUNA flow cell method to characterize a large regional area such as that shown in Figure 5.4, then use the results to plan a more detailed sampling regime, possibly including the vertical profiling or RTRM methods developed in this project (see sections 4.2.2 and 4.2.3).
Figure 5.4: Regional nitrate concentrations, sampled using the SUNA flow cell method from 23 wells within the LPT3 monitoring network over a two day period from April 29 to 30, 2015. Groundwater levels (GW Elev.) were measured manually and contoured using kriging in ESRI ArcMap Version 10.0. The town of Simcoe is shown on the eastern portion of the map (visible dense road networks), with Delhi just west of the map’s extents. In locations with wells at multiple depths, the largest of the measured concentrations is shown. Map created using ESRI ArcMap Version 10.0, with satellite imagery from SWOOP (2006).
5.2 Vertical Geochemical Profiling

The vertical profiling method developed is flexible in its requirements for testing time, and can be adjusted based on the needs of the user. In large production wells (i.e. those having diameters of 6” or larger), vertical profiles were collected in less time than if the user was to purge the well and collect discrete samples for laboratory analysis. The profiling method was also useful because measurements were obtained without exposure to the environment at the surface, which may have important implications on the measured values, particularly for parameters such as DO and pH (Nielsen & Nielsen, 2007). The resulting vertical profiles with lithology and well construction details are provided from Figure 5.5 to Figure 5.13. Raw profiling data used to generate these Figures is available as complementary data (see Appendix C:).

Port Rowan

The four profiles collected from the Port Rowan site are shown in Figure 5.5, Figure 5.6, Figure 5.7, and Figure 5.8. There are distinct changes in nitrate, EC, DO and turbidity upon entry into the screened interval in these wells. No significant changes were observed in pH or temperature along the screened interval. Due to the relatively short length of the screens of approximately one metre, no clear stratifications of parameters were observed along the screens. The evidence provided by the profiles across the site suggests that while that water column above the screen contains stagnant water having different chemistry, the screened interval contains fresher water that is likely subject to ambient flow conditions within the aquifer. Therefore, the SUNA and EXO sensors can and should be deployed within the screen for any RTRM or other in situ monitoring initiatives. Based on profiling results, wells PR11 and PR8 were chosen for RTRM, as they contained the highest nitrate concentrations of any production wells on site, which approached 5 mg L\(^{-1}\) and 1 mg L\(^{-1}\), respectively.

Analyzing the changes in profiles more specifically, clear increases in nitrate were observed along the screen in wells PR8 and PR11, with minor increases likely in PR6 and PR9, although concentrations were essentially zero (i.e. close to non-detect) in those two wells and were therefore more difficult to interpret. Large increases in EC on the order of 200 to 400 \(\mu\)S cm\(^{-1}\) were observed along the screen in wells PR6, PR8 and PR11, but no significant increase was observed in PR9. Increases in DO of approximately 4 to 6 mg L\(^{-1}\) were observed along the screen in wells PR6 and PR11, with a smaller increase of approximately 1 mg L\(^{-1}\) at PR8 and no clear increase at PR9. Increases in ORP towards the screen and/or bottom portion of the well were observed across all wells. This suggests that strongly reducing conditions are present.
along the water column, but a transition towards conditions that are neither reducing nor oxidizing occurs within the well screen, and by extension the surrounding aquifer, at that depth. Strongly reducing conditions and low DO suggest that denitrification processes are most favourable at PR8, which may help to explain why nitrate-N concentrations are lower there (i.e. 1 mg L\(^{-1}\)), while they approach 5 mg L\(^{-1}\) and 3 mg L\(^{-1}\) in wells PR11 and MW2, which are located on either side of PR8, as shown in Figure 3.8. It is possible that denitrification reactions are more rapidly attenuating the nitrate plume in the area surrounding PR8, while concentrations are more persistent around PR11 and MW2 because conditions are less favourable for denitrification. Nitrate concentrations are low at PR6 because denitrification processes are likely favourable, and because the well is located east of the nitrate plume. Nitrate concentrations are low at PR9 because the well is located significantly down-gradient from the nitrate plume and its potential source(s), and is therefore subject to dilution within the aquifer. Evidence does suggest that conditions may also favour denitrification at PR9, so nitrate would likely be attenuated at that location if concentrations were not already decreased through dilution.

Profiles collected at the Port Rowan site do not appear to display much temporal variability. The SUNA nitrate profiling method is consistent, since profiles showed very little change between two profiling runs on August 28 and October 11, 2014. EXO profiles appear to be more temporally variable, which may be partly due to slight differences in calibration of the device, and partly due to sensitivities and response times within the measured parameters. For example, turbidity appears to be sensitive to profiling and therefore displays more variability in measured results. It is likely that the movement of the sensors during profiling disturbs the water column, suspending sediments and increasing turbidity readings. The straighter profiles for nitrate, EC, DO, temperature and pH suggest that these parameters may be less sensitive to mixing within the water column. However, changes in the absolute values being measured for pH during different profiling runs, particularly at PR6 and PR8, suggests that pH can be quite temporally variable on site (i.e. changes of approximately 1 pH over different profiling runs), or that readings may be sensitive to calibration values. A similar conclusion was observed for EC at wells PR6 and PR9, although EC profiles were less temporally variable in wells PR8 and PR11. It was also interesting to note the change in the DO profile from August 28 at well PR8. Oxygen readings were much higher during this profiling run, even though they remained consistent in other wells during the same period. It is unclear if this result is some sort of methods-based aberration, or if a natural process caused an increase in DO at PR8. It is possible that the observed increase could be partly due to purging of the nearby monitoring well,
or by profiling with the EXO too quickly, resulting in mixing of the oxygen rich water located higher in the water column as the EXO sonde was lowered down-hole.

It is critical to be conscious of vertical profiling speeds, which can have a large effect on the measured concentrations. Profiling at a faster rate (i.e. on the order of 2 m min⁻¹ or faster) likely induces more mixing within the water column and may result in a coarser resolution that captures chemical gradients poorly. This was evident in the October 11 profiling run with the SUNA at PR11. The faster profiling speed resulted in readings being obtained at depths of approximately 10.5 and 12.5 metres from surface, with no measurements in between. The measured profile therefore has no data available near the entrance into the screened interval, which is where large changes in nitrate concentrations are expected to occur. By profiling more slowly (i.e. on the order of 0.5 m min⁻¹ or slower), the user would better capture this transitional region, as shown in the earlier run conducted on August 28. This could be particularly important in open bedrock boreholes, where well concentrations at along the entire open borehole are probably more representative of aquifer conditions compared to the stagnant water in cased overburden wells. A benefit of the profiling method developed is that the user can customize the profiling and logging rates of both sensors. Thus, the spatial resolution of the profiles can be adjusted depending on site-specific project requirements.

Region of Waterloo
Similar profiling results as those from Port Rowan were observed in the screened overburden wells located in the Region of Waterloo, shown in Figure 5.9 and Figure 5.10. Increases in nitrate, EC and turbidity were observed along the screened intervals of Test Wells 1 and 2, with decreasing pH and no observable changes in DO or temperature. The nitrate profiles measured were consistent, with slight temporal variation at Test Well 1 between the profiling runs on September 4 and October 15, 2014. It is interesting to note two distinct plateaus or zones of nitrate concentrations within the longer screened interval in Test Well 2. The deeper zone is probably more representative of concentrations at that depth in the aquifer, while the zone closer to the top of the well screen is probably a mixture of the deeper water having high nitrate and shallower water having low nitrate. It is therefore evident that vertical profiling with the SUNA can capture vertically stratified nitrate concentrations along the screened interval. To the best of the author’s knowledge, this is the only method that can measure stratified nitrate concentrations (with observable differences) directly down-hole, without the use of multilevel systems, packer equipment, or depth-discrete interval sampling equipment such as the Snap
EXO profiles from the Region of Waterloo showed little temporal variation, especially for Test Well 2; however, there was some variation in pH between profiling runs. It is difficult to assess whether this variation is due to sensitivity in calibration, or perhaps due to recharge processes introducing water having lower pH into the aquifer. It is likely that freshly recharging groundwater would also induce temporal changes in parameters such as DO or EC in addition to pH, but this was not observed in either well, so it is therefore difficult to conclude that temporal changes in pH are due to natural processes. It would be prudent to repeat vertical profiling at different times throughout the year to further evaluate any potential effects of groundwater recharge on the observed profiles. It would also help in assessing whether or not denitrification processes are favoured at each site. Although isotope testing and ORP readings were not obtained in Test Well 1 and Test Well 2, the low DO values observed through profiling suggest that both sites might be favourable for denitrification reactions. Denitrification processes have been observed in other locations throughout the Waterloo Moraine in previous studies (e.g. Robertson et al., 1996), but further testing including isotope analyses would be required to confirm this at Test Wells 1 and 2.

Guelph
Open bedrock borehole profiles from the Stone Well and GDC-10 at the BAFF (shown in Figure 5.11 and Figure 5.13) show different results compared to the overburden wells in Port Rowan and the Region of Waterloo. Two distinct peaks in turbidity were observed at depths of approximately 12.5 and 17.5 metres below ground surface and may serve as indicators for flow through fractures at those depths. This evidence would not have the same resolution as methods such as ALS heat pulse techniques (e.g. Pehme et al., 2010), but may serve as a quick method for identifying flowing fractures, especially to locate intervals of active groundwater flow to place the sensors for future RTRM on site (see section 5.3). Geophysical logging techniques would be useful for confirming the presence of fractures near the depths where these increases in turbidity were observed. It is very important to note that due to the nature of the Stone Well, which was drilled decades prior to this study, no borehole logs or information about lithology or well construction was made available. Lithology was inferred from another borehole located approximately 300 metres east of the site. It is assumed that a well casing extends to a depth just below the overburden, but this could not be confirmed.
Geophysical methods cannot be performed on site due to issues with site access (i.e. physically transporting the required equipment to the Stone Well). However, low nitrate and DO concentrations at depths corresponding to the inferred overburden depths were observed, which suggests the presence of stagnant water due to the probable existence of a well casing to depths of approximately 4 metres to 8 metres below ground surface, depending on the thickness of the overburden. The interpretation of results at the Stone Well would be aided by provision of lithological and well construction details, along with the previously mentioned geophysical techniques.

The nitrate profile at the Stone Well shows three distinct zones of concentration that decrease with depth. The uppermost zone has concentrations of approximately 8.0 mg L\(^{-1}\), which decreases to 7.5 mg L\(^{-1}\) at depths of approximately 9 to 14 metres and then to approximately 6.5 mg L\(^{-1}\) from depths of 14 to 19 metres. This is easier to visualize in Figure 5.11, in which nitrate and DO profiles were specifically isolated. The decreases in nitrate appear to correlate with decreases in DO at the same depths, suggesting that denitrification processes might be favourable in what is presumed to be the lower depths of the Guelph formation or the upper portion of the Eramosa formation. A slight decrease in pH and increase in EC were observed at depths corresponding to the aforementioned decrease in DO, which suggests the presence of groundwater having different composition, possibly due to changes in lithology or from flow through fractures. The evidence therefore suggests that the lower depths of the Guelph formation or the Eramosa formation is capable of naturally attenuating nitrate concentrations in the area surrounding the Stone Well, which is in agreement with Opazo (2012). The middle zone having nitrate concentrations of approximately 7.5 mg L\(^{-1}\) may represent the zone of mixing between the water from the overburden or upper portion of the Guelph formation having higher nitrate concentrations, and the water from the deeper portion of the Guelph formation having lower nitrate concentrations. The effects of borehole mixing should be further investigated using techniques such as borehole flowmeter testing (e.g. Hess, 1986), which would help in interpreting the different zones of geochemistry at the Stone Well.

Profiling results from GDC-10 (Figure 5.13) show distinct and rapid decreases in DO and a transition towards reducing conditions below the Eramosa formation, with a slight decrease in DO towards 0 mg L\(^{-1}\) towards the bottom of the Reformatory Quarry member. Although SUNA profiling could not be performed at GDC-10 due to size constraints, it is likely that if any nitrate did exist on site, it would not persist below the Eramosa Formation due to the presence of
reducing conditions favouring denitrification, as suggested by Opazo (2012). A large increase in EC of over 3000 μS cm\(^{-1}\) was observed from the upper dolostone units to the deeper shale units, which was expected. Slight decreases in pH appear to occur at the bottom of the Eramosa formation and near the top of the Gasport Formation. Similar to the Stone Well results, distinct increases in turbidity were observed at two depths along the borehole within the Reformatory Quarry member. A more systematic increase in turbidity was observed at all locations towards the bottom of the Gasport formation, which is known to contain actively flowing fractures. It is unclear whether or not these increases in turbidity are indicative of active groundwater flow.

It is evident that vertical profiling methods can be used to identify stratified geochemistry within the water column of a well, particularly in open bedrock boreholes or in overburden wells having long screened intervals. In situations in which lithology information is not known, profiling can serve as a useful tool for quickly obtaining general information about the chemistry within a well at different depths, and might provide evidence for changes in lithology or well construction. If fracture location information is not known and if more robust techniques such as ALS or flowmeter testing cannot be applied, it may be possible to quickly identify flowing fractures using turbidity values at different depths from vertical EXO profiles. However, the absolute values being measured are undoubtedly affected by vertical flow and mixing within the water column. If highly accurate, depth-discrete geochemical data is a project requirement, it would still be beneficial to use multilevel monitoring systems. It would also be interesting to refine the developed vertical profiling techniques by creating a method that integrates the SUNA and EXO with borehole linear or packer-type equipment. Such methods would isolate specific intervals within the borehole and eliminate errors due to vertical flow and mixing within the water column. At present, vertical profiling techniques would be most useful for identifying suitable zones for placing the sensors for future RTRM initiatives, and may also be useful as an initial screening tool for the placement of monitoring ports during the design of multilevel well systems.
Figure 5.5: Vertical geochemical profiles for PR6, obtained at the Port Rowan site on July 31, August 28 and October 11, 2014
Figure 5.6: Vertical geochemical profiles for PR8, obtained at the Port Rowan site on July 31, August 28 and October 11, 2014.
Figure 5.7: Vertical geochemical profiles for PR9, obtained at the Port Rowan site on July 31, August 28 and October 11, 2014
Figure 5.8: Vertical geochemical profiles for PR11, obtained at the Port Rowan site on July 31, August 28 and October 11, 2014
Figure 5.9: Vertical geochemical profiles for Test Well 1, obtained from the Region of Waterloo site on September 4 and October 15, 2014
Figure 5.10: Vertical geochemical profiles for Test Well 2, obtained from the Region of Waterloo site on September 4 and October 15, 2014
Figure 5.11: Vertical geochemical profiles for the Stone Well, obtained on September 4 and October 16, 2014. It is unclear how far the well casing extends, but it probably extends to approximately 8 m below ground surface, to contact with the bedrock.
Figure 5.12: Vertical geochemical profiles for the Stone Well, obtained on September 4 and October 16, 2014. The results for nitrate and DO have were isolated and placed on longer axes to clarify their interpretation and analysis. It is unclear how far the well casing extends, but it probably extends to approximately 8 m below ground surface, to contact with the bedrock.
Figure 5.13: Vertical geochemical profiles for GDC-10, obtained from the BAFF site on July 15, 2014. SUNA profiling could not be conducted due to size constraints within the borehole.
5.3 Real-time Remote Monitoring

5.3.1 Isotope Sampling

Isotope and chemical analyses were completed for a purged sample from MW1 obtained on March 27, 2015, as discussed in section 4.2.3. The isotope analyses provide information about groundwater source and age, as well as potential nitrate sources at the Port Rowan site, so it is important to discuss their results prior to interpreting RTRM data from Port Rowan. Sampling results are provided in Table 5.2, with a plot showing $\delta^{18}$O v. $\delta^{2}$H relative to the global meteoric water line (GMWL) shown in Figure 5.14. Measured tritium concentrations (8.8 T.U.) suggest the presence of fresh groundwater that is younger than 50 years, as older groundwater has tritium <5 T.U. (Stotler et al., 2011). Results for $\delta^{18}$O and $\delta^{2}$H fall very close to the GMWL, suggesting that the groundwater is sourced from modern precipitation, since little fractionation has occurred for either isotope reading (Merlivat & Jouzel, 1979). This result is logical given that MW1 is screened in an unconfined aquifer having a shallow water table (i.e. water table is approximately 3.80 m BGS). Recharge to the aquifer is probably quite rapid following precipitation events. It is likely that the aquifer unit has freshly recharged groundwater at all locations across the site, but additional purged samples across the site would help confirm this. Groundwater chemistry in the shallow aquifer on site is probably affected by recharge processes, since residence times are not very long. Therefore, RTRM data should be evaluated knowing that responses in groundwater chemistry should occur at small lag times after precipitation events, since groundwater in the aquifer is modern.

Potential nitrate sources were evaluated by plotting $\delta^{15}$N and $\delta^{18}$O. It was believed that the nitrate might be sourced from an agricultural field located up-gradient from PR8 and PR11 (see the nature of the plume shown in Figure 3.8). Analysis of Figure 5.14 suggests that nitrate at the site is sourced from either ammonium-based fertilizer or human/animal manures, which confirms that the agricultural operation up-gradient is likely a contributing source. High nitrate and DO concentrations at MW1 of 10.8 and 7.15 mg L$^{-1}$, respectively, suggest the presence of strong oxidizing conditions that are favourable for nitrification. Low DOC (<1.0 mg L$^{-1}$) and nitrite (0.007 mg L$^{-1}$) concentrations do not suggest that denitrification is occurring around MW1. It would be valuable to further isotope analyses, particularly near PR8 and PR11, to better understand nitrification and denitrification processes across the site.
Table 5.2: Results from isotope and chemical analyses for purge sample obtained from MW1 on March 27, 2015. NO₃⁻ was measured using the SUNA. DOC, NO₂⁻, and SO₄²⁻ were measured at the University of Guelph's AFL. Isotopic analyses were conducted at the University of Waterloo's Environmental Isotope Laboratory. Duplicates were performed for all isotopic analyses.

<table>
<thead>
<tr>
<th>Analysis (units)</th>
<th>Result</th>
<th>Duplicate</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg L⁻¹)</td>
<td>&lt;1.0</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻ (mg L⁻¹)</td>
<td>10.80</td>
<td>n/a</td>
<td>± 8%</td>
</tr>
<tr>
<td>NO₂⁻ (mg L⁻¹)</td>
<td>0.007</td>
<td>n/a</td>
<td>± 8%</td>
</tr>
<tr>
<td>DO (mg L⁻¹)</td>
<td>7.15</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>δ¹⁸O (VSMOW)</td>
<td>-10.34</td>
<td>-10.13</td>
<td>± 0.2%</td>
</tr>
<tr>
<td>δ¹⁵N (VSMOW)</td>
<td>2.29</td>
<td>-</td>
<td>± 0.3%</td>
</tr>
<tr>
<td>δ²H (TU)</td>
<td>8.8</td>
<td></td>
<td>± 0.8 T.U.</td>
</tr>
<tr>
<td>δ²H (VSMOW)</td>
<td>-67.53</td>
<td>-66.97</td>
<td>± 0.8%</td>
</tr>
<tr>
<td>SO₄²⁻ (mg L⁻¹)</td>
<td>40</td>
<td>n/a</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.14: Isotopic analysis results for δ¹⁸O v. δ²H and δ¹⁵N v. δ¹⁸O for a purged sample from MW1 compared to GMWL. Results for δ¹⁸O v. δ²H are used for estimating groundwater age and source, and results for δ¹⁵N v. δ¹⁸O are used for estimating nitrogen sources.
5.3.2 Quality Control, Drift and Equipment Performance

Before presenting and interpreting the results from RTRM, it would be valuable to recall the quality control practices implemented during monitoring and discuss their potential implications on the measured data. As discussed in section 4.2.3, the SUNA and EXO were retrieved approximately every three weeks to one month, cleaned and re-calibrated, and checked for spectral and optical drift. It should again be noted that it is generally easier to test for drift within the SUNA, as standard solutions are readily available and are not temperature dependent, and because it is easier to maintain the calibration environment for the SUNA. Results showed that no spectral or optical drift was observed in the SUNA throughout monitoring, so measured RTRM concentrations were expected to be accurate relative to those in the well. It may be possible to extend the length between checking drift and re-calibrating the SUNA (i.e. for longer than periods of three weeks), but that would depend on the environment in which the sensor is deployed. No significant drift was observed within the EXO after comparing to a DIW baseline, and any intermittent drift would have been corrected during calibration. However, it is still possible that some drift is occurring within the EXO, as it is more difficult to quantify compared to the SUNA. Therefore, additional methods were also used to check for drift in the EXO, which will be discussed below. Any drift present is expected to be linear and is largely corrected for during differencing of the data prior to calculating the cross-correlation functions.

A simple strategy used to investigate the accuracy of RTRM observations from PR11 and PR8 was to compare RTRM values (from Figure 5.15 and Figure 5.17) with those obtained along the screened interval from vertical profiles within the same well. The profiling values used are shown in Table 5.3 and were estimated based on averages along the well screen and then used to obtain “ballpark” comparisons to RTRM data. RTRM readings for temperature, EC, pH and turbidity readings fell into an acceptable range close to values from Table 5.3 for PR11, but nitrate and DO showed some divergence. Nitrate values obtained from profiling and previous purge sampling approached and exceeded 4 mg L\(^{-1}\), while most RTRM values did not exceed 3 mg L\(^{-1}\). This may in part be due to seasonal effects that cause differences in nitrate concentrations at different times throughout the year. Monitoring over several years would help in investigating these effects. DO values from RTRM regularly exceeded 6 mg L\(^{-1}\), while profiling values were closer to 4 mg L\(^{-1}\). All RTRM values from PR8 were in reasonable agreement with those from Table 5.3, with the exception of EC. Vertical profiling estimates suggested EC was on the order of 600 uS cm\(^{-1}\), while RTRM readings ranged from approximately 700 to 900 uS cm\(^{-1}\).
Table 5.3: Estimated averages along screened interval from PR11 and PR8 vertical profiles. These values were used for making a simple “ballpark” comparison to RTRM data from the same wells.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PR11</th>
<th>PR8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>4.0 mg L⁻¹</td>
<td>1.0 mg L⁻¹</td>
</tr>
<tr>
<td>GW Temp</td>
<td>8.5 to 9.0 °C</td>
<td>8.5 to 9.0 °C</td>
</tr>
<tr>
<td>EC</td>
<td>550 uS cm⁻¹</td>
<td>600 uS cm⁻¹</td>
</tr>
<tr>
<td>DO</td>
<td>4.0 mg L⁻¹</td>
<td>0 to 1.0 mg L⁻¹</td>
</tr>
<tr>
<td>pH</td>
<td>7.5 to 7.9</td>
<td>7.0 to 8.0</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0 to 30 NTU</td>
<td>0 to 20 NTU</td>
</tr>
</tbody>
</table>

The RTRM data was also compared to three purged samples obtained from MW3, which is located less than 20 metres from PR8. Samples were measured in a flow cell using the SUNA for nitrate and the YSI 6820 multi-parameter sonde for field parameters, after three borehole volumes were purged. Field parameters could not be obtained on April 22 because the YSI sonde was not available. Purged samples could not be completed for comparison at PR11 because the nearby monitoring well MW4 had warping in the PVC stick-up and could not accommodate a submersible pump. The results of the comparison for PR8 are shown in Table 5.4. Upon inspection, it appears that nitrate, temperature and pH readings are quite similar between the two methods. The purged sample for nitrate was only slightly lower than RTRM data on April 22nd, and was very close on the other sampling dates. Minor differences in nitrate might be due to the slight differences in locations between the two wells, but overall it appears that nitrate readings are consistent between RTRM and purged samples. DO readings are not close with one another, but are believed to have been caused by a faulty calibration of the 6820 handheld multi-parameter sonde, because concentrations appear to be unreasonably large. Profiling results indicate that well PR8 is likely an environment having low DO, so it is very unlikely that concentrations would exceed 10 mg L⁻¹. EC readings from RTRM are significantly higher than their respective purged samples, especially around May 13. It is possible that some differences in conductivity exist between MW3 and PR8, but vertical profiling in PR8 also suggested that EC concentrations are on the order of 600 µS cm⁻¹, which is significantly lower than RTRM readings. The EC readings for the EXO in PR8 may have therefore been affected by drift or error, which is difficult to correct for, but should be considered when analyzing RTRM results. Ideally, more purged samples should have been obtained at both PR8 and PR11, but constraints related to site access and equipment availability made that difficult. Having more purged samples available would supplement the comparisons made with RTRM data.
Table 5.4: RTRM data compared to purged samples from PR8, sampled on March 27, April 22 and May 13, 2015.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RTRM</td>
<td>Purged Sample</td>
<td>RTRM</td>
<td>Purged Sample</td>
<td>RTRM</td>
<td>Purged Sample</td>
</tr>
<tr>
<td>Nitrate (mg L(^{-1}))</td>
<td>0.94</td>
<td>1.00</td>
<td>1.38</td>
<td>1.01</td>
<td>1.23</td>
<td>1.36</td>
</tr>
<tr>
<td>GW Temp. ((^\circ)C)</td>
<td>8.91</td>
<td>9.20</td>
<td>8.85</td>
<td>-</td>
<td>8.85</td>
<td>9.47</td>
</tr>
<tr>
<td>EC ((\mu S cm(^{-1}))</td>
<td>835.55</td>
<td>774</td>
<td>946.11</td>
<td>-</td>
<td>919</td>
<td>742</td>
</tr>
<tr>
<td>DO (mg L(^{-1}))</td>
<td>0.39</td>
<td>10.21*</td>
<td>0.61</td>
<td>-</td>
<td>0.51</td>
<td>20.43*</td>
</tr>
<tr>
<td>pH</td>
<td>7.70</td>
<td>7.38*</td>
<td>7.64</td>
<td>-</td>
<td>7.76</td>
<td>7.37</td>
</tr>
</tbody>
</table>

* Measurement is suspect due to poor calibration

Based on ballpark profiling and purged sample comparisons from both wells, it appears that similar results can be achieved for many parameters, which suggests that RTRM and vertical profiling can be used as alternatives to traditional sampling methods. However, site specific discrepancies can affect the reproducibility of the measured data for some parameters at each site. It is difficult to determine whether the discrepancies result from experimental differences or environmental differences. For example, mixing within the borehole column during profiling probably affects the raw values observed, which constitutes a potential experimental difference. Other experimental differences occur between methods because the sensors sample at a constant depth in the middle of the screen during RTRM, sample along most of the screened interval during profiling, and sample from the aquifer outside the screen during purging. As discussed in section 5.2, vertical profiling results suggested that absolute measured values are dependent on the position of the sensors within the screen. Thus, each of the methods is likely to produce somewhat different results. Environmental differences could arise because the surface and subsurface are two distinctly different environments and have been shown to affect values such as DO and pH depending on which environment the groundwater is sampled in (Nielsen & Nielsen, 2007). There is also temporal variability to consider at the Port Rowan site, since the parameters clearly change with time. Thus, while there are obvious differences in nitrate and DO at PR11 and in EC at PR8, it does not necessarily imply that RTRM methods are inaccurate. Rather, they provide a different means of obtaining information about the geochemistry within a well intersecting the formation. This is important to consider when formulating conclusions about the RTRM datasets, especially considering the objectives of this research, where investigating trends in parameters is desired.
The time series datasets collected using RTRM were analyzed visually using both daily averaged and hourly data, and the datasets from PR11 and PR8 were further analyzed statistically using the framework developed in section 4.2.3. Hourly and daily averaged time series graphs for PR11, PR8 and the Stone Well are shown in Figure 5.15 to Figure 5.20. Cross-correlation functions between groundwater levels, precipitation and measured water quality parameters are shown in Figure 5.22 to Figure 5.32. Detailed statistical charts including histograms and autocorrelation functions (ACFs) for all RTRM parameters can be found in Appendix C, along with raw datasets and figures documenting how outliers were removed from the raw data.

As expected, the hourly datasets show more variability compared to daily averages for all RTRM stations. Gaps in the data are a result of three separate processes: 1) calibration events, (which are specifically shown in the Appendix B) in which the equipment was either powered off or because the data from the first 24 hours after calibration was removed, as discussed in section 4.2.3; 2) outlying data points, which were removed using Tukey's Hinges (Tukey, 1977) as discussed in the methodology section, and; 3) missing data points, which occurred for the SUNA (i.e. nitrate) data but not the EXO data (e.g. Figure 5.15). The SUNA did not function properly at times and it does not have internal logging. The EXO does have internal logging capabilities, so it was able to record data internally following a power outage at the PR11 station from December 13, 2014 to January 9, 2015. Diagnostics did not clarify what caused the SUNA to malfunction at times. Battery voltage, SUNA supply voltage and relative internal humidity did not seem to be underlying factors. It was theorized that perhaps the malfunctioning was driven by external temperatures or disabling of field communication cables, but no evidence directly supported that. In most cases, the SUNA would start spontaneously measuring again without having to examine the device in the field; however, there was no period in which the SUNA at PR11 worked for several weeks straight with no interruptions. There were no patterns in the missing nitrate data between both PR8 and PR11. There was significantly more missing data at PR11 compared to PR8, with a total of 29% and 1.5% missing within their respective hourly datasets. It is therefore more likely that the missing data may have resulted from some sort of defect in the equipment, which only seemed to be a significant issue in the one device present at PR11.
5.3.3 Visual Analysis

PR11
Since PR11 was the first RTRM station to be commissioned, the daily averaged and hourly datasets from Figure 5.15 and Figure 5.16 are the most extensive of any collected. Climate data suggests that the equipment was deployed for two of the major recharge events in late November 2014 and early January 2015, as discussed in section 3.1.2, with no additional recharge events until after snowmelt in late March 2015. There was a period of extreme cold from late January to early March 2015 in which a large amount of snow accumulated on site, with no apparent periods of melting. A period of significant precipitation occurred in late March and early April, and likely contributed to spring recharge in addition to snowmelt. The volume of recharge in spring 2015 appears to be smaller than in the two previous years, based on groundwater levels in Figure 3.7; however, the groundwater levels were not depleted as significantly in summer 2014 compared to summer 2013, so the absolute values of measured groundwater levels in spring 2013, 2014 and 2015 were reasonably similar. The three distinct recharge periods noted from fall 2014 to spring 2015 are important to note for interpretation of the measured RTRM data at PR11.

Observed turbidity values may offer the most interesting results from this study. Upon visual inspection, it appears that turbidity might serve as the most viable indicator for groundwater recharge, which supports similar findings by Fournier et al. (2007) and Pronk et al. (2009). There were clear pulses (>5 NTU) in hourly and daily averaged turbidity readings corresponding to recharge events in late November and early January 2015. The pulses had little or no time lag between precipitation, groundwater levels and increased turbidity values. These distinct pulses lasted approximately two to five days before turbidity readings returned to ambient levels. A second pulse occurred around January 23, 2015 and lasted until approximately February 15; a period of about 22 days. The source of this larger pulse is more difficult to identify, as it occurred during a period where no recharge occurred. It is possible that this pulse resulted from a larger flux of groundwater moving through the site from up-gradient; however, this likely would likely have been reflected in observed groundwater levels. Groundwater elevations decreased during the same time period. It is also possible that the prolonged turbidity pulses resulted from field visits on January 9, January 30 and February 13, in which the water column was disturbed and freed sediments settled slowly. However, the water column appears to have returned to ambient levels within two or three days following the field visit on February 13. Field activities conducted do not suggest that the water column was disturbed any more
significantly on January 9 or 30, so it is not likely that the water column remained disturbed for 22 days straight. A third potential source of the prolonged turbidity increase is snowmelt in conjunction with rainfall events in late January. Examination of observed air temperatures suggests that this may have been the case; however, again it should be noted that groundwater levels decreased during this time, which does not suggest the presence of freshly recharging water.

Other responses in turbidity were observed and appear to correspond to spring recharge. A slight, gradual increase from approximately 1 to 4 NTU was observed starting in late March, with two larger pulses in early April of approximately 10 NTU. The larger pulses resembled those in fall 2014 and also appeared to follow significant precipitation events in early April, but the turbidity pulses did appear to have a slightly longer lag time following precipitation compared to fall 2014 recharge events. This is probably due to the presence of more vegetation on site in April compared to late November, which would uptake some of the precipitation as it travels through the unsaturated zone. It is expected that lag times would increase through the summer and into early fall, until eventually little or no pulses in turbidity are observed, as increases in evapotranspiration restrict recharge from occurring on site. Lag times do not appear to be any larger than about two to four days for all turbidity pulses. Based on the visual trends of RTRM parameters with respect to groundwater levels, it is likely reasonable to assume that turbidity could serve as the best indicator of recharge of all parameters measured, at least for the PR11 site.

Additional changes were observed which appear to correspond to the major spring recharge event in late March and early April 2015. An increase in EC of approximately 15 to 20 μS cm\(^{-1}\) was observed over a period of about two weeks from March 30 until April 12, which seemed to peak and then recede with groundwater levels. Nitrate also increased during the same period by almost 1 mg L\(^{-1}\) and then receded with groundwater levels. DO decreased significantly and appeared to respond to significant precipitation events in early April, then continued to gradually decrease with groundwater levels. No significant trends were observed in groundwater temperature or pH, which are likely quite consistent in the unconfined overburden aquifer in Port Rowan. It is possible that the increases in EC and nitrate were due to freshly recharging groundwater, as it can intercept nitrate in the unsaturated zone and salts at or close to ground surface, which would contribute to elevated EC concentrations (Rivett et al., 2008). It is more difficult to explain the decrease in DO, which was not necessarily expected. Freshly recharging
groundwater should theoretically have higher DO concentrations since it was more recently exposed to atmospheric oxygen. However, it may be possible that what has been postulated as freshly recharging groundwater is actually slightly older groundwater that has been pushed deeper through the saturated zone by fresher groundwater as it reaches the top of the water table. The older groundwater could have lower DO concentrations, which may explain why decreases in DO were observed following recharge events.

As previously discussed in section 5.3.1, tritium dating and δ¹⁸O-δ³H analyses conducted on site suggested the presence of modern groundwater with short residence times. However, these methods provide “ball park” estimates of groundwater age (i.e. less than 5 years), and cannot confirm age or residence time with high resolution. Therefore, although groundwater from the shallow, unconfined aquifer in Port Rowan is fresh, it is possible that it may still reside near the top of the saturated zone for some time before reaching the depths that the SUNA and EXO sensors were located at. There was no consistent pumping on site that would artificially induce locally confined vertical travel through the saturated zone, so any of this travel or mixing would be occurring through natural recharge processes. The dynamics of mixing of groundwater through the saturated zone are not very well understood at the Port Rowan site, so it might be valuable to conduct a tracer experiment to evaluate vertical travel times through the saturated zone.

**PR8**

Monitoring results from PR8 (shown in Figure 5.17 and Figure 5.18) also appeared to have responses in groundwater chemistry due to 2015 spring recharge. Again, it appears that turbidity might serve as the most viable indicator of recharge. Similar increases in turbidity of approximately 10 to 15 NTU were observed at PR8 beginning around March 28 and persisted almost until the end of April, which was a slightly longer time period compared to the increase observed at PR11. Two additional pulses in turbidity occurred between March 17 and March 28 and probably correspond to infiltrating snowmelt, which will be further discussed. There was also an increase in EC of approximately 100 µS cm⁻¹ and an increase in nitrate of approximately 0.4 mg L⁻¹ which appear to correspond to the aforementioned increases in turbidity and groundwater levels during spring recharge. These observed increases are in agreement with similar increases at PR11. There was another small increase in nitrate of approximately 0.4 mg L⁻¹ that occurred in early February but did not seem to result from a recharge event. It may instead result from groundwater from up-gradient having higher nitrate concentrations moving
across the area around PR8. It is also possible that the increase could be due to some unforeseen issue with the SUNA sensor during monitoring, although such an issue would be difficult to verify without disturbing the aquifer and therefore affecting the measured nitrate values. Furthermore, since no optical or spectral drift was observed in the SUNA throughout monitoring at both PR11 and PR8, it is believed that the measured nitrate concentrations are accurate with respect to the true concentrations in each well. However, concentrations within a well may not necessarily agree with concentrations in the surrounding aquifer because of effects such as vertical flow and mixing. While the increase in nitrate observed in PR8 in early February was not necessarily expected, the small magnitude of change suggests that it may not be linked to recharge or other hydrogeological mechanisms.

The pH and DO data in Figure 5.17 and Figure 5.18 seems to contradict the results for pH and DO from PR11. A sharp increase in pH of about 0.4 occurred around March 17, the causes of which are difficult to interpret. The pH then seems to continue to increase through March and early April. At about the same time as the increase in pH, the DO concentration increased to 1 mg L\(^{-1}\) from essentially zero or non-detect and then persisted around 0.5 mg L\(^{-1}\). The changes in both parameters in April seem to be related to spring recharge when compared with groundwater levels, but it is the increases prior to March 28 that are not easily understood. The results from vertical profiling at PR8 (see Figure 5.6) suggest that the observed DO and pH readings from RTRM are consistent with those observed in profiling, but the values are obviously affected by the depth in the water column, even within the same screened interval. Thus, it follows that a potential source for the observed changes in pH and DO preceding spring recharge might be that the position (i.e. depth) of the EXO was altered slightly. However, the depth was maintained by a stainless cable which did not change length throughout monitoring, so it is unlikely the position of the EXO changed.

Upon closer inspection of the air temperature data, it appears that a period of above zero temperatures occurred starting around March 9, 2015. The sharp observed increases in pH and DO occurred starting around March 17. A slight but distinct increase in groundwater temperature was observed at the same time. It is therefore possible that the observed increases in pH, DO and temperature resulted from snowmelt reaching the saturated zone, with a lag time of less than eight days following the initiation of snowmelt. This would explain the rapid observed increases in pH and DO beginning about March 17. The increases are more gradual beginning about March 28, probably because recharge was occurring less rapidly after the
snowmelt reached the water table. No real increases in groundwater temperature were observed later in March or in early April. A sequence of precipitation events throughout late March suggests that a more gradual recharge period through April was onset by rainfall, while recharge from about March 17 to March 28 resulted from snowmelt at the Port Rowan site. The recharge period that may have resulted from snowmelt induced sharp changes in pH, DO, groundwater temperature and turbidity, while the recharge period likely resulting from spring rainfall induced more gradual but distinct increases in nitrate, EC, DO and turbidity. The evidence from PR11 suggests that the RTRM parameters affected by recharge, as well as the rates of change of the parameters, are probably dependent on whether the recharge was sourced from either recharging snowmelt or recharging rainfall.

**PR11 and PR8**

While many of the results have been discussed, it is important to compare the results from PR11 and PR8 with one another to evaluate the effectiveness of the RTRM methods. Since the wells are located in the same unconfined aquifer less than 500 metres from one another, the observed data should hypothetically show some spatial correlation. Figure 5.21 compares the datasets from each well visually. The groundwater elevations appear to be very strongly correlated, suggesting that groundwater reaches each well at about the same time. Similar increases in nitrate and EC were also observed and likely correspond to spring recharge. Turbidity appears to show similar peaked responses related to recharge, albeit with time lags between the two datasets, which may indicate different response or travel times. An increase in DO at PR8 and a decrease at PR11 was observed around the same time, which is difficult to interpret. While few changes were observed in groundwater temperature and pH at PR11, changes were observed at PR8 around March 17 and may correspond to recharging snowmelt. Comparing the values of the measured data, it is evident that PR8 generally had higher observed turbidity and EC readings, while PR11 had higher pH and DO readings. Groundwater temperature was approximately the same between the two sites, but increased by approximately 0.2 °C at PR11 during monitoring while decreasing by approximately 0.2 °C at PR8. It is unlikely that the observed temperature readings resulted from instrument drift, as the EXO’s temperature thermistors are quite stable and do not require re-calibration (YSI Inc., 2013).

Many studies have investigated the chemistry of snowmelt. These can help in supporting the hypothesis that snowmelt in late March induced changes in groundwater chemistry at the Port
Rowan site. It is well established that atmospheric pollutants and ionic compounds can be stored in snowpack, especially in winters with uninterrupted cold periods (Johannessen & Henriksen, 1978). Compounds such as $\text{H}^+$, $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ can then be released during spring melt, resulting in “ionic pulses” (Harrington & Bales, 1998) that typically increase EC and decrease pH of the receiving body due to the acidic nature of natural precipitation (Johannessen & Henriksen, 1978). The initial pulse is typically stronger in the first few days following snowmelt, as the initial meltwater has concentrations stronger than the parent snowpack (Harrington & Bales, 1998). However, studies are often limited by sampling frequencies, which are often too short to detect these recharge pulses (Piatek et al., 2005), which underlines the potential utility of hourly monitoring using RTRM methods. Snowmelt can also store $\text{NO}_3^-$ from atmospheric deposition, but much of it is probably uptaken by plants (Piatek et al., 2005), so the main source of groundwater nitrate in spring is microbial nitrate from soil (Spoelstra et al., 2001). This supports the observation that snowmelt was initiated around March 9 and reached the water table at PR8 around March 17, which caused rapid changes in the measured parameters as previously discussed. More gradual changes were then brought upon due to recharge from rainfall events through late March and early April.

It is important to consider the thickness of the unsaturated zone and the effect it can have on vertical travel times and groundwater quality. The unsaturated zone at PR11 is more than twice as thick as the unsaturated zone at PR8, which were approximately 4.61 and 1.86 metres thick on October 14, 2014, respectively. Although both sites have shallow groundwater tables, advective travel time from the surface can be much longer at PR11. This probably explains why EC and turbidity are generally higher at PR8, as shown in Figure 5.21. It may also explain why PR8 appeared to show a sharper, more rapid response to snowmelt compared to PR11. Meltwater having higher turbidity and EC probably reached the water table more quickly, resulting in generally higher readings that changed more quickly. It may also explain why PR8 saw a small decrease in temperature with recharge, which may be in part to lower temperatures in the meltwater. The thicker unsaturated zone at PR11 can both delay the response and “dampen” the effects of recharge pulses through dilution or adsorption onto the porous media matrix. However, DO and pH results are again more difficult to explain at PR8. The thin unsaturated zone at PR8 should probably have resulted in a decrease in pH with snowmelt that was likely acidic. Further, DO concentrations should hypothetically be higher at PR8 due to the thinner unsaturated zone; however higher concentrations were observed at PR11. It seems that some localized site conditions at PR8 have resulted in reducing conditions with low DO that are
probably favourable for denitrification, despite the presence of a thin unsaturated zone. Nitrate concentrations are probably less affected by unsaturated zone thicknesses at PR11 and PR8 because the probable nitrate source is located up-gradient in an agricultural field (see Figure 3.8).

Stone Well
Since only about three weeks of RTRM data from the Stone Well was available at the time of this publication, it is difficult to infer any significant conclusions from the results shown in Figure 5.19 and Figure 5.20. From the hourly data, it is evident that there is more variability in all parameters. For example, nitrate concentrations appear to change by up to 1 mg L\(^{-1}\) on a daily basis, while EC can change by as much as 15 µS cm\(^{-1}\) and DO can change by as much as 2 to 3 mg L\(^{-1}\). This is likely because the discharging groundwater being monitored was sourced from a bedrock aquifer, which generally have faster contaminant travel times due to fracture flow, and could therefore have more variable responses in water quality compared to porous media. Turbidity values are very close to zero or non-detect at the Stone Well, which supports the notion that the water is sourced from a bedrock aquifer. It is known that bedrock aquifers can have rapid responses and more variability in nitrate and may therefore require more frequent monitoring (Levison & Novakowski, 2009), and it is evident that the RTRM station installed at the Stone Well was able to detect some of the variability at that site.

There were only two major rainfall events in the Guelph area during monitoring up until the production of this thesis, which occurred on May 31 and June 1, 2015. Initial inspection within the RTRM data suggest that a distinct decrease in pH, increase in nitrate and increase in EC was observed, possibly in response to these rainfall events. If these changes are indeed due to precipitation, it would follow that the bedrock aquifer in question appears to have rapid responses in water quality that likely occur within the same day as the rainfall event. More monitoring is required to support these initial observations and explore the relationships between groundwater quality, response times and recharge at the Stone Well site.
Figure 5.15: Time series graph showing daily averaged RTRM data (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) with climate data and groundwater levels (GW Elev.), collected at PR11 from November 11, 2014 to June 11, 2015.
Figure 5.16: Time series graph showing hourly RTRM data (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) with climate data and groundwater levels (GW Elev.), collected at PR11 from November 11, 2014 to June 11, 2015.
Figure 5.17: Time series graph showing daily averaged RTRM data (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) with climate data and groundwater levels (GW Elev.), collected at PR8 from January 9, 2014 to June 11, 2015
Figure 5.18: Time series graph showing hourly RTRM data (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) with climate data and groundwater levels (GW Elev.), collected at PR8 from January 9, 2014 to June 11, 2015.
Figure 5.19: Time series graph showing daily averaged RTRM data (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) with climate data, collected at the Stone Well from May 14, 2014 to June 1, 2015
Figure 5.20: Time series graph showing hourly RTRM data (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) with climate data, collected at the Stone Well from May 14, 2014 to June 1, 2015.
Figure 5.21: Time series graph comparing daily averaged RTRM data (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) and groundwater levels (GW Elev.) from PR11 and PR8, collected from February 1, 2015 to June 11, 2015
5.3.4 Statistical Analysis

As discussed in section 4.2.3, two CCFs were constructed for daily precipitation and groundwater elevation, with data from April through October isolated for 2013 and 2014. The CCFs are shown in Figure 5.22. The same CCFs were constructed with time lags up to 100 days, but it was determined that the highest correlations are clustered between zero and two days. It appears that the response of the water table to precipitation events is on the order of two days, as significant positive correlations were observed at two days lag time in both 2013 ($r=0.203$) and 2014 ($r=0.229$). It is unclear as to why additional significant negative correlations were observed at each well at lag time zero; there is no probable explanation as to why precipitation would lead to a decrease in groundwater levels, so that correlation was not considered. The CCF results from Figure 5.22 had important implications for the numerous CCFs constructed using RTRM data, which were plotted at time lags as suggested by results from MW3. The CCFs were plotted over 14 lags, allowing for a “safety factor” extending past the potential lag time of two days.

The method of using CCF analysis using precipitation and groundwater levels may by complemented by “back of the envelope” calculations, unsaturated zone modeling, or the van Genuchten equation as a means of estimating unsaturated zone travel time, as discussed by Sousa et al. (2013). It would be interesting to evaluate the method using CCFs in addition to the methods from Sousa et al. (2013) across several different sites. While the aquifer response time and unsaturated zone travel time are represent different phenomena, both can provide insight regarding the dynamics of contaminant transport through the unsaturated zone on site. While it is known that the relationship between precipitation and groundwater levels is certainly non-linear, the CCF lag time of two days gives a potential response time at one location on site. It must be noted that this lag time was calculated specifically during periods of recharge and is likely variable throughout the year due to climatic conditions. Lag times may also be different between MW3/PR8 and PR11 due to differences in thickness of the unsaturated zone.
CCFs comparing water quality parameters to groundwater levels and precipitation for PR11 and PR8 (Figure 5.23 to Figure 5.30) were analyzed to identify any significant correlations (i.e. those that exceeded 95% confidence intervals). Significant correlations and the time lag that they occurred at are shown in Table 5.5. Since several of the CCFs contained significant correlations at several different lags, the highest correlation was chosen. Correlations at negative lags were not included because it is known that precipitation and groundwater elevation should affect groundwater quality, but not vice versa. Any correlations at negative lags in the CCF imply that the second variable (water quality parameter) leads or predicts the first variable (groundwater level or precipitation), which is untrue. The correlation matrix in Table 5.5 makes it easier to examine trends and patterns within the correlations to support and/or refute any of the relationships previously discussed from visually inspecting the time series data. The matrix was analyzed for the types of correlations, the strengths of the correlations, and the values of the lag times for significant correlations. Any cell left blank means that no significant correlations were identified for those parameters.
Table 5.5: Correlation matrix using CCFs from Port Rowan RTRM data. Values of significant correlations are provided with time lags shown in parentheses. In the event that multiple significant correlations were seen for each parameter, the highest of the correlations was chosen. Positive correlations are shown in green and negative correlations are shown in red.

<table>
<thead>
<tr>
<th></th>
<th>PR11 (Nov – June)</th>
<th>PR11 (Mar – June)</th>
<th>PR8 (Feb – June)</th>
<th>PR8 (Mar – June)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td></td>
<td></td>
<td>0.21 (9)</td>
<td>0.32 (2)</td>
</tr>
<tr>
<td>EC</td>
<td></td>
<td></td>
<td>-0.16 (6)</td>
<td></td>
</tr>
<tr>
<td>GW Temp.</td>
<td>-0.19 (5)</td>
<td></td>
<td>0.20 (2)</td>
<td>-0.17 (2)</td>
</tr>
<tr>
<td>DO</td>
<td>0.17 (2)</td>
<td></td>
<td>-0.27 (3)</td>
<td>0.29 (0)</td>
</tr>
<tr>
<td>pH</td>
<td>0.17 (2)</td>
<td>0.30 (7)</td>
<td>-0.45 (9)</td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.14 (2)</td>
<td>-0.15 (2)</td>
<td>-0.27 (2)</td>
<td>0.27 (3)</td>
</tr>
</tbody>
</table>

Analysis of the correlation matrix yielded some interesting results that merit further discussion. No correlations across the site can be classified as “strong,” as the highest observed correlation was 0.49. The strength of association of Pearson’s r is often classified by small (0.10-0.29), moderate (0.30-0.49) or large (≥0.50), as suggested by Cohen (1977). This indicates a lack of strong linear relationships of groundwater quality with respect to recharge across the site. Correlations are generally stronger for data from March to June, which was expected since data from winter (i.e. when recharge did not occur) was not considered. It would be useful to compare the strength of the correlations between spring and fall recharge periods, but monitoring at both sites was not initiated early enough in fall 2014. It was expected that correlations would be stronger with respect to groundwater elevation rather than precipitation, as groundwater levels more directly imply the occurrence of recharge. This was true for PR8 but not for PR11, where correlations were actually stronger with respect to precipitation. Only two significant correlations were even identified for PR11 with respect to groundwater elevation, but 9 significant correlations were observed with respect to precipitation. It is puzzling as to why no significant correlations were observed with respect to groundwater levels at PR11 from March to June 2015, since responses to recharge were observed for some parameters in time series figures from visual analysis. Stronger correlations were observed for DO, pH and turbidity with respect to precipitation, but with the exception of DO, the relationships from CCF analysis seemed to refute observations from using visual analysis. Correlations at PR8 appear to generally agree with results from visual analysis, with the possible exception of pH; these relationships will be explored further.
It does not appear that there are significant differences in lag times during spring recharge (i.e. potential vertical travel times through the unsaturated zone) at PR11 and PR8, considering daily intervals. Significant correlations at PR11 with respect to precipitation occurred twice at lag times of two days, once at a lag time of three days, and once at a lag time of nine days. Significant correlations at PR8 with respect to precipitation occurred once at a lag time of one day, and once at a lag time of two days. Lag times appear to be shorter during the spring recharge period compared to when data over winter is included. The parameter that likely has the most interesting results concerning lag times is again turbidity, where significant correlations were observed at lag times of two or three days for almost every dataset. Considering the potential water table response time of two days as identified from Figure 5.22, the correlation results for turbidity appear to be in agreement. In fact, lag times of two days were identified in six other instances throughout the correlation matrix, with many other lag times of 1 to 3 days. This evidence supports the hypothesis that the aquifer response time during is on the order of two days. It also implies that the source of turbidity is probably located nearby the well, and turbidity pulses are detected after recharge moves vertically through the unsaturated zone, displacing slightly older groundwater that is pushed deeper into the saturated zone. It is noteworthy that negative correlations for turbidity with respect to precipitation were observed for PR11, which does not agree with the observed responses from visual analysis, which suggested increases in turbidity due to spring recharge. It is possible that the strength and direction of the relationship at PR11 is complicated by the thickness of the unsaturated zone, making it hard to evaluate the relationship between turbidity and precipitation. It may also be that the source of turbidity at PR11 is located slightly upgradient (where the overburden is thinner) and takes longer to travel to the well/receptors. It did appear that the observed turbidity pulses at PR11 with respect to recharge had a longer lag time in spring compared to fall; perhaps the CCF did not approach significance at larger lag times because of the lack of response to recharge at earlier times within the data.

It is evident that the presence and strength of correlations is dependent upon the endpoints of the data used to construct CCFs. Selecting start and end dates of data that will be analyzed is an arbitrary process that depends upon what the user is looking to explore. In this study, two distinct periods were chosen: one including all available data and only considering data from spring recharge, approximately March to June. The spring recharge period was chosen because visual analysis suggested that there was likely a response in RTRM variables during that time. Correlations between the two time periods for PR11 vary significantly and sometimes produce
contradictory results. For example, a negative correlation was observed between groundwater temperature and precipitation from November to June, yet a positive correlation was observed between the same parameters from March to June. Positive correlations were observed between DO and pH with respect to precipitation from November to June, while stronger negative correlations were observed for the same parameters from March to June. It follows, then, that the user should be conscious of the range of data selected when constructing CCFs, because correlations are clearly and significantly variable throughout the year. Climatic differences alter conditions on site and control when natural processes such as recharge can occur. There are ultimately endless combinations of dates that could be included, and they depend on the nature of the raw data and the objectives of the researcher. The selected dates should be carefully documented to avoid any confusion when interpreting CCFs, and efforts should be made to make comparisons between sites using the same range of dates.

It is important to remember when analyzing CCFs that they essentially represent the strength of the linear relationship between variables (Meko, 2015). Therefore, the lack of any significant correlation does not necessarily imply with certainty that one variable does not affect or predict the other; it only suggests that the variables are not linearly related. Similarly, a strong correlation only suggests the strength of the linear relationship between the two variables. It can be used as evidence to infer relationships between variables, but the underlying mechanisms need to be analyzed to demonstrate causal relationships between predictor and response variables. The strength of the relationship can also be biased through errors in statistical methodology such as autocorrelation (Montgomery et al., 1987), experimental errors such as data drift, and environmental errors such as vertical flow and mixing within the well. Therefore, the results of the CCFs should not be taken as absolute certainties, but should be used in conjunction with complementary analyses such as visual inspection. Considering the visual analyses from section 5.3.3 and correlation results from Table 5.5, Table 5.6 shows the inferred relationships for each RTRM parameter at PR11 and PR8. Parameters are marked as either increasing or decreasing with spring recharge. While the conclusions are subjective and the strength of the relationships are not shown, the trend matrix is a useful tool for comparing the results of visual CCF analyses.
Table 5.6: Trend matrix comparing results from visual and statistical (CCF) analyses of RTRM data. Trends in parameters are marked as either increasing (green) or decreasing (red) with respect to spring 2015 groundwater recharge. Only CCFs using data from March to June 2015 were considered, but both precipitation and groundwater levels were included as predictor variables.

<table>
<thead>
<tr>
<th></th>
<th>PR11 Visual</th>
<th>PR11 CCF</th>
<th>PR8 Visual</th>
<th>PR8 CCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW Temp.</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>DO</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>pH</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td></td>
<td></td>
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</tbody>
</table>

Visual and CCF analyses did not generally result in similar conclusions for PR11. While increasing trends in nitrate and EC were observed visually in response to spring recharge, CCF results found no significant correlations. It is likely that nitrate correlations were strongly influenced by a large amount of missing SUNA data in early April (see section 5.3.2). Although it was most applicable given the nature of the missing data, the linear interpolation applied to impute the missing data may not account for important responses in nitrate during that period. The lack of significant correlations for EC might be explained by the nature of the response; EC concentrations rose briefly and then receded by early April. It is interesting that positive and negative correlations were identified for temperature and pH, respectively, while visual analysis did not really identify particular trends for each variable. Both parameters did not show much temporal variance, so it may be an issue of scales used during visual analysis, such that it was difficult to identify any responses to recharge. It is therefore possible that the CCF method of analysis may be more useful when a parameter does not show much variance with time, as it can be difficult to identify trends or responses when there are no large peaks visible within the data. The only parameter in which visual and CCF analyses inferred similar relationships was DO, which decreased with respect to recharge at PR11. It is interesting to note that a positive correlation was observed if the entire dataset was considered; this suggests that perhaps some sort of error or drift in measured DO readings in spring 2015 lead to the observation of a false negative correlation. It is difficult to rule out that oxygen increased with respect to recharge given the results from PR8 and knowledge of the sandy, unconfined aquifer at the Port Rowan site. It is also interesting that a positive correlation was observed for turbidity considering the entire dataset, but a negative correlation was observed using March to June data. This was the
only occurrence in which a negative correlation with respect to turbidity was observed, so similarly to DO, it is difficult to rule out an increase in turbidity with recharge at PR11.

Visual and CCF analyses at PR8 produced very similar results. Increases in nitrate, EC, DO and turbidity, and decreases in temperature with respect to spring recharge were observed using both methods of analysis. The only parameter where results were not in agreement was pH, in which no significant correlations were observed. This result is interesting because visual analysis suggested an increase in pH occurred which corresponded to spring recharge; this was difficult to explain due to the inherently acidic nature of precipitation and snowmelt in southern Ontario (Goodison, Louie & Metcalfe, 1986). Since no significant positive correlation between pH and groundwater levels was observed during the spring recharge period, it may help refute the conclusions regarding pH from visual analysis. The observed increases do not seem to have resulted from recharge, and may instead result from drift in the pH sensor of the EXO. However, no drift in pH was documented during site visits.

It was noted that more significant correlations were observed with respect to groundwater levels at PR8 compared to PR11. It is likely that the correlations were stronger at PR8 because of the thinner unsaturated zone, which probably allows for more direct responses to precipitation and recharge since there is less time for any constituents in the precipitation to adsorb onto the surrounding porous media. Correlations between groundwater levels and groundwater quality parameters from RTRM are probably strongest after snowmelt or large storms, where rapid recharge can occur due to translator flow, flow through macropores, and groundwater ridging, as explained by Sophocleous (2002). The consistency in conclusions between methods at PR8 suggests that the CCF method is effective in developing relationships between RTRM parameters. However, the inconsistency of conclusions at PR11 suggests that CCF methods may not always be appropriate, especially in deeper wells or in those having complex stratigraphy or thick unsaturated zones, since the relationships between recharge and groundwater quality are almost certainly non-linear.
Figure 5.23: Cross-correlation functions for groundwater levels (GW Elev.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR11 daily averaged data, November 2014 to June 2015. CCFs were plotted for ±14 time lags (days), and were evaluated to determine if groundwater levels lead (predict) groundwater quality.
Figure 5.24: Cross-correlation functions for precipitation (Precip.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR11 daily averaged data, November 2014 to June 2015. CCFs were plotted for ± 14 time lags (days), and were evaluated to determine if precipitation leads (predicts) groundwater quality.
Figure 5.25: Cross-correlation functions for groundwater levels (GW Elev.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR11 daily averaged data, March 2015 to June 2015. CCFs were plotted for ± 14 time lags (days), and were evaluated to determine if groundwater levels lead (predict) groundwater quality.
Precip with Nitrate | Precip with EC
---|---
![Precip with Nitrate](image1)

Precip with GW Temp | Precip with DO
---|---
![Precip with GW Temp](image2)

Precip with pH | Precip with Turbidity
---|---
![Precip with pH](image3)

Figure 5.26: Cross-correlation functions for precipitation (Precip.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR11 daily averaged data, March 2015 to June 2015. CCFs were plotted for ± 14 time lags (days), and were evaluated to determine if precipitation leads (predicts) groundwater quality
<table>
<thead>
<tr>
<th>GW Elev with Nitrate</th>
<th>GW Elev with EC</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>GW Elev with GW Temp</td>
<td>GW Elev with DO</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>GW Elev with pH</td>
<td>GW Elev with Turbidity</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
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</tbody>
</table>

Figure 5.27: Cross-correlation functions for groundwater levels (GW Elev.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR8 daily averaged data, February 2015 to June 2015. CCFs were plotted for ± 14 time lags (days), and were evaluated to determine if groundwater levels lead (predict) groundwater quality.
Figure 5.28: Cross-correlation functions for precipitation (Precip.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PRB daily averaged data, February 2015 to June 2015. CCFs were plotted for ± 14 time lags (days), and were evaluated to determine if precipitation leads (predicts) groundwater quality.
Figure 5.29: Cross-correlation functions for groundwater levels (GW Elev.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR8 daily averaged data, March 2015 to June 2015. CCFs were plotted for ± 14 time lags (days), and were evaluated to determine if groundwater levels lead (predict) groundwater quality.
Figure 5.30: Cross-correlation functions for precipitation (Precip.) and water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR8 daily averaged data, March 2015 to June 2015. CCFs were plotted for ± 14 time lags (days), and were evaluated to determine if precipitation leads (predicts) groundwater quality.
Spatial correlation between the RTRM stations in Port Rowan was tested by plotting CCFs using the same parameters from PR11 and PR8. For example, nitrate from PR11 was cross-correlated with nitrate from PR8, and this was repeated for all RTRM parameters. Daily data from March to June was used. The results for daily and hourly groundwater levels are shown in Figure 5.31. Daily groundwater levels were strongly correlated ($r=0.82$) at a lag time of zero days, and hourly groundwater levels also displayed their highest correlations at lags around zero hours. This suggests that response times due to spring recharge are similar between PR11 and PR8. This implies that the thickness of the unsaturated zone may not be an important factor for response times at the Port Rowan site. It also means that groundwater quality CCFs should be expected to show significant correlations, if any, around a lag time of zero, since the groundwater levels are correlated at a lag of zero. There could be some small deviations from zero because the time lag with respect to groundwater levels at PR11 and PR8 is related to the unsaturated zone travel time, while the time lag for groundwater quality parameters is more related to the unsaturated zone travel time plus additional time to reach the receptor (i.e. sensor) through the saturated zone.

As mentioned in section 5.3.3, it is difficult with the available data to assess travel times due to advection, dispersion and diffusion processes under ambient conditions in the saturated zone, so it is difficult to estimate how long it might take for groundwater quality changes to be noticed after recharging groundwater reaches the water table. However, since most lag times in Table 5.5 were on the order of zero to three days, it was believed that the aquifer response time was on the order of zero to three days. The observed changes likely result from water having been previously stored in the unsaturated zone being pushed deeper due to the advancing recharge flux from the surface. This is supported by calculated vertical travel times through the unsaturated zone, using methods described by Sousa et al. (2013). Using both the van Genuchten equation assuming no flow, and the surface to aquifer advection time (SAAT), vertical travel times at PR8 ranged from approximately 53 days to 1.72 years (627 days), and from 93 days to 2.70 years (981 days) at PR11, depending on the assumed values for recharge and soil properties (effective porosity, residual saturation, van Genuchten coefficients $A/n$). The travel times through the unsaturated zone are much longer compared to the aquifer response time of approximately zero to three days. Thus, it is unlikely that changes observed chemistry changes reflect the chemistry of rainfall observed only days previously at the surface. Rather, the observed changes in groundwater quality result from slightly older (i.e. ≤3 years)
groundwater previously stored in the saturated/unsaturated zone that is pushed deeper by freshly infiltrating precipitation at the surface.

Once recharge encounters the unsaturated zone, it does not appear to take long for a response to occur within the groundwater quality in wells PR11 and PR8. A simple saturated zone vertical travel time \( (t_s) \) calculation was performed for PR8. Assuming a distance \( (D) \) from the receptor of 1 m, an effective porosity \( (\eta_{ef}) \) for sand of 0.37, a vertical saturated hydraulic conductivity \( (k_z) \) of 11.4 m day\(^{-1}\) that was determined from pumping tests conducted by Banks (2013), and a vertical gradient \( (\Delta h) \) of 7.93 m (from the water table to the top of screen at PR8), a vertical travel time \( (t_s) \) of only 5.89 minutes was calculated. The value \( t_s \) would increase if the radial distance \( (D) \) from the well was increased, but this calculation supports the hypothesis that the time lag associated with the saturated zone is very small, especially in comparison to the unsaturated zone.

Since groundwater levels between PR11 and PR8 were strongly correlated and the wells are screened in the same aquifer, it was expected that groundwater quality parameters should display some spatial correlation. Scatter plots comparing PR11 and PR8 groundwater quality at zero lag time were created and are shown in Figure 5.33 in addition to the groundwater quality CCFs in Figure 5.32. Significant positive correlations for nitrate and EC were observed at lags of one and two days respectively. This implies that as nitrate and EC increase in PR8, a similar increase is expected to occur at PR11. Positive correlations for nitrate EC persisted past eight positive lags, which were likely caused by some minor underlying autocorrelation in both parameters due to missing nitrate data at both stations. First differencing the data removes much of this autocorrelation, but it still seems to persist at non-problematic levels in the CCFs. The only other parameter with a significant correlation was turbidity, which had a negative correlation approaching -0.5 at lag zero. This suggests that as turbidity increases at PR8, there is a corresponding decrease at PR11 that is reasonably strong, which is a relationship that is difficult to clarify. No significant correlations were observed for temperature, DO or pH.

The scatterplots shown in Figure 5.33 demonstrate that with the exception of turbidity, no parameters showed a significant correlation between PR11 and PR8 at lag zero. While it appears that nitrate and EC display similar responses to spring recharge, there is no apparent spatial correlation for temperature, pH and DO at the Port Rowan site, and the accuracy of the observed spatial correlation for turbidity is questionable. This suggests that RTRM methods are
probably not very repeatable or consistent at this location. It is unclear if this results from inconsistencies within the equipment and methods, spatial differences in groundwater quality between the two sites, or some combination of the two. While some differences in groundwater quality are inevitable, it was initially hypothesized that the RTRM data at PR11 and PR8 are spatially correlated, but this was not observed. Stronger spatial correlations may have resulted for nitrate if there was less missing data at PR11, or for EC if the results from PR8 were not affected by drift. However, it is difficult to determine how the spatial correlations were affected by errors, if any. It is entirely possible that the differences in groundwater quality between PR11 and PR8 are indeed the result of natural processes at the two locations, perhaps influenced by the difference in elevation between the sites. It is evident that the nitrate plume shown in Figure 3.8 is significantly spatially variable, so other groundwater quality parameters including temperature, pH, EC, DO, and turbidity may not be spatially correlated. It would be valuable to continue monitoring across the site or at additional sites to further evaluate the efficacy of RTRM methods and how the results may vary spatially and temporally.
Figure 5.31: Cross-correlation functions for daily averaged and hourly groundwater levels (GW Elev.), and scatterplot of first differenced, daily averaged groundwater levels at zero time lag from PR11 and PR8 (March 2015 to June 2015), shown with linear best fit and Pearson’s $R^2 = 0.664$.
Figure 5.32: Cross-correlation functions for daily averaged water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) from PR11 and PR8 (March 2015 to June 2015)
Figure 5.33: Scatterplots of first differenced, daily averaged water quality parameters (nitrate-N, electrical conductivity (EC), groundwater temperature (GW Temp.), dissolved oxygen (DO), pH, turbidity) at zero time lags (days) from PR11 and PR8 (March 2015 to June 2015), shown with linear best fit and Pearson’s $R^2$. 

Image 1: PR11 Nitrate vs. PR8 Nitrate

Image 2: PR11 EC vs. PR8 EC

Image 3: PR11 GW Temp. vs. PR8 GW Temp.

Image 4: PR11 DO vs. PR8 DO

Image 5: PR11 pH vs. PR8 pH

Image 6: PR11 Turbidity vs. PR8 Turbidity

Table 1:

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<td>PR11 DO vs. PR8 DO</td>
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<td>PR11 Turbidity vs. PR8 Turbidity</td>
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6 Conclusions and Recommendations

It is evident that innovative measurement techniques will be required in order to meet growing demands for advanced groundwater quality monitoring. The main objective of this research was to apply an innovative platform of sensor equipment to develop and evaluate methods for: 1) obtaining *in situ* nitrate measurements; 2) down-hole groundwater quality profiling, and; 3) continuous groundwater quality monitoring. Three unique techniques were successfully tested during this research to address the aforementioned objectives: modified flow cell testing, vertical geochemical profiling, and real-time remote monitoring (RTRM). The sensors used included Satlantic Inc.’s submersible ultraviolet nitrate analyzer (SUNA) and YSI Inc.’s EXO water quality sondes. Nitrate was the contaminant of focus in this study, but field parameters including EC, temperature, DO, pH and turbidity were also measured. Testing was conducted in diverse hydrogeological settings, including a shallow, unconfined overburden aquifer (Norfolk County, Ontario, Canada), a deeper, confined to semi-confined overburden aquifer (Waterloo, Ontario), and a shallow to deep Silurian dolostone bedrock aquifer (Guelph, Ontario) over a period of approximately one year. The monitoring methods developed provided insight such that additional objectives were successfully investigated. Depth-discrete measurements were obtained to examine vertical variability of nitrate concentrations within the well column. Temporal trends in groundwater quality parameters with respect to recharge event timing and magnitude were assessed. The unique datasets obtained using RTRM methods provided some of the highest temporal resolution groundwater quality datasets available at the time of this research, which will serve as input or calibration datasets for future nitrate transport and fate modeling initiatives.

The modified flow cell method complements traditional purge sampling and allows for concentrations to be measured directly and accurately in the field at high precision. Water is pumped from a well and discharges through a simple flow cell, where the SUNA can measure nitrate concentrations continuously (i.e. one measurement per second). A total of 32 independent field trials were conducted at nine wells located in Norfolk County, over four different testing periods from July 2014 to February 2015. Purged samples for each trial were analyzed in a laboratory and compared to SUNA nitrate concentrations. SUNA concentrations ranged from approximately 0 to 15 mg L\(^{-1}\) (nitrate-N) and were strongly correlated (\(R^2=0.99\)) to laboratory concentrations for each testing period, with an average error and average absolute error of -0.25 and 0.28 mg L\(^{-1}\), respectively. This suggests that the SUNA can obtain precise
and highly accurate nitrate concentration measurements relative to traditional purge sampling techniques in groundwater environments. To the best of the author’s knowledge, this is probably the most precise method for measuring nitrate concentrations in the field. The potential value of the flow cell method was demonstrated by testing a network of 23 monitoring wells such that regional nitrate concentrations and groundwater elevations were measured and mapped over a period of only two days. The flow cell method is clearly useful for initial screening of regional areas in order to plan field sampling campaigns. The SUNA could also be used in flow cell systems at municipal supply wells, and would be particularly useful for municipalities or drinking water authorities that require regular nitrate sampling at the regional scale.

Vertical profiling is a down-hole method for observing changes in groundwater chemistry with depth along a borehole, similar to temperature (e.g. Pehme et al., 2010) and fluid conductivity logging methods which are commonly used. Testing was conducted over two periods in fall 2014, using six overburden wells in Norfolk County (Port Rowan) and the Region of Waterloo, plus an additional two bedrock boreholes in Guelph. The method is similar to other down-hole geophysical methods, in which a sensor (the SUNA and then the EXO) is lowered down the borehole at a specified rate and then retrieved, with data from the downward log being used. Size constraints related to the diameter of the SUNA limits profiling methods to wells exceeding four inches (4") in diameter, but initial profiling results were promising. Future profiles can be compared to grab samples collected at specific depths, using devices such as the Snap Sampler (Britt et al., 2010), and analyzed in lab for comparison. To the best of the author’s knowledge, this method represents the first down-hole method for measuring groundwater nitrate concentrations in situ. Profiling results from the Port Rowan research site showed the presence of fresher groundwater along the screened interval, which is likely subject to ambient flow conditions and was therefore an ideal location for RTRM. Profiling results from the Waterloo research site showed the presence of vertically stratified nitrate concentrations in the long screened interval of one well ranging from approximately 0-5 mg L⁻¹. Profiling results from the Guelph research site indicated the presence of vertically stratified nitrate concentrations at distinct zones along an open bedrock borehole, which seemed to correspond to DO concentrations. Evidence from a second bedrock borehole in Guelph suggested that turbidity may serve as an indicator of active groundwater flow in this type of environment.

For RTRM methods, the SUNA and EXO sensors can be deployed directly downhole for a period of several months. Snapshot measurements of groundwater quality can be obtained
every 15 minutes and transmitted wirelessly, such that they can be observed remotely and in real-time. In this study, measurements were averaged hourly and then analyzed in conjunction with air temperature and precipitation data. Testing was initiated in well PR11 at the Port Rowan research site in November 2014, with a second RTRM station commissioned at well PR8 starting in January 2015. A third station was tested at the Stone Well in Guelph beginning in May 2015. All stations were operated continuously through June 2015. The datasets obtained were analyzed visually and then correlations between RTRM parameters in Port Rowan were assessed using a statistical framework. Cross-correlation functions (CCFs) were calculated for groundwater quality parameters with respect to groundwater levels and then precipitation, using first differencing to account for autocorrelation within the measured data. Evidence suggested that the aquifer response time to fall and spring recharge from 2013 to 2015 may be on the order of 2 days at both Port Rowan wells. Visual analysis at PR11 suggested the presence of significant responses in nitrate, EC, DO and turbidity corresponding to the initial timing of spring recharge, but CCF results provided contradicting evidence, with the exception of DO. Visual analysis at PR8 suggested that significant changes were observed for all parameters in response to spring recharge, and CCF results were similar with the exception of pH. RTRM datasets from PR11 and PR8 were not strongly spatially correlated, despite a strong correlation \((r=0.82)\) between daily groundwater levels, which raises some concern about the consistency of RTRM methods. However, inconsistencies may also result from differences in the nature of the hydrogeological settings between PR11 and PR8, where a spatially variable nitrate plume suggests that conditions (due to spatially variable inputs) in the shallow aquifer on site are heterogeneous. Having the ability to obtain hourly measurements of groundwater quality is certainly promising, and clearly demonstrates the novelty of RTRM methods developed in this research study.

It is recommended that further studies should either test the developed methods in alternative settings, or refine the techniques with modifications that may help to mitigate impacts related to sources of error or uncertainties within this research. More open bedrock boreholes should be investigated with vertical profiling combined with measurements of open borehole flow metering, and it would also be interesting to outfit a bedrock borehole with an RTRM station to compare response (due to recharge) magnitudes and timing between granular porous media and fractured bedrock aquifers. Preference should be given to bedrock aquifers having thin overburden, if possible, because it would be interesting to examine sites that are prone to rapid recharge and therefore may have the most significant responses to precipitation events. It would
also be useful to operate RTRM stations for a longer period of time (i.e. multiple years), which would likely allow for better characterization of responses due to both fall and spring recharge and timing and distribution of nitrate inputs, and might provide the opportunity for robust statistical techniques such as ARIMA models and time series forecasting (e.g. Changnon, Huff & Hsu, 1988). Another potentially useful experiment would involve comparing multilevel well systems to vertical profiling. If an open bedrock borehole was scheduled to be fitted with a multilevel system, it would be interesting to profile the borehole beforehand and then sample multilevel ports (once installed) to compare the profiles between the two techniques. This would help to quantify the effects of vertical flow and borehole mixing on vertical profiles obtained using down-hole techniques. A prudent study would involve developing and testing a means of isolating the SUNA and EXO sensors during profiling and RTRM such that borehole mixing does not occur. This could be developed using a similar system to packer equipment or FLUTE™ liners in conjunction with the sensors, which would hopefully eliminate cross-contamination of water within the borehole.
Bibliography


Appendices
Appendix A: Flow cell testing raw data and linear regression model specifics

Table A-1: Raw data collected during flow cell testing at the LPT3 site from July 2014 to February 2015. SUNA measurements were calculated by taking the average of samples during the last minute of flow cell testing before a bottle sample was collected for laboratory analysis. Precision for SUNA and Lab analysis is ±8% and ±10%, respectively.

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Figure A-1: Simple linear regression models (with $R^2$ given) comparing SUNA and Lab nitrate concentrations for (clockwise, from top left): testing round one (Jul-Aug 2014), testing round two (02-Oct-2014), testing round three (25-Nov-2014), and testing round four (13-Feb-2015).
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Least Squares Fit ($y=mx+b$)

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Figure A-2: SUNA and LAB nitrate data from flow cell testing with linear regression model and statistics describing the model fit, including $R^2$, standard error (S.E.) of the regression, slope, and intercept, and the slope and intercept for confidence bands (CBs) and prediction bands (PBs)
Figure A-3: a) Histogram and b) Q-Q plot for residuals from the linear regression model constructed using raw data from SUNA flow cell testing (see Figure 5.3), with c) an additional histogram and d) Q-Q plot for residuals for the linear regression model constructed using log transformed data from SUNA flow cell testing.

It is evident that the log transformed data results in a better fitting model in which the residuals are approximately normally distributed. However, the raw data is also reasonably normally distributed, so the constructed 95% confidence and prediction bands in Figure 5.3 are still acceptable for use in this research. The log transformed model would only be required if it was essential to examine the cause-and-effect relationship between SUNA and Lab nitrate concentrations. The SUNA and Lab datasets do not truly have an independent-dependent relationship; rather, they are two independent variables that refer to the same value. An example of a cause-and-effect relationship in which a well fitted regression model would be more useful is the relationship between smoking and incidences of lung cancer.
Appendix B: Time Series Figures with Raw and Corrected Data

Figure B-1: Raw and corrected hourly nitrate data obtained using RTRM methods at PR11, shown with daily precipitation and hourly groundwater levels
Figure B-2: Raw and corrected hourly groundwater temperature data obtained using RTRM methods at PR11, shown with daily precipitation and hourly groundwater levels.
Figure B-3: Raw and corrected hourly EC data obtained using RTRM methods at PR11, shown with daily precipitation and hourly groundwater levels
Figure B-4: Raw and corrected hourly pH data obtained using RTRM methods at PR11, shown with daily precipitation and hourly groundwater levels
Figure B-5: Raw and corrected hourly DO data obtained using RTRM methods at PR11, shown with daily precipitation and hourly groundwater levels.
Figure B-6: Raw and corrected hourly turbidity data obtained using RTRM methods at PR11, shown with daily precipitation and hourly groundwater levels.
Figure B-7: Raw and corrected hourly nitrate data obtained using RTRM methods at PR8, shown with daily precipitation and hourly groundwater levels.
Figure B-8: Raw and corrected hourly groundwater temperature data obtained using RTRM methods at PR8, shown with daily precipitation and hourly groundwater levels.
Figure B-9: Raw and corrected hourly EC data obtained using RTRM methods at PR8, shown with daily precipitation and hourly groundwater levels
Figure B-10: Raw and corrected hourly pH data obtained using RTRM methods at PR8, shown with daily precipitation and hourly groundwater levels
Figure B-11: Raw and corrected hourly DO data obtained using RTRM methods at PR8, shown with daily precipitation and hourly groundwater levels.
Figure B-12: Raw and corrected hourly turbidity data obtained using RTRM methods at PR8, shown with daily precipitation and hourly groundwater levels
Figure B-13: Raw and corrected hourly nitrate data obtained using RTRM methods at the Stone Well, shown with daily precipitation.
Figure B-14: Raw and corrected hourly groundwater temperature data obtained using RTRM methods at the Stone Well, shown with daily precipitation.
Figure B-15: Raw and corrected hourly EC data obtained using RTRM methods at the Stone Well, shown with daily precipitation.
Figure B-16: Raw and corrected hourly pH data obtained using RTRM methods at the Stone Well, shown with daily precipitation
Figure B-17: Raw and corrected hourly DO data obtained using RTRM methods at the Stone Well, shown with daily precipitation
Figure B-18: Raw and corrected hourly turbidity data obtained using RTRM methods at the Stone Well, shown with daily precipitation.
Appendix C: Autocorrelation Functions (ACFs) and Histograms for Port Rowan RTRM Data

ACFs were plotted for 14 time lags using daily averaged RTRM data for each parameter measured (nitrate, groundwater temperature, EC, pH, DO, turbidity, and groundwater levels). Two ACFs were created for each variable: one using raw data and one with the first differenced data. Comparing the two ACFs can evaluate the effectiveness of first differencing on removing autocorrelation from the raw data, transforming the series such that it is stationary.

Similarly, histograms were plotted using daily averaged data for each RTRM variable, for both pre- and post- first differenced data. Comparing histograms for the two datasets can evaluate the effectiveness of first differencing on transforming datasets towards normality. The degree to which the datasets are normal affects the accuracy of confidence intervals constructed for cross-correlation functions (CCFs), as discussed in section 4.2.3.2.

All ACFs and histograms are provided below. Tabulated ACF and CCF correlations from SPSS outputs are also available upon request.
Figure C-1: ACFs for pre- and post-differenced daily averaged nitrate, groundwater temperature and EC data from RTRM at PR11 (Nov 2014 to Jun 2015)
Figure C-2: ACFs for pre- and post- differenced daily averaged pH, DO and turbidity data from RTRM at PR11 (Nov 2014 to Jun 2015)
Figure C-3: ACFs for pre- and post-differenced daily averaged groundwater levels at PR11 (Nov 2014 to Jun 2015)
Figure C-4: ACFs for pre- and post- differenced daily averaged nitrate, groundwater temperature and EC data from RTRM at PR8 (Feb 2015 to Jun 2015)
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Figure C-5: ACFs for pre- and post- differenced daily averaged pH, DO and turbidity data from RTRM at PR8 (Feb 2015 to Jun 2015)
Figure C-6: ACFs for pre- and post-differenced daily averaged groundwater levels at PR8 (Feb 2015 to Jun 2015)
Figure C-7: Histograms for pre- and post- differenced daily averaged nitrate, groundwater temperature and EC data from RTRM at PR11 (Nov 2014 to Jun 2015)
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<th>First Differenced DO</th>
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</thead>
<tbody>
<tr>
<td><img src="image3" alt="Histogram" /></td>
<td><img src="image4" alt="Histogram" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raw Turbidity</th>
<th>First Differenced Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5" alt="Histogram" /></td>
<td><img src="image6" alt="Histogram" /></td>
</tr>
</tbody>
</table>

Figure C-8: Histograms for pre- and post- differenced daily averaged pH, DO and turbidity data from RTRM at PR11 (Nov 2014 to Jun 2015)
Figure C-9: Histograms for pre- and post- differenced daily averaged groundwater levels at PR11 (Nov 2014 to Jun 2015)
Figure C-10: Histograms for pre- and post- differenced daily averaged nitrate, groundwater temperature and EC data from RTRM at PR8 (Feb 2015 to Jun 2015)
Figure C-11: Histograms for pre- and post-differenced daily averaged pH, DO and turbidity data from RTRM at PR8 (Feb 2015 to Jun 2015)
Figure C-12: Histograms for pre- and post- differenced daily averaged groundwater levels at PR8 (Feb 2015 to Jun 2015)
Appendix D: Vertical Profiling and RTRM Datasets

Any of the raw datasets collected using vertical profiling or RTRM methods for this research are available upon request, and can be viewed in Microsoft Excel (.xlsx file extension), or as plain text files. The datasets are extensive and were omitted from these appendices due to their length. Vertical profiling and RTRM data is structured as shown below.

Table D-1: Example vertical profiling dataset from PR9. Only the first three of 89 samples are shown. Depths available relative to water table, top of casing (TOC), and ground surface. Datasets with the same structure are available for all vertical profiling runs.

<table>
<thead>
<tr>
<th>Site</th>
<th>Well ID</th>
<th>Direction</th>
<th>Time</th>
<th>Temp °C</th>
<th>SpCond µS/cm</th>
<th>pH</th>
<th>ORP mV</th>
<th>ODO mg/L</th>
<th>Turbidity NTU</th>
<th>Depth from WT (m)</th>
<th>Depth from TOC (m)</th>
<th>Depth from Surface (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Port Rowan</td>
<td>PR9</td>
<td>Down</td>
<td>17:08:00</td>
<td>12.295</td>
<td>319.7</td>
<td>8.00</td>
<td>-</td>
<td>10.21</td>
<td>78.20</td>
<td>0.00</td>
<td>2.54</td>
<td>1.69</td>
</tr>
<tr>
<td>Port Rowan</td>
<td>PR9</td>
<td>Down</td>
<td>17:08:05</td>
<td>12.467</td>
<td>321.0</td>
<td>7.92</td>
<td>-</td>
<td>6.68</td>
<td>83.99</td>
<td>0.01</td>
<td>2.55</td>
<td>1.70</td>
</tr>
<tr>
<td>Port Rowan</td>
<td>PR9</td>
<td>Down</td>
<td>17:08:10</td>
<td>12.629</td>
<td>319.8</td>
<td>7.87</td>
<td>-</td>
<td>4.90</td>
<td>89.29</td>
<td>0.03</td>
<td>2.57</td>
<td>1.71</td>
</tr>
</tbody>
</table>

Table D-2: Example RTRM dataset from PR8. Only the first hourly sample of over 4000 is shown. Daily averaged data with standard deviations calculated is also available upon request.

<table>
<thead>
<tr>
<th>Datetime</th>
<th>Day</th>
<th>Month</th>
<th>Year</th>
<th>Nitrate (mg/L)</th>
<th>SpCond (µS/cm)</th>
<th>Temp (°C)</th>
<th>DO (mg/L)</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>EXO Depth (m)</th>
<th>GW Elev (m)</th>
<th>Air Temp (°C)</th>
<th>Precip. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31/01/2015 12:00</td>
<td>31</td>
<td>1</td>
<td>2015</td>
<td>0.65</td>
<td>770.89</td>
<td>8.97</td>
<td>0.19</td>
<td>7.22</td>
<td>27.66</td>
<td>8.11</td>
<td>211.14</td>
<td>-12.5</td>
<td>0</td>
</tr>
</tbody>
</table>
Appendix E: Well Construction Details

Well construction details for each of the production wells that were tested during this research are summarized in the table below. Well logs for the production wells (PR9, PR11, PR6 and PR9) at the Port Rowan site, and Test Well 1 and Test Well 2 at the Region of Waterloo are available upon request. Monitoring well logs from the LPT3 site can also be provided upon request. All well records can also be accessed by inputting coordinates and searching the Ontario Water Well Record Database (Government of Ontario, 2015 – accessed here: http://www.ontario.ca/environment-and-energy/map-well-records).

No log was available for the Stone Well. Detailed fracture and lithology logs for GDC-10 can be made available upon request, but the lithological interpretations from those logs are reflected in Figure 5.13.

Table E-1: Well construction details for production wells tested in this research. Depths are given below ground surface (BGS). Wells are classified as overburden (OB) or open bedrock (BR) boreholes. The length of open borehole at the Stone Well was inferred assuming an overburden thickness of 7.92 m, since no well log was available.

<table>
<thead>
<tr>
<th>Well ID</th>
<th>OB/BR?</th>
<th>Northing</th>
<th>Easting</th>
<th>Ground Elev. (m)</th>
<th>Well Depth (m BGS)</th>
<th>Depth to WT (m BGS)</th>
<th>Length of Screen/Open Borehole (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR6</td>
<td>OB</td>
<td>4726666</td>
<td>542101</td>
<td>213.17</td>
<td>11.58</td>
<td>1.82</td>
<td>3.00</td>
</tr>
<tr>
<td>PR8</td>
<td>OB</td>
<td>4726488</td>
<td>541779</td>
<td>213.24</td>
<td>13.08</td>
<td>2.10</td>
<td>3.00</td>
</tr>
<tr>
<td>PR9</td>
<td>OB</td>
<td>4726369</td>
<td>542090</td>
<td>212.59</td>
<td>11.13</td>
<td>1.31</td>
<td>3.00</td>
</tr>
<tr>
<td>PR11</td>
<td>OB</td>
<td>4726586</td>
<td>541952</td>
<td>216.16</td>
<td>14.78</td>
<td>4.94</td>
<td>3.00</td>
</tr>
<tr>
<td>Test Well 1</td>
<td>OB</td>
<td>4805044</td>
<td>536526</td>
<td>336.40</td>
<td>16.80</td>
<td>3.99</td>
<td>4.20</td>
</tr>
<tr>
<td>Test Well 2</td>
<td>OB</td>
<td>4803953</td>
<td>530865</td>
<td>359.17</td>
<td>42.7</td>
<td>7.23</td>
<td>7.60</td>
</tr>
<tr>
<td>Stone Well</td>
<td>BR</td>
<td>4820606</td>
<td>565452</td>
<td>329.00</td>
<td>19.81</td>
<td>1.33</td>
<td>11.89</td>
</tr>
<tr>
<td>GDC-10</td>
<td>BR</td>
<td>4821595</td>
<td>562877</td>
<td>329.02</td>
<td>72.69</td>
<td>16.18</td>
<td>60.69</td>
</tr>
</tbody>
</table>
Appendix F: SUNA Calibration Details

Detailed video instructions can be found here:
https://www.youtube.com/watch?v=UO4Ea_Z2QI4

1. Use a Q-tip and isopropyl alcohol to clean the sampling window, especially around the UV light source window
2. Connect sensor bulkhead to USB cable
3. Attach cable leads to 12 V battery
4. Using parafilm, create a seal around the SUNA’s sampling window. It is a good idea to tape around the edges of the parafilm using electrical tape to ensure there is a good seal around the sampling window.
5. Poke a small hole through the parafilm and fill the sampling window with deionized water (DIW).
6. Connect to the SUNA using SUNACom software, making sure to identify the correct communications port
7. Select “Update Settings,” and then ensure that the SUNA is operated in Continuous mode prior to re-calibrating
8. Select “Update Calibration,” and the SUNA will establish a new baseline for its internal algorithm, which will be automatically updated to the calibration file
9. Check drift during and after deployment by measuring concentrations in DIW using the same steps outlined above. If the nitrate concentration in DIW reads ± 2 μM, then drift has occurred and the device should be re-calibrated before deployment