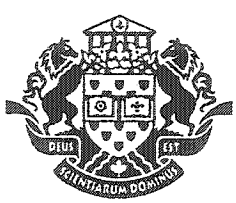

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ABSTRACT

Groundwater is a major source of water for many Canadians. It has been shown that in many parts of Canada, wells exceed the guidelines for nitrate and bacteria and there is a lack of detailed information available on the state of wells in general.

Water samples from 54 private potable wells in the South Nation River and Raisin River watershed areas were collected for water quality analysis in 2003. Water quality indicators tested for in the well water samples consisted of the following: nitrate, total coliforms (TC), *Escherichia. coli* (EC), background colonies (BC), conductivity, oxygen (dissolved oxygen), redox potential (Eh), pH, total inorganic carbon (TIC), total organic carbon (TOC) and methyl mercury (MeHg). Overall, more than 50 % of the wells tested positive for TC; 7 % tested positive for EC and over 60% had background colonies (BC). The mean conductivity was 908 µS/cm + 570 standard deviation (SD). pH ranged from 6.9 to 8.1. The average redox potential was 197 mV ± 103 SD. TIC ranged from 22 ppm to 255 ± 31 SD. TOC was very low, with an average of 2 ppm ± 2 SD. The water was low in oxygen (mean of 2 mg/L ± 2 SD). Nitrate concentrations varied from less than the detectable limit of 0.01 mg/L to 56 mg/L. Many samples had a sulfide smell, hence, we also tested for methyl mercury (MeHg), a by-product of sulphate reducing bacteria in anoxic water. The levels of MeHg were minimal (mean of 0.05 ng/L ± 0.01 standard error).

Dug wells have a greater risk of contamination than drilled wells. I predicted that there would be a difference in the bacteria and nitrate levels in these two type of wells. Dug wells tested positive 1.6 more times for total coliforms (TC) than drilled wells, 13 times more for *E.coli* and 1.5 times more for background colonies. With respect to bacterial counts, there was a significant difference in the means of TC counts ($p<0.05$) and BC counts ($p< 0.05$), but not with

EC ($p>0.05$) between the dug and drilled wells. Nitrate levels were on average significantly higher in shallow dug wells as compared to drilled wells ($p<0.001$). For TC and BC, the bacteria counts decreased with increasing well depth ($p<0.05$).

Well water samples were subdivided based on three categories of land use: residential, agricultural and agricultural intensive. In this study there was no significant difference in the occurrence of TC, BC and EC in the water samples between the three land use sites ($p>0.05$). In addition, there were no significant differences in the mean bacterial counts between the three land use types. There was a significant difference in the nitrate levels between the three land use types ($p<0.05$).

Factors such as land use, type of aquifer and climate change can affect quality of groundwater. These factors should be carefully considered in keeping our water supply healthy.

RÉSUMÉ

L'eau souterraine est la principale source d'eau pour un grande nombre de Canadiens. Il est évident qu' il ya beaucoup de puits au Canada qui dépassent les directives pour le nitrate et aussi pour les bactéries. Ici, j'ai fait une étude de la qualité de l'eau de 54 puits dans les résidences rurales du bassin de la rivière South Nation et de la rivière Raisin.

À l'été de 2003, des échantillons d'eau de 54 puits furent recueillis dans les résidences privées du bassin de la rivière South Nation et de la Rivière raisin pour analyse qui consiste: l'azote, coliformes totales (TC), *E. coli* (EC), les colonies background (BC), la conductivité hydraulique, l'oxygène, redox (Eh), pH, le carbone inorganique total (TIC), le carbone organique total (TOC) et le mercure méthyle (MeHg). En général, plus que 50% des puits ont été positifs pour TC, 7% ont été positifs pour EC, et plus que 60% ont eu les BC. La moyenne de la conductivité hydraulique a été 908 µS/cm + 570 (DS). pH a varié de 6.9 à 8.1. Le Redox a été en moyenne de 197 mV ± 103 DS. TIC a varié de 22 ppm à 255 ± SD. TOC a été bas (en moyenne de 22 ppm ± 2 DS). Il n'y pas beacoup d'oxygène dan l'eau (en moyenne de 2 mg/L ± 2 DS). L'azote a variê de < 0.01 mg/L à 56 mg/L. Plusieurs d'échantillons avaient l'odeur de sulphide, et à cause de cette odeur on a analysé l'eau pour MeHg. Le niveau de MeHg a été très bas (en moyenne de 0.05 ng/L ± 0.01DS

Les puits creusés ont plus de risque d'être contaminé que les puits qui sont percés. J'ai prédit qu'il y aurait une différence entre les niveaux des bactéries et de nitrate dans l'eau qui provient de ces deux genres des puits. Les mesures indiquent que les puits creusés sont 1.6 fois plus positives pour le TC que les puits percés, 13 fois plus positifs pour *E.coli* et 1.5 fois plus positifs pour BC. Les mesures indiquent aussi qu'il y a une différence considérable dans les

moyenes de compte de bactéries TC ($p<0.05$) et BC ($p<0.05$), mais pas pour EC. Le niveau de nitrate est plus haut dans le puits creusés. Les mesures indiquent qu' il y a une considérable différence entre les moyennes d'azote ($p<0.001$) entre les puits creusés et percés. Pour TC et BC, les résultats indiquent que le compte de bactéries diminue quand la profondeur de puits augmente ($p<0.05$). Les résultants indiquent aussi qu'il n'y pas de relation entre EC et la profondeur et entre l'azote et la profondeur.

L'utilisation des terres agricoles peut avoir un effet sur la qualité de l'eau. Les échantillons étaient divisé en le categories trois: 1. l'aire residentiel 2. l'aire agricole 3.l' aire agricole intensive. Les résultants indiquent qu'il n'y pas de relation entre la présence de bacterium TC, BC, EC et entre les trois categories. Il n'y a pas de différence considerable entre la moyenne de compte de bactéries et les trois catégories ($p>0.05$). Les resultants indiquent qu'il y a une différence considerable entre la moyenne d'azote entre les trois categories.

L'utilisation des terres et aussi les changements climatiques peuvent affecter la qualité de l'eau souterraine. Donc, il est évident qu' il faut les considérer pour conserver la santé de notre eau.

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1. INTRODUCTION

This section is divided into eight subsections. The first one will provide a brief overview of groundwater and climate change effects, including potential climate effects on water contamination. Following the overview section, nitrate in groundwater is introduced, with respect to some possible sources and health effects. Following nitrate, a short review of methyl mercury; its production in groundwater and its potential implications for surface water is discussed. The next section discusses the linkage between this project and the Community University Research Alliance Project (CURA), entitled "*Institutional Adaptation of Water-Related Infrastructures to Climate Change in Eastern Ontario*" which was an interdisciplinary and comprehensive analysis of a variety of issues (e.g. groundwater) in conjunction with some possible adaptation strategies that would reduce the impact of climate change on these issues and infrastructures (Crabbé and Robin, 2003). Following this section, the significance of aquifers and wells in the study area is discussed, followed by a detailed summary of variables tested; finally concluding with the rationale.

1.1 BACKGROUND ON GROUNDWATER AND CLIMATE CHANGE

Groundwater is the major source of water for approximately 26% of Canadians, or approximately 8 million people (Chambers et al., 2001). In Ontario alone, approximately 30% of the total population and 90% of the population in rural areas rely on groundwater as the main water source (Piggott et al., 2001). Much of the supply in rural areas is extracted from private wells that were constructed to provide a reliable water supply subject to then-current climate and water use. Even partial loss of the capacity of these wells in response to factors such as climate change and increased water use will have tangible economic and societal implications (Piggott et al., 2001).

Water well survey programs are patchy across the country, but show that some wells are above or close to the guidelines for nitrate and bacteria (Chambers et al., 2001). Regional surveys of nitrate contamination in ground water wells show that from 1.5 to more than 60% have nitrate-N concentrations greater than the acceptable drinking water concentration of 10 mg/L nitrate-N (Chambers et al., 2001). It is estimated that 20 to 40% of rural wells across Canada have nitrate or coliform bacteria concentrations exceeding drinking water guidelines (Corkal et al., 2003).

A major survey of rural wells in Ontario entitled the "*Ontario Farm Groundwater Quality Survey*" conducted in 1991/1992 found that out of 1292 wells, 34% contained elevated levels of coliform bacteria, 14% had elevated levels of nitrates, 7% were contaminated with both nitrate and bacteria, and close to 10% had detectable levels of pesticides (Goss et al., 1998). In total, about 40% of the wells contained one or more target contaminants above the maximum acceptable concentration (MAC) drinking water objectives for at least one of the targeted contaminants. In another study of 131 wells, 50% tested positive for nitrates, and 9% had levels that exceeded the MAC (Health Canada, 2002).

In the period of 1974-1996, more than 20% of Canada's reported waterborne disease outbreaks occurred in private water supplies, and an additional 45% of the reported outbreaks occurred in non-municipal systems, largely in rural or remote areas (Corkal et al. 2003).

Climate change is expected to make the situation worse. Every region of Canada is likely to be affected by climate change (Charron et al., 2003). Some of the forecasted changes in weather for Ontario include: warmer temperatures, more frequent and intense rainstorms, flash flooding, increased drought, increased erosion, and in general, less water to recharge aquifers (EC, 2001). It has also been shown on several occasions that excessive precipitation (e.g., heavy rainfall,

snowfall, snowmelt) is associated with waterborne disease outbreaks (Charron et al., 2003) (Rose et al., 2001) (Patz et al., 2001). As an example, in Walkerton, it was concluded that the extraordinary rainfall between May 8 and May 12 was responsible in part, for the waterborne disease resulting from *E.coli* 0157:H7 and *Campylobacter* that originated from cattle manure from a nearby farm. *E.coli* 0157:H7 is a pathogenic bacteria strain that produces potent toxins which cause abdominal pain, bloody diarrhoea and haemolytic uraemic syndrome and has been implicated in many foodborne and a few drinking water outbreaks (Health Canada, 2002). It has been suggested that in certain watersheds, by virtue of the land use, fecal contaminants from both human sewage and animal wastes are transported into waterways and drinking water supplies by precipitation events (Rose et al., 2001).

A few other examples of excess rainfall causing outbreaks include the outbreak of *Giardia lamblia* in Montana in 1983, and the largest reported waterborne outbreak ever documented in the United States in Milwaukee, Wisconsin in 1993, which resulted in 54 deaths, and more than 403,000 people ill (Auld et al., 2003). This was associated with heavy rainfall and the associated run-off.

In addition, high temperatures and drought have been linked to an increased risk of water contamination. In the Walkerton case, it is not known whether temperature had a role in the outbreak, however, temperatures had been warmer prior to the contamination, specifically >25 ° C or 10-13 ° C above normal for these dates (Auld et al., 2003). In September 1999, the largest waterborne associated outbreak of *E.coli* 0157:H7 occurred at a fairground in New York, and was linked to contaminated well water. In this case, heavy rains were preceded by a period of drought (Rose et al., 2001).

Drought increases the demand for water when the supply is significantly reduced and vulnerable (Charron et al., 2003). Drought followed by heavy rain can lead to more severe run-off and risk of surface water contamination because the capacity of a very dry soil to absorb water is very low (although this capacity increases as the soil gets wetter) (Robin, 2004). Drought can also affect the water supply in that the salinity of water may increase due to the forecasted increased rate of evaporation, and decreased rate of recharge of groundwater.

The general consensus seems to be that the impacts of climate change on groundwater will be led by variations in the rates and timings of recharge (Pigott, 2002). Groundwater recharge is the water that infiltrates to the water table and is affected by climatic conditions. Groundwater levels and river baseflows will respond to these changes. The groundwater discharge to surface water produces baseflow in surface waters. Groundwater has a simultaneous function in the maintenance of aquatic ecosystems. Therefore, a reduction in discharge due to varying climate can affect the health of the aquatic habitat (Piggott et al., 2001).

The sustainable yield of an aquifer depends on how much recharge it receives. An aquifer is an underground geologic formation that is water bearing (CH2MHILL, 2001). Shallow aquifers overlain by permeable materials are sensitive to climate, and fluctuate according to how much recharge is received seasonally and annually. These aquifers are sensitive to drought, and may not be useful during periods of prolonged drought. Also, they are more vulnerable to contamination than deeper aquifers overlain by low-permeability deposits (AAFC, 2002). Deep aquifers are less vulnerable to drought and contamination, however, the danger is that when recharge rates are low, these aquifers may be pumped beyond sustainable yields (AAFC, 2002) This in turn will affect the ability of a well to meet water supply demands if the rate of groundwater recharge is less than the

rate of withdrawal. The water level in the aquifer will gradually drop below the elevation of the pump, or in some extreme cases the bottom of the well. Robin and Daneshfar (2003) studied groundwater quantity in the South Nation and the Raisin river watersheds and found that some areas are particularly and consistently vulnerable to droughts during the summer months, while other regions are vulnerable only during dry years. They strongly recommended the installation of piezometers (monitoring wells) at locations of high groundwater vulnerability and areas of regional groundwater recharge and the metering of large groundwater users.

Climate change also has implications for the integrity of private wells (Simpson, 2003) For example, increased flooding can result in shallow wells being contaminated when the wellheads and associated aquifers are inundated. Also, the increased predicted surface temperatures, particularly in the winter months, could result in the increased survival and movement of waterborne pathogens, and increased enteric disease (Simpson, 2003). Likewise, shorter winters may result in a reduced snow accumulation and could lead to a reduced groundwater recharge in spring and summer, which would further stress shallow aquifers.

There are many knowledge gaps with respect to climate and waterborne diseases issues (Patz et al., 2001). Figure 1.1 (modified from Patz et al., 2001) illustrates some potential effects of climate change on water quality which in turn has health effects. Climate involves several changes (e.g. precipitation), which in turn can affect the fate and transport microbial and chemical agents, which ultimately affects the quality of water (Rose et al. 2001). Determinants of transport and the fate of microbial pollutants associated with rainfall and melting snow are not well quantified and further studies should address the influence of varying land use on the water quality in watersheds (Patz et al., 2001). Regional and localized projections of changes in the intensity and frequency of

storms and changes in land use are required for improving climate variability /health assessments (Patz et al., 2001). Advances in monitoring are necessary to improve the knowledge base and enhance early warning and prevention capabilities (Patz et al., 2001).

The microbial contamination of drinking water supplies can have serious health consequences and this fact has been illustrated dramatically in two recent incidents in Canada, in Walkerton, Ontario and in North Battleford, Saskatchewan (Krewski et al., 2003). The significant link between excess rainfall and waterborne disease outbreaks indicates that meteorological and climatological conditions need to be considered by water managers, public health officials and private citizens as a significant risk factor for water contamination (Auld et al., 2003).With advance notice of weather, proactive measures can be taken by people dependant on private wells (e.g. monitor water quality more frequently) or those in charge of water treatment.

Currently, there is a project underway that is assessing the nature, frequency and geographic distribution of water-related diseases in Canada, both in terms of outbreaks and sporadic and endemic cases. The links between these disease occurrences and the weather-related events most likely affected by climate change, and most plausibly causing waterborne illness (extreme rainfall, soil conditions, drought) will be examined closely (Charron et al., 2003)

1.2 GROUNDWATER AND NITRATE

Groundwater samples from all over the world are showing high levels of nitrate concentration (Luk and Au-Yeung, 2002). The release of nitrate to groundwater from poor farming practice increases concentrations at an alarming rate (Luk and Au-Yeung, 2002). Several factors contribute to nitrate in groundwater.

Landuse plays a role in nitrate leaching into groundwater. In Ontario, corn takes up the majority of acreage of cropland, next to soybean (OMAF, 2002). Corn is a high acreage crop with high nitrogen application rates (Drury, 2002). The fertility needs of corn tend to be higher, when expressed on per-hectare basis than other crops, however, when adjusted to reflect differences in average crop yields, the fertility needs for corn are similar, or lower than for other grain species (Ontario Corn Producers Association, 2002). In addition, often other forms of nitrogen (e.g. manure) may not be taken into consideration (Drury, 2002). Nitrogen recovery by agronomic crops averages about 50%, however, only 35% or less of the amount applied is removed in the harvest grain of corn (Papendick et al., 1987).

Agriculture is the major contributor to the contamination of groundwater with nitrate. In general there is a direct relationship between nitrate concentrations in ground water and nitrogen fertilization rate (Canter, 1997). The continuous application of excess nutrients to soils affects the storage capacity of the soil and results in nutrients in streams and lakes, which leads to ammonia toxicity to fish, elevated nitrates in groundwater, eutrophication affecting the oxygen supply for aquatic biota, and microbial problems that impact water use and consumption (Berka et al., 2001).

The additional effects of uncontrolled animal-feeding practices, waste contamination through storm and urban runoff are also considered important (Luk and Au-Yeung, 2002), as well as geological variables, such as type of aquifer and soil conditions (Chambers et al., 2001) (Canter, 1997).

Climate change affects several critical processes in nature and in farming systems. It affects plant growth rates, soil oxygen status, mineralization and nitrification processes, as well as crop yield and nitrate leaching (Power et al. 2001). Heavy rains cause movement of nitrate from the root

zone as well as cause run-off from agricultural fields and manure containment facilities. Drought affects crop growth and crop yield which results in a lower uptake of nitrogen from soil and leaves more soil for leaching(Drury, 2002). One study showed that the concentration of nitrate in tile water was higher after a drought due to the decreased yields and decreased nitrogen uptake (Drury, 1993).

Nitrate concentration in groundwater exists as a pseudo-steady state which results from a balance between inputs and outputs. One major loss process is bacterial denitrification. The four basic requirements for denitrification are nitrate (or other N oxides), the presence of bacteria to facilitate the process, suitable electron donours, and suboxic conditions (<2 mg/L) (Burton et al., 2000). While organic carbon is the most common electron donor for denitrification, reduced iron and sulfide can also act as donors (Spalding and Parrott, 1994). Denitrification occurs in groundwater and can reduce nitrate levels in aquifers (Starr et al., 1987). In some aquifers, denitrification can attenuate nitrate levels, often to very low levels (Robertson et al., 1996).

Groundwater redox studies have shown that nitrate levels drop dramatically when the groundwater redox potential (Eh) falls below ~0.25 volts (Spalding and Parrott, 1994). Rapid decreases in nitrate concentrations with increasing depth in aquifers are common and generally are attributed to biological denitrification in the less oxygenated, deeper parts of aquifers. Spalding and Parrott, (1994) found that there was a clear sharp contrast in nitrate levels above and below 0.28 volts, and that nitrate and well depth was not highly associated because nitrate loss is controlled more by lateral than vertical changes in redox potential. Roberston et al., (1996) found that elevated levels of nitrate (5-50 mg/L) in shallow groundwater were attenuated to low levels (<0.05 mg/L) at

the redoxcline (in soil, the horizon which separates the overlying oxidizing environment from the underlying reducing environment found at 3-5 metres in that study).

Although poorly advertised and not generally known, high levels of nitrate can be harmful and fatal to bottle-fed infants up to the age of three months. The Ontario Ministry of Health advises that "for families on wells, ***no infant*** up to the age of six months should be fed formula made with water from ***any*** well (Health Canada, 1998). Infants ingesting formula made with water containing high levels of nitrate will develop methemoglobinemia, or "blue-baby syndrome", a condition that involves an impaired hemoglobin which is unable to transport oxygen to tissues. Symptoms include cyanosis, asphyxia and it can result in death (Chambers et al., 2001). Pregnant women, adults with reduced stomach activity, and individuals deficient in the methemoglobin reductase enzyme are also at increased risk for developing methaemoglobinemia (Luk and Au-Yeung, 2002)(Bourchard et al., 1992). The maximum acceptable concentration (MAC) of nitrate in drinking water is 10 mg/L.

1.3 GROUNDWATER AND METHYLMERCURY

Climate change can affect water quality to a significant extent, but what role does climate play in methylmercury levels in surface and groundwater? The South Nation River has a concentration of methyl mercury, of approximately 0.20 to 0.25 nanograms/L (ng/L) (Holmes, 2003). About 60% of the water in the South Nation River is fed by groundwater (Haughton and Pick, 2002). Since methyl mercury is an indicator of natural microbial activity in groundwater, could groundwater be the source of methylmercury in the South Nation River. Consumption restrictions on fish from the South Nation have been reported . The source of this mercury

contamination may be from a variety of sources including industry, fertilizer and fungicide application or leaching from landfill sites (Haugton and Pick, 2002).

The methylation of mercury is known to occur in anoxic water and is thought to be generally mediated by sulfate-reducing bacteria (SRB) (Jay et al., 2000). SRB are important mediators of mercury methylation in lacustrine sediments and provide a possible mechanism for increased methyl mercury bioaccumulation in water bodies affected by sulfate deposition (Gilmour et al., 1992).

Murphy et al., (1993) found levels of methylmercury at $\leq$0.2 to 137 ng/L in a survey of 78 private potable wells in southern New Jersey. It was unknown however, whether the methyl mercury found in the groundwater represented mercury that was methylated after reaching groundwater or mercury that entered the groundwater as methyl mercury. It was concluded that the historical use of mercury-based pesticides may have been a potential source of contamination to the groundwater.

In another study of groundwater collected from wells near the Nevada Test Site, it was found that mercury concentrations were very low, generally at levels of approximately 10 ng/L to 20 ng/L (Cizdziel, 2004).

Multiple field studies have showed that SRB are the key methylating organisms in nature, however, little is known about the biochemical mechanism of methyl mercury in SRB (Ekstrom et al., 2003). Choi et al. (1994) concluded that the corrinoid-containing protein responsible for mercury methylation in *Desulfovibrio desulfuricans* LS is involved in the acetyl-coenzyme A (CoA) pathway. This is now the generally accepted pathway for mercury methylation (Ekstrom et al., 2003). The only other biochemical pathway that has been suggested for Hg methylation is the

methionine synthase pathway in *Neurospora crassa*, however, this is not considered to be an important producer of methylmercury in nature (Ekstrom et al., 2003).

1.4 THE LINKAGE BETWEEN THIS STUDY AND THE CURA PROJECT

This study is a component of the Community University Research Alliance Project (CURA) entitled "Institutional Adaptation of Water-Related Infrastructures to Climate Change in Eastern Ontario" This project was a joint partnership between the Federation of Canadian Municipalities, the Eastern Ontario Water Resources Committee, the St. Lawrence River Institute of Environmental Sciences and the University of Ottawa, and was funded by the Social Sciences and Humanities Research Council. The goal of this multi-interest group project was to examine the ability of the study area to adapt to climate change. While the full impact of climate change is predicted to take place over many years, we can only take measurements over shorter time frames relative to unusually warm dry or cold wet years.

Adaptation to climate change is local as well as global. It includes policies, actions, or measures that will reduce the present and projected impacts of climate change in a given regional area, as well as reducing the vulnerabilities of some infrastructures to these impacts (e.g. ice storm of 1998) (Crabbé and Robin, 2003). This project consisted of a review of the geography and demography of the region, and a development and application of climatic scenarios to groundwater quantity and groundwater quality. There were several other areas explored (e.g. views of city councilors), however, the groundwater quality issue was the primary focus of this Master's thesis.

Given that the South Nation River watershed area is a primarily rural area with approximately 57% (South Nation Conservation, 2003) of the watershed being used for farming,

climate change should be of major interest to this region. Recognizing that climate change is an additional stress on Eastern Ontario water-related infrastructures, on top of the increase in the number of households, agri-businesses, industrial and recreational changes, and existing pollution loadings, the CURA study provided some recommendations to complement an earlier study entitled the Eastern Ontario Resources Management Study (EOWRMs) which provided recommendations in various areas including groundwater.

1.5 AQUIFERS

An aquifer is a water-saturated rock with sufficient porosity and permeability to be a usable source of water for wells (Drever, 1997). Aquifers are classified as either unconfined or confined. An unconfined aquifer is one where the water table occurs within the aquifer layer. In confined aquifers, the whole thickness of the aquifer layer is saturated and there is a confining layer above (Fitts, 2002). Generally, unconfined aquifers have a greater tendancy to be contaminated because they are open to infiltration from the surface. Contaminants from the surface must only migrate to the water table to cause potential impact (MOE, 2001). Unconfined aquifers are often shallow and frequently overlie one or more confined aquifers. Confined aquifers usually occur at considerable depths (Washington State University, 1986). In a study entitled "Ground Water Quality Fluctuations" done for the Ministry of Ontario, Miller (1982) concluded that wells obtaining water from confined aquifers, showed a lesser degree of variability than wells obtaining water from unconfined and leaky aquifer conditions. This conclusion was based on the observation that four out of five of the lowest ranking wells in variability were in confined aquifers, whereas four out of the five highest ranking wells in variability were in unconfined or leaky aquifers. The wells in the

unconfined aquifers tended to show more variability in the parameters often related to near-surface pollutants such as those from septic tank effluent, agricultural fertilizers and road salting. These parameters included nitrate and chloride.

In Eastern Ontario, the primary aquifer consists of the upper portion of the fractured Paleozoic bedrock and sand and gravel deposits, which directly overlie the bedrock in the lower portion of the overburden (CH2MHill, 2001). Pleistocene and recent deposits overlie the Paleozoic bedrock. These deposits are called overburden or unconsolidated deposits and include pre-glacial sands, till and moraine, post-glacial sands and Champlain Sea deposits. This aquifer system is called the Contact Zone Aquifer. Clay and fine-grained deposits in the region act as a confining layer for the Contact Zone Aquifer, and this layer is instrumental in preserving the quality of the water in the fractured bedrock and sand and gravel aquifer as it significantly decreases the downward migration of recharge from the surface to the aquifer. In regions where the glacial till is absent, the aquifer is more exposed to contamination (CH2MHill, 2001). The degree of geologic protection from contamination varies throughout the study area. In general, the deeper overburden aquifers have a lower potential for contamination than the shallow overburden. However, in many cases the two aquifers may be connected such that the deeper overburden aquifer may be as vulnerable as the upper overburden aquifer (CH2MHill, 2001). Two important characteristics of aquifer vulnerability (sensitivity of aquifer to contamination) are: 1. the vertical hydraulic conductivity of the geologic material overlying the aquifer (Kd) and the hydraulic gradient and porosity (Robin, 2004).

It has been shown that there is a large data gap with respect to ground water quality in Eastern Ontario and that there are many areas of high aquifer vulnerability (CH2MHill, 2001). It

has also been shown that there are many areas in the Ottawa area that have a high risk for groundwater contamination due to conditions such as sandy soil and a high water table (CH2MHILL, 2002). Information on well water quality is difficult to find and is located in various places. The compilation of groundwater quality data from a variety of sources (eg. bacteriological testing reports, hydrogeology reports, engineering reports) into a data-base would be of significant help in developing watershed-based monitoring programs (CH2MHiLL, 2001). Recently, a provincial groundwater monitoring network has been set up to provide a database that will characterize the location, quality, and sustainable yield of water and will describe how and why it is changing (MOE, 2001). Despite the recent, groundwater monitoring network, data on local groundwater quality is difficult to find or is unavailable at this time.

1.6 WELLS

Climate change may affect the integrity of private wells (Simpson 2003). Shallow wells are typically more susceptible to running dry during periods of low precipitation than drilled wells that draw water from deeper aquifers (Simpson 2003). Conversely, flooding from an extreme precipitation event can also affect the ability of the well to produce a steady and safe supply of water by causing surface water to enter older, shallow or improperly capped wells. This can also result in the increased movement of water and contaminants through the soil profile and flood water infiltrating and contaminating groundwater sources.

1.7 VARIABLES STUDIED

As a component of the overall study this investigation focused on general drinking water quality. To illustrate the potential impacts of variables such as land use and climate change on ground water, the following variables were measured using well water samples. Well water samples provide a convenient way to obtain groundwater samples and may be important during extreme weather conditions.

1. Nitrate: a highly soluble form of nitrogen which is an indication of either chemical fertilizers, or organic waste (human or animal) leaching into groundwater.
2. Total coliforms and *Escherichia coli* (*E.coli*): Bacteria indicative of faecal sewage contamination. Total Coliforms (TC) are defined by Health Canada (2002) as:
   (1) all facultative anaerobic, Gram-negative, non-spore-forming, rod-shaped bacteria that ferment lactose with gas and acid formation within 48 hours at 35 ° C;
   (2) many facultative anarobic, Gram-negative, non-spore-forming, rod-shaped bacteria that develop red colonies with a metallic (golden) sheen within 24 hours at 35 ° C on an Endo-type medium containing lactose; or
   (3) all bacteria possessing the enzyme β-galactosidase, which cleaves a chromogenic substrate (for example, ortho-nitrophenyl-β-D-galactopyranoside), resulting in release of a chromogen (ortho-nitrophenol).

Total coliforms occur naturally in soil and in the gut of humans and animals, and their presence in well water is a result of surface water infiltration or seepage from a septic system. Their presence in water may indicate faecal contamination. Water should not contain more than 10 total coliform bacteria per 100 mL of water. Water that contains more

than this amount should be re-sampled, and if the repeat sample contains more than 10 total coliform bacteria per 100 mL, corrective action should be taken immediately. Water containing fewer than 10 total coliform bacteria per 100 mL is considered marginally safe to drink; however, the sample should be re-tested, and if fewer than 10 total coliform bacteria per 100 mL are detected, the cause of contamination should be determined if possible and corrective action taken as appropriate (Health Canada, 2003).

Escherichia coli (E.coli) is the only species in the coliform group that is exclusively found in the intestinal tract of humans and other warm-blooded animals and is exreted in large numbers in faeces. The presence of this organism indicates *definite* recent faecal (sewage) pollution, and the possible presence of pathogenic microorganisms (e.g. *E.coli* 0157:H7). Water containing *E coli* is not safe to drink and corrective action should be taken immediately.

In this study, background colonies were also measured. These organisms are all non-coliform bacteria that grow on agar at 35 ° C. They include such bacteria as fecal streptococcus and staphyloccus.

3. Conductivity: a measure of the concentration of ionic solutes such as salt. It is closely related to total dissolved solids (TDS), and is dependant on the geology of the surrounding material (Fitz 2003) as well as inputs from road salt and backwash from water softeners. TDS are comprised of inorganic salts and small amounts of organic matter that are dissolved in water (Health Canada, 1991).

4. Oxygen: This variable is important in characterizing the hydrochemical nature of groundwater. The concentration of oxygen in water (dissolved oxygen)(DO) depends on a

number of factors. For example, as water moves from recharge to discharge in an aquifer, a progressive decrease in DO may result, and when DO becomes depleted, the water becomes anaerobic, and sometimes highly reducing such that H_2S, CH_4, or NH_4^+ may be present (Hounslow, 1995). DO is consumed by bacterial processes when organic matter is present (e.g. respiration). In addition, the type of soil and the type of rock also play a role in DO concentration in groundwater (e.g. in areas with little or no soil overlying permeable fractured rock, DO at detectable levels commonly persists far into the flow system) (Freeze and Cherry, 1979). In this study of interest DO in the groundwater samples were of interest, due its role in denitrification.

5. Redox potential (Eh): This is a potential within a system observed at equilibrium and indicates whether the system is reducing or oxidizing (Hounslow, 1995). Redox levels in groundwater are determined essentially by the introduction of oxygen by circulation and the consumption of oxygen by bacterially mediated decomposition of organic matter (Drever, 1997). Eh plays a role in denitrification.

6. pH: This is a measure of the hydrogen ion concentration. Most groundwater falls in the range $6.5 < pH < 10$ (Fitts, 2002). Variations in pH can be an indicator of surface water influence.

7. Methyl mercury (MeHg): Mercury is methylated to methylmercury by sulfate reducing bacteria producing a sulfide odour. This reaction occurs in anoxic environments found in groundwater where sulfate persists. The formation of MeHg in groundwater will be used to predict the contribution to levels in nearby rivers.

8 . Total Inorganic Carbon (TIC): Carbon found in species such as bicarbonate and

carbonate. In groundwater, this is derived from and depends on the geological structure/weathering of rock material through which the water passes, (e.g. HCO_3^-).

9. Total Organic Carbon: The organic carbon content of groundwater that has not been filtered through a 0.45 μ filter (Drever, 1997). Nearly all of the organic carbon of natural waters consists of dissolved organic carbon (DOC) and dead particulate organic carbon (POC). DOC is separated from POC by filtration.

1.8 RATIONALE

Land use has been implicated in impacting water quality through point or non-point source contamination (Corkal et al., 2003). Factors influencing the leaching of agricultural chemicals to groundwater (e.g. nitrate) include type and intensity of agricultural practices (e.g. livestock production), crop and land management practices, the type and chemicals used, soil characteristics, and weather (Environment Canada (EC), 2002; Agriculture and Agri-Food Canada (AAFC), 2002). In addition, the risk of water quality problems is directly related to the type of well, its condition, and how close it is to potential sources of contamination. The general rule is –the deeper the well, the longer it will take for surface water to enter the well, which lessens the risk of contamination (Simpson, 2003).

I hypothesized that there would be a difference in the levels of bacteria and nitrate in different land use sites. I compared these levels in residential, agricultural (i.e. areas adjacent to or near farm land) and agricultural intensive sites (i.e., with mixed farming/crops and animals on site). Also, I hypothesized that there may be a difference in levels of bacteria and nitrate in dug and drilled wells. To test this, I compared these levels in the two kinds of wells. In conjunction with the type of well, another important factor is the type of aquifer. The type of aquifer, and the degree of geologic protection varies throughout this area (CH2MHill, 2001). I hypothesized that there may be a difference in the contamination levels of the wells, based on characteristics of the aquifer.

Biological denitrification occurs naturally when denitrifying bacteria use nitrate as a terminal electron acceptor in their respiratory process, in the absence of oxygen (Soares, 2000). This process leads to a decrease in nitrate concentrations in aquifers (Spalding and Parrott, 1994). I predicted that in those water samples low in dissolved oxygen concentrations would also have low

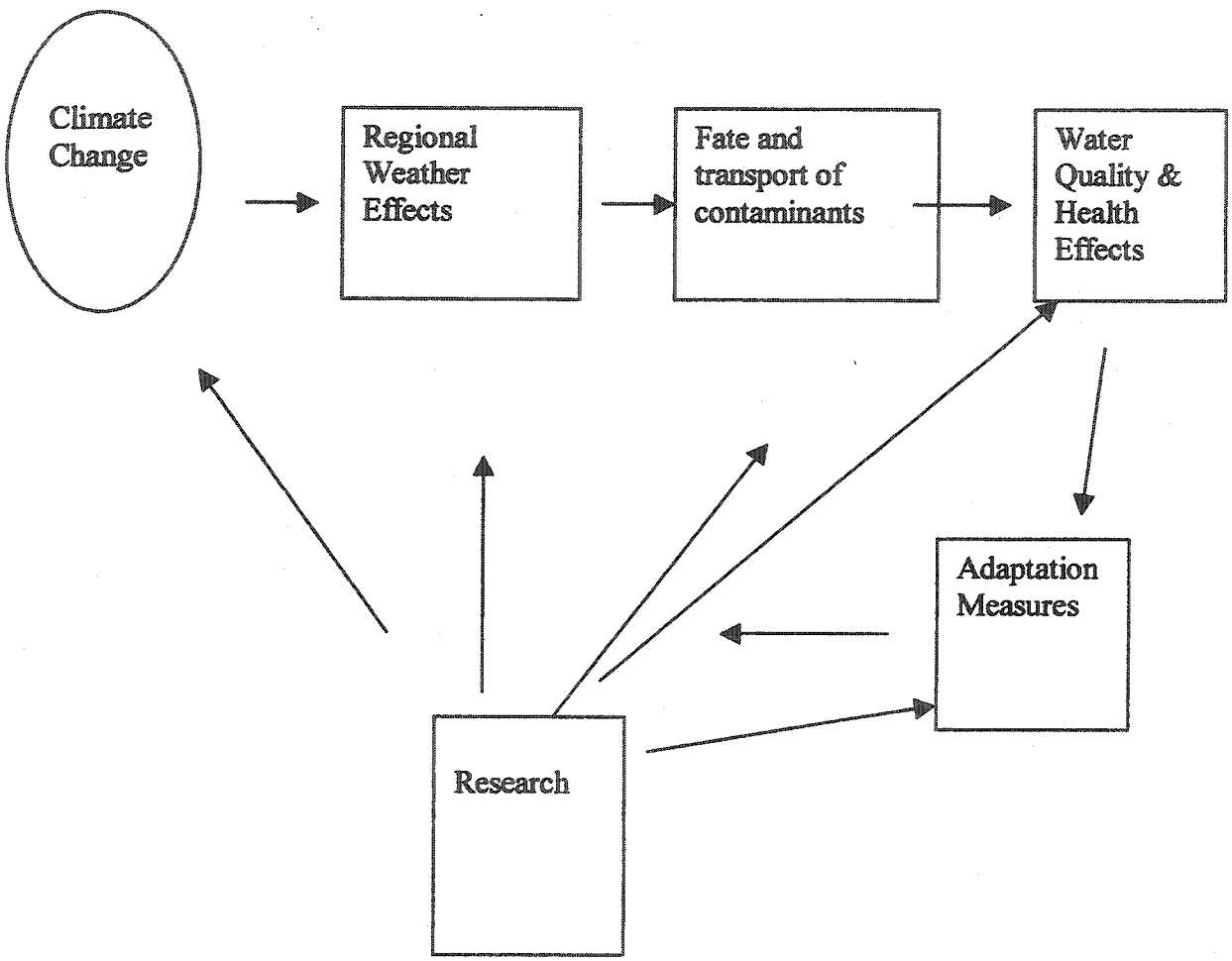
nitrate concentrations due to biological denitrification. Also, those samples with a redox potential of less than 250 mV would have a lower nitrate concentration.

Approximately, 60% of the water in the South Nation River is fed by groundwater sources (Haughton and Pick, 2002). The levels of methylmercury (MeHg) in this river are in the range of 0.20 to 0.25ng/L (Holmes, 2003). I hypothesized that groundwater could be a contributing source of MeHg to the South Nation River.

Given the recent groundwater challenges in Ontario (e.g. Walkerton) and due to the lack of information on groundwater quality in Ontario, and in the South Nation River and Raisin River regions, and also due to the unavailability of this information as affected by climate change, the objectives of this study were:

1) to provide detailed information and data on groundwater quality.
2) to test whether land use has an impact on groundwater quality
3) to test whether type of well (e.g. dug or drilled) and the characteristics of the aquifer (e.g. vertical hydraulic conductivity) have an impact on water quality
4) to test the levels of MeHg in well water, and to test whether these levels are impacting the MeHg levels in the surface water, specifically, the South Nation River.
5) These data could then be used as a basis to make future predictions on the impact of climate change on groundwater systems, or as a comparison with future data.

Figure 1.1 The Effects of Climate Variability on Water Quality (modified from Patz et al., 2001).


Climate Change
Regional Weather Effects
Fate and transport of contaminants
Water Quality & Health Effects
Adaptation Measures
Research

2. MATERIALS AND METHODS

2.1 Study Site and Water Sampling Collection Procedure

In 2002, homeowners in the South Nation River and Raisin River watershed areas were contacted to see whether there was interest in participating in my study. It should be noted that prior to setting out and distributing information sheets, Research Services of the University of Ottawa was contacted for guidance on ethics. It was advised by them that since the object of study was to study water samples, it would not be required to proceed through the university's ethics review process. Interested participants were given an information sheet, to read, sign and send back to me. South Nation River Conservation Authority produced an article for their newsletter in conjunction with my team explaining the nature of the study. Further to this newsletter, several local papers also ran articles about the groundwater study. The articles explained that a researcher from the University of Ottawa was setting out to test local drinking water. As a result of these articles, approximately 54 people wrote or called me in order to sign up and participate in the research.

Due to the interest of the public in the research , the study became an investigation in the drinking water situation in this part of Eastern Ontario. In June and July of 2003, drinking water samples were collected from 54 homes in the South Nation River and Raisin Region watershed areas across an area of 6800 square kilometres (Figure 2.1). These 54 samples were divided into the following categories to test whether land use and type of well play a role in contamination level in the well water.

1. according to land use: residential, agricultural, and intensive agricultural (R, A, and AI). There were 22, 17 and 15 water samples in R, A, and AI, respectively.
2. type of well: dug or drilled (DU, DR). There were 10 and 41 DU and DR wells, respectively.

After the water samples were collected, all analysis were then conducted in the laboratory of Dr. David Lean and the St. Lawrence River Institute (SLRIES) following the procedures below.

2.2. Bacterial Enumeration

During sampling, Dynamarex Safe-Touch latex gloves were worn. The cold tap was left running for five minutes prior to collection. The sterilized sampling bottle provided by the St. Lawrence River Institute was opened; the cap was removed, and the bottle was filled to the line. The water sample bottles were immediately placed on ice in coolers, and driven to SLRIES at the end of the collection day or were sent by Purolater packed in ice to arrive by 9:00 AM the next day. All samples were analyzed within 24 hours.

The first six samples were analyzed for total coliforms (TC), *E.coli* (EC) and faecal coliforms, and thereafter, all samples were analyzed for TC, EC and background colonies (BC). Since, faecal coliforms provide similar information as EC (i.e. indicators of animal/human waste), doing both faecal and EC tests was not necessary. Background colonies can be done on the sample plate as TC and EC, and it provides an indication of general bacteria in the water (i.e. the level of sterility) (Ridal, 2004). The method used for enumerating TC and EC is called the Differential Coliform Method and was developed by the Ontario Ministry of the Environment. It is the standard procedure used by most laboratories across Ontario for enumerating TC and EC. EC colonies are

blue, non-EC coliform are red, and all the other colonies are background colonies. All bacteria colonies were counted by enumeration using a dissecting scope (Ridal, 2004).

For the first 11 samples, there were no duplicates, and thereafter, all samples were collected in duplicate.

2.3 Water Chemistry

2.3.1 *Conductivity, Eh, pH, TOC, TIC*

Single 50 mL Polypropylene Conical Falcon tubes Blue Max (Becton Dickinson Labware) were rinsed three times with sample water, which was discarded, and then filled with sample water to be analyzed immediately for: conductivity, redox potential (Eh), and pH. Other duplicate tubes were rinsed with sample water. This water was discarded and the tubes were filled , capped and stored on ice in coolers to be later analyzed for total inorganic carbon (TIC) and total organic carbon (TOC). Another tube was filled as an extra.

Both pH and Eh was measured with a VWR Scientific Products waterproof SP21 meter. The pH probe used was a VWR SympHony Series Gel-Filled Combination Electrode. Samples were standardized against Thermo Orion pH buffers at pH's 7, 10 and 4. The probe was kept in VWR Symphony pH electrode Storage Solution when not in use.

Eh was measured with aVWR Platinum Redox Electrode. The filling solution for the probe was probe VWR Scientific Products #14002-824 4 M KCl. The probe was placed in standard solutions of 234 mV and 300 mV prior to measurement. The standard solutions were prepared in the laboratory prior to sampling.

Conductivity was measured by filling the above 50 mL falcon tubes with sample water and using the Hand Held Traceable Conductivity Meter (Model #21800-012).

All samples that were collected and analyzed for pH, Eh, conductivity were discarded after analysis.

2.3.2 *Oxygen*

Oxygen levels in the water samples were measured by using a YSI Model 57 Oxygen Meter with a YSI 5720 probe. The water was collected by attaching a hose to the cold water tap (in some cases outdoor taps), and allowing the water to fill an 300 mL Wheaton glass Biological Oxygen Demand bottle. Approximately 2 volumes of the bottle was overflowed so that there were no air bubbles, and the bottle was quickly capped. Then, the cap was quickly removed and the YSI 5720 probe was inserted into the bottle to avoid getting air into the bottle. Oxygen values were calibrated using air oxygen at ambient temperature. After taking the reading, the water was discarded.

2.3.3 *Nitrate*

Wheaton Redi-Pak 4 oz square glass bottles with the Teflon lined caps were washed with deionized water in the laboratory prior to water collection. On site, the bottles were also rinsed with sample water from the tap and duplicate samples were collected for the analysis of nitrate. After filling both bottles with water, samples were put in coolers on ice. Analysis was performed by University of Ottawa using the Lachat Instruments, QuikChem Method 10-107-04-1-C.

Most samples were analyzed within 24 hours. Some samples were re-tested after the following weeks: samples 40 and 41 after 4 weeks; sample 31 after 5 weeks, sample18 after 6

weeks. Samples 48, 49, 50, and 51 were tested after 1 week and 46 and 47 after 2 weeks. It was found that since the amount of nitrate found at the initial testing was either less than the detection limit (0.01 mg/L), or close to it, the change in nitrate over time was minimal.

2.3.4 *Methyl Mercury (MeHg)*

Nalgene Wide-Mouth High Density Poly Ethylene 1000 mL bottles were prepared in the laboratory by rinsing with deionized water. New bottles were rinsed with deionized water, whereas bottles that had been re-used were washed with dish soap, scrubbed with a bottle brush and rinsed. On site, bottles were rinsed with sample water from the tap and filled to the top with sample water. 5 mL of concentrated hydrochloric acid GR ACS UN1789 (EM Science/Merck KgaA) were added to the sample and the sample was placed in a cooler on ice. Analysis was performed at the University of Ottawa following the method of Cai et al., (1996).

2.3.5. *Aquifer Information*

Maps of the type of aquifer (i.e. shallow or deep) of the study area were provided by Dr. Bahram Daneshvar and Dr. Michel Robin. The Eastern Ontario Water Resources Management Study (2001) maps were consulted for the estimated vertical conductivity (K) of the overburden of the study area.

2.4 Statistical analyses

All statistical analyses were performed with SYSTAT® 10 for Windows® (2000) . Rejection of the null hypothesis occurred when $p < 0.05$. All the results for statistical analysis are found in Appendix A. Statistical Analysis.

A chi-square test (2 by 3 contingency table) was used to determine whether the occurrence/presence or absence of the three types of bacteria measured (total coliforms:TC, E.coli: EC, and Background colonies: BC) differed between the three land use types (i.e., residential, agricultural, and agricultural intensive). A chi-square test was also used to determine whether the occurence of these bacteria differed between the dug wells and the drilled wells.

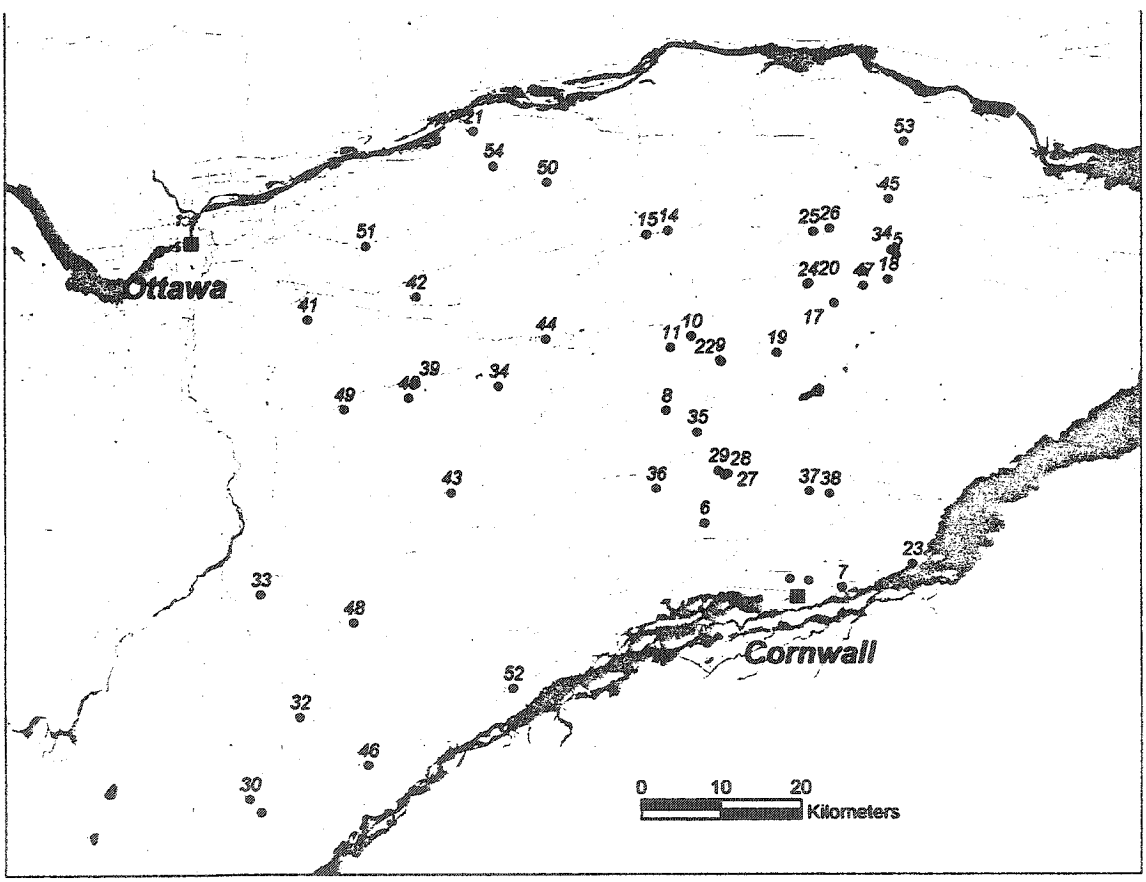
A one-way analysis of variance (ANOVA) was used to test whether there was a difference between the means in the following cases. The Lilliefors test was used to determine normality of residuals. The Levene's test was used to determine whether there was heteroscedasticity. The Kruskall-Wallis test was used to confirm the results of the parametric ANOVA:

1. bacterial cell counts for TC, BC and EC in the three different land use types (i.e, residential, agricultural, and agricultural intensive).
2. nitrate levels in the three different land use types.
3. bacterial cell counts for TC, BC, and EC in the two different types of well (i.e. dug and drilled)
4. nitrate levels in the two different types of well
5. nitrate levels at two different concentrations of dissolved oxygen (1mg/L and <1mg/L).
6. nitrate levels measured at the two different redox potential (Eh) of less than or greater than 250 mV.

A one-tailed T test was used to test whether there as a difference in the means of the methyl mercury concentrations between the samples that exibited a sulphide odour and those samples that did not.

Simple Linear Regressions (SNL) were done to determine if there was a relationship between the variables of conductivity as a function of total inorganic carbon; nitrate concentration as a function of dissolved oxygen, MeHg as a function of total organic carbon; bacterial counts as a function of well depth (BC, TC and EC) and nitrate as a function of well depth.

Figure 2.1 Map showing the location of sampling in the South Nation River and Raisin River watershed areas. Note 4 sampling points are not shown. Points 1 and 2 are indicated by a square. Points 12 and 13 are not shown (Daneshfar and Robin, 2003).


Ottawa
Cornwall
0 10 20
Kilometers

3. RESULTS

3.1. Samples

More than 50% of the well water samples, tested positive for total coliforms (TC) (Figure 3.1). 11% of the samples showed total coliforms counts >50 colony forming units/100 mL water; cfu/100mL). Sample 52 was not included, but showed 12 500 cfu/100mL TC. 67% of these samples also had elevated *E.coli* counts (samples 26, 36, 41 and 52). 13% of the total samples had elevated levels of background colonies (Figure 3.12).

Only 4 % of the samples had nitrate concentrations that exceeded the maximum acceptable concentration (MAC) of 10 mg/L (Figure 3.13). 25% of the samples had values that exceeded zero, but were not over the MAC. The rest of the samples were below the detection limit for nitrate (0.01 mg/L) (Figure 3.13).

Conductivity was high, with a mean of 908 µS/cm + 570 SD (Table 3.1). 8% of the samples had conductivity greater than or equal to 2000 µS/cm. The mean Total Inorganic Carbon (TIC) was 65 ppm ± 32 SD.

The samples were low in oxygen, averaging 1.5 mg/L ± 1.7 SD. Samples 12, 14, 15, 28, 35, 40, 42, 47, 49, 53 and 54 had considerably higher oxygen concentrations than the mean.

The redox potential of the samples was mostly positive with a mean of 197 mV ± 102 SD (Table 3.1). Some samples showed negative redox potential as follows: 1, 9, 10, 37, 43, 44, 50 (Figure 3.17).

The methylmercury (MeHg) concentration in the samples was very low with a mean of 0.05 ng/L ±0.01 SD. Figure 3.14 shows that three samples showed a very slightly elevated MeHg (48, 49, and 50).

3.2 Bacteria

More than 50% of the 54 well water samples were contaminated by total coliform bacteria (TC), about 7% were contaminated by *E.coli* (EC), and more than 60% were contaminated by background colonies (BC); (Figure 3.1). The average count was high at 25 cfu/100 mL + 77 standard deviation (SD) when a major outlier was excluded (Table 3.1). When included , the average count rose to 231 cfu/100 mL +1699 SD. According to Health Canada, a water sample having a count of more than 10 cfu/100mL of TC should be resampled, and if the repeated sample contains more than 10 cfu/100mL TC, then corrective action should be taken immediately (Health Canada, 2003). Furthermore, Health Canada (2003) also recommends that water containing fewer than 10 cfu/100 mL be resampled, the cause of the contamination should be determined and corrective action taken as appropriate. In this survey, 28% of the well water samples had TC counts over 10 cfu/100 mL. 7.4% had EC counts that were over the maximum acceptable concentration of 0 cfu/ 100 mL of water (Health Canada, 2003) The average count for EC was 0.42 ± 0.25. For BC, 11% of the well water samples had counts greater than 200 with an average count of 70 + 145 SD.

Table 3.2, indicates a comparison of the proportions of samples testing positive within the three land use sites (i.e., residential, agricultural and agricultural intensive). While samples testing positive for TC increased from 50% in residential areas to 53% in agricultural areas, and to 73% in the agricultural intensive areas, the proportions of samples testing positive were not significant

(chi-square test, p=0.335). Neither BC nor EC occurrence was significant (chi-square test, p=0.689, p=0.794) (Appendix A.1).

Furthermore, there was no difference in the means of the bacterial counts of TC, BC, or EC between the three land use types (1-way ANOVA p=0.763, p=0.315, p=0.743) (Appendix A.3,A.4 and A.5).

Dug wells tested positive 1.6 times more for TC than drilled wells did ; 13 times more for *E.coli*, and 1.4 times more for background colonies (Table 3.4). It was found that other than for *E.coli*, there was no difference in the proportions of the bacteria in the dug and drilled wells (chi-square test; p=0.075, p=0.004, p=0.389) for TC, EC, and BC, respectively (Appendix A.2).

Figure 3.2 shows the mean TC, EC, and BC cell counts in dug and drilled wells. Although the average cell counts were higher in dug wells than in drilled wells, a significant difference was found only in the means of TC counts (1-way ANOVA, p=0.015) and in background colonies (1-way ANOVA, p=0.051), but not in *E.coli* (1-way ANOVA, p=0.429) (Appendix A.6 to A.8).

Another way to analyze the above observations is to look at the levels of bacteria versus well depth. For both TC and BC, their counts show a general decrease with increasing well depth (p=0.024 for TC; p=0.055 for BC) (Figure 3.3). The relationship was significant only for TC and BC; although the R^2 was relatively small for TC ($R^2 = 0.253$) and even smaller for BC ($R^2 = 0.165$). No relationship could be drawn between *E.coli* (EC) and well depth due to the large number of zero counts (Figure 3.4).

3.3 Water Chemistry

48% of the well water samples had a very low concentration of nitrate (i.e., below the detection limit of 0.01 mg/L) nitrate. The average nitrate concentration was 1.95 mg/L ± 7.78 SD

(Table 3.1). Nitrate levels were below the maximum acceptable concentration (MAC) of 10 mg/L, except in two cases. These samples had nitrate concentrations of 56 and 15 mg/L.

Dissolved oxygen (DO) concentrations in the well water samples were generally very low, with 44% of the samples being below 1 mg/L DO. The average concentration of DO in the samples was 1.51 mg/L ± 1.74 SD (Table 3.1). A significant positive linear relationship was observed between DO and nitrate ($p<0.001$), although it was weak ($R^2=0.320$) (Figure 3.5). There was a significant difference in the means (0.879 ± 0.214 ; 2.613 ± 0.292) of nitrate concentrations at the two different concentrations of DO (<1 mg/L DO and >1mg/L DO) (1-way ANOVA, $p=0.000$). At DO concentrations > 1mg/L, the nitrate concentrations increased, and at DO concentrations <1mg/L, the nitrate levels decreased.

Nitrate levels were on average highest in the agricultural intensive sites (Figure 3.6). The average levels were well below the MAC (Table 3.3) There was a significant difference in the means of the nitrate concentrations between the three land use sites (1-way ANOVA, $p=0.006$). The means and the standard errors for the three land use types are 0.610 ± 0.127 SE for residential, 1.107 ± 0.141 SE for agricultural, and 1.341 ± 0.156 SE for the agricultural intensive site.

No relationship could be drawn between nitrate concentration as a function of well depth (Figure 3.4) due to so many of the samples having such low concentrations of nitrate. On average, the nitrate concentrations was higher in the dug wells than in the drilled wells (Table 3.5). There was a significant difference between the means (7.639 ± 2.531 SE, 0.408 ± 1.201 SE) of nitrate concentrations in the dug and drilled wells, respectively (1-way ANOVA; $p<0.05$).

The redox potential (Eh) of the samples ranged from –63.6 to 274.6 mV, with an average of 197.45 ± 102.87 SD (Table 3.1). A significant difference was found in the means of nitrate

concentrations between samples that had an Eh less than 0.25 V and samples that had an Eh greater than 0.25 V (1-way ANOVA; p=0.001; Appendix A.15). The means were 0.481 ± 0.087 SE, and 1.246 ± 0.106 mg/L for samples with less than 0.25 V Eh, and samples that had greater than 0.25 V, respectively. Redox plays an important role in biological denitrification. High nitrate concentrations in groundwater were associated with relatively oxidizing groundwater (i.e, > +0.28 v ± 0.02). Nitrate levels have been found to dramatically decrease when Eh dropped to below +0.25 V (Spalding and Parrott, 1994).

MeHg concentrations in all of the samples were very low with a mean of 0.05 ng/L ± 0.01 SE (Appendix B). Values ranged from below the detection limit of 0.02 ng/L to 0.90 ng/L. The MeHg values were subdivided into samples that emitted a sulphide like odour and those that did not. The samples that emitted a sulphide odour had significantly higher levels of MeHg than those that did not emit this odour (Figure 3.7; One-tailed T test: p=0.043; Appendix A.17).

Since a portion of the total organic carbon (TOC) may be a substrate for microbial metabolism, with products such as sulfide and methane (Chappelle et al., 1993), I wanted to see if there was a relationship between the concentration of TOC and MeHg since the sulfate reducing bacteria that are involved in producing MeHg need specific organic carbon materials as substrate. There was no relationship between these two variables (Figure 3.8) (Simple Linear Regression, p=0.885) suggesting that much of the TOC is not metabolically active.

Conductivity is the concentration of ionic solutes (e.g. salt) and is closely related to total dissolved solids (TDS). The mean conductivity in the water samples was 908 µS/cm + 570 SD (Table 3.1), and ranged from 225 µS/cm to 9669 µS/cm. 80% of the samples were under 1000 µS/cm. Conductivity is a good estimator of total dissolved solids (TDS) (Hounslow, 1995). High

TDS (or conductivity) is due to natural dissolution, but can also be attributed to inputs from road salt; backwash from water filters and the groundwater flow pathway. TDS is comprised of inorganic salts and small amounts of organic matter dissolved in water (Health Canada, 1991). In groundwater, the TDS depends on the surrounding geology, consists of a short list of inorganic solutes (e.g. Ca^{2+} and $HCO3^-$) (Fitts, 2002).

Figure 3.9 illustrates the relationship between conductivity and total inorganic carbon (SLR, $p<0.001$, $r^2 = 0.54$). There is a signficant positive relationship between the concentration of total inorganic carbon and conductivity in the well water samples due to the geology of the study area.

3.4 Aquifers

Figure 3.19 and 3.20 are maps indicating the position of the aquifer above sea level (m) (red indicating shallow parts of the aquifer and blue indicating deep aquifers), and the estimated vertical hydraulic conductivity of the overburden (K), respectively. The sample points (location) were superimposed on both of these maps. In total, 52 of the sample points are shown, excluding sample numbers 12 and 13. Samples 1 and 2 are indicated by a square on the map. Samples 1, 4, 7, 8, 11, 14, 15, 17, 19, 24, 26, 32, 36, 41, 45, 46, 47, 48, and 52 had elevated TC counts (Figure 3.10). Of these samples, over 70 % were located on a shallow part of the aquifer (shown in red) (Figure 3.13) and about 17 % of these samples had a high K value (Figure 3.14). Samples, 26, 36, 41 and 52 also had high *E.coli* counts (Figure 3.10). All of these points were found on shallow parts of the aquifer. Only one of these points (36) had a very high K value.

Samples 21, 26, 28, 36, 46 and 47 had elevated levels of background colonies (Figure 3.10). All of these, except for sample 21 are also located on shallow parts of the aquifer (Figure 3.13). 66% of these points had a high K.

Similiarly, samples 8, 12, 14,15, 16, 18, 26, 27, 28, 35, and 47, had the elevated nitrate levels (Figure 3.11). Of these 18% were found on shallow aquifers and 13% had high K. Samples 48, 49, 50 showed higher levels of MeHg than the rest of the samples (Figure 3.12). These wells were also found on shallow aquifers with a high K.

Table 3.1 Average Values for Variables Measured for all 54 Sampling Sites.

*note that this was the average value with one outlier excluded, if the value was included the average count=231 cfu/100mL and standdev.=1699

Variable	Average Value
Total Coliforms (TC)*	25 cfu/100mL* ± 77 SD
E.coli (EC)	0 cfu/100 mL ± 2 SD
Background Colonies (BC)	70 cfu/100 mL ± 145
Conductivity	908 uS/cm ± 570 SD
pH	7.4 ± 0.3 SD
Eh	197 mV ± 102 SD
Nitrate	1.9 mg/L ± 7.8
MeHg	0.05 ng/L ± 0.01 SD
Total Inorganic Carbon (TIC)	65 ppm ± 32 SD
Total Organic Carbon (TOC)	1.5 ppm ± 2.0 SD
Dissolved Oxygen (DO)	1.5 mg/L ± 1.7 SD

Table 3.2 Occurrence of Bacteria in Three Different Landuse Types

Sampling site	% of samples testing positive		
	Total Coliforms	E.coli	Background colonies
Overall	57	7.4	62
Pearson Chi-Square for land use impact	0.335	0.689	0.794
Residential	50	4.5	68
Agricultural	53	11.7	53
Intensive Agricultural	73	6.7	60
One way ANOVA for landuse impact	0.763	0.743	0.315

Note* the land use impact is based on the three land use types (Residential, Agricultural, and Agricultural Intensive).

Table 3.3 Average Nitrate Levels in Three Different Landuse Types
± 1 Standard Deviation (SD)

Landuse type	Average Nitrate Concentration (mg/L)
Residential	0.61 ± 0.12
Agricultural	1.11 ± 0.14
Intensive Agricultural	1.34 ± 0.16

Table 3.4 Occurrence of Bacteria in Dug and Drilled Wells.

Total Number of Wells are 11 Dug and 40 Drilled.

Type of Well	% Wells Testing Positive for Bacteria		
	Total coliforms	E.coli	Background Colonies
Dug	80	30	80
Drilled	49	2.4	56

Table 3.5 Nitrate Levels in Dug and Drilled Wells

± Standard Deviation

Well Type	Average Nitrate Concentration (mg/L)
Dug	7.63 ± 2.53
Drilled	0.40 ± 1.20

Table 3.6 Mean Bacteria Counts in the three Land Use Types

Number of Samples are (N) = 22, 17, and 15 in residential, agricultural and agricultural intensive land use types. Bacteria counts are measured in colony forming units per 100 mL (cfu/100 mL of liquid) ± Standard Deviation (SD).

Variable	Residential	Agricultural	Agricultural Intensive
Total coliforms	10 ± 27	52 ± 134	14 ± 18
E.coli	0.36 ± 1.7	0.24 ± 0.68	0.73 ± 2.8
Background colonies	51 ± 112	111 ± 200	51 ± 133

Figure 3.1 Percentage of total well samples (n=54) testing positive with total coliforms (TC; light shade), *E.coli* (EC; in white) or background colonies (BC; dark diamonds).

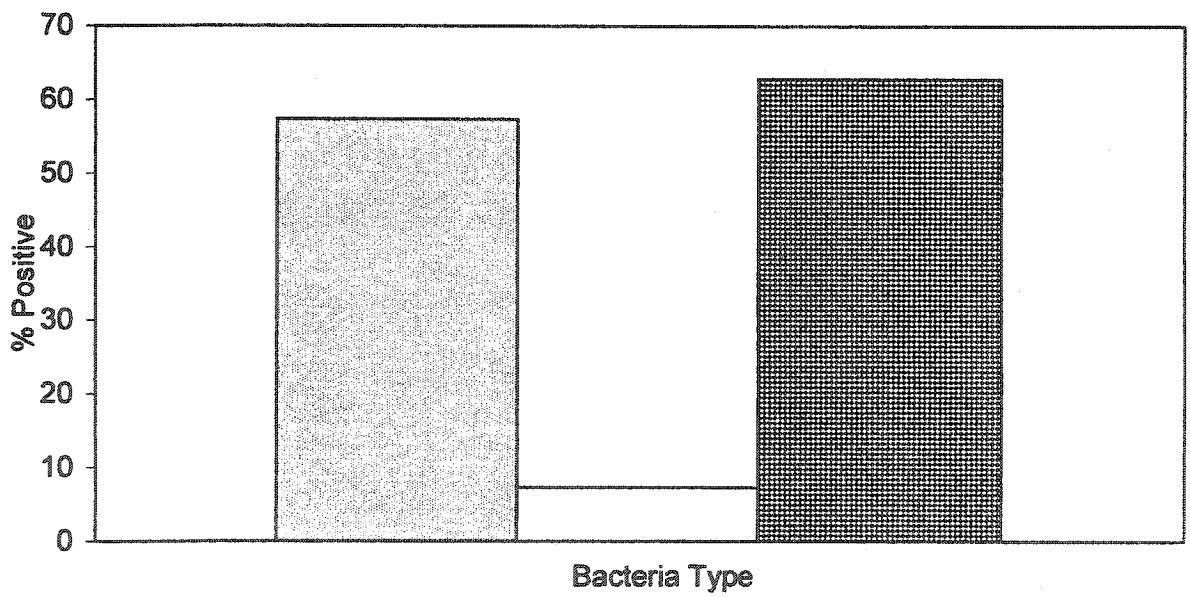
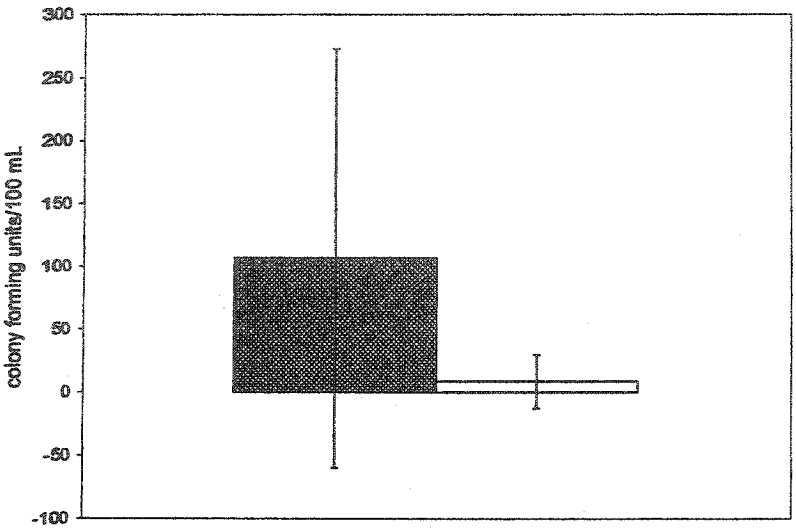
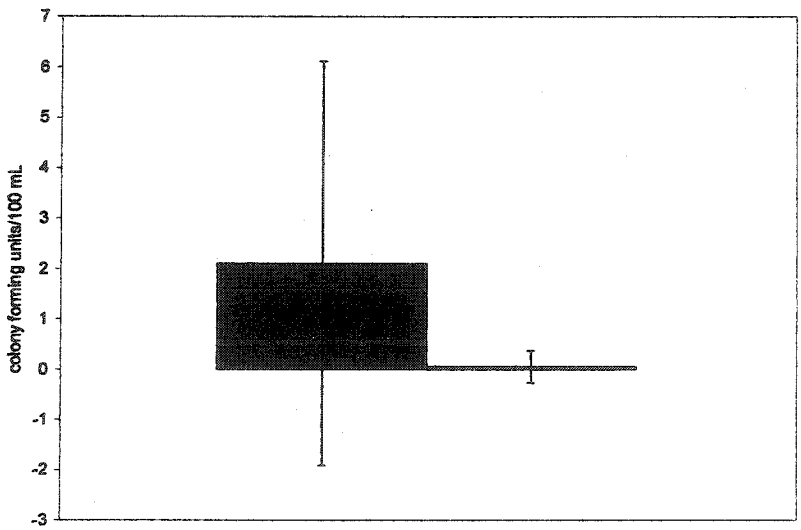

70
60
50
40
30
20
10
0
% Positive
Bacteria Type

Figure 3.2 Mean Cell Counts (±1SD) of total coliform (TC; top graph), E.coli (EC; middlegraph), and background colonies (BC; bottom graph) in dug (dark shade; n=10) and drilled wells (white; n=41)

TC


colony forming units/100 mL
300
250
200
150
100
50
0
-50
-100

EC


colony forming units/100 mL
7
6
5
4
3
2
1
0
-1
-2
-3

BC

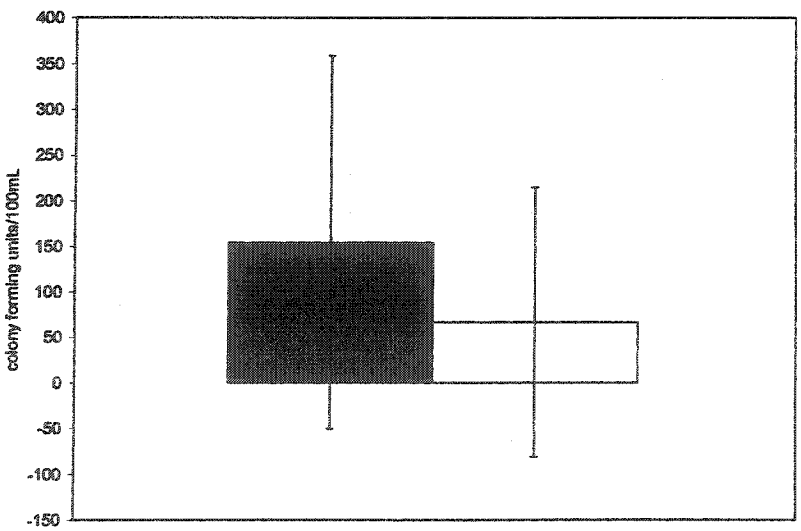

colony forming units/100mL
400
350
300
250
200
150
100
50
0
-50
-100
-150

Figure 3.3 Relationships between mean cell counts (log cfu/100 mL) of total coliform (TC: n=20; top graph), *E.coli* (EC: n=54; however only 4 detectable samples; middle graph), and background colonies (BC: n=23; bottom graph) and well depth.

The regression analyses resulted in the following models:

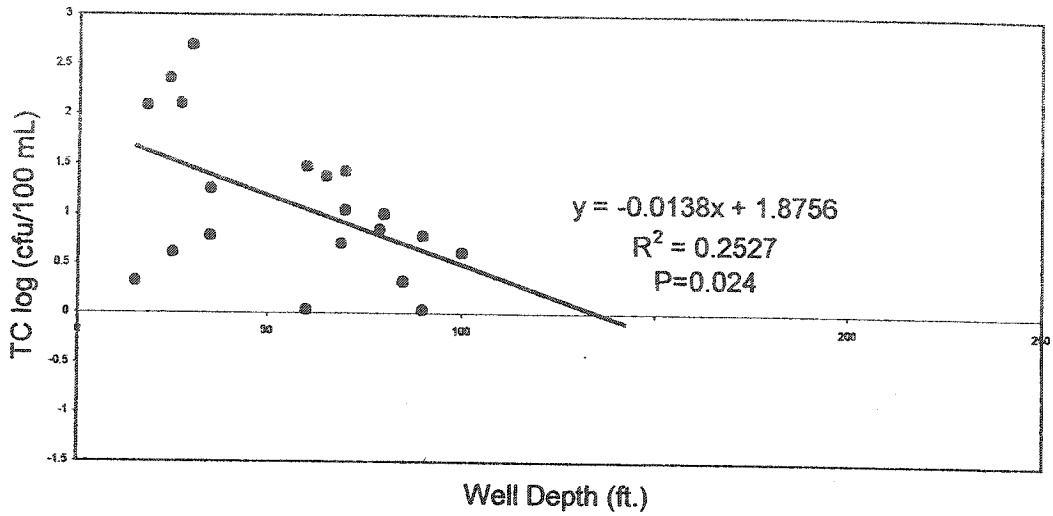
Total coliforms (TC)

Log TC count = 1.876 + -0.014 Depth, r^2=0.25, p=0.02

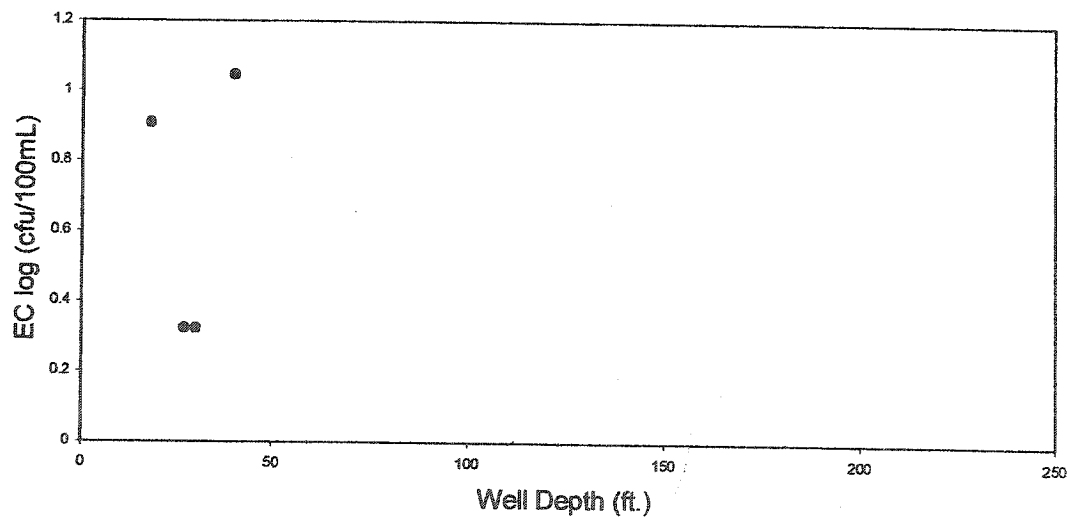
Background colonies (BC)

Log BC count = 1.894 + -0.009 Depth, r^2=0.16, p=0.05

TC


y = -0.0138x + 1.8756
R2 = 0.2527
P=0.024
TC log (cfu/100 mL)
Well Depth (ft.)

EC


EC log (cfu/100mL)
Well Depth (ft.)

BC

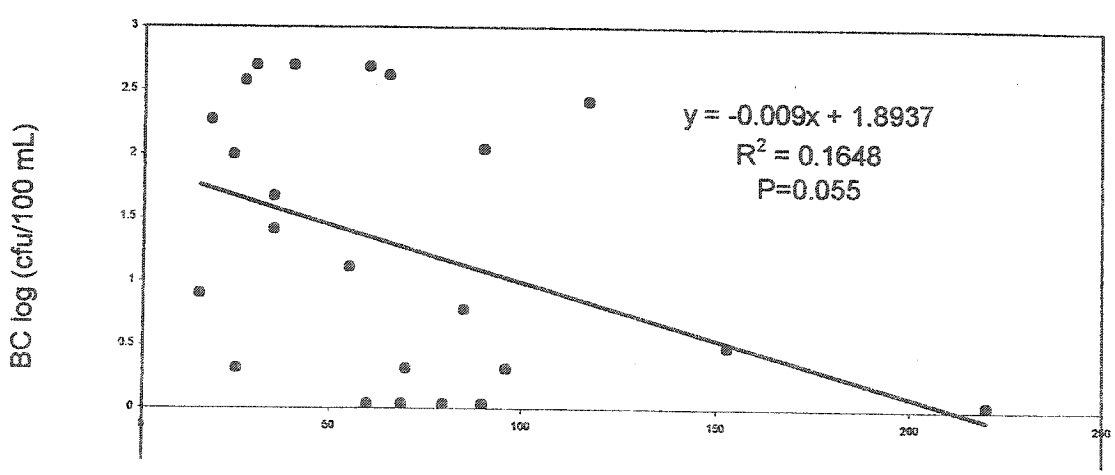

y = -0.009x + 1.8937
R2 = 0.1648
P=0.055
BC log (cfu/100 mL)

Figure 3.4 Plot of nitrate (mg/L) and well depth (feet) (n = 53). The value for sample 8 was removed (56 mg/L).

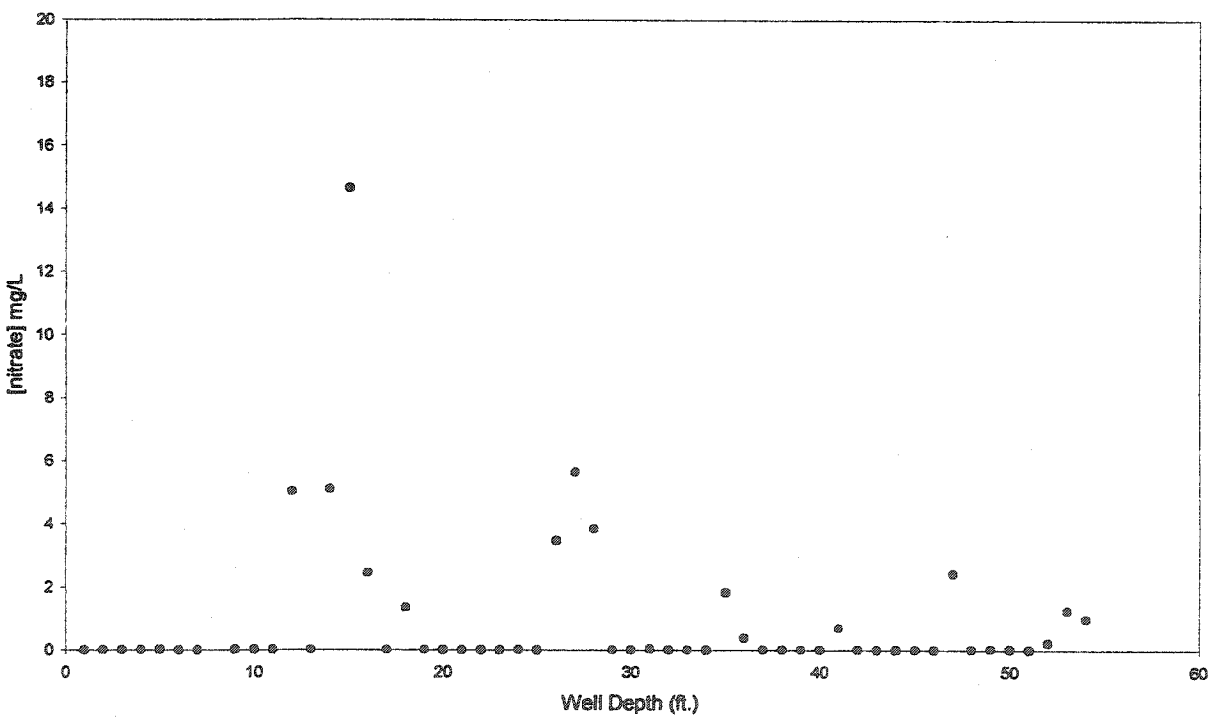

[nitrate] mg/L
Well Depth (ft.)
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60

Figure 3.5. Relationship between nitrate (mg/L) and dissolved oxygen (mg/L) (n=41) in the well samples. 11 samples were excluded due to methods, and 2 points were outliers.

The regression analyses resulted in the following model:

Nitrate concentration = 0.041 + 0.505 dissolved oxygen, r^2=0.32, $p < 0.001$

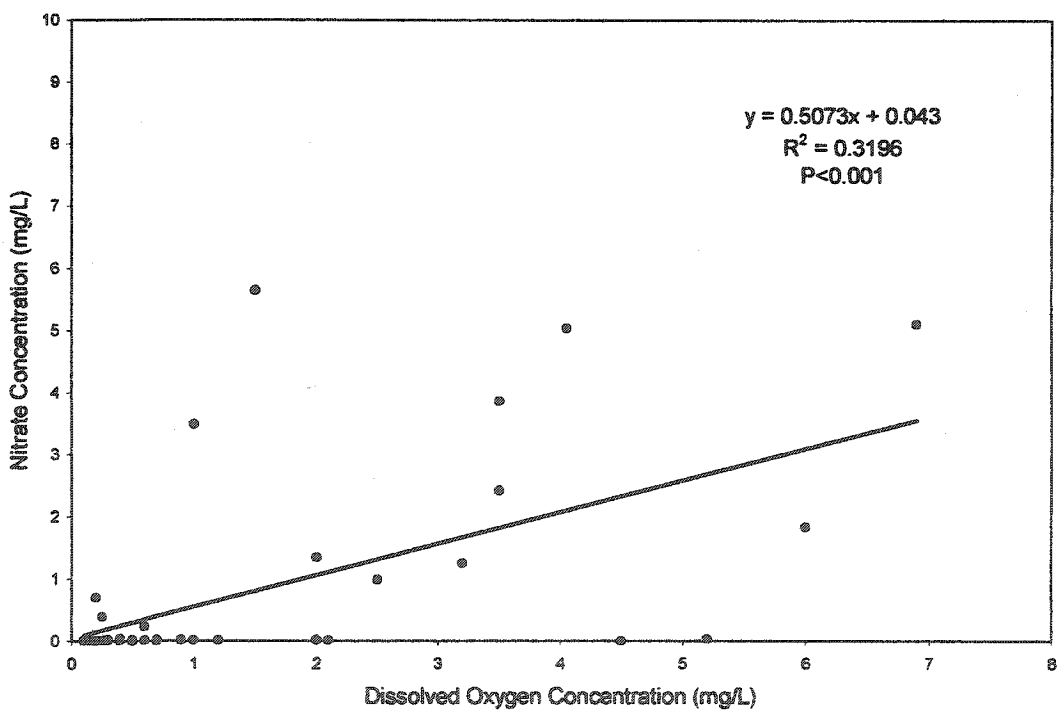

y = 0.5073x + 0.043
R2 = 0.3196
P<0.001
Nitrate Concentration (mg/L)
Dissolved Oxygen Concentration (mg/L)
0
1
2
3
4
5
6
7
8
9
10

Figure 3.6 Mean nitrate concentration (± 1 SE) in the wells from the three land use types. Residential (white: n=21), agricultural (lightly shaded: n=16) and agricultural intensive (darkly shaded: n=15).

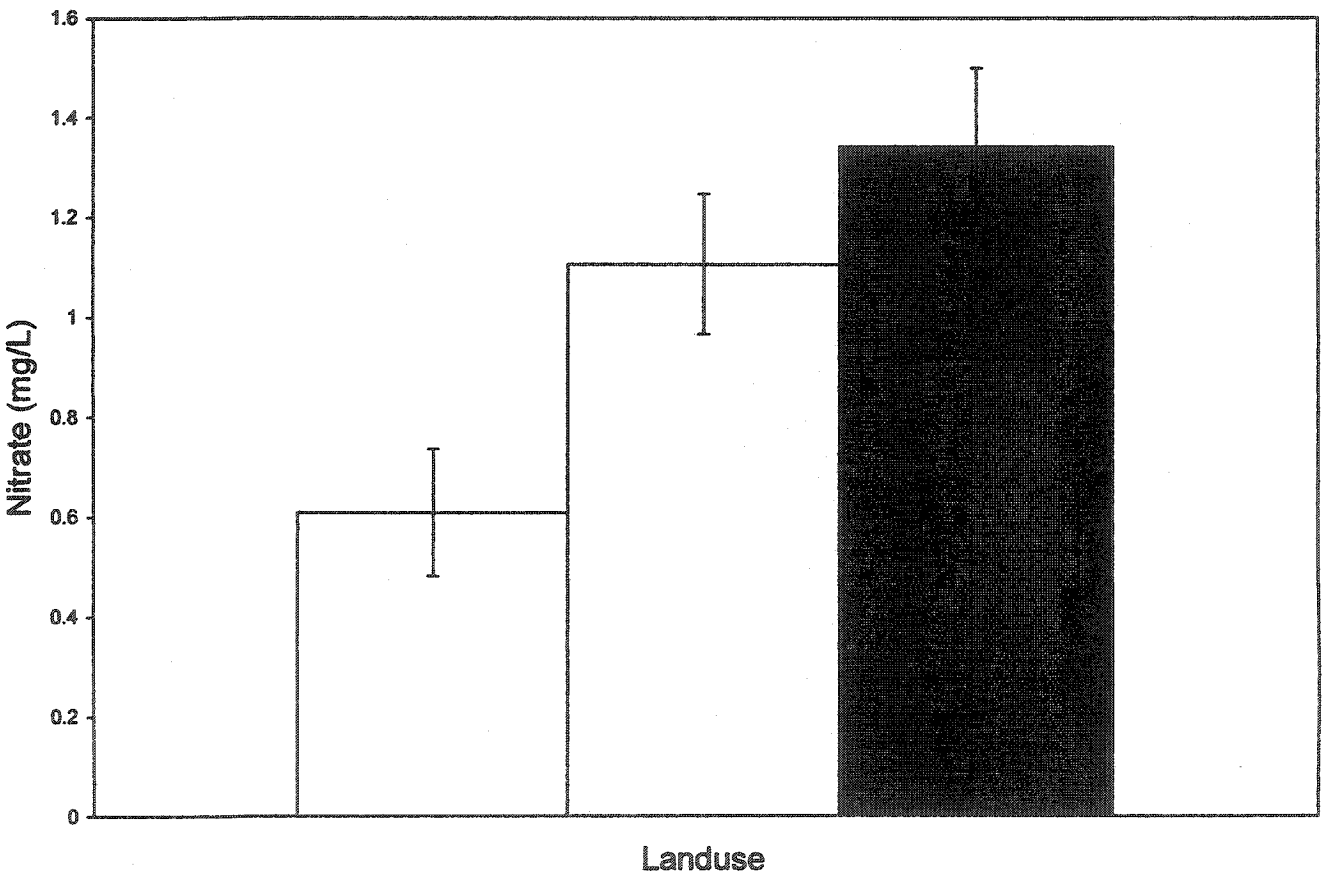

1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Nitrate (mg/L)
Landuse

Figure 3.7 Mean methylmercury concentration (±SE) in the wells with sulphide odour (represented by dark shade: n=9) and without sulphide odour (represented by white: n=27). Analysis by T test (p=0.043)(Appendix A.16).

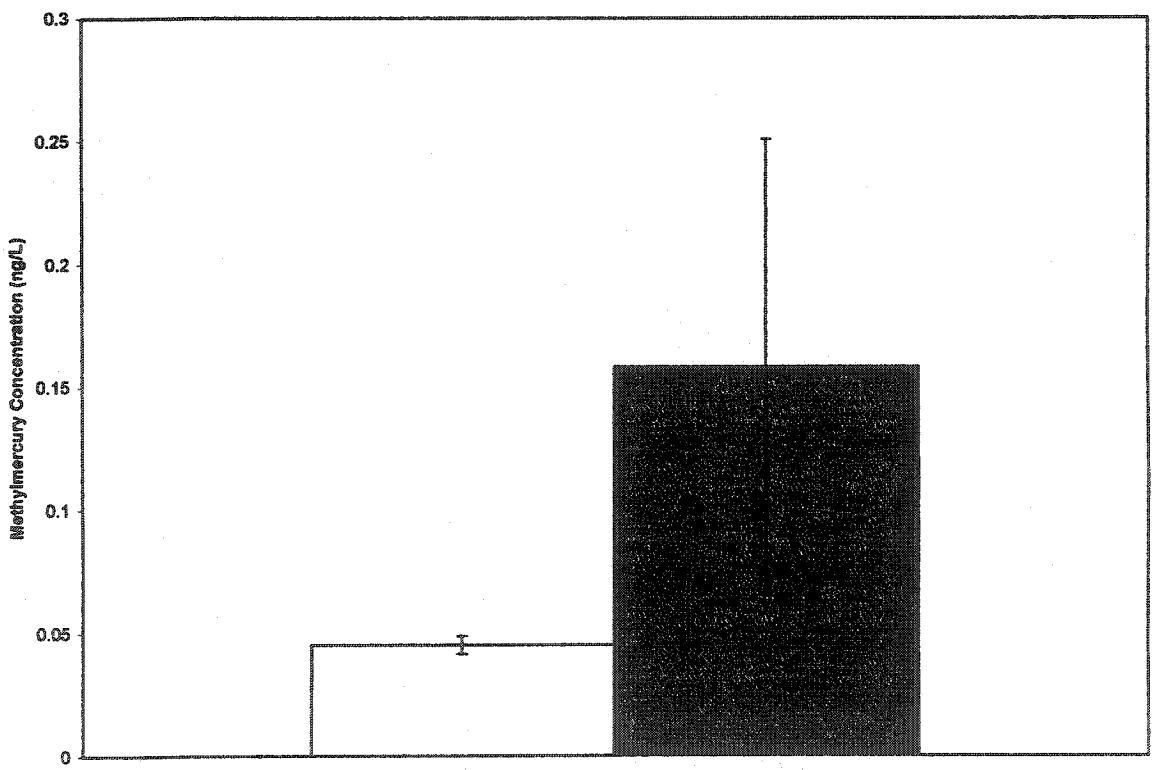

0.3
0.25
0.2
0.15
0.1
0.05
0
Methylmercury Concentration (ng/L)

Figure 3.8 Relationship between methylmercury concentration (ng/L) and total organic carbon (ppm) (n=52) in the well samples. Methyl mercury

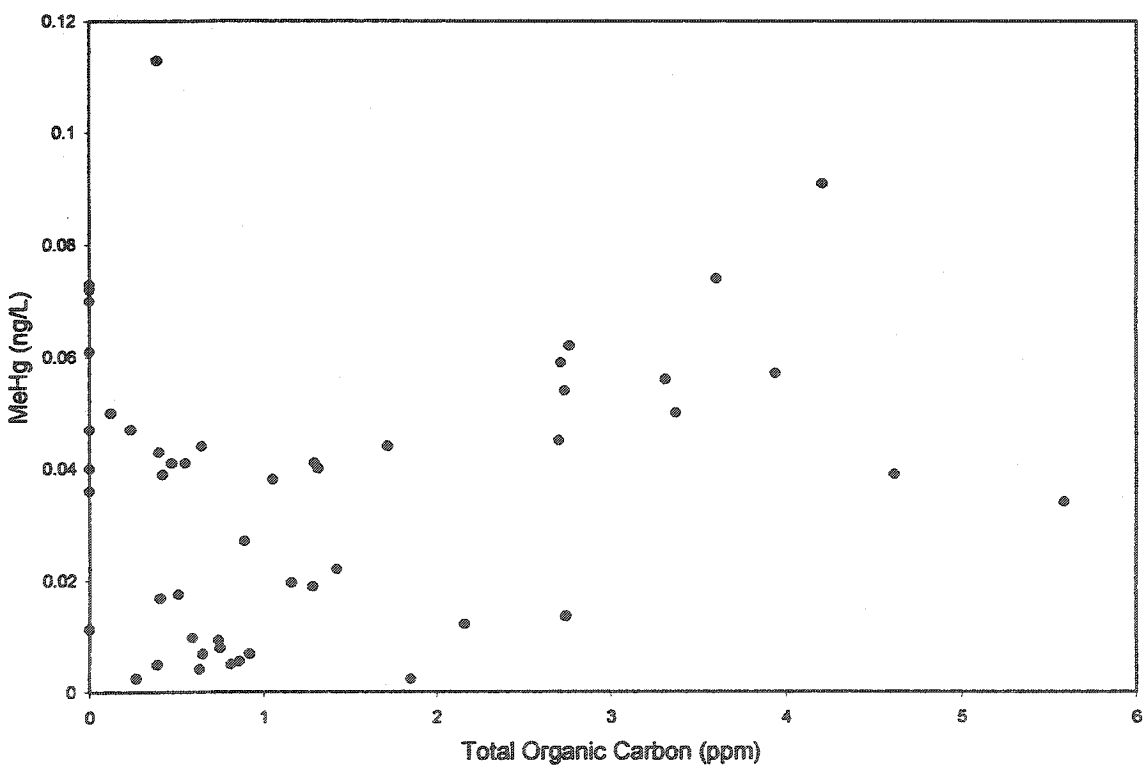

0.12
0.1
0.08
0.06
0.04
0.02
0
MeHg (ng/L)
0
1
2
3
4
5
6
Total Organic Carbon (ppm)

Figure 3.8.1 Mean methyl mercury concentration (n=51) in the wells versus depth (ft.). Sample 52 deleted (0.895 ng/L).

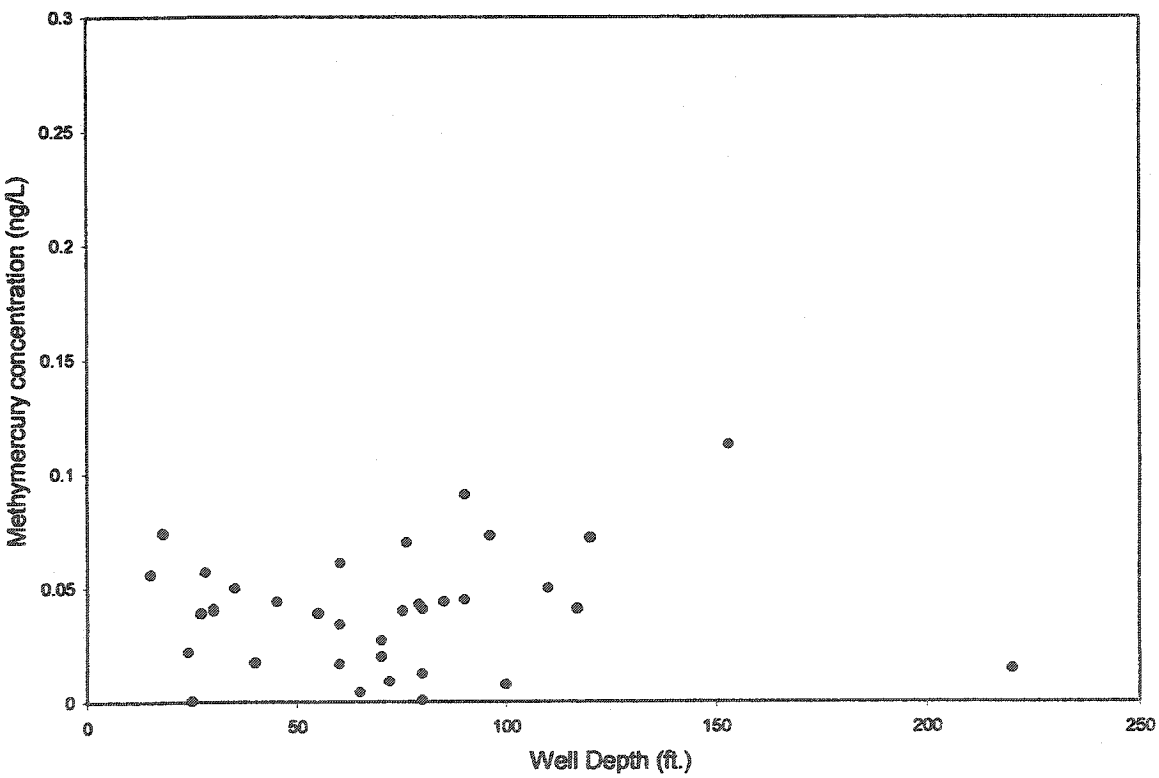

0.3
0.25
0.2
0.15
0.1
0.05
0
Methymercury concentration (ng/L)
0
50
100
150
200
250
Well Depth (ft.)

Figure 3.9 Regression of conductivity (μS/cm) and total inorganic carbon (ppm) in well water samples (n=44).

The regression analyses resulted in the following model:

Conductivity= 0.264 + 0.007 TIC, r^2=0.548, $p<0.001$

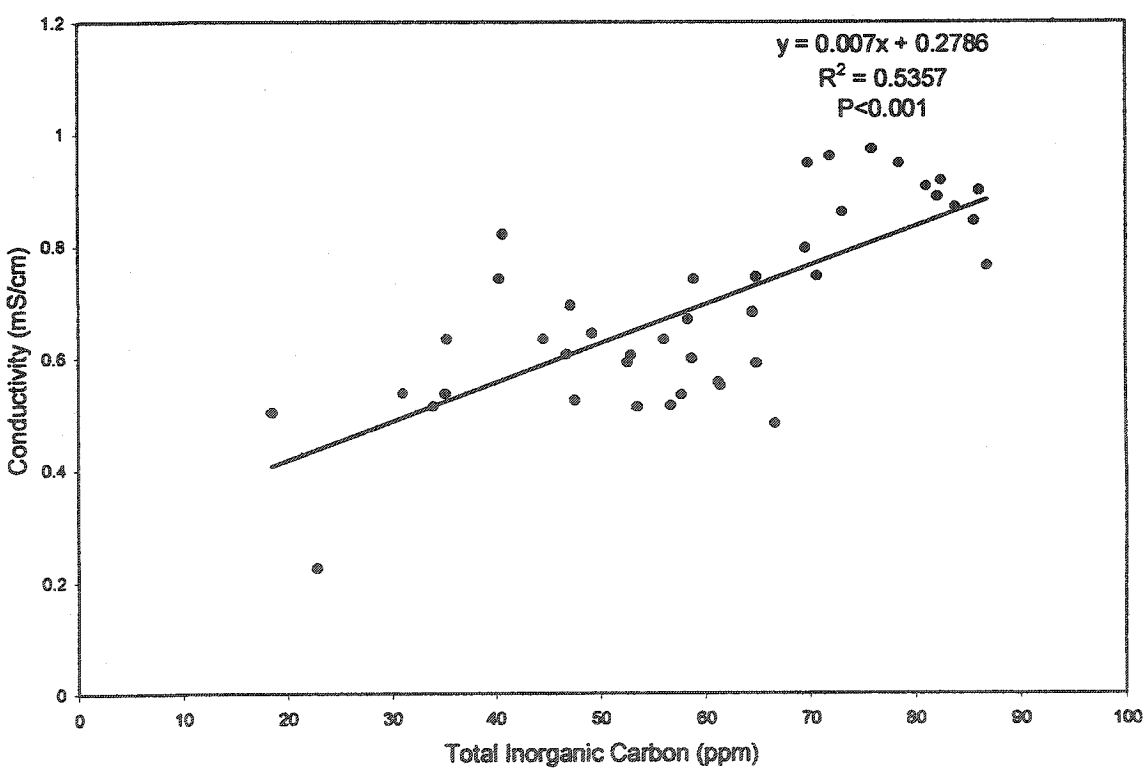
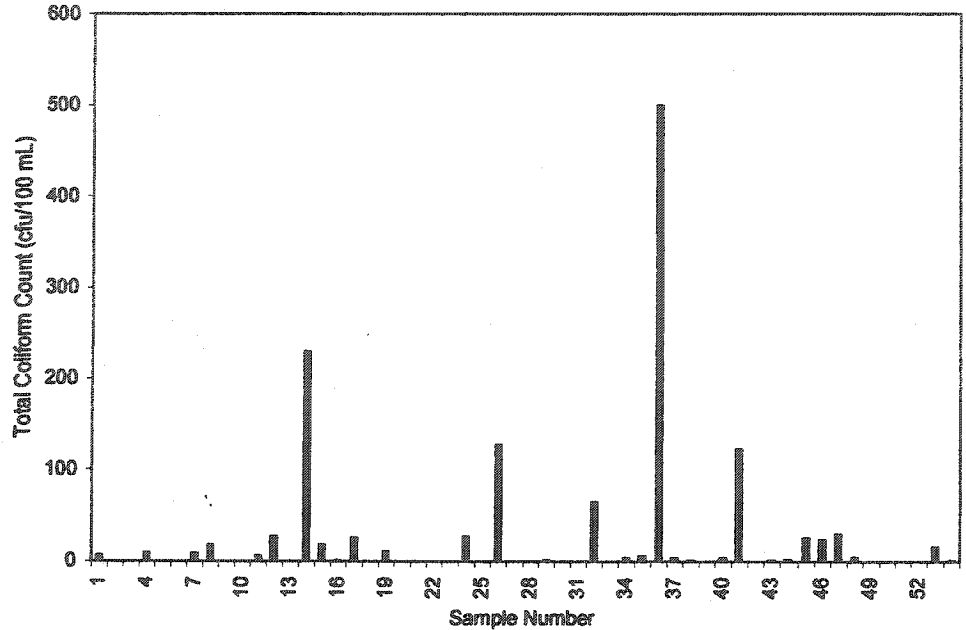
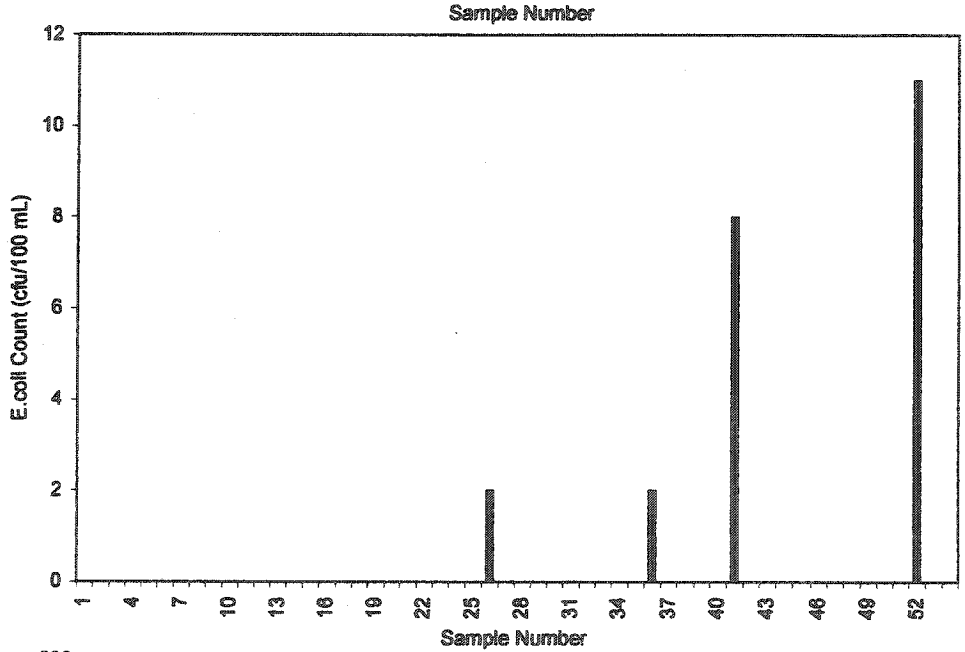

y = 0.007x + 0.2786
R2 = 0.5357
P<0.001
Conductivity (mS/cm)
Total Inorganic Carbon (ppm)
0
0.2
0.4
0.6
0.8
1
1.2
0
10
20
30
40
50
60
70
80
90
100

Figure 3.10 Total Coliforms (n=53), *E.coli* (n=54) and background colonies (n=47). This figure depicts mean bacterial cell counts versus sample number. Sample 52 TC, and BC count not included and the first six background colony counts were not included.


Total Coliform Count (cfu/100 mL)
0
100
200
300
400
500
600
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52
Sample Number


E.coli Count (cfu/100 mL)
0
2
4
6
8
10
12
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52
Sample Number

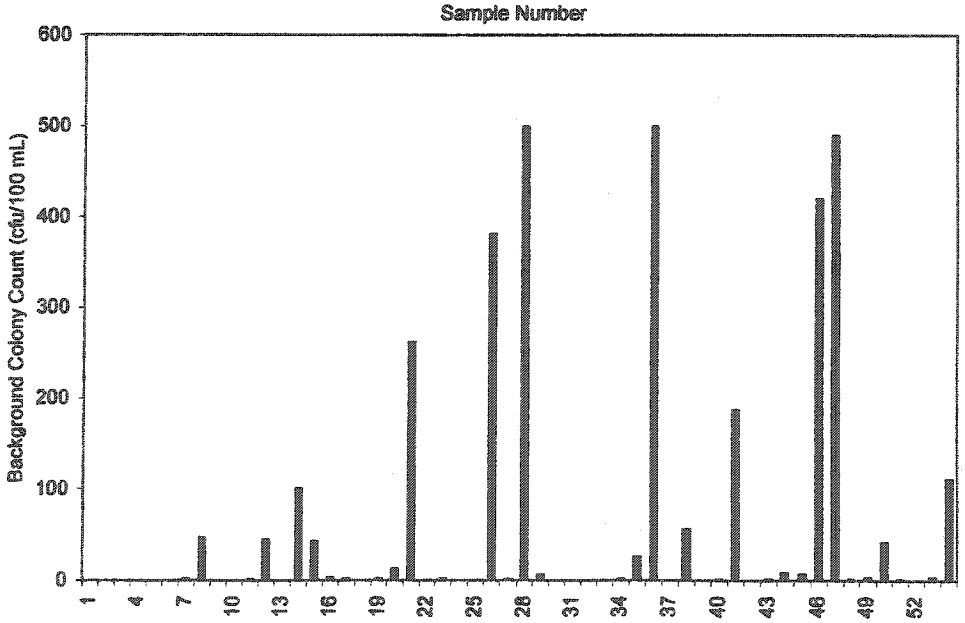
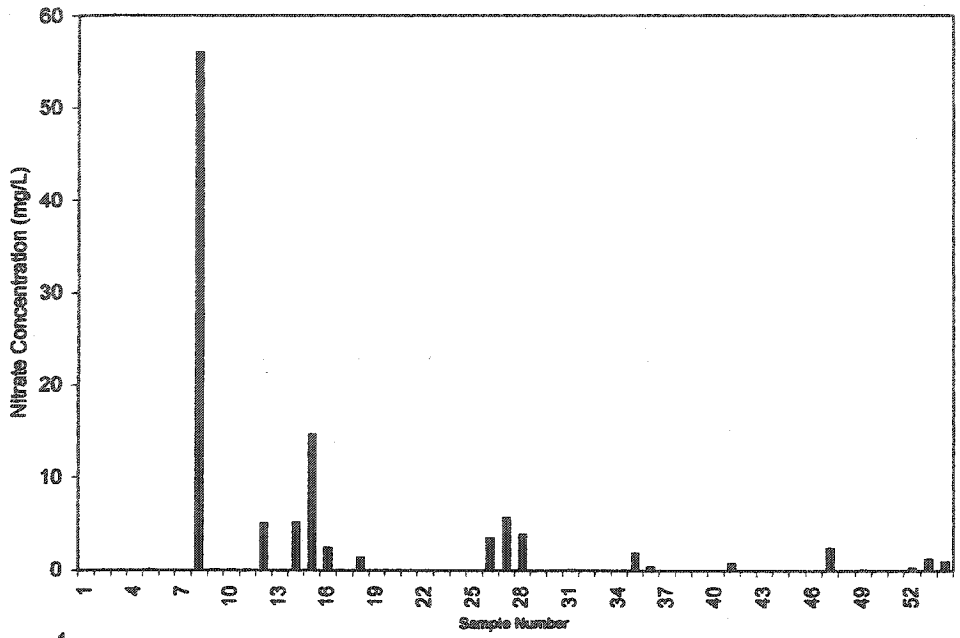
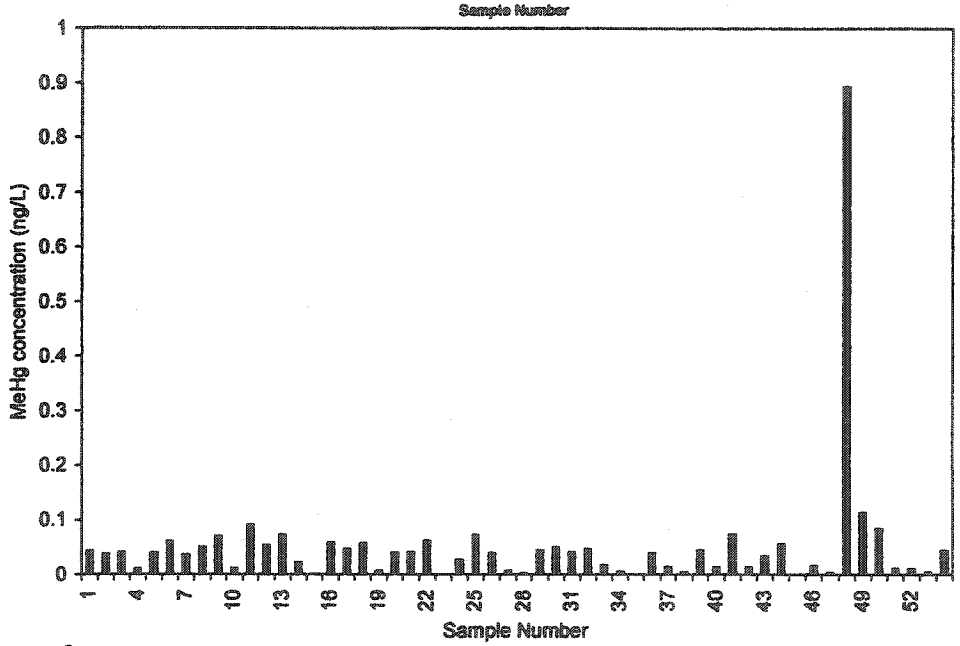

Background Colony Count (cfu/100 mL)
0
100
200
300
400
500
600
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52

Figure 3.11 Nitrate Concentration (mg/L) (n=54), methyl mercury (ng/L) (n=52) and dissolved oxygen (mg/L) concentration (n=46) in the well water samples.


Nitrate Concentration (mg/L)
0
10
20
30
40
50
60
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52
Sample Number


MeHg concentration (ng/L)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52
Sample Number

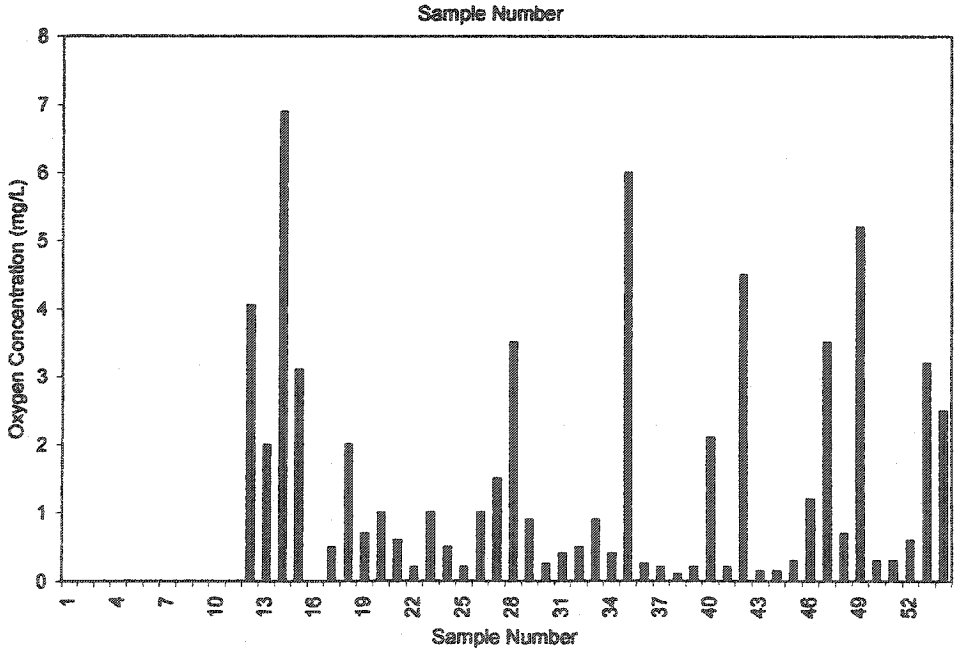
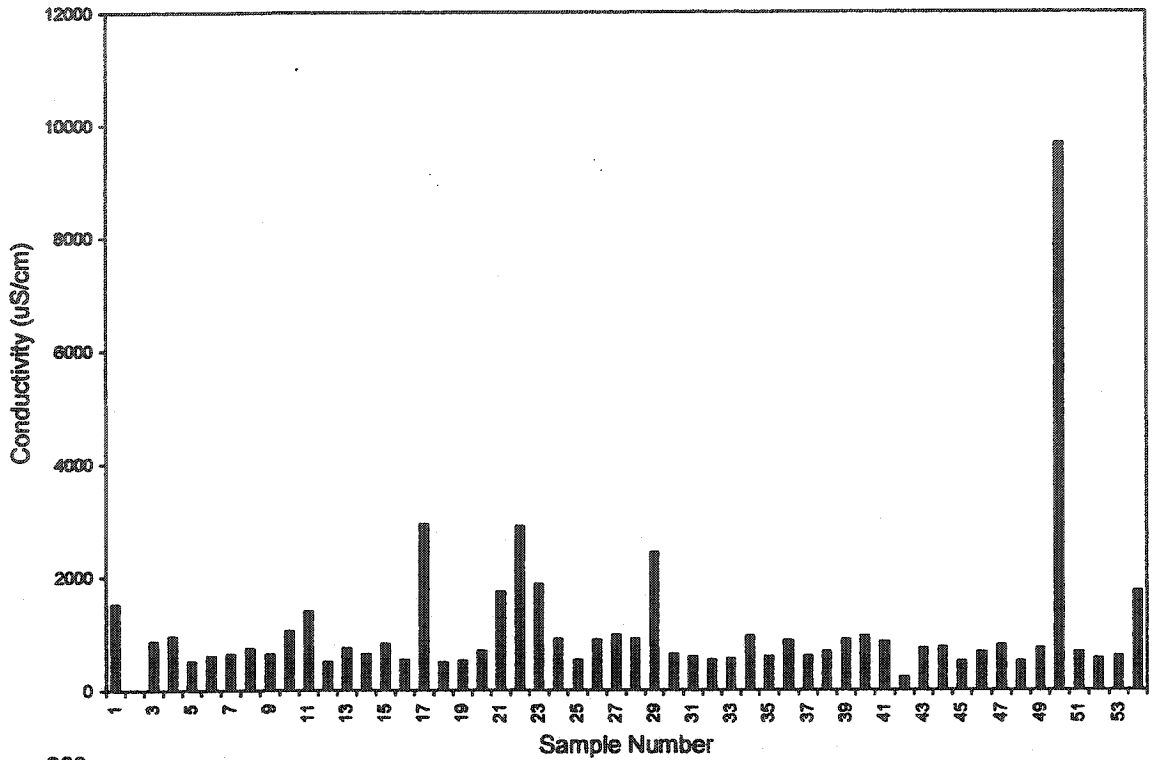

Oxygen Concentration (mg/L)
0
1
2
3
4
5
6
7
8
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52
Sample Number

Figure 3.12 Conductivity (μSiemens/cm) (n=53) and total inorganic carbon (n=53) in the well water samples


Conductivity (uS/cm)
12000
10000
8000
6000
4000
2000
0
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
33
35
37
39
41
43
45
47
49
51
53
Sample Number

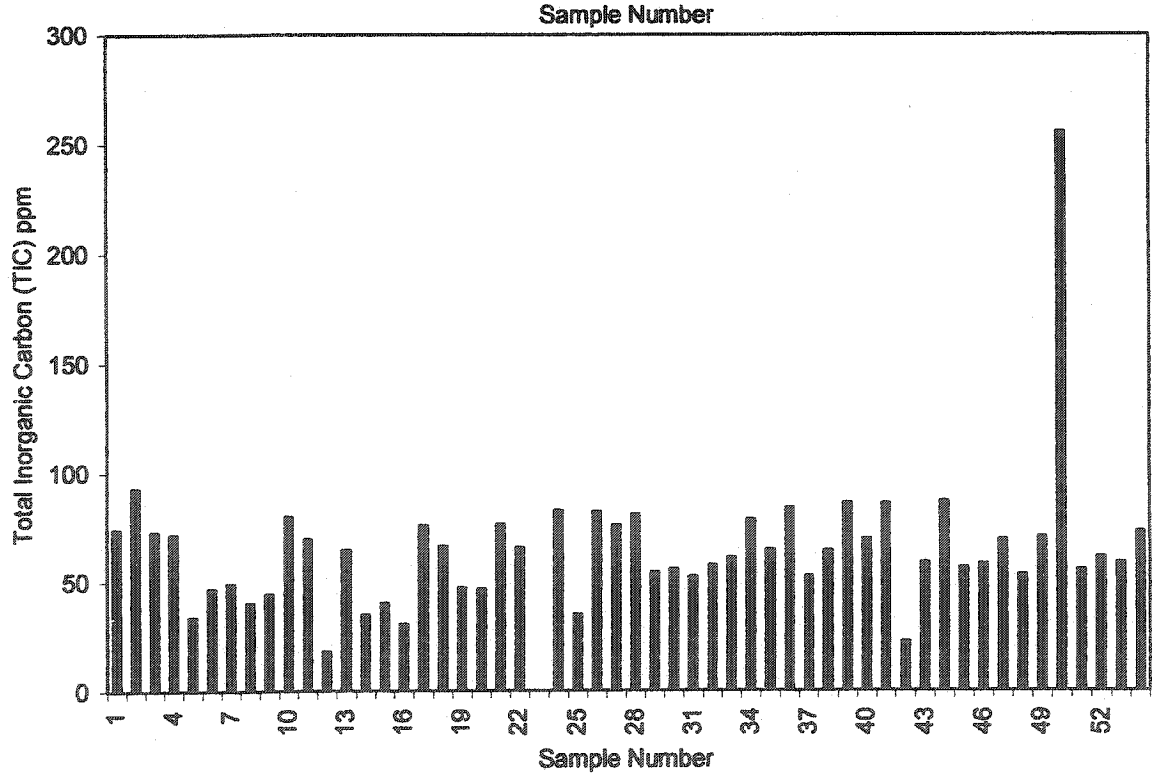

Total Inorganic Carbon (TIC) ppm
300
250
200
150
100
50
0
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52
Sample Number

Figure 3.13 Map of the sampling area indicating the position of the bottom of the upper aquifer (m) above sea level (N=52). Map courtesy of Dr. B. Daneshfar and Dr. M. Robin.

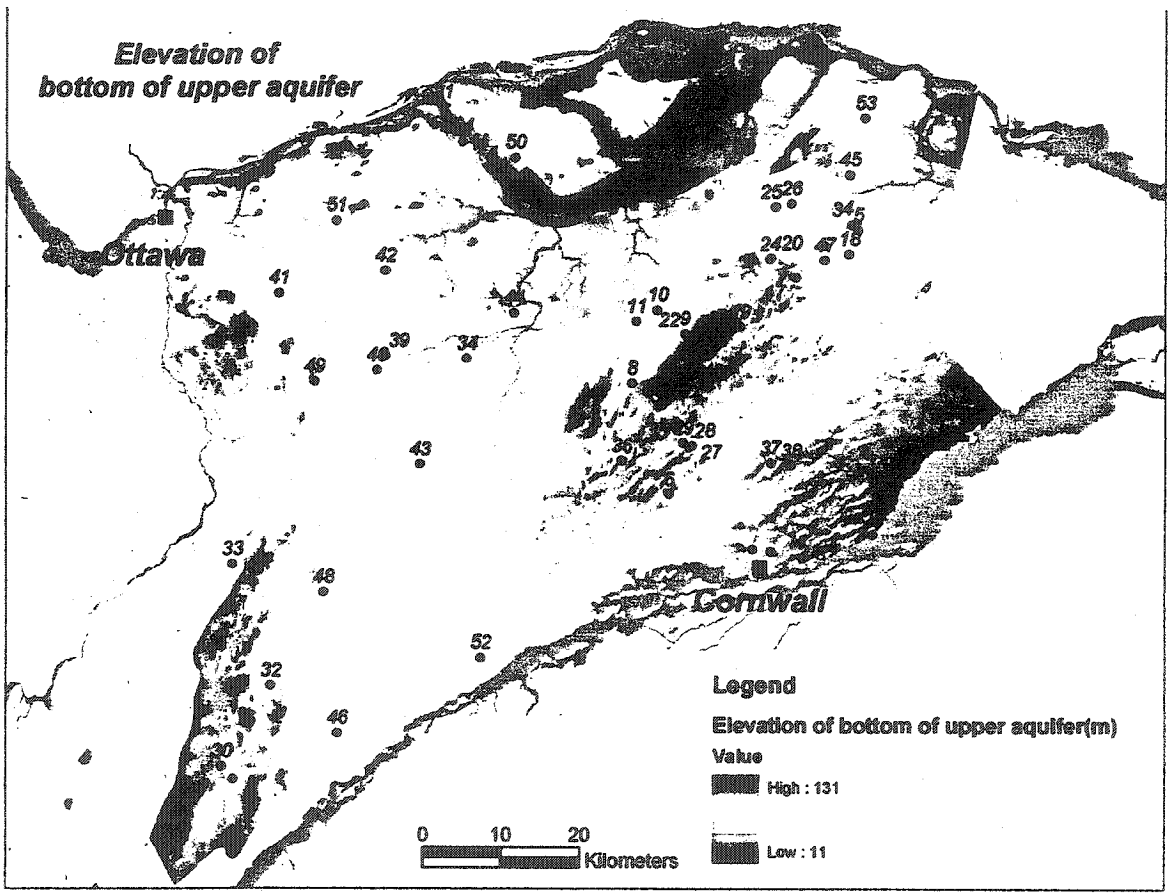
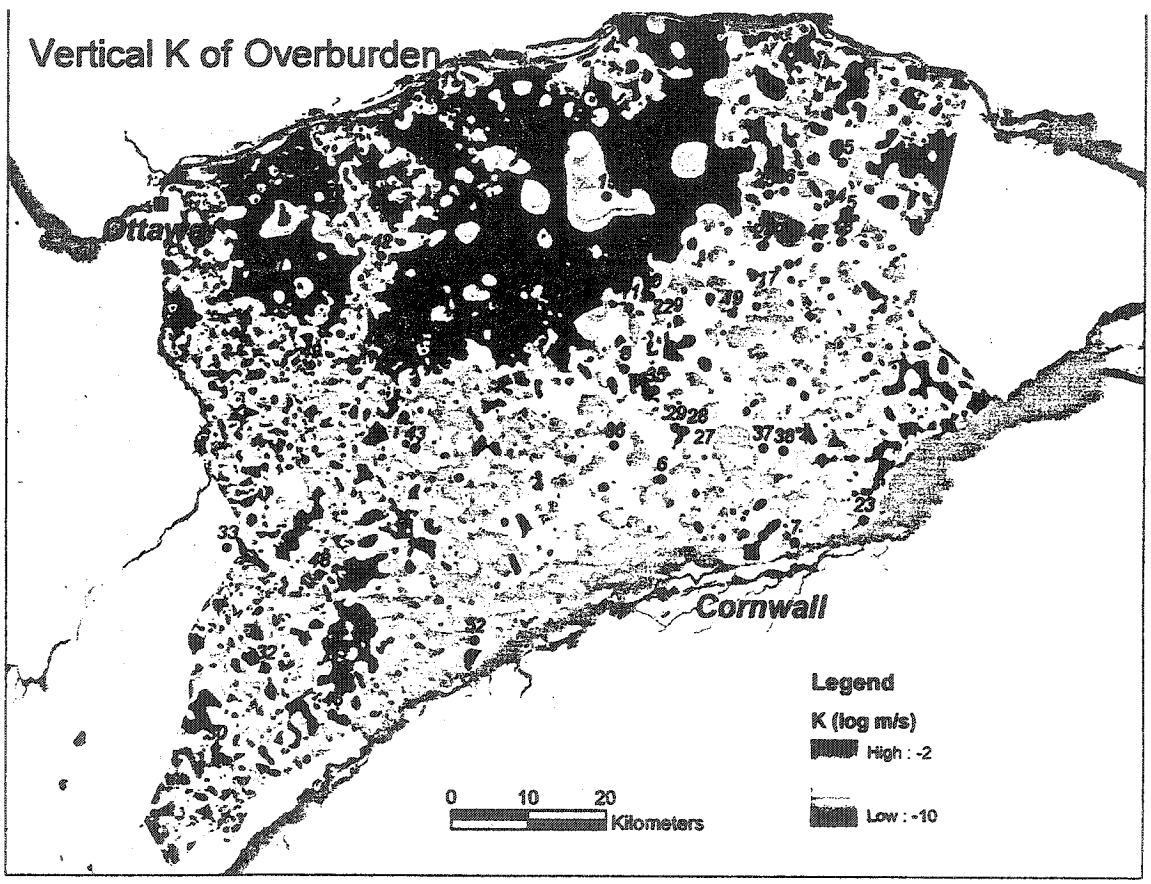

Elevation of
bottom of upper aquifer
Ottawa
Cornwall
Legend
Elevation of bottom of upper aquifer(m)
Value
High : 131
Low : 11
0 10 20
Kilometers

Figure 3.14 Map of the sampling area indicating the vertical hydraulic conductivity (K) (N=52). Map courtesy of Dr. B. Daneshfar and Dr. M. Robin.


Vertical K of Overburden
Ottawa
Cornwall
Legend
K (log m/s)
High : -2
Low : -10
0 10 20
Kilometers

4. DISCUSSION

4.1 Bacteria

This study showed that many wells were contaminated by bacteria (Figure 3.1). Drinking water should not contain any bacteria, although Health Canada advises that water containing fewer than 10 TC bacteria per 100 mL is considered marginally safe to drink (Health Canada, 2003).). It is also recommended however, that if after re-testing fewer than 10 cfu/100 mL TC is still found, the cause of the contamination should be determined if possible and corrective action taken as appropriate (Health Canada, 2003).

In this survey, 30% of the wells had TC levels over 10 cfu/100mL. In a previous survey, 34% of rural wells in Ontario contained elevated levels of coliform bacteria (O'Connor, 2002). With respect to *E .coli* (EC), however, there is no acceptable concentration since the presence of this bacteria indicates *definite* fecal (sewage) pollution (Health Canada, 2003). In this study over 7% of the well water samples tested over this level. Water containing EC is not safe to drink, and corrective action should be taken immediately (Health Canada, 2003). These observations are of concern since currently, the onus is on the homeowner to do regular testing of their own drinking water, and in many of the cases, regular testing had not been done, or had been done infrequently. Participants, were recommended to re-test their water by their local public health authorities.

Given the relatively short lifespan of these organisms, the presence of fecal bacteria in the groundwater indicates the presence of a source of fecal contamination, a short travel time from the surface, and a lack of adequate natural filtration by subsurface materials surrounding a well intake screen (O'Connor, 2002). Geology and hydrogeology (i.e., fracturing of bedrock, thinness of

overburden, and point source breaches) and meterology (ie., rainfall) can all be contributing factors to ground water contamination.

The other aspect investigated was the type of well, more specifically, the level of contamination between dug and drilled wells. Dug wells are generally shallow while drilled wells tend to be deeper. Generally, the deeper the well, the longer it will take for surface water to enter the well, which lessens the risk of contamination (Simpson, 2003). In our study, all dug wells were less than or equal to 40 ft. and drilled wells ranged from 55-220 ft. in depth. Only the contamination by *E.coli* was found to be significantly higher in dug wells as compared to drilled wells. In terms of actual bacteria counts (cfu/100 mL), there was a significant difference between dug and drilled wells and the mean TC and BC counts (Appendix A.6 and A.8). These results agree with a previous study that showed that dug and bored wells or shallow sandpoints were more frequently contaminated than drilled wells regardless of depth, although the occurrence of contamination tended to decrease with depth for all well types (Goss et al., 1998). Also, dug or bored wells are often limited in depth to shallow water-bearing formations, and will penetrate only a short distance within the saturated zone below the water table; conversely, drilled wells can tap deeper water-bearing formations (Miller, 1982). Wells that are 40 m deep or less are generally considered equivalent to surface water since there is the risk of contamination from land use and surface activities (Corkal et al., 2003). In this study, a significant and inverse relationship was found for TC and well depth ($R^2 = 0.25$, $p = 0.024$) and BC and well depth ($R^2 = 0.16$, $p = 0.055$) (Figure 3.3).

The above findings underscore the need for vigilance in regular testing/monitoring of wells, especially shallow wells for *E.coli* contamination. Considering these recent findings, it is expected

that climatic extreme events such as excessive rainfall causing major run-off could exacerbate bacterial contamination. It has already been forecasted that Ontario may expect an increased precipitation, more dramatic weather events, and a greater degree of surface runoff and flooding, among other events (O'Connor, 2002). If these changes occur, they will have long-term impacts on the quality and quantity of drinking water sources in Ontario (O'Connor, 2003). In the Walkerton disaster, excessive rainfall was one of the causative factors of the waterborne disease tragedy. Various studies have concluded that there is a significant link between excess rainfall and waterborne disease outbreaks, and therefore, meteorological and climatological conditions need to be considered by water managers, public health officials and private citizens as a significant risk factor for water contamination (Auld et al., 2003). Meterological and climatological information should also be considered both for the design and siting of new and safer wellheads (e.g. height of wellhead) in order to reduce risks during more challenging weather conditions (Auld et al., 2003).

In addition to excessive rainfall, climate change is expected to alter drought events. Drought increases the demand for water when the supply is significantly reduced and vulnerable (Charron et al., 2003). Heavy rain following drought can lead to more severe run-off and risk of water contamination (Charron et al., 2003). The most plausible events causing these problems are extreme rainfall, soil conditions and drought, however there are a number of inherent complex socio-ecological systems that are involved that cause an uncertainty in the knowledge base (Charron et al., 2003). Work is currently going on that will review the local socio-ecological systems, specifically to understand why there are disease outbreaks in some communities but not in others faced with the same stressors.

Land use is a major factor impacting ground water quality (Corkal et al., 2003)(Environment Canada, 2002)(OMAFRA, 2002) (Canter, 1997) (Alley, 1993). Contamination of groundwater by livestock can result if runoff from manure storage or a feedlot yard percolates through the soil close to a well, or when manure is spread on to cropped land (Goss et al., 1998). In this study, the occurrence of TC, EC, or BC did not differ significantly between the three land use types (residential, agricultural and agricultural intensive) (Appendix A.1). The mean bacterial cell counts had a wide range (e.g., 0 to 500 cfu/100mL for TC in the agricultural site) for each land use site so, therefore, the counts did not differ significantly between the sites (Appendix D). In a previous study, there was no obvious correlation between a particular land use and the occurrence of bacterial contamination in the groundwater, either from the analysis of water-well results or the multilevel monitoring wells beneath the fields (Rudolph et al., 1998). There are several complexities in relating groundwater to land use (Alley, 1993). For example, land use is not homogeneous throughout large areas, and more than one land use can exist near a well. In evaluating the effects of land use on groundwater quality, the most reliable approach is to select wells that are located in recharge areas and directly down gradient from a single land use setting, which will help to avoid the influence of other land use activities and complications from upward movement of water that originated from distant areas (Alley, 1993). In our study, the above reasons could be applicable for no apparent difference in the occurrence of bacteria or bacterial counts between the three land use sites. Also, this study was a survey where participants showed interest in having their wells sampled , and specific sites/locations were not pre-determined (i.e., as in the above method of selecting wells located in recharge areas and directly down gradient from a single land use setting).

To summarize this section, many wells were contaminated by bacteria. Dug wells showed a greater occurrence of *E. coli* contamination than drilled wells, and in terms of bacteria counts, there was a significant difference between dug and drilled wells for total coliforms and background colonies. Finally, it was shown that well depth plays an important role, specifically, TC and BC bacteria decreased with increasing depth.

4. 2. Water Chemistry

4.2.1 *Nitrate*

In the present study, the nitrate levels of the wells were low with an average of 1.95 mg/L (Appendix B). Only 4% of the well water samples had nitrate levels exceeding the maximum acceptable concentration (MAC) of 10 mg/L. These results were much lower than a previous survey that showed that 14% of rural wells exceeded the MAC (Goss et al., 1998).

The concentration of nitrate is expected to be higher in dug wells than in drilled wells as there is more opportunity for surface contaminants/run-off to reach shallow wells. Surveys have shown that shallow (sandpoint, dug, or bored) wells had nitrate concentrations greater than 10 mg/L more often than drilled wells (Simpson, 2003). In this study, we found that there was a significant difference in nitrate levels between dug and drilled wells (Appendix A.11). The two wells that exceeded the MAC, were shallow dug wells (35 and 3 feet, respectively). In the first situation, the well was dug and located near a septic bed, and in the other situation the well was located in a crop field. Agricultural fields form the main diffuse sources of nitrate that is leached to groundwater (Goss et al., 1998). Nitrate contamination of groundwater is usually due to over-application of fertilizer or manure on agricultural land, domestic waste from septic disposal systems, and losses of

soil organic nitrogen produced by plough down of old meadows, legumes and other crop residues (Chambers et al., 2001). Nitrates can also result from human or animal waste (O'Connor, 2002).

It has also been shown previously that nitrate concentrations decrease with increasing well depth (Goss et al., 1998). In the present study, there was no relationship between nitrate concentration and well depth. This is likely due to the many values of nitrate that were below the detection limit (Figure 3.4), as a result of the low dissolved oxygen concentration leading to denitrification.

Other factors influencing the amount and rate of leaching of agricultural chemicals into groundwater include the type and intensity of agricultural practices, crop and land management practices, the type and amount of chemicals used, soil characteristics, and weather (Environment Canada, 2002). It was expected that there would be a difference in the amount of nitrate in the three land use sites (residential, agricultural and agricultural intensive). In the present study, there was a significant difference in the mean concentrations of nitrate between the three land use sites (Appendix A13).

Low values of nitrate in groundwater are attributed to denitrification (Burton and Ryan, 2000) (Robertson et al., 1996) (Gilham et al., 1987). Denitrification is the biological reduction of nitrate and nitrite to nitrous oxide and molecular oxygen, and is carried out by bacteria of almost all major groups of prokaryotes, being the Gram-negative aerobic heterotrophs most abundantly found in water and soil. Under anoxic conditions, nitrogenous oxides are reduced and carbonaceous substrates are oxidized to carbon dioxide by these bacteria (Gomez et al., 2000). Denitrification requires suboxic conditions (<2 mg/L oxygen) (Burton et al., 2000).

It was expected that nitrate concentration would decrease with decreasing oxygen concentration due to denitrification. In this study, Figure 3.5 indicates that there is a positive linear relationship between nitrate concentration and dissolved oxygen concentration (R^2=0.3196, P<0.001). In fact, it was found that there was a significant difference in the means of nitrate below 1 mg/L oxygen (Appendix A.13), further supporting that denitrification is occuring at these low oxygen conditions.

In addition to low oxygen conditions, denitrification requires Eh values of less than 0.28 V (Burton and Ryan, 2000). It has been found in a previous study that nitrate levels were lowered dramatically when the groundwater Eh dropped below ~ +0.25 V (Spalding and Parrott, 1994).

In this study it was expected that there would be a difference in nitrate concentration above and below this Eh value. A significant difference was found in the nitrate concentrations for the redox potential of <250 mV and >250 mV (Appendix A.16), further supporting that denitrification was occurring in these areas.

4.2.2. *Methyl Mercury*

There was a significant difference in the mean methyl mercury levels between the samples that had a sulphide odour and those that did not (Figure 3.7) (P=0.043; Appendix A.16). The higher values of methyl mercury in the sulphide-smelling samples were expected since many studies have shown that sulfate-reducing bacteria (SRB) are the key mercury-methylating organisms in nature (Ekstrom et al., 2003). This typically occurs in anoxic waters and sediments (Ekstrom et al., 2003) (Jay et al., 2000). Our water samples were on average very low in oxygen (e.g. mean 1.5 mg/L)(Appendix B). The mechanism by which mercury is methylated is generally accepted to be the acetyl-CoA

pathway in *Desulfovibrio desulfuricans* LS. However, Ekstrom et al. (2003) reported that mercury methylation occurs in several species of SRB that do not utilize this pathway as a major metabolic pathway and it was suggested that mercury methylation is independent of this pathway. It has also been shown that there is a correlation between mercury methylation and methionine synthase activity in *Escherichia coli* cell extracts and in sediments (Siciliano and Lean, 2002).

Total organic carbon (TOC) is a ready substrate for microbial metabolism and results in the accumulation of final metabolites such as sulphide and methane (Chapelle et al., 1993). In the current study, no relationship could be drawn from TOC and MeHg as the level of TOC was low ranging from less than the detectable limit to 12 ppm with a mean of 1.54 ppm (Appendix C). TOC is generally low in most groundwaters because water percolating through soil loses its dissolved organic carbon, and by the time it reaches the water table, most of it has been removed (Drever, 1997). No relationship could be found between MeHg and well depth (Figure 3.8). Mercury concentration in well water samples were also independent of the depth and the volcanic lithology of the aquifer in a recent study in southern Nevada (Cizdziel, 2004).

Mercury-based pesticides were raised as a potential source of contamination of methyl mercury in 78 private wells in southern New Jersey (Murphy et al., 1993). With respect to the South Nation River (SNR), land use has had a profound impact on the ecological state of the river which is considered by Ontario and Quebec standards in "poor ecological health" (Crabbé and Robin, 2003). Nutrients and herbicides are the major pollutants of this river, and stem from runoff from fertilized fields (Crabbé and Robin, 2003). The levels of MeHg measured in the SNR are between 0.20 to 0.25 ng/L (Holmes, 2003). It is known that approximately, 60% of the SNR is fed by groundwater (Haughton and Pick, 2002). Haughton and Pick, (2002) raised industry, fertilizer

and fungicide application as a possible source of mercury to the SNR. Given that the South Nation River and the Raisin River are drainage basins where agriculture is a major land use type, it is possible that the above-mentioned sources may have played a role in the methyl mercury concentration of the South Nation River and also to some extent of the groundwater. Some mercury resulting from natural biological processes of the sulphate reducing bacteria, in addition to run off from agricultural fields may have contributed to methyl mercury in groundwater, which may in turn be contributing to the South Nation River.

4.2.3 *Total Inorganic Carbon and Conductivity*

Conductivity of the groundwater samples in this study varied from 225 to 2900 µS/cm with a mean of 908 µS/cm (Appendix B). Conductivity is a good estimator of the total dissolved solids (TDS) (Hounslow, 1995), increasing in proportion to dissolved solids (O'Connor, 2002). A study of groundwater in Saskatchewan showed a relatively high concentration of total dissolved solids (mean and maximum conductivity of 2 157 and 12 400 µS/cm) (Thompson, 2003).

In groundwater, the TDS consists primarily of a short list of inorganic solutes (i.e., Ca^{2+}, $HCO3^-$). It was expected that the conductivity of the well water samples would increase with an increase in the total inorganic carbon concentration and this trend was observed (Figure 3.9). In a study of ten wells in Southern Ontario, Miller (1982) found that 80% of the wells showed a predominance of calcium- bicarbonate. In the current study, an analysis of the major ion concentration of the well water was not done, however, it is expected that the major ions would be Ca^{2+}, Mg^{2+} Na^{+}, Cl^{-1}, HCO3, and $SO4^{2-}$ (Robin, 2004).

TDS in groundwater tends to be higher than TDS of surface water since groundwater is in contact with a much larger mineral surface area for a much longer time (Fitts, 2002). The degree of dissolved constituents in groundwater depends on a combination of factors. Precipitation, spring thaw events, flooding, and atmospheric conditions affect the pH of precipitation and affect the initial input into groundwater. As soon as groundwater enters the subsurface, it dissolves minerals in its path and a chemical equilibrium is approached with the mineral constituents of the surrounding geological formations. Other factors affecting the general composition of groundwater include: permeability of the host formation, temperature of groundwater, the degree of solubility of the minerals comprising the formation, the length of contact time of the water within the formation, the pressure of the formation and the degree of microbiological activity within the formation . In general, formations at great depths will contain waters that will have a high dissolved solid content, whereas waters in shallower formations will be younger in age, will contain less dissolved solids, and will be generally more suitable for use and consumption (Miller, 1982).

Finally, the primary aquifer in Eastern Ontario consists of the upper portion of the fractured Paleozoic bedrock and sand and gravel deposits, which directly overlie the bedrock. TDS levels in Paleozoic and Mesozoic sedimentary rock ranges from 195-1100 mg/L due to the presence of carbonates, chlorides, calcium, magnesium and sulphates (Health Canada, 1991). This chemical composition probably contributes to the TDS levels in the Eastern Ontario region.

With climate change, Ontario is expected to show a variety of changes, specifically increased temperatures, increased evaporation rates of water, a lowering of the levels of surface water, thereby reducing the rate of recharge of groundwater. The concern is that an increased evaporation rate would increase groundwater salinity in areas where the water table is shallow

which will affect the suitability of this water for human consumption (Dubrovsky et al., 1993). During times of drought, water is taken from deeper aquifers, however, deep aquifers are often of poor quality since they are usually highly mineralized (Corkal et al., 2003).

4.2.4 *Aquifer properties*

Aquifer properties such as elevation above sea level (m) (i.e., shallow or deep) and vertical conductivity were examined with respect to the levels of various contaminants in the well water samples. A large percentage of the samples contaminated with bacteria (TC, EC and BC), nitrate and MeHg were found on aquifers that were shallow. Vertical conductivity of the geologic material overlying the aquifer (CH2MHill, 2001) is also a key variable in aquifer vulnerability. Many of the samples containing a high level of contaminant originated from an area with a high vertical conductivity.

4. 3. Future studies

Future studies investigating the bacteriology and chemistry of groundwater in Eastern Ontario region at different times of year (i.e., spring thaw, and fall) and for the next number of years would be helpful in monitoring the water quality as affected by changes in climate, precipitation, water levels etc. Sampling groundwater for other contaminants would provide yet another layer of information and detail to this study.

Conclusions

From this study, it can be seen that many well water samples have tested positive for bacteria, specifically total coliforms (TC). Total cell counts (cfu/100 mL) are also quite high for TC. This is a concern since these bacteria are an indicator of fecal contamination, and in many

cases wells have been tested infrequently, or in some cases water had not been tested for several years. In addition, 7.4 % of the water sampled had a presence of *E.coli* which is also a *definite* indicator of fecal contamination.

It was found that there was no significant difference in the proportions of bacteria in different land use sites (residential, agricultural and agricultural intensive). For nitrate, however, land use played a key role since a significant difference was found between the means of nitrate in the three land use sites.

Type of well was important. Dug wells were more contaminated with *E.coli* and nitrate than drilled wells. Well depth is a also key factor in contamination, as it was found that bacteria counts decreased with increasing depth of the well.

Climate change is of key significance to these findings as it is expected to make the situation worse both in terms of water quality. Climate, along with a shallow aquifer within this region, and the high conductivity of the overburden could lead to elevated levels of various contaminants in groundwater.

MeHg was found in higher concentrations in water samples that smelled like sulfide. This can be attributed to the sulfate reducing bacteria. MeHg in the South Nation River has been attributed to a variety of sources including industry, fertilizer and fungicide application, leaching from land fill sites, and in addition, as can be seen from this study, may be partly a result of the natural bacterial process of the sulfate reducing bacteria in groundwater.

The current lack of information on groundwater in the province, combined with infrequent monitoring, raises a need for increased awareness, education, and emergency preparedness. It is

crucial to learn from past lessons (i.e., Walkerton and North Battleford, Saskatchewan); to prevent future disasters.

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Appendix A Statistical Analyses

Table A.1. Pearson Chi-Square to test whether the occurrence (presence or absence) of bacteria was different between the three land use types (residential, agricultural, and agricultural intensive).

	Total Coliforms (TC)	*E.coli* (EC)	Background Colonies (BC)
Pearson Chi-Square (P)	0.335	0.689	0.794
Degrees of Freedom (df)	2.000	2.000	2.000

Table A.2. Pearson Chi-Square to test whether the occurrence (presence or absence) of bacteria differed between the dug and drilled wells.

	TC	EC	BC
P	0.075	0.004	0.389
df	1.000	1.000	1.000

Table A.3 ANOVA to test whether there was a difference in means of the bacteria counts for TC and the three land use types. Least Square Means (LS) ± Standard Error (SE)

P	Residential	Agricultural	Agricultural Intensive
	LS Mean	LS Mean	LS Mean
0.763	0.962 ± 0.222	1.202 ± 0.243	1.044 ± 0.230

Table A.4 ANOVA to test whether there was a difference in the means of the background colonies and the three land use types.

P	Residential	Agricultural	Agricultural Intensive
	LS Mean	LS Mean	LS Mean
0.315	0.959 ± 0.250	1.580 ± 0.323	1.083 ± 0.323

Table A.5. ANOVA to test whether there was a difference in the means of *e.coli* and the three land use types

P	Residential	Agricultural	Agricultural Intensive
	LS Mean	LS Mean	LS Mean
0.743	0.235 ± 0.092	0.000 ±0.101	0.000 ± 0.083

Table A.6 ANOVA to test whether there was a difference in the means of the TC bacteria cell counts between the dug and drilled wells.

P	Dug	Drilled
	LS Mean	LS Mean
0.015	1.764 ± 0.276	0.902 ± 0.185

Table A.7 ANOVA to test whether there was a difference in the means of EC bacteria cell count between the dug and drilled wells.

P	Dug	Drilled
	LS Mean	LS Mean
0.429	0.749 ± 0.227	0.301 ± 0.394

Table A.8 ANOVA to test whether there was a difference in the means of BC bacteria cell count between the dug and drilled wells.

P	Dug	Drilled
	LS Mean	LS Mean
0.051	0.623 ± 0.161	0.875 ± 0.091

Table A.9 Simple Linear Regression for TC as a function of well depth

P	R^2
0.024	0.253

Table A.10 Simple Linear Regression for BC as a function of well depth

P	R^2
0.055	0.165

Table A.11 ANOVA to test the difference of means of nitrate between dug and drilled wells

Table A.11 Simple Linear Regression for Nitrate as a function of oxygen

P	R^2
P <0.001	0.320

Table A.12 ANOVA to test whether there was a difference in means of nitrate at less than or greater than 1 mg/L oxygen.

P	< 1 mg/L Oxygen	>1 mg/L Oxygen
	LS Mean	LS Mean
P<0.001	0.879 ± 0.214	2.613 ± 0.292

Table A.13 ANOVA to test whether there was a difference in means of nitrate between the three land use types.

P	Residential	Agricultural	Agricultural Intensive
	LS Mean	LS Mean	LS Mean
0.006	0.610 ± 0.127	1.107 ± 0.141	1.343 ± 0.156

Table A.14 ANOVA to test whether there was a difference in means of nitrate in the dug and drilled wells.

P	Dug	Drilled
	LS Mean	LS Mean
<0.05	7.639 ± 2.531	0.408 ± 1.201

Table A. 15 ANOVA to test whether there was a difference in means of nitrate at two different redox potentials

P	<250 mV	>250 mV
	LS Mean	LS Mean
0.001	0.481 ± 0.087	1.246 ± 0.106

Table A.16 Two sample T test to determine whether there was a difference in the means of methyl mercury concentration between samples that exibited a sulphide odour and those that did not.

P	df	t
0.043	8	-2.321

Table A.17 Simple Linear Regression of Conductivity as a function of Total Inorganic Carbon.

P	R^2
<0.001	0.548

APPENDIX B

Sample number, total coliforms count (colony forming units (cfu)/100 mL), *E.coli* (cfu/100 ml), background colonies (cfu/100mL), conductivity (µS/cm), pH, Eh (mV), temperature (° Celsius), oxygen (mg/L), nitrate (mg/L), methyl mercury (ng/L and pg/L).

sample no.	Total Colif.	*E. coli*	Back. colon.	cond (ug/cm)	pH	Eh	temp. ° C.	oxygen (mg/L)	nitrate (mg/L)	nitrate (ug/L)	MeHg (ng/L)	MeHg (pg/L)
1	7	0		1515	7.33	-50.00			0.01	8.13	0.04	43.00
2	0	0		0	7.49	241.90			0.01	5.89	0.04	38.00
3	0	0		861	7.38	232.70			0.02	16.00	0.04	41.00
4	10	0		960	7.17	254.80			0.01	5.30	0.02	15.21
5	0	0		514	7.91	245.00			0.01	6.20	0.04	40 00
6	0	0		607	7.62	227.70			0.00	1.75	0.06	61 00
7	9	0	2	644	7.73	240.50			0.00	1.00	0.04	36 00
8	18	0	47	742	7.45	255.50			56.01	56013.50	0.05	50 00
9	0	0	0	634		-27.90			0.02	20.00	0.07	70 00
10	0	0	0	1050		-11.60	13.7		0.02	20.00	0.01	8 77
11	6	0	1	1393		248.50			0.02	20.00	0.09	91.00
12	27	0	45	503		268.00	14.5	4.1	4.93	4925.00	0.05	54.00
13	0	0	0	745		218.00	9.5	2.0	0.01	7.50	0.07	73 00
14	230	0	100	634		265.50	10.7	6.9	5.11	5105.00	0.02	22.00
15	18	0	43	821		269.50		3.1	14.55	14545.00	0.01	11.14
16	1	0	3	538		261.30	14.9		2.44	2440.00	0.06	59.00
17	26	0	2	2930	6.95	210.50	13.9	0.5	0.01	10.00	0.05	47.00
18	0	0	0	483	7.33	275.50	17.9	2.0	1.35	1350.00	0.06	57.00
19	11	0	2	525	8.05	250.00	17.4	0.7	0.01	10.00	0.02	18.24
20	0	0	13	694	8.2		15.2	1.0	0.01	8.09	0.04	39.00

sample no.	Total Colif.	*E. coli*	Back. colon.	cond (ug/cm)	pH	Eh	temp. ° C.	oxygen (mg/L)	nitrate (mg/L)	nitrate (ug/L)	MeHg (ng/L)	MeHg (pg/L)
21	0	0	261.5	1740	7.22	260.70	12.6	0.6	0.01	8.36	0.04	41.00
22	0	0	0	2900	7.18	192.00	15.7	0.2	0.01	8.91	0.06	62.00
23	0	0	2	1882	7.36	267.90	16.4	1.0	0.01	6.11		0.00
24	27	0	0	917	7.21		15.4	0.5	0.01	10.00	0.03	27.00
25	0	0	0	537	8.05	262.30	14.7	0.2	0.00	2.15	0.07	72.00
26	128	2	381	888	7.23	274.90	20.4	1.0	3.49	3485.00	0.04	39.00
27	0	0	1	973	7.23	252.60	16.4	1.5	5.65	5645.00	0.02	19.22
28	0	0	500	907	7.31	271.80	16.5	3.5	3.86	3860.00	0.01	8.30
29	2	0	6	2430	7.33	265.90	16.0	0.9	0.02	15.00	0.04	44.00
30	0	0	0	633	7.68	261.10	17.0	0.3	0.01	10.00	0.05	50.00
31	0	0	0	592	7.62	258.60	15.6	0.4	0.04	40.00	0.04	41.00
32	65	0	0	535	7.62	228.20	16.2	0.5	0.01	9.17	0.05	47.00
33	0	0	0	557	7.45	257.10	17.7	0.9	0.00	3.86	0.00	3.74
34	4	0	2	948	7.12	190.30	17.6	0.4	0.01	6.74	0.01	13.52
35	6	0	26	590	7.38	267.90	22.1	6.0	1.83	1830.00		0.00
36	500	2	500	870	7.3	255.50	20.2	0.3	0.39	390.00	0.04	40.00
37	4	0	0	605	7.56	-63.60	19.2	0.2	0.01	6.05	0.02	19.12
38	1	0	56	682	7.48	186.50	22.2	0.1	0.00	0.50	0.00	4.90
39	0	0	0	899	8.14	227.30	20.4	0.2	0.01	5.00	0.04	44.00
40	4	0	1	948	7.33	79.90	23.0	2.1	0.01	5.00	0.01	10.21
41	123	8	187	845	7.15	245.50	23.5	0.2	0.70	700.00	0.07	74.00
42	0	0	0	225	7.14	267.10	19.9	4.5	0.01	7.40	0.00	4.39
43	1	0	1	740	7.49	-29.30	22.3	0.2	0.00	3.63	0.03	34.00
44	2	0	8	765	7.15	-53.60	18.5	0.2	0.01	9.93	0.06	56.00
45	26	0	7	515		150.00	18.8	0.3	0.01	7.82	0.01	14.38
46	24	0	420	669	7.58	79.90	15.9	1.2	0.01	7.78	0.00	3.35
47	30	0	490	796	7.38	274.60	21.4	3.5	2.42	2420.00	0.00	4.92
48	5	0	1	513	7.54	191.10	17.7	0.7	0.01	9.83	0.90	895.00
49	0	0	3	746	7.4	267.50	16.4	5.2	0.03	30.00	0.11	113.00
50	0	0	42	*9669	7.78	-11.00	20.9	0.3	0.02	15.00	0.09	85.00
51	0	0	1	673	7.71	120.10	17.9	0.3	0.00	1.70	0.00	4.56
52		11		550	6.86	212.40	19.5	0.6	0.23	230.00	0.01	14.41

sample no.	Total Coli.	*E. coli*	Back. colon.	cond (ug/cm)	pH	Eh	temp. ° C.	oxygen (mg/L)	nitrate (mg/L)	nitrate (ug/L)	MeHg (ng/L)	MeHg (pg/L)
53	16	0	3	599	7.25	247.50	17.8	3.2	1.25	1250.00	0.01	10.87
54	1	0	111	1754	6.86	233.20	17.0	2.5	0.99	985.00	0.05	45.00
st.dev.	77	2	145	570	0.3	102.87	3.1	1.7	7.86		0.12	
st.err	10	0	20	78	0.0	14.27	0.5	0.3	1.07		0.01	
AVR	25	0	70	908	7.4	197.45	17.5	1.5	1.95		0.05	

*note value 50 of conductivity not used to calculate mean of conductivity; value 52 of TC, BC not used to calculate mean.

APPENDIX C

Sample number, the presence of sulphide odour (0 no odour, 1 odour), Total inorganic carbon (TIC) (ppm), and Total organic carbon (TOC) (ppm).

sample no.	Sulphide odour detected	TIC Conc. (ppm)	TOC Conc. (ppm)
1	0	74.23	0.40
2	0	92.92	1.05
3	0	73.08	0.55
4	0	71.91	0.51
5	0	33.92	0.00
6	0	46.80	0.00
7	0	49.23	0.00
8	0	40.30	0.13
9	0	44.58	0.00
10	1	79.95	0.41
11	0	69.79	4.21
12	0	18.43	2.73
13	1	64.82	0.00
14	0	35.29	1.42
15	0	40.61	1.16
16	1	30.97	2.71
17	1	75.92	0.24
18	0	66.62	3.94
19	0	47.57	0.39
20	0	47.10	0.42
21	0	76.49	1.29
	1	66.08	2.76

sample no.	Sulphide odour detected	TIC Conc. (ppm)	TOC Conc. (ppm)
22			
23	0		
24	0	82.43	0.89
25	0	35.12	0.00
26	0	82.10	4.62
27	0	75.86	1.85
28	0	81.05	0.92
29	0	54.57	0.64
30	1	56.09	3.37
31	1	52.61	0.47
32	0	57.73	0.00
33	0	61.27	0.00
34	1	78.45	2.74
35	0	64.87	2.16
36	0	83.80	1.31
37	1	52.98	0.75
38	0	64.52	0.81
39	0	86.11	1.71
40	1	69.82	0.86
41	0	85.63	3.60
42	0	22.76	0.63
43	0	58.89	5.59
44	0	86.84	3.31
45	0	56.70	0.59
46	0	58.34	0.65
47	0	69.57	1.28
48	1	53.54	0.16
	1	70.68	0.39

sample no.	Sulphide odour detected	TIC Conc. (ppm)	TOC Conc. (ppm)
49			
50	1	255.86	12.38
51	1	55.76	2.16
52	0	61.41	0.74
53	0	58.71	0.27
54	0	73.05	2.70
st.dev.		31.79	2.05
st.err		4.33	0.28
AVR		65.16	1.54

APPENDIX D

Sample number, total coliforms (cfu/100 mL) , *e.coli* (cfu/100 mL), background colonies (cfu/100 mL), and well depth (ft.) in the three different land use types (residential, agricultural, and agricultural intensive).

Residential					Agricultural				
sample	Tc	Ec.	B.c. .	depth	sample	tc	ec	b.c	depth
2	0	0			3	0	0		80
6	0	0		60	5	0	0		75
7	9	0	2		13	0	0	0	120
17	26	0	2		14	230	0	100	24
19	11	0	2	70	18	0	0	0	
21	0	0	262	117	20	0	0	13	55
22	0	0	0		25	0	0	0	120
23	0	0	2	96	26	128	2	381	27
29	2	0	6	85	36	500	2	500	30
30	0	0	0	110	37	4	0	0	
31	0	0	0		42	0	0	0	
33	0	0	0	25	44	2	0	8	15
34	4	0	2	35	48	5	0	1	69
35	6	0	26	45	53	16	0	3	50
39	0	0	0		28	0	0	500	40
40	4	0	1	18	1	7	0		70
41	123	8	187		38	1	0	56	
45	26	0	7	65					
46	24	0	420	80					
49	0	0	3	90					
51	0	0	1						
54	1	0	111						
totalsites	22	22	22		total	17	17	17	
Average	11	0	52		average	53	0	112	
Max.	123	8	420		max	500	2	500	
min.	0	0	0		min	0	0	0	
%pos.	50	5	68		% pos.	53	12	53	
stdev.	27	2	112		stdev.	134	1	200	
sterror	6	0	24		st.err	34	0	50	

APPENDIX D

Sample number, total coliforms (cfu/100 mL), *e.coli* (cfu/100 mL), background colonies (cfu/100 mL), and well depth (ft.) in the agricultural intensive land use site.

sample	tc	e.c.	b.c	depth
4	10	0		80
8	18	0	47	35
9	0	0	0	76
10	0	0	0	72
11	6	0	1	90
12	27	0	45	
15	18	0	43	3
16	1	0	3	4
24	27	0	0	70
27	0	0	1	220
32	65	0	0	30
43	1	0	1	60
47	30	0	490	60
50	0	0	42	
52	12500	11		
Total sites	15	15	15	
average	847	1	52	
max	65	11	490	
min	0	0	0	
% pos.	73	7	60	
stdev.	3224	3	133	
sterror	832	1	34	