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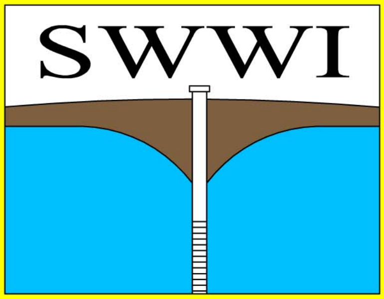
Sustainable Water Well Initiative



In-Situ Remediation of Nitrate in Groundwater
Phase 1: Site Characterization

Prepared by:
Earth Sciences Unit
Prairie Farm Rehabilitation Administration
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Canada

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EXECUTIVE SUMMARY

Elevated concentrations of nitrate in drinking water is a concern to rural Canadians as nitrate in excess amounts can cause environmental and health problems. Rural areas, where livestock and drinking water supplies are found in a common location, are particularly at risk as animal manure contains high levels of nitrogen. When nitrogen in the form of nitrate reaches groundwater it becomes very mobile and can migrate long distances from the area of input, leading to the contamination of groundwater supplies.

To address the issue of nitrate contamination of groundwater, the Prairie Farm Rehabilitation Administration (PFRA) of Agriculture and Agri-Food Canada is conducting a study of nitrate plumes in groundwater originating from livestock waste. The study will provide information on the properties of groundwater environments that impact the natural attenuation and reduction of nitrate. This information will contribute to the development of preventative strategies and mitigative measures to protect groundwater from nitrate contamination and will help to improve knowledge on the siting of water wells and the management of groundwater resources in proximity to agricultural production systems.

An evaluation of in-situ groundwater nitrate remediation technologies and processes will be performed during the second phase of the study. Evaluations will focus on enhanced in-situ bioremediation, a treatment process by which microbiological activities are used to reduce the concentration or toxicity of a pollutant. Electrokinetics will also be evaluated as a means to concentrate contaminants in the aquifer within a defined treatment zone.

The PFRA Caledonia-Elmsthorpe Pasture was chosen as the research site to begin this study based on previous testing of the residence well which showed nitrate levels exceeded the Canadian Drinking Water Quality Guidelines. Livestock pens, located close to the residence well, were suspected to be the source of nitrate contamination

As part of this Phase 1 study, PFRA completed a site investigation at the Caledonia-Elmsthorpe Pasture to characterize the site hydrogeology and groundwater quality. Test holes were drilled at the site to define the geology and the source and configuration of nitrate contamination. Twenty piezometers were installed at the research site to act as monitoring wells. Water levels were monitored in each of the piezometers, and water samples were collected from select wells. These samples were tested for nitrate concentrations to: 1) determine the source and areal extent of nitrate contamination in groundwater at the research site, 2) benchmark the change in nitrate concentrations with respect to time, 3) identify vertical variations in nitrate concentrations with respect to the different geologic units, and 4) identify events that may increase or decrease the concentration of nitrates in the aquifer. A series of diagnostic tests were also performed on groundwater samples from the site, to compare initial site conditions to a known set of conditions required for successful remediation. These included tests for chloride (Cl), dissolved oxygen (DO), dissolved organic carbon (DOC) and biological activity. Information from this Phase 1 investigation will be used during the Phase 2 study to: 1) identify the best location for

remediation efforts, 2) guide further sampling and testing procedures, and 3) design and implement the remediation process.

The aquifer at the research site contains high concentrations of nitrate. The source of nitrate is animal waste from livestock pens which are located south of the residence well. A plume of nitrate is moving to the east and north of the livestock pens which is the direction of groundwater flow. The nitrate plume extends to the residence well, resulting in unacceptable concentrations in the well. In general, nitrate concentrations are highest in the winter months when groundwater elevations are low. Nitrate is also present in the bedrock which underlies the aquifer at the site. However, nitrate levels in this bedrock unit are below maximum acceptable levels and are believed to be natural background levels in this unit.

Nitrate (NO_3^-)/chloride (Cl^-) ratios were used to identify areas where biochemical reduction of nitrate (i.e. denitrification) may be occurring at the site. These ratios show that denitrification may be occurring in the aquifer north of the livestock pens, at monitoring wells C-17, C-14, C-18 and C-19. Diagnostic tests performed at the site show low levels of DO in these areas, which may contribute to the denitrification process. In addition, some of the wells in these areas contain active populations of denitrifying bacteria.

If measures are taken to prevent nitrate leaching into the groundwater, the effects of dilution along with the process of denitrification will cause nitrate concentrations in the aquifer to decrease over time. Dilution has a significant impact on nitrate concentrations at this site. As the aquifer is recharged the contaminated water is diluted, leading to a reduction in nitrate concentrations. As a result, nitrate concentrations will decrease in the aquifer if the source of contamination is removed.

Due to the low transmissivity and the discontinuous nature of the aquifer at the Caledonia-Elmsthrope site, it is unlikely that the whole area of contamination can be remediated. It is therefore recommended that any evaluation of in-situ nitrate remediation technologies be limited to a small area of the aquifer. The most favourable conditions for in-situ nitrate remediation, are found in the aquifer north of the pens in an area that encompasses monitoring wells C-14, C-16, C-17 and C-18.

Evaluations of in-situ bioremediation may require a carbon amendment. In most areas of the aquifer, the level of dissolved organic carbon (DOC) is too low and the concentration of dissolved oxygen (DO) is generally too high for bioremediation to proceed. Adding a carbon source to the aquifer in the area chosen for remediation will provide the substrate necessary to increase biomass and will provide the electron donor necessary for oxygen and nitrate reduction.

Once the area for the in-situ remediation evaluation has been established, further tests will be required to ensure that all other geochemical parameters are adequate for successful remediation to occur. Regular monitoring of groundwater nitrate concentrations will continue during phase 2 of this study to provide a measure of nitrate reduction resulting from mitigation or remediation efforts.

ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

1.1 ORIGIN AND SCOPE OF STUDY

Nitrate contamination of groundwater resources, arising from livestock waste, is a concern as elevated nitrates in water supplies may have an impact on human health. The entry of nitrate into groundwater can often be reduced or eliminated by the use of best management practices for agriculture. However, where nitrate is already at high concentrations in groundwater, a means to eliminate the contaminant may be required.

The Prairie Farm Rehabilitation Administration (PFRA) of Agriculture and Agri-Food Canada is conducting a study to address the issue of nitrate contamination of groundwater. The objectives of this study are to:

1) Develop knowledge on the occurrence and development of nitrate plumes from point sources originating from livestock contamination.

2) Identify physical, chemical and microbiological properties of groundwater environments that impact the natural attenuation and reduction of nitrates.

3) Develop preventative strategies and mitigative measures to protect groundwater from nitrate contamination.

4) Evaluate and develop innovative in-situ groundwater nitrate remediation technologies and processes.

5) Improve knowledge for the siting of water wells and the management of groundwater resources in proximity to agricultural production systems.

The PFRA Caledonia-Elmsthorpe Pasture was chosen as the research site for this study based on previous testing of the residence well which showed nitrate levels exceeded the Canadian Drinking Water Quality Guideline of 45 mg/L. Livestock pens, located close to the residence well, were suspected to be the source of nitrate contamination.

As part of this Phase 1 study, PFRA completed a site investigation at the Caledonia-Elmsthorpe Pasture to characterize the site hydrogeology and groundwater quality. The site investigation provided data necessary to establish the existence, source and extent of nitrate contamination and to establish baseline fluctuations in groundwater nitrate concentrations with respect to time and seasonal events. In-situ nitrate remediation processes will be evaluated during the second phase of this study. Therefore, diagnostic tests for chloride (Cl), dissolved oxygen (DO), dissolved organic carbon (DOC) and biological activity were performed to compare initial site conditions to a known set of conditions required for successful remediation. This report is a summary of results from the Phase 1 investigation.

1.2 INVESTIGATIVE APPROACH

The Caledonia-Elmsthorpe Pasture headquarters is located on SW36 - Twp11 - Rge 21 - W2M and consists of a residence, several buildings, sheds, a barn, corrals, bins and other facilities common to pasture operations. An intermittent creek flows northeasterly through the quarter and a dam has been constructed across it, creating a small reservoir area (See Figures 1 and 2).

An analysis of groundwater obtained from the residence well, located north of the livestock pens, indicated nitrate concentrations of 46 mg/L . This exceeds the Canadian Drinking Quality Guideline (MAC) of 45 mg/L. An investigation involving test drilling, piezometer installations and water sampling was undertaken to define site geology, as well as the source and configuration of the nitrate contamination.

Options for the placement of test holes and piezometers were limited due to the number of building structures on site, the presence of the creek bed and reservoir to the west and northwest, private property immediately east of the study site, use of the available open area as hay bale storage, and generally poor surface conditions within the livestock pens.

Air photographs, topographic maps and the provincial groundwater database were reviewed prior to initiation of the test drilling program. Information obtained from PFRA pasture personnel revealed that the residence well was constructed in 1987 and consists of a 76.2-cm diameter galvanized steel casing to a depth of 18.3 metres. Further details on the well design were not available. However, the interior of the well casing was viewed with a downhole video camera which revealed intermittent slots at depths of 6 metres and 15 metres below ground. The average non-pumping water level in the well was determined to be approximately 4 metres below ground, and the submersible pump was set at a depth of 14 metres below ground.

2.0 PHYSICAL ENVIRONMENT OF STUDY AREA

2.1 PHYSIOGRAPHY AND DRAINAGE

The pasture headquarters is situated within the Qu'Appelle River basin on the eastern flank of the northwest-trending Missouri Couteau, at an elevation of about 590 metres above sea level (masl). Immediate drainage is toward the northeast-flowing intermittent stream which is tributary to the Moose Jaw River several kilometres north of the site (see Figure 1).

2.2 SURFICIAL GEOLOGY

There is a very thin cover of glacial drift consisting primarily of stiff, clayey till with occasional thin lenses of fine sand containing partings of silt and clay. Effectively, the base of groundwater exploration in the area is the contact between the drift and the bedrock Bearpaw Formation which occurs at an average depth of 3 to 6.5 metres. Given the nature and thickness of the drift, there is very low potential for groundwater development at this site.

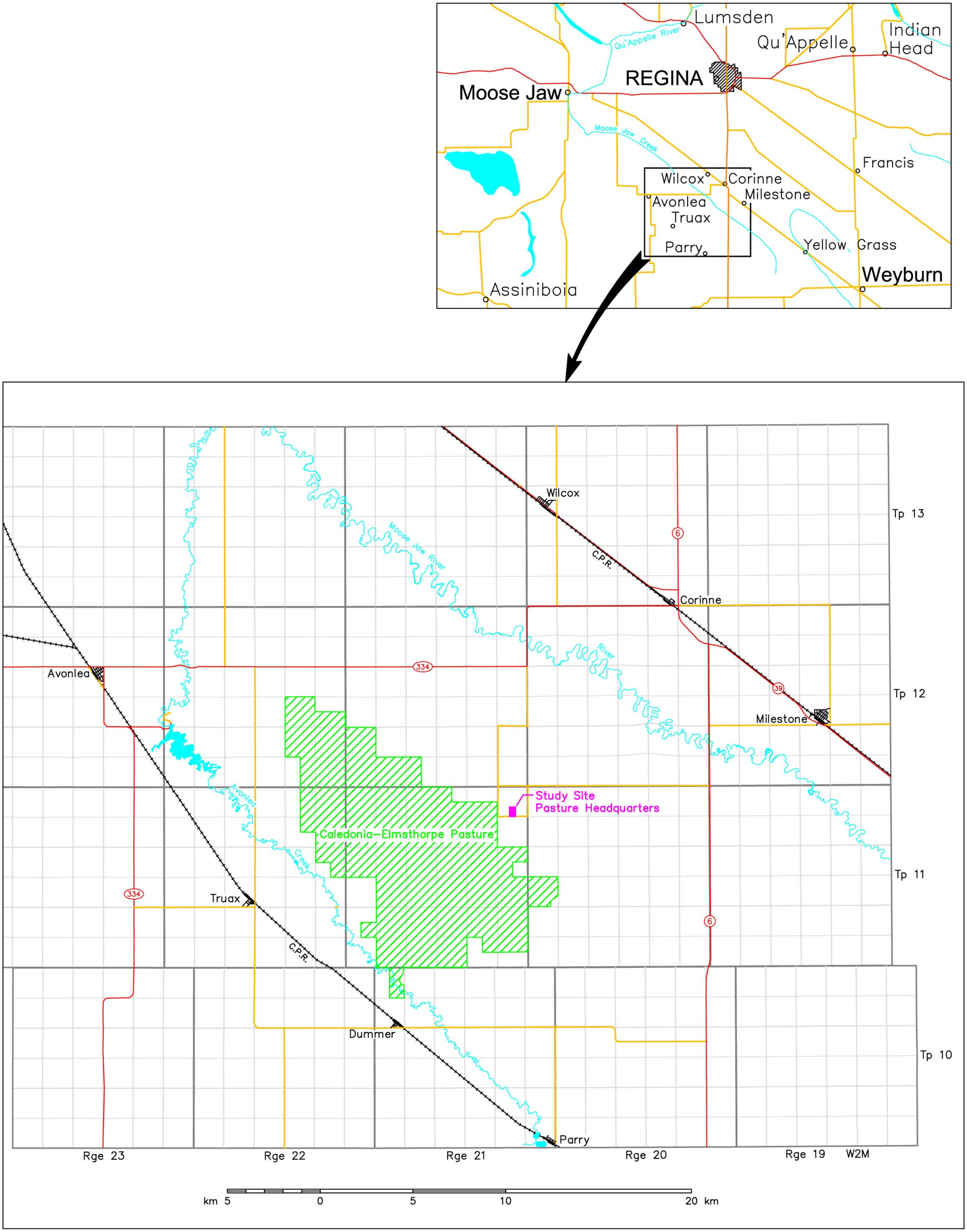


FIGURE 1: General plan showing location of Caledonia Study Site

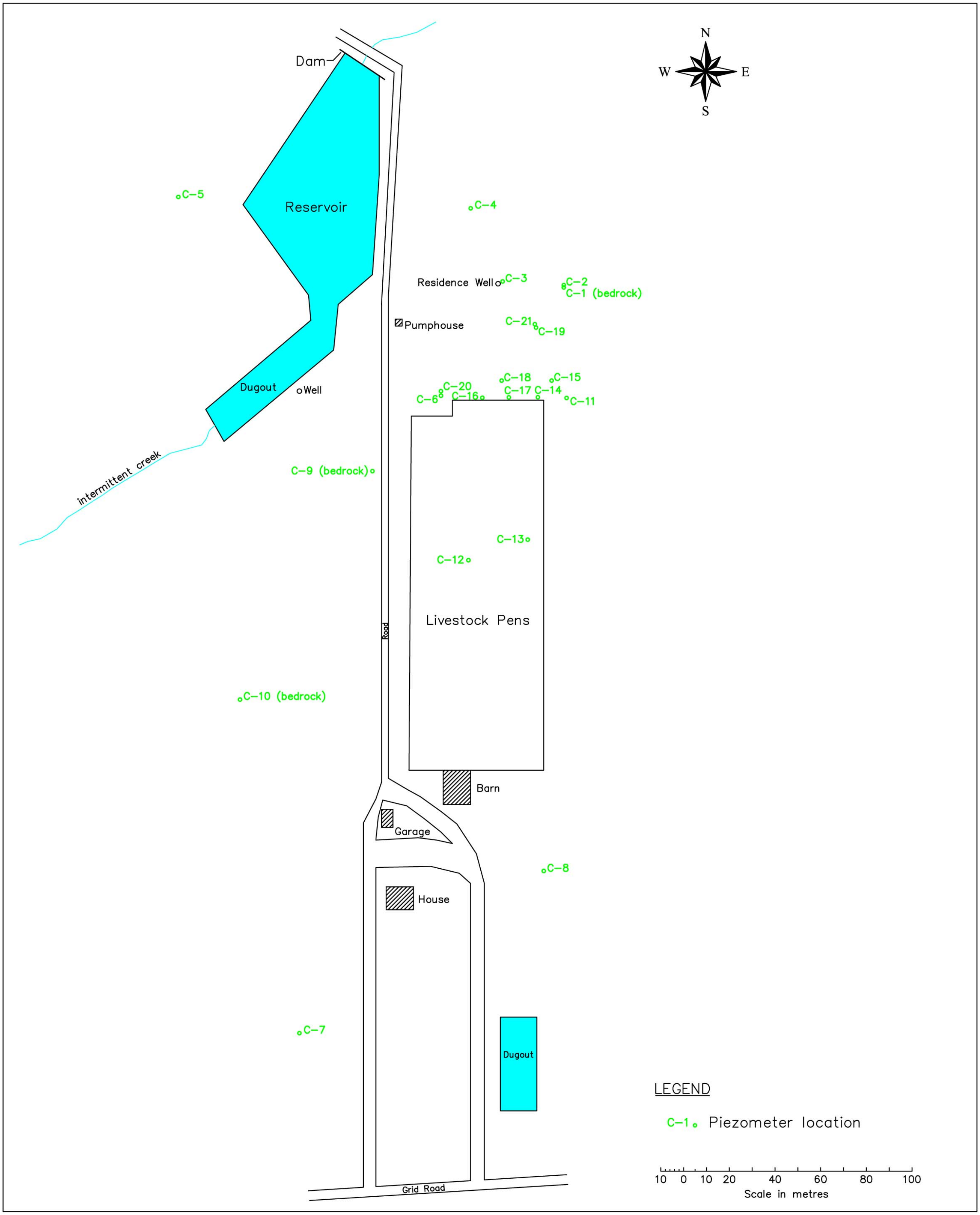


FIGURE 2: Plan of study site showing location of piezometers

2.3 BEDROCK GEOLOGY

The Bearpaw Formation is encountered at an elevation of approximately 585 masl and consists of a grey, noncalcareous clay which is locally bentonitic and concretionary. Occasionally, there are small inclusions of sandstone, and oxides within local fractures. There is very little potential for groundwater development from these units, however, some supplemental production to surficial groundwater supplies is possible with the use of large diameter seepage wells.

2.4 CLIMATE

Precipitation averages from 25 to 38 centimetres annually, the majority of which occurs in the summer months. Evaporation exceeds precipitation for the seven months from April to October (Atlas of Saskatchewan, 1999)

3.0 FIELD INVESTIGATION

3.1 TEST DRILLING AND MONITORING WELL CONSTRUCTION

Test drilling on the pasture headquarters site was initiated on November 14, 2000. During the initial investigation 21 test holes were drilled with a cable tool rig, with the installation of 17 standpipe piezometers into the drift and 3 casagrande piezometers into the Bearpaw Formation. A survey of casing top elevations and establishment of GPS locations for all drill sites was also completed. A plan showing the piezometer locations is provided in Figure 2, and plan drawings of Bearpaw Formation elevations and general surface elevations at the study site are provided in Appendix A. Test hole logs and casing diagrams are provided in Appendix B.

Drift sand units were found to be discontinuous, thin, and often silty, and therefore, relatively unproductive of groundwater (see Appendix B). These sand units in contact with jointed till and bedrock shales, which together yield quantities of groundwater to a seepage well sufficient for domestic purposes, form the aquifer at the study site. An isopach map of surficial deposits, and cross sections outlining the surface-to-bedrock stratigraphy are also provided in Appendix B.

3.2 AQUIFER TESTING AND EVALUATION OF AQUIFER SAMPLES

A falling head permeability test was performed in the PFRA Maxwell facility on a sample of sand obtained from C-6. The permeability of the sand was calculated to be approximately10^{-4} cm/sec. The details of the test are provided in Appendix C.

Falling head slug tests were also performed on piezometer installations C-14, C-16, C-17, C-18 and C-19. The value of permeability from the tests ranged from $1.2x10^{-5}$ to$1.2x10^{-3}$ cm/sec. Details of these slug tests are provided in Appendix C.

Groundwater elevations obtained from each of the piezometers indicate local influence from the reservoir, located northwest of the headquarters residence, and from the dugout, located southeast of the headquarters residence, on groundwater movement in the shallow domain. Overall groundwater flow is to the northeast at an approximate gradient of 0.01, as shown in Appendix C. Readings obtained from the casagrande piezmeters show that groundwater elevations are typically higher in the Bearpaw Formation than those in surficial sediments, suggesting some movement from the Bearpaw unit into overlying surficial deposits.

On July 3, 2001, an aquifer test was conducted on the residence well. The flow rate was set at 10.9 m^3/day (1.7 igpm) for the first 20 minutes of the test, and thereafter, at 16.35 m^3/day (2.5 igpm) until test completion at 426 minutes. Aquifer transmissivity and storativity near the residence well, as provided by the data from C-3, was determined to be 2.2 m^2/day and 0.013, respectively. Aquifer transmissivity increased and storativity decreased in areas further from the pumped well, as determined from piezometer response during the test. Details of the aquifer test are provided in Appendix C.

4.0 GROUNDWATER DIAGNOSTIC TESTING AND RESULTS

Diagnostic tests were performed during the site investigation to establish the existence, spatial extent (i.e. vertical and horizontal) and source of nitrate contamination at the site. In addition, groundwater nitrate levels and water levels were monitored from Nov. 26, 2000 to Feb. 20, 2002, to record changes in nitrate concentrations with respect to time and seasonal events.

Nitrate concentrations, in subsurface environments, can vary with depth, areal extent, and with time. Understanding the variations in nitrate levels is essential when developing and evaluating mitigation strategies or remediation processes. Monitoring nitrate levels for a period of time before the mitigation measures or remediation processes are applied, provides the data needed to distinguish between natural nitrate fluctuations and nitrate reductions resulting from the mitigation or remediation. Understanding the horizontal and vertical extent of the nitrate plume is necessary to design and implement the remediation process.

One of the objectives of this study is to evaluate innovative in-situ nitrate remediation technologies and processes. During the second phase of the study, evaluations will focus on enhanced in-situ bioremediation, a treatment process by which microbiological activities are used to reduce the concentration or toxicity of a pollutant. Electrokinetics will also be evaluated as a means to retain contaminants within a confined zone of the aquifer.

Microorganisms found in soil and groundwater are often involved in the transformation or destruction of a specific compound. These microorganisms require favourable environmental conditions in order to complete their biochemical reactions and remediate the compound of concern. The objective of phase 2 will be to provide the environment and resources required by the native microbes to reduce the concentration of nitrates in a specific area of the aquifer.

When in-situ bioremediation is considered as a remediation technology, a series of diagnostic tests are required to compare initial site conditions to a known set of conditions required for successful remediation. In groundwater environments the conditions required for effective bioremediation include: 1) a proper balance of nutrients (e.g. nitrogen and phosphorus), 2) a sufficient source of food (i.e. carbon), 3) the required electron acceptor in sufficient supply (e.g. nitrates) 4) a conducive environment (e.g. proper DO and pH levels), and 5) a viable microbial population that can degrade the contaminant of concern. The bioremediation process must be designed to correct any unfavourable conditions or deficiencies.

Diagnostic tests performed during this phase of the project included tests for nitrate, chloride (Cl), dissolved oxygen (DO), dissolved organic carbon (DOC) and biological activity, which were measured at various locations in the groundwater below the research site. This information will be used during Phase 2 investigations to: 1) identify the best location for remediation efforts, 2) guide further sampling and testing procedures, and 3) design and implement the remediation process.

4.1 NITRATE MONITORING AND ASSESSMENT

Water samples, collected from select piezometers (i.e. monitoring wells), were tested for nitrate concentrations to: 1) determine the source and areal extent of nitrate contamination in groundwater at the research site, 2) benchmark the change in nitrate concentrations with respect to time, 3) identify vertical variations in nitrate concentrations with respect to the different geologic units, and 4) identify events that may increase or decrease the concentration of nitrates in the aquifer. Sampling and testing procedures and nitrate analytical results are included in Appendix D. The location of the residence well and the location of the piezometers, which were used as monitoring wells, are shown in Figure 3. Using isocontours, Figure 3 illustrates the areal extent and nitrate concentrations measured in the groundwater on August 08, 2001.

Water samples collected from monitoring wells, C-5 (see Figure 2 for location) and C-4, show that background nitrate (NO_3^-) concentrations in groundwater at the study area are generally below 10 mg/L. Since C-5 and C-4 are outside the area of influence from contaminated groundwater flowing under the livestock pens, nitrate concentrations at these sites represent background nitrate levels in the aquifer.

4.1.1 Source and Areal Extent of Nitrate Contamination

The distribution of nitrates clearly shows that the nitrate plume originates below the livestock pens, as shown in Figure 3. Nitrate concentrations are highest in groundwater below the livestock pens and movement of the nitrate plume is in a northeastward direction in accordance with the hydraulic gradient and also under the influence of the residence well and the presence of the reservoir located to the northwest of the pens.

A finger of high nitrate concentrations is moving towards C-3 which is located just 2 metres from the residence well (see Figure 3). Pumping the well may cause preferential movement of contaminated groundwater towards this area. In addition, the aquifer consists of discontinuous layers of sand, silt and clay. These heterogeneities may cause the pattern of nitrate movement to be variable.

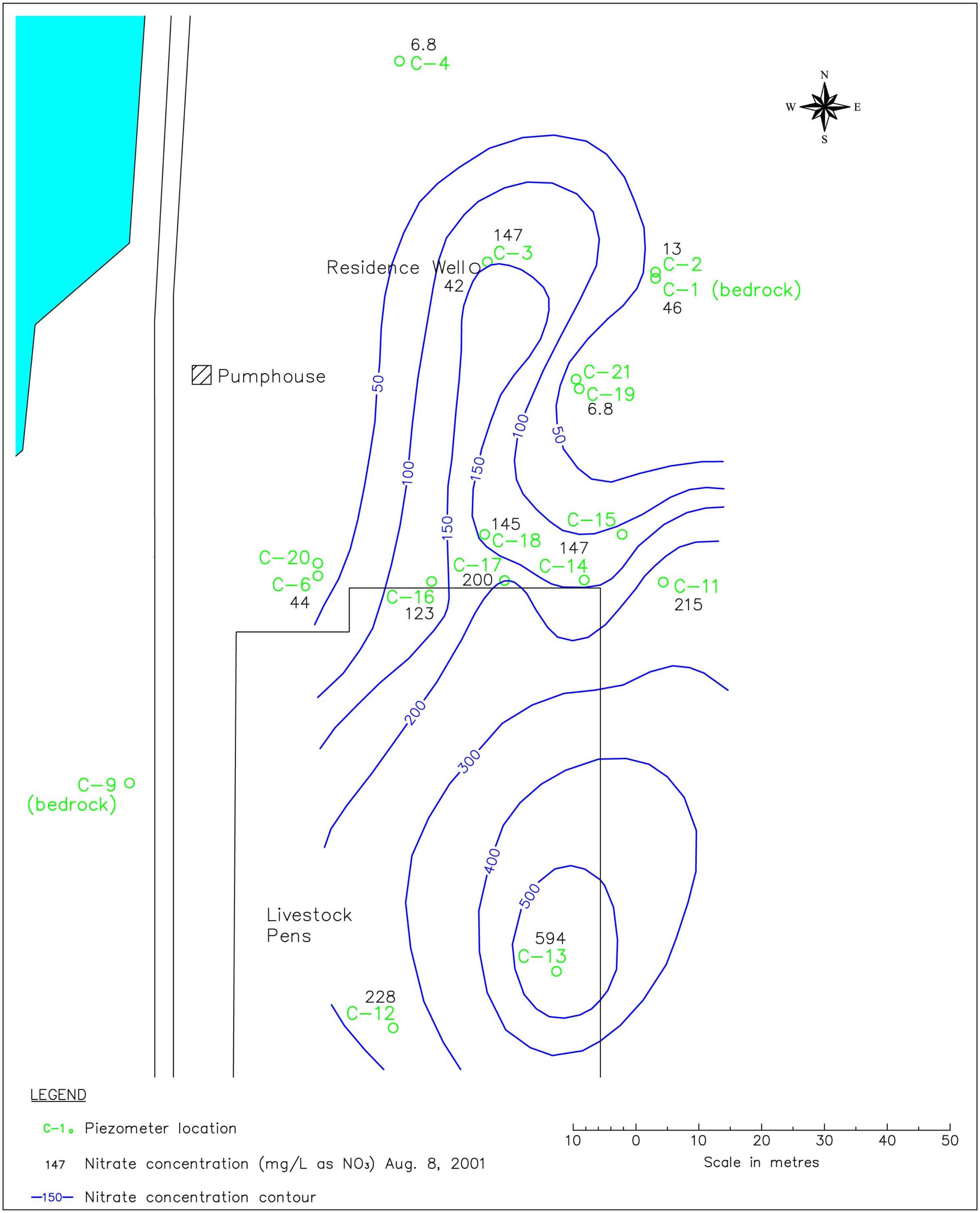
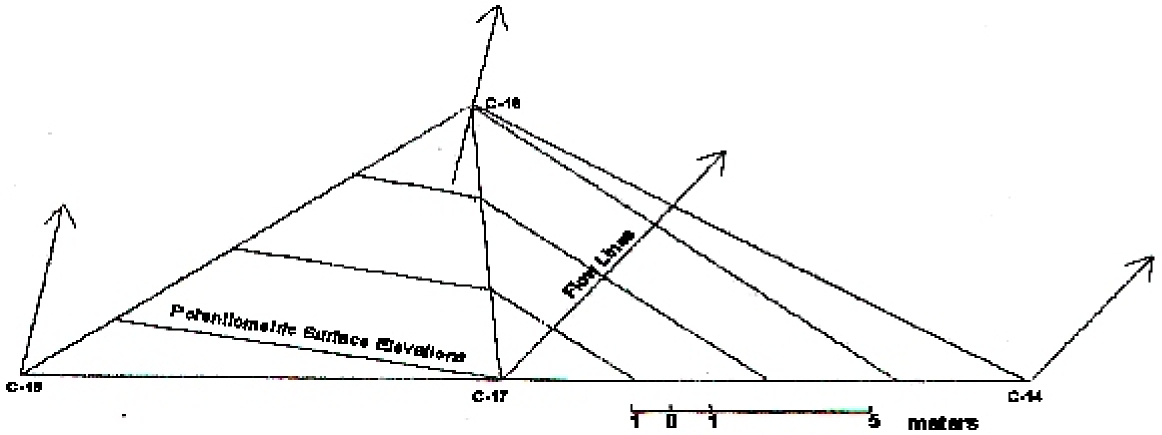


FIGURE 3: Plan of study site showing contours of nitrate concentrations

Nitrate appears to enter the groundwater within the livestock pens near C-13. Through the process of diffusion and mechanical dispersion, the nitrates spread in all directions away from the source and decrease in concentration with distance from the source. However, the nitrate plume moves primarily north and northeast of the pen, which is the direction of ground-water flow as shown in Figure 4.



Note: The slope of the water table or potentiometric surface elevations were established using data from a level survey performed at the site and from water levels measured in the monitoring wells (see data Appendix D).

Figure 4 Groundwater Flow in the Aquifer North of the Livestock Pens

The livestock pens contain cattle throughout the year and the livestock waste which collects in these pens is the source of nitrate contamination at the site. Solid waste from cattle contains high levels of organic nitrogen and cattle urine contains a significant amount of nitrogen, principally in the form of urea ($CO(NH_2)_2$). This nitrogen is converted to ammonia and ammonium, and then to nitrate by soil bacteria. Nitrate moves through the soil and enters the groundwater below the pens during snow melt and rainfall events.

It is well documented that organic nitrogen compounds from wastes and remains of plants or animals are converted to ammonia or ammonium compounds by decomposing bacteria and fungi. The decomposers use released amino acids and proteins for growth and release the excess as ammonia or ammonium, some of which is used by plants. If the ammonia or ammonium made available by decomposing bacteria or fungi is not used by plants, it may be utilized as an energy source by other bacteria that sequentially oxidize it to nitrite and nitrate.

The chemical process in which nitrogen from plant and animal wastes is oxidized to nitrites and then to nitrates is termed, "***nitrification***". Ammonium is oxidized in aerobic environments to nitrite and nitrate. Nitrification is primarily initiated by nitrifying bacteria, which gain energy by oxidizing ammonium, while using CO_2 as their source of carbon to synthesize organic compounds.

When nitrogen in the form of nitrate reaches groundwater, it becomes very mobile because of its solubility and anionic form. Nitrate is nonsorptive and for the most part does not exchange on sediment surfaces. Nitrate solutions tend to move through soils at virtually the same speed as groundwater flow, and can migrate long distances from input areas if present in highly permeable subsurface materials that contain dissolved oxygen. The only condition that can affect this process is a decline in the redox potential of the groundwater. In this case, biodenitrification can occur (Canter, 1997).

4.1.2 Nitrate Levels in the Residence Well

Initial testing provided evidence that the residence well was contaminated with nitrates. On November 2, 2000, three water samples were collected from inside and outside house taps. These samples were sent to the Saskatchewan Provincial Health Lab for nitrate (NO_3^-) testing. Test results indicated nitrate concentrations at 46 mg/L in each of the 3 samples (see Appendix D). The Canadian Drinking Water Quality Guidelines identify the maximum acceptable concentration (MAC) of nitrates to be 45 mg/L, which is equivalent to 10 mg/L as nitrate-nitrogen.

Nitrates were monitored in the residence well over a 16-month period, with initial samples collected in November, 2000. Nitrate concentrations ranged from 25 mg/L to 70 mg/L during this period, with the highest concentrations recorded in December, 2001 (see Appendix D for test results).

Although the residence well and C-3 are in close proximity to one another, nitrate concentrations in C-3 are considerably higher than in the residence well. Nitrate levels in C-3 range from 77 mg/L to over 200 mg/L, compared to 25 to 70 mg/L in the residence well. Pumping the well may have an impact on the level of nitrates entering the well. During pumping, groundwater is drawn to the well from both contaminated and uncontaminated areas of the aquifer. This would result in dilution of the nitrates entering the well. Presently, the effects of dilution are beneficial to the well, however, if nitrate concentrations continue to rise as the plume moves further to the north, nitrate levels in the well may increase.

4.1.3 Seasonal Effects on Nitrate Concentrations

Nitrate concentrations and groundwater elevations were monitored at the Caledonia research site from November, 2000 to February, 2002 (see Appendix D). Nitrate concentrations were highest in most of the monitoring wells, in December, 2001. During this time, nitrate levels peaked in wells C-3, C-6, C-11, C-12, C-13, C-14, C-18, C-21. This peak corresponds to a significant drop in groundwater elevations, which indicates that there was less recharge to the groundwater during the fall and winter months of 2001, resulting in less dilution of nitrate.

A comparison of nitrate concentrations was made for three different areas of the Caledonia Aquifer (see Figures 5, 6 and 7). Nitrate levels in the groundwater below the livestock pen at C-13 range from 440 mg/L in March, 2001 to 792 mg/L in December, 2001. Nitrate in C-3, just 2 metres from the residence well, range from 77 mg/L in November, 2000 up to 233 mg/L in December, 2001. Nitrate in the residence well range from 25 mg/L in November, 2000 to 70 mg/L in December, 2001. Nitrate levels were highest in each of these wells in December, 2001.

Figure 5 Nitrate Levels vs Time: Residence Well

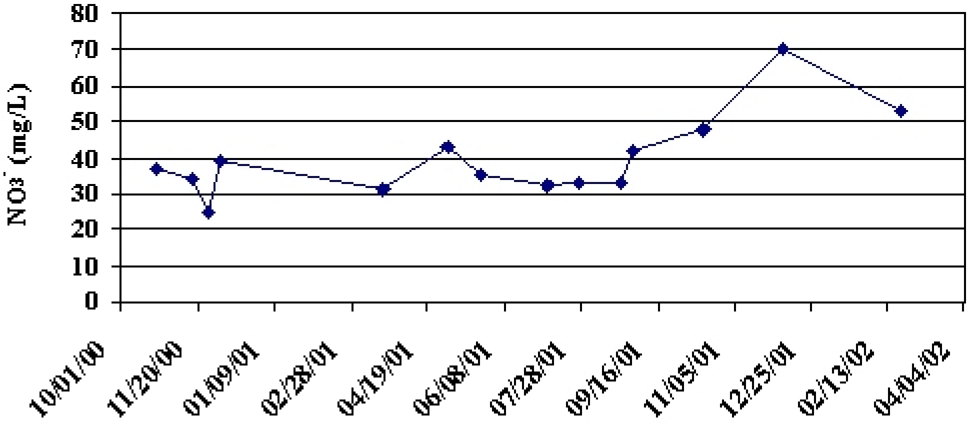


Figure 6 Nitrate Levels vs Time: Piez. C-13

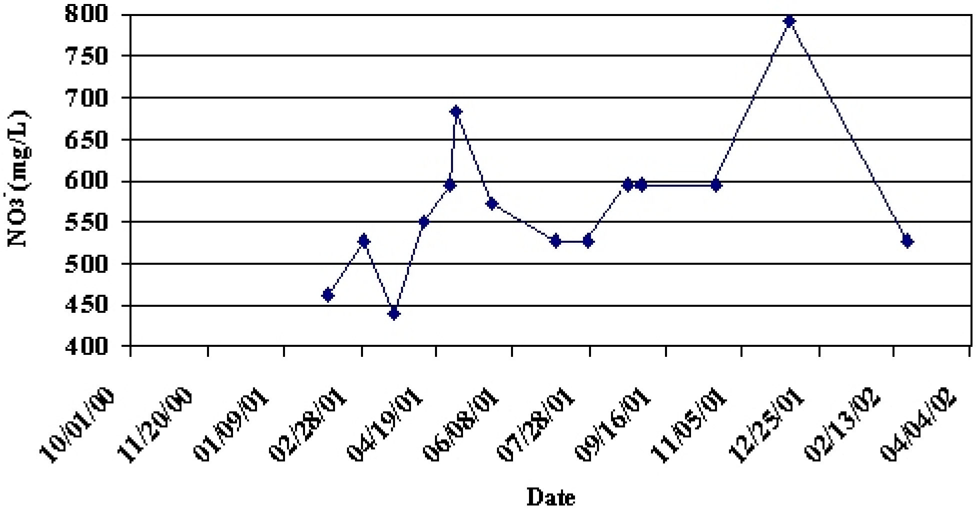
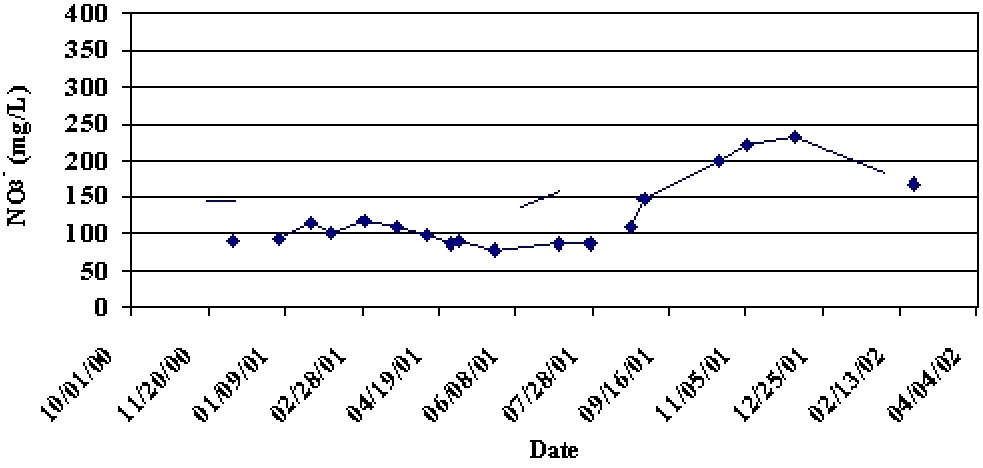


Figure 7 Nitrate Levels vs Time: Piez. C-3



A comparison of groundwater elevations to nitrate concentrations at C-3 is shown in Figure 8. Nitrate concentrations at C-3 were lowest from April 9, 2001 to July 26, 2001. Fresh water from snow melt and spring rains entering the aquifer outside the livestock pens probably diluted nitrate concentrations during this period. In the late summer and fall of 2001, water levels decreased at C-3 while nitrate concentrations increased. During this time there was very little regional precipitation, resulting in a reduction in groundwater recharge and less dilution of the nitrates.

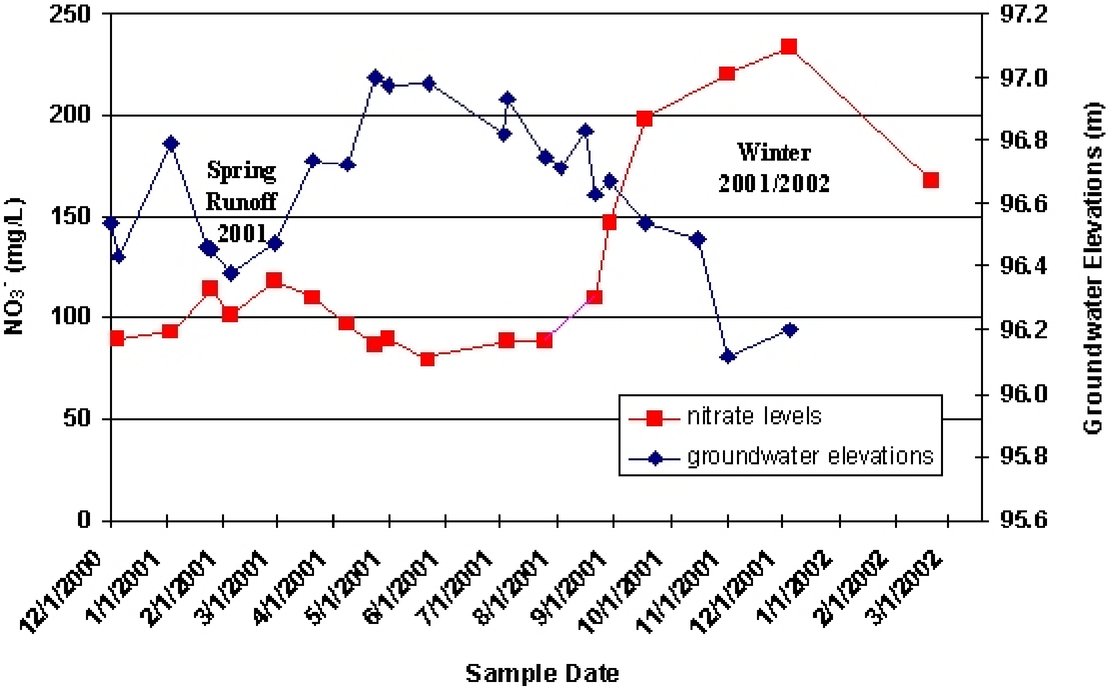


Figure 8 Groundwater Elevations vs Nitrate Levels: Piez. C-3

In addition to having less fresh water available for dilution, the conversion of ammonium to nitrates (i.e. nitrification) may be higher during early winter months. In subsurface environments the availability of oxygen and ammonium, more than temperature, regulate the rate of nitrification in sediments. Blackburn (1983) found that the maximum rate of nitrification occurred at 1°C in sandy sediment cores. Blackburn suggests that oxygen is more available in the sediment during the winter months, when competition from heterotrophic processes and hydrogen sulphide production is least. Therefore, conversion of ammonium to nitrates may increase in the winter months.

There was an increase in nitrate concentrations below the livestock pens at C-13, in May, 2001 (see Figure 5). Unlike the fresh water from spring melt infiltrating though the soil *outside* the pens, the water infiltrating through the soil *inside* the pens contains high levels of ammonium and nitrate from livestock waste that has accumulated over the winter months. The accumulated nitrate enters the groundwater below the pens in the early spring when the soil thaws, which causes a temporary increase in nitrate concentrations.

4.1.4 Vertical Variations in Nitrate Concentrations

Nitrate is also present in the bedrock (Bearpaw Formation) at the research site. However, the livestock pens are not likely the source of nitrate in the bedrock unit. Water samples collected from this unit, both under the nitrate plume and east of the plume, contain similar concentrations of nitrate. This implies that nitrate in the bedrock may originate from a source other than the livestock pens. Three casagrande piezometers (C-1, C-9 and C-10) were installed in the bedrock. Due to the low permeability of the unit, no water could be extracted from hole C-9. However, given sufficient time, C-1 and C-10 produced sufficient water for nitrate testing. C-1 is located under the area of contamination, while C-10 is located east of the contamination plume. Water samples collected from these sites show nitrate concentrations in both areas of the bedrock at 39 mg/L in May, 2001, and 31 mg/L in July, 2001.

Background nitrate concentrations in the overlying units are lower than nitrate concentrations in the underlying bedrock. Nitrate levels in C-4 and C-5 are approximately 25 to 35 mg/L lower than in C-1 and C-10. C-4 and C-5 are completed in overlying units outside the area of contamination while C-1 and C-10 are installed in the underlying bedrock. C-2 is completed in the overlying units at the fringe of the nitrate plume and is only 1 metre horizontally from C-1, yet the nitrate concentrations in C-2 are approximately 20-30 mg/L lower than in C-1.

4.2 CHLORIDE TEST RESULTS

Water samples were collected from selected monitoring wells at the Caledonia research site and tested for chloride concentrations in August, 2001. Chloride (Cl^-) serves as a tracer, which enables quantification of dilution effects on a contamination plume. Liquid manure generally contains high concentrations of Cl^- which is a negative (and soluble) ion similar to NO_3^-, and therefore, it does not adsorb to soil and moves readily in groundwater. However, unlike NO_3^-, Cl^- concentrations are not reduced by biochemical processes. Therefore, reductions in Cl^- levels in a contamination plume are generally caused by dilution, mechanical dispersion or diffusion. Chloride concentrations in monitoring wells at the site are shown in Figure 9.

Chloride levels in the bedrock are much higher than background chloride levels in the overlying units. Chloride concentrations in C-4, which is completed into the overlying units outside the area of contamination., are below 20 mg/L. Tests performed on C-1 show much higher concentrations of chloride (i.e. 2060 mg/L) in the underlying bedrock unit.

The movement and vertical extent of the chloride plume closely resembles the nitrate plume. Chloride levels were highest below the livestock pens at C-13, with levels at 572 mg/L in August, 2001. Chloride leaches into the groundwater below the livestock pens and then decreases in concentration with distance from the pens. The chloride spreads north and northeast of the pens, in the direction of groundwater flow. Chloride levels are reduced to background levels at C-4, which is located 90 metres north of the livestock pens.

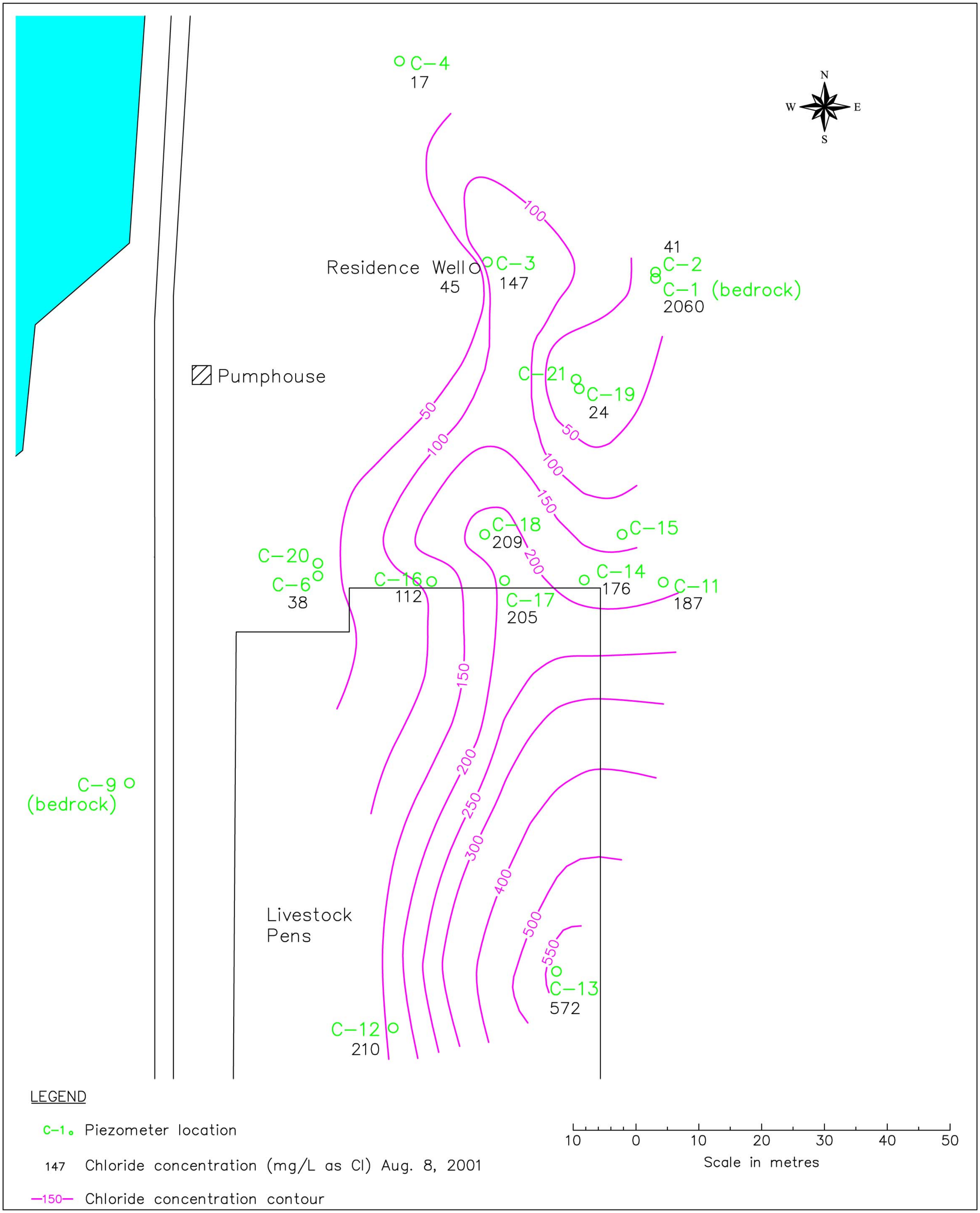


FIGURE 9: Plan of study site showing contours of chloride concentrations

Similar to the nitrate plume, the chloride plume extends to the residence well and chloride levels are lower in the residence well than chloride levels in C-3. In August, 2001, chloride concentrations were at 147 mg/L in C-3 and at 45 mg/L in the residence well. Pumping the residence well may not only impact the nitrates levels in the well, but also the chloride levels. During pumping, groundwater is drawn to the well from both contaminated and uncontaminated areas of the aquifer, resulting in a dilution of the chlorides entering the well.

4.2.1 Nitrate/Chloride Ratios

Nitrate (NO_3^-)/chloride (Cl^-) ratios were used to identify areas where biochemical reduction of nitrates (i.e denitrification) may be occurring at the research site. Nitrate and chloride concentrations are at similar levels below the livestock pens at C-13. Water samples collected from C-13 contained 594 mg/L of nitrate and 572 mg/L of chloride. This provides a NO_3^-/Cl^- ratio of 1.04 in the groundwater where the main source of nitrate leaching is occurring (see Figure 10). Since nitrate and chloride do not adsorb to soil and both move readily in groundwater, the NO_3^-/Cl^- ratio should remain fairly constant in the area of contamination. However, this ratio will change if nitrification or denitrification is occurring in the aquifer. These processes will increase or decrease nitrate levels, but will not impact chloride levels.

Denitrification is likely occurring in the aquifer around C-17, C-14, C-18 and C-19. These wells show a progressive decrease in NO_3^-/Cl^- ratios from 0.98 at C-17 to 0.28 at C-19. At these sites the nitrate concentrations are decreasing at a faster rate than the chlorides. This indicates that denitrification may be occurring in the aquifer around these wells.

Denitrification, as defined by Canter (1997), is the biological reduction of nitrate to gaseous end-products, such as N_2 or N_2O. Nitrogen oxides serve as terminal electron acceptors during denitrification. These nitrogen oxides constitute what is sometimes referred to as the pathway of denitrification, which may proceed as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Certain bacteria are capable of reducing nitrate right through to N_2. However, the combined activities of organisms individually capable of catalysing only one or a few steps of this pathway also bring about denitrification (Ingraham, 1981). Blackburn (1983) describes nitrate reduction as an anaerobic process in which a reduced substrate (e.g. CH_2O, H_2S, H_2) is oxidized at the expense of nitrate. When the product of such a reaction is a nitrogenous gas (i.e. N_2, N_2O), the process is defined as denitrification.

In some monitoring wells, NO_3^-/Cl^- ratios are higher than below the livestock pens at C-13. This indicates that *nitrification* continues below the pens as groundwater moves away from the source of contamination. Water samples collected from C-12 , C-16, C-6 and C-11 show NO_3^-/Cl^- ratios of 1.09, 1.10, 1.16 and 1.15, respectively. Although both chloride and nitrate levels are lower at these sites due to dilution, diffusion and mechanical dispersion, there is a greater reduction in the concentration of chlorides than nitrates. This may be a result of continued nitrate production under the pens where oxygen levels are high.

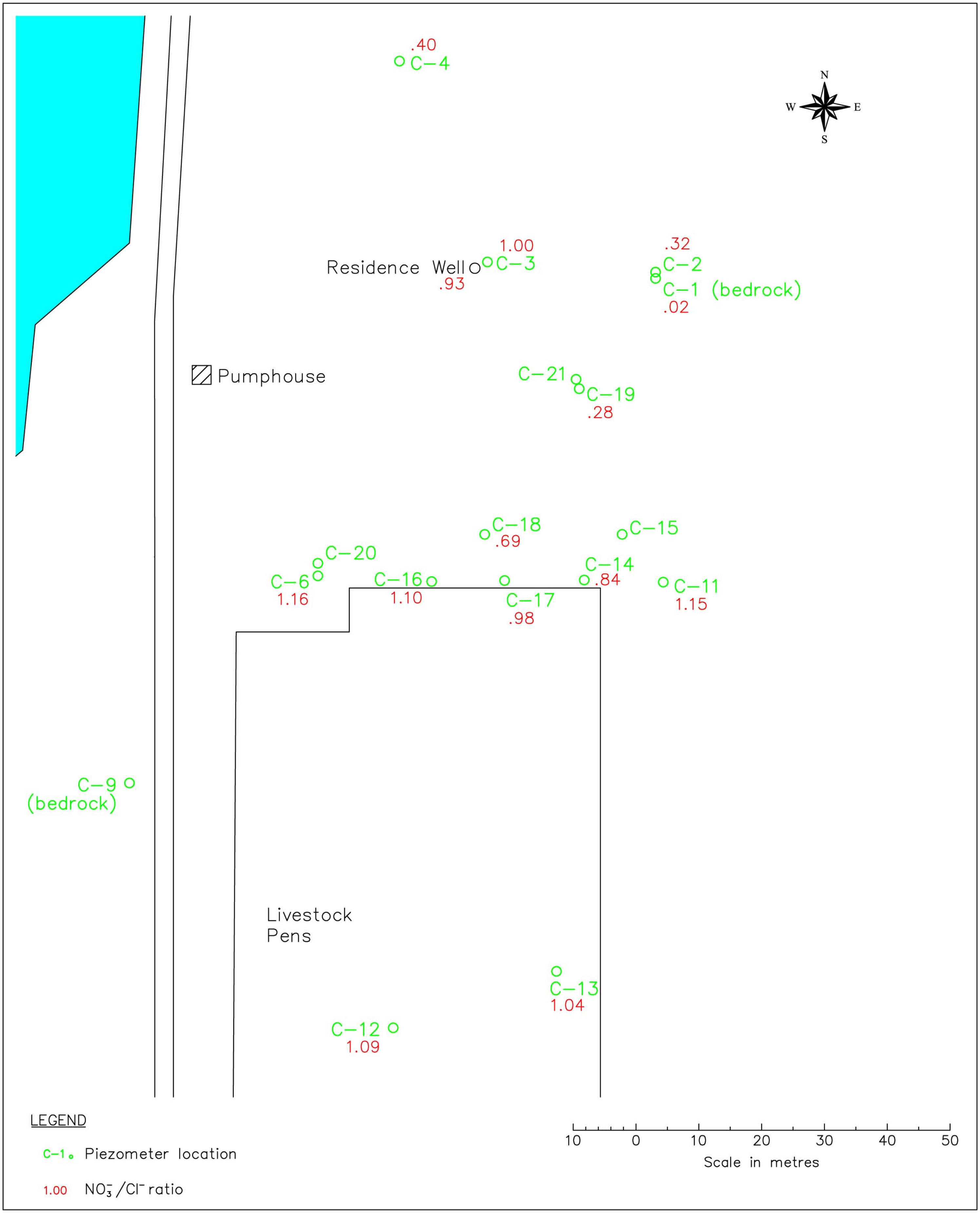


FIGURE 10: Plan of study site showing nitrate/chloride ratios

4.3 DISSOLVED OXYGEN (DO) TEST RESULTS

The level of dissolved oxygen (DO) in soil and groundwater environments can have a significant impact on nitrification and denitrification processes. Generally, oxygen levels must be above 1.0 mg/L for nitrification to occur. However, oxygen concentrations greater than 1.0 mg/L also have an inhibitory effect on denitrification. Denitrification is carried out under anaerobic conditions by either anaerobic or facultative heterotrophic bacteria or by certain chemoautotrophic bacteria.

Heterotrophic bacteria use organic compounds as an energy and carbon source. If available, facultative heterotrophic bacteria will use free dissolved oxygen as the terminal electron acceptor in this process. If oxygen is unavailable, facultative heterotrophic bacteria will use nitrate, nitrite or nitrous oxide as the electron acceptor.

Organisms which obtain cell carbon from an inorganic source (e.g. CO_2) and energy from the oxidation of inorganic chemical compounds are termed ***chemoautotrophs*** (Henry and Heinke, 1989). Certain autotrophic bacteria are capable of denitrification by oxidizing an inorganic compound (e.g. sulfur or sulfide, Fe^{+2}, H_2) for energy, and using carbon dioxide or bicarbonates for synthesis (Kapoor and Viraraghaven, 1997). During this process the inorganic compound acts as an electron donor and nitrate acts as the final electron acceptor (i.e. nitrate is reduced).

Dissolved oxygen levels were monitored in several wells at the Caledonia research site over a six- month period from May, 2001, to February, 2002, and are recorded in Table 1.

Date	Monitoring Wells										
	C-2	C-3	C-6	C-11	C-12	C-13	C-14	C-16	C-17	C-18	C-19
5/9/01	8.1	4.8	0.9	1.7	1	8.8	-	-	-	-	-
5/23/01	5.6	0.6	0.6	0.6	0.9	7.6	-	-	-	-	-
9/18/01	-	-	1.2	1.1	0.9	4	3.8	0.9	0.9	1.6	0.7
10/16/01	1.2	0.7	0.6	0.9	0.7	3.4	2.4	1.1	0.7	0.9	0.7
11/1/01	-	0.9	0.6	1.1	-	-	1.8	1.4	0.7	1.1	0.8
12/5/01	1.2	0.5	1.2	0.5	0.6	2.1	0.7	0.7	0.5	0.6	0.3
2/20/02	4.7	0.9	2.7	0.8	3.4	1.9	0.3	0.9	0.3	0.3	0.8

Table 1 Groundwater Dissolved Oxygen Levels: May 2001 to February 2002

Dissolved oxygen concentrations, below the livestock pens at C-13, were sufficiently high throughout the six-month period to permit conversion of ammonium to nitrate. In May, 2001, DO levels reached 8.8 mg/L at C-13, and although levels decreased over the fall and winter months they still remained above 1.0 mg/L.

The lowest DO levels were recorded in C-14, C-17, C-18 and C-19. The DO levels in each of these monitoring wells reached a low of 0.3 mg/L. This suggests that there may be anaerobic zones in the aquifer around these wells. These monitoring wells also showed a progressive decrease in NO_3^-/Cl^- ratios. The low levels of oxygen in these areas may contribute to denitrification, as nitrate would become the electron acceptor used by facultative denitrifying bacteria instead of oxygen.

4.4 DISSOLVED ORGANIC CARBON (DOC)

Water samples were collected from 8 monitoring wells at the research site in December, 2001, and tested to determine dissolved organic carbon (DOC) concentrations in the groundwater. Test results are provided in Table 2. DOC is a measure of the fraction of total organic carbon (TOC) that passes through a 0.45 µm-pore-diameter filter. These tests were required because insufficient amounts of organic carbon may limit the application of in-situ bioremediation.

Denitrifying bacteria, as with all microorganisms, require a carbon source for cellular growth. They also require a source of energy to propel metabolic reactions. Without sunlight, metabolism requires chemical energy derived from oxidation-reduction reactions. Whenever a microbe degrades an organic substrate for its carbon content and energy needs, electrons are removed from the substrate and passed on to a suitable electron acceptor. In this process, carbon, the electron donor, is oxidized while the electron acceptor (e.g. oxygen or nitrates) is reduced (King, Long and Sheldon, 1998).

For these biotransformations to occur, nutrients must be present in soil and groundwater. Generally an organic source of carbon is required, however, certain chemoautotrophic bacteria use carbon dioxide or bicarbonates for synthesis. Ideally, the C/N/P ratio should be 100/10/1. This ratio corresponds to the approximate ratio of these macronutrients found in microorganisms. It also represents the macronutrient requirements for new microorganism development (2001, Nyer et al). Using this ratio, approximately 230 mg/L of carbon would be required to reduce 100 mg/L of nitrate (i.e @ 23 mg/L as N).

4.4.1 Dissolved Organic Carbon (DOC) Test Results

Dissolved organic carbon concentrations are highest (70 mg/L) in water samples collected from C-13 (see Table 2). This is due to the high levels of organic compounds found in livestock waste. However, very little of these organic compounds reach the groundwater north of the livestock pens. With the exception of C-13 and C-21, each of the wells tested contained DOC levels less than 20 mg/L. This suggests that an additional carbon source will be required in this area of the aquifer to stimulate the growth and activity of indigenous heterotrophic denitrifying bacteria.

Dissolved Organic Carbon Levels (mg/L) in Monitoring Wells								
C-6	C-12	C-13	C-14	C-16	C-17	C-18	C-21	Residence Well
6	18	70	15	15	16	18	33	9

Table 2 Dissolved Organic Carbon Levels: December 2001

4.5 BIOLOGICAL ACTIVITY TEST RESULTS

Biological Activity Reaction Tests (BART™) were used to measure microbial activity in the groundwater at the Caledonia research site. Water samples were collected from 9 monitoring wells in September, 2001, and tested for Denitrifying Bacteria (DN), Heterotrophic Aerobic Bacteria (HAB) and Sulphate Reducing Bacteria (SRB). The BART™ system was developed by Droycon Bioconcepts Inc. and offers a simple method for detecting the presence and activity level of a select group of bacteria in a water sample. Test procedures are described in Appendix E.

DN BART™ s were used to determine the presence of denitrifying bacteria (DN) in groundwater at the research site. These tests were required since in-situ bioremediation becomes a treatment option if test results show the presence of a viable native population of nitrate reducing bacteria. Tests for Heterotrophic Aerobic Bacteria (HAB) and Sulphate Reducing Bacteria (SRB) were performed to identify areas were a natural progression in reduction-oxidation conditions may be occurring.

Two forms of data can be obtained by using the BART™ system: 1) the days of delay (DD) or time lag which is the time elapsed from the addition of water to the biodetectors until the initial reaction occurs, and 2) the reaction type (RX). The DD is used to determine the activity level (e.g. high, medium, low) of a bacteria group. The shorter the days of delay for a reaction to occur, the more aggressive or active the bacteria. The various reactions observed provide an indication of the types of bacteria present in the water sample (Cullimore, 1993).

Table 3 is a summary of the data, supplied by Droycon Bioconcepts Inc., which is used as a guide to determine bacteria activity levels in a water sample. Table 4 shows BART™ results from tests performed in September, 2001.

Bacterial Activity Level	DD Days to Initial Reaction in the IRB BART™	DD Days to Initial Reaction in the DN BART™	DD Days to Initial Reaction in the SRB BART™	DD Days to Initial Reaction in the HAB BART™
High	1 - 4	1 - 2	1 - 6	1 - 2
Medium	5 - 8	any DD greater than 2 suggests Low aggressivity	7 - 8	3 - 4
Low	9 - 10		9 - 10	5 - 10

Table 3 Determining Bacterial Activity Levels

BART™	Days to First Reaction (DD)									
	C-6	C-12	C-13	C-14	C-16	C-17	C-18	C-19	C-21	Residence Well
HAB	3	2	3	2	2	1	2	1	2	6
DN	3	3	3	3	2	2	2	3	2	3
SRB	6	6	6	3	6	6	3	3	6	NR

Table 4 BART™ Results: September 2001

DN BART^{TM} results show denitrifying bacteria present in each of the water samples tested. However, these bacteria were most active in water samples from C-16, C-17, C-18 and C-21. Samples from these monitoring wells caused a DN reaction within 2 days. These results indicate that a viable and active population of denitrifying bacteria can be found in areas of the aquifer which supply groundwater to these sites.

SRB reactions occurred within 3 days in C-14, C-18 and C-19. In general, sulfate reducers require an environment free of oxygen. Therefore, the high levels of SRB activity provide evidence of anaerobic zones near these wells.

Heterotrophic Aerobic Bacteria (HAB) were highly active (i.e DD < 3) in water samples collected from each monitoring well with the exception of C-6, C-13 and the residence well. The residence well and C-6 both contain low DOC levels, which may explain the low levels of heterotrophic activity in these wells, while in C-13, the activities of nitrifying bacteria may decrease HAB activity.

5.0 SUMMARY OF FINDINGS

1. The Caledonia-Elmsthorpe Pasture aquifer is contaminated with nitrate from animal wastes. Livestock pens are located south of the residence well. A nitrate plume originates beneath the livestock pens and extends between 60 to 90 metres north of the pens. Monitoring well C-13, which is located in one of the pens, contains the highest concentrations of nitrate. Although nitrate concentrations decrease with distance from the source, the nitrate plume is moving north and northeast of the pens, which is the direction of ground-water flow.

2. The nitrate plume extends to the residence well causing nitrate concentrations in the well to reach unacceptable levels. Water samples collected from the residence well in October, 2001, December, 2001 and February, 2002, show nitrate concentrations in the residence well exceeded 45 mg/L. However, nitrate concentrations are lower in the residence well than in the groundwater east and south of the well. During pumping, groundwater is drawn to the well from both contaminated and uncontaminated areas of the aquifer. This results in dilution of nitrate entering the well.

3. Nitrate is present in the bedrock (Bearpaw Formation) at the research site. However, nitrate levels in this unit are below maximum acceptable levels. Water samples collected from the bedrock unit, both under the nitrate plume and away from the plume, contain similar concentrations of nitrate. This indicates that nitrate in the bedrock unit is not derived from the livestock pens.

4. Nitrate concentrations are highest in the winter months when groundwater elevations are low. Nitrate concentrations peaked in December, 2001 at C-3, C-6, C-11, C-12, C-13, C-14, C-18 and C-21. This peak in nitrate levels corresponds to a significant drop in groundwater elevations. With less fresh water entering the aquifer there is less dilution of nitrate. In addition to having less fresh water available for dilution, the conversion of ammonium to nitrate (i.e. nitrification) below the pens may be higher during winter months when competition from heterotrophic processes and hydrogen sulphide production is least.

5. Since background levels of chloride are quite low in groundwater at the research site, chloride tests can be effectively used to quantify the effects of dilution on the nitrate plume. Livestock waste generally contains high concentrations of chloride which is a negative (and soluble) ion, and therefore, like nitrate, it does not adsorb to soil and moves readily in groundwater. For this reason the effects of dilution on chloride concentrations are very similar to dilution effects on nitrate concentrations. Nitrate/chloride ratios can also be used to identify areas where nitrate, is reduced by biochemical processes since chloride is not affected by this process.

6. Chloride test results provide further evidence that waste from livestock pens is the source of contamination at the research site. Chloride concentrations in the aquifer are highest below the livestock pens at C-13 and decrease in concentration with distance from the pens.

7. Nitrate (NO_3^-)/chloride (Cl^-) ratios show that denitrification (i.e. biochemical reduction of nitrate) is occurring in some areas north of the livestock pens. The NO_3^-/Cl^- ratio in water samples collected from C-13 and C-12 were 1.04 and 1.09 in August, 2001. Wells C-17, C-14, C-18 and C-19 show a progressive decrease in NO_3^-/Cl^- ratios (e.g 0.98, 0.84 0.69 and 0.28). Although both chloride and nitrate concentrations are decreasing in these wells due to dilution, diffusion and mechanical dispersion, the nitrate concentrations are decreasing at a faster rate than the chloride. This indicates that denitrification may be occurring in the aquifer around these wells.

8. Groundwater, below the livestock pens, contains sufficient dissolved oxygen (>1.0 mg/L) for nitrification (i.e. biochemical oxidation of ammonium) to proceed. In May, 2001, DO levels were up to 8.8 mg/L below the livestock pens at C-13. Although DO levels decreased over the fall and winter months, the DO levels remained above 1.0 mg/L at this location.

9. Anaerobic zones, which support the process of denitrification, may have developed in the aquifer north of the livestock pens near C-14, C-17, C-18 and C-19. DO levels of 0.3 mg/L were recorded in each of these wells at least once during the study period.

10. Denitrifying bacteria are likely present in all areas of the aquifer. However, these bacteria are most active north of the pens around C-16, C-17, C-18 and C-21. Reactions occurred within 2 days when water samples from these wells were tested using the DN Biological Activity Reaction Tests ($BART^{TM}$). Reactions occurring within 2 days indicate that denitrifying bacteria are active in the water sample.

11. Nitrate concentrations will decrease in the aquifer if the source of contamination is removed. Dilution has a significant impact on nitrate concentrations in the aquifer at this site. As the aquifer is recharged the contaminated water is diluted leading to a reduction in nitrate concentrations. This process, along with the process of denitrification which is occurring in some areas of the aquifer, will cause nitrate concentrations to decrease over time, provided that measures are taken to stop nitrate leaching into the groundwater.

12. The low levels of nutritional substrate (i.e. carbon), in the groundwater north of the livestock pens, may be limiting the ability of heterotrophic denitrifying bacteria to fully reduce nitrate entering the aquifer. DOC levels were highest (70 mg/L) in water samples collected from C-13 which is due to

the high levels of organic compounds found in livestock waste. However, very little of these organic compounds reach the groundwater north of the pens. With the exception of C-13 and C-21 each of the wells tested contained DOC levels less than 20 mg/L. The process of denitrification, which is occurring in some areas of the aquifer, may be a result of chemoautotrophic bacterial activity as these bacteria do not require an organic carbon source.

13. The most favourable conditions for in-situ nitrate remediation, are found in the aquifer north of the pens in an area that encompasses C-14, C-16, C-17 and C-18. Wells C-16, C-17 and C-18 contain active populations of denitrifying bacteria. DO tests indicate that anaerobic zones have developed near C-14, C-17 and C-18 and NO_3^-/Cl^- ratios show that denitrification is already occurring to some extent at these sites. However, to completely reduce the level of nitrate in the aquifer, a nutrient substrate (e.g. carbon source) may be required.

6.0 RECOMMENDATIONS

1. Due to the low transmissivity and the discontinuous nature of the aquifer at the Caledonia Elmsthrope site it is unlikely that the entire area of contamination can be remediated. It is therefore recommended that any evaluation of in-situ nitrate remediation technologies be limited to a small area of the aquifer. For the evaluation of in-situ bioremediation, efforts should focus on an section of the aquifer north of the livestock pens near wells C-14, C-16, C-17 and C-18, as this area offers the most favourable conditions for denitrification.

2. A carbon amendment is recommended for the evaluation of in-situ bioremediation. The level of dissolved oxygen in most areas of the contaminated aquifer is generally too high for bioremediation to proceed. Adding a carbon source, to the aquifer, will provide the substrate necessary to increase cellular biomass and will provide the electron donor necessary for oxygen and nitrate reduction. Once the area for in-situ bioremediation evaluation has been established further tests will be required to establish that all other geochemical parameters are adequate for successful remediation to occur.

3. During the Phase 1 investigation, nitrate levels were monitored throughout the aquifer to establish baseline fluctuations in nitrate concentrations with respect to time and seasonal events. It is recommended that regular monitoring continue in all areas of the aquifer during Phase 2 of this study. The nitrate data collected during Phase 1 and Phase 2 of the study, along with the nitrate/chloride ratios, will provide the information needed to distinguish between natural nitrate fluctuations and nitrate reductions resulting from mitigation or remediation efforts.

7.0 REFERENCES

1. Canter, Larry W., 1997. **Nitrates in Groundwater**. Boca Raton, Florida: Lewis Publishers.

2. Cullimore, D.R., 1993. **Practical Manual of Groundwater Microbiology.** Chelsea, Michigan: Lewis Publishers.

3. Blackburn, T. Henry, 1983. **Microbial Geochemistry**. Oxford: Blackwell Scientific Publications.

4. Delwiche, C., 1981. **Denitrification, Nitrification, and Atmospheric Nitrous Oxide.** New York, NY: John Wiley & Sons.

5. Henry, Glynn J.; Heinke, Gary W., 1989. **Environmental Science and Engineering.** New Jersey: Prentice-Hall Inc.

6. Ingraham, John, 1981. **Microbiology and Genetics of Denitrifiers.** New York, NY: John Wiley & Sons.

7. Kapoor, A.; Viraraghavan, T., 1997. **Nitrate Removal From Drinking Water - Review. Journal of Environmental Engineering.** Vol 123, No 4

8. King, Barry R.; Long, Gilbert M.; Sheldon, John K.; 1998. **Practical Environmental Bioremediation-The Field Guide.** Boca Raton, Florida: Lewis Publishers, CRC Press.

9. McCarty, Perry; Parkin, Gene; Sawyer, Clair, 1994. **Chemistry For Environmental Engineering.** New York, NY: McGraw Hill, Inc.

10. Nyer, Evan K.; Boettcher, Gary, 2001. **In Situ Treatment Technology (Second Edition) Chapter 7.** Boca Raton, Florida: Lewis Publishers, CRC Press.