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GRADE / DEGREE

Faculty of Science

FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Nitrate and Ammonium Transformation and Fate in Groundwater of an Agricultural Watershed : An Isotope and Geochemistry Approach

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Nitrate and Ammonium Transformation and Fate in Groundwater of an Agricultural Watershed: An Isotope and Geochemistry Approach

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Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
University of Ottawa

In partial fulfillment of degree requirements for a

Masters of Science (M.Sc.)
in Earth Sciences

Ottawa-Carlton Geoscience Centre
and
University of Ottawa
Ottawa, Canada

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ISBN: 978-0-494-79695-5
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ISBN: 978-0-494-79695-5

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ABSTRACT

The management of soil fertility to augment crop yields has been the pre-occupation of farmers for thousands of years. In agricultural environments, the use of synthetic fertilizers and animal manure has the potential to contaminate underlying aquifers and the surface waters into which they discharge. As such, a proper understanding of the nitrogen dynamics involved is critical to the health of the environment.

The purpose of this study was to characterize the groundwater recharge environment and evaluate the fate and processes affecting agricultural nutrients in groundwater. This consisted of three agricultural sites and one naturally vegetated background site. The fields were located in the intensely cultivated Raisin River watershed of eastern Ontario, where approximately 45% of land cover is used for crop or pasture. One field used only urea fertilizer, a second used a mostly manure with minor urea, while the third applied both manure and urea during corn rotations. Samples were collected monthly over a 15 month period between August 2005 and October 2006 from a series of piezometers, tile drains, suction-lysimeters and domestic wells. In addition, three meteoric stations were setup with the participation of home owners to measure precipitation and collect samples to evaluate the meteoric isotopic input signal.

Naturally occurring stable isotopes ($\delta^{18}O$ and $\delta^{2}H$), which are sensitive to seasonality of recharge, were used in groundwater and precipitation to provide an estimate of recharge and mass loading to the aquifer. The significance of direct infiltration through cultivated corridors where corn is grown (C_4 vegetation), versus naturally forested C_3 vegetation, which is predominant in the headwater environment, $\delta^{13}C$ analysis of DIC and DOC were conducted. To assess geochemical reactions, isotopes of nitrate and ammonium ($\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NH4}$) were used to provide insights into the transformation and attenuation processes in the nitrogen cycle.

Groundwater $\delta^{18}O$ and $\delta^{2}H$ results indicate that recharge occurs predominantly in late fall as photosynthetic transpiration declines and in late spring following spring thaw, when vegetation is inactive. The abundance of wormholes observed in an excavated test pit, suggests macro-porosity in the sediments aids the infiltration and contributes to the rapid transmission of the meteoric signal to the water table and thus accounting for the rapid shift in trends observed in the temporal monitoring in the overburden material.

Observations of shallow groundwater suggest the presence and concentrations of NO_3 and NH_4 may be dependent on the type of fertilizer application. The presence and attenuation of nitrate and ammonium varied between the three agricultural sites. There was no one dominant attenuation process throughout, nor were nitrate and ammonium consistent in the unsaturated zone and groundwater. Findings indicate the urea only site has possibly longer retention of NH_4 in soil water, low concentrations of NH_4 but the presence of moderately higher NO_3 concentrations (up to 20 ppm-N) in shallow groundwater. The infiltration of nitrified NO_3 appears to be followed by some level of denitrification, resulting in bedrock aquifer NO_3 concentrations below 5 ppm-N. Observations from the agricultural site where liquid manure was the dominant fertilization method, suggest the chronic loading of NH_4 in the subsurface. There is possibly less retention of NH_4 in soil water (> 20 ppm-N), resulting in the infiltration of NH_4 (2 ppm-N in piezometers), while NO_3 concentrations in shallow groundwater are below detection. Lastly, the mixed application site shows the presence of both NO_3 and NH_4 at similar concentration in shallow groundwater, with nitrogen attenuation by dilution, denitrification and potentially anammox.

Overall, irrespective of the type of fertilization, findings suggest that reactive losses of nitrogen together with crop uptake, greatly limit the total nitrogen flux that is reaching the underlying bedrock aquifer, indicating that agricultural activities do not have an excessive adverse impact on the aquifer. While total nitrate and ammonium concentrations of nitrogen in the unsaturated zone, as sampled in the lysimeters and tile drains reached over 30 ppm-N, concentrations in groundwater were typically <10 ppm-N, and most often <0.5 ppm-N in the bedrock aquifer. The attenuation of high ammonium concentrations in soil water was attributed to plant uptake prior to recharge to the water table, with minor loss by volatilization as groundwater ^{15}N values exhibited slight enrichment.

Geochemical and isotopic results from a couple domestic wells exhibited signs of leaking well casings/seals, thus permitting potentially contaminated surface and/or shallow groundwater to enter the well, thereby potentially impacting the groundwater resource. If the proportion of such wells is significant throughout the region, this represents a principle threat to water quality.

This study provides insight into attenuation processes affecting nitrogen species and the effects on groundwater conditions from differing fertilizer applications.

RÉSUMÉ

La gestion de la fertilité des sols pour augmenter les rendements des cultures a été la préoccupation des agriculteurs pour des milliers d'années. Dans les milieux agricoles, l'utilisation d'engrais synthétiques et le fumier animal a le potentiel de contaminer les nappes phréatiques et les eaux de surface dans lesquels ils s'acquittent. En tant que tel, une bonne compréhension de la dynamique de l'azote en cause est essentielle à la santé de l'environnement.

Le but de cette étude était de caractériser l'environnement recharge des eaux souterraines et d'évaluer le devenir et les processus affectant les éléments nutritifs agricoles dans les eaux souterraines. Il s'agissait de trois sites agricoles et un site de fond de végétation naturelle. Les champs étaient situés dans le bassin intensément cultivée de la rivière Raisin a l'est de l'Ontario, où environ 45% de couverture des terres est utilisée pour des cultures ou le pâturage. Un terrain utilisé d'engrais d'urée seulement, un deuxième a utilisé principalement du fumier avec de l'urée mineures, tandis que le troisième s'applique à la fois du fumier et d'urée au cours des rotations maïs. Les échantillons ont été collectés chaque mois sur une période de 15 mois entre Août 2005 et Octobre 2006 à partir d'une série de piézomètres, drains, lysimètres d'aspiration et les puits domestiques. En outre, trois stations météorique ont été d'installation avec la participation des propriétaires de maison à la mesure des précipitations et de recueillir des échantillons pour évaluer le signal d'entrée isotopique.

Les isotopes stables ($\delta^{18}O$ et $\delta^{2}H$), qui sont sensibles à la saisonnalité de la recharge, ont été utilisés dans les eaux souterraines et des précipitations pour fournir une estimation de la recharge et la masse de chargement de l'aquifère. L'importance de l'infiltration directe à travers les corridors cultivées où le maïs est cultivé (C_4 végétation), par rapport à la végétation naturelle boisée (type C_3), qui est prédominante dans l'environnement amont, l'analyse $\delta^{13}C$ de la DIC et le DOC ont été menées. Pour évaluer les réactions géochimiques, les isotopes de nitrate et d'ammonium ($\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ et $\delta^{15}N_{NH4}$) ont été utilisés pour fournir des indications sur les processus de transformation et d'atténuation dans le cycle de l'azote.

Les résultats $\delta^{18}O$ et $\delta^{2}H$ des eaux souterraines indiquent que la recharge se produit principalement lorsque la végétation est inactif, en fin d'automne quant la photosynthèse et la transpiration se baisse, et après le dégel du printemps. L'abondance des trous de ver observé

dans une fosse de contrôle, suggère que la macro-porosité dans les sédiments aides l'infiltration et contribue à la transmission rapide du signal météorique de la nappe phréatique et donc tenir compte du déplacement rapide des tendances temporel observées dans le matériau souterraines.

Les eaux souterraines peu profondes suggèrent la présence et les concentrations de NO_3 et NH_4 peut dépendre du type de l'application d'engrais. La présence et l'atténuation du nitrate et l'ammonium et variait entre les trois sites agricoles. Il n'y avait pas de processus d'atténuation plus dominante tout au long, ni nitrates et d'ammonium ont été cohérents dans la zone non saturée et les eaux souterraines. Les résultats indiquent que le site d'urée a de rétention peut-être plus de NH_4 dans l'eau du sol, de faibles concentrations de NH_4, mais la présence de concentrations légèrement plus élevées de NO_3 (jusqu'à 20 ppm-N) dans les eaux souterraines peu profondes. L'infiltration de NO_3 nitrifié semble être suivi par un certain niveau de dénitrification, avec les résulta que l'aquifère profonde a des concentrations de NO3-dessous de 5 ppm-N. Observations sur le site agricole où le fumier liquide est la méthode de fertilisation dominante, suggèrent le chargement chronique de NH_4 dans le sous-sol. Il ya peut-être moins de rétention de NH_4 dans l'eau du sol (> 20 ppm-N), résultant de l'infiltration de NH_4 (2 ppm-N dans les piézomètres), tandis que les concentrations de NO_3 dans les eaux souterraines peu profondes sont inférieurs à la détection. Enfin, le site d'application mixtes montre la présence de NO_3 et NH_4 à une concentration similaire dans les eaux souterraines peu profondes, avec une atténuation d'azote par dilution, la dénitrification et potentiellement l'anammox.

Dans l'ensemble, quel que soit le type de fertilisation, les résultats suggèrent que les pertes d'azote réactif avec absorption par les cultures, limite fortement les flux d'azote total qui atteint l'aquifère du substratum rocheux, ce qui indique que les activités agricoles n'ont pas un impact trop négatif sur l'aquifère. Bien que les concentrations du nitrate et l'ammonium dans la zone non saturée, comme détecter dans les échantillon des lysimètres et les drains souterrains ont atteint plus de 30 ppm-N, les concentrations dans les eaux souterraines ont été typiquement <10 ppm-N, et le plus souvent <0,5 ppm-N dans l'aquifère du substratum rocheux. L'atténuation des concentrations d'ammonium dans l'eau du sol élevée a été attribuée à absorption par les plantes avant de recharger la nappe phréatique,

avec une perte par volatilisation mineures que les eaux souterraines ^{15}N valeurs exposées léger enrichissement.

Les résultats géochimiques et isotopiques à partir des quel que puits domestique présentait des signes de fuite tubages de puits et joints, ce qui permet de potentiellement permettre la pénétration des le puits par des eaux contaminés, ce qui pourrait un impact sur la ressource en eau souterraine. Si la proportion de ces puits est importante dans toute la région, cela représente une menace principe de qualité de l'eau. Cette étude donne un aperçu des processus d'atténuation affectant les espèces d'azote et les effets sur les eaux souterraines à partir des applications d'engrais différents.

ACKNOWLEDGEMENTS

First and foremost, special thanks go to my supervisor Dr. Ian Clark, for giving me the opportunity to participate in this project, for his enthusiasm and financial commitment to develop the isotope analysis methods locally, for his insight, and at the end his patience for never failing to believe that I would get this done. I would like to thank Dr. Michel Robin for leading and coordinating the Watershed and Environmental Research Assessment Project (WERAP), and to the Canadian Water Network for funding the holistic study of the Raisin River watershed. I thank my committee members, Dr. Francis Pick and Dr. Fred Michel for their helpful and constructive comments.

The installation of numerous piezometers, and groundwater sampling over a 15 month period could not have been done without the assistance of many others. Thanks go to all the graduate students who helped out in the field, while having their own busy programs on the go. Also, thanks to Dr. Brewster Conant Jr. from the University of Waterloo, for providing and operating the GPS survey equipment. From the various labs, I thank Paul Middlestead at the G.G. Hatch Stable Isotope Laboratory, for the hours of help setting up, trouble shooting and rebuilding the instrumentation to run my nitrate isotopes. From Dr. Clarks Geochemistry Lab, I thank Monika Wilk and particularly Ping Zhang for helping in preparing the denitrifier bacteria. From Dr. Lean's lab in CAREG, I thank Serena Maharaj for analysing the ammonium and total phosphorus samples.

And last but not least, I thank my wife Vetina, for uprooting and moving to Ottawa for a couple years, and her patience afterwards as I struggled to complete this thesis. I couldn't have done it without your support.

1.0 INTRODUCTION

1.1. Background

The following thesis study was part of a larger Canadian Water Network (CWN) and Eastern Ontario Water Resources Committee (EOWRC) funded research project called the Watershed & Environmental Resource Assessment Project (WERAP), which assembled several scientific disciplines to holistically monitor and assess the health of an agricultural watershed. The main focus of the project was the Raisin River watershed, of Eastern Ontario, with field work being conducted in 2005 and 2006. The overall project consisted of four main disciplines: Geography, Biology, Aquatic Chemistry / Biochemistry and Hydrogeology. This project engaged many of the problems associated with agricultural and rural landscapes and communities. Social Geography was applied to understand the activities and perceptions of those using the river, ecological indicators were evaluated, genomics was used to study the amphibian population health, geochemistry was used to evaluate the rivers nutrient, pesticide load and methyl mercury levels, and finally, the hydrogeology component investigated groundwater recharge, nitrate dynamics and groundwater discharge *[WERAP, 2006]*.

Other hydrogeological related graduate theses undertaken concurrently for the WERAP project included: Drag-probe electrical Conductivity Survey of the Castor and Raisin River Used to Determine Deep Groundwater Discharge, by Elyse Bustros-Lussier, and Using Ecohydrology to Predict Algal Biomass in the Raisin River Watershed, Ontario, Canada, by Lieserl Woods, both of the Department of Earth Sciences at the University of Ottawa.

1.2 Scope of Work

The increased use of synthetic nitrogen fertilizers in the last 100 years has resulted in an almost 20-fold increase in application rates, resulting in a current global rate of 1 billion tons of nitrogen annually *[Glass, 2003]*. Combined with the use of animal manure, agricultural environments have the potential to contaminate underlying aquifers. However, previous studies in the Raisin River Watershed *[Cane, 1996; Porter, 1996]*, have

demonstrated that the underlying contact zone bedrock aquifer, from which approximately 83% of the domestic wells draw their water *[Singer et al., 2003]*, is not adversely impacted with elevated nitrate concentrations above the drinking water nitrate standard of 10 mg/L-N *[Health Canada, 2008]*. As such, this thesis aims to determine what is occurring between the surface and the underlying bedrock aquifer.

The Raisin River watershed is located in Eastern Ontario and drains into the St. Lawrence River (Lake St. Francis) east of Cornwall, Ontario (Figure 1.1). This watershed was chosen as part of the WERAP project because it was representative of a small agricultural watershed which flows into the St. Lawrence River, which was previously identified as part of the Cornwall Area of Concern (AOC), and where a Remedial Action Plan (RAP) was initiated in 1987 *[Environment Canada, 2008]*.

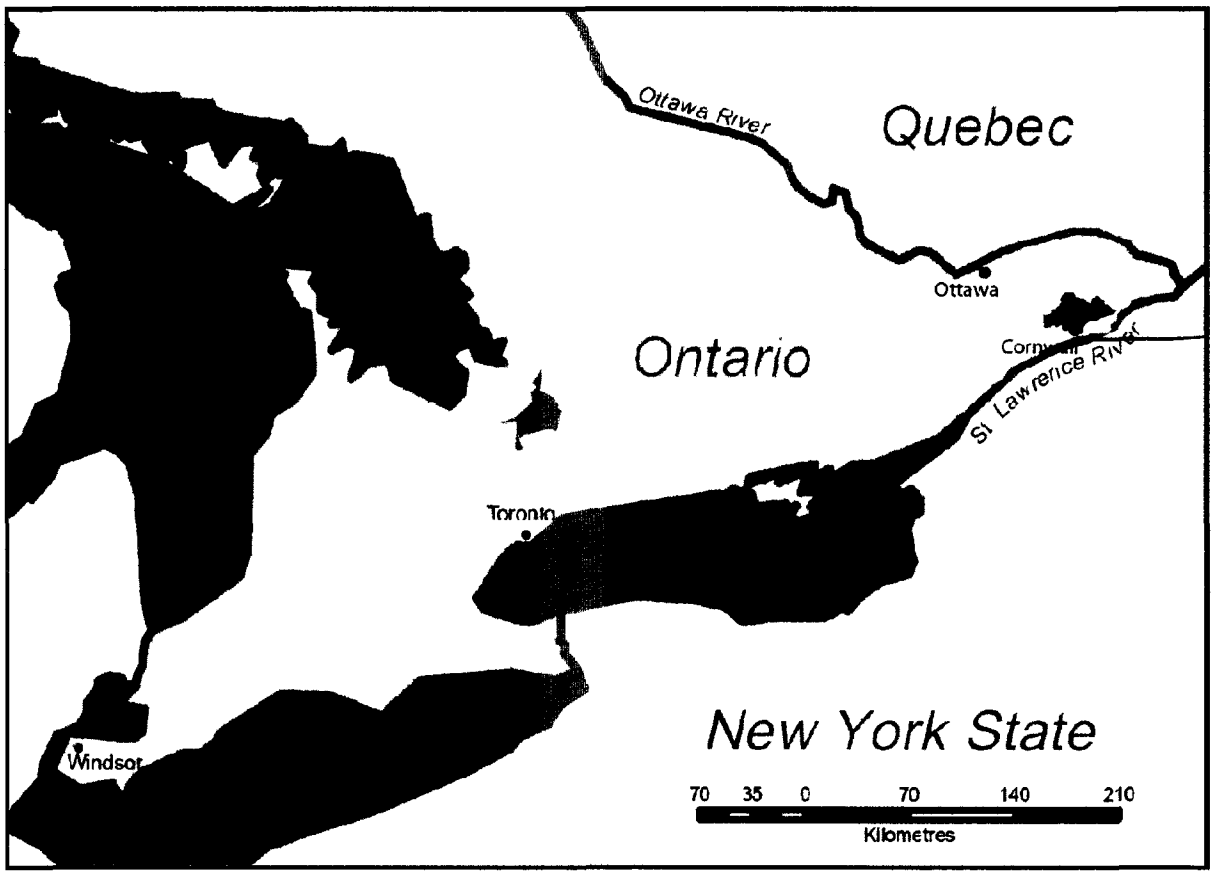

Figure 1.1: Location of the Raisin River watershed (red) within Eastern Ontario, Canada. Reproduced from *[Raisin-South Nation SWPR, 2007]*.

1.3 Objectives

The overall objective of this investigation is to evaluate subsurface nitrogen pathways, transformations, attenuation processes and their seasonal variations within the agricultural watershed. Specifically: (1) monthly precipitation samples were collected to establish seasonal trends in $\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$ values, determine any local variations at different meteoric stations, and to compare against the Ottawa meteoric water line (2) naturally occurring stable isotopes ($\delta^{18}O_{H2O}$, $\delta^{2}H_{H2O}$ and $\delta^{13}C_{DIC}$,), which are sensitive to seasonality of recharge, were used to examine temporal variations, and provide an estimate of recharge and mass loading to the aquifer; (3) ,$\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, and $\delta^{15}N_{NH4}$ provided insight into nitrogen attenuation (namely plant uptake, geochemical transformations and dilution). In addition to the environmental isotopes identified above, nutrients (NO_3^-, NH_4^+ and PO_4^{2-}), dissolved organic and inorganic carbon (DOC and DIC) and major ion concentrations were measured monthly to reconstruct the seasonal variations of biogeochemical reactions involving DOC and nitrogen species as they recharge through the agricultural setting. These parameters are key elements in assessing the groundwater impacts on the river, and the ecotoxicology and ecology component of the greater multidisciplinary project.

2.0 LITERATURE REVIEW

2.1 Introduction

In Canada, almost one third of the population (30.3%), more than 10 million people, rely on groundwater as a primary source of drinking water *[Statistics Canada, 1996]*. More then 80% of the rural population depends on groundwater for its entire water supply, while in Ontario 28.5% of the population actively relies on groundwater *[Canadian Council of Academies, 2009]*. Groundwater is a critical natural resource which is often taken for granted, but is subject to significant threats including: climate change, industrialization, urbanization, and agricultural intensification, that in rural environments results in pollutants such as pathogens, pesticides, and nutrients being found in shallow drinking water wells. Events such as the tragic groundwater contamination of municipal water by pathogenic *E. coli* in Walkerton, Ontario in May of 2000, remind us of the vulnerability of the resource. However, of all agricultural contaminants in rural groundwater, nitrate is the most widespread in exceeding drinking water standards in North America. It is estimated that between 5 - 46% of drinking water wells exceed the nitrate standard of 10 mg/L-N *[Spalding and Exner, 1993; Goss et al., 1998; Wassenaar et al., 2006; Health Canada, 2008]*, while an estimated 57% contain elevated concentrations *[USEPA, 1990]*.

The consumption of nitrate from drinking water sources can be a health concern. In the human body, an estimated 10% of nitrate intake is reduced to nitrite, which is formed from ammonium and nitrate by micro-organisms in the stomach and mouth. It is then rapidly absorbed from the stomach into the blood stream where it forms methaemoglobin because nitrite oxidizes the iron in heamoglobin to the ferric state *[Kendall, 1998]*. The result is that the molecule is no longer able to complex with oxygen, thereby potentially resulting in hypoxia. Methaemoblobinemia (blue baby syndrome) in infants under 6 months, results from high levels of nitrite, and indirectly from nitrate *[Canter, 1997]*.

2.2 Nitrogen Dynamics

The nitrogen cycle is one of the most important nutrient cycles in the terrestrial ecosystem. Nitrogen is found in various forms, and is used by organisms to produce many

complex organic molecules like proteins, amino acids and nucleic acids. Nitrogen accounts for 4% of plant matter and 3% of animal matter, while the atmosphere contains 78.08% nitrogen (N_2 gas) *[Canter, 1997]*. Nitrogen is however often the most limiting nutrient for plant growth as most plants can only take up nitrogen in two ionic forms: nitrate (NO_3^-) and ammonium (NH_4^+); because the energy required to convert atmospheric nitrogen to usable forms is limited as a result of the strong bond of the N_2 molecule. Nitrogen and oxygen dynamics in soil and groundwater are regulated by both biologically-mediated reactions and physical processes, where isotope fractionation is possible at each step of a reaction *[Kendall, 1998]*. The resulting fractionations provide a tool in isotope hydrogeology to distinguish between nitrogen from various sources and evaluate transformation processes in agricultural settings *[Kendall, 1998; Clark and Fritz, 1997; Canter, 1997]*. Fractionation depends on local environmental conditions, the reservoir size for each compound, the type and number of reactive steps, and available organisms *[Kendall, 1998]*. The schematic representation of the flow of nitrogen through the agricultural ecosystem, and the transformation processes affecting $\delta^{15}N$ and $\delta^{18}O$ values is presented in Figure 2.1. Bacteria are critical to nitrogen cycling, as they provide different forms of nitrogen available to higher organisms *[EPA, 2007]*.

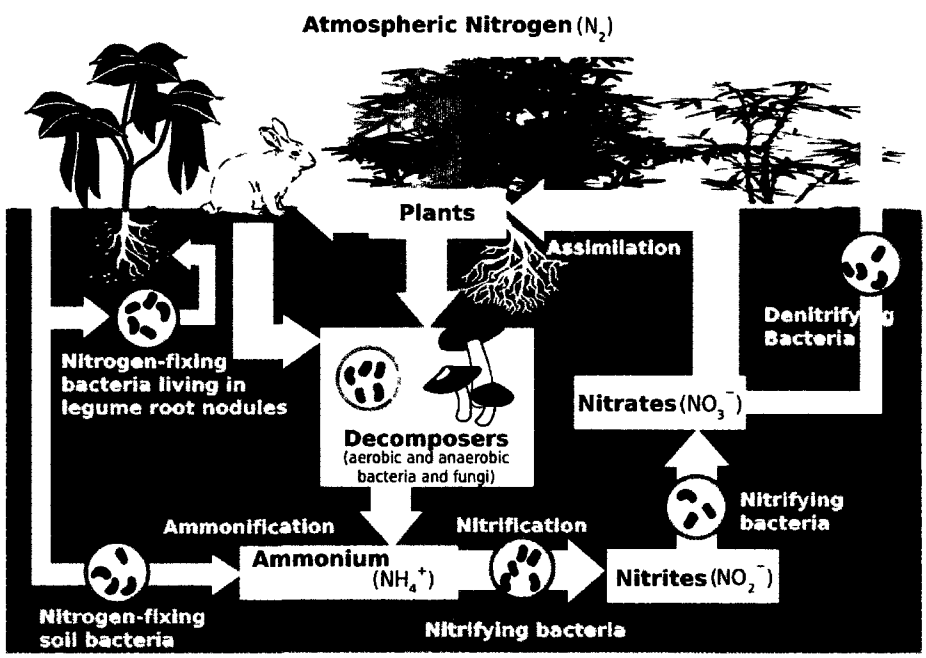

Figure 2.1: The Nitrogen Cycle. Reproduced from *EPA, [2007]*.

2.2.1 *Isotope Fundamentals*

Globally, there are two stable nitrogen isotopes: ^{15}N and ^{14}N, with ^{14}N accounting for 99.634%, while there are three stable isotopes of oxygen ^{16}O, ^{17}O and ^{18}O *[Canter, 1997]*. Because measuring the absolute abundance of stable isotopes is difficult and expensive, isotope abundances are measured with respect to international references whose isotopic content is known. Both nitrogen and oxygen are measured as a ratio relative to the most abundant isotope for each element ($^{15}N/^{14}N$ and $^{18}O/^{16}O$), and expressed in parts per thousand (i.e. permil ‰) with the delta (δ) notation, either higher or lower then their respective standard references. Isotopic composition of nitrogen samples is reported relative to air (AIR), while the reference standard material for oxygen is Vienna Standard Mean Ocean Water (VSMOW), according to Equation 2.1:

$$\delta(‰) = (R_{sample}/R_{standard} - 1) \times 1000 \qquad (2.1)$$

Where $\delta(‰)$ is the isotopic ratio relative to a standard, R_{sample} (i.e. $(^{15}N/^{14}N)_{sample}$) and $R_{standard}$ represent the atomic ratios in the sample and reference material, respectively. Positive values imply the sample contains more of the isotope of interest than the standard (enrichment), while negative values imply less (depletion).

2.2.2 *Isotope Fractionation*

The nitrogen stable isotope, along with hydrogen, carbon, oxygen and sulphur, are considered light elements, which bestow large relative mass differences in their isotopes, resulting in an easily measurable fractionation from thermodynamic reactions. Different transformation processes (i.e., thermodynamic reactions) lead to isotope fractionation because of differences in rates of reaction between various molecular species, resulting in disproportionate amounts of one isotope over another. These reactions can be driven by either physiochemical or biological processes, and viewed either as reversible *equilibrium* reactions, or irreversible *kinetic* reactions. Both processes result in significant isotope fractionation, and are commonly modeled using Rayleigh equations *[Kendall, 1998]*. For equilibrium reactions, the ratio of isotope ratios for the reactant and products is defined as

the fractionation factor (α), expressed as Equation 2.2, where R is $^{15}N/^{14}N$. In low temperature environments (groundwater), kinetic fractionations are typically more relevant than equilibrium fractionation effects, with the fractionation factor expressed as Equation 2.3 *[Clark and Fritz, 1997]*. The fractionation between two compounds can also be expressed as an isotope enrichment factor (ε), where the isotopic difference in ‰ notation is defined by Equation 2.4.

$$\alpha_{reactant\text{-}product} = (R_{reactant}/R_{product}) \quad (2.2)$$

$$\alpha_{product\text{-}reactant} = (R_{product}/R_{reactant}) \quad (2.3)$$

$$\varepsilon_{product\text{-}reactant} = (\alpha_{product\text{-}reactant} - 1) \times 1000 \quad (2.4)$$

Additional information on the effects of isotopic fractionation from reactions is discussed in section 2.2.3.

2.2.3 Transformation Processes

There are several transformational processes affecting nitrogen-bearing compounds such as nitrate and ammonium, and it is therefore important to understand how this cycling affects the isotopic composition of these forms of nitrogen. Figure 2.2 illustrates both biochemical and physiochemical transformation processes that result in the oxidation and reduction of nitrogen, and its isotope fractionation *[Böhlke et al., 2006]*. Many processes consist of multiple steps, each of which has the potential for fractionation. The overall fractionation is dependant on the intermediate steps, along with environmental conditions such as size of compound reservoirs, soil pH, and types of organisms *[Kendall et al., 2007]*. However, typically it is the rate-determining (slowest step) that causes most of the fractionation. Rate-limiting steps are often large reservoirs of substrate, where only small amounts react slowly at one time. Conversely, non rate-limiting steps are generally small reservoirs that react quickly from reactant to product, resulting in limited net fractionation.

The primary microbial mediated reactions in ecosystems that control nitrogen dynamics are: fixation, mineralization, assimilation, nitrification and denitrification. Unless the entire reactant pool is consumed (reaction goes to completion), these reactions will result

in an increase of the $^{15}N/^{14}N$ ratio of the substrate and decrease of $^{15}N/^{14}N$ ratio of the product *[Kendall et al., 2007]*. The volatilization of ammonia, which is a physical process, also results in the enrichment of the $^{15}N/^{14}N$ ratio of the residual NH_4^+ reactant. These processes are discussed below.

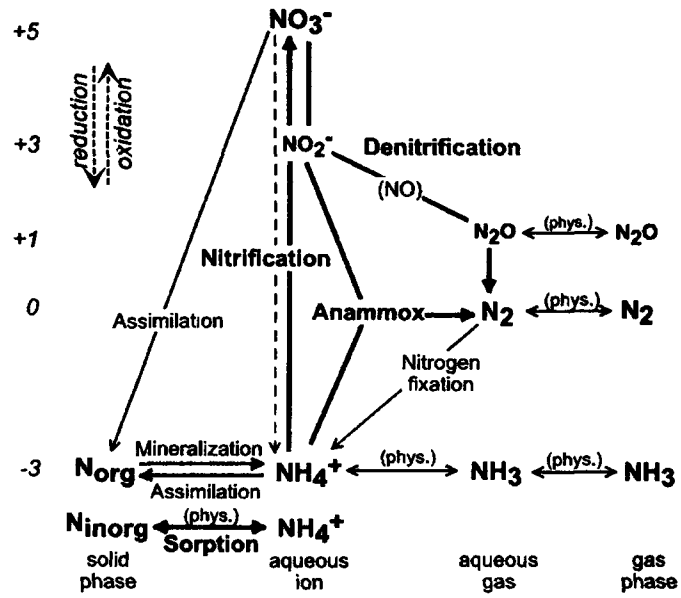

Figure 2.2: Biochemical and physiochemical nitrogen transformations. Repreduced from *[Böhlke et al., 2006]*.

Fixation

Fixation refers to the process where unreactive atmospheric N_2 is converted into other forms of nitrogen such as NH_4^+. The process typically refers to the fixation by bacteria, but can also include lightning, and human activities (i.e., energy production, fertilizer production and crop cultivation) which produce reactive N *[Kendall, 1998]*. Bacteria and algae that possess the *nitrogenase* enzyme are primarily responsible for N_2 fixation that commonly produces organic materials with $\delta^{15}N$ values slightly less then 0 ‰, and fractionation ranging from -3 to +1 ‰. *[Kendall et al., 2007]*.

Mineralization

Mineralization, also known as ammonification or remineralization, refers to the aerobic and anaerobic microbial conversion of organically-bound nitrogen, which is a component of all proteins and plant biomass, to the reduced inorganic nitrogen as ammonium (NH_4) *[Pierzynski et al., 2005; Kendall et al., 2007; Kendall, 1998]*, see Figure 2.2. It should be noted that more then 95% of the reduced soil N is in the organic form *[Kendall and Aravena, 2000]*. There is only a small fractionation (±1‰) between soil organic matter and NH_4^+ *[Kendall, 1998]*. When this occurs in unsaturated materials such as soils or manure, the ammonia can volatilize, or dissolve into water. Volatilization would result in additional fractionation (see section on Volatilization). Organic N can be naturally present in soils, may be added as manure or urea, or released during the decay of biomass *[Kendall, 1998]*. Mineralization is a necessary process for terrestrial plants that are not able to fix atmospheric nitrogen. Ploughing or tilling generally increases mineralization of soil organic N due to soil aeration, thereby increasing the availability of oxygen for microbial activity *[Kreitler et al., 1975]*. Urea ($CO(NH_2)_2$) an organic compound that is often applied as a granular fertilizer, will begin decomposing as soon as it is applied to the soil. For dry soils, typically no reaction will occur. However, in even slightly moist soils it will be broken down by bacterially mediated reactions (*urease* enzyme), which will cause urea to hydrolyze and release ammonia and carbon dioxide for plants (Equation 2.5) *[Overdahl et al., 2007]*:

$$CO(NH_2)_2 + H_2O + \text{urease} \rightarrow 2NH_3 + CO_2 \qquad (2.5)$$

Assimilation

Assimilation, also known as immobilization, refers to the transformation of inorganic nitrogen-bearing compounds (i.e., nitrate and ammonium) into organically-bound nitrogen by living organisms during biosynthesis. Typically oxidized forms of N are first reduced to NH_4^+ then assimilated to organic matter *[Kendall et al., 2007]*. As with other biological reactions, assimilation results in isotope fractionation, with a large range of N fractionation (-30 to 0‰) reported in field studies, while there is limited research of the effects of $\delta^{18}O$ fractionation during assimilation of residual NO_3. There is evidence of strong 1:1 fractionation changes in the $\delta^{15}N$ and $\delta^{18}O$ of nitrate *[Kendall et al., 2007]*. However,

because ammonium concentrations are often low in soils and aquatic environments, the availability of nitrogen may be the limiting condition, resulting in a low (<4‰) overall fractionation *[Kendall et al., 2007]*.

Nitrification

Nitrification is a multi-step biologically driven process where organic and inorganic nitrogenous compounds are converted from a reduced state to a more oxidized state *[Wetzel, 2001]*. The reactant NH_4^+ may originate as fertilizers, septic waste, manures, and mineralized soil organic N. Various aqueous (NO_2^-) and gaseous (NO and N_2O) intermediate compounds can also be produced during nitrification, and released into the environment. It is mediated by autotrophic organisms (bacteria and fungi) for the purpose of obtaining metabolic energy *[Kendall, 1998]*. Equation 2.6 shows the first step (NH_4^+ to NO_2^-), which is mediated by *Nitrosomonas* (Nitrobacteriacea), followed by oxidation of NO_2^- to NO_3^- by *Nitrobacter* bacteria, as shown by the following (Equation 2.7) reaction *[Alexander, 1965; Kendall, 1998]*. Nitrification conditions must be aerobic, where dissolved oxygen levels must exceed 0.3 mg/L *[Wetzel, 2001]*. Regardless of the source, nitrification will generate acidity due to the release of protons (H^+), as shown in Equations 2.6 and 2.8. Equation 2.8 shows the complete process from NH_4^+ to NO_3^- *[Freeze and Cherry, 1979]*.

$$NH_4^+ + 1½O_2 \leftrightarrow 2H^+ + NO_2^- + H_2O \quad (2.6)$$

$$NO_2^- + ½O_2 \leftrightarrow NO_3^- \quad (2.7)$$

$$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3^- + H_2O \quad (2.8)$$

In addition, the resulting acidification causes the replacement of hydrogen, and aluminum ions on calcium and magnesium exchange sites, resulting in the leaching of Ca^{2+} and Mg^{2+} *[Brady and Weil, 2002]*.

During nitrification the sources of N and O atoms are unrelated, and therefore considered "decoupled". Nitrogen atoms originate from NH_4^+ and/or NO_2^- molecules, while O comes from O_2 and/or H_2O. As such, the processes that control $\delta^{15}N$ and $\delta^{18}O$ values during nitrification are separate *[Kendall et al., 2007]*.

The fractionation of N during nitrification is dependant on which of the two steps is rate-limiting. Typically, the oxidation of NH_4^+ to NO_2^- is the slower and rate-limiting step, while oxidation of NO_2^- to NO_3^- proceeds rapidly in nature, and is not rate-limiting. NH_4^+ to NO_2^- N fractionation has been reported at between -38 and -14 ‰ *[Mariotti et al, 1981; Casciotti et al., 2003; Kendal et al., 2007]*. However, at low NH_4^+ concentrations, nitrification will also be limited by NH_4^+ diffusion (resulting in a smaller isotope effect) and/or the non-fractionating mineralization of NH_4^+, indicating the relevance of the reactant reservoir size *[Casciotti et al., 2003; Kendall et al., 2007]*. In the N-limited system, fractionation will be small and the product $\delta^{15}N_{NO3}$ of soil will be within a few permil of the $\delta^{15}N_{N\text{-}ORG}$ composition, while if a large reservoir is present (i.e., following the application of fertilizer or manure), large amounts of NH_4^+ will be available and nitrification will be stimulated, but limited by the oxidation of NH_4^+ *[Mariotti et al, 1981; Casciotti et al., 2003; Kendal et al., 2007]*.

$\delta^{18}O$ resulting from nitrification is controlled by the oxidant sources (i.e., H_2O and O_2). During the first step of NH_4^+ oxidation to NO_2^-, *Andersson and Hooper, [1983]* show that the one O atom is incorporated from dissolved O_2, and one from H_2O; however, additional isotopic exchange between the O in H_2O and NO_2^- also occurs *[Kendall et al., 2007]*. During the second step oxidation of NO_2^- to NO_3^-, it has been shown that O atoms are only incorporated from H_2O. Overall, the process (Equation 2.9) derives two O atoms from oxygen in water molecules and one O atom from dissolved O_2 *[Kendall et al., 2007; Aravena, et al, 1993]*.

$$\delta^{18}O_{NO3} = {}^{2}/_{3}\delta^{18}O_{H2O} + {}^{1}/_{3}\delta^{18}O_{Dissolved\ O2} \qquad (2.9)$$

Where $\delta^{18}O_{H2O}$ is that of ambient H_2O, and $\delta^{18}O_{O2}$ is that of ambient O_2. Therefore, by making some general assumptions, if $\delta^{18}O_{H2O}$ values are in the normal range of -25 to +4 ‰, and soil O_2 $\delta^{18}O$ is that of atmospheric O_2 $\delta^{18}O$ (+23.5 ‰), then soil $\delta^{18}O_{NO3}$ should be approximately -10 to +10 ‰ *[Kendall and Aravena, 2000]*. Overall, there is no significant O isotope fractionation during nitrification *[Clark and Fritz, 1997]*.

Denitrification

Denitrification is a multi-step bacterially driven process (Equation 2.10) of biochemically reducing oxidized nitrogen compounds (NO_3) to N_2 gas (Figure 2.2), with N_2O and N_2O as intermediate compounds *[Kendall, 1998]*. The process has several requirements such as: denitrifying bacteria, reducing conditions (low oxygen levels), and an electron donor source.

$$NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2 \qquad (2.10)$$

The process occurs when denitrifying bacteria such as heterotrophic *Pseudomonas denitrificans* obtain energy by reducing NO_3 with concurrent respiration of CO_2 from oxidizing organic matter (electron donor) *[Kendall, 1998; Rodvang and Simpkins, 2001]*. The bacteria use NO_3^- as a terminal H acceptor in the oxidation of organic substrate *[Alexander, 1961]*. Alternatively, denitrification occurs by autotrophic respiration *(Thiobactillus denitrifican)*, where reduced sulphur or iron are the electron donors *[Kendall and Aravena, 2000]*. Other bacteria responsible for this conversion include: *Archromobacter*, *Escherichia,* and *Micrococcus [Wetzel, 2001]*.

Denitrification causes residual ^{15}N and ^{18}O of NO_3 to enrich exponentially as NO_3 concentrations decrease, resulting in 2:1 enrichment in $^{15}N_{NO3}$ and $^{18}O_{NO3}$. In addition, denitrification causes soil acidity to decrease due to bicarbonate production, as shown by Equation 2.11 *[Kendall, 1998; Amberger and Schmidt, 1987]*.

$$4NO_3^- + 5C + 2H_2O \rightarrow N_2 + 4HCO_3 + CO_2 \qquad (2.11)$$

Volatilization

Volatilization refers to the loss of ^{15}N-depleted gaseous ammonia (NH_3) to the atmosphere, as shown in Equation 2.12. The multi-step process is highly fractionating, resulting in ammonia gas with a much lower $\delta^{15}N$ than residual NH_4^+ *[Kendall, 1998]*. First, equilibrium fractionation occurs between ammonium ions and ammonia in solution, and between aqueous and gaseous ammonia; and second, the kinetic fractionation of ^{15}N-depleated ammonia from diffusive loss *[Kendall et al., 2007]*.

$$NH_{3(aq)} \rightarrow NH_{3(g)} \quad (2.12)$$

Because of the relatively high Henry's law constant for ammonia, and the negligible partial pressure of NH_3 in air, diffusive loss from manure, soils and surface waters with high concentrations of un-ionized ammonia will occur. However, volatilization from groundwater below the water table is greatly minimized by the slow rate of aqueous diffusion *[Clark, 2006]*. In agricultural environments, volatilization occurs within manure piles and from the field application of manure and urea fertilizer. The mineralized ammonium can have $\delta^{15}N$-enriched values up to +25 ‰ due to ammonia loss, but is dependant on pH, temperature, humidity and other environmental factors *[Hubner, 1986; Kendall et al., 2007]*. Because Urea volatilization is temperature dependant, losses are typically 8-10%, and as high as 15%. At temperatures over 30°C, losses of 20% after 10 days would be expected, although losses might be quite low during the spring if the soil temperature is cold. *[Overdahl et al., 2007]*. Unless it rains, urea must be incorporated within a few days to avoid ammonia loss. The key to the most efficient use of urea is to incorporate it into the soil during a tillage operation, or blend it in as a liquid application. As little as 6 mm of rain is sufficient to blend urea into the soil to a depth where ammonia volatility will be significantly reduced *[Overdahl et al., 2007]*. *Kreitler [1975]* reported that $\delta^{15}N_{NO3}$ in groundwater may be 2–3 ‰ enriched compared to applied fertilizer due to volatilization. The remaining ^{15}N-enriched NH_4 is also converted to ^{15}N-enriched NO_3 during nitrification *[Kendall et al., 2007]*.

Ammonia Ionization

Ammonia ionization is the inorganic reaction that provides the high solubility of ammonia in water at neutral pH, where most ammonia is ionized to ammonium (Equation 2.13) *[Clark, 2006]*. The two species have equal concentrations at pH 9.23 (dissociation constant), so higher NH_3 concentrations are only present at high pH values.

$$NH_3 + H^+ \rightarrow NH_4^+ \quad (2.13)$$

Anammox

Anammox is an abbreviation for **AN**aerobic **AMM**onium **OX**idation, and represents a biologically-mediated reaction where nitrite and ammonium are simultaneously converted to aqueous dinitrogen (N_2) and subsequently nitrogen gas, first identified by *Mulder et al., [1995]*. The anammox bacteria use NH_4^+ as an electron donor, and NO_2^-, generated through partial reduction of NO_3^-, as an electron acceptor, according to Equation 2.14 *[Clark et al., 2008]*. The nitrite for this reaction can be produced by partial denitrification of NO_3^-. This process has been observed in anaerobic environments where both ammonium and nitrate species are present, such as in waste-water streams *[Strous et al., 1997]*, anoxic marine waters *[Dalsgaard et al., 2003; Devol, 2003; Kuypers et al., 2003]* and soils *[Jetten, 2001]*. Anammox is the only known microbial reaction that converts ammonium to N_2 *[Kendall, 1998]*. Similar to the nitrogen enrichment during nitrification and denitrification in NH_4^+ and NO_3^-, respectively, the residual ammonium and nitrate measured in the groundwater during anaerobic oxidation of NH_4^+ should also become enriched in ^{15}N.

$$3\ NO_3^- + 5\ NH_4^+ \rightarrow 4\ N_2 + 9\ H_2O + 2H^+ \qquad (2.14)$$

2.2.4 Nitrogen Sources

Elevated soil and groundwater nitrate concentrations are typically associated with one or more of the following sources: (1) natural; (2) animal and human waste; and (3) synthetic fertilizer. Table 2.1 summarizes the reported isotopic signatures of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ from various nitrogen sources.

Soil Nitrogen

Natural sources, although typically not major sources, include atmospheric deposition (from lightning fixation), baseline organic N in soils from plant decomposition, and geological nitrogenous sources that become mobilized and leach into groundwater due to system changes (such as commencement of irrigation) *[Canter, 1997]*. Table 2.1 summarizes $\delta^{15}N_{NO3}$ values from soil organic N, with an average value of +5 ‰. *Choi et al. [2003]*

reports that when NO_3^- concentration are consistently below 3 mg/L-N, and $\delta^{15}N_{NO3}$ values range between +5 and +8‰, then soil organic N is likely the source.

Table 2.1: Literature isotopic values for various nitrogen and oxygen sources.

$\delta^{15}N$ ‰	$\delta^{18}O$ ‰	Source	References
+10 to 20		Cow manure	*Kreitler, 1975*
+10 to +25		Animal waste	*Heaton, 1986*
+7.9 to +8.6		Poultry manure	*Wassenaar, 1995*
	+18 to +22	Synthetic NO3	*Amberger and Schmidt, 1987*
+1.5		Synthetic fertilizer	*Fogg et al., 1998*
	+13	NH_4-NO_3 fertilizer	*Aravena et al., 1993*
-2.2 to +1.0		Synthetic fertilizer	*Kaplan and Magaritz, 1986*
-4 to +4		Synthetic fertilizer	*Kendall, 1998*
-5.0 to +3.0		Synthetic fertilizer	*Kreitler, 1975*
-1.5 to -0.6		Synthetic fertilizer	*Wassenaar, 1994*
-0.91±1.88		NH_4 Fertilizer	*Hübner, 1986*
+2.75±0.76		NO_3 Fertilizer	*Hübner, 1986*
+0.18±1.27		Urea Fertilizer	*Hübner, 1986*
-5 to +2		Plants	*Fry, 1991*
+6.4 to +58.3		Septic System	*Aravena and Robertson, 1998*
+19.0 to +28.8		Septic System	*Kaplan and Magaritz, 1986*
+10 to +25		Septic System	*Heaton, 1986*
+9.9		Soil Organics	*Aravena et al., 1993*
+2.0 to +5.0		Soil Organics	*Broadbent et al., 1980*
+4.7 to +11.4		Soil Organics	*Kaplan and Magaritz, 1986*
+2.0 to +8.0		Soil Organics	*Kreitler, 1975*
+2.0 to +9.0		Soil Organics	*Heaton, 1986*

Manure and Septic Waste

Nitrate sources from waste include: animal manure from commercial operations; land application of municipal and industrial sludge; and septic system loss *[Canter, 1997]*. Farm manure typically originates from poultry, hog or cattle, and enters the ground either from leaky pits and lagoons, or from field applications. When applied to fields, high nitrate concentrations may be a result of: excessive application, incomplete uptake, or off-season mineralization (non-growing season) of soil nitrogen *[Canter, 1997]*. Where aerobic conditions exist, either surface or subsurface, NO_3^- can form from nitrification of NH_4^+ from septic waste or manure application *[Aravena et al, 1993]*. Because of the volatilization of gaseous NH_3 from NH_4^+ during the storage and/or application of manure, $\delta^{15}N_{NO3}$ is isotopicaly enriched *[Kendall 1998]*. $\delta^{15}N$ values from septic waste typically range from +10

to +25 ‰ *[Heaton, 1986; Aravena and Robertson, 1998]*, while those from manure typically range between +10 and +20‰, depending on animal type, indicating little difference between the two sources (Table 2.1) *[Wassenaar, 1995; Kreitler, 1975]*.

Approximately 25% of US population are not connected to municipal sewage utilities, and instead use individual septic systems. The release of effluent from these septic systems, which moves through the unsaturated zone and into groundwater, typically undergoes rapid nitrification under aerobic conditions. Cation exchange is responsible for NH_4^+ loss in soils; however, if cation exchange sites become saturated, NH_4^+ will leach into the aquifer. Conversely, NO_3^- remains soluble and leaches readily into the aquifer *[Canter, 1997; Aravena et al, 1993]*.

Synthetic Fertilizer

Presently in the US, urea ($CO(NH_2)_2$) (46-0-0), which indicates that it contains 46% Nitrogen, is the most common form of synthetic (anthropogenic) fertilizer applied *[Overdahl et al., 2007]*. Other forms of synthetic fertilizer include Ammonium-nitrate (NH_4-NO_3) (34-0-0) and Potassium Nitrate (KNO_3), although their use has decreased over the past several decades. A liquid mix of urea and ammonium-nitrate (UAN 28% N) is also available and popular in some areas *[Kendall et al., 2007]*. Each of these is produced by the fixation of atmospheric N ($\delta^{15}N = 0$) using the Haber-Bosch process, and have $\delta^{15}N$ values ranging from -4 to +4‰ *[Kendall, 1998; Wassenaar, 1995; Amberger and Schmidt, 1987]*. $\delta^{18}O$ values from synthetic nitrate are reported as +18 to +22 ‰, where all three oxygens originate from atmospheric O_2 ($\delta^{18}O = +23.5$ ‰) *[Amberger and Schmidt, 1987]*. NO_3^- from synthetic NH_4-NO_3 fertilizers, where 50% of oxygen is from nitrification of NH_4 fertilizer and 50% is from synthetic NO_3 fertilizer, has a reported $\delta^{18}O$ value of approximately 13 ‰ *[Aravena et al, 1993]*.

2.2.5 Fertilization

Modern agricultural practices often apply fertilizers at rates higher than required by crops, leading to the loss of nitrogen *[Canter, 1997]*. However, because of economic impacts, the practice of conducting seasonal soil N testing is becoming increasingly popular

to optimize the availability of existing soil N, and minimize losses *[Canter, 1997]*. Aside from crop uptake of nitrate and ammonium, losses from the soil system typically include: leaching of nitrate, erosion of soil containing both organic and mineral N, and gaseous loss processes such as denitrification and ammonia volatilization *[Fairchild, 1987]. Fried et al., [1976]* showed that crop uptake efficiency is more important than the quantity of N application, in terms of the absolute amount of N available for leaching. Varying tillage practices, along with crop rotation (legumes such as alfalfa and soybean do not require fertilization), can influence NO_3^- leaching, as different plants require different nutrients. Current rates of nitrogen fertilization (manure and urea) for corn production at the participating agricultural field sites varied from as little as 50 kg-N/ha to >120 kg-N/ha, while *Fairchild [1987]* reported application rates for corn of 30-80 kg-N/ha. Depending on soil conditions, approximately 10-20 kg-N/ha is required for base soil conditioning, and 50-65 kg-N/ha for crop yield, with approximately 10% remaining from previous applications *[Fairchild, 1987].*

2.2.6 Groundwater Investigations

The use of synthetic and manure fertilizers as sources of nitrogen is considered a required practice in global agriculture to produce sustainable crop yields. As a result, leaching of nitrate to the water table and subsequent impacts on aquifers has been widely documented in studies throughout the world *[Böhlke, 2002; Fried et al., 1987; Goss et al., 1998; Hamilton and Helsel, 1995; Hasleur et al., 2005; Heaton, 1986; Hill, 1982; Rodvang and Simpkins, 2001; Spalding and Exner, 1993].* Soil nitrate is very soluble, is mobile and easily moves with water as it infiltrates through the soil to the water table. Other investigations have looked more specifically at the origin, transformation processes, and fate of agricultural contaminants using stable isotopes *[Aravena and Robertson, 1998; Böhlke and Denver, 1995; Hendry et al., 1984; Mengis et al., 2005; Cey et al, 1999; Savard et al., 2007; Tesoriero et al., 2000; Wassenaar, 1995; Wassenaar, 2006; Wilhelm et al., 1994],* while others have used isotopes to evaluate and determine the source of nitrogen-bearing nutrients *[Aravena et al, 1993; Moore et al., 2006; Bohlke et al., 2006; Amberger and Schmidt, 1987; Fogg et al., 1998; Kreitler, 1975; Mayer et al., 2002; Moore et al., 2006; Verstraeten et al., 2005].*

2.3 Carbon Dynamics

2.3.1 Dissolved Inorganic Carbon

Dissolved Inorganic carbon (DIC) is the sum of four main dissolved carbon-bearing species ($CO_{2(aq)}$, H_2CO_3, HCO_3^-, and CO_3^{2-}). Carbon can diffuse into water from $CO_{2(g)}$ or from the dissolution of carbon-bearing minerals, such as calcite and dolomite. The distribution (concentration) of these species is a function of pH (Figure 2.3), and is defined by the following net reaction (Equation 2.15).

$$CO_2(g) + H2O \leftarrow K_{CO2} \rightarrow H_2CO_3 \leftarrow K_1 \rightarrow H^+ + HCO_3^- \leftarrow K_2 \rightarrow 2H^+ + CO_3^{2-} \qquad (2.15)$$

Where K are the species dissociation constants *[Clark and Fritz, 1997]*. The partial pressure of soil CO_2 (P_{CO2}) is ~ 10^{-3} to 10^{-1} (atm), while that of atmospheric (P_{CO2}) is $10^{-3.5}$(atm), which is significantly lower. The high soil CO_2 produces carbonic acid, which further lowers the soil pH.

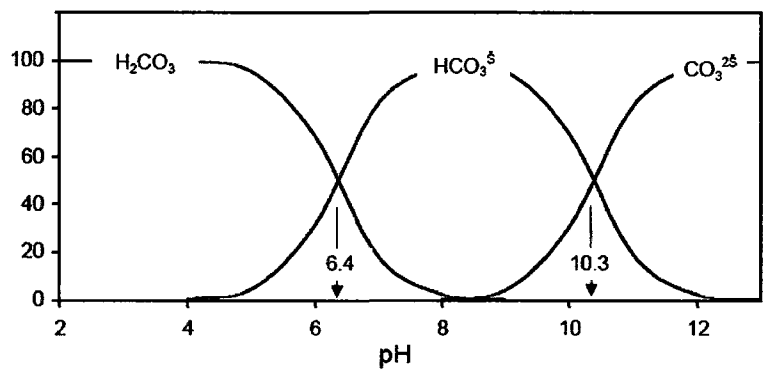

Figure 2.3: The distribution of three DIC species according to pH and molar concentration. Reproduced from *Clark and Fritz, [1997].*

In nature there are three carbon isotopes: ^{12}C, ^{13}C and ^{14}C, of which the last is radiogenic. Almost 99% of atmospheric CO_2 contains the least heavy carbon ^{12}C, 1.1% comprises the heavier ^{13}C, and only a small fraction contains ^{14}C. The isotopic composition is reported relative to the Vienna Pee-Dee Belemnite (VPDB) standard, and is expressed in the delta permil δ(‰) notation (Equation 2.1). During photosynthesis, terrestrial vegetation and marine phytoplankton discriminate against heavy molecules preferring ^{12}C to ^{13}C when absorbing CO_2. As such, carbon trapped in flora contains smaller proportions of ^{13}C than

atmospheric CO_2. The evolution of $\delta^{13}C$ values in groundwater starts with atmospheric CO_2, which has a $\delta^{13}C$ value of -7‰ *[Clark and Fritz, 1997]*. During plant uptake of CO_2, isotopic fractionation results in overall $\delta^{13}C$ depletion of 22‰. On average, terrestrial organic matter in vegetation and soils has a mean $\delta^{13}C$ value of -26‰, however because plants belong to two large groups (C_3 and C_4), which differ in their photosynthetic pathways, they each have very different $\delta^{13}C$ values. The numerations are because in the C_3 group, the first photosynthesized organic compound has three C atoms, while the C_4 group has four C atoms. Most natural vegetation in temperate and high latitude climates follows the C_3 photosynthesis pathway and has lower values of $\delta^{13}C$, between -24‰ and -30‰, with an average of -27‰ *[Vogel, 1993]*, while the remaining 1% of species (5% plant biomass) are of C_4 type *[Bond et al., 2005]*. The majority are tropical herbs, but also common agricultural plants such as sugar cane, corn (maize) and sorghum *[Bond et al., 2005]*are C_4 type, and have more enriched $\delta^{13}C$ values between -10‰ and -16‰, with an average of -12.5‰ *[Vogel, 1993]*. There is also a third smaller group called CAM, which is a combination of the C_3 and C_4 processes, which some cactus and succulents belong to. Figure 2.4 illustrates how differences in $\delta^{13}C$ values in various terrestrial carbon reservoirs can be used to evaluate geochemical reactions in groundwater systems *[Clark and Fritz, 1997]*.

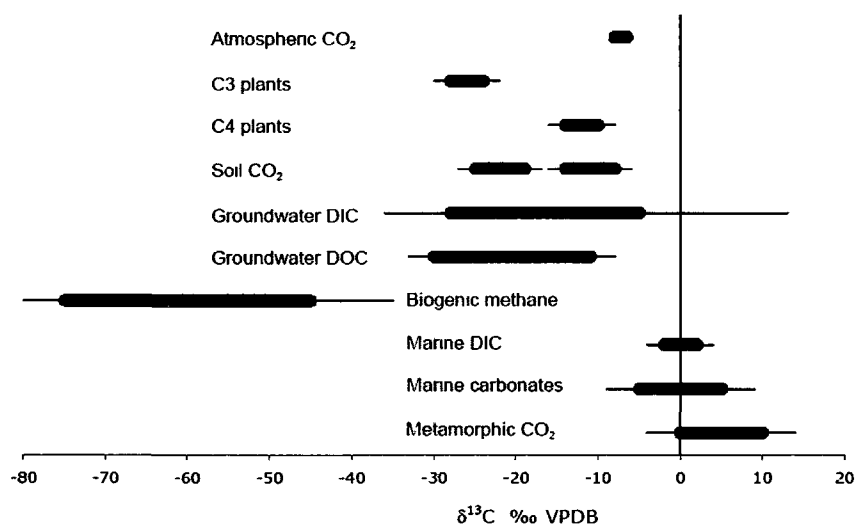

Figure 2.4: Ranges of organic and inorganic $\delta^{13}C$ values from terrestrial reservoirs. Reproduced from *Clark and Fritz, [1997]*.

When vegetation dies, aerobic bacteria convert it back to CO_2. Initially, microbially-respired CO_2 typically has the same $\delta^{13}C$ as the original vegetation; however, due to outgassing there is subsequent fractionation of approximately 4‰, resulting in soil CO_2 with a $\delta^{13}C$ value of -23‰ in C_3 landscapes, and -9‰ in C_4 landscapes *[Cerling et al., 1991; Clark and Fritz, 1997]. Cane and Clark [1999]* reported groundwater $\delta^{13}C_{DIC}$ values from the Raisin River agricultural watershed between -13 and -16‰ during periods of high water table reflecting stronger mixing with natural C_3 vegetation, and values between -11 and -7‰ during periods of low water table, reflecting the C_4 type vegetation source.

Following the dissolution of soil CO_2, the hydration into infiltrating water results in the dissociation of HCO_3^- and CO_3^{2-}, which further fractionates $\delta^{13}C$ from naturally vegetated environments to -15‰ (pH dependant) *[Clark and Fritz, 1997]*. In geologic settings containing carbonate minerals, the dissolution of carbonate causes the evolution of more enriched values of $\delta^{13}C_{DIC}$, depending on whether the dissolution is occurring in an open or closed system with regard to CO_2 *[Clark and Fritz, 1997]*.

2.3.2 Dissolved Organic Carbon

Dissolved organic carbon (DOC) refers to various organic molecules derived from the decomposition of biomass that are soluble in groundwater, and can pass through a 0.45μm filter. They are composed of C, O, N, H and S in varying proportions, such as humic substances. DOC plays an important role in the geochemical evolution of groundwater through reduction-oxidation (redox) reactions, such as the fixing of carbon by photosynthesis. Soil structure and soil water conditions influence the transport or organic carbon. In the root zone soil water DOC concentrations can reach 10 to 1000 mg-C/L, but drops off toward the water table *[Aiken et al., 1985]*. Groundwater often contains less than 1 to 2 mg-C/L, but under certain conditions; such as agricultural areas, periods of high water table, in spring when soil microbial activity is low, and around septic fields, concentrations can be higher *[Wassenaar, 1990]. Cane and Clark [1999]* reported groundwater DOC concentrations from the Raisin Rover agricultural watershed between 10 and 30 mg-C/L, while *Aravena et al. [1995]* reported concentrations from bog areas exceeding 100 mg-C/L. In addition, buried peat in Quaternary sediments, known as sedimentary organic matter

(SOM) may be found within an aquifer, although they likely contribute little to the groundwater DOC pool as they tend to be insoluble and at low concentrations *[Aravena and Wassenaar, 1993; Artinger et al., 1995]*. In Canada, the suggested maximum drinking water DOC concentration is 5 to 10 mg-C/L, beyond which water often looks yellow *[Health Canada, 2008]*.

Generally, $\delta^{13}C_{DOC}$ values in most groundwater tend to reflect the carbon isotopic composition of local overlying vegetation. The reported range of groundwater $\delta^{13}C_{DOC}$ values is -18 to -46‰, however, a narrower range of values between -26 to -30‰ is reported for C_3 type vegetation, and up to -18‰ for C_4 vegetation *[Yang et al., 1998]*.

2.4 Stable Isotopes of Water

The water molecule contains three stable isotopes of oxygen: ^{16}O, ^{17}O, and ^{18}O, and two stable isotopes of hydrogen: ^{2}H and ^{1}H. The natural abundances of the stable isotopes relevant to this investigation are 0.204% (for $^{18}O/^{16}O$) and 0.015% (for $^{2}H/^{1}H$) *[Clark and Fritz, 1997]*. The isotopic compositions of both elements are reported relative the Vienna Standard Mean Ocean Water (VSMOW) reference, and are expressed in the delta permil δ(‰) notation *[Clark and Fritz, 1997]* (Equation 2.1).

2.4.1 Isotope Fractionation

The process of fractionation, which is the isotopic ratio between the reactants and products of a reaction, results in a somewhat predictable isotopic composition in precipitation. The temperature controlled thermodynamic processes of evaporation and condensation partition heavier isotopes between the liquid and vapour phases. During the process of evaporation from an open surface of water under an air column with 0% humidity, there is a 1% difference in the vapour pressure between $H_2{}^{16}O$ and $H_2{}^{18}O$ *[Clark and Fritz, 1997]*. Because vapour pressure increases with temperature, and the vapour pressure of $H_2{}^{16}O$ is greater then that of $H_2{}^{18}O$, the evaporative flux of $H_2{}^{16}O$ is greater than $H_2{}^{18}O$, resulting in the isotopic depletion of $H_2{}^{16}O$ in the water body (reservoir), while ^{16}O and ^{1}H are preferentially accumulated in the vapour phase. The enrichment of heavier isotopes in the reservoir follows the Rayleigh distillation function (Equation 2.16).

$$R = R_o f^{(\alpha-1)} \quad (2.17)$$

Where R_o is the initial isotope ratio, R is the ratio when only a fraction, f, of the reservoir remains, and α is the equilibrium fractionation factor (Equation 2.2) *[Clark and Fritz, 1997]*. The reverse process, where clouds and precipitation form by condensation with 100% humidity, is dominated by equilibrium fractionation, such that the condensation flux of $H_2{}^{16}O$ is greater than $H_2{}^{18}O$ and $^2H_2{}^{16}O$. Further, the isotopic fractionation from both thermodynamic processes is greater at colder temperatures *[Clark and Fritz, 1997]*.

For condensation to occur, the vapour mass must cool, which can only occur by two methods. First, by adiabatic expansion, where warm air rises to lower pressures, second, by radiative heat loss, where water vapour condenses to maintain equilibrium as the temperature drops and the dew point is passed. As rainout continues because of decreasing temperatures, both the precipitation and the condensed phase become increasingly depleted in ^{18}O and ^2H, and the process follows Rayleigh distillation *[Clark and Fritz, 1997]*.

2.4.2 Relationship of $\delta^{18}O$ - δ^2H in Precipitation

The Global Meteoric Water Line (GMWL) defines the strong linear relationship between ^{18}O and ^2H in global fresh water, relative to the reference Standard Mean Ocean Water (SMOW), and is expressed by Equation 2.17 *[Craig,1961]*.

$$\delta^2H = 8\delta^{18}O + 10 \text{ (SMOW)} \quad (2.18)$$

The slope represents a theoretical 8 times greater enrichment under equilibrium conditions (i.e. 100% humidity) of ^2H in water than that of ^{18}O, because of differences in vapour pressures of heavier and lighter molecules. Because net evaporation and condensation would not occur under equilibrium conditions, it suggests that non-equilibrium evaporation (by molecular diffusion) is equally important in the formation of water vapour and precipitation *[Clark and Fritz, 1997]*. In fact, the intercept of 10 is a function of the non-equilibrium evaporation of the ocean surface from where precipitation originates. However, because the GMWL is an annual average of many local meteoric water lines (LMWL), seasonal and spatial deviations are attenuated. *Rozanski et al. [1993]* determined a more precise

relationship (Equation 2.19) based on precipitation from the Global Network of Isotopes in Precipitation (GNIP) worldwide stations, relative to the currently used reference of Vienna Standard Mean Ocean Water (VSMOW). The partitioning of ^{2}H and ^{18}O between warm and cold regions is a result of the distillation during rainout (Rayleigh distillation) *[Clark and Fritz, 1997]*. The Ottawa LMWL is expressed by Equation 2.20 *[Fritz et al., 1987]*:

$$\delta^{2}H = 8.17(\pm 0.07)\delta^{18}O + 11.27(\pm 0.65) \text{ (VSMOW)} \quad (2.19)$$

$$\delta^{2}H = 7.6\delta^{18}O + 16.5 \text{ (VSMOW)} \quad (2.20)$$

When humidity is 100% (i.e. water vapour and seawater are at equilibrium) precipitation will plot on a line through seawater with a slope of 8. However, precipitation will be enriched over water vapour when humidity is less than 100%, resulting in a positive displacement from the seawater line. On average, global precipitation forms at just over 85% humidity; which results in a displacement of +10‰ of $\delta^{2}H$ over seawater *[Clark and Fritz, 1997]*. Presently known as deuterium excess (d), Dansgaard characterized it as the ^{2}H deviation from the slope of 8 in global precipitation, and is defined by Equation 2.21 *[Dansgaard, 1964; Gat, 1996, Clark and Fritz, 1997]*.

$$d = \delta^{2}H - 8\delta^{18}O \quad (2.21)$$

Deuterium excess will vary spatially for all areas where humidity is less than 100%, especially for exceptionally dry regions.

2.4.3 Spatial and Temporal Variations in Precipitation

Because spatial and temporal variations of ^{2}H and ^{18}O in precipitation are typically characterized by strong linear correlations, due to mass-dependant partitioning, adequate characterization of precipitation is necessary for proper investigations of groundwater systems *[Fritz et al., 1987; Gibson et al., 2005]*. These variations are related to both non-

equilibrium (kinetic) and equilibrium isotopic fractionation processes that occur in evaporation and condensation of atmospheric water vapour *[Clark and Fritz, 1997]*.

Dansgaard, [1964] described several empirical relationships or "effects" between the isotopic composition of precipitation and environmental conditions of any given region. These effects include: temperature, altitude, continentality, latitude, amount, and seasonality.

The temperature effect describes the relationship between surface air temperatures and the isotopic content of precipitation, which had been observed as a 1‰ increase in average $\delta^{18}O$ for every ~1.1 to 1.7°C increase in average annual temperature *[Dansgaard, 1964]*. The altitude effect is caused by orographic lifting of a vapour mass over elevated topography, thus reducing pressure and decreasing temperatures and forming isotopically depleted precipitation. Depending on local conditions, gradients of 0.15-0.5‰ $\delta^{18}O$ and 1.2-4‰ $\delta^{2}H$ per 100m altitude are common *[Gat, 1980]*. The continental effect describes that continental precipitation tends to be more isotopically depleted, because it is further from the moisture source, and thus at the end of a Rayleigh distillation. Furthermore, temperatures in coastal areas are moderated by large water bodies (oceans), thus continental regions experience greater temperature extremes *[Clark and Fritz, 1997]*. The latitude effect describes how precipitation at higher latitudes is more depleted because average temperatures are colder than in equatorial regions, and precipitation is often at the end of a Rayleigh distillation similar to continental regions *[Gibson et al., 2005; Clark and Fritz, 1997]*. The amount effect is described as secondary evaporation, where kinetic fractionation will occur on a drop of precipitation as it falls through an unsaturated air column, resulting in isotopic enrichment with respect to the composition at the time of condensation *[Clark and Fritz, 1997]*. Seasonal temperature variations will impart fractionations on local meteoric water in summer and winter, where summer precipitation will be isotopically enriched with respect to winter precipitation *[Gibson et al., 2005; Clark and Fritz, 1997]*.

2.4.4 Isotopic Composition of Groundwater

The isotopic composition of ^{2}H and ^{18}O in water represent the best possible tracers of the hydrological cycle. To investigate the sources and pathways to recharge of shallow groundwater, seasonal variations in the isotopic content of meteoric waters can be used

[Fontes, 1980; Clark and Fritz, 1997; Buttle, 1998]. The isotopic composition of groundwater is a reflection of its location, period, and processes of the recharge, while a changing isotopic composition along a flowpath is a reflection of the groundwater's history, where history refers to mixing, salinization, and discharge processes *[Fontes, 1980].* As precipitation enters the ground, its isotopic composition is often modified as it mixes with soil water, and infiltrates through the unsaturated zone *[Fontes, 1980; Clark and Fritz, 1997].* Furthermore, evaporative isotopic enrichment can occur during infiltration in warmer environments or seasons *[Gat, 1996; Clark and Fritz, 1997].*

Infiltration through the unsaturated zone can occur in one of two primary ways: (1) through a homogenous porous matrix, or (2) through (rapid) preferential pathways such as fractures, fissures or macro-pores (e.g. wormholes). It is these flowpaths that are responsible for the "smoothing out" of the precipitation signal, while the type pathway (slow or rapid) are distinguishable by the degree of attenuation *[Clark and Fritz, 1997].* Groundwater, whose isotopic signal is similar to that of local mean annual precipitation, is well hydrodynamically dispersed, where multi-seasonal and/or multi-annual meteoric signals are adequately mixed. In recharge environments with (slow) infiltration, mixing often occurs with stored soil water or with more regional groundwater once the water table is reached. In either case, sufficient residence times and transit times are required, respectively. Recharge through rapid or preferential pathways often incurs much less mixing, and will better preserve seasonal variations of the input signal *[Clark and Fritz, 1997].* Meanwhile, deeper regional aquifers will have little or no seasonal or annual variations due to advective mixing *[Clark and Fritz, 1997].*

For continental temperate climates, such as those of Eastern Ontario, there is more variation in the meteoric signal because of the effects of seasonal temperature partitioning. Recharge, however, is more seasonally biased to late fall and spring, because in summer evapotranspiration approaches or exceeds infiltration, while winter precipitation typically experiences overland run off in spring due to ground frost before infiltration can occur *[Clark and Fritz, 1997].*

3.0 STUDY AREA

3.1 Location and Topography

The 546 km^2 Raisin River watershed is located in Eastern Ontario, flows south-easterly, and drains into Lake St. Francis on the St. Lawrence River near Lancaster, east of Cornwall, Ontario (Figure 3.1) The watershed lies within the Municipalities of North and South Stormont, North and South Glengarry, and the City of Cornwall, Ontario. The Raisin River consists of a main branch, which originates as Dixon Creek in an organic-rich bog near Lunenberg, Ontario, and two large tributaries, the North and South Branches, which originate near Monkland and Long Sault, Ontario, respectively. The main branch passes the towns of St. Andrews West, Martintown, and Williamstown.

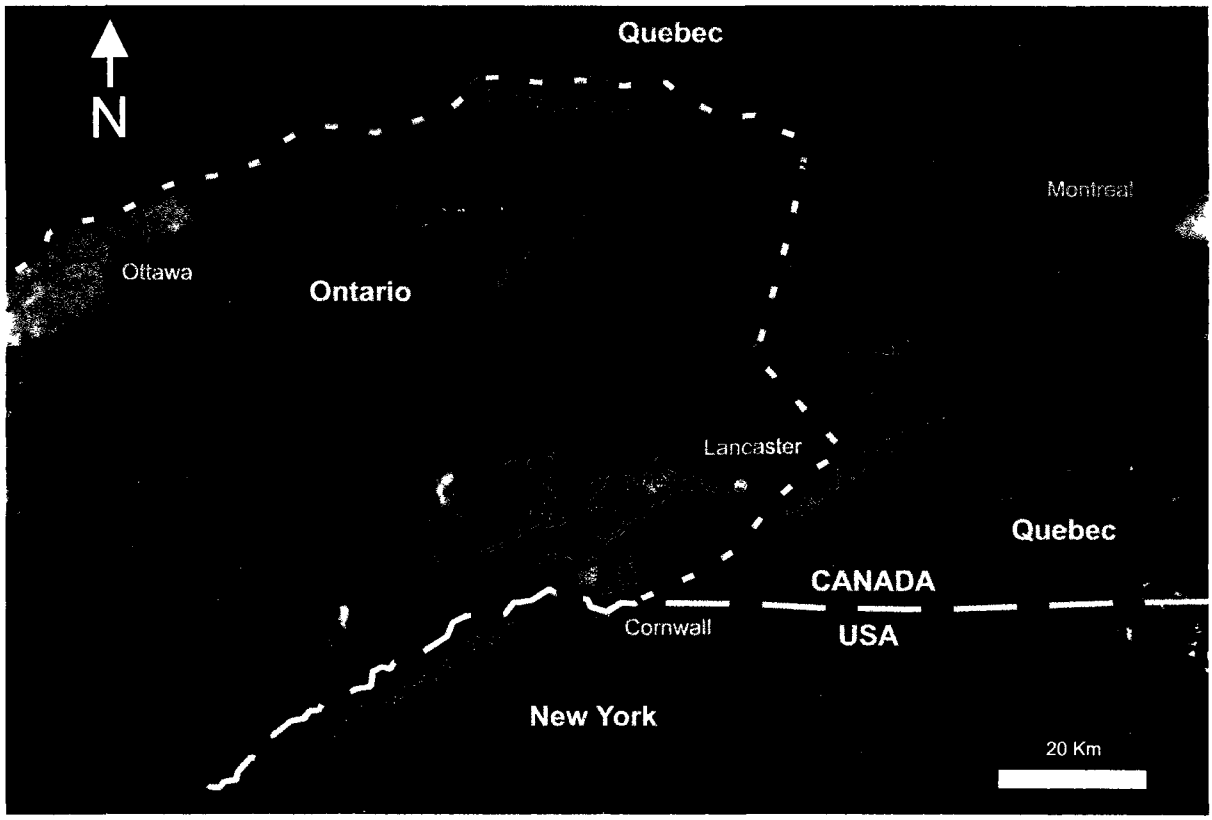

Figure 3.1: Location of the Raisin River watershed in Eastern Ontario, Canada. Image from *[Google Maps].*

The terrain is generally hummocky throughout the watershed with minimal relief, locally sloping towards the various branches, while regionally, the topography slopes gently

from the North-West to the South-East, from a high of 130 meters above sea level (masl) to 40 masl at the confluence with the St. Lawrence River (Figure 3.2).

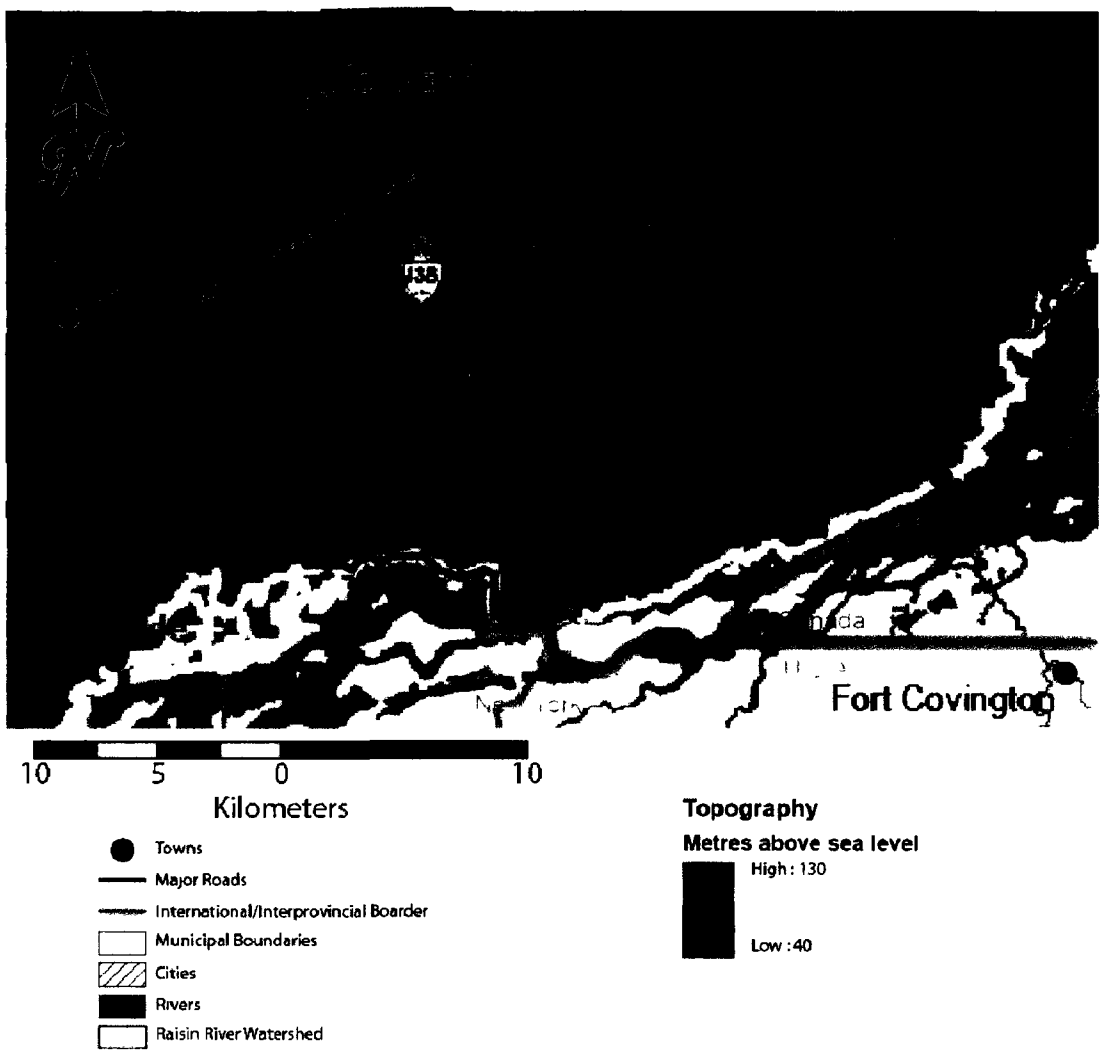

Figure 3.2: Regional topography. Modified from *Raisin-South Nation SWPR, [2007].*

3.2 Climate

The area is characterized by a temperate climate, with an average annual temperature of 7.2°C, with a maximum daily average temperature of 26.7°C in July, and minimum daily average of -12.9°C in January. Subzero temperatures typically commence in November, while spring thaw begins in March-April *[Canadian Climate Normals, 1971-2000].* Total annual precipitation in Cornwall is approximately 1002 mm, with 794.8 mm falling as rain, and 207 mm falling as snow (as rainfall equivalent). Rainfall in the area is predominant between June and September, while January and February represent the lowest precipitation.

Based on long term climate normals (1971-2000), annual precipitation for Cornwall, is approximately 9% greater than that at Ottawa, which has total annual precipitation of 914.2 mm. Environment Canada Climate Normals (1971-2000), for stations in Cornwall and Ottawa, IDs 6101874 and 6105976, respectively, are located in Tables A1 and A2 in Appendix A

Regionally, evapotranspiration has been estimated at between 579 and 664 mm/year, and highest during the growing months between May and August, where approximately 60% of the annual losses occur. Losses from agricultural fine textured soil are estimated at 340 mm/year *[Raisin-South nation SWPR, 2007].*

3.3 Land Use

As illustrated in Figure 3.3, and summarized in Table 3.1, land use in the watershed is dominated by forest (deciduous, coniferous and mixed tree cover) and agriculture (crop and pasture), with 46.3% and 44.4%, respectively. The majority of agricultural land consists of corn, soybean, alfalfa and winter wheat crop cover, with crop type rotation occurring depending on economics and soil nutrient levels. Wetlands, and in particular the Newington Bog in the northwest portion of the watershed account for 7.1% of the area, while urban areas, and specifically the City of Cornwall, which borders on the South branch of the Raisin River, occupy 1.3%. Other than the higher population density within the City of Cornwall (>700 people/km^2), the rural population of the four counties in which the watershed is located, have a population density of <20 people/km^2 (Table 3.2).

Table 3.1: Raisin River watershed land use summary *[Raisin-South Nation SWPR, 2007].*

Land Use	Cover (%)
Water	0.6
Swamp/Wetland	7.1
Forest	46.3
Mining	0.3
Urban	1.3
Crop/Pasture	44.4

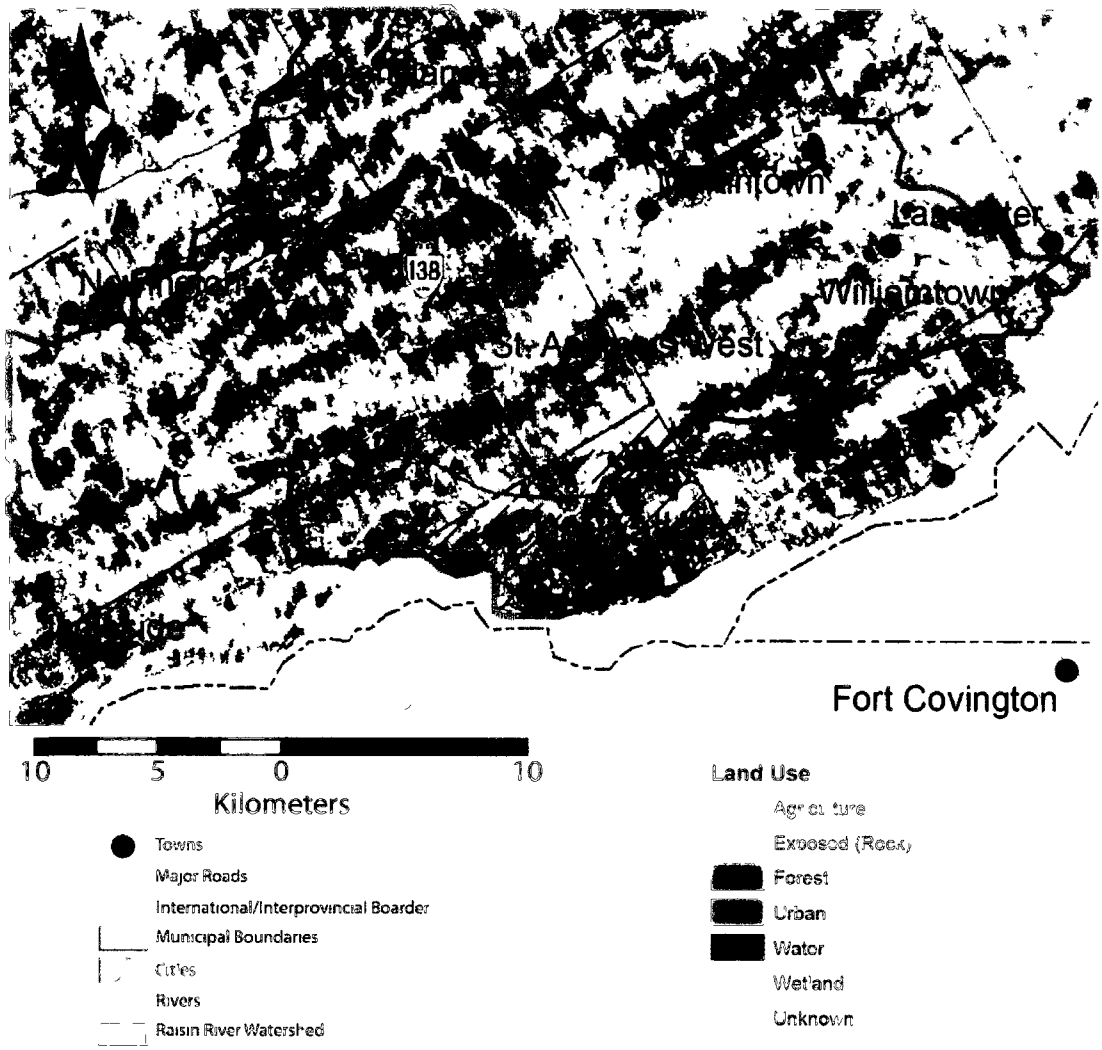

Figure 3.3: Regional land use. Modified from *Raisin-South Nation SWPR, [2007].*

Areas of urban land use and close to roads are more susceptible to urban runoff such as road salts and other potential contaminants, which may leach into the groundwater and/or flow into the river, while the cultivated portion of the watershed is more at risk from agricultural contaminants such as manure and synthetic fertilizers, which are applied in April-May to stimulate microorganism growth. In comparison, pesticides are typically applied in early-June when corn is in the three-leaf stage.

Table 3.2: County populations, areas, and density. ***[Statistics Canada, 2006]***

	Population	Area (km^2)	Population Density ($persons/km^2$)
North Glengarry	10635	642	17
South Glengarry	12880	605	21
North Stormount	6769	516	13
South Stormount	12520	447	28
City of Cornwall	45965	62	743
Total	88769	2272	39

3.4 Geology

3.4.1 Surficial Geology and Soils

The Raisin River watershed lies in a geological region called the Ottawa-St. Lawrence Lowlands, which was eroded by the Laurentide Ice Sheet as part of the last (Wisconsin) glaciation beginning 110,000 years ago, until its maximum extent 20,000 years ago *[Eyles and Miall, 2007]*. Two glacial tills were deposited during separate sequences of glaciations; the lowermost sequence (Malone Till) is described as dark blue-grey clayey silt, with a large compact sandy silt component with Paleozoic pebbles (3-15 m in thickness), while the uppermost sequence (Fort Covington Till) is a sandy till (with stratified sand and gravel) containing crystalline pebbles and is approximately 0.3-9 m in thickness *[Terasmae, 1965; Porter, 1996]*.

The area was later covered by three phases of post-glacial Champlain Sea (11,500 to 10,000 year ago) deposits, which overlaid the glacial till *[Eyles and Miall, 2007]*. These consisted of: invasion phase marine clays with silt and sand beds, deep-sea massive to stratified clay, followed by regression phase beach sand and gravel pockets *[Terasmae, 1965; Gadd, 1960]*. Once the Champlain Sea receded, stratified gravel, sand, silty-sand and clay alluvial sediments where deposited in the eastern portions of the region, with a total thickness of 1-3 meters. In the Northwest portion of the watershed, younger organic dark peat formations are found within Newington Bog *[Terasmae, 1965; Gadd, 1960]*. Figure 3.4 illustrates the surficial geology of the region.

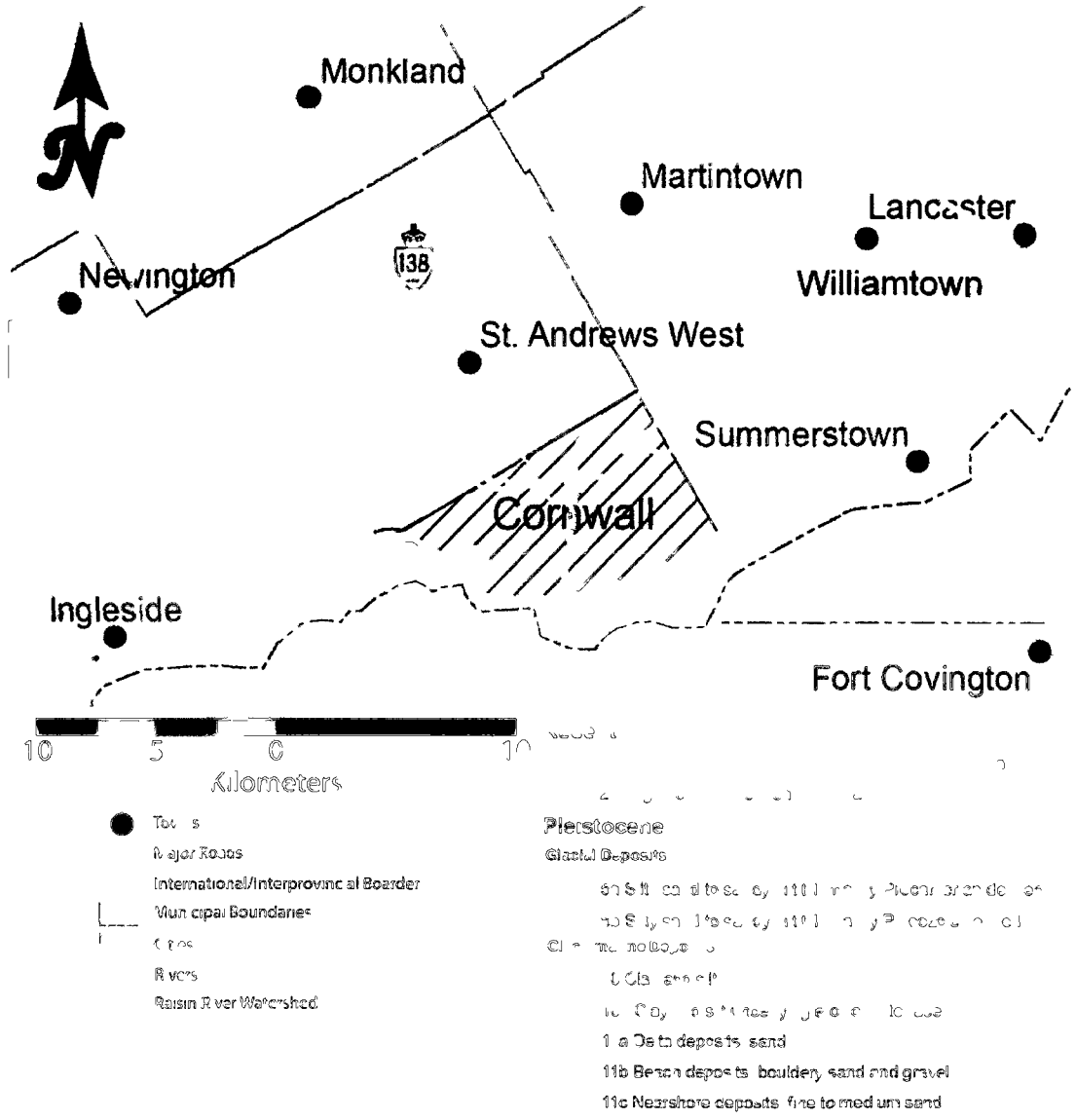

Figure 3.4: Surficial Geology of the region. Modified from *[Terasmae, 1965; Raisin-South Nation SWPR, 2007].*

Figure 3.5 illustrates the two primary types of Quaternary deposits which comprise the physiographic units of the region; 1) the Glengarry Till Plain begins at the headwaters of the watershed and extends east to St. Andrews West and Martintown, and 2) the topographically lower Landcaster Flats, comprised of both marine and alluvial deposits which extend to the St. Lawrence River *[Chapman and Putnam, 1966; Raisin-South Nation SWPR, 2007; Porter, 1996].*

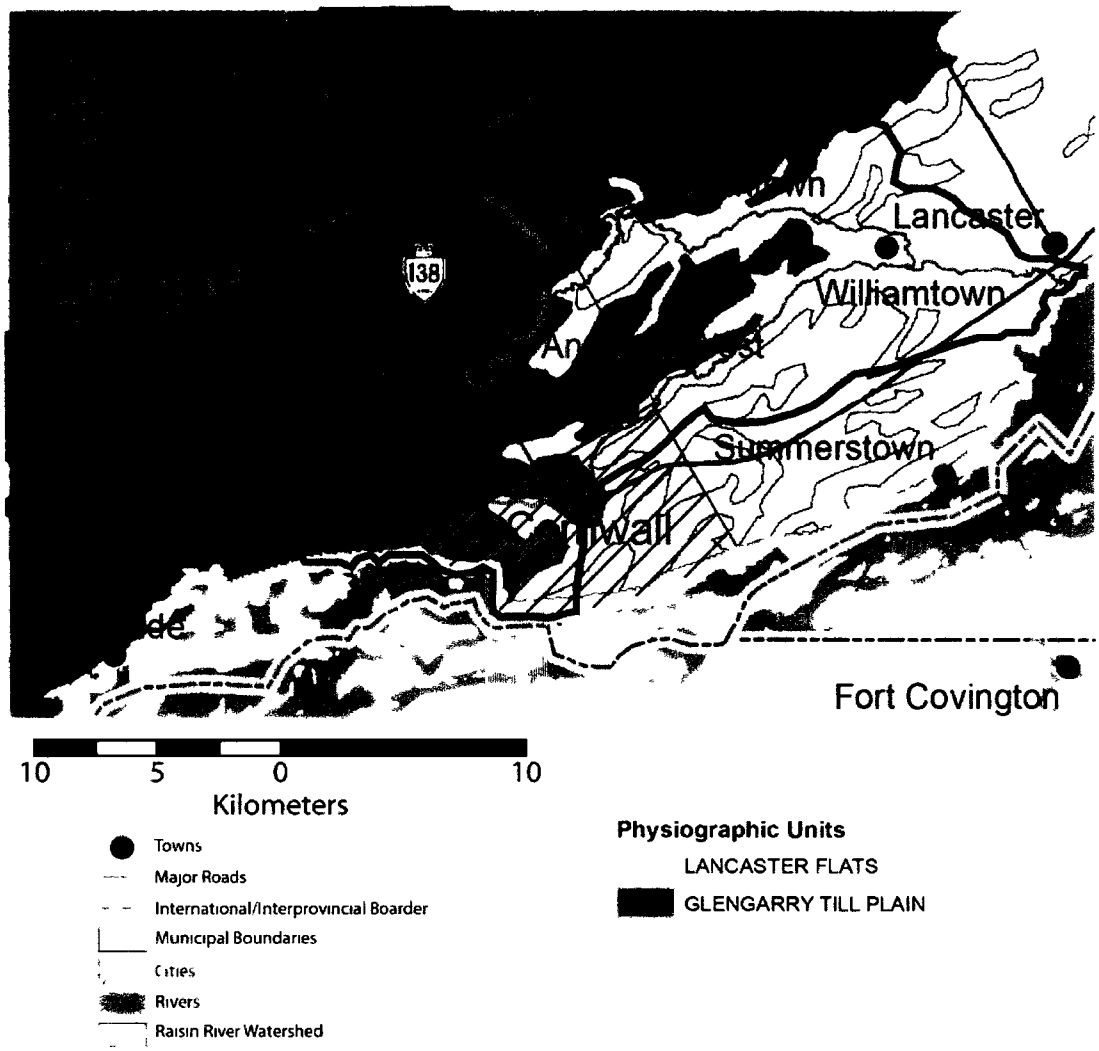

Figure 3.5: Physiographic units of the region. Modified from *Raisin-South Nation SWPR, [2007].*

The primary soils in the watershed consist of loam (Sand, Silt & Clay, 40-40-20%, respectively) and sandy loam (Sand, Silt & Clay, 65-25-10%, respectively). Figure 3.6 shows the distribution of soil type throughout the watershed. Or state that loam and sandy loam signifies this or that.

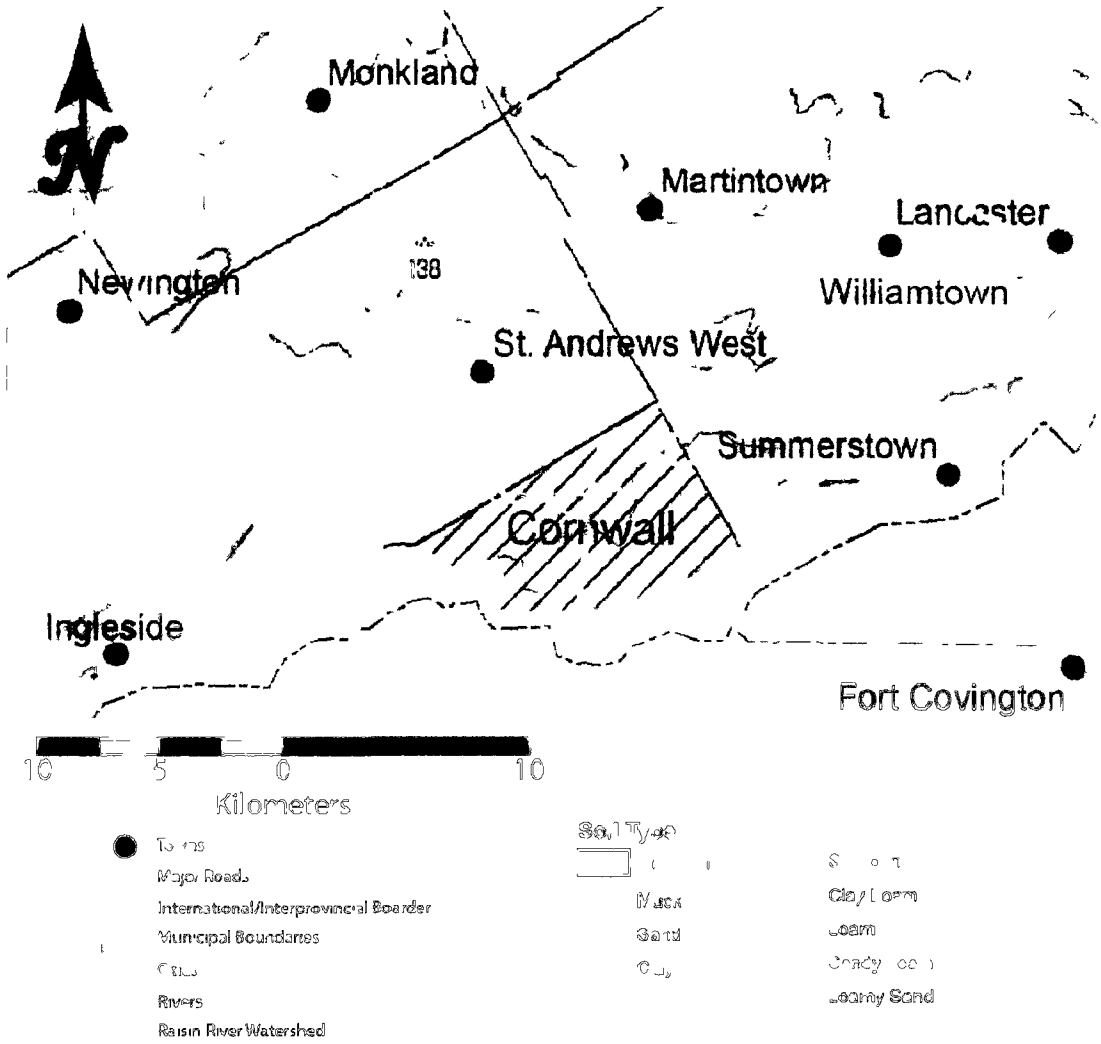

Figure 3.6: Soil classification for the region. Modified from *Raisin-South Nation SWPR, [2007].*

3.4.2 Bedrock Geology

The underlying bedrock geology consists of five major Ordovician Period (444-488 Ma) *[GSA, 2009]* formations, four of which are part of the Ottawa Group (from youngest to oldest; Lindsay, Verulam, Bobcaygeon, and Gull River Formations) *[Williams, 1991]*. Figure 3.7 illustrates the bedrock geology of the Raisin River watershed. The Lindsay Formation consists of Limestone with undulating shale partings and calcareous shale interbeds, and approximately 23 m thick in the region (20m to 25m). The Verulam Formation is composed of thin to medium bedded limestone with calcareous shale interbeds, and approximately 40 m thick (32 m to 65 m). The Bobcaygeon Formation consists of limestone with shaley partings, and approximately 83 m thick (51 m to 87 m). The Gull River formation is

composed of carbonate rocks – interbedded limestone and silty dolostone with minor quartz sandstone, and is approximately 71 m thick in the area (42 m to 71 m). While the Rockcliffe Formation, which lies below the Ottawa Group and is located near the St. Lawrence River, was formed at the bottom of an ancient sea and consists primarily of Interbedded quartz sandstone and shale, with dessication cracks often present, and is approximately 48 m thick locally (52 m to 125 m regionally) *[Williams, 1991].*

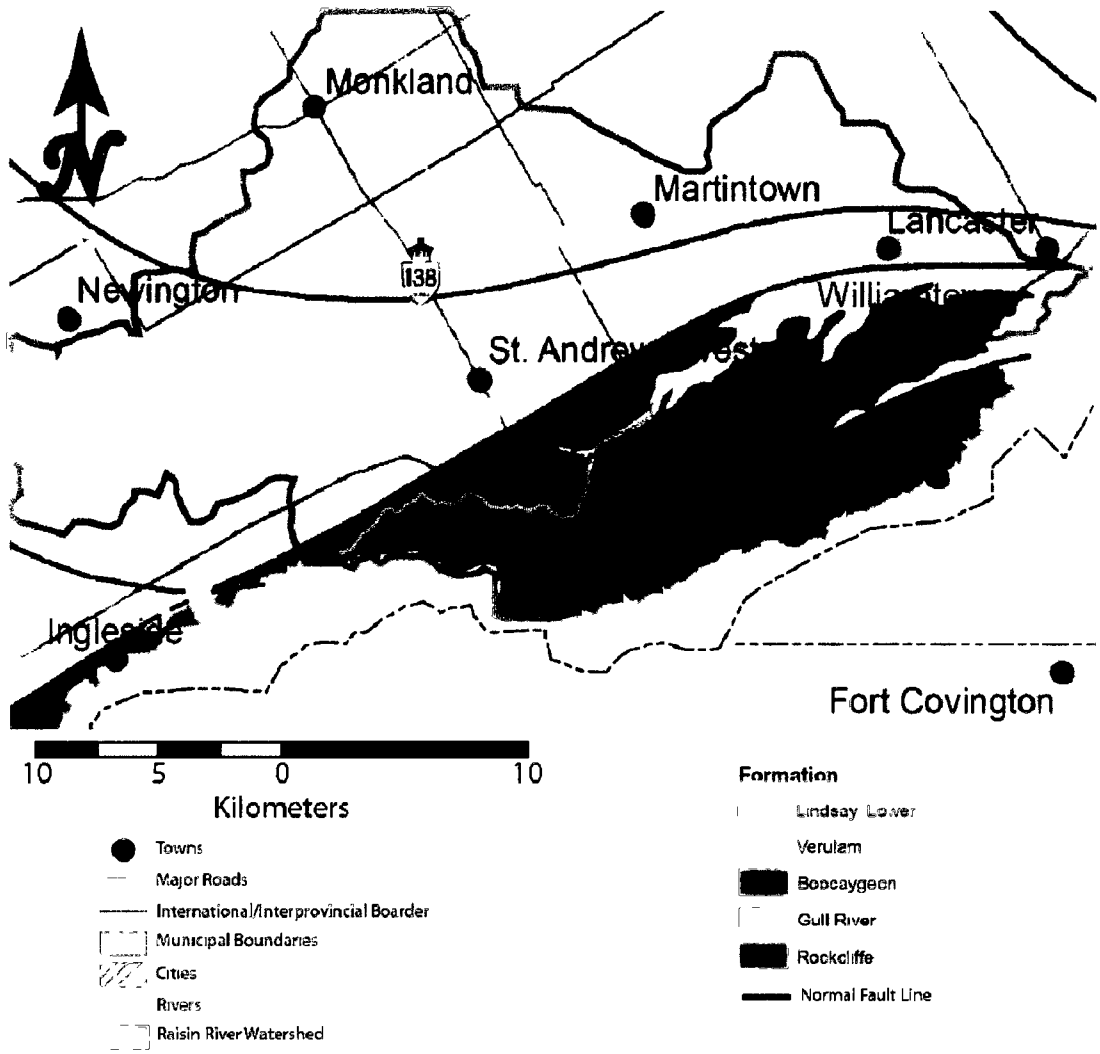

Figure 3.7: Bedrock Geology and faults of the region, ***[Williams, 1991; Raisin-South Nation SWPR, 2007].*** **Modified from** ***Raisin-South Nation SWPR, [2007].***

3.4.3 Structural Geology

There are four normal faults in the region, all part of the Ottawa valley rift zone, and striking sub-parallel to the Raisin River *[Williams et al., 1985]* (Figure 3.6). The faults are all steeply dipping; however, bedding is generally flat-lying away from the fault zones. The fault displacement ranges from 355 m in the north to 515 m in the south *[Williams,1991]*, and the faults act as contacts between the various formations.

3.5 Hydrology

The Raisin River has a main branch, a north branch, and a south branch totalling 809 km of streams, and a width of < 20 m. The Raisin is a sixth order stream system with 83% of its waterway classified as first through third order (headwater) streams. The mean annual discharge of Raisin River near Williamstown is 5.09 m^3/s *[Raisin River Conservation Authority, 2007]*.

Typically, intense summer storm events coupled with saturated ground, cause the river to flood its banks, resulting in dilution of the ionic concentration of river water due to greater runoff. While in the winter, the Raisin River will freeze in sections from January to mid-March.

The Watershed was characterized by evaluating the ratio of effective discharge (or event flow) Q_{ef}, to total rainfall W_t, by analyzing four storm hydrographs (Williamstown Environment Canada gauge station), and precipitation from the Cornwall Environment Canada rain gauge. Results indicated the Raisin River watershed has a very low Q_{ef} / W_t ratio, ranging between 0.02 and 0.04, which may be explained by the low gradient of the watershed, and the prevalence of high water uptake crops such as corn *[Woods, 2009]*. *Dingman, [2002]* indicated this ratio is generally lower than 0.5, and as low as 0.1 for many watersheds. *Woods, [2009]* evaluated the flow duration curve at the Williamstown gauge from 1960 to 2004. Results showed a steep curve, indicating discharge is primarily due to runoff, and not from groundwater discharge, which corresponds to the sandy silt and till deposits that have low dynamic storage *[Thomas 1966]*.

3.6 Hydrogeology

Within the Raisin River watershed, there is only one primary aquifer, that of the Contact Zone Bedrock Aquifer (herein called the bedrock aquifer), located beneath the overlying sediments. A second aquifer, known as the Lancaster-Cornwall Aquifer, consists of a basal gravel deposit located along the shore of the St. Lawrence River, between the Quebec border and the City of Cornwall; however, except for the area near Lancaster, at the mouth of the Raisin River, this aquifer is not within the study area, and is not further discussed. The unconsolidated Quaternary sediments, which lay atop the bedrock, and are of limited thickness, and consist of fine sand, silt and clay. Several coarser-grained Esker deposits are located regionally, but none are in the study area [*Raisin-South Nation SWPR, 2007]*. As such, the overburden sediments, through which locally infiltrated water passes, will be considered as the Surficial Aquitard.

Cane [1996], reported there have been over 4000 wells drilled in the Raisin River watershed, of which more then 88% of the domestic groundwater wells in the region draw water from the bedrock aquifer *[Singer et al., 2003]*.

3.6.1 Bedrock Aquifer

The bedrock aquifer consists of the upper fractured limestone zone of the Ottawa Group Units (Lindsay, Verulam, Bobcaygeon and Gull River Formations) and Rockcliffe Unit. The vertical extent of the fracturing below the contact is not known; however, *Singer et al., [2003]* rated these units (and others) on their water-yielding capabilities and water quality. The Ottawa Group Units where reported as being good producers and of fair quality, while the Rockcliffe Unit was a poor producer and fair quality. Figure 3.8 illustrates the shallow Bedrock Aquifer potentiometric surface and regional groundwater flow direction within the Bedrock Aquifer. Areas of high bedrock topography in the northwest represent regional zones of recharge, while regional groundwater discharge would be in areas of topographic lows in the southeast along the St. Lawrence River, suggesting a regional flow direction from the Northwest to the Southeast. In addition, because portions of the south branch of the Raisin River lie in a very low-relief valley, shallow contact zone bedrock groundwater along the south branch may be influenced by sub-regional flow.

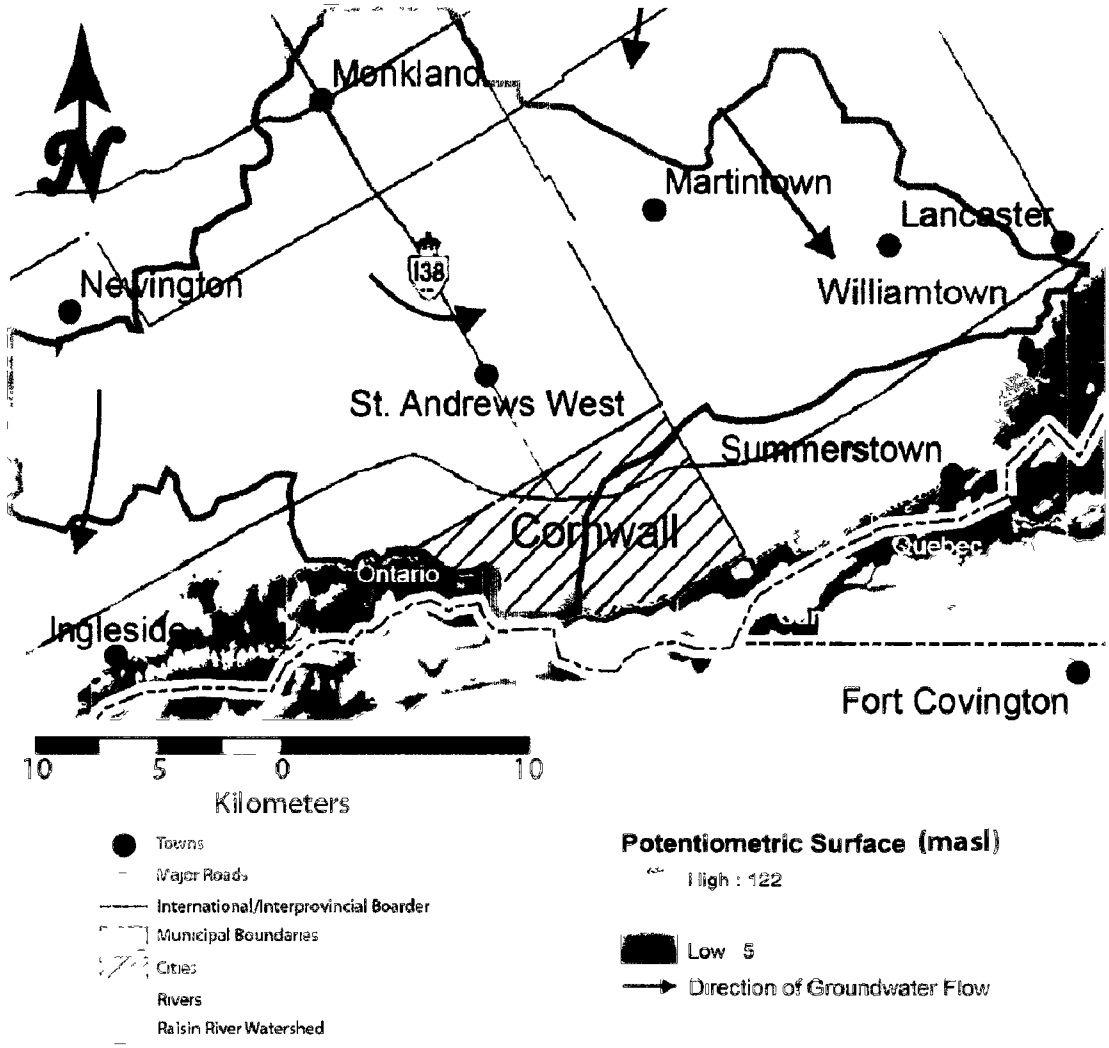

Figure 3.8: Shallow Bedrock Aquifer potentiometric surface and groundwater flow direction. Modified from *Raisin-South Nation SWPR, [2007].*

As previously indicated in section 3.4.3, there are four faults in the regions, which, along with stratigraphy and lithology are often important to groundwater flow. Because structures (fault zones) can have a higher hydraulic conductivity compared to the adjacent geology, they can increase an aquifers transmisivity. As such, local influences on regional groundwater flow may result from these vertical faults.

3.6.2 Surficial Aquitard

Most overburden deposits are of limited thickness and aerial extent, and consist of glacial-marine, glacial-fluvial and till deposits. *Raisin-South Nation SWPR, [2007],*

subdivides these further into a Glacial-marine Aquitard, a Till Aquitard, and a Glacial-fluvial Aquifer; however, for the purpose of this investigation, they will not be differentiated. Regionally, the Surficial Aquitard varies in thickness, generally between 18 and 50 m, depending on the degree of erosion. This aquitard does not extend throughout the region, but is segmented by bedrock outcrops and river channels, and consists of low permeability tills, silts, fine sands and clays. This results in groundwater and overland flow likely following local topography and draining into the various branches of the Raisin River.

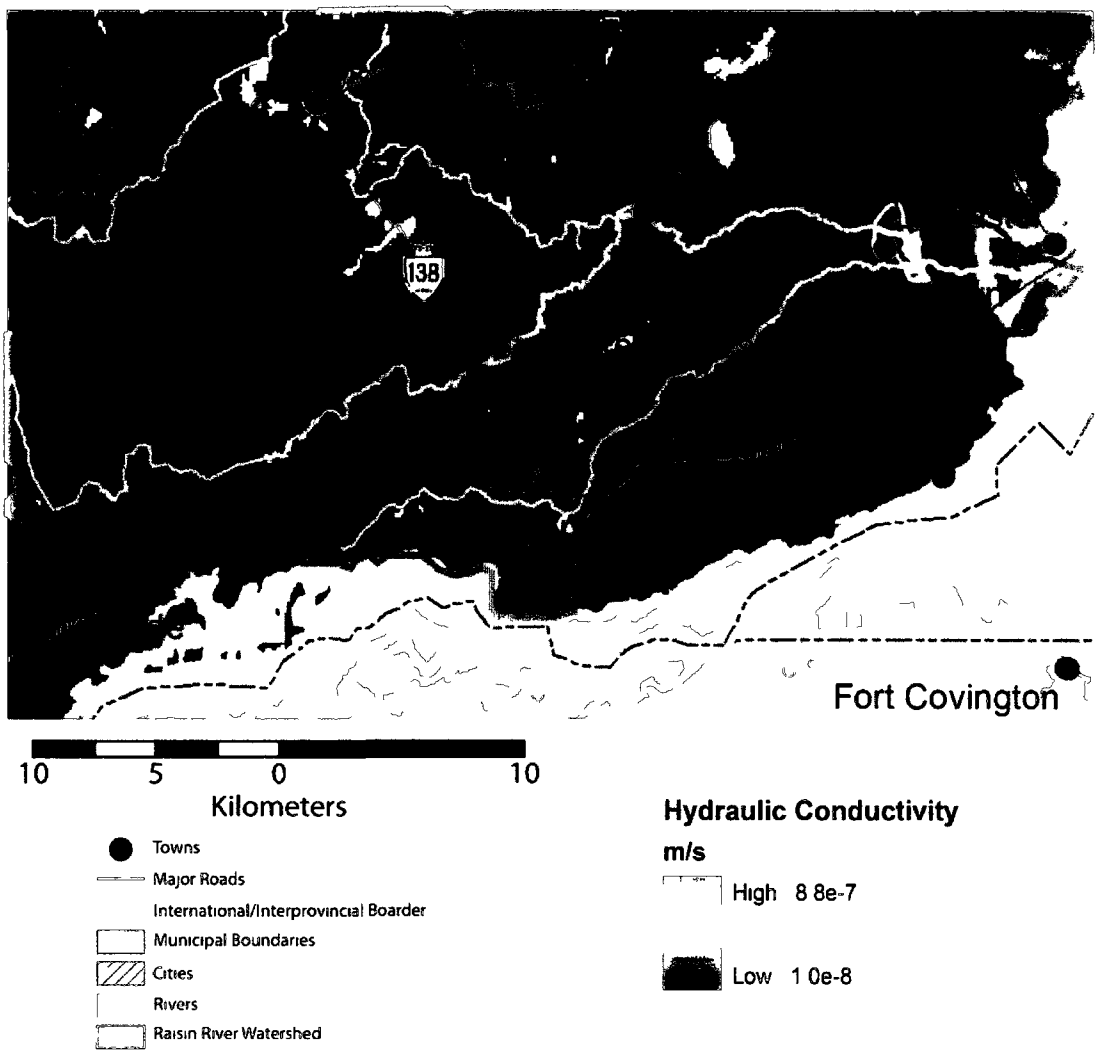

Figure 3.9: Hydraulic conductivity of overburden sediments (Surficial Aquitard). Modified from *Raisin-South Nation SWPR, [2007].*

On average, the hydraulic conductivity of the Surficial Aquitard is low at $3.0x10^{8}$ and increases in areas to $2.25x10^{-6}$ m/s *[Raisin-South Nation SWPR, 2007]. Porter [1996]* reported that Malone Till has hydraulic conductivity values of 10^{-7} m/s, while the older Fort Covington Till has a hydraulic conductivity between 10^{-6} m/s and $1.9x10^{-8}$ m/s. These values, as illustrated in Figure 3.9, are consistent with those of glacial till and silty sand as reported by *Freeze and Cherry [1979]*, and correspond with the physiographic units shown in Figure 3.5.

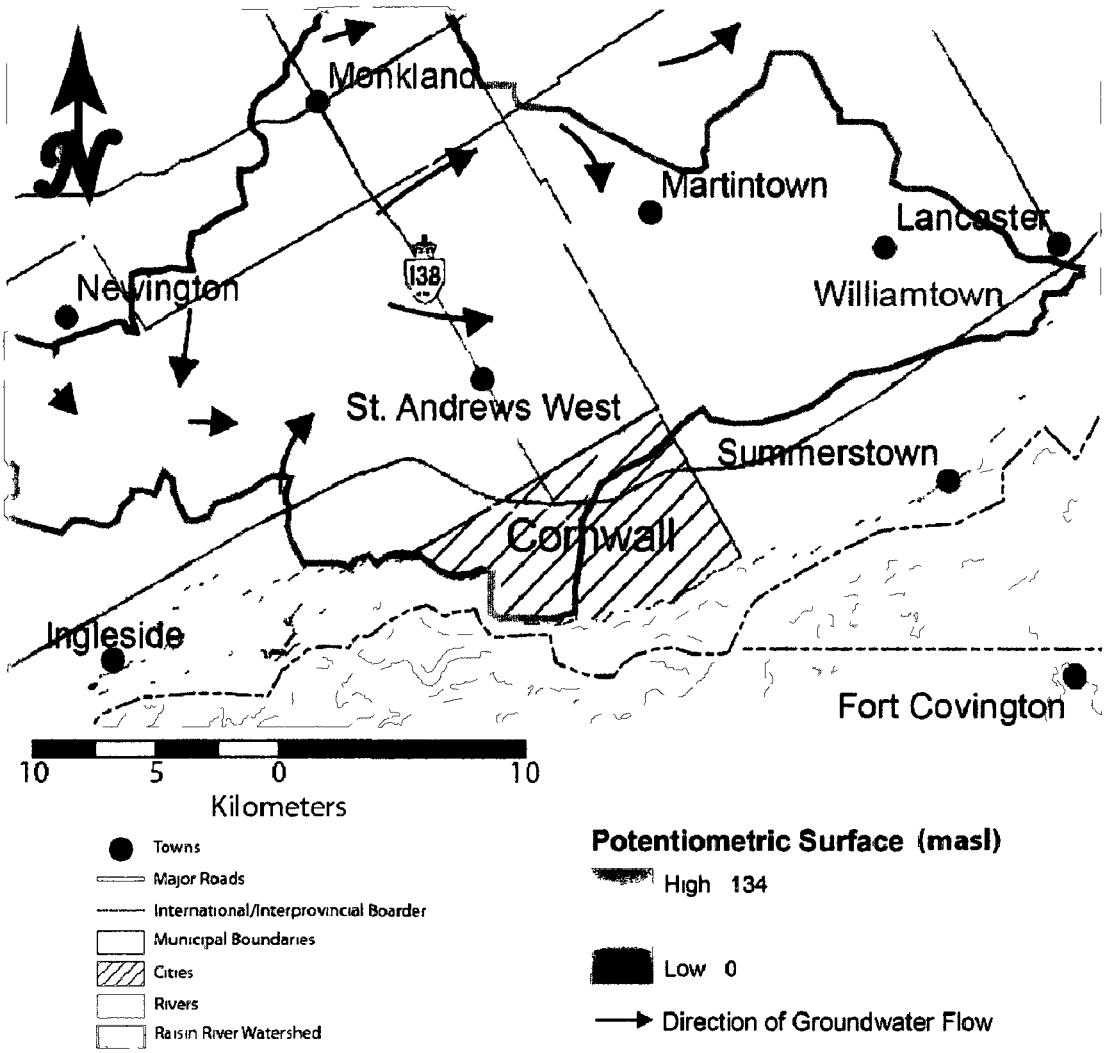

Figure 3.10: Surficial aquitard potentiometric surface and groundwater flow direction. Modified from *Raisin-South Nation SWPR, [2007].*

Figure 3.10 illustrates the local groundwater flow direction, which suggests that it follows local topography, and likely discharges locally along reaches of the Raisin River. In addition, the small vertical relief throughout the watershed adds to low vertical hydraulic conductivities, possibly suggesting limited connection between the overburden sediments and the Bedrock Aquifers. Furthermore, clay pockets within the overburden will act as confining layers on the local scale. Figure 3.11, shows the average annual recharge to the overburden and contact aquifers, which shows that the annual recharge is generally less than 100 mm/yr for the majority of the watershed, and only in the more permeable sediments in the vicinity of Lancaster (Lancaster-Cornwall Aquifer), does the recharge increase to values above 200 mm/yr *[Raisin-South Nation SWPR, 2007]*.

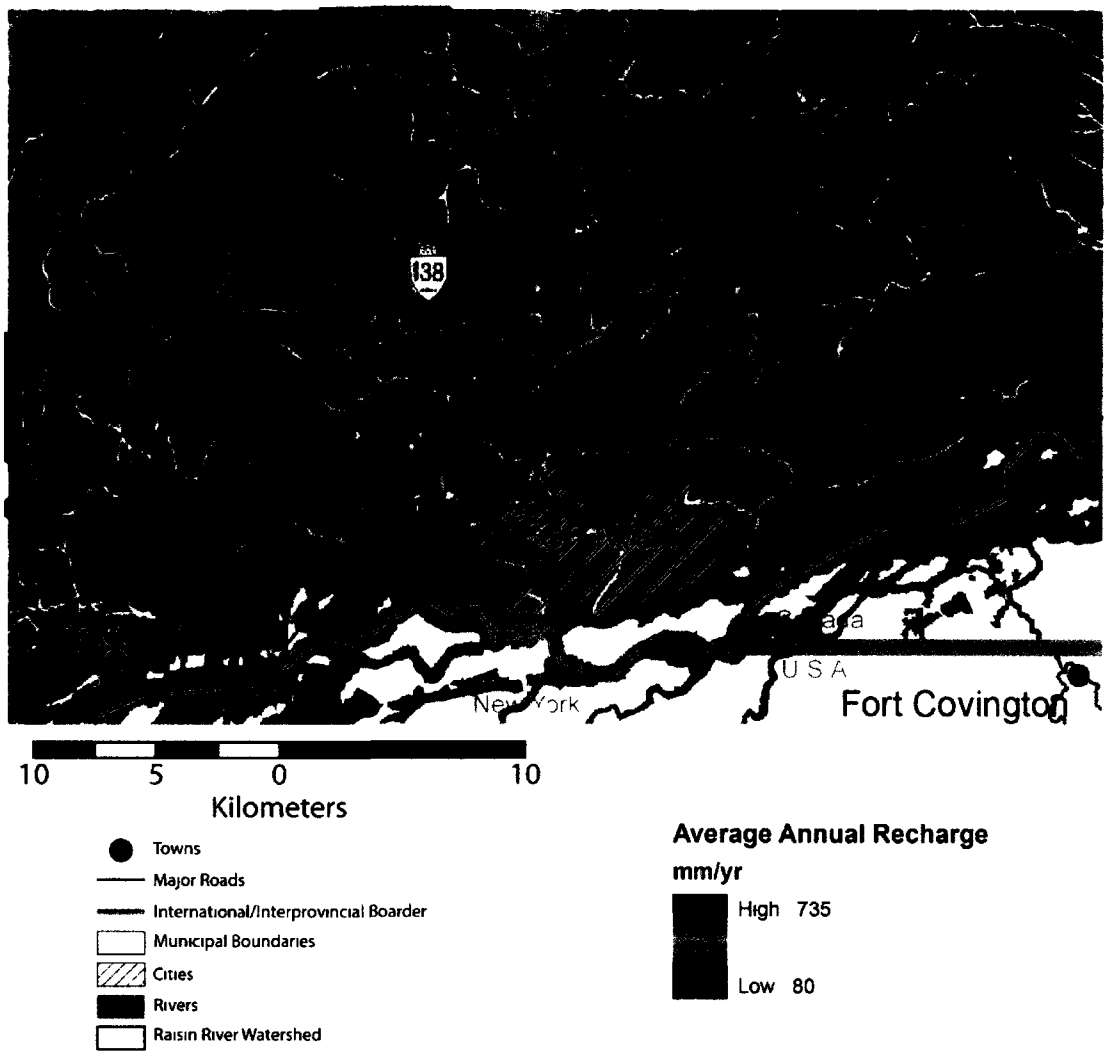

Figure 3.11: Average annual recharge to the overburden and contact bedrock aquifers. Modified from *Raisin-South Nation SWPR, [2007].*

3.6.3 Groundwater Quality

The extent of agricultural activities within the watershed, poses a potential risk to the underlying groundwater resources. Nutrient loading from point sources such as manure pits and septic fields, and non-point source applications of manure and synthetic fertilizers are evident throughout the watershed. However, previous studies, such as *Cane [1996]*, have shown that the Bedrock Aquifer from which most domestic wells draw groundwater is not impacted above maximum allowable concentrations (MAC) for drinking water for nitrates. Other potential pollutants of concern such as phosphate and trace metals were also found to be below relevant MACs.

4.0 METHODOLOGIES

4.1 Site Selection

Local land owners were contacted with the assistance of the Raisin River Conservation Authority (RRCA), who had existing relationships with many farmers in the regional, particularly those whose fields abut the Raisin River. Project objectives were discussed with interested farmers, and their properties were evaluated based on a number of important parameters. The local surficial geology, abundance of proximal cultivated fields, proximity to the river, presence of tile drains, year-round access, availability of neighbouring domestic wells, and fertilizer application. Following this process, three agricultural sites and one naturally vegetated background site were selected. Each of the three field sites were further divided into stations where lysimeters and piezometers were installed to varying depths. Available tile drains and domestic wells were chosen in the immediate vicinity of the stations. Although the installations (lysimeters, tile drains, piezometers and domestic wells) were not situated along specific groundwater flow-paths, samples from each site were considered as representative of the migration of water from the field surface to the underlying overburden and the bedrock aquifers at each site. Figure 4.1 illustrates the distribution of each site throughout the watershed.

4.2 Installations

In total, 8 lysimeters and 11 piezometers were installed, while 12 domestic wells and 6 tile drains were selected at 4 field sites, along with the establishment of three meteoric rain collection sites. Tile drains and domestic wells did not require any installation; however, they were selected based on location and availability. Exterior taps left open year round, that by-passed any water softerners and filtration systems accommodate monthly sampling. In a few cases, water level measurements were not possible to obtain because the well heads were sealed for flood protection purposes. Table 4.1 summarizes the domestic well construction information as obtained from the homeowners, while Table 4.2 summarizes the tile drain information. Appendix B provides additional location and construction information.

Table 4.1: Summary information for domestic wells used in this research.

Name	Site	Vegetation Type	Aquifer	Ground Elevation	Mid-Screen Depth	Well Diameter	Screen Length
			m	masl	mbgs	m	m
W1-A	1	Agricultural	Bedrock	57.014	56.9*	0.156	n/a
W1-B	1	Agricultural	Bedrock	54.619	54 5*	0.156	n/a
W1-C	1	Agricultural	Bedrock	53.700	53.5*	0.156	n/a
W2-A	2	Agricultural	Bedrock	53.619	53.5*	0.156	n/a
W2-B	2	Agricultural	Bedrock	53.404	53.2*	0.156	n/a
W2-C	2	Agricultural	Bedrock	55.512	55.4*	0.156	n/a
W2-F	2	Agricultural	Overburden	52.250	51.6	0.700	3.0
W3-B	3	Agricultural	Bedrock	57.129	57.0*	0.156	n/a
W3-C	3	Agricultural	Overburden	54.723	53.7	1.000	1.0
W3-D	3	Agricultural	Bedrock	56.545	56.4*	0.156	n/a
W9-A	Background	Natural	Overburden	89.178	88.2	1 000	2.0
W9-B	Background	Natural	Bedrock	89.056	88 9*	0.156	n/a

Notes: * = Estimated value as screen length is unknown

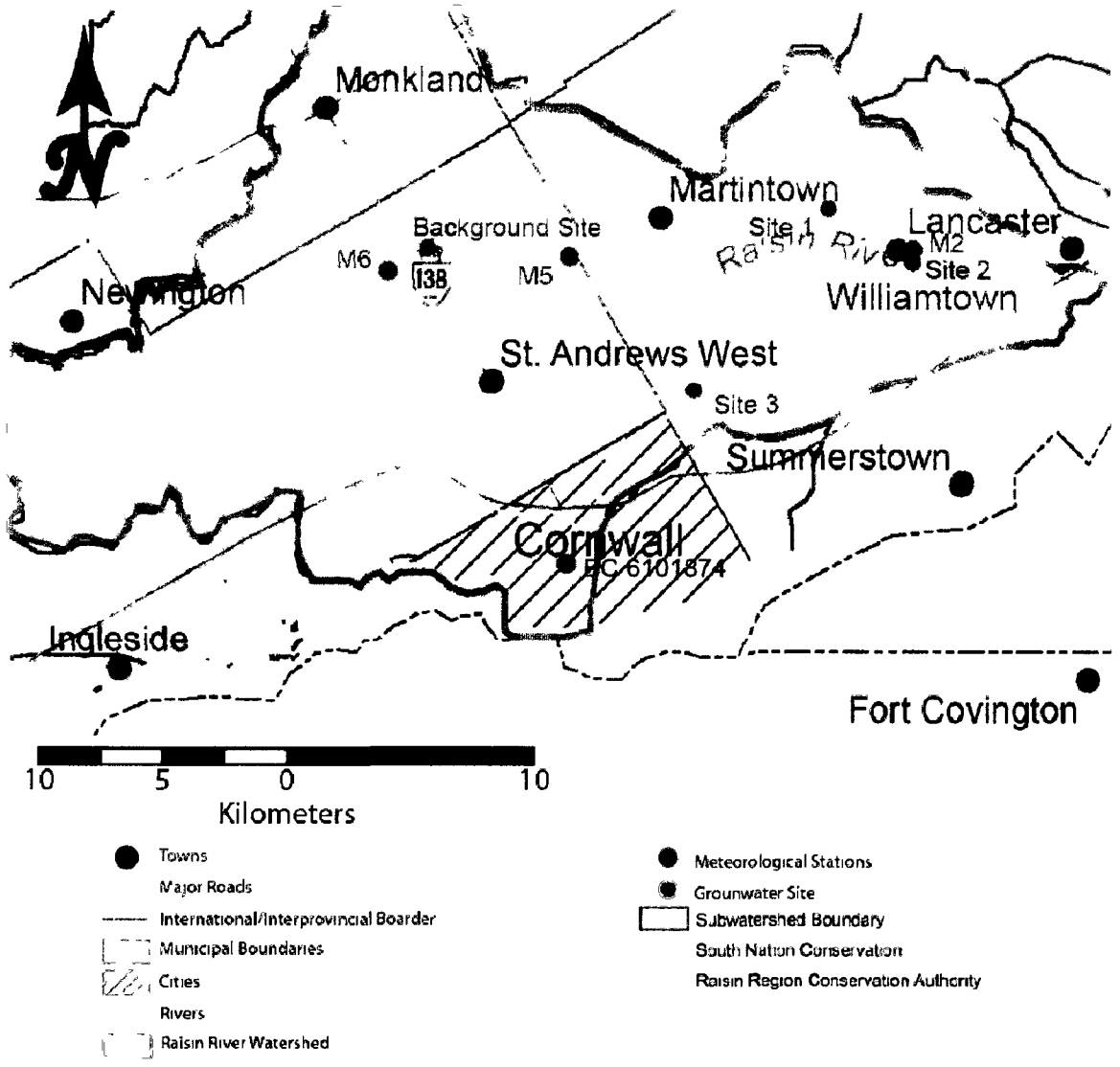

Figure 4.1: Research site locations. Modified from *[Raisin-South Nation SWPR, 2007].*

Table 4.2: Summary information for tile drains used in this research.

Name	Site	Ground Elevation	Outlet Depth
-		masl	mbgs
T1-A	1	54.195	1.5
T1-B	1	54.012	1.8
T2-A	2	52.653	1.0
T2-B	2	51.678	1.5
T3-A	3	52.270	1.0
T3-B	3	52.987	1.3

4.2.1 Lysimeters

The prefabricated lysimeters consisted of Soilmoisture Equipment Corp.® 1900 series in-situ soil water large-volume samplers, designed for near-surface installations at depths ranging from 6 inches (15 cm) to 6 feet (1.8 m). The units consist of a 1.9" (4.8 cm) outside diameter PVC tube, a porous ceramic cup with a 2 bar (200 kPa) air-entry value, and a Santoprene stopper *[Soilmosture, 2007]*. Neoprene tubing was used as an access port for evacuation. A Soilmoisture vacuum pump was required to evacuate the sampler, and clamping rings were slipped over the folded tubing to seal the sampler after evacuation. Table 4.3 summarizes the lysimeter installation information.

Table 4.3: Summary information for lysimeters installed for this research.

Name	Site	Bottom of Cup
		mbgs
L1-1A	1	0.30
L1-1B	1	0.91
L1-1C	1	1.82
L2-1A	2	0.30
L2-1B	2	0.91
L2-1C	2	1.82
L3-1A	3	0.30
L3-1B	3	0.91

4.2.2 Piezometers

Piezometers were advanced by first driving a 1-inch steel pipe into the ground using a 60 pound Bosch® electric jackhammer with a modified drive head. After extracting the steel pipe using a chain hoist, 1-inch schedule 40 PVC piezometers were pushed in before the hole collapsed in on itself. Construction scaffolding was set up to drive the steel pipe to the desired depth, and to suspend the chain hoist for pipe removal. Since the water table was

shallow at all sites (seasonal mean from 0.50 m to 2.5 m below ground surface), a one piece section of steel pipe was required with no couplings. To facilitate the insertion of the PVC piezometer, a bead (extruding approximately 3mm) was welded onto the circumference of the pipe every 5 feet to enlarge the drive-hole and facilitate the piezometer installation.

The piezometers were constructed from 5 and/or 10 ft sections of PVC joined together with flush threads, while 5 foot screened sections consisted of #10 sized slots. The PVC piezometer pipe was purchased from an environmental supplier in Ottawa. Table 4.4 summarized the piezometer installation information.

Table 4.4: Summary information for installed piezometers.

Name	Site	Ground Elevation	Mid-Screen Depth
		m.a.s.l.	m.b.g.s.
P1-1B	1	55.04	3.91
P1-1C	1	55.06	5.37
P1-2B	1	54.55	3.86
P2-1A	2	52.62	3.90
P2-1B	2	52.61	5.47
P2-2B	2	52.09	3.93
P3-1A	3	52.37	3.83
P3-1B	3	52.43	4.84
P3-1C	3	52.37	6.91
P3-2A	3	52.27	3.88
P3-2B	3	52.30	5.49
P9-1A	Background	87.72	2.94

4.2.3 Meteoric Stations and Rain Collectors

Rain gauges/collectors where installed at three private properties, distributed in the watershed at varying elevations, whose home owners volunteered to make daily recording of precipitation and collect samples for $\delta^{18}O$ and $\delta^{2}H$ isotope analysis. The three meteoric stations, consisted of a stainless steel rain collector with a 150mm diameter aluminum funnel, and 1L bottle for water collection. They were installed on steel posts (approximately 1.5 m above the ground) which were located in open clearings with no structures or trees within 30 meters. The Environment Canada weather station ID 6101874 at Cornwall, Ontario, was also used as a comparison for precipitation data. Meteoric stations are summarized in Table 4.5.

Table 4.5: Summary of meteoric stations and rain collectors used.

ID	Location	Type	Setup	Elevation masl	Latitude	Longitude
M2	Site 2	gauge / sample	project specific	55	45 14'N	74 59'W
M5	Site 5	gauge / sample	project specific	65	45 12'N	74 76'W
M6	Site 6	gauge / sample	project specific	100	45 11'N	74 87'W
6101874	Cornwall	gauge only	Environment Canada	64	45 02'N	74 75'W
6105976	Ottawa	gauge only	Environment Canada	79 2	45 38'N	75 72'W

4.2.4 Survey

All domestic wells and piezometers were surveyed using a Thales® Z-max RTK GPS system from the University of Waterloo. An HT2 Geoid and NAD83 coordinate system was used to establish latitudes and longitudes. Top of pipe and ground surface vertical and horizontal coordinates were measured after three newly installed benchmarks were created by post processing, in the vicinity of each of the study sites. The mean vertical and horizontal RMS errors for all measurements were ±0.011m and ±0.007m, respectively.

4.2.5 Test Pit Excavation

One test pit was excavated at Site 2 during the summer to observe the soil profile and evaluate the presence of macro pores (i.e. wormholes). Located close to piezometer P2-2B (Station 2), the pit was dug by shovel to an approximate depth of 1 metre.

4.3 Field Measurements

Physical and chemical parameters were measured concurrently during sample collection. Parameters included: pH, temperature, conductivity, oxidation-reduction potential, total dissolved solids, salinity and dissolved oxygen. All electrodes/probes were rinsed with deionized-distilled (DDI) water between samples to prevent cross-contamination then pre-rinsed with sample water. Specific sampling procedures for lysimeter, piezometer, tile drain and domestic well measurements are discussed in detail in Section 4.4.

4.3.1 Water Levels

Static water levels in piezometers and domestic wells were measured using a Solinst™ model 101 water level tape, prior to pump deployment and activation. The water level probe was rinsed with distilled water between uses to prevent cross-contamination. Water level measurements were made to three decimal places, with an accuracy of +/- 0.001m.

4.3.2 pH and Temperature

pH and temperature measurements were performed using a VWR™ SP21 handheld meter and tri-gel electrolyte electrode. Three-point calibration was performed daily using pH 4, 7 and 10 buffer solutions, as specified by the manufacturer.

4.3.3 Conductance

Electrical conductivity measurements were performed using an Orion™ model 110 conductivity meter. Calibration was performed on a daily basis using a manufactured sodium chloride (*NaCl*) solution with a conductance of 1413 $\mu S \cdot cm^{-1}$ at 20°C. Instrument precision for conductivity is reported as; ±1 $\mu S \cdot cm^{-1}$. Specific Conductance (SpC) was later calculated based on the conductivity and water temperature measurement, using equation (4.1), taken from *[Eaton et al., 1996]*:

$$SpC_{T'} = \sigma_T / 1 + \alpha(T - T') \qquad (4.1)$$

where, SpCT' represents the Specific Conductance at the common temperature T' (25°C), expressed in degrees Celsius, °C, and σ_T is the Conductivity at the measured groundwater temperature T, also expressed in degrees Celsius, °C. While α represents the temperature compensation slope, which for most natural waters ranges between 1-3 %/°C, *Eaton et al., [1996]* uses a slope value of 1.9 %/°C.

4.3.4 Oxidation-Reduction Potential (Eh)

Oxidation -reduction potential measurements were performed using a VWR™ SP21 handheld meter with a Ag/AgCl electrode. Redox electrodes respond directly to potential and so calibration is not possible; however, the electrode was tested daily against a standard Zobell's™ solution ($E_{measured}$ = 228 mV at 25°C) to assure proper readings, or to make a linear correction. The Zobell™ solution was first cooled to approximate groundwater temperatures (10°C). Measurements of E were then converted to Eh using Equation 4.2, using a temperature-dependant value for $E_{Ag/AgCl}$ determined by Equation 4.3, from data taken from *Clark [2006]*.

$$E_H = E_{measured} + E_{Ag/AgCl} \tag{4.2}$$

$$E_{Ag/AgCl} = (-0.7203 \cdot T) + 220 \tag{4.3}$$

where *T* represents in-situ groundwater temperature expressed in degrees Celsius, °C.

4.3.5 Dissolved Oxygen

Dissolved Oxygen (DO) measurements were conducted using a YSI™ model 55 DO meter, which uses a membrane and KCL electrolyte solution. Calibrations were performed daily based on the current barometric pressure and elevation; however, instrument problems were often encountered (readings above 100% oxygen saturation) and measurements were not made on numerous months.

4.4 Sample Collection and Handling

4.4.1 Groundwater

Sample collection was conducted on a monthly basis over a 15 month period from August 2005 to October 2006. Water samples obtained from piezometers and lysimeters were collected using a Geopump™ peristaltic pump with dedicated tubing. Because of the low hydraulic conductivities of the surficial sediments in which the piezometers were

installed, and the inherently long recovery times following piezometer purging, sampling was conducted at low-flow (<100 mL/minute). The sampling tube was located within the screen length following *Robin and Gillham, [1987]*, where water within the screen length is considered transient, and therefore representative of formation water, thus eliminating the need to purge prior to sampling. Sample collected from tile drains and domestic wells were filled directly from the outlet pipe and tap, respectively. Domestic wells were sampled using the wells submersible/jet pump and allowed to purge for 15 to 30 minutes, until field parameters stabilized for three consecutive measurements so as to allow stagnant well casing water to be removed and replaced with formation water.

Field filtration was conducted using a re-usable 47mm diameter polycarbonate Nalgene™ filter holder and a 0.45 μm Pall™ Supor™ disposable membrane. The filter holder was extensively rinsed between sites to prevent cross-contamination, and equipment blanks were collected for conformation. All samples were placed in an ice-pack filled cooler while in the field. Table 4.6 summarizes the bottle type used, quantity, filtration and sample handling. In case of the carbon samples, particular care was taken to ensure that no air bubbles (i.e., no head-space) were trapped beneath the septa, to prevent fractionation, while mercuric chloride ($HgCl_2$) was not used to kill bacterial activity as DIC/DOC samples were analyzed within 1 or 2 weeks of collection. Ammonium isotope samples were not field filtered because of the larger volume, they were instead filtered in the lab.

4.4.2 Precipitation

Each morning, the participating home owner checked the rain collector to record the precipitation volume and collect a sample if precipitation had occurred during the previous 24 hours. If rain water had accumulated in the 1L bottle, a graduated cylinder was used to record the amount, and subsequently determine the daily precipitation by dividing by the funnel area. After which, approximately 20mL were placed in a scintillation vial, sealed then frozen, with the remaining volume discarded. Samples and recordings were picked up monthly at the time of groundwater sampling.

Evaporation from the collector was not considered for this study. The rain collectors did not function during winter months, and the caretakers were asked to collect snow

samples, along with estimated daily accumulation amounts. However, home owner participation was inconsistent during the winter season.

Table 4.6: Sample bottle collection and handling summary.

Analyses	Bottle Type	Quantity	Field Filtered	Comments
Anions	30 mL PEL	1	No	Frozen, filtered during analysis
Major Cations	15 mL PEL	1	Yes	Acidified to pH 2 with HNO_3
DIC/DOC and Isotopes	40 mL borosilicate	2	Yes	None, rubber septa used
Total Phosphorus	50 mL PEL	1	No	Frozen
Ammonium	50 mL PEL	1	Yes	Frozen
Ammonium Isotope	1L PEL	1	No	Frozen
Nitrate Isotope	50 mL PEL	1	Yes	Frozen
H_2O Isotope	20 mL PEL	1	No	Sealed

4.4.3 Sampling QAQC

A total of 570 discrete samples, and an additional 49 field duplicate samples were collected over a 15 month period during this investigation. The ratio of duplicate to discrete samples was approximately 9%, which is close to the recommended ratio of 10% for Quality Assurance and Quality Control (QAQC), as specified by *Eaton et al., [1996]*. Duplicate sample results were compared against discrete samples by absolute percentage difference (APD). The results are discussed in Section 4.5, specific to each analytical method.

4.5 Analytical Methods

4.5.1 Oxygen and Hydrogen Isotopes of Water

The oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) isotope content in groundwater and precipitation samples were analysed within one or two weeks of sample collection and pickup, respectively. Analysis was conducted using a Finnigan Matt DeltaPlus isotope ratio mass spectrometer (IRMS) at the G.G. Hatch Isotope Laboratory, University of Ottawa. Within a few days of sample collection, a copper strip was placed in each vial to limit interference with the catalyst and hydrogen analysis. The $^{18}O/^{16}O$ ratios of water samples (R_{SAMPLE}) were measured by the standard CO_2-H_2O equilibration technique *[Epstein and Mayeda, 1953]*, while the $^{2}H/^{1}H$ ratios of water samples were determined using the zinc

reduction technique *[Coleman et al., 1982]*. Oxygen-18 and deuterium ratios are expressed as the δ values, which represent the deviation in parts per thousand (‰) of the sample (where R_{SAMPLE} represents either $^{18}O/^{16}O$ or $^{2}H/^{1}H$), from Vienna-Standard Mean Ocean Water (VSMOW) ($R_{STANDARD}$), using Equation 2.1. $\delta^{18}O$ and $\delta^{2}H$ measurements were normalized using internal laboratory standards and IAEA reference materials, including Greenland Ice Sheet Precipitation (GISP), VSMOW, and Standard Light Antarctic Precipitation (SLAP). The 2σ analytical precision was ±0.1‰ for $\delta^{18}O$ and ±2‰ for $\delta^{2}H$. The APD results from field duplicate analysis were 2% for $\delta^{18}O$ and 9% for $\delta^{2}H$, which is considered acceptable.

4.5.2 Aqueous and Isotope Carbon Composition

Water samples were analyzed for DIC and DOC concentrations and isotopic content on a monthly basis within 1 or 2 weeks of collection. Concentrations and $^{13}C/^{12}C$ ratios were determined using an IO® total inorganic carbon–total organic carbon analyzer interfaced to a Finnigan Conflo II and Finnigan Matt DeltaPlus isotope ratio mass spectrometer (IRMS) for analysis by continuous flow at the G.G. Hatch Isotope Laboratory, University of Ottawa *[St-Jean, 2003]*. Sample vials were first run for DIC, after which 5 drops (0.25 mL) of phosphoric acid (H_2PO4) were added to reduce the pH, and vials were then flushed with helium for 30-45 minutes to degas potentially interfering high CO_2 concentrations when samples are re-run for DOC. DIC and DOC concentration are expressed in mg-C·/L, while $^{13}C/^{12}C$ content is expressed by standard delta (δ) notation, which represents a deviation in parts per thousand (‰) from the standard Vienna Pee Dee Belemnite (VPDB), using Equation 2.1. Isotope data were normalized using three internal standards, with 2σ analytical precision for concentrations and δ ^{13}C values, and are reported to 0.002 ppmC or 2% (whichever is higher) and ±0.2‰, respectively. The APD results from field duplicate analysis were 6% for DIC and 12% for DOC, and 4% for $\delta^{13}C$-DIC and 3% for $\delta^{13}C$-DOC. All results are considered acceptable, although the DOC value is high.

4.5.3 Major Ions and Nutrients

The major anion concentrations (F^-, Br^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) in water samples were analyzed by Ion Chromatography (IC) using a Dionex® DX-100 coupled to a Dionex®

AS40 autosampler. Samples were filtered in-line with a 0.45 micron filter. Major cation concentrations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a Variant® Vista-Plus. Analyses were conducted in the Geochemistry Laboratory at the University of Ottawa. All samples were run in duplicate together with internal standards and the analytical reproducibility was ±5%.

Additionally, total phosphorus and ammonium (NH_4^+) concentrations in water were determined by flow injection analysis (FIA) photo colorimetry using a Lachatte® 8500 Flow Injection analyzer. Analyses were performed in Dr. David Lean's lab in CAREG, at the University of Ottawa. The average APD results from field duplicate analysis were 7% for anions and 5% for major cations, and are considered acceptable. Results for total phosphorus and ammonium were 7% and 12% respectively.

4.5.4 Nitrogen and Oxygen Isotopes of Nitrate

The isotopic compositions of nitrate nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) were determined using the "Denitrifier Method" developed at Princeton University. The basic protocol is described in *Sigman et al., 2001* for $\delta^{15}N_{NO3}$, while *Casciotti et al., [2002]* further describe the method with regard to $\delta^{18}O_{NO3}$. The method involves the isotopic analysis of nitrous oxide (N_2O), which is generated by the classical denitrification pathway of nitrate (Equation 4.4) by denitrifying bacteria (*Pseudomonas aureofaciens*) that lack N_2O-reductase activity (the enzyme that reduces N_2O to N_2).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (4.4)$$

The process consists of preparing denitrifier cultures, inoculation, incubation and purging, to finally produce a bacterial broth into which the samples are injected. A complete step-by-step write-up of the method is provided in Appendix B. After injection of 20 nmoles of NO_3-N in a helium purged *Pseudomonas aureofaciens* broth, the reaction is allowed to sit overnight. Using a helium carrier gas, N_2O is removed from each vial using an automated on-line extraction. Purification, cryogenic trapping, and chromatographic separation from CO_2 is completed using a Finnigan Precon, with subsequent analysis by continuous flow

using a Thermo-Finnigan Matt DeltaPlus XP isotope ratio mass spectrometer (IRMS) at the G.G. Hatch Isotope Laboratory, University of Ottawa.

Isotope data were referenced against an automated injection of N_2O from a gas cylinder; however, this was not the absolute reference, as each batch also included replicates of the international KNO_3 reference standards IAEA-N3. The method precision for $\delta^{15}N$ and $\delta^{18}O$ values is reported as ±0.2‰; however, the average uncertainty from all the batches for $\delta^{15}N$ and $\delta^{18}O$ was determined to be ±0.6‰ and ±1.3‰, respectively. All samples were run in triplicate, while blanks and standards were included every four samples (12 vials) to ensure consistency. The major advantage of this method is that it requires approximately three orders of magnitude less nitrate than conventional methods, with concentrations as little as 0.1 mg/L NO_3-N. Field duplicate samples were not specifically analysed, since all samples were run in triplicate, and only a limited number of samples could be analyzed.

Additional issues associated with the $^{18}O/^{16}O$ analysis of nitrate by this method also exist. They include: (1) the oxygen isotopic difference between nitrate samples and the N_2O analyte due to isotopic fractionation associated with the loss of oxygen atoms from nitrate *[Casciotti et al., 2002]*; (2) the exchange of oxygen atoms with water during the conversion of NO_3 to N_2O *[Casciotti et al., 2002].* However, it is also reported that water exchange contributes to less then 10% and often less than 3% of the oxygen atoms, while both issues can be corrected for by applying the isotopic reference materials (IAEA-N3, $\delta^{18}O_{H2O}$) and $\delta^{18}O_{BLANK}$, following the mass and isotopic balance Equations 4.5 and 4.6:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (4.5)$$

$$\delta^{18}O_m m = (\delta^{18}O_s + \varepsilon)s(1 - x) + \delta^{18}O_{H2O} sx + \delta^{18}O_b b \qquad (4.6)$$

where m is the total amount of measured N_2O N in the sample, s is the amount of sample nitrate N added, b is the amount of blank N, and x is the fraction of oxygen atoms in the product N_2O from the exchange with water during denitrification. $\delta^{18}O_m m$ is the measured $\delta^{18}O$ value, $\delta^{18}O_s$ is the true $\delta^{18}O$ value, while the oxygen isotopic compositions of water and the blank are $\delta^{18}O_{H2O}$ and $\delta^{18}O_b$, respectively. ε is the isotopic fractionation from the removal of oxygen atoms during nitrate reduction. Further explanation is reported in

Casciotti et al., [2002], including assumptions and estimated values if amounts of blank or exchange are not measured. The uncertainty is proportionally lower for results that are similar in $\delta^{18}O$ to N3.

4.5.5 Nitrogen Isotopes of Ammonium

Groundwater samples were analyzed for nitrogen ($^{15}N/^{14}N$) isotope content of NH_4, using the 'Ammonium Diffusion' method, as described by *Sebilo et al., [2004]; Schleppi et al., [2006]*; *Holmes et al., [1998]*, with a few modifications due to available supplies and equipment, as this method was newly developed in the laboratory. This method was first developed in 1939 for quantitative analysis of nitrogen, and then adapted in the 1990s for isotope measurements *[Holmes et al., 1998; Sebilo et al., 2004].*

The method involves the conversion of 50 to 150 µg of dissolved NH_4^+-N to NH_3 by increasing the pH and subsequently trapping the NH_3 onto a H_2SO_4 saturated glass fiber filter, to produce $(NH_4)_2SO_4$. Because of the degree of nitrogen fractionation involved during volatilization, it is critical that >98% of the sample nitrogen is diffused onto the filter to obtain an accurate isotope ratio *[Sebilo et al., 2004].* As such, the samples were incubated for one week, and subsequently freeze-dried prior to analysis by mass spectrometry.

The $^{15}N_{(NH4)2SO4}$ content and concentration was then determined by packing the freeze-dried glass fiber filters into large (10 × 10 mm) silver cups and thermally decomposing them (to N_2 gas) using an Elementar® Vario EL III elementar analyzer interfaced to a Finnigan Conflo II and Thermo-Finnigan Matt DeltaPlus XP isotope ratio mass spectrometer (IRMS) for analysis by continuous flow at the G.G. Hatch Isotope Laboratory, University of Ottawa. The amount of N content on the glass fiber filter was determined by evaluating the area of the N_2 peak, and compared to the original dissolved NH_4^+-N amount in the incubation bottle. Only if the recovery was >95%, was the nitrogen isotope ratio considered acceptable *[Sebilo et al., 2004].* Similarly, blank samples and the IAEA-N3 standard were prepared, incubated, freeze-dried and thermally decomposed to determine the impact on the N signal. It was determined that typically less than 2% of the total N signal was a result of the nitrogen blank, which was later corrected for by mass

balance. *Sebilo et al., [2004]* concluded their blank contributions were mainly derived from small N_2 leaks in the autosampler, which is also likely for our setup.

Isotope data were normalized using internal standards previously calibrated with International standards. The method uncertainty for $\delta^{15}N$ values is reported as ±0.2‰; however, the 2σ analytical precision was determined to be ±1.9‰. All samples were run in duplicate. Field duplicate samples were not specifically analysed, since all samples were run in duplicate, and only a limited number of samples could be analyzed. A complete step-by-step write-up of the method is provided in Appendix B.

5.0 RESULTS AND DISCUSSION

5.1. Stable Isotopes in Precipitation

As previously described, the objective of the meteoric sampling was to establish seasonal trends in $\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$ values, determine any spatial variations from the three meteoric stations, and to compare values against the long-term Ottawa MWL. Seasonal variations in $\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$ values were expected to be similar to those in Ottawa, while spatial variations from meteoric stations was expected to be minimal; however, because of the short sampling period, having three stations should have compensated for any anomalous results at any one station. With regards to the Ottawa LMWL, it was expected that the LMWL would have had a slightly more enriched signal because of the slightly warmer and wetter climate and lower elevation.

5.1.1. Precipitation Data

Between August 2005 and October 2006, precipitation samples were collected daily (when available) from three meteoric stations (M2, M5 and M6), distributed throughout the Raisin River watershed (Figure 4.1). Table 5.1 summarized both the total frequency of events (number of samples collected), and total monthly precipitation at each station, including the Environment Canada station ID 6101874, located in Cornwall, Ontario (herein referred to as station EC). Figure 5.1 plots the mean monthly precipitation, showing the wettest period as fall and spring. Basin wide recharge is likely greatest during the fall when precipitation totals are significant and temperatures begin decreasing, resulting in lower evapotranspiration, and following spring thaw, when ground ice has thawed permitting precipitation to infiltrate. Monthly temperature and precipitation values for station EC are summarized in Table 5.2, while complete Climate Normals (1971-2000), and Daily and Monthly Climate Data for station EC are located in Tables A1, A3, and A4 in Appendix A. The period of August to November 2005 appears to have been significantly wetter than normal, while the second summer period, June to August 2006 appears to be similar to recorded normals. Similarly, the 2006 winter and spring periods, appear to be similar to recorded normals.

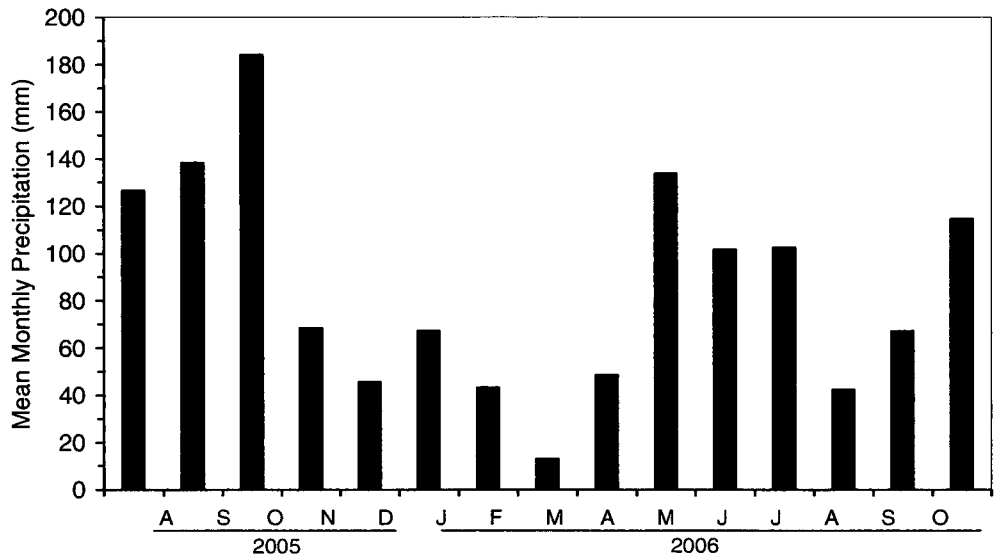

Figure 5.1: Mean monthly total precipitation data from EC Cornwall Station ID 6101874 ***[Environment Canada, 2007b].***

Table 5.1: Total frequency of events, samples collected and monthly precipitation totals.

		Total Monthly Precipitation			
Station		M2	M5	M6	EC*
Elavation (masl)		55	65	100	64
Precipitation Frequency (days) / # Samples		62	61	33	183
Date		(mm)	(mm)	(mm)	(mm)
Aug	2005	139	121	117	143
Sep	2005	123	94	110	143
Oct	2005	144	185	178	221
Nov	2005	14	63	5	103
Dec	2005				64
Jan	2006	63	33		115
Feb	2006	30			78
Mar	2006	12			22
Apr	2006	52	50	19	66
May	2006	180	169	110	126
Jun	2006	119	127	96	83
Jul	2006	97	131	119	104
Aug	2006	39		21	33
Sep	2006	88	89	73	77
Oct	2006	120	15	94	109
Mean Monthly Precipitation (Aug 05 - Jul 06)		89	108	94	106

Notes: "*" Indicates no samples collected at this site.

Mean monthly precipitation was determined from the total precipitation (for the period of August 2005 to July 2006), to evaluate the adequacy of sample collection by participating home owners (Table 5.1). The data suggest strong similarities between the three meteorological stations and station EC. The relative percentage difference of the mean monthly precipitation for stations M2, M5 and M6, were 9%, 1%, and 6% from that of

station EC, respectively. However, there was limited participant sample collection during the winter months (December to March), particularly for station M6. As a result, the $\delta^{18}O$ and $\delta^{2}H$ values (discussed in the Section 5.1.2), specifically those from station M6 should be used with caution, as they will disproportionally exhibit more enriched values because of incomplete winter sampling.

Table 5.2: Monthly temperature and precipitation values for meteoric station EC.

Month	Year	Min Temp °C	Max Temp °C	Mean Temp °C	Total Rain mm	Snow (Rain Equivalent) mm	Total Precipitation mm
Aug	2005	17.7	27.1	22.4	143		143
Sep	2005	14	23	18.5	143		143
Oct	2005	7.3	14.1	10.7	221		221
Nov	2005	0.2	8.4	4.3	95	8	103
Dec	2005	-7.9	-2	-5	19	45	64
Jan	2006	-7.8	-0.2	-4	66	48	115
Feb	2006	-9.4	-2.4	-5.9	37	41	78
Mar	2006	-4.4	4.4	0	19	3	22
Apr	2006	2.8	13.4	8.2	60	6	66
May	2006	10.2	19.6	14.9	126		126
Jun	2006	14.4	24.1	19.3	83		83
Jul	2006	17.6	28.7	23.2	104		104
Aug	2006	15.6	25.5	20.6	33		33
Sep	2006	11.7	19.0	15.4	77		77
Oct	2006	4.7	12.7	8.7	109		109

5.1.2. Meteoric $\delta^{18}O$ and $\delta^{2}H$ Values

Raw $\delta^{18}O$ and $\delta^{2}H$ values for each of the three stations are summarized in Table 5.3. Both the $\delta^{18}O$ and $\delta^{2}H$ mean raw values from each station are very similar, with pooled average raw values for $\delta^{18}O$ and $\delta^{2}H$ of -9.9‰ and -74.4‰, respectively. The minimum (depleted) values represent those of snow samples collected in January and February 2006 from station M2. Table C1 in Appendix C presents the event-weighted $\delta^{18}O$ and $\delta^{2}H$ values for meteoric waters collected from stations M2, M5 and M6 between August 2005 and October 2006. The event-weighted calculation consisted of grouping concurrent days of precipitation into storm events, then conducting an isotopic mass-balance based on each day's precipitation amount within the storm event. If meteoric samples were collected, but precipitation measurements were missing for any particular day or storm event, precipitation results from the Cornwall station were used.

Table 5.3: Statistical summary of meteoric $\delta^{18}O$ and $\delta^{2}H$ raw values.

	M2		M5		M6	
	$\delta^{18}O$ (VSMOW)	$\delta^{2}H$ (VSMOW)	$\delta^{18}O$ (VSMOW)	$\delta^{2}H$ (VSMOW)	$\delta^{18}O$ (VSMOW)	$\delta^{2}H$ (VSMOW)
Min	-24.2	-183.7	-21.1	-161.9	-21.4	-163.0
Max	-3.7	-24.0	-2.7	-8.5	-3.5	-27.4
Mean	-10.0	-75.0	-9.9	-72.0	-9.9	-76.2
SD	5.1	38.6	4.1	32.5	4.4	33.9
Count	75	55	64	51	56	26

Table 5.4 summarizes the amount-weighted mean monthly $\delta^{18}O$ and $\delta^{2}H$ values for each station, the amount-weighted mean annual values for the period of September 2005 to August 2006, along with pooled $\delta^{18}O$ and $\delta^{2}H$ values from stations M2 and M5. Station M6 was excluded from the pooled values for reasons explained in Section 5.1.1, and because of limited $\delta^{2}H$ data analysis (Table 5.4). The amount weighted mean-monthly values were determined by averaging the event-weighted values for any particular month.

Table 5.4: Amount weighted mean-monthly and mean-annual meteoric $\delta^{18}O$ and $\delta^{2}H$ values.

		M2		M5		M6		Pooled M2 & M5 Avg	
		$\delta^{18}O$ (VSMOW)	$\delta^{2}H$ (VSMOW)	$\delta^{18}O$ (VSMOW)	$\delta^{2}H$ (VSMOW)	$\delta^{18}O$ (VSMOW)	$\delta^{2}H$ (VSMOW)	$\delta^{18}O$ (VSMOW)	$\delta^{2}H$ (VSMOW)
Aug	2005	-8.9	-62.2	-6.9	-48.0	-8.8	-63.0	-7.9	-55.1
Sep	2005	-7.5	-56.9	-5.8	-38.5	-7.7	-50.0	-6.7	-47.7
Oct	2005	-10.1	-72.6	-12.0	-88.5	-12.2	-84.6	-11.1	-80.5
Nov	2005	-8.0	-51.3	-9.8	-66.0	-8.8	-57.4	-8.9	-58.6
Dec	2005								
Jan	2006	-17.4	-127.3	-12.1	-80.1			-14.8	-103.7
Feb	2006	-21.4	-159.8					-21.4	-159.8
Mar	2006	-9.2	-84.5					-9.2	-84.5
Apr	2006	-6.9	-62.2	-10.3	-68.4	-15.6		-8.6	-65.3
May	2006	-9.6	-69.0	-9.0	-65.9	-11.9	-98.5	-9.3	-67.5
Jun	2006	-11.9	-81.2	-8.4	-62.8	-11.4		-10.1	-72.0
Jul	2006	-7.7	-38.5	-7.5	-45.1	-5.9		-7.6	-41.8
Aug	2006	-7.3				-9.5		-7.3	
Sep	2006	-5.9		-9.9		-10.5		-7.9	
Oct	2006	-17.4		-19.5		-17.3		-18.5	
Annual*		-10.2	-70.0	-9.3	-64.8	-10.1	-48.1	-9.9	-69.1

Notes: The weighted mean-annual values are for the period September 2005 to August 2006.

Because of incomplete sample collection (as previously discussed) and incomplete analysis of $\delta^{2}H$ values in August to October 2006, it was difficult to make comparisons between stations for every month. Pooled amount-weighted mean monthly meteoric water $\delta^{18}O$ and $\delta^{2}H$ values were most depleted (-21.4‰ and -159.8‰, respectively) in February 2006 (snow samples only at station M2). Most enriched values varied between stations, but

values for $\delta^{18}O$ (-5.9‰ to -7.6‰) and $\delta^{2}H$ (-41.8‰ to -47.7‰) were observed between July and September. The absences of results from December 2005 indicates that no samples were collected from any of the three stations, while the large discrepancy of values from stations M2 and M5, is a result of incomplete sample collection from M5. These findings suggest that only results from station M2 are credible, and only partially due to limited sampling through winter months.

The event-weighted $\delta^{18}O$ distribution for stations M2 and M5 shows strong seasonal variations typical of a northern continental station (Figure 5.2). Temperature extremes and significant isotopic seasonal variations occur because of the distance of the moderating effect of marine influences *[Clark and Fritz, 1997]*. Heavily depleted meteoric signals are evident in two continental storm events (October 2005, portion of Hurricane/Storm Wilma), and a major storm system from October 2006. The extremely depleted signals are attributed to consecutive days of precipitation, where the effects of Rayleigh distillations occur in storm systems that travel long distances from the Caribbean, with depleted $\delta^{18}O$ and $\delta^{2}H$ values were as low as -21 and -160‰.

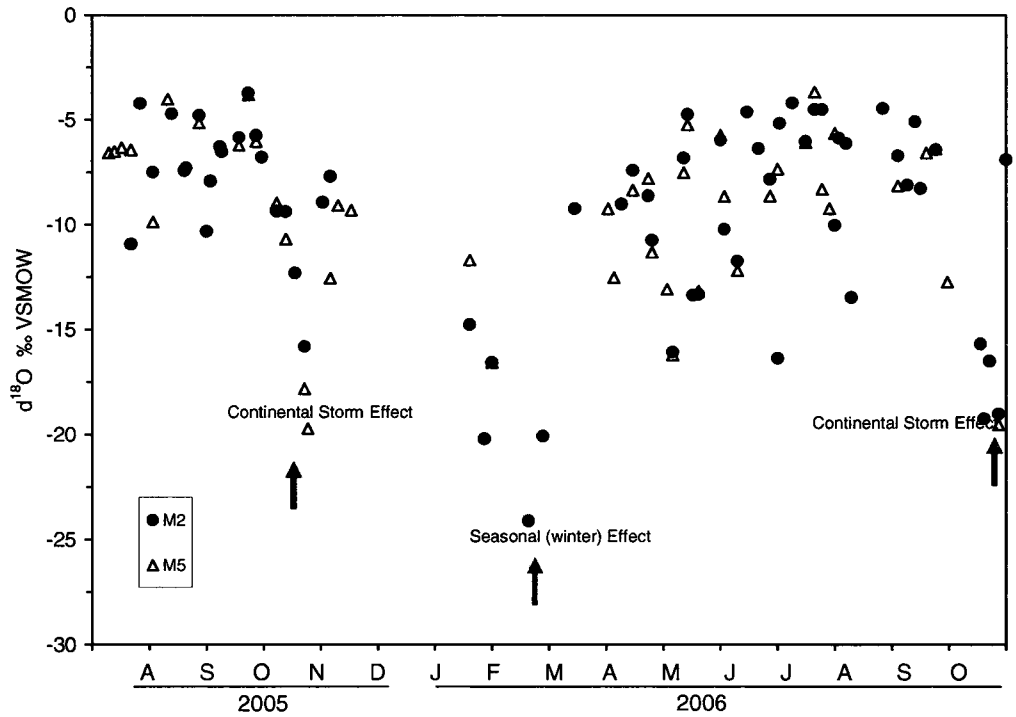

Figure 5.2: Event-weighted $\delta^{18}O$ distribution for stations M2 and M5. Three periods of depletion occur, two as a result of continental effect storm precipitation events (October 2005 and October 2006) (red arrow), and one due to seasonal (winter) depleted precipitation (green arrow).

However, despite the extremes in meteoric inputs, recharge in temperate northern climates is seasonally biased towards the moderate isotope signals of late fall and late spring precipitation events *[Clark and Fritz, 1997]*, as the mean meteoric $\delta^{18}O$ values is approximately -10‰.

The M2 amount-weighted mean annual meteoric $\delta^{18}O$ and $\delta^{2}H$ values are -10.2‰ and -70.0‰, respectively. In comparison, the amount-weighted mean annual $\delta^{18}O$ and $\delta^{2}H$ values for Ottawa precipitation, which is the nearest regional meteoric water line (1973-1994; 1999-2002), are -11.1‰ and -77.0‰, respectively *[Birks et al, 2003]*. The amount-weighted mean annual $\delta^{18}O$ and $\delta^{2}H$ values from the watershed stations likely exhibit more enriched values because of systematic incomplete winter sampling, resulting in meteoric water values over-weighted with isotopically heavier precipitation. For comparison both are plotted on Figure 5.3.

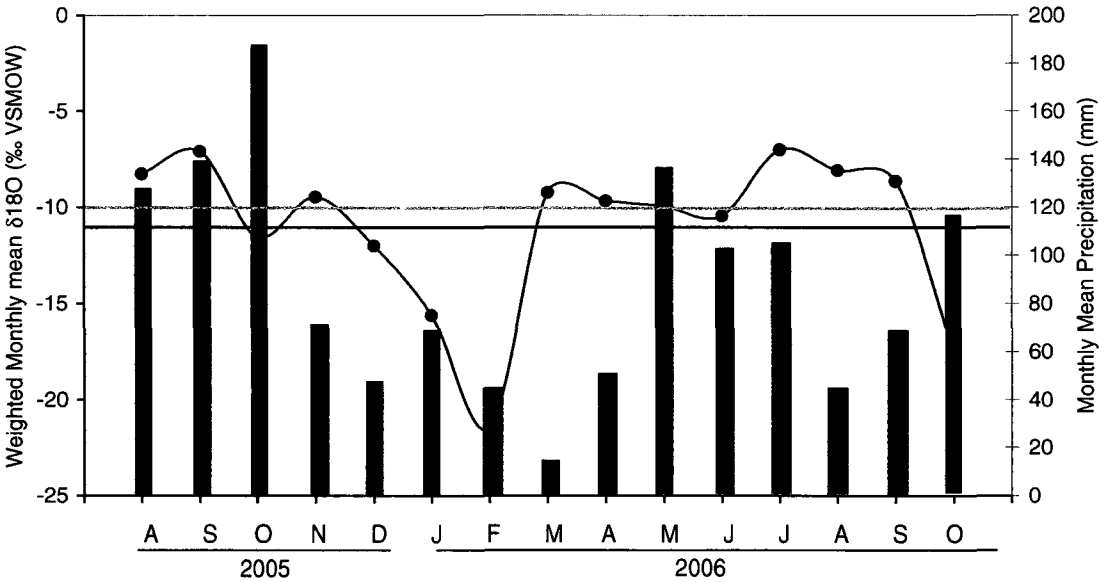

Figure 5.3: Amount-weighted mean monthly $\delta^{18}O$ distribution for pooled station data, and mean monthly precipitation for Cornwall, Ontario. For comparison the weighted mean annual $\delta^{18}O$ values for Ottawa and M2 values are presented as black and grey lines, respectively.

Regarding the differences in climate between the two areas, the Raisin River watershed is located approximately 80 km southeast of Ottawa and exhibits a slightly warmer climate, based on Climate Normals (meteorological stations for Cornwall and Ottawa, Ontario) (Tables A1 and A4 in Appendix A, respectively). For these reasons, it is

not surprising that the mean annual average of $\delta^{18}O$ and $\delta^{2}H$ contents in Raisin River basin precipitation would be slightly enriched with respect to that of Ottawa.

The event-weighted $\delta^{18}O$ – $\delta^{2}H$ values (all stations), and linear regression trend line (station M2) are plotted in comparison to the Ottawa LMWL (Figure 5.4). Differences in slope and intercept of the various MWLs can likely be attributed in part to the aforementioned imbalanced sampling, a slightly different climate, and to a short 15 month sampling record. In comparison, the Ottawa record extends back to 1973, therefore smoothing out short term climatic extremes. Results suggest the M2 LMWL is closest to the Ottawa LMWL than then pooled values, yet it is not statistically different from the Ottawa LMWL.

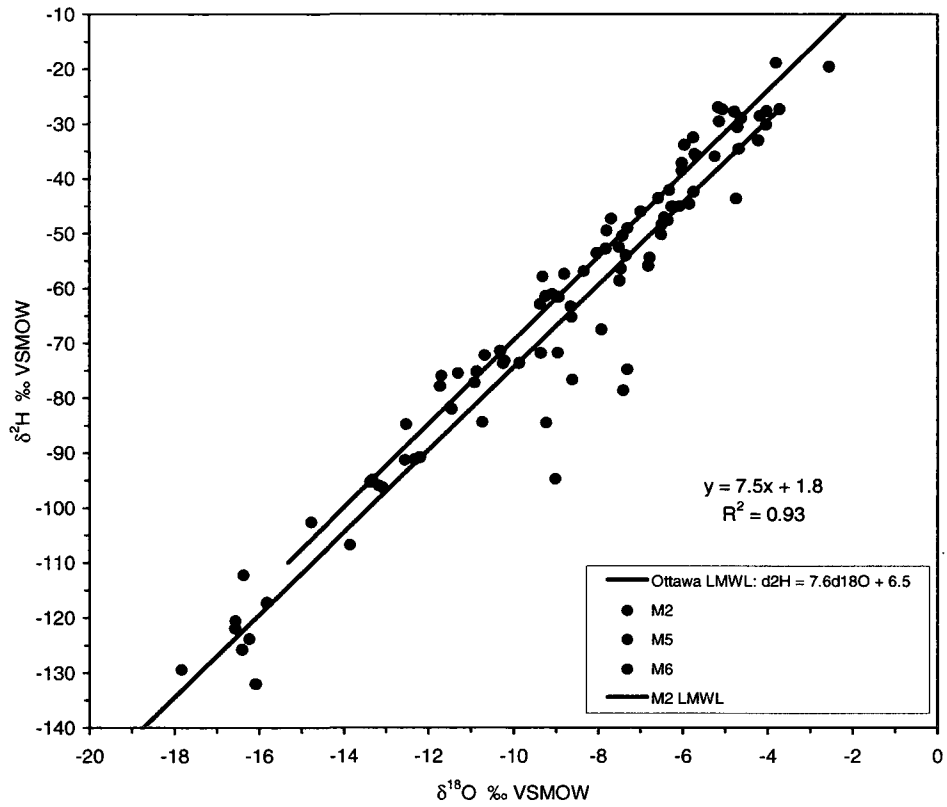

Figure 5.4: Event-weighted precipitation $\delta^{2}H$ and $\delta^{18}O$ values for all stations, and M2 and Ottawa LMWL *[Fritz et al., 1987].*

5.1.3. Summary and Conclusions

Precipitation totals suggest remarkable similarities between the three meteorological stations and those from the Environment Canada station in Cornwall, Ontario. Extremely depleted meteoric $\delta^{18}O$-$\delta^{2}H$ values were measured from a limited set of winter snow samples. Two continental storm events (October 2005, portion of Hurricane/Storm Wilma), and a major storm system from October 2006, resulted in depleted meteoric water at that time. These signals are attributed to consecutive days of precipitation, where the effects of Rayleigh distillations occur in storm systems that travel long distances from the Caribbean. Despite the extremes in meteoric inputs, recharge in temperate northern climates is seasonally biased towards the moderate isotope signals of late fall and late spring precipitation events, which was observed in these findings.

Meteoric results indicated that only values from station M2 are of any significant value, as sampling from stations M5 and M6 were incomplete, which resulted in biased local meteoric lines. Even so, the amount-weighted mean annual meteoric water $\delta^{18}O$ and $\delta^{2}H$ values for station M2 ($\delta^{18}O$ = -10.2‰ and $\delta^{2}H$ = -70.0‰) were more enriched than established values from Ottawa precipitation. In comparison, the amount-weighted mean annual $\delta^{18}O$ and $\delta^{2}H$ values for Ottawa precipitation, which is the nearest regional meteoric water line are -11.1‰ and -77.0‰, respectively. The discrepancy is certainly a result of limited sample collection during the winter months, resulting in a systematic exclusion of the winter meteoric signal.

Results indicate that establishing the local meteoric stations was not necessary for numerous reasons. First, the sampling record was too short to properly evaluate $\delta^{18}O$ and $\delta^{2}H$ values against the long-term Ottawa record. Second, it was critical that participating home-owners collect snow samples in winter to properly account for depleted values. Third, although the climate and elevation differ slightly between the Raisin Rover watershed and Ottawa, there is little overall difference between the $\delta^{18}O$ and $\delta^{2}H$ meteoric values, and any recorded difference is likely statistically insignificant. Accordingly, the Ottawa precipitation series is used as the best representation of the local meteoric water line, for comparison against groundwater values.

5.2. Background Site – Natural Vegetation

The objective for establishing this site was to collect shallow overburden and Bedrock Aquifer groundwater samples which have not been impacted by agricultural practices in the immediate vicinity. The Background Site is located in a rural naturally forested setting (dominated by C_3 type vegetation) west and up-gradient of the agricultural sites (Figure 4.1), and closer to the groundwater recharge area at higher topographic elevations. It consists of one piezometer and one dug domestic well, both located in a sand and gravel alluvial deposit, and one drilled domestic well completed in the Bedrock Aquifer. Only the piezometer was advanced specifically for this project, the two wells belonged to a participating home owner. Tables 4.4 and 4.1 in Section 4 summarize the installation details for the piezometer and wells, respectively, while Table 5.5 summarizes the physiographic and geologic settings (maps in Section 3) found in the vicinity of the Background Site.

Complete field parameter measurements, geochemical and isotopic results, and seasonal summaries of samples collected from the Background Site are located in Table D1 of Appendix D.

Table 5.5: Background Site - Summary of physiographic and geologic settings

Land Use	Forest
Soil Type	Loam: Sand, Silt & Clay (40-40-20%)
Physiographic Unit	Till Plain
Surficial Geology	Alluvial: Sand and Gravel
Bedrock Geology	Lindsay Formation: sublithographic to fine crystalline limestone with beds of calcarenite and shale
Overburden Thickness	15-20 m
Comments	None

5.2.1. Field Measurements

The water level, temperature, pH, conductivity, dissolved oxygen, and EH concentrations of Background Site groundwater samples are summarized in Table 5.6. The overburden summary consists of results from the shallow piezometer P9-1A and the dug well W9-A, except for water level, which only represents the piezometer. Seasonally the piezometer water table fluctuates by approximately 1.6 m, with water levels rising in September and dropping in June Figure 5.5. A lower water table corresponds to the periods

of high evapotranspiration *[Raisin-South Nation SWPR, 2007]* and is inversely related to periods of highest precipitation (Table A1).

Table 5.6: Background Site – Field parameter statistical summary.

	Overburden Groundwater					Bedrock Groundwater				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
W.L. (mbgs)	0.53	0.49	0.01	1.59	15	1.72	0.51	1.09	2.66	15
Temp. (°C)	10.9	3.8	2.5	19.0	30	11.1	1.2	9.0	12.6	15
pH	7.1	0.2	6.8	7.6	30	7.1	0.2	6.4	7.3	15
SpC. (µS/cm)	1323	352	768	1999	28	1155	333	764	1932	14
DO (mg/L)	0.92	1.23	0.11	3.24	10	0.19	0.06	0.10	0.27	8
Eh (mV)	430	270	132	946	13	183	86	108	366	7

Notes: 1) Overburden statistics are a compilation of piezometer P9-1A and the shallow dug well (W9-A).
2) Bedrock Well statistics are those of W9-B.
3) Overburden water level measurements are those from piezometer P9-1A.
4) Bedrock water level measurements are those from W9-B.

The mean bedrock groundwater temperature is 11.1°C, while that of the overburden varies more significantly from seasonal atmospheric influences, with highs and lows of 19.0°C and 2.5°C, respectively. The mean pH value in both shallow and bedrock groundwater was 7.1, and did not vary significantly seasonally. Shallow, recently recharged groundwater often has lower pH values than deeper groundwater due to the effects of soil CO_2 and acid rain; however, this was not evident. The range in specific conductance values was identical for both overburden and bedrock samples, with a mean value higher in the overburden samples than those from the bedrock well. This may be attributed to road salt application on Hwy 38 which passes the site; mean Cl^- concentrations in the overburden samples are 2-3 times higher then those in the bedrock well (17-37 mg/L versus 10-14 mg/L). Seasonally, overburden Cl^- concentrations appear highest in spring and summer after the winter thaw, while concentrations in the bedrock well do not vary significantly seasonally (Table D1). Mean dissolved oxygen values from the shallow piezometer are 3.2 mg/L, although only 2 measurements were taken, while mean values from the dug and bedrock wells were 0.8 mg/L and 0.2 mg/l, respectively, which is typical for groundwater in recharge areas with silty soils *[Drever, 1982; Freeze and Cherry, 1979]*. The average EH value in the bedrock well was 183 mV, with highest values (366 mV) measured in summer. As expected, mean overburden EH values (410 mV) were on average twice those of the bedrock well, with the highest value (946 mV) again in the summer, representing oxidized

water (Table D1). Mean values represent stable waters that are neither oxidizing nor reducing *[Freeze and Cherry, 1979].*

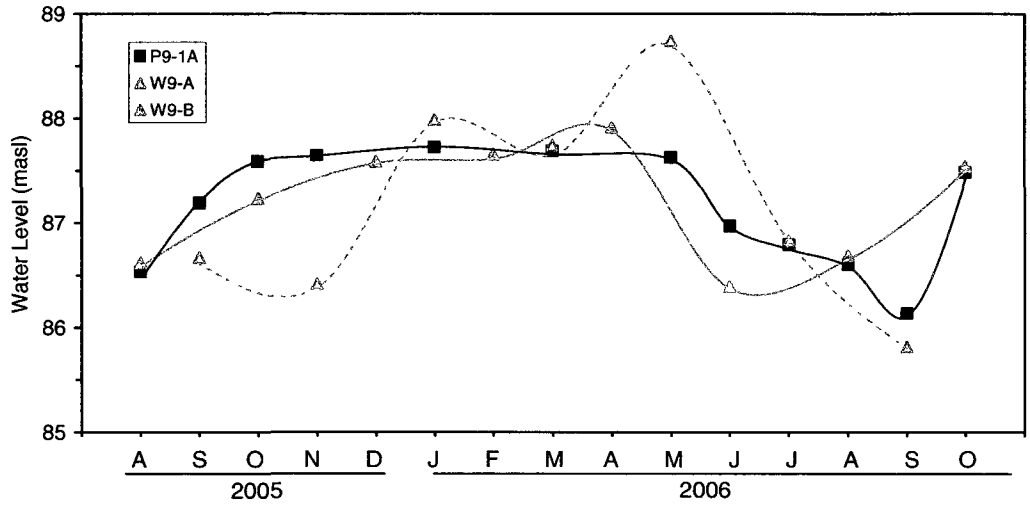

Figure 5.5: Background Site – Monthly water level fluctuations in piezometers and wells, presented as elevations in meters above sea level.

5.2.2. Groundwater $\delta^{18}O$ and $\delta^{2}H$

Results, as summarized in Table 5.7, indicate that groundwater $\delta^{18}O$ and $\delta^{2}H$ values from both overburden material and the bedrock aquifer vary little. However, mean bedrock aquifer values appear marginally more enriched compared to those from overburden groundwater. This is the opposite of what would be expected with more isotopically depleted values in the regional bedrock aquifer, representative of well mixed regional groundwater. Shallow and deeper groundwater $\delta^{18}O$ and $\delta^{2}H$ values do not appear to deviate from the local meteoric water line, suggesting they are both locally recharged. More depleted shallow groundwater may be a result of local summertime evaporation; however, such a trend is not apparent in the mean seasonal values in Table D1. Figure 5.6 shows that both shallow and deeper $\delta^{18}O$ and $\delta^{2}H$ values do not appear to deviate from the LMWL, suggesting they are both locally recharged waters. More depleted shallow groundwater may be a result of local summertime evaporation; however, such a trend is not apparent in the mean seasonal values in Table D1 (Appendix D).

Table 5.7: Background Site – Statistical summary of groundwater $\delta^{18}O$ and $\delta^{2}H$ values.

	Piezometer				Overburden Well				Bedrock Well			
	Mean	Min	Max	n	Mean	Min	Max	n	Mean	Min	Max	n
Water												
$\delta^{18}O_{H2O}$ (‰)	-10.4	-10.9	-9.9	13	-10.4	-10.8	-9.5	14	-10.1	-10.4	-8.4	10
$\delta^{2}H_{H2O}$ (‰)	-74.4	-78.4	-65.5	9	-73.4	-82.8	-67.1	10	-72.0	-75.9	-64.1	10

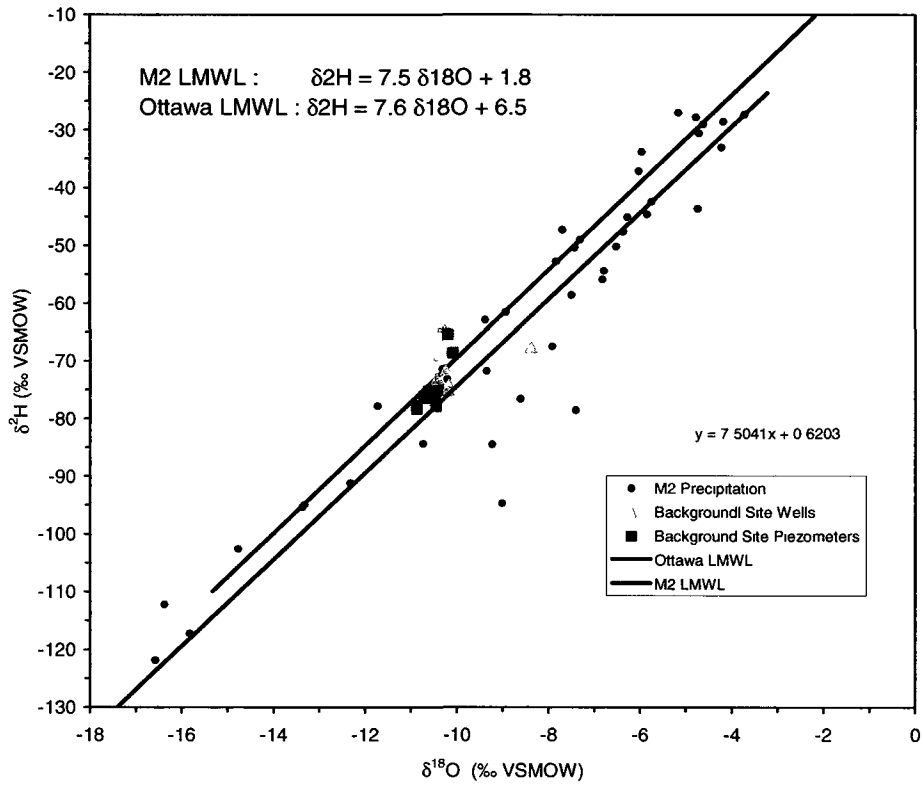

Figure 5.6: Background Site – $\delta^{18}O$ and $\delta^{2}H$ values for event-weighted precipitation and Background Site piezometers and wells samples, plotted along with the M2 and Ottawa LMWLs.

5.2.3. Geochemistry, Nutrients and Isotope Composition

Major ions, nutrient concentrations and isotope values of Background Site groundwater samples are summarized in Table 5.8. Major ion chemistry shows little difference between shallow and deeper bedrock water samples, suggesting groundwater is locally recharged, corroborating $\delta^{18}O$ and $\delta^{2}H$ observations. As previously noted, mean Cl^- concentrations in shallow samples are higher then those in deeper samples, possibly related to road salt (NaCl) applications. Mean SO_4^{2-} concentrations decrease marginally with depth, with mean values of 100, 86 and 70 mg/L in the piezometer, shallow well and bedrock well, respectively. Pyrite is a common constituent of till and glacial-marine deposits *[Rodvang and*

Simpkins, 2001], possibly resulting in higher SO_4^{2-} concentrations in shallow more oxygenated groundwater, such as these in the alluvial sand and gravel deposit.

Table 5.8: Background Site – Groundwater geochemistry and isotope results and statistical summary.

	Piezometer				Overburden				Bedrock			
	Mean	Min	Max	n	Mean	Min	Max	n	Mean	Min	Max	n
Major Ions and Nutrients												
Ca^{2+} (mg/L)	145	126	162	15	189	158	216	15	119	99	139	15
Na^{+} (mg/L)	5 2	4 0	8 6	15	21 2	12 4	41 0	15	11 4	8 1	16 8	15
Mg^{2+} (mg/L)	31	26	33	15	26	14	36	15	37	32	41	15
K^{+} (mg/L)	1 9	1 2	3 9	15	4 3	3 0	5 4	15	2 6	2 3	2 9	15
P (mg/L)	0 38	0 02	0 89	13	0 04	0 01	0 10	13	0 06	0 01	0 24	13
NH_4^{+} (mg-N/L)	0 008	0 003	0 022	8	0 054	0 011	0 107	9	0 064	0 041	0 093	8
Cl (mg/L)	31	25	40	15	23	15	51	15	12	8	19	15
SO_4^{2} (mg/L)	100	87	108	14	86	55	110	13	70	49	82	14
NO_3 (mg-N/L)	0 76	0 21	1 38	15	0 22	0 14	0 30	4	0 01	0 01	0 01	1
HCO_3 (mg/L)	397	229	524	15	614	293	980	15	440	166	605	15
Calculations												
pCO_2 (exp) (atm)	-1 59	-1 93	-1 35	15	-1 26	-1 80	-0 95	15	-1 49	-1 72	-1 23	15
$SI_{calcite}$	1 634	0 692	2 868	15	2 253	0 986	7 103	15	1 431	0 101	2 702	15
Nitrogen Isotopes												
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	13 9	10 7	17 0	5	7 9	7 9	7 9	1	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	6 1	3 7	7 9	5	-2 3	-2 3	-2 3	1	-	-	-	-
Carbon												
DIC (ppmC)	95	59	121	15	160	72	261	15	108	69	140	15
DOC (ppmC)	2 6	1 1	4 9	14	6 5	4 0	11 1	15	3 5	1 4	5 9	15
$\delta^{13}C_{DIC}$ (‰)	-15 9	-16 8	-14 3	14	-15 0	-16 2	-13 0	14	-13 9	-15 0	-7 8	15
$\delta^{13}C_{DOC}$ (‰)	-26 0	-27 4	-21 6	14	-25 9	-27 1	-22 6	14	-26 8	-31 4	-22 6	15

Notes
1) Piezometer statistics are those of piezometer P9-1A
2) Overburden Well statistics are those of W9-A
3) Bedrock Well statistics are those of W9-B
4) P = Total Phosphorus
5) pCO_2 is the exponent value with base 10
6) "-" indicates that no samples were analysed

No pattern of DIC concentrations exist with depth, the shallow well having a greater mean concentrations (160 mg/L), while the piezometer and deep well have similar but lower concentrations of 95 and 108 mg/L, respectively. $\delta^{13}C_{DIC}$ appears to become more enriched with depth; however, the difference in values is small (-15.9‰, -15.0‰, and -13.9‰). $\delta^{13}C_{DIC}$ values suggest open system (non-saturated) conditions, where $\delta^{13}C_{DIC}$ is controlled by soil CO_2 ($\delta^{13}C_{DIC}$ -23‰), with a HCO_3^- to $CO_{2(g)}$ fractionation of -9 ‰ *[Clark and Fritz, 1997]*. In areas of forested (C_3) type vegetation, at neutral pH and groundwater temperatures of 15°C, this results in final $\delta^{13}C_{DIC}$ values of -14‰ *[Cane and Clark, 1999]*, which

corresponds with results at the naturally vegetated Background Site. Mean DOC concentrations range between 2.5 and 11 mg-C/L, which is significantly higher then the 1 to 2 mg-C/L typically observed in natural groundwater, although likely the result of a shallow water table close to the root zone *[Aiken et al., 1985; Drever, 1997]*, which results in higher levels of organic decomposition, thus higher DOC concentrations. Average $\delta^{13}C_{DOC}$ values of -25.9 to -26.8±2.4‰ are constant both temporally and with depth.

Mean nitrate concentrations appear to decrease with depth, with piezometer, dug and bedrock well concentrations of 0.76, 0.22 and 0.01 mg-N/L, respectively; however, all but one value from the bedrock well was reported as below the detection limit of 0.002 mg-N/L. Five $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ samples were available for analysis from the piezometer, with results suggesting that denitrification may be occurring at shallow depths (Figure 5.7). Additional analyses could not be conducted at depth, as NO_3^- concentrations were mostly below the method's lower quantifiable limit of 0.124 mg-N/L.

Following Equation 2.8, which indicates that during nitrification two O atoms originate from $\delta^{18}O_{H2O}$ (-10.4‰), while a third originates from $\delta^{18}O_{O2}$, (+23‰), calculations suggest a starting $\delta^{18}O_{NO3}$ of +2.2‰. Determining the original residual fraction of NO_3^-, and the enrichment factors for ^{15}N and ^{18}O (Figure 5.7), yields a starting $\delta^{15}N_{NO3}$ value of 8.5‰. Because the domestic septic field is located down-gradient of the piezometer (>40 m), and there are no agricultural fields in the area where manure could be applied, the nitrate source is likely nitrified soil-N. In addition, low NO_3^- concentrations correspond to natural background concentrations of 1 mg-N/L as reported by *Drever [1986]*, ammonium concentrations are near zero at all depths, suggesting that any mineralized organic N is rapidly nitrified.

5.2.4. Summary and Conclusions

Groundwater conditions at the Background Site are representative of naturally forested type vegetation, where soil CO_2 is controlled by C_3 $\delta^{13}C$ values under open system dissolution ($\delta^{13}C$ is approximately -14‰), and NO_3^- concentrations are close to 0 mg-N/L. The water table fluctuates approximately 1.6m within the piezometer, with lowest levels in September following the peak evapotranspiration period (June to August). Water levels

begin increasing sharply in October, in conjunction with heavy precipitation and reduced rates of evapotranspiration. Shallow groundwater had higher conductivity values compared to that of the underlying Bedrock Aquifer, likely because of winter road salt application on the nearby highway.

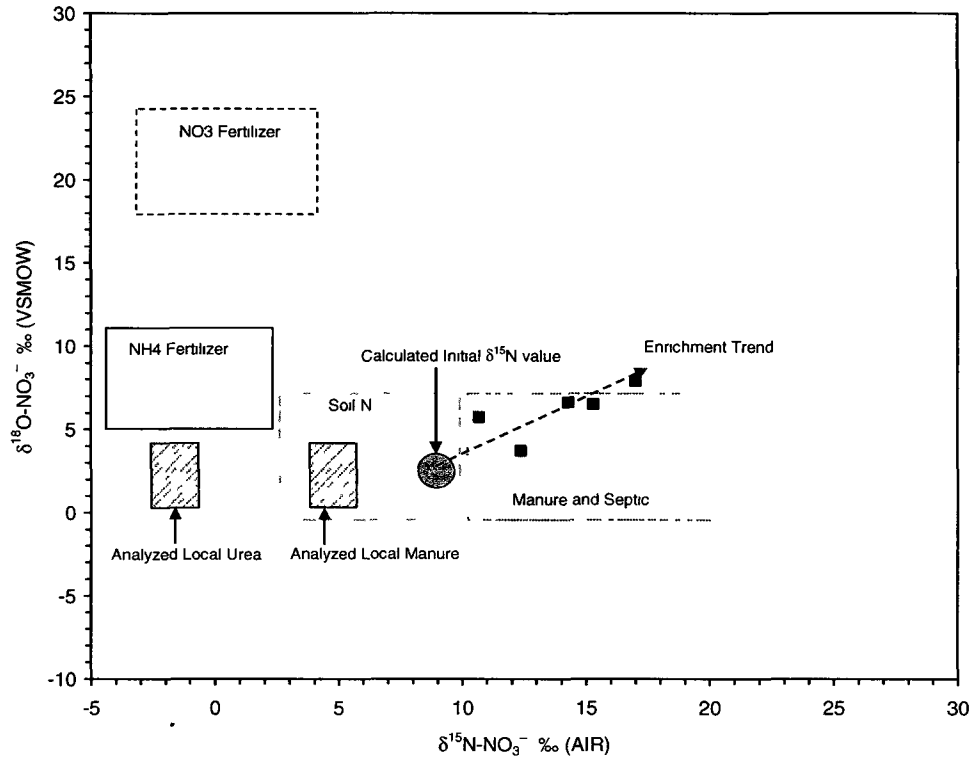

Figure 5.7: Background Site – $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$ individual values for piezometer P9-1A. The arrow represents the enrichment trend for NO3- during denitrification, while the boxes represent literature and measured ranges for various NO_3 sources, from *[Clark and Fritz, 1997]*. Local urea and manure boxes represent analyzed values from this investigation.

The $\delta^{18}O$ and $\delta^{2}H$ values plot slightly above the M2 LMWL, and slightly below the Ottawa MWL, attributed to an incomplete long term local meteoric record, and an exclusion of winter meteoric sampling. As such, both surficial and bedrock groundwaters are locally recharged, this is further supported by similarities in major ion chemistry. Evidence of denitrification is present in shallow groundwater samples, with $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ results supporting a nitrogen source from soil organic matter. Enrichment factors (□) for $\delta^{15}N$ and $\delta^{18}O$ were determined to be, -8.4‰ and -5.7‰, respectively. Average background nitrate concentrations in the overburden material and Bedrock Aquifer were determined to be <0.3 and <0.01 mg-N/L, respectively, with no measurable ammonium. Shallow groundwater also contained marginally higher concentrations of dissolved oxygen (0.9 mg-N/L) than deeper

groundwater (0.2 mg-N/L). This is significant as denitrification typically occurs when DO is below 0.3 mg-N/L, although it should be noted that limited data was available (two measurements).

5.3. Site 1 – Agricultural Field

Site 1 is a cropland agricultural site located in an area of extensive agriculture, near the main branch of the Raisin River (Figure 4.1). It consisting of three lysimeters, two tile drains, and three piezometers all located in a glacial-marine deltaic deposit (Surficial Aquitard), and three drilled wells keyed into the Bedrock Aquifer. The lysimeters and piezometers were advanced directly into the middle of the fields, while the tile drains and wells belonged to the participating farmer and neighbouring home owners. The tile drains discharged into a ditch, which subsequently entered the main branch of the Raisin River approximately 20 m away. Tables 4.3, 4.2, 4.4 and 4.1 in Section 4, summarize the installation details for lysimeters, tile drains, piezometer and wells, respectively, while Table 5.9 summarizes the physiographic and geologic settings (maps in Section 3) found in the vicinity of this site. Figure 5.8 identifies sampling point locations and local land use distribution.

Silage corn was planted in the season preceding the investigation (2004), and the two years (2005 and 2006) of the investigation. Each year the total Urea fertilizer application was (50-80 kg-N/ha), and was applied as a starter (April-May depending on the year), and sidedress once corn was at the 3-4 leaf stage.

Table 5.9: Site 1 – Summary of physiographic and geologic settings.

Land Use	Agricultural
Soil Type	Silt Loam Sand, Silt & Clay (20-15-65%)
Physiographic Unit	Lancaster Flats
Surficial Geology	Glacial-marine Delta Deposits Sand, Silt and Clay
Bedrock Geology	Lindsay Formation fine crystalline limestone with beds of calcarenite and shale
Overburden Thickness	5-10 m
Comments	Close to Fault Zone

Field measurements, geochemical and isotopic composition of samples collected from Site 1 are summarized in the tables below, while complete results and seasonal summaries are located in Table D2 of Appendix D.

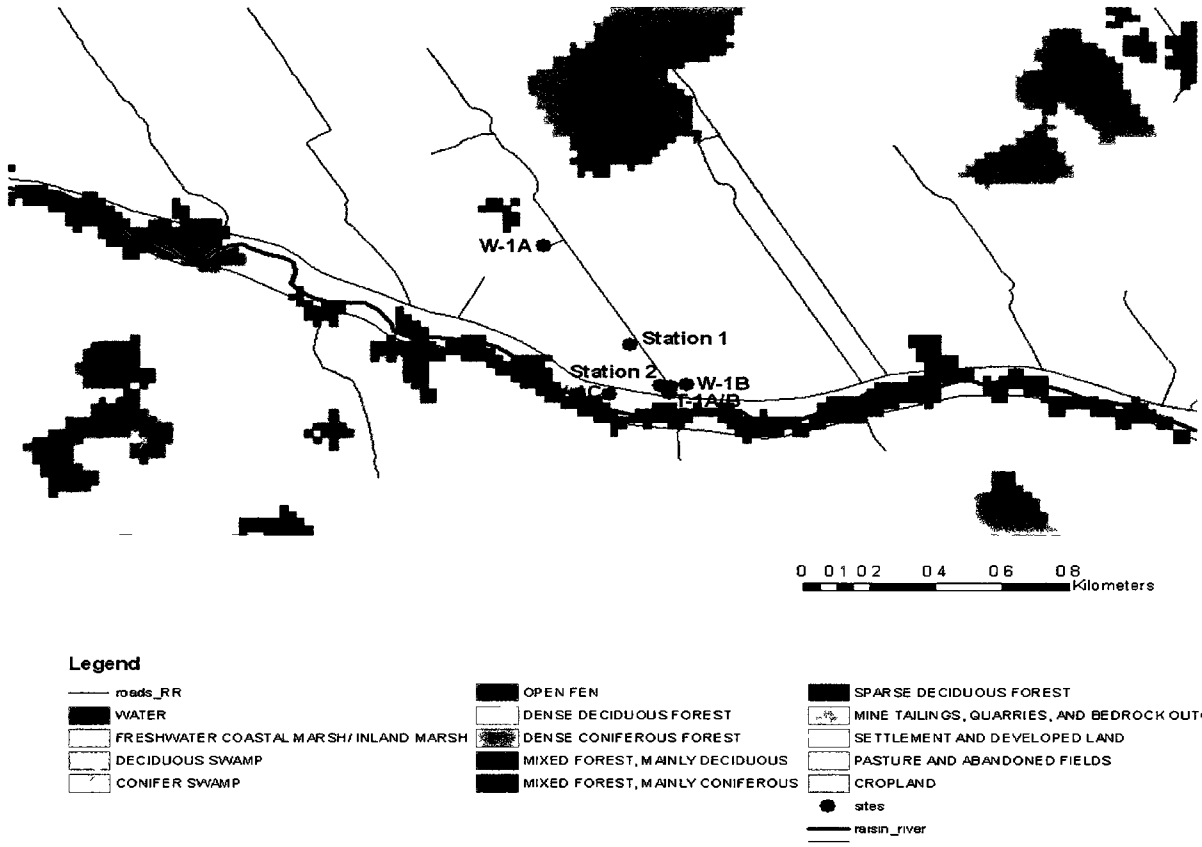

Figure 5.8: Site 1 – Location map of sampling points and local land use along the Main Branch of the Raisin River. Station 1 consists of three lysimeters (L1-1A, L1-1B and L1-1C) and piezometers (P1-1B and P1-1C), while Station 2 consists only of piezometer P1-2B. All grey colouration represents agricultural fields.

5.3.1. Field Measurements

The water level, temperature, pH, conductivity, dissolved oxygen, and EH concentrations from Site 1 groundwater samples (piezometers and bedrock wells) are summarized in Table 5.10. Aside from conductivity and pH readings, other soil moisture field measurements (lysimeters and tiles drains) are not summarized or discussed as they represent an unsaturated oxygenated environment which is exposed to atmospheric influences, and which were typically dry in summer. All available field measurements are located in Table D2.

The mean pH values for lysimeters and tile drains were 7.2 and 7.1, respectively, while specific conductance values were similar to those recorded in shallow groundwater samples (approximately 800 µS/cm).

Table 5.10: Site 1 – Groundwater field parameter statistical summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field										
W.L. (mgbs)	1.43	0.80	0.48	2.98	15	4.05	0.57	2.79	4.93	14
Temp. (°C)	11.4	3.5	4.8	19.5	45	10.3	1.3	8.3	15.2	43
pH	7.5	0.27	7.0	8.0	45	7.3	0.29	6.5	8.2	43
SpC. (µS/cm)	792	256	440	1424	45	974	284	542	1866	41
DO (mg/L)	2.3	0.78	0.93	3.6	8	0.5	0.3	0.05	1.0	17
Eh (mV)	332	115	128	461	15	350	122	83	665	18

Notes: 1) Piezometer statistics are a compilation of three piezometers (P1-1B, P1-1C and P1-2B).
2) Bedrock Well statistics are a compilation of three wells (W1-A, W1-B and W1-C).
3) Piezometer water level measurements are those from P1-1B.
4) Well water level measurements are those from W1-C.
5) DO summary excludes measurements from well W1-A

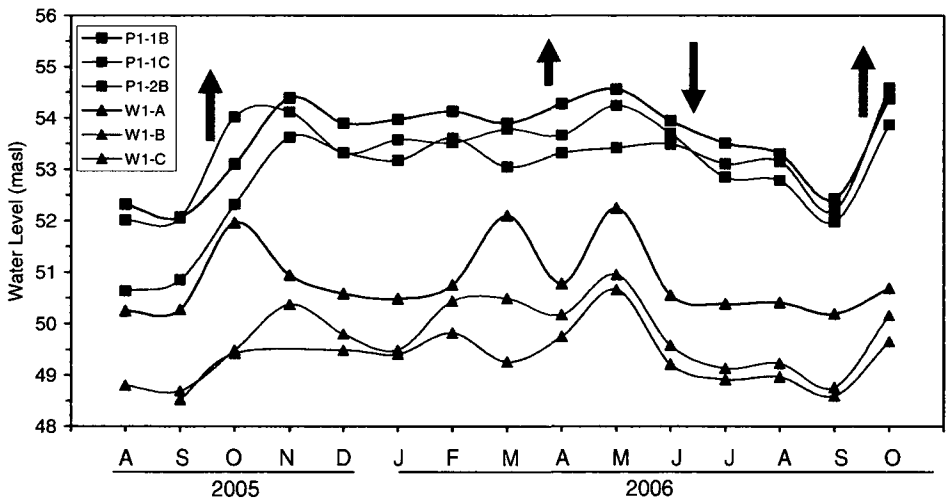

Figure 5.9: Site 1 – Monthly water level fluctuations in piezometers and bedrock wells, presented as elevations in meters above sea level. The red arrows indicate major periods of rising water levels, the blue arrow indicates rising water levels following spring thaw, and surface water infiltration, while the black arrow identifies decreasing water levels due to high rates of evapotranspiration resulting in decreased or limited infiltration.

Shallow groundwater and the bedrock groundwater levels generally responded to precipitation equally, with the exception of well W1-A, which responded more rapidly to precipitation, suggesting a more direct hydraulic connection, such as a leaking well seal (Figure 5.9).

The mean Bedrock Aquifer temperature was 10.3°C, while that of shallow groundwater varied more significantly from seasonal atmospheric influences, with highs and lows of 19.5°C and 4.8°C, respectively. The mean pH value was slightly higher in the overburden than the Bedrock Aquifer, with no discernable seasonal pattern, and was generally consistent with those from the Background Site. Specific conductance values were marginally lower in shallow groundwater samples compared to the Bedrock Aquifer, which is expected as deeper bedrock groundwater generally has longer residence times, allowing for more mineral dissolution. Both values were lower than concentrations found at the Background Site, which was expected since that site was likely under road salt influence. The mean DO value from piezometer samples was 2.3 mg/L, which is expected in younger oxygenated groundwater, while the mean value for bedrock wells was 0.5 mg/L, which is similar to Bedrock Aquifer readings from the Background Site. Seasonal DO trends were not evident in either piezometer or well measurements. Mean EH values from both shallow overburden and deeper bedrock groundwater were 332mV and 350mV, respectively, and both with a standard deviation value of approximately 120 mV. Average EH values from individual piezometer and wells ranged between 240 mV and 440 mV, which represent stable waters that are neither reducing (<-400 mV) nor oxidizing (>800 mV). Highest measurements were always recorded in summer following spring recharge and when the unsaturated zone is at a maximum depth (Table D2), while lowest values were recorded in winter.

5.3.2. Vadose and Groundwater $\delta^{18}O$ and $\delta^{2}H$

Water sampled from lysimeters and tiles drains represents that from the unsaturated zone, as their only source of moisture is from locally infiltrated precipitation. As a result, any attenuation of the monthly meteoric signal is solely due to mixing with older precipitation stored in the soil. However, water samples collected from either shallow groundwater or the Bedrock Aquifer, may be composed from both locally attenuated infiltrated precipitation and regional system groundwater. Summarize the $\delta^{18}O$ and $\delta^{2}H$ values for both soil moisture samples and groundwater samples are located in Tables 5.11 and 5.12, respectively.

Soil moisture and groundwater $\delta^{18}O$ values are compared to the weighted monthly mean meteoric signal and the weighted mean annual values for Ottawa and M2 LMWLs (Figure 5.10). April 2006 samples were not analyzed due to problems with instrumentation.

Table 5.11: Site 1 – Lysimeter and tile drain summary of $\delta^{18}O$ and $\delta^{2}H$ values.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Water										
$\delta^{18}O_{H2O}$ (‰)	-10 2	0 7	-11 0	-7 4	35	-10 8	0 4	-11 6	-10 2	12
$\delta^{2}H_{H2O}$ (‰)	-73 2	4 8	-84 3	-63 0	25	-76 9	2 1	-79 8	-72 7	12

Notes 1) Lysimeter statistics are a compilation of three lysimeters (L1-1A, L1-1B and L1-1C)
2) Tile Drain statistics are a compilation of two tile drains (T1-A and T1-B)

Table 5.12: Site 1 – Piezometer and bedrock well summary of $\delta^{18}O$ and $\delta^{2}H$ values.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Water										
$\delta^{18}O_{H2O}$ (‰)	-10 8	0 4	-11 1	-8 6	42	-11 0	0 7	-11 7	-8 5	40
$\delta^{2}H_{H2O}$ (‰)	-76 4	2 6	-79 8	-67 5	30	-78 9	4 2	-85 1	-67 2	28

Notes 1) Piezometer statistics are a compilation of three piezometers (P1-1B, P1-1C and P1-2B)
2) Bedrock Well statistics are a compilation of three wells (W1-A, W1-B and W1-C)

During the fall of 2005, the 0.3m lysimeter exhibited the most enriched signal. An apparent 2 month lag in response to meteoric inputs is observed, with an enrichment peak occurring in November following a meteoric peak in September. For the remainder of the sampling period, only 4 additional samples were collected from this lysimeter, because in winter soil moisture was locked in ground frost, while in summer infiltration was not occurring due to high evapotranspiration rates. However, when samples were available, a similar delayed enriched or depleted pattern was observed. At depths of approximately 0.6-1.2m (0.60m lysimeter and tile drains at 1.2m), further attenuation of the meteoric signal and response lag was observed when samples were available. The strongly depleted winter precipitation signal observed in February 2006, was only partially represented by more depleted values in lysimeters and tile drains, but with a one month lag. The lack of an immediate response indicates that limited infiltration occurs in winter. The $\delta^{18}O$ values from the 1.8m lysimeter were even further attenuated and the total range was only 0.7‰, indicating significant mixing with older precipitation. For the most part, $\delta^{18}O$ values from these samples were more depleted than the weighted mean annual M2 signal (-10.2‰), yet

enriched when compared to the Ottawa annual meteoric signal (-11.1‰). The mean $\delta^{18}O$ value for L1-1C was -10.8‰, only 0.3‰ off the long term Ottawa mean. However, it should be noted that seasonal variation in soil moisture values would likely be greater if a more complete sampling set were available, including winter and summer extremes.

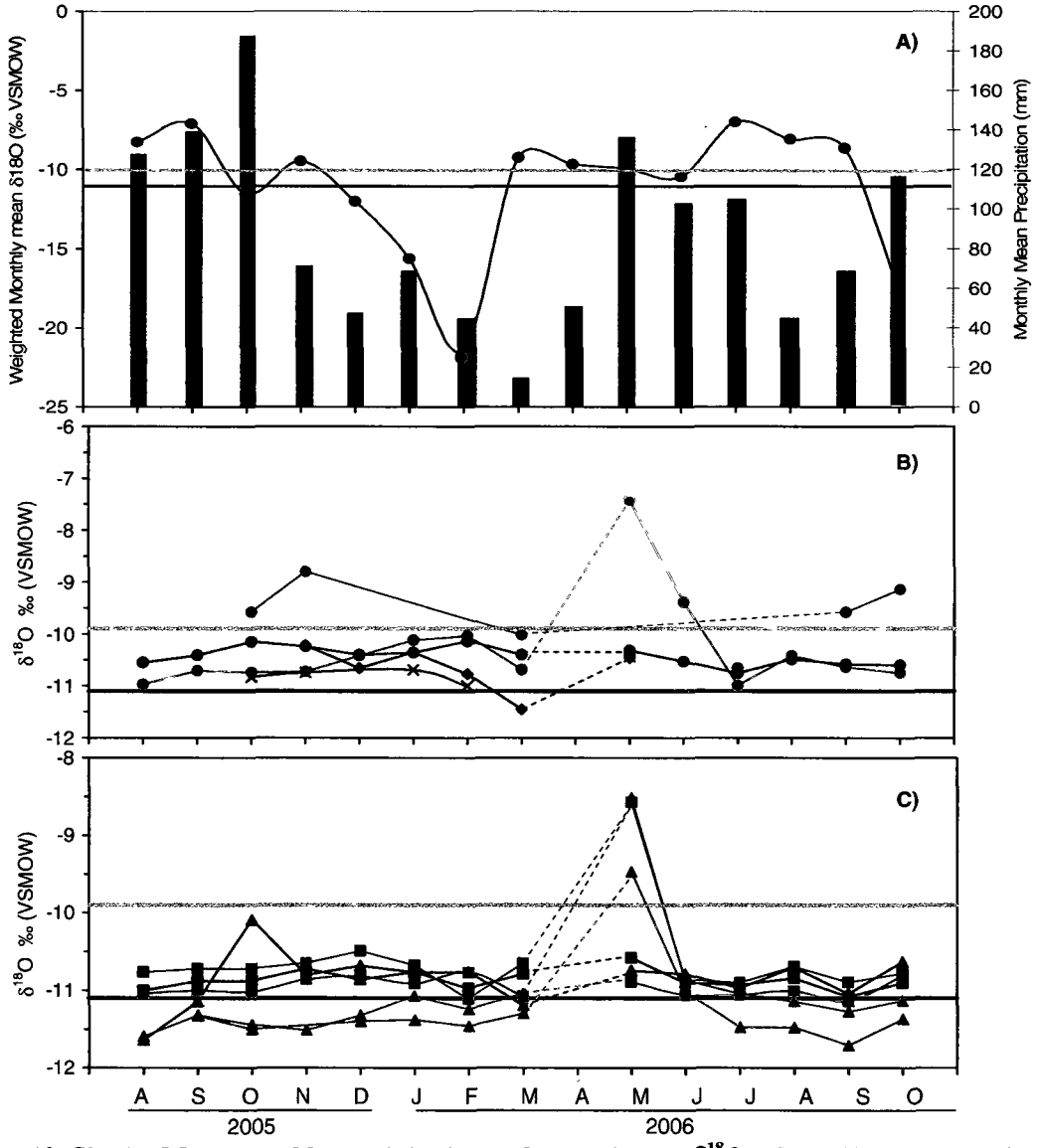

Figure 5.10: Site 1 – Mean monthly precipitation and groundwater $\delta^{18}O$ values. A) Amount-weighted mean monthly meteoric $\delta^{18}O$ values and mean monthly precipitation histogram for Cornwall, Ontario. B) Monthly soil moisture $\delta^{18}O$. C) Monthly groundwater $\delta^{18}O$. The grey and black lines represent the weighted mean annual meteoric $\delta^{18}O$ signals, for the M2 LMWL (-10.2‰) and Ottawa MWL (-11.1‰), respectively. A symbol legend for each sampling point in located in Appendix F.

The shallow groundwater meteoric signal exhibits stronger attenuation (less variability) compared to the unsaturated zone samples. Piezometer P1-1C, with a screen approximately 3.7 meters below the average water table is consistently more depleted than the two shallower piezometers; however, the variability in all three piezometers is consistent. The strongest variability occurs during the late-spring early-summer (May) when heavily enriched values are observed in unsaturated samples, shallow groundwater and bedrock groundwater alike. The mean $\delta^{18}O$ piezometer value varies about the meteoric annual signal by approximately only 0.3‰. The bedrock aquifer $\delta^{18}O$ signal is equally attenuated to the piezometer signal; however, the mean value is further depleted by 0.2‰, and is almost identical to the Ottawa mean annual meteoric input of -11.1‰ (Table 5.12).

Well W1-A again exhibits anomalous behaviour in that the October 2005 $\delta^{18}O$ value is enriched by 0.9‰ above the mean. The enrichment is concurrent to a significant rise in water level, and is consistent with elevated conductivity readings which together suggest a leaking well seal, where surface water of shallow groundwater are able to directly enter the well.

Figure 5.11 plots $\delta^{18}O$ against $\delta^{2}H$; indicating shallow groundwaters are more enriched relative to bedrock groundwaters. While recharge at higher elevations in the catchment may contribute to some of the depletion observed in the bedrock groundwaters, a potential altitude effect of 0.15-0.5‰ $\delta^{18}O$ per 100m elevation *[Gat, 1980]*, unlikely contributes all of this depletion due to the rather subdued topography (approximately 70 m). Piezometer groundwaters have similar trends and $\delta^{18}O$ and ^{2}H values compared with the deep lysimeter (Figure 5.11B and C), demonstrating local recharge through the fields, while the well groundwater (Bedrock Aquifer), is systematically depleted, indicating a more regional signal from the basin. This may reflect a systematic exclusion of winter precipitation infiltrating to the water table and piezometer groundwater due to drainage of snow melt-water preferentially by the tile drains. This would account for the non-evaporative enrichment of the piezometer groundwaters (fields) over the wells (regional) observed in Figure 5.11.

Furthermore, piezometer $\delta^{18}O$ and $\delta^{2}H$ values plot on the Ottawa MWL but above the M2 LMWL (Figure 5.11), enforcing the observations made in Section 5.1, which indicated

the M2 LWML record was too short and incomplete due to unavailable winter meteoric sampling.

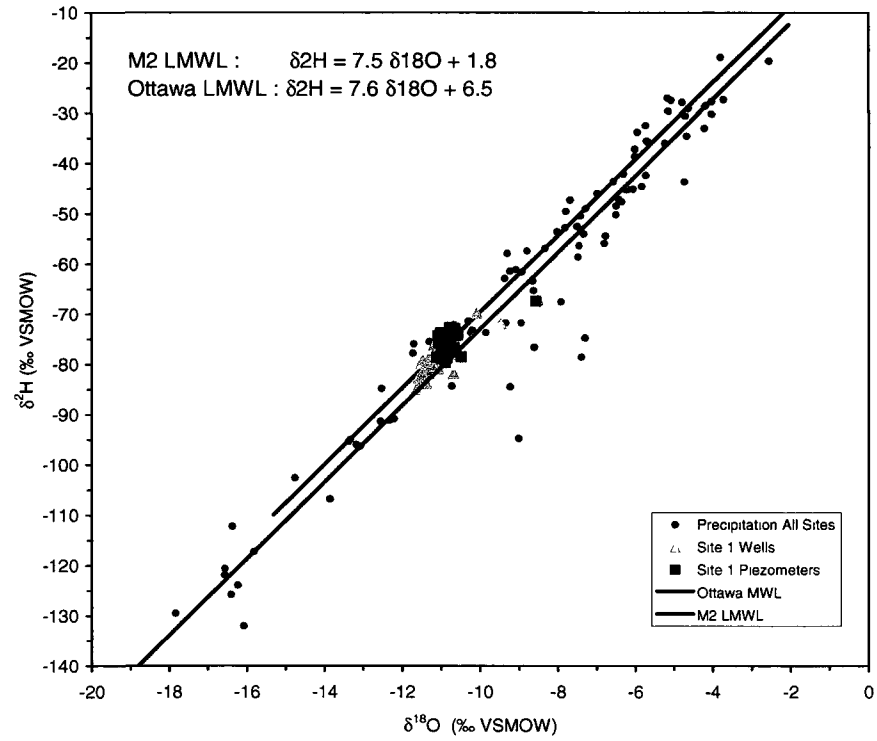

Figure 5.11: Site 1 – δ^2H and $\delta^{18}O$ values for weighted mean monthly precipitation, and monthly individual piezometer and well samples.

5.3.3. Geochemistry

Major ions, nutrient concentrations and isotope values of unsaturated zone and groundwater samples are summarized in Table 5.13 and Table 5.14, respectively. Major ion chemistry of the following analytes; Ca^{2+}, Na^{+}, Mg^{2+} and SO_4^{2-}, shows little variability between unsaturated zone, shallow groundwater and deeper bedrock groundwater samples. This may suggests that mineral dissolution is occurring rapidly following infiltration of local precipitation. The mean calcite saturation indices for the lysimeters, tile drains, piezometers and bedrock wells are 0.895, 0.345, 1.759 and 1.270, respectively, indicating that calcite is under-saturated in the soil water, while supersaturated in both shallow and deeper groundwater. Of interest is the near saturated mean lysimeter value compared to the tile drain value, possibly suggesting the lysimeter is drawing in pore water with longer residence times, while tile drains are rapidly flushing infiltrating precipitation by macro-pore

"wormhole" channels. Such wormholes were observed when a test pit was dug at Site 2, and will be discussed in Section 5.4. All major ion concentrations in general and bicarbonate in particular, are lower in the tile drains compared to the lysimeters.

Total phosphorus concentrations are similar in both unsaturated and groundwater samples, except for piezometer P1-1B, whose phosphorous concentration is almost one order of magnitude higher. Potassium concentrations are higher in groundwater samples compared to unsaturated zone values, suggesting they may be originating from a different source.

Table 5.13: Site 1 – Lysimeter and tile drain summary of major ion results.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
Ca^{2+} (mg/L)	71	20	30	100	39	59	9.5	33	71	16
Na^{+} (mg/L)	11	3.1	4.2	18	39	9.1	2.0	5.3	12	16
Mg^{2+} (mg/L)	25	7.2	10	38	39	19	3.5	11	25	16
K^{+} (mg/L)	1.0	0.59	0.37	2.4	35	1.2	0.96	0.57	3.9	16
P (mg/L)	0.063	0.17	0.0001	0.94	29	0.08	0.18	0.01	0.71	15
Cl^{-} (mg/L)	27	13	2.3	58	38	25	3.9	20	31	16
SO_4^{2-} (mg/L)	30	15	17	85	35	26	9.3	13	39	14
HCO_3^{-} (mg/L)	247	86	125	451	39	171	43	110	270	16
Calculations										
pCO_2 (exp) (atm)	-1.84	0.27	-2.69	-1.47	39	-1.96	0.21	-2.51	-1.57	16
$SI_{calcite}$	0.895	1.228	0.164	7.335	38	0.348	0.291	0.054	1.206	16

Notes:
1) Lysimeter statistics are a compilation of three lysimeters (L1-1A, L1-1B and L1-1C).
2) Tile Drain statistics are a compilation of two tile drains (T1-A and T1-B).
3) P = Total Phosphorus
4) pCO_2 is the exponent value with base 10
5) "-" indicates that no samples were analysed

Table 5.14: Site 1 – Piezometer and bedrock well summary of major ion results.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
Ca^{2+} (mg/L)	66	11	53	85	45	73	48	0 17	135	39
Na^{+} (mg/L)	10	0 74	8 7	12	45	8	3 2	1 6	13	43
Mg^{2+} (mg/L)	25	3 9	20	32	45	10	7 0	0 027	19	38
K^{+} (mg/L)	3 0	1 0	1 3	4 8	45	11	10	2 3	29	28
P (mg/L)	0 43	0 69	0 0069	2 8	37	0 049	0 057	0 0092	0 32	39
Cl (mg/L)	13	6 4	2 9	22	45	13	2 5	7 8	21	42
SO_4^{2} (mg/L)	19	11	3 1	37	42	34	9 3	17	45	39
HCO_3 (mg/L)	276	62	149	422	45	311	81	139	522	43
Calculations										
pCO_2 (exp)	-2 14	0 26	-2 66	-1 58	45	-1 83	0 28	-2 68	-1 34	43
$SI_{calcite}$	1 759	1 115	0 247	4 493	45	1 270	0 887	0 091	3 946	28

Notes
1) Piezometer statistics are a compilation of three piezometers (P1-1B, P1-1C and P1-2B)
2) Bedrock Well statistics are a compilation of three wells (W1-A, W1-B and W1-C)
3) K^{+} results from well W1 B were excluded from the bedrock well summary because values are altered by an inline KCl water softener that was discovered after sampling had commenced
4) P = Total Phosphorus
5) pCO_2 is the exponent value with base 10

5.3.4. DIC and DOC

DIC and DOC concentrations and $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ values of unsaturated zone samples and groundwater samples are summarized in Tables 5.15 and 5.16, respectively.

Table 5.15: Site 1 – Lysimeter and tile drain carbon chemistry and isotope results suumary.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
HCO_3 (mg/L)	247	86	125	451	39	171	43	110	270	16
Calculations										
pCO_2 (exp) (atm)	-1 84	0 27	-2 69	-1 47	39	-1 96	0 21	-2 51	-1 57	16
Carbon										
DIC (ppmC)	58	19	26	96	39	42	9 1	30	61	16
DOC (ppmC)	5 8	5 0	1 4	25	37	2 7	1 4	1 3	6 1	16
$\delta^{13}C_{DIC}$ (‰)	-12 6	1 9	-17 0	-7 4	39	-12 6	1 1	-13 7	-9 8	16
$\delta^{13}C_{DOC}$ (‰)	-25 5	2 5	-33 3	-19 8	37	-24 4	1 7	-26 2	-19 7	16

Notes
1) Lysimeter statistics are a compilation of three lysimeters (L1-1A, L1-1B and L1 1C)
2) Tile Drain statistics are a compilation of two tile drains (T1-A and T1-B)
3) pCO_2 is the exponent value with base 10

Table 5.16: Site 1 – Piezometer and bedrock well carbon chemistry isotope results summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
HCO_3 (mg/L)	276	62	149	422	45	311	81	139	522	43
Calculations										
pCO_2 (exp) (atm)	-2 14	0 26	-2 66	-1 58	45	-1 83	0 28	-2 68	-1 34	43
Carbon										
DIC (ppmC)	60	13	30	90	45	73	18	43	125	43
DOC (ppmC)	2 1	0 81	1 1	4 8	42	3 2	1 8	0 93	9 1	43
$\delta^{13}C_{DIC}$ (‰)	-16 1	0 7	-17 4	-14 6	44	-14 5	1 3	-16 8	-11 7	43
$\delta^{13}C_{DOC}$ (‰)	-25 8	1 4	-28 0	-21 7	42	-26 5	1 9	-30 6	-20 1	43

Notes 1) Piezometer statistics are a compilation of three piezometers (P1-1B, P1-1C and P1-2B)
2) Bedrock Well statistics are a compilation of three wells (W1-A, W1-B and W1-C)
3) pCO_2 is the exponent value with base 10

DIC concentrations show a general increase through the unsaturated zone and shallow groundwater, reflecting biodegradation (Figure 5.12A). Mean DIC concentrations are constant with depth, with mean DIC concentrations between 50-70 mg-C/L, although with considerable seasonal variability (30 to 90 mg-C/L), suggesting intermittent, rapid recharge from the surface. The $\delta^{13}C$ of DIC shows a similar variability; however, values become more depleted through the unsaturated zone to a minimum mean value of -16.1‰ in the piezometers. This suggests a mixing pattern from C_4 (corn) type vegetation (~-4‰) under open system dissolution, to natural C_3 type vegetation (~-14 to -16‰). Mean pCO_2 values decrease with depth, reflecting increased weathering; however, higher pCO_2 in the Bedrock Aquifer and lower $SI_{calcite}$ suggests a different weathering pathway.

Mean DOC concentrations range between 2.1 and 5.8 mg-C/L, with higher concentrations present closer to the root zone (<1 meter) where there is a greater abundance of decomposing organic mater (Figure 5.13A). The slight decreasing trend of DOC concentration with depth suggests that organic mater is being oxidized towards the low values in groundwaters (1 to 2 mg-C/L typically observed in natural groundwater *[Drever, 1997]*). $\delta^{13}C$ of DOC shows a similar seasonal variability at all depths, with values becoming slightly more depleted through the unsaturated zone and shallow groundwater (Figure 5.13B). Such values represent a predominantly natural C_3 type vegetation pattern (~-26 to -30‰), with very little C_4 vegetation influence, and is not concurrent with $\delta^{13}C$ of DIC observations.

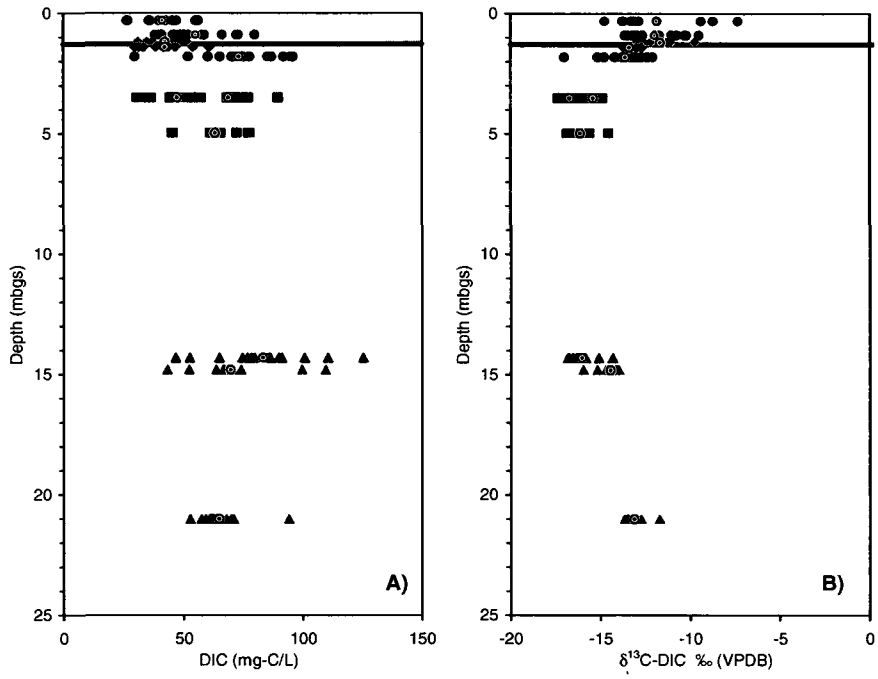

Figure 5.12: Site 1 – Depth vs. DIC. A) DIC concentrations. B) $\delta^{13}C_{DIC}$ values. The blue lines represent the average depth of the water table, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F.

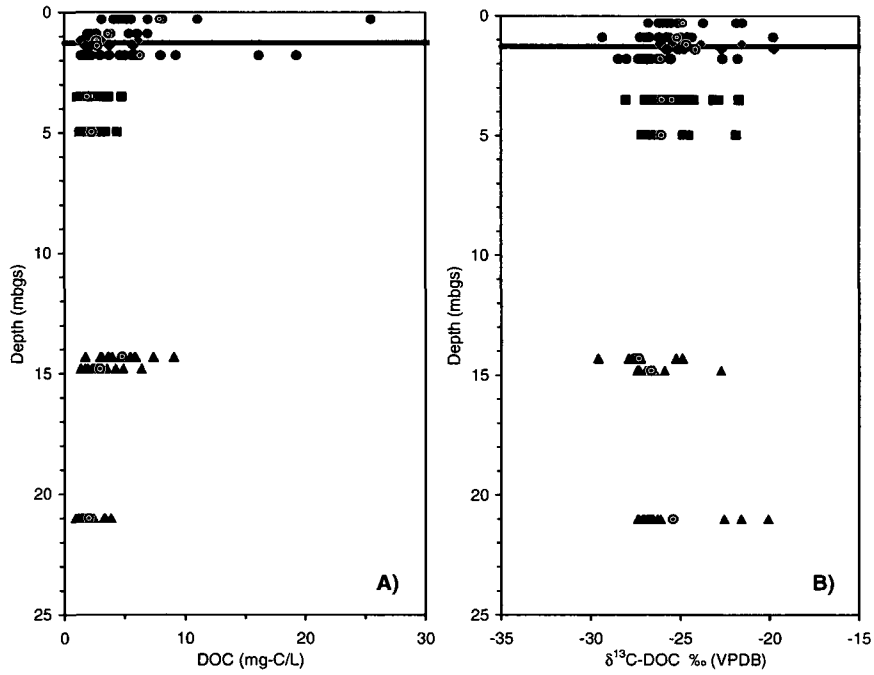

Figure 5.13: Site 1 – Depth vs. DOC. A) DOC concentrations. B) $\delta^{13}C_{DOC}$ values. The blue lines represent the average depth of the water table, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F.

5.3.5. *Nitrate and Ammonium*

Table 5.17 and Table 5.18 summarize nitrate and ammonium concentrations and $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values for unsaturated zone samples and groundwater samples, respectively. Nitrate concentration in the suction lysimeters (ranging between 3.4 and 5.7 mg-N/L) are lower than concentration from tile drains, which have a mean of 9.4 mg-N/L. Concentrations decrease further in shallow and bedrock groundwaters to mean values of 1.7 and 1.2 mg-N/L (Figure 5.14A), excluding the anomalous leaking well W1-A, which is discussed separately. The groundwater NO_3^- concentrations are all below the drinking water standard of 10 mg-N/L, and could be considered as background *[Drever, 1997]*. The seasonality for nitrification of this ammonium source would be responsible for the variable $\delta^{18}O_{NO_3}$, which would be influenced by the $\delta^{18}O$ of the ambient water and $\delta^{18}O$ soil O_2. This downward trend towards decreased NO_3^- concentrations in the unsaturated zone may reflect uptake by crops. However, for some sampling points it is also accompanied by a small increase in $\delta^{15}N_{NO_3}$ suggesting some attenuation by denitrification.

Excluding well W1-A, $\delta^{15}N_{NO3}$ values range between +2.0 and +10.9‰. The enrichment of nitrate $\delta^{15}N$ values , together with decreasing NO_3^- concentrations, and the accompanied by a slight increase in DIC and depletion in the $\delta^{13}C$ of DOC, is consistent with denitrification in shallow groundwater (Figure 5.14A and B). Alternatively, nitrification of NH_4^+ concurrently with crop uptake of NO_3^- could be occurring. Minimal NH_4^+ concentration present in any samples (Figure 5.14C), reflects active nitrification of applied urea in the soil, and is consistent with the oxidizing E_H levels measured at the site.

Table 5.17: Site 1 – Lysimeter and tile drain nitrate and ammonium results summary.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
NH_4^+ (mg-N/L)	0.023	0.020	0.002	0.073	25	0.026	0.048	0.003	0.145	11
NO_3^- (mg-N/L)	4.0	2.6	0.88	15	37	8.1	1.9	4.7	12	16
Nitrogen Isotopes										
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	6.3	1.7	2.0	9.5	16	5.7	1.3	4.1	8.1	6
$\delta^{18}O_{NO3}$ (‰)	0.2	3.2	-6.9	5.6	16	9.3	12.7	0.2	25.9	6

Notes: 1) Lysimeter statistics are a compilation of three lysimeters (L1-1A, L1-1B and L1-1C).
2) Tile Drain statistics are a compilation of two tile drains (T1-A and T1-B).
3) "-" indicates that no samples were analysed

Table 5.18: Site 1 – Piezometer and bedrock well nitrate and ammonium results summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
NH_4^+ (mg-N/L)	0.061	0.073	0.004	0.278	26	0.104	0.228	0.002	1.12	29
NO_3^- (mg-N/L)	1.7	1.5	0.11	4.1	36	1.2	0.26	0.81	1.7	15
Nitrogen Isotopes										
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	8.3	1.1	7.0	10.9	9	10.3	2.7	4.3	13.5	11
$\delta^{18}O_{NO3}$ (‰)	3.6	3.3	-3.1	7.1	9	5.2	7.0	0.4	25.3	11

Notes:
1) Piezometer statistics are a compilation of three piezometers (P1-1B, P1-1C and P1-2B).
2) Bedrock Well statistics are a compilation of three wells (W1-A, W1-B and W1-C).
3) NO_3^- results from well W1-A are excluded from the bedrock well summary because values are unusually high, likely a result of a leaky well seal which allows surface water from a nearby cow pasture to enter the well.
4) "-" indicates that no samples were analysed

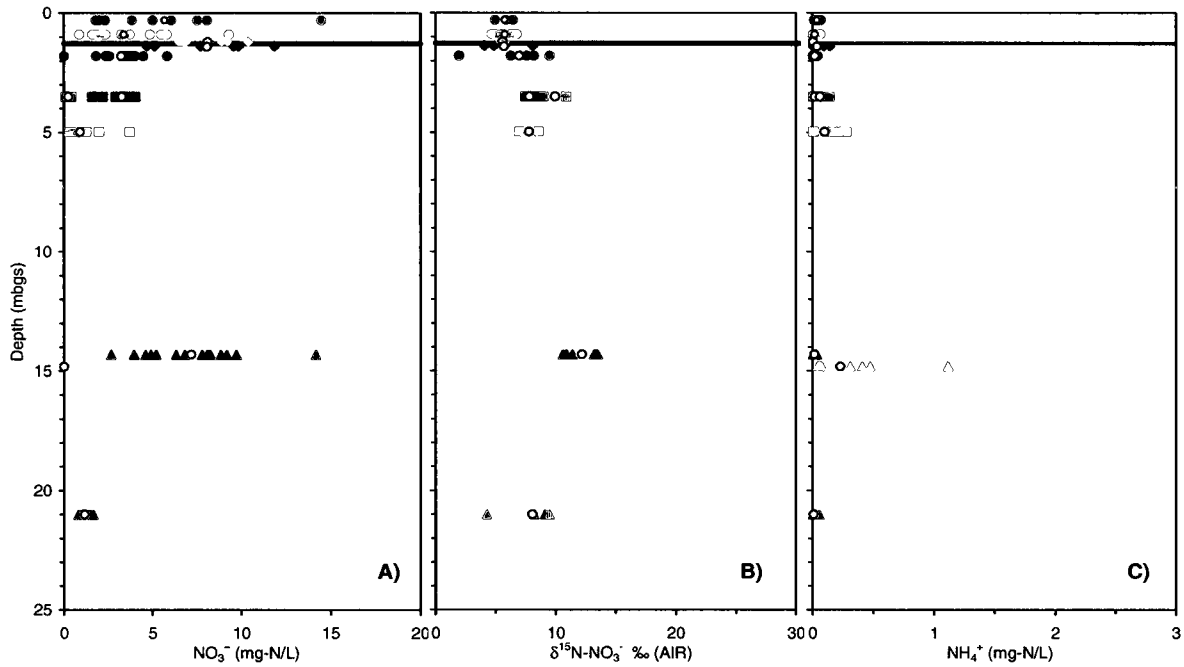

Figure 5.14: Site 1 – Depth vs. nitrate and ammonium. A) NO_3^- concentrations. B) $\delta^{15}N_{NO3}$ values. C) NH_4^+ concentrations. The blue lines represent the average depth of the water table, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point is located in Appendix F. Well W1-A at 14.3 m likely represents a leaking well seal, resulting in a surface water 'short-circuit', with elevated nutrient concentrations.

Most groundwater and unsaturated samples generally plot $\delta^{15}N_{NO3}$ within the range for soil N (Figure 5.15), and partially enriched from the analyzed value from local manure (measured $\delta^{15}N$ of manure was +4.4‰), while $\delta^{18}O_{NO_3}$ values show both enrichment and depletion around the hydrolyzed urea value of +2.2‰ (Section 5.2.3). Other boxes represent

literature ranges for various NO_3^- sources, from *[Clark and Fritz, 1997]*. These observations do not correspond with knowledge that only urea fertilizer (measured $\delta^{15}N$ of urea was 0.4‰) has been used on these fields recently; however, $\delta^{15}N_{NO_3}$ values enriched by up to 10‰ above values from nitrification of urea, suggesting losses by denitrification. Three samples (two tile drains and one well) show highly enriched $\delta^{18}O_{NO_3}$ values (approximately +25‰), suggesting a potential source from NO_3^- fertilizers.

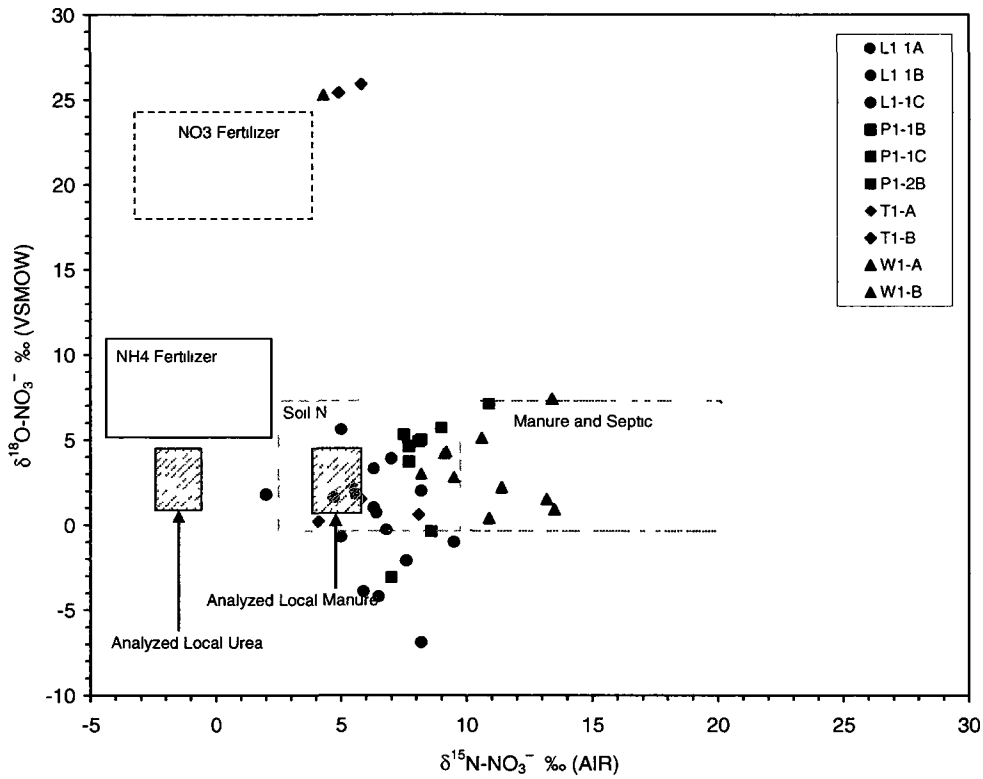

Figure 5.15: Site 1 – $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$, individual values for unsaturated zone and groundwater samples. The boxes represent literature ranges for various NO_3 sources, from *[Clark and Fritz, 1997]*, and the analyzed local urea and manure ^{15}N values.

Elevated NO_3^- and NH_4^+ concentrations in well W1-A (14 m well depth) relative to other Bedrock Aquifer samples stand out, supporting previous findings that the well has a leaking seal, allowing surface water and/or shallow groundwater to enter the casing following periods of precipitation. The well is located in the vicinity of a few cattle, and down-gradient of the farm equipment storage area. The mean NO_3^- concentration of well W1-A is 7.2 mg-N/L, which is comparable to concentrations found in lysimeters and tile drain; however, it is higher then the mean piezometer concentration of 1.7 mg-N/L. $\delta^{15}N_{NO3}$

and $\delta^{18}O_{NO_3}$ values from the leaking well (W1-A) plotted on Figure 5.15, suggests the nitrate originated from the nearby cattle manure.

5.3.6. Summary and Conclusions

Both shallow Surficial Aquitard and Bedrock Aquifer groundwaters show rapid response to precipitation indicating direct connection to the surface with macroporosity. A vertical downward hydraulic gradient was observed in mid-field piezometers. Stable isotopes of water showed direct recharge through fields, with a signal more enriched than regional groundwaters due likely to the preferential drainage of spring melt-water by tile drains. The shallow and bedrock groundwater meteoric signals exhibit stronger attenuation compared to those of the unsaturated zone.

Only urea fertilizer was applied to the fields, and is readily transformed to nitrate in the unsaturated zone, although there is attenuation through to shallow groundwaters attributable to both plant uptake and minor denitrification, as demonstrated by increased $\delta^{15}N$ of NO_3^- in some samples. Ammonium concentrations in groundwaters are consistently below 1 mg-N/L. Nitrate concentrations also remain low, with concentrations from 0.1 mg-N/L to only 4 mg-N/L. Further, $\delta^{15}N_{NO_3}$ values are enriched by up to 10‰ above values from nitrification of urea, suggesting losses by denitrification.

Carbon showed increased weathering with depth, supported by decreasing pCO_2 and increasing DIC. The $\delta^{13}C$ of DIC; however, showed a decrease with depth that is consistent with contributions of organic carbon through denitrification.

5.4. Site 2 – Agricultural Field

Site 2 is situated in an agricultural environment used for crop production, located near the town of Williamstown at confluence of the main and south branches of the site Raisin River (Figure 4.1). It consisting of three lysimeters, two tile drains, three piezometers and one dug overburden well all located in a glacial-marine deltaic deposit (Surficial Aquitard), and three drilled wells keyed into the Bedrock Aquifer. The lysimeters and piezometers were advanced directly into the middle of the fields, while the tile drains and wells belonged to the participating farmer and neighbouring home owners. The tile drains

discharged into a ditch which subsequently entered the Main Branch of the river approximately 50 m away. Tables 4.3, 4.2, 4.4 and 4.1 in Section 4, summarize the installation details for lysimeters, tile drains, piezometer and wells, respectively. Table 5.19 summarizes the physiographic and geologic settings (maps in Section 3) found in the vicinity of this site. Figure 5.16 identifies sampling point locations and local land use distribution.

Crops at Site 2 consisted of silage corn, which was planted in the season preceding the investigation (2004), and the two years (2005 and 2006) of the investigation. Each growing season, manure (80-100 kg-N/ha) and Urea (20 kg-N/ha) were applied as pre-plant (April-May depending on the year) and sidedress (June), respectively. The farm owner noted that typically approximately 10% (10 kg-N/ha) are likely still available each year from the manure applications of the previous year.

Table 5.19: Site 2 – Summary of Physiographic and Geologic settings.

Land Use	Agricultural
Soil Type	Sandy Loam Sand, Silt & Clay (65-25-10%)
Physiographic Unit	Lancaster Flats
Surficial Geology	Glacial-marine Delta Deposits Sand
Bedrock Geology	Verulam Formation interbedded bioclastic limestone, and sublithographic to fine crystalline limestone and shale
Overburden Thickness	10-15 m

Field measurements, geochemical and isotopic composition of samples collected from Site 2 are summarized in tables below, while complete results and seasonal summaries are located in Table D3 of Appendix D.

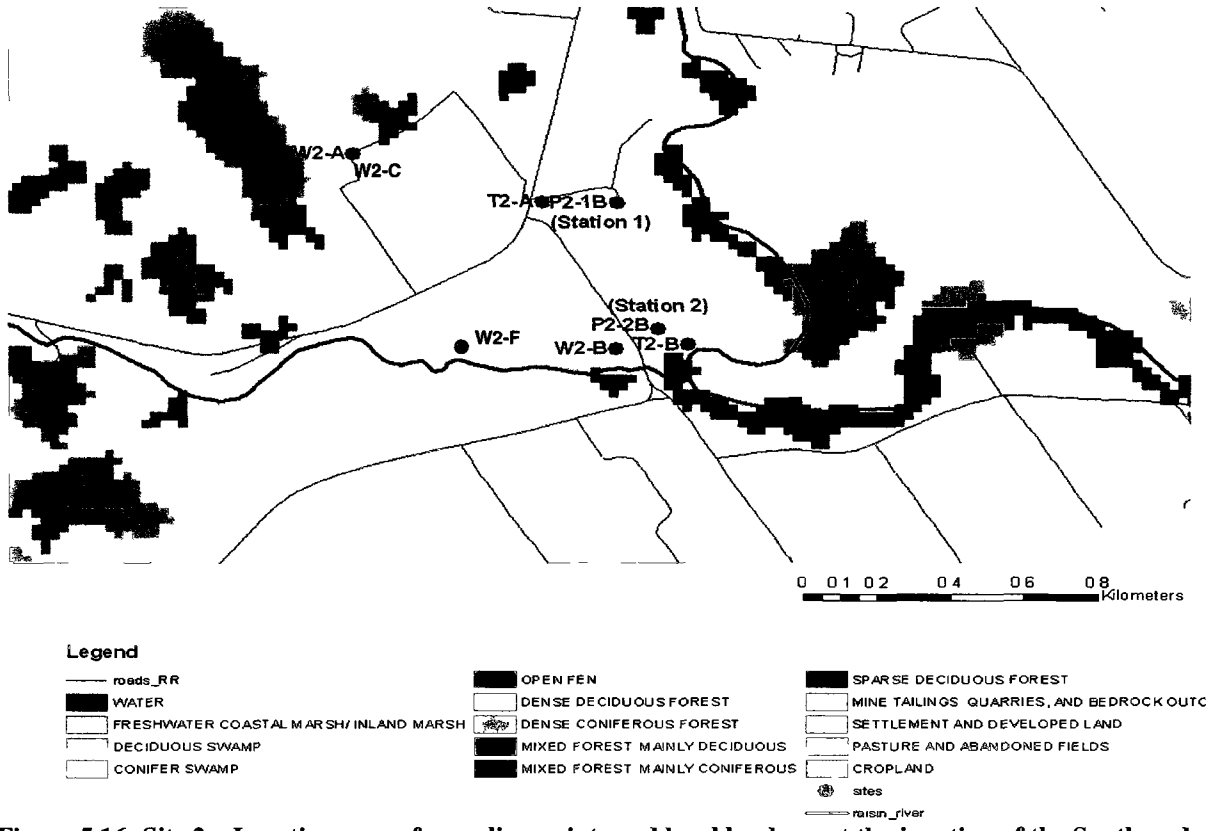

Figure 5.16: Site 2 – Location map of sampling points and local land use at the junction of the South and Main Branches of the Raisin River. Station 1 consists of lysimeters (L1-1A, L1-1B and L1-1C) and piezometers (P1-1B, P1-1C), while Station 2 consists only of piezometer P2-2B. All grey colouration represents agricultural fields.

5.4.1. Field Measurements

The water level, temperature, pH, conductivity, dissolved oxygen, and EH concentrations from Site 2 groundwater samples (piezometers and bedrock wells) are summarized in Table 5.20. The mean pH values for lysimeters and tile drains were 7.3 and 7.0, respectively, while specific conductance values were 804 and 1725 µS/cm, respectively.

Shallow and bedrock groundwater levels generally responded to precipitation equally, (Figure 5.17). Seasonally the water table fluctuations between fall highs and summer lows are approximately 1.4 m in the piezometers and 2.2 m in the Bedrock Aquifer. Full recharge occurs by October or November, followed by a slow steady decline until March, when water levels increase again following spring thaw, after which they start declining in June until a September low. The steady decline throughout the summer corresponds to periods where evapotranspiration is greater than infiltration *[Raisin-South Nation SWPR, 2007]*. A vertical gradient could not be determined as the piezometers were not nested, while

the horizontal groundwater flow gradient was south towards the South Branch of the Raisin River.

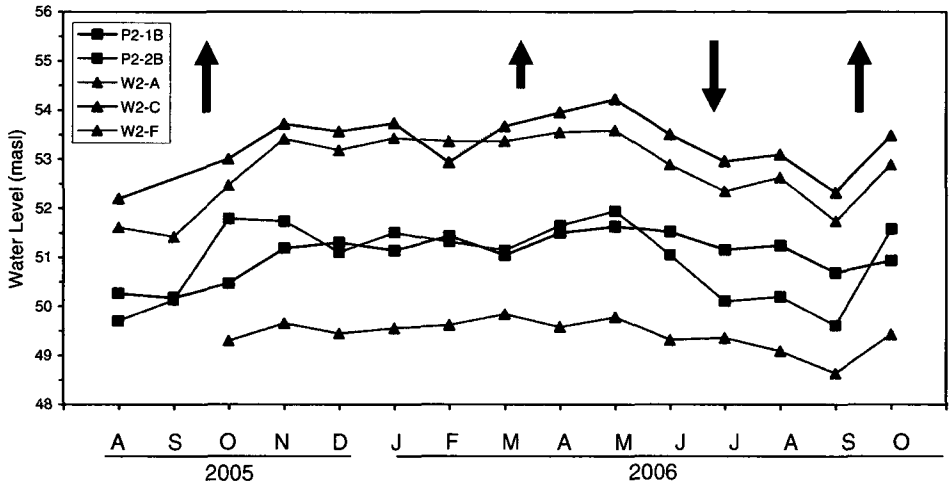

Figure 5.17: Site 2 – Monthly water level fluctuations in piezometers and wells, presented as elevations in meters above sea level. The red arrows indicate major periods of rising water levels (fall), the blue arrow indicates rising water levels following spring thaw and surface water infiltration, while the black arrow identifies decreasing water levels due to high rates of evapotranspiration resulting in decreased or limited infiltration.

The mean bedrock aquifer temperature is 10.4°C (similar to that of other sites), while the shallow groundwater temperature varied more significantly from seasonal atmospheric influences, with a mean of 11.5°C, and high - low values of 19.5°C and 3.0°C, respectively. The mean pH values were slightly higher in overburden than bedrock groundwaters, there was no discernable seasonal pattern, and they were generally consistent with those from the other sites. Specific conductance values were marginally lower in shallow groundwater samples compared to the bedrock aquifer, which is expected as deeper bedrock groundwater generally has a longer residence time, allowing for more mineral dissolution. Again, values were similar to those of other agricultural sites. The range in DO values from piezometer samples was 0.63 - 2.0 mg/L, as expected in shallow groundwater, and similar to other agricultural sites. The mean bedrock DO value was 0.3 mg/L, again similar to other bedrock aquifer readings. The shallow dug well W2-F, had DO measurements of 4.4 mg/L. Seasonal DO trends were not evident in either piezometer or well measurements. Average Eh values from shallow groundwater and Bedrock Aquifer measurements were all positive and below 375 mV, with the highest reading always recorded in summer following spring recharge and

when the unsaturated zone is at a maximum depth (Table D2). This same pattern was observed at the other sites as well.

Table 5.20: Site 2 – Piezometer and bedrock well summary of field parameters.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field										
W L (mbgs)	1 56	0 45	0 98	2 43	15	0 83	0 73	0 03	2 20	15
Temp (°C)	11 5	4 0	3 0	19 5	30	10 4	1 4	7 5	15 0	57
pH	7 7	0 28	7 0	8 0	30	7 3	0 36	6 7	8 0	57
SpC (µS/cm)	1060	378	560	1980	30	1251	712	7	3067	53
DO (mg/L)	1 1	0 50	0 63	2 0	6	0 3	0 5	0 03	2 0	24
Eh (mV)	139	55	80	238	9	180	78	52	328	29

Notes
1) Piezometer statistics are a compilation of two piezometers (P2-1B and P2-2B)
2) Bedrock Well statistics are a compilation of four wells (W2-A, W2-B, and W2-C)
3) Piezometer water level measurements are those from P2-1B
4) Well water level measurements are those from W2-A

5.4.2. Soil Test Pit

A test pit was dug by hand at Site 2 in order to evaluate the presence and prevalence of wormhole macro-pores in an agricultural field. Soils consist of sandy loam comprising of sand, silt and clay, approximately 65-25-10%, respectively. The test pit was dug to approximately 1.0 m, and on a surface prepared at a depth of 0.60 m, the prevalence of worm holes was calculated at 246/m^2 (Figure 5.18). The wormhole channels (approximately 5mm in diameter) were lined with darker coloured material, possibly excrement.

Water level measurements from piezometer P2-2B located close to the pit indicted maximum water table fluctuations of 0.15 - 2.5 meters below ground surface (mbgs); however, water levels ranged primarily between 0.5 – 1.0 mbgs. The maximum extent of the wormhole penetration was not fully delineated; however, channels were evident down to the bottom of the pit. Further, soil mottling (iron oxidation of minerals) was observed below 0.3 m depth. The abundance of wormholes suggests macro-pore flow aids in infiltration, and would contribute to the rapid transmission of any meteoric $\delta^{18}O$ and $\delta^{2}H$ signal to the water table and thus provide the rapid shift in trends observed in the temporal monitoring.

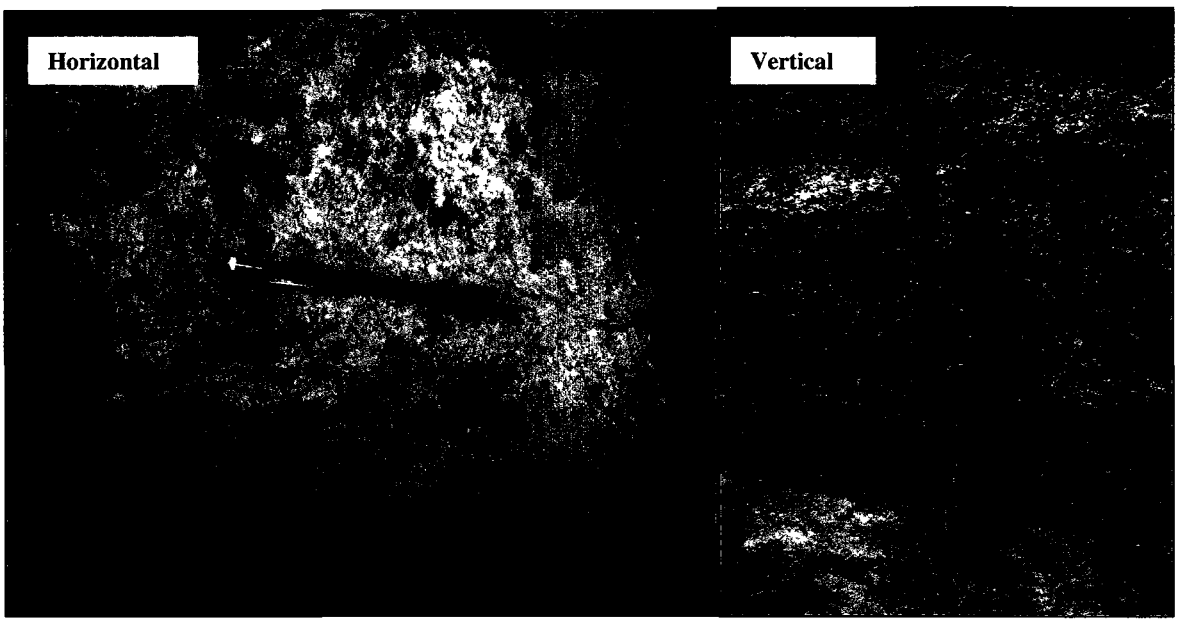

Figure 5.18: Site 2 – Test pit horizontal and vertical cross-sections with wormholes. The pit was dug in the field next to piezometer P2-2B. Approximately 246 holes per square meter measured at 0.60 m depth. Mineral oxidation (mottling) was also observed, identified by rust coloration.

5.4.3. Vadose and Groundwater $\delta^{18}O$ and $\delta^{2}H$

Table 5.21 and Table 5.22 summarize the $\delta^{18}O$ and $\delta^{2}H$ values for both soil moisture samples and groundwater samples, respectively. Soil moisture and groundwater $\delta^{18}O$ values are compared to the weighted monthly mean meteoric signal, and the weighted mean annual values for Ottawa and the pooled Raisin River signal (Figure 5.19).

Table 5.21: Site 2 – Lysimeter and tile drain summary of water isotope results.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Water										
$\delta^{18}O_{H2O}$ (‰)	-10.1	0.8	-11.2	-8.0	28	-10.6	0.4	-11.1	-10.0	12
$\delta^{2}H_{H2O}$ (‰)	-71.8	5.8	-80.8	-59.0	22	-74.9	3.4	-80.2	-69.9	12

Notes: 1) Lysimeter statistics are a compilation of three lysimeters (L2-1A, L2-1B and L2-1C).
2) Tile Drain statistics are a compilation of two tile drains (T2-A and T2-B).

During the fall of 2005, the 0.3 m lysimeter exhibited the most enriched values; however, a meteoric signal lag was not obvious due to limited data. A potential enrichment peak may be 1 or 2 months behind; however, there was limited data because the lysimeter was typically

dry in both summer and winter. The 0.6 m lysimeter displayed an apparent lag of about 2 months in the fall of 2005 and 2006 when samples were available, while the signal attenuation was similar to the 0.3 m lysimeter. At depths beyond 0.6 m, limited tile drain data were available (not plotted) and the 1.8 m lysimeter was not functional at this site. $\delta^{18}O$ lysimeter values are more enriched than the Ottawa annual meteoric signal (-11.1‰) reflecting the lack of data for the winter months. The mean $\delta^{18}O$ values for L2-1A and L2-1B were -9.4 and -9.8‰, respectively, and plot close to the M2 LWML, suggesting infiltration without significant evaporative loss; however, in relation to the Ottawa MWL, the minor enrichment could be explained by evaporative loss.

Table 5.22: Site 2 – Piezometer and well summary of water isotope results.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Water										
$\delta^{18}O_{H2O}$ (‰)	-10.0	0.4	-10.5	-9.1	28	-11.0	0.3	-11.4	-10.2	41
$\delta^{2}H_{H2O}$ (‰)	-71.5	3.5	-77.4	-63.8	20	-77.9	3.8	-83.3	-64.1	37

Notes: 1) Piezometer statistics are a compilation of two piezometers (P2-1B and P2-2B).
2) Bedrock Well statistics are a compilation of four wells (W2-A, W2-B, W2-C and W2-F).
3) All results from well W2-C were excluded from the bedrock well summary as most values were anomalous.

The shallow groundwater meteoric signal is more subdued, suggesting stronger attenuation towards the mean value compared to the unsaturated zone samples. Piezometer (P2-1B) is the shallower at 3.5 m (2.0 m below the mean water table), with a mean $\delta^{18}O$ of -9.7‰, and ranging from -10 to -9.1‰. This is consistently more enriched than piezometer P2-2B, which is deeper at 5.1 m (3.6 m below the mean water table) and has a mean $\delta^{18}O$ of -10.3‰ with a range from -10.5 to -9.9‰. Both piezometer signals vary coherently with one another, track similarly (Figure 5.19), and suggest different mixing ratios of regional flow and direct infiltration through the tiled field. The deeper piezometer (P2-2B) is closer to the river, suggesting it receives greater contributions of regional groundwater, as it travels upward towards to the discharge zone (river). The mean $\delta^{18}O$ values from the shallow and deep piezometer vary about the M2 annual meteoric signal by 0.4 and 1.1‰, respectively, suggesting a difference in the contribution of enriched summer precipitation (Figure 5.20). The mean $\delta^{18}O$ values vary more significantly when compared to the Ottawa signal.

Winter values are depleted by about 0.3‰ in both piezometers, with a 1 month lag from the meteoric signal. Both sites were sampled at the same frequency throughout the period, so there is no systematic exclusion of winter precipitation. The strongest variability (heavy enrichment, followed by steep depletion) from one month to the next occurs during the late-spring (May-July) following the ground thaw and presumed reopening of macro-pore flow, similar to observations at Site 1. The common tracking of seasonal variations suggests that the rapid contribution of direct infiltration through macro-pores (worm holes as presented above) is significant in this material.

An isotope mass balance between $\delta^{18}O$ of the local meteoric signal and $\delta^{18}O$ of the regional bedrock flow system allows calculation of mixing ratios, according to Equation 5.1:

$$\delta^{18}O_{mixed} = f_{local} \bullet \delta^{18}O_{local} + (1 - f_{local}) \bullet \delta^{18}O_{regional} \qquad (5.1)$$

This shows that the shallow piezometer (P2-1B) comprises 93% local contribution whereas the deeper piezometer (P2-2B) incorporates only 53% local contribution. When conducting a mass balance using the Ottawa meteoric precipitation signal -11.1‰, and the above distributions, results show that local $\delta^{18}O$ contribution to each piezometer is -9.65‰ and -9.68‰, for the shallow and deep, respectively. Compared to the mean lysimeter and tile drain $\delta^{18}O$ values of -10.1 and -10.6, respectively, these values suggest the difference is a result of enriched summer precipitation input.

The $\delta^{18}O$ signals from the Bedrock Aquifer (wells W2-A and W2-B) are equally subdued as the piezometer signal, although they are more depleted. The mean $\delta^{18}O$ values are -11.2 and -10.9‰, respectively, which very similar to the mean Ottawa meteoric signal of -11.1‰. W2-A and W2-B winter values are depleted from the mean by 0.3‰ and 0.4‰, respectively, with a similar 1 month lag as observed in the two piezometers. Thus, although a regional groundwater isotope signal dominates in these wells, there appears to be significant connectivity to the surface that allows rapid incorporation of meteoric signals on a seasonal to monthly basis (Figure 5.19).

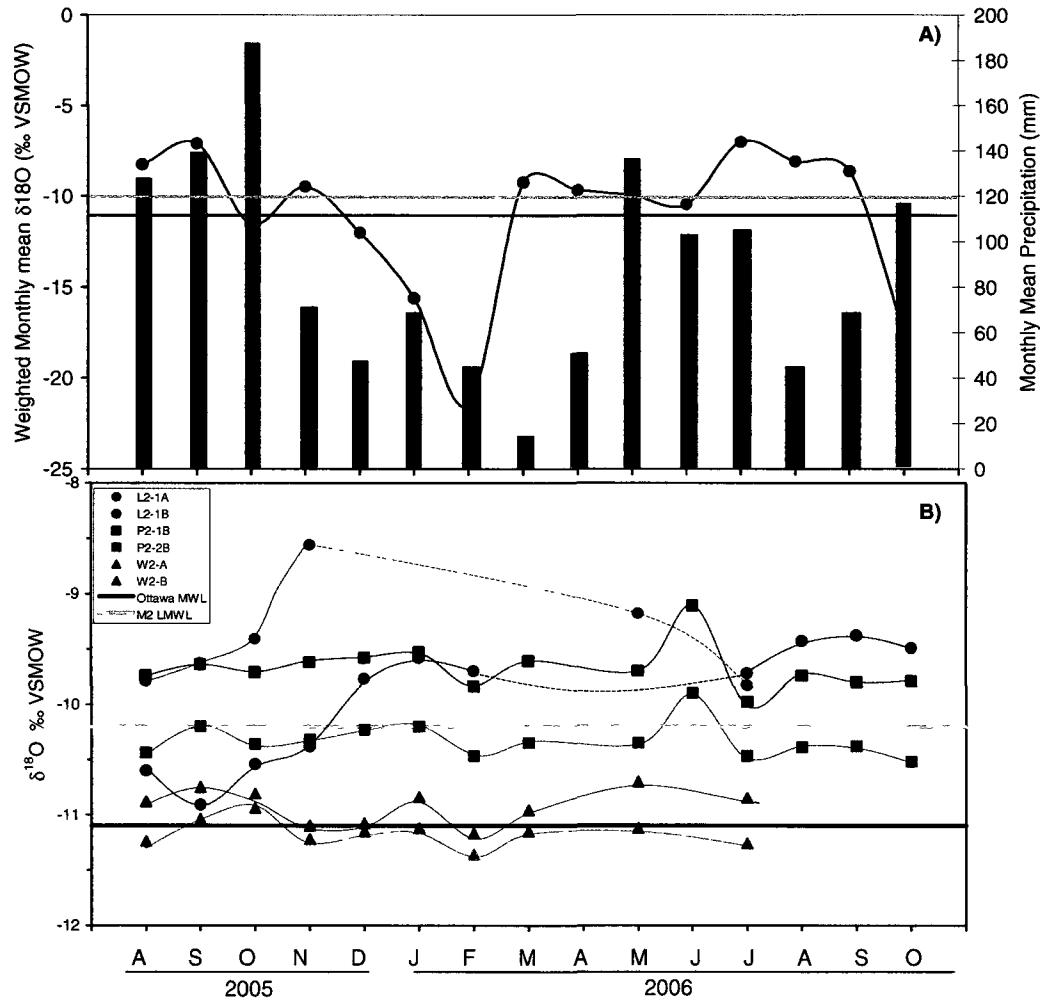

Figure 5.19: Site 2 – Temporal plot vs. mean monthly precipitation and $\delta^{18}O_{H2O}$. A) Amount-weighted mean monthly meteoric $\delta^{18}O$ and monthly precipitation. B) Monthly unsaturated zone and groundwater $\delta^{18}O$ seasonal trend. The grey and black lines represent the weighted mean annual meteoric $\delta^{18}O$ signals for the M2 LMWL (-10.2‰) and Ottawa MWL (-11.1‰), respectively.

Figure 5.20 plots $\delta^{18}O$ against $\delta^{2}H$. As with Site 1, shallow groundwater from piezometers are more enriched relative to bedrock aquifer groundwater, suggesting groundwaters comprise local infiltration (with summer bias) mixing with the regional, more depleted groundwaters. On average, bedrock groundwaters are depleted over piezometers in $\delta^{18}O$ by 1‰. Similarly as in Site 1, a potential altitude effect of 0.15-0.5‰ $\delta^{18}O$ per 100m elevation *[Gat, 1980]*, is unlikely to contribute all of this depletion due to the rather subdued topography (approximately 70 m).

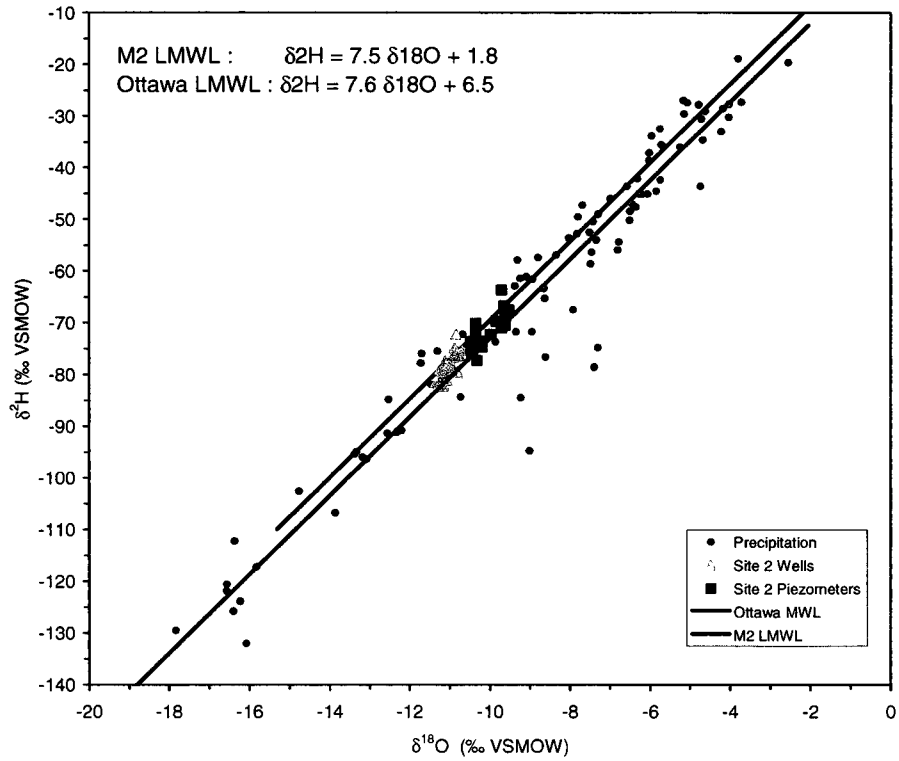

Figure 5.20: Site 2 – δ^2H and $\delta^{18}O$ values for monthly-weighted precipitation, piezometers and wells.

The piezometer groundwaters have $\delta^{18}O$ and δ^2H values and trends more similar to the lysimeters, demonstrating a local recharge through the fields, while the well groundwater (Bedrock Aquifer), is systematically depleted, indicating a more regional signal from the basin, which is similar to the long term Ottawa meteoric signal.

5.4.4. Geochemistry

Major ions, nutrient concentrations and isotope values from Site 2 unsaturated zone and groundwater samples are summarized in Table 5.23 and Table 5.24, respectively. Major ion chemistry was not dissimilar to that from Site 1, except for well W2-C, which is located within a barn and in close proximity to an older clay lined dairy cow manure pit. Although the steel wellhead is above grade, capped, and set into the concrete floor of the barn and not at risk to flooding, preferred pathways likely exist beneath the concrete slab. Concentrations of most major ions and nutrients from well WC-2 vary significantly from those found in other bedrock wells in the vicinity, as such it was not included in the bedrock well summary. The well is further discussed in Section 5.4.5.

Table 5.23: Site 2 – Lysimeter and tile drain summary of analytical results.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
Ca^{2+} (mg/L)	51	16	31	79	34	109	48	31	223	16
Na^{+} (mg/L)	18	3 3	12 7	25	34	90	64	23	239	16
Mg^{2+} (mg/L)	19	9 2	7 3	36	34	30	10	10	54	16
K^{+} (mg/L)	2 3	1 3	0 54	4 7	34	1 9	0 74	0 78	3 42	16
P (mg/L)	0 055	0 11	0 0066	0 56	24	0 092	0 11	0 019	0 40	16
Cl (mg/L)	22	6 7	9 4	32	30	229	162	53	640	16
SO_4^{2} (mg/L)	27	8 8	15	51	28	25 6	8 0	11 6	45 3	14
HCO_3 (mg/L)	142	118	14	370	33	217	79	88	335	15
Calculations										
pCO_2 (exp)	-2 10	0 41	-3 18	-1 34	33	-1 87	0 42	-2 61	-1 31	15
$SI_{calcite}$	0 805	1 471	0 006	7 102	33	0 590	0 538	0 048	2 221	15

Notes
1) Lysimeter statistics are a compilation of three lysimeters (L2-1A, L2-1B and L2-1C)
2) Tile Drain statistics are a compilation of two tile drains (T2-A and T2-B)
3) P = Total Phosphorus
4) pCO_2 is the exponent value with base 10
5) "-" indicates that no samples were analysed

Table 5.24: Site 2 – Piezometer and bedrock well summary of analytical results.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
Ca^{2+} (mg/L)	37	15	19	56	30	77	18	52	119	43
Na^{+} (mg/L)	86	47	33	159	30	26	8 7	11	40	43
Mg^{2+} (mg/L)	25	4 7	17	31	30	26	4	19	32	43
K^{+} (mg/L)	8 6	2 3	5 1	13	30	6	3	2 9	11	43
P (mg/L)	1 1	0 64	0 236	2 2	27	0 062	0 042	0 015	0 16	38
Cl (mg/L)	16	5 3	8 1	24	30	26	14	9 8	79	43
SO_4^{2} (mg/L)	3 7	1 5	0 52	6 9	16	42	18	14	80	40
HCO_3 (mg/L)	419	82	270	624	30	343	88	165	604	43
Calculations										
pCO_2 (exp)	-2 11	0 27	-2 69	-1 49	30	-2 02	0 33	-2 52	-1 40	43
$SI_{calcite}$	1 854	0 911	0 235	3 858	30	1 940	1 084	0 416	5 215	43

Notes
1) Piezometer statistics are a compilation of two piezometers (P2-1B and P2-2B)
2) Bedrock Well statistics are a compilation of three wells (W2-A, W2-B and W2-F)
3) All results from well W2-C were excluded from the bedrock well summary as most values were anomalous
4) pCO_2 is the exponent value with base 10

5.4.5. DIC and DOC

Table 5.25 and Table 5.26 summarize DIC and DOC concentration and $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ values from unsaturated zone samples and groundwater samples, respectively.

Results from bedrock well W2-C, previously identified as being located in a barn next to a manure pit, are discussed separately.

Table 5.25: Site 2 – Lysimeter and tile drain carbon chemistry and isotope results summary.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Carbon Species and Isotopes										
HCO_3 (mg/L)	142	118	14	370	33	217	79	88	335	15
pCO_2 (exp)	-2 10	0 41	-3 18	-1 34	33	-1 87	0 42	-2 61	-1 31	15
DIC (ppmC)	35	23	3 7	81	33	57	21	21	90	15
DOC (ppmC)	6 1	4 7	1 4	16	31	4 1	1 4	2 2	7 1	16
$\delta^{13}C_{DIC}$ (‰)	-15 3	1 2	-17 3	-13 4	33	-11 8	0 5	-12 8	-11 1	15
$\delta^{13}C_{DOC}$ (‰)	-26 2	1 4	-28 6	-22 4	31	-24 3	1 7	-26 6	-21 4	16

Notes 1) Lysimeter statistics are a compilation of three lysimeters (L2-1A, L2-1B and L2-1C)
2) Tile Drain statistics are a compilation of two tile drains (T2-A and T2-B)

Table 5.26: Site 2 – Piezometer and bedrock well carbon chemistry and isotope results summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Carbon Species and Isotopes										
HCO_3 (mg/L)	419	82	270	624	30	343	88	165	604	43
pCO_2 (exp)	-2 11	0 27	-2 69	-1 49	30	-2 02	0 33	-2 52	-1 40	43
DIC (ppmC)	89	16	55	128	30	76	21	37	137	43
DOC (ppmC)	5 2	2 54	1 6	10 5	28	5 0	13 5	0 87	91 0	43
$\delta^{13}C_{DIC}$ (‰)	-13 5	1 9	-15 6	-9 2	30	-13 8	0 6	-14 9	-12 6	43
$\delta^{13}C_{DOC}$ (‰)	-27 8	2 3	-33 4	-22 9	28	-26 0	1 8	-28 5	-20 5	42

Notes 1) Piezometer statistics are a compilation of two piezometers (P2-1B and P2-2B)
2) Bedrock Well statistics are a compilation of three wells (W2-A, W2-B and W2-C)
3) All results from well W2-C were excluded from the bedrock well summary as most values were anomalous

DIC concentrations show a general increase through the unsaturated zone reflecting biodegradation and weathering. In groundwaters, DIC concentrations are on average constant with depth, as seen in Figure 5.21, with mean DIC concentrations between 75-90 mg-C/L at all depths, although with considerable seasonal variability (40 to 130 ppm-C), suggesting intermittent, rapid recharge from the surface. The $\delta^{13}C$ of DIC shows a similar variability, in that values become more enriched through the unsaturated zone to a maximum mean value of -11.9‰ in the deeper piezometers, while bedrock groundwater has a slightly more depleted mean value of -13.8‰. This suggests that C_4 (corn) type vegetation (~-4‰) is influencing the signal at shallow groundwater depths; however, the overall deeper bedrock

signal is that of DIC from C_3 (natural) type vegetation (~-14 to -16‰) which had evolved under open system dissolution.

Infiltrating water will equilibrate with soil CO_2, after which bacterial oxidation of soil organic matter, and respiration of CO_2 in the root zone will maintain pCO_2 levels of approximately 10^{-3} to 10^{-1} (100,000 ppmv) *[Clark and Fritz, 1997]*. Calculations show that mean pCO_2 values are on average constant with depth and lower than typical soil pCO_2 values, suggesting increased weathering is not occurring past the water table, as $SI_{calcite}$ values move from under-saturated in the vadose zone to super-saturated in groundwaters.

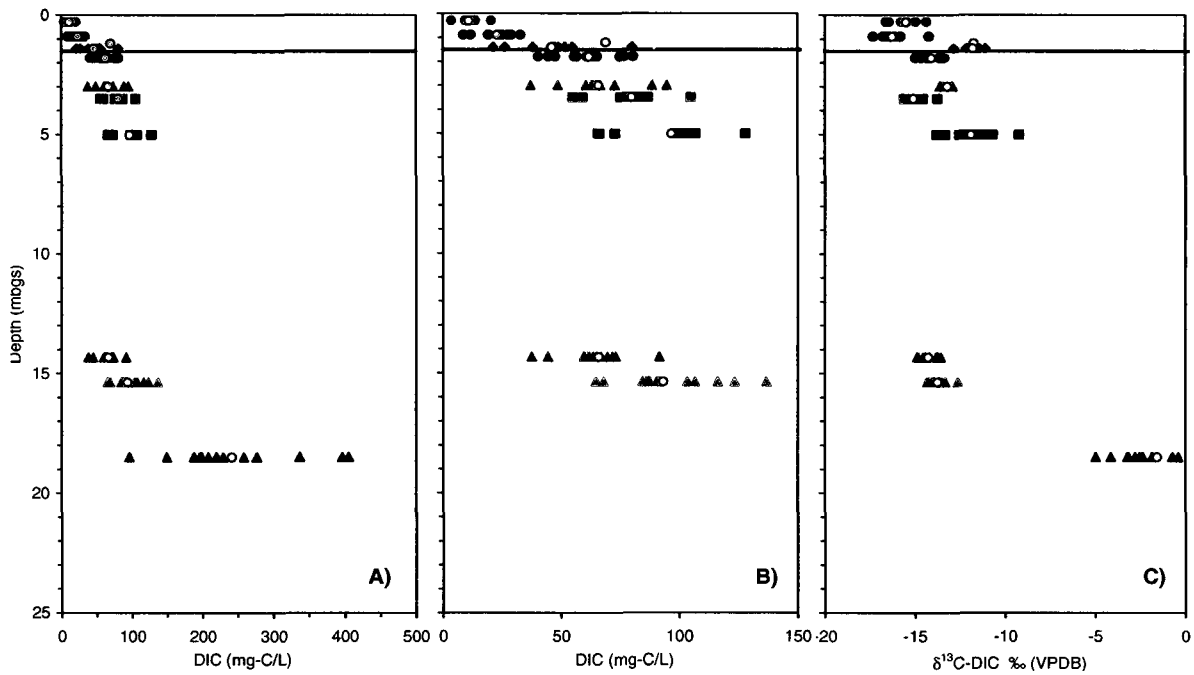

Figure 5.21: Site 2 – Depth vs. DIC. The blue lines represent the mean water table depth, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F. A) DIC concentrations. B) DIC concentrations, cropped range. C) $\delta^{13}C_{DIC}$ values.

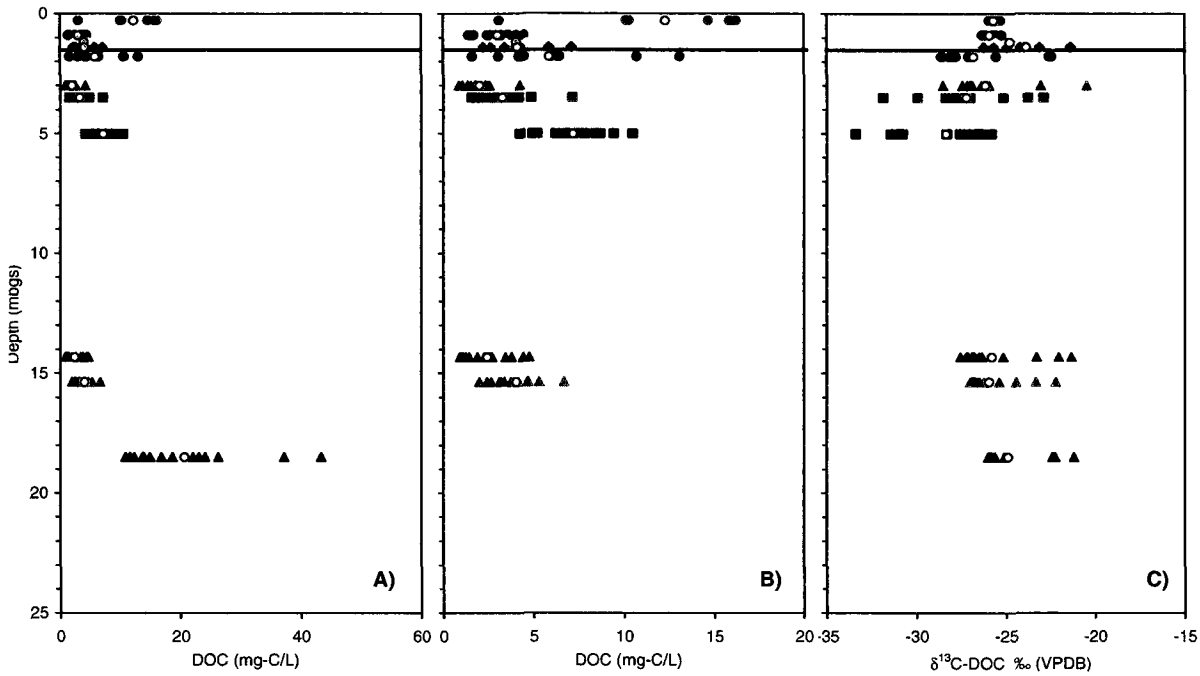

Figure 5.22: Site 2 – Depth vs. DOC. The blue lines represent the mean water table depth, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F. A) DIC concentrations. B) DOC concentrations, cropped range. C) $\delta^{13}C_{DOC}$ values.

Mean DOC concentrations are constant through both the unsaturated zone and below the water table (Figure 5.22), with values between 4.1 and 6.1 mg-C/L. The $\delta^{13}C$ of DOC values on average are constant with depth, with mean $\delta^{13}C$ values ranging between -26.0 and -27.8‰. However, because of the considerable seasonal variability at all depths, $\delta^{13}C$ of DOC values appear to be decreasing in the unsaturated zone, and then increasing in the groundwater (Figure 5.21). Constant average DIC and DOC concentrations with depth suggest that oxidation of organic compounds is not a major process at this site.

Highly elevated DIC concentrations in bedrock well W2-C, coupled with enriched $\delta^{13}C$ of DIC values suggests that more than regular non-point source agricultural impacts are involved. Because of the close proximity of the manure pit, high pCO_2 ($10^{-1.05}$), the elevated presence of DOC, and slight enrichment of $\delta^{13}C_{DOC}$, biogenic methane gas (CH_4) production through bacterial decomposition of organic mater (CH_2O) is suspected. For this to occur, the environment must be free of atmospheric oxygen and of other free electron acceptors (NO_3^- and SO_4^{2-}) *[Clark and Fritz, 1997]*. The absence of NO_3^- and abundance of reduced NH_4^+,

confirms this requirement, while SO_4^{2-} is present with a mean concentration of 36 mg/L. Complete analytical and isotopic results from well W2-C are located in Table D3 in Appendix D. One groundwater sample was analyzed for CH_4 and $\delta^{13}C$ of CH_4, giving a result of -37.2‰. Biogenic methane origins in groundwater has been reported as being between -50 to -90‰ *[Fritz et al., 1992; Aravena et al., 1993, 1995; Clark and Fritz, 1997]*, while thermocatalytic methane from sedimentary basins have more enriched $\delta^{13}C_{CH4}$ values *[Clark and Fritz, 1997]*. However, given the high NH_4^+ and Fe (~7 ppm) present in this well, and no natural gas has been reported in the region, a biogenic source is most likely. The more enriched $\delta^{13}C_{CH4}$ signal may be due to microbial oxidation of CH_4. Additional comments for well W2-C regarding nitrogen results are discussed in the next section.

5.4.6. Nitrate and Ammonium

Tables 5.27 and 5.28 summarize nitrate and ammonium concentrations and $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values for unsaturated zone samples and groundwater samples, respectively. Results from bedrock well W2-C are excluded from the summary table, and are discussed separately; however complete results are located in Table D3 in Appendix D.

Table 5.27: Site 2 – Lysimeter and tile drain nitrate and ammonium results summary.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Nitrogen Species										
NH_4^+ (mg-N/L)	0.060	0.104	0.004	0.37	22	0.024	0.053	0.003	0.198	13
NO_3^- (mg-N/L)	22	12	0.42	35	30	4.9	2.3	2.3	9.4	16
Nitrogen Isotopes										
$\delta^{15}N_{NH4}$ (‰)	6.7	-	6.7	6.7	1	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	8.0	1.5	5.7	10.8	16	5.4	1.5	3.5	7.3	7
$\delta^{18}O_{NO3}$ (‰)	1.5	1.6	0.0	6.4	16	8.9	11.1	-1.0	24.8	7

Notes: 1) Lysimeter statistics are a compilation of three lysimeters (L2-1A, L2-1B and L2-1C).
2) Tile Drain statistics are a compilation of two tile drains (T2-A and T2-B).
3) "-" indicates that no samples were analysed

Ammonium concentrations in the unsaturated zone are on average very low and constant (<0.1 mg-N/L), as seen in Figure 5.23A and B; however, they do increase slightly (up to concentrations of 3 mg-N/L) at shallow groundwater depths. The absence of NH_4^+ in the unsaturated zone, and the presence in groundwater coupled with the presence of NO_3^- in

the unsaturated zone and absence below the water table (Figure 5.24A) suggests that NH_4^+ (applied as both synthetic urea and manure) is possibly being oxidized to NO_3^- in lysimeters and tile drains prior to sample collection.

Table 5.28: Site 2 – Piezometer and bedrock well nitrate and ammonium results summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Nitrogen Species										
NH_4^+ (mg-N/L)	1 88	0 678	0 760	2 96	30	0 584	0 361	0 096	1 41	41
NO_3 (mg-N/L)	trace	trace	trace	trace	-	0 41	0 20	0 17	0 75	6
Nitrogen Isotopes										
$\delta^{15}N_{NH4}$ (‰)	6 0	2 8	2 0	13 5	29	5 4	2 2	0 2	8 3	30
$\delta^{15}N_{NO3}$ (‰)	11 9	-	11 9	11 9	1	19 1	2 2	17 0	21 3	3
$\delta^{18}O_{NO3}$ (‰)	-10 8	-	-10 8	-10 8	1	9 7	3 9	7 3	14 2	3

Notes
1) Piezometer statistics are a compilation of two piezometers (P2-1B and P2-2B)
2) Bedrock Well statistics are a compilation of three wells (W2-A, W2-B and W2-F)
3) All results from well W2-C were excluded from the bedrock well summary as most values were anomalous
4) "-" indicates that no samples were analysed

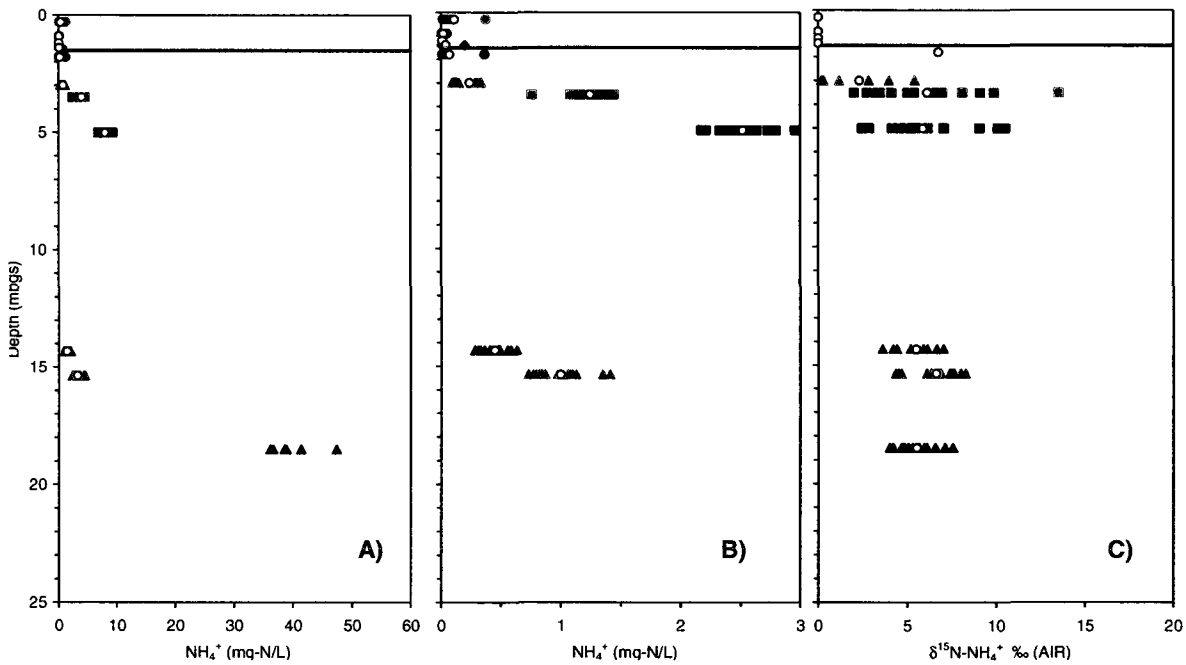

Figure 5.23: Site 2 – Depth vs. Ammonium. The blue lines represent the mean water table depth, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F. A) NH_4^+ concentrations (reduced range <3 ppmN). B) NH_4^+ concentrations (full range, including well W2-C at 18.5m). C) $\delta^{15}N_{NH4}$ values.

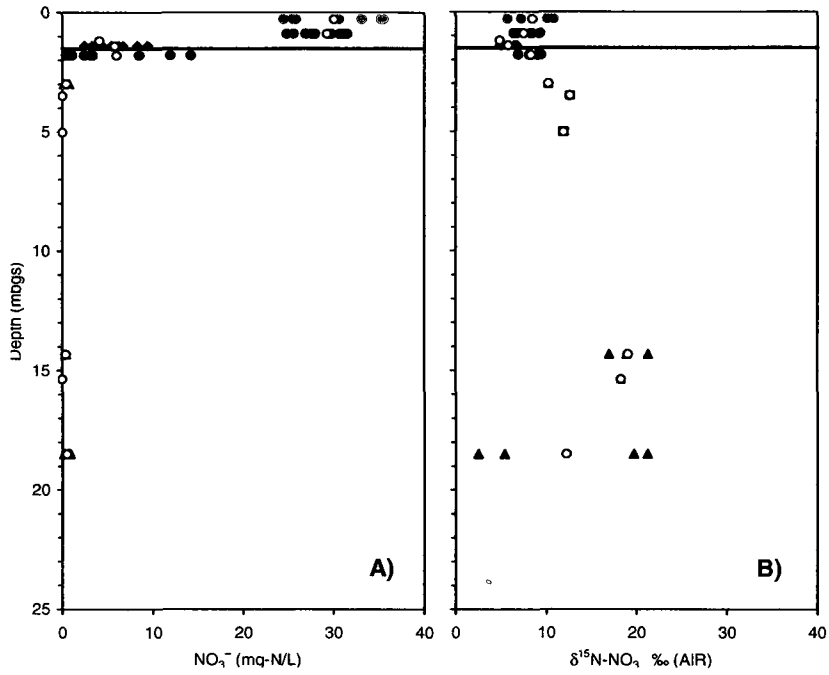

Figure 5.24: Site 2 – Depth vs. Nitrate. The blue lines represent the mean water table depth, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F. A) NO_3^- concentrations. B) $\delta^{15}N_{NO3}$ values.

Mean $\delta^{15}N_{NO3}$ values in lysimeters and tile drains are 8.0 and 5.4‰, respectively, very close to the $\delta^{15}N_{NH4}$ values in piezometers and bedrock wells of 6.0‰ and 5.4‰, respectively. This supports the concept that soil water NH_4^+ is quantitatively converted to NO_3^- as a result of the oxidizing environment in the lysimeters. Considering a simple ^{15}N mass balance, and assuming zero net fractionation between N reactant and N product, complete ammonium oxidation to nitrate in lysimeters and tile drains would result in ^{15}N values of ~5.8‰.

As previously stated at the beginning of Section 5.4, the ratio of total N fertilizer application at this site (manure vs. urea) is approximately 5:1, 80-100 kg-N/ha vs. 20 kg-N/ha. A urea analysis provided a $\delta^{15}N_{NH4}$ value of 0.4‰, while a manure analysis yielded a $\delta^{15}N$ value of 4.4‰. Isotope mass balance provides a combined fertilizer ^{15}N value of ~3.7‰, which suggests 2‰ enrichment to the average of 5.8‰ measured. This is likely due to either mineralization of urea, or partial volatilization of NH_3 prior to fertilizer nitrification.

Lysimeters were installed at depths of 0.3 m, 0.6 m, and 1.8 m, while the two tile drains are buried at approximately 1.2 m. The corresponding mean NO_3^- concentrations, in order of increasing depth (L2-1A, L2-1B, T2-A, T2-B and L2-1C) are 30, 29, 4.1, 5.8, and

6.0 mg-N/L, which is presumed to represent largely ammonium concentrations in the soil water (converted to NO_3^- in the lysimeters). Conversely, the mean NH_4^+ piezometer concentration (P2-1B and P2-2B), is 1.8 mg-N/L, suggesting a 33 to 1.8 mg-N/L reduction in N concentrations, or roughly 18:1 attenuation. This non-fractionating attenuation of N is likely a combination of crop uptake, sorption and mixing of local and regional groundwater.

As discussed in Section 5.4.5, elevated NH_4^+ concentrations in well W2-C, are likely due to infiltration of manure leachate (Figure 5.23A). The mean $\delta^{15}N_{NH4}$ value of 5.5‰ (Figure 5.23C) closely corresponds with the isotopic composition of manure ($\delta^{15}N$ of 4.4‰) with little modification by volatilization or nitrification (absence of NO_3^-).

Figure 5.25 illustrated that most unsaturated samples have $\delta^{15}N_{NO3}$ values (resulting from NH_4^+ oxidation, followed by mineralization or volatilization) which are enriched in comparison to the analyzed value of cattle manure fertilizer (measured $\delta^{15}N$ of manure was 4.4‰; see grey), while $\delta^{18}O_{NO_3}$ values show both enrichment and depletion around the manure value. Other boxes in Figure 5.25 represent literature ranges for various NO_3^- sources, from *[Clark and Fritz, 1997]*. A number of samples from well W2-B also show both $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO_3}$ enrichment, suggesting that denitrification is also occurring at this site. Figure 5.25 also identifies two tile drain samples that show highly enriched $\delta^{18}O_{NO_3}$ values (approximately +25‰); in conjunction with no $\delta^{15}N_{NO3}$ enrichment, suggesting a potential source from NO_3^- fertilizers.

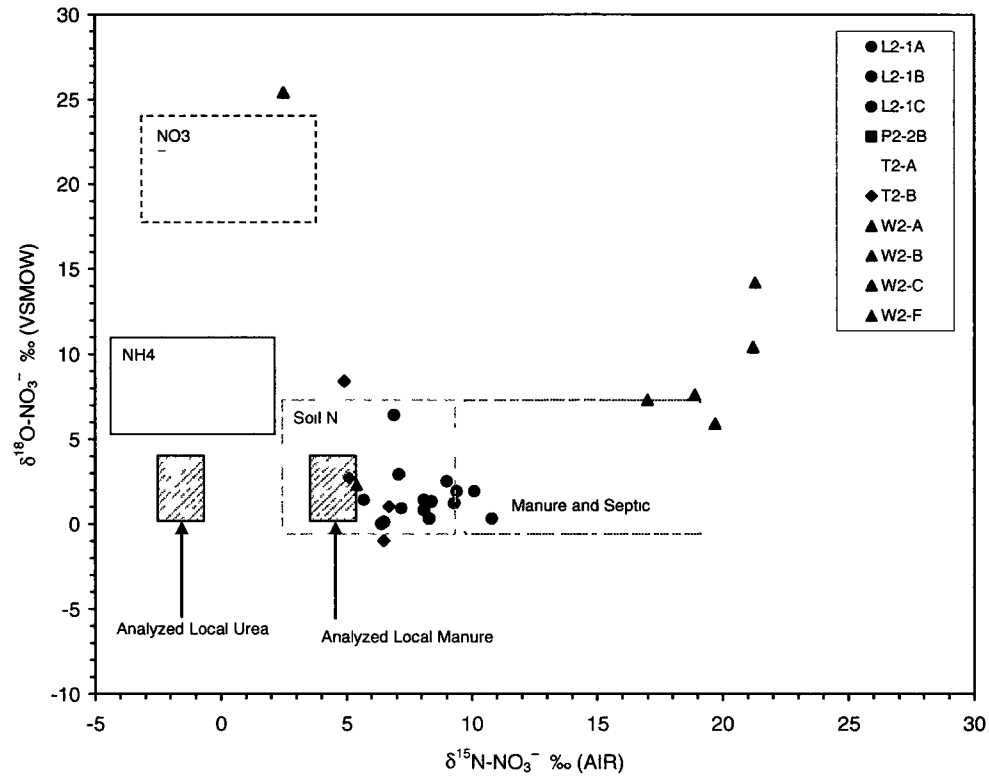

Figure 5.25: Site 2 – $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$ groundwater, tile drain and lysimeter values from indivual samples. The boxes represent literature ranges for various NO_3 sources, from *[Clark and Fritz, 1997]*, while the grey boxes represent analyzed $\delta^{15}N$ values for hydrolyzed local urea ($\delta^{15}N$ = +0.4‰) and manure $\delta^{15}N_{ORG}$ = +4.4‰).

Exclusive of well W2-C, there is minimal seasonal variability in NH_4^+ concentrations (Figure 5.26C), while $\delta^{15}N_{NH4}$ values for piezometer and bedrock groundwaters (Figure 5.26A) vary monthly; however, no trend is apparent. The attenuations of NH_4^+ isotope values from piezometers to wells is attributed to dilution, given the lack of coherent enrichment in ^{15}N which would be associated with reactive loss. With regards to well W2-C, interestingly the NH_4^+ concentrations level off at their lowest concentration of approximately 12 mg-N/L between February and June, possibly a result of ground frost. Following this low period, concentrations climb steeply, with corresponding high concentrations in the months of September and October (max 50 mg-N/L) during both years of the investigation.

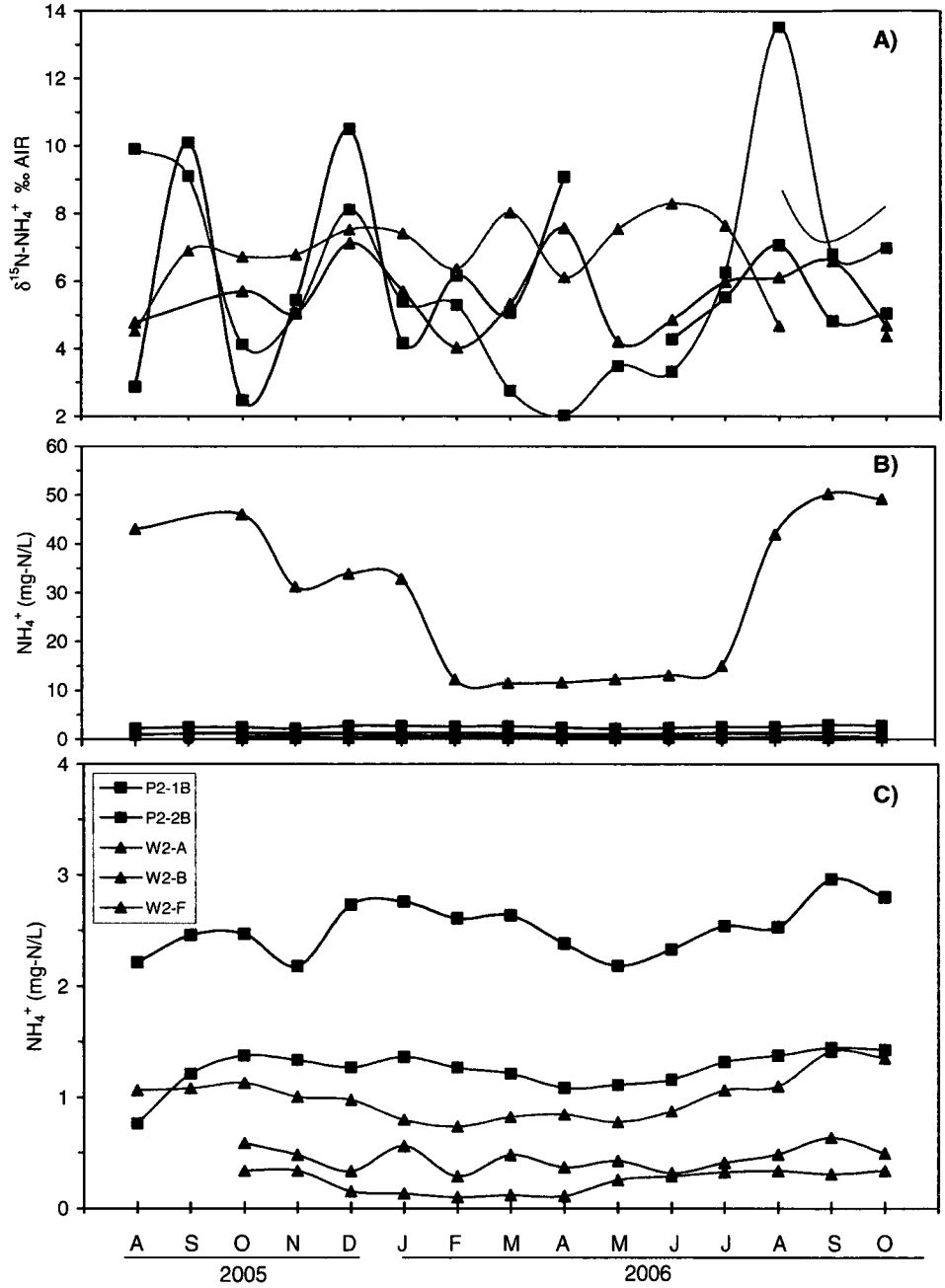

Figure 5.26: Site 2 – Temporal plots of NH_4^+ $\delta^{15}N$ of NH_4^+ values and NH_4^+ concentrations A) $\delta^{15}N_{NH4}$ values. B) NH_4^+ concentrations (full range with elevated concentrations of well W2-C). C) NH_4^+ excluding well W2-C.

5.4.7. Summary and Conclusions

Stable isotopes demonstrate infiltration through the fields to groundwaters is mixed with regional groundwaters recharged in the distal regions of the catchment. Rapid response to precipitation observed for water levels is also observed with the stable isotope trends,

although with significant attenuation. The abundance of wormholes identified (250/m^2) following the excavation of a test pit suggests macro-porosity in the sediments aids the infiltration and contributes to the rapid transmission of any meteoric $\delta^{18}O$ and $\delta^{2}H$ signal to the water table and thus providing the rapid shift in trends observed in the temporal monitoring is significant in this material. Piezometer groundwaters have stable isotope values that are on average intermediate between lysimeter and bedrock groundwaters, again demonstrating a mixture of direct infiltration and regional groundwaters.

Constant average DIC and DOC concentrations with depth suggest that oxidation of organic materials is not a major process at this site. This is consistent with the nitrogen data, which show no evidence for reaction during infiltration of NH_4^+ from the soils to groundwaters. High soil water nitrate values (up to 35 mg-N/L in lysimeters) are concluded to be mainly NH_4^+ (although the lysimeters report NO_3^- due likely to quantitative oxidation of soil NH_4^+) are reduced to less than 3 mg-N/L in the piezometer groundwaters. Thus, infiltration is dominated by NH_4^+, with only trace NO_3^- in the piezometers and minor but persistent NH_4^+. Enriched values for $\delta^{15}N_{NO_3}$ indicate reactive loss of NO_3^- from ammonium nitrification in the soils. Accordingly, the high NH_4^+ concentrations in soil water (~30 mg-N/L assumed from the high NH_4^+ in lysimeters) is highly attenuated by plant uptake prior to recharge at the water table, where groundwater concentrations are on the order of 1 to 5 mg-N/L. The ^{15}N of ammonium is close to that of the combined urea and manure signal with a slight 2‰ enrichment likely associated with volatilization, and no evidence for nitrification is observed. This is consistent with the low E_H (mean of 139 mV) and low DO (1.1 mg/L).

In contrast, the wells have low but measureable NO_3^- concentrations with higher $\delta^{15}N$ values indicating possible denitrification. The low E_H of well waters supports this and suggests that this nitrate is of a regional source rather than by infiltration through the fields. These findings correspond with $\delta^{18}O$ and $\delta^{2}H$ results suggesting a regional source for groundwater in the Bedrock Aquifer. Although a regional groundwater isotope signal dominates in these wells, there appears to be significant connectivity to the surface that allows rapid incorporation of meteoric signals on a seasonal to monthly basis (Figure 5.19).

5.5. Site 3 – Agricultural Field

Site 3 is an agricultural site located along the south branch of the Raisin River (Figure 4.1). It consists of two lysimeters, two tile drains, 5 piezometers, and one dug well, all located in a glacial-marine deltaic deposit (Surficial Aquitard), while two drilled domestic wells are completed in the Bedrock Aquifer, and specifically the Bobcaygeon Formation. The lysimeters and piezometers were advanced directly into the field, while the tile drains and wells belonged to the participating farmer and neighbouring home owners. Figure 5.27 identifies the installation locations (three piezometers at Station 1, two piezometers at Station 2), domestic wells, and the tile drains which discharged directly into the river. Tables 4.3, 4.2, 4.4 and 4.1 in Section 4, summarize the installation details for lysimeters, tile drains, piezometer and wells, respectively, while Table 5.29 summarizes the physiographic and geologic settings (maps in Section 3) found in the vicinity of this site.

Topography in the vicinity of Site 3 indicates the south branch lies in a very low-relief valley, and that local Bedrock Aquifer groundwater likely has sub-regional source influences, compared to Bedrock Aquifer groundwater from the other sites.

Table 5.29: Site 3 – Summary of Physiographic and Geologic settings.

Land Use	Agricultural
Soil Type	Loam: Sand, Silt & Clay (40-40-20%)
Physiographic Unit	Lancaster Flats
Surficial Geology	Glacial-marine Delta Deposits: Sand, Silt and Clay
Bedrock Geology	Bobcaygeon Formation: interbedded calcarenite and sublithographic to fine crystalline limestone
Overburden Thickness	10-15 m

During this investigation, crops at Site 3 consisted of silage corn and soybean. Silage corn was planted in the growing season preceding the investigation (2004), while during the investigation, silage corn was planted in 2005, followed by and soybean in 2006. Fertilizer application varied at this site in that approximately 120 kg-N/ha of manure was applied in the 2004 season, while 60 kg-N/ha of urea was applied in 2005, and no fertilizer (manure or synthetic) was applied in 2006 when soybean was the crop. *Fairchild, [1987]* indicates that approximately 12 kg-N/ha (10%) were likely still available in 2005, from the 2004 manure application.

Field measurements, geochemical composition and isotopic values from samples collected at Site 3 are summarized in tables below, while complete results and seasonal summaries are located in Table D4 of Appendix D.

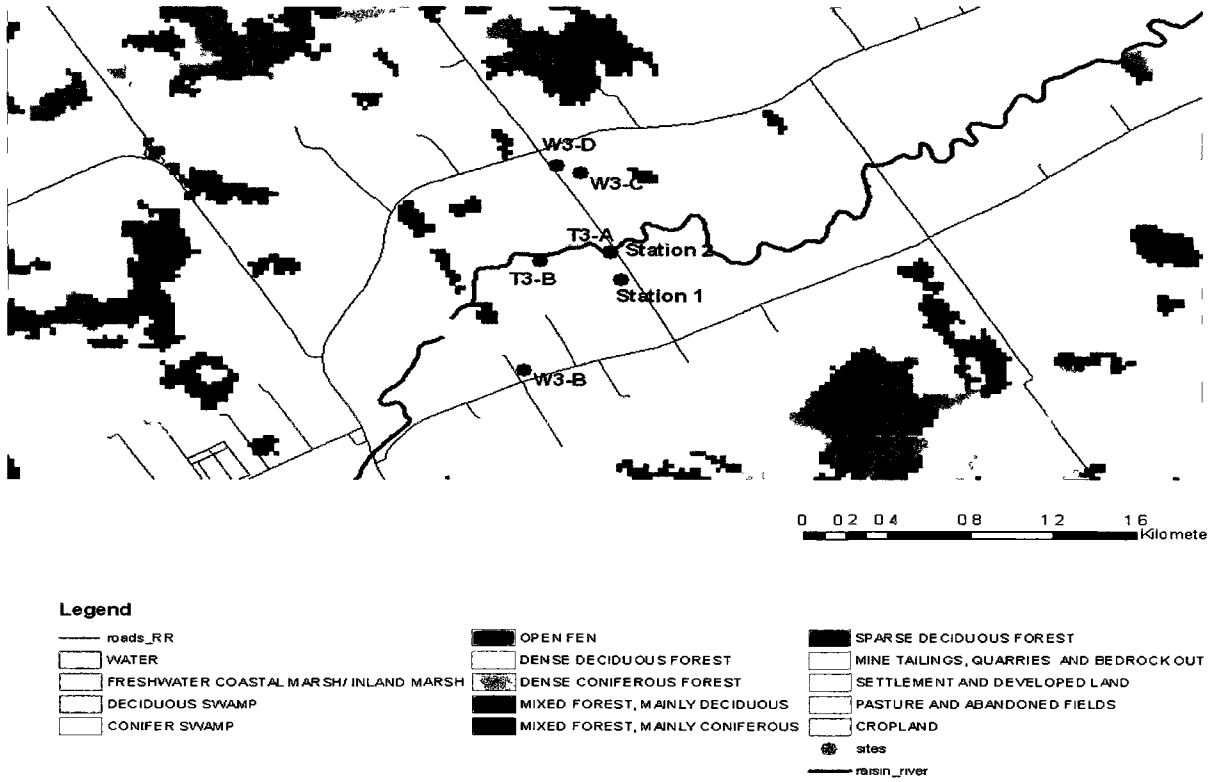

Figure 5.27: Site 3 – Location map of sampling points and local land use along the South Branch of the Raisin River. Station 1 consists of lysimeters (L3-1A and L3-1B) and piezometers (P3-1A, P3-1B and P3-1C), while Station 2 consists of piezometers (P3-2A and P3-2B). All grey colouration represents agricultural fields.

5.5.1. Field Measurements

The water level, temperature, pH, conductivity, dissolved oxygen, and EH concentrations from Site 3 groundwater samples (piezometers and bedrock wells) are summarized in Table 5.30. As with the two previous sites, only pH and conductivity are discussed for unsaturated zone samples as Temperature, DO and EH are not relevant in the unsaturated zone oxygenated environment. Mean pH values for lysimeters and tile drains were 7.3 and 7.0, respectively, while specific conductance values (816 and 950 µS/cm) were similar in magnitude to those recorded in groundwater samples.

Table 5.30: Site 3 – Field parameters statistical summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field										
W.L. (mbgs)	1.03	0.27	0.54	1.49	15	3.85	0.34	3.47	4.58	14
Temp. (°C)	11.3	3.4	4.6	19	74	10.8	1.2	8.9	14	24
pH	7.5	0.22	7.0	8.0	74	7.5	0.13	7.2	7.7	23
SpC. (µS/cm)	1039	385	511	1966	74	986	307	531	1548	21
DO (mg/L)	0.99	0.48	0.51	2.4	15	0.44	0.41	0.070	1.5	10
EH (mV)	235	167	45	752	23	205	110	49	375	12

Notes: 1) Piezometer statistics are a compilation of five piezometers (P3-1A, P3-1B, P3-1C, P3-2A and P3-2B).
2) Bedrock Well statistics are a compilation of two wells (W3-B and W3-D).
3) Piezometer water level measurements are those from P3-1A.
4) Well water level measurements are those from W3-B.

Shallow groundwater and the bedrock groundwater levels generally responded to precipitation equally, seasonally the water table fluctuations between fall highs and summer lows are approximately equal at 1 m in both piezometers and deeper wells. Full recharge occurs by October, followed by declining water levels throughout the winter until February-April, when water levels increase again following spring thaw. Water levels in piezometers from Station 2 located next the river (Figure 5.27), declined rapidly from October to December (Figure 5.28C), which corresponded with declining mean monthly discharge levels (Figure 5.28B), while mid-field piezometers (Station 1) had a longer period of declining water levels (Figure 5.28C). Bedrock Aquifer groundwater appeared to have a 1 or 2 month lab behind the mid-field piezometers, with spring water levels increasing in April. All water levels declines throughout the winter, with lowest water levels recorded systematically in September. The steady decline throughout the summer corresponds to periods where evapotranspiration is greater than infiltration.

Water level measurements generally suggest a downward vertical gradient in the nest of piezometers mid-field (Station 1), although it is very minor suggesting near horizontal flow beneath the field towards the river. Station 2 piezometers next to the river bank show an upward gradient at all times except for October in both years, when minor downward gradients are present. Conditions at Station 2 correspond to peak water levels following two months of precipitation, as shown in Figure 5.28A. Interestingly; the periods of elevated river discharge are generally not linked to periods of high precipitation. Elevated river discharge for the period (October to May) follows heavy fall precipitation and persists

throughout the winter and spring, reflecting the importance of groundwater discharge to river baseflow. Complete river discharge data are provided in Table E1 in Appendix E.

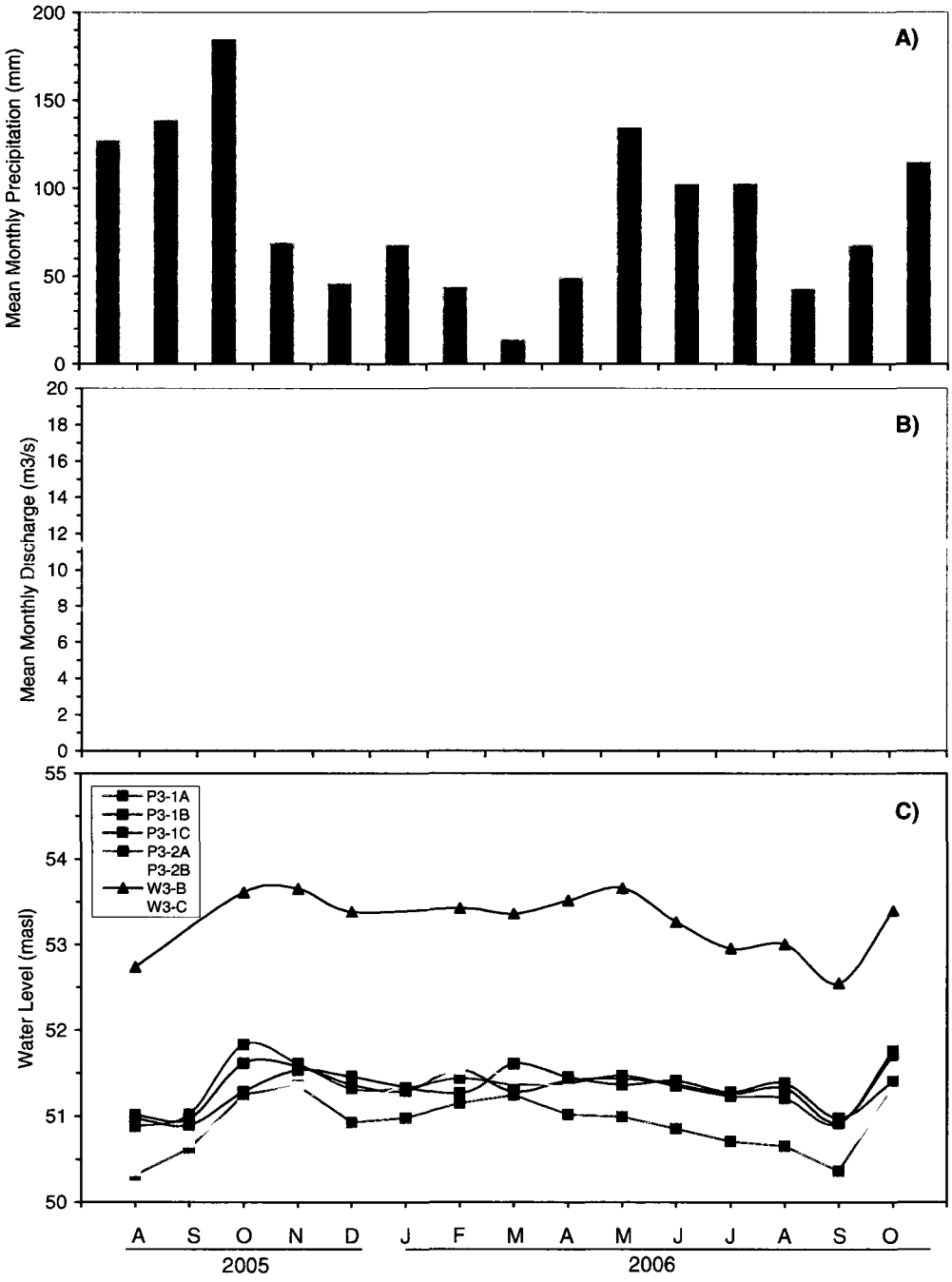

Figure 5.28: Site 3 – Temporal precipitation, Raisin River discharge Monthly water level fluctuations in piezometers and wells, presented as elevations in meters above sea level. A) Mean monthly precipitation for station EC at Cornwall, Ontario *[Environment Canada, 2006b]*. B) Mean monthly main branch Raisin River discharge (m^3/s) at Williamstown *[Environment Canada, 2006c]*. C) Monthly water level measurements, reported as elevations in meters above sea level.

The mean bedrock aquifer temperature is 10.8°C, and varied little seasonally, while that of shallow groundwater had a mean temperature of 11.3°C, and exhibited more variability. Mean pH values were identical in both shallow and deep groundwaters; there was no discernable seasonal pattern, and were consistent with those from other sites. Specific conductance values were marginally lower in shallow groundwater compared to bedrock groundwater as expected, and both were similar to values measured elsewhere. DO concentrations at this site parallel those measured elsewhere, mean piezometer and bedrock groundwater values were 1.0 and 0.4 mg/L, respectively. Seasonal DO trends could not be evaluated because of insufficient data due to equipment malfunctions. Average E_H values for shallow and bedrock groundwater ranged between 45mV and 750mV, with means of 235 and 205 mV, respectively. As with all previous sites, these average values represent stable waters that are neither oxidizing nor reducing; however, maximum values were recorded during the summer when water levels were lowest.

5.5.2. Vadose and Groundwater $\delta^{18}O$ and $\delta^{2}H$

Table 5.32 and Table 5.32 summarize the $\delta^{18}O$ and $\delta^{2}H$ values for both soil water and groundwater samples, respectively. Soil water and groundwater $\delta^{18}O$ values are compared to the weighted monthly mean meteoric signal (Figure 5.29A), and the weighted mean annual values for Ottawa and M2 LMWL signal.

As in other sites, the lysimeter data is limited because of dry summertime conditions, or ground frost in winter, which both restrict sampling capabilities. The lysimeter results show a systematic bias towards enriched $\delta^{18}O$ and $\delta^{2}H$ reflecting a dominance of summer infiltration that was sampled (Figure 5.29A). Consistent with other sites, the monthly monitoring of shallow mid-field piezometers (P3-1A and P3-1B) shows an attenuated signal compared to that of meteoric precipitation, but one that trends similarly through time as the Bedrock Aquifer well data, but which is enriched by up to 1 ‰ for $\delta^{18}O$. The most depleted soil water and groundwater values are reported in February, which corresponds to the depleted winter meteoric signal.

Table 5.31: Site 3 – Lysimeters and tile drains summary of water isotope results.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Water										
$\delta^{18}O_{H2O}$ (‰)	-9 9	0 5	-10 7	-8 5	20	-10 4	0 3	-10 9	-10 0	9
$\delta^{2}H_{H2O}$ (‰)	-72 2	3 4	-75 7	-65 5	14	-74 3	3 8	-80 2	-67 3	9

Notes 1) Lysimeter statistics are a compilation of three lysimeters (L3-1A, L3-1B and L3-1C)
2) Tile Drain statistics are a compilation of two tile drains (T3-A and T3-B)

Table 5.32: Site 3 – Piezometers and bedrock well summary of water isotope results.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Water										
$\delta^{18}O_{H2O}$ (‰)	-10 3	0 3	-10 8	-9 5	48	-11 0	0 1	-11 1	-10 8	14
$\delta^{2}H_{H2O}$ (‰)	-73 9	3 6	-80 4	-66 4	48	-77 4	2 5	-82 0	-71 2	14

Notes 1) Piezometer statistics are a compilation of five piezometers (P3-1A, P3-1B, P3-1C, P3-2A and P3-2B)
2) Bedrock Well statistics are a compilation of two wells (W3-B and W3-D)

Noteworthy are the muted but discernable shifts for piezometer groundwaters from Nov 2005 to Feb 2006, followed by the uniform increase for all groundwaters in Mar 2006, all of which follow the isotope trends in precipitation (Figure 5.29). This is accounted for by a two component mixing involving both regional groundwaters and a component derived from infiltration through the fields. This mixing ratio then varies for each of the piezometers and the wells. This remains consistent with observations by *Cane and Clark [2000]*. The direct infiltration component through the field is clearly aided by macro-pores including the vertical worm holes as described earlier, and must give rise to the rapid response to precipitation events for both water level and isotope trends.

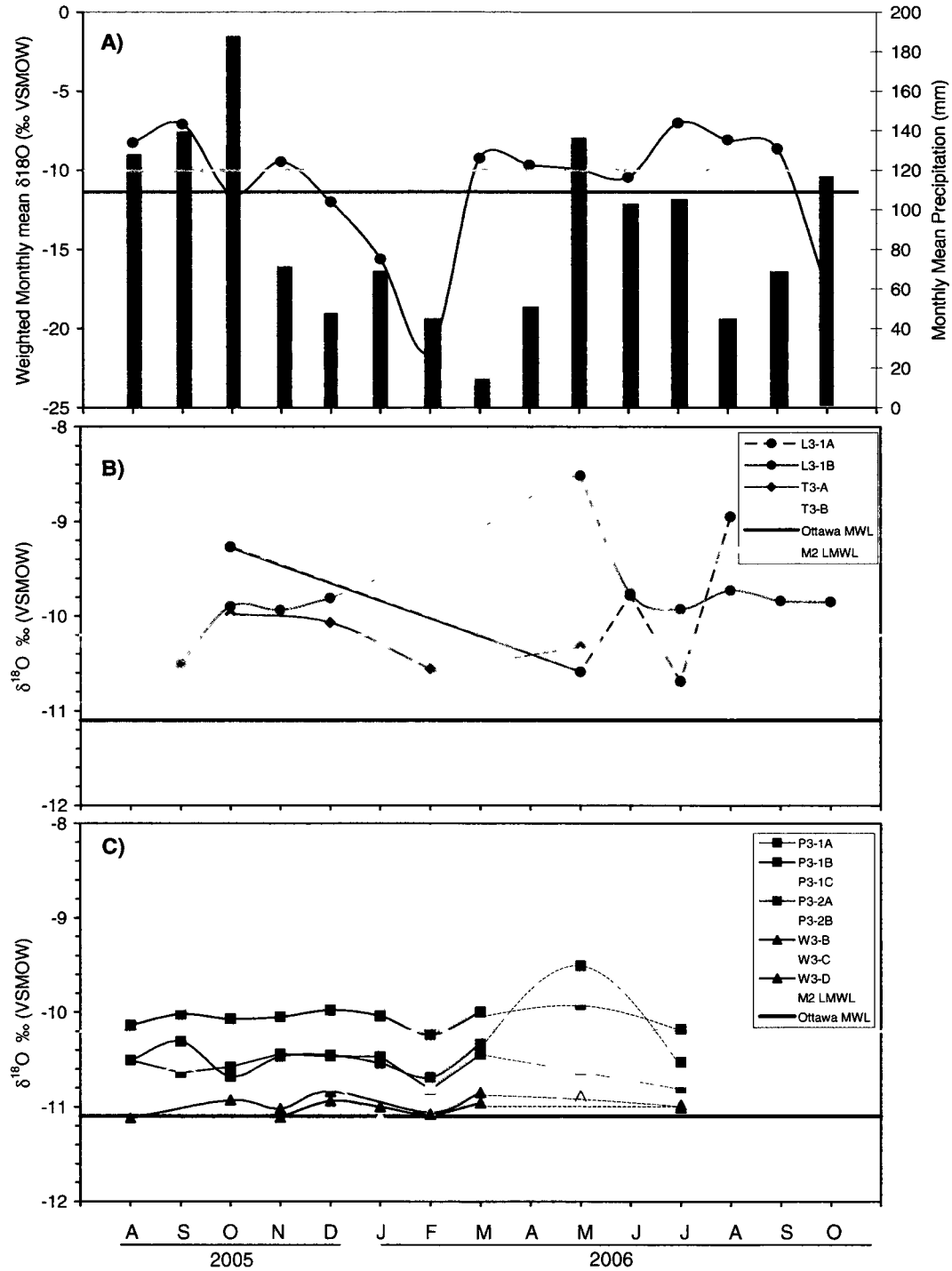

Figure 5.29: Site 3 – Temporal plot of $\delta^{18}O_{H2O}$. A) Amount-weighted mean monthly meteoric $\delta^{18}O$ and monthly precipitation. B) Monthly unsaturated zone $\delta^{18}O$ seasonal trend. C) Monthly groundwater $\delta^{18}O$ seasonal trend. The grey and black lines represent the weighted mean annual meteoric $\delta^{18}O$ signals, for the M2 LMWL (-10.2‰) and Ottawa MWL (-11.1‰), respectively.

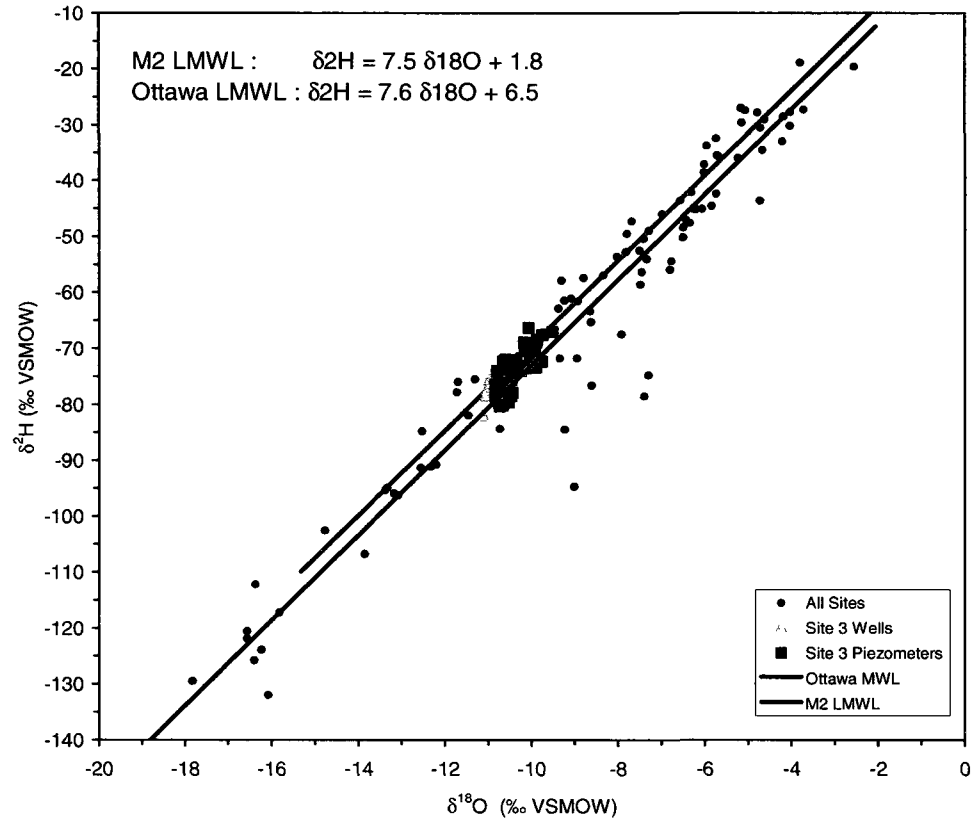

Figure 5.30: Site 3 – δ^2H and $\delta^{18}O$ values for monthly-weighted precipitation, piezometers and wells.

5.5.3. Geochemistry

Major ion concentrations from Site 3 unsaturated zone and groundwater samples are summarized in Tables 5.33 and 5.34, respectively. Concentrations of Ca^{2+}, Na^{+}, Mg^{2+}, SO_4^{2-} and HCO_3^{-}, were not dissimilar to those from Site 1, and show little variability between the unsaturated zone, shallow groundwater and deeper bedrock groundwaters. Typically this suggests that mineral dissolution is occurring rapidly following infiltration of local precipitation; however, because of the upward groundwater flow gradient observed at Station 2 next to the river, a different weather dynamic may be occurring The mean calcite saturation indices for the lysimeters, tile drains, piezometers and bedrock wells are 1.105, 0.504, 2.243 and 1.656, respectively, with a similar distribution as that from Site 1, where lysimeters were at or near saturation, tile drains were under-saturated, while groundwater samples where supersaturated. The prevalence of macro-pores, as seen at Site 2, suggests that they allow tile drains to effectively drain the soil from November to May, thereby reducing the time for mineral dissolution.

Table 5.33: Site 3 – Lysimeters and tile drains summary of analytical results.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
Ca^{2+} (mg/L)	80	21	24	108	24	77	8 2	66	93	14
Na^{+} (mg/L)	21	7 4	10	35	24	19	12	5 3	35	14
Mg^{2+} (mg/L)	29	11	5 6	51	24	21	9 1	11	34	14
K^{+} (mg/L)	1 5	1 6	0 22	8 0	21	8 0	7 2	1 4	19	14
P (mg/L)	0 077	0 079	0 0077	0 29	17	0 046	0 022	0 014	0 076	14
NH_4^{+} (mg-N/L)	0 034	0 024	0 004	0 081	9	0 008	0 004	0 003	0 013	9
Cl (mg/L)	38	28	6 9	106	21	38	37	5 8	106	14
SO_4^{2} (mg/L)	23	3 1	19	28	19	24	2 5	20	27	12
NO_3 (mg-N/L)	14	6 0	0 5	23	14	7 8	3 0	4 5	16	14
HCO_3 (mg/L)	275	111	113	495	22	244	64	115	334	14
Calculations										
pCO_2 (exp)	-1 80	0 33	-2 37	-1 24	22	-1 67	0 20	-1 93	-1 24	14
$SI_{calcite}$	1 105	0 908	0 028	3 408	22	0 504	0 331	0 028	1 178	14

Notes
1) Lysimeter statistics are a compilation of three lysimeters (L3-1A, L3-1B and L3-1C)
2) Tile Drain statistics are a compilation of two tile drains (T3-A and T3-B)
3) P = Total Phosphorus
4) pCO_2 is the exponent value with base 10
5) "-" indicates that no samples were analysed

Table 5.34: Site 3 – Piezometers and bedrock well summary of analytical results.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
Ca^{2+} (mg/L)	66	13	42	88	73	83	15	61 49	106	23
Na^{+} (mg/L)	30	11	14	50	73	28	16 7	12 8	51	23
Mg^{2+} (mg/L)	37	10	22	50	73	31	6 4	22 683	40	23
K^{+} (mg/L)	7 2	3 2	2 4	13	73	3	0	2 6	3	23
P (mg/L)	0 45	0 25	0 11	1 0	55	0 027	0 011	0 0078	0 06	20
NH_4^{+} (mg-N/L)	0 760	0 524	0 004	1 8	64	0 131	0 298	0 017	1 28	17
Cl (mg/L)	10	5 2	3 2	19	72	65	56 3	7 7	150	23
SO_4^{2} (mg/L)	20	9 3	0 39	30	59	52	5 9	29	57	22
NO_3 (mg-N/L)	0 56	0 57	0 004	3 2	39	0 10	0 14	0 20	0 2	2
HCO_3 (mg/L)	410	123	130	652	71	311	78	121	492	23
Calculations										
pCO_2 (exp)	-1 99	0 26	-2 65	-1 49	71	-2 04	0 20	-2 65	-1 72	23
$SI_{calcite}$	2 243	1 274	0 348	5 294	71	1 656	0 605	0 759	2 818	23

Notes
1) Piezometer statistics are a compilation of five piezometers (P3-1A, P3-1B, P3 1C, P3-2A and P3-2B)
2) Bedrock Well statistics are a compilation of two wells (W3-B and W3-D)
3) P = Total Phosphorus
4) pCO2 is the exponent value with base 10
5) "-" indicates that no samples were analysed

Total phosphorus concentrations are similar in both unsaturated and groundwater samples except for the piezometers, where total phosphorus concentrations are at least an order of magnitude higher.

5.5.4. DIC and DOC

DIC and DOC concentrations and $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ values from unsaturated zone samples and groundwater samples are summarized in Tables 5.35 and 5.36, respectively.

Table 5.35: Site 3 – Lysimeter and tile drain carbon chemistry and isotope results summary.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions										
HCO_3 (mg/L)	275	111	113	495	22	244	64	115	334	14
Calculations										
pCO_2 (exp) (atm)	-1 80	0 33	-2 37	-1 24	22	-1 67	0 20	-1 93	-1 24	14
Carbon										
DIC (ppmC)	66	25	24	118	24	65	9 4	53	82	14
DOC (ppmC)	8 5	9 0	2 0	37	23	3 4	1 1	2 0	5 3	14
$\delta^{13}C_{DIC}$ (‰)	-12 3	1 9	-17 2	-8 1	23	-13 4	1 7	-14 9	-8 1	13
$\delta^{13}C_{DOC}$ (‰)	-24 9	1 3	-26 6	-21 6	23	-26 1	1 2	-27 7	-23 5	14

Notes 1) Lysimeter statistics are a compilation of three lysimeters (L3-1A, L3-1B and L3-1C)
2) Tile Drain statistics are a compilation of two tile drains (T3-A and T3-B)
3) pCO_2 is the exponent value with base 10

Table 5.36: Site 3 – Piezometers and bedrock wells carbon chemistry and isotope results summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions										
HCO_3 (mg/L)	410	123	130	652	71	311	78	121	492	23
Calculations										
pCO_2 (exp) (atm)	-1 99	0 26	-2 65	-1 49	71	-2 04	0 20	-2 65	-1 72	23
Carbon										
DIC (ppmC)	88	26	28	141	71	68	17	25	106	23
DOC (ppmC)	4 3	1 93	0 7	9 8	68	2 0	1 1	0 10	4 0	23
$\delta^{13}C_{DIC}$ (‰)	-16 3	1 3	-18 4	-14 0	72	-13 6	0 4	-14 2	-12 5	23
$\delta^{13}C_{DOC}$ (‰)	-26 1	0 9	-28 4	-22 8	68	-26 2	2 2	-28 7	-19 5	23

Notes 1) Piezometer statistics are a compilation of five piezometers (P3-1A, P3-1B, P3-1C, P3-2A and P3-2B)
2) Bedrock Well statistics are a compilation of two wells (W3-B and W3-D)
3) pCO_2 is the exponent value with base 10

Because of seasonal variability, DIC concentrations appear to show a general increasing trend through the unsaturated zone, reflecting biodegradation and mineral weathering. However, mean groundwater concentrations suggest constant concentrations with depth, where calcite saturation has been achieved. Unsaturated zone and shallow groundwater DIC concentrations, as seen in Figure 5.31A, have mean values of 65mg-C/L, and 88mg-C/L, respectively. This is followed by a minor decrease in concentrations from shallow Surficial Aquitard water to the Bedrock Aquifer (mean DIC concentration of 68mg-C/L), suggesting a different source and history for carbon in the Bedrock Aquifer.

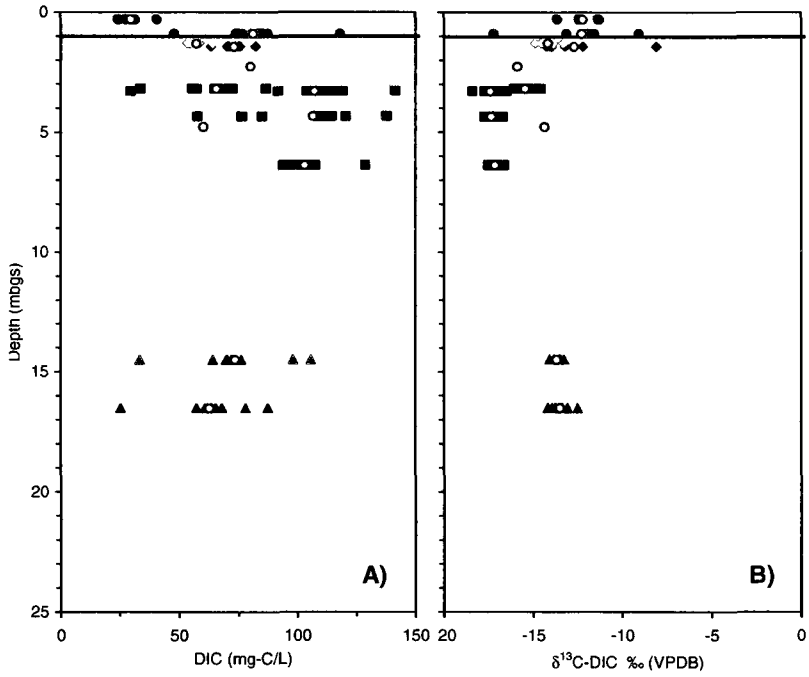

Figure 5.31: Site 3 – Depth vs. DIC concentration and isotopic value. A) DIC concentration. B) $\delta^{13}C_{DIC}$. The blue lines represent the mean water table depth, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F.

A 1.8 m lysimeter was not installed at this site because water table depths are shallow, as summarized in Table 5.30 (mean of 1 mbgs and range of 0.5 to 1.5 mbgs). As such, the thickness of the unsaturated zone is significantly less than at previous sites, limiting aerobic activities and facilitating denitrification, which requires anoxic reducing conditions (low oxygen levels), and an electron donor source such as decomposing organic matter, all of which are found at this site. This downward trend to anaerobic conditions is observed in the $\delta^{13}C$ of the DIC, which shows a decrease towards more negative values in the piezometer

groundwaters. Closed system oxidation of DOC will impart this more negative $\delta^{13}C$ signal on the accumulating DIC. This is consistent with the low DO, low Eh, and as will be seen below, the evidence for denitrification at this site.

DOC results indicate corresponding mean concentrations appear to decrease with depth in both the unsaturated zone and groundwater, which is expected with organic oxidation; however, Table 5.35 and 5.37 show otherwise. Considerable seasonal DIC and DOC variability (25 to 140 p mg-C/L and 0.1 to 10 p mg-C/L, respectively) is observed at all depths, suggesting intermittent, rapid recharge from the surface. Assuming open system calcite dissolution, the $\delta^{13}C$ of DIC and DOC values both plot close to or on the natural C_3 type vegetation signal ($\delta^{13}C_{DIC}$ -14 to -16‰, and $\delta^{13}C_{DOC}$ -26 to -30‰). However both show a slight trend from C_4 (corn) influenced vegetation in the unsaturated zone ($\delta^{13}C_{DIC}$ ~-4‰, and $\delta^{13}C_{DOC}$ >-18‰), to C_3 organics at depth.

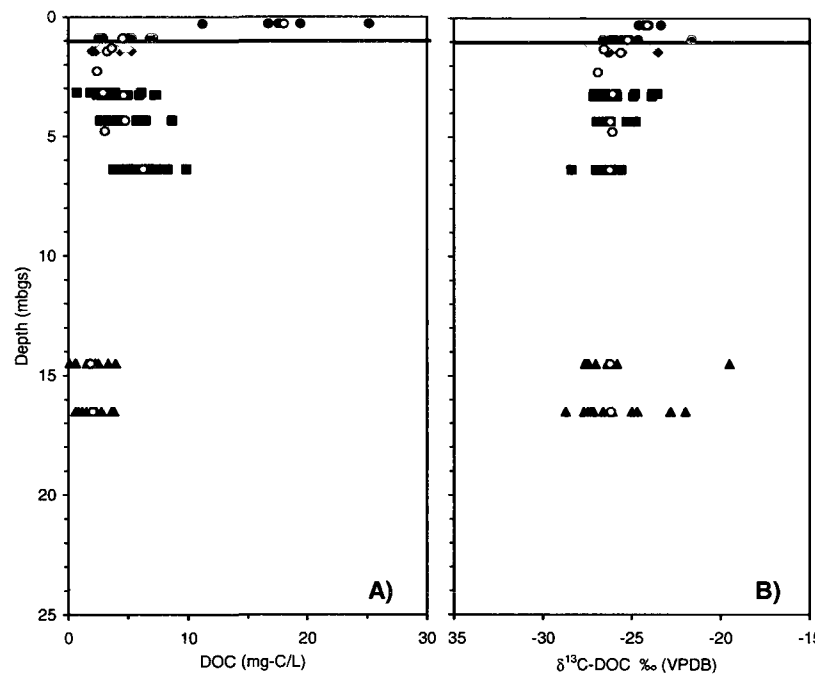

Figure 5.32: Site 3 – Depth vs. DOC concentration and isotopic value. A) DOC concentration. B) $\delta^{13}C_{DOC}$. The blue lines represent the mean water table depth, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F.

As previously discussed in Section 5.5.1, water level measurements generally suggest a downward vertical gradient in the nest of piezometers mid-field (Station 1), while station 2 piezometers next to the river bank have an upward gradient, reflecting that deeper

groundwater is discharging into the river, and geochemistry results may be reflective of other sources. The $\delta^{13}C$ of DIC and DOC both show less seasonal variability, as seen in Figure 5.31 and Figure 5.32, suggesting well mixed groundwater. Mean pCO_2 values generally decrease with depth ($10^{-1.8}$ to $10^{-2.0}$), reflecting increased weathering. This corresponds with increasing $SI_{calcite}$ values, which are all supersaturated, suggesting open system weathering.

5.5.5. Nitrate and Ammonium

Tables 5.37 and 5.38 summarize nitrate and ammonium concentrations and $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values for unsaturated zone samples and groundwater samples, respectively.

Table 5.37: Site 3 – Lysimeter and tile drain; NO_3^-, NH_4^+ and isotope results, summary.

	Lysimeters					Tile Drains				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Nutrients										
NH_4^+ (mg-N/L)	0.034	0.024	0.004	0.081	9	0.008	0.004	0.003	0.013	9
NO_3^- (mg-N/L)	14	6.0	0.5	23	14	7.8	3.0	4.5	16	14
Nitrogen Isotopes										
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	8.1	2.2	4.9	11.5	8	15.3	3.6	11.2	20.4	6
$\delta^{18}O_{NO3}$ (‰)	1.8	2.6	-3.7	4.5	8	6.7	2.1	3.3	9.2	6

Notes: 1) Lysimeter statistics are a compilation of three lysimeters (L3-1A, L3-1B and L3-1C).
2) Tile Drain statistics are a compilation of two tile drains (T3-A and T3-B).
3) "-" indicates that no samples were analysed.

Table 5.38: Site 3 – Piezometers and bedrock wells; NO_3^-, NH_4^+ and isotope results, summary.

	Piezometers					Bedrock Wells				
	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Major Ions and Nutrients										
NH_4^+ (mg-N/L)	0.760	0.524	0.004	1.8	64	0.131	0.298	0.017	1.28	17
NO_3^- (mg-N/L)	0.56	0.57	0.004	3.2	39	0.10	0.14	0.20	0.2	2
Nitrogen Isotopes										
$\delta^{15}N_{NH4}$ (‰)	8.6	3.0	3.2	18.7	51	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	15.3	12.4	-0.9	47.8	21	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	9.1	6.3	-1.9	21.3	21	-	-	-	-	-

Notes: 1) Piezometer statistics are a compilation of five piezometers (P3-1A, P3-1B, P3-1C, P3-2A and P3-2B).
2) Bedrock Well statistics are a compilation of two wells (W3-B and W3-D).
3) "-" indicates that no samples were analysed.

The vertical profiles of NO_3^- (Figure 5.33) and NH_4^+ (Figure 5.34) concentrations and isotopes, essentially show similar unsaturated zone and shallow groundwater conditions as those at Site 2. The presence of NH_4^+ in the unsaturated zone at very low concentrations (essentially <0.05 mg-N/L), along with increased concentrations in piezometers (mean of 0.81 mg-N/L, maximum of 1.8 mg-N/L), coupled with the presence of NO_3^- in the unsaturated zone (mean lysimeter and tile drain concentrations of 14 and 7.8 mg-N/L, respectively), and presence of NO_3^- at very low concentrations in shallow groundwater (mean 0.56 mg-N/L, maximum of 3.2 mg-N/L) suggests that NH_4^+ (applied as both synthetic urea and manure) is again being oxidized to NO_3^- in lysimeters and tile drains prior to sample collection. The mean $\delta^{15}N_{NO3}$ value in lysimeters is 8.1‰, while the mean $\delta^{15}N_{NH4}$ value in the piezometers of 8.6‰, which further supports the concept that soil water NH_4^+ is quantitatively converted to NO_3^- as a result of the oxidizing environment in the lysimeters.

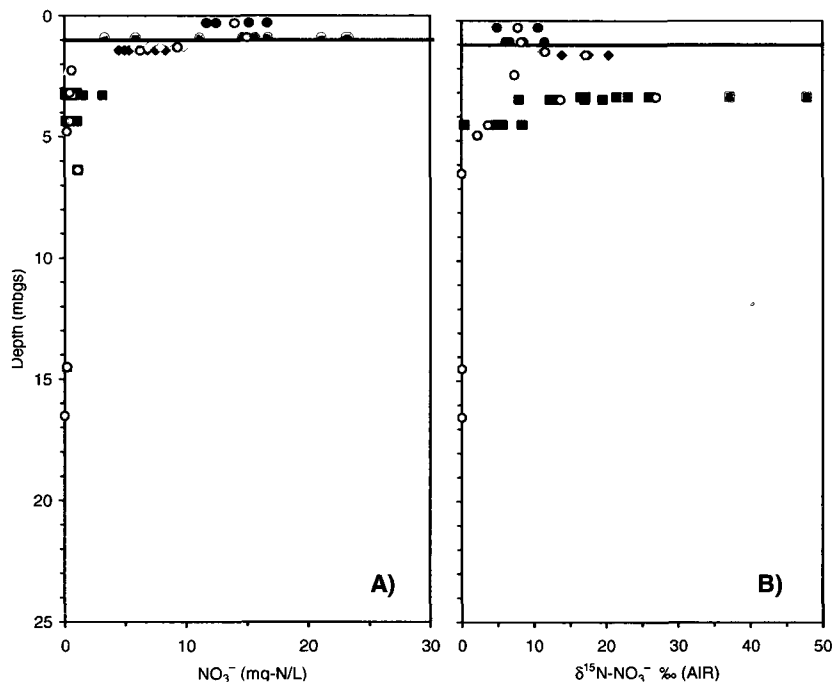

Figure 5.33: Site 3 – Depth vs. Nitrate concentration and isotope value. A) NO_3^- concentration. B)$\delta^{15}N_{NO3}$ The blue lines represent the mean water table depth, while the black and yellow dots represent the mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F.

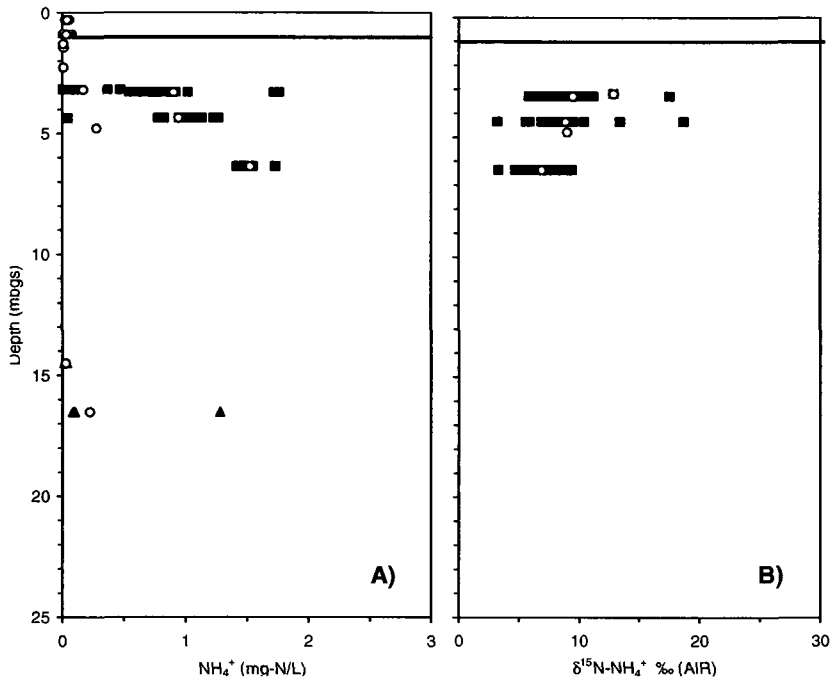

Figure 5.34: Site 3 – Depth vs. Ammonium concentration and isotope value. A) NH_4^+ concentration. B) $\delta^{15}N_{NH4}$. The blue lines represent the mean water table depth, while the black and yellow dots represent mean value for each sampling depth. A symbol legend for each sampling point in located in Appendix F.

One significant physical difference between the two sites is that the unsaturated zone is much shallower at Site 3, compared to that of Site 2, with a more rapid shift with depth to anoxic conditions. As a consequence, incomplete oxidation of NH_4^+ in the soils allows infiltration of both NO_3^- and NH_4^+ to the deeper groundwaters sampled by the piezometers. In this zone, the unusual combination of both NO_3^- (range of 0.004 to 3.2 mg-N/L) and NH_4^+ (range of 0.004 to 1.8 mg-N/L) are present in samples at the same depth. Further, both demonstrate partial trends towards enrichments of ^{15}N, particularly in the fall and winter (Figure 5.35), demonstrating that reactive attenuation of both NO_3^- and NH_4^+ is occurring. Denitrification can account for the strong enrichment observed for the NO_3^- (Figure 5.36), although reactive loss of NH_4^+ under these conditions is less clear, while fractionation due to sorption during transport from the surface imparts only a minor to negligible enrichment on the ^{15}N of ammonium.

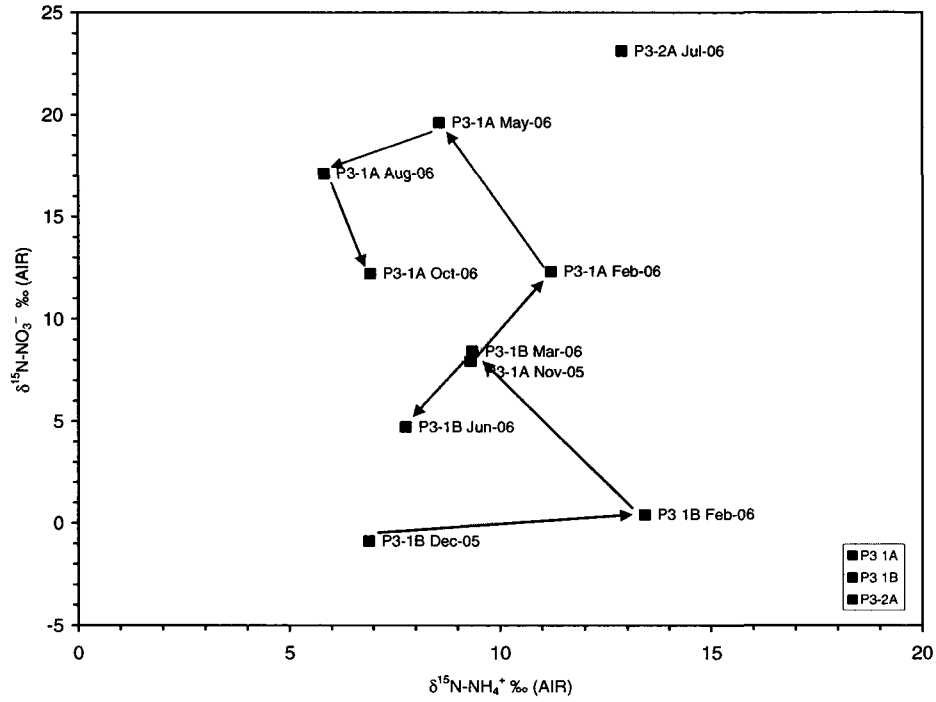

Figure 5.35: Site 3 – $\delta^{15}N_{NO3}$ vs $\delta^{15}N_{NH4}$ values show parallel enrichment adn depletion in piezometers P3-1A (shallower) and P3-1B (deeper).

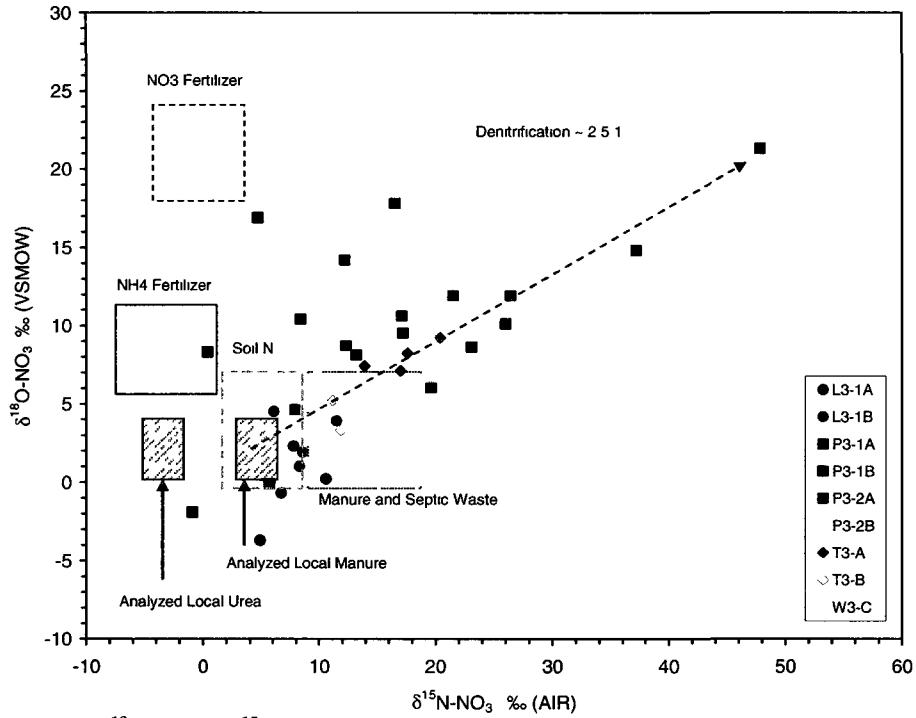

Figure 5.36: Site 3 – $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$. Groundwater, tile drain and lysimeter values, boxes represent literature ranges for various NO_3 sources, from *[Clark and Fritz, 1997]*.

To account for the coupled loss of ammonium and nitrate in groundwaters, and the accompanying enrichment in ^{15}N, the possibility of anaerobic oxidation of ammonium by anammox bacteria exists *[Clark et al., 2008]*. As described in Section 2.2.3, the biologically-mediated anammox reaction, whereby oxidation of NH_4^+ is facilitated using NO_3^- as the terminal electron acceptor (Equation 2.14) may be occurring.

$$3NO_3^- + 5NH_4^+ \rightarrow 4N_2 + 9H_2O + 2H^+ \quad (2.14)$$

Piezometer $\delta^{15}N_{NO3}$ and $\delta^{15}N_{NH4}$ values plotted on Figure 5.35, show a parallel enrichment and depletion of ^{15}N values. Parallel enrichment in piezometers P3-1B (deeper) and P3-1A (shallow) may be occurring in fall and winter, which correspond to an upward groundwater gradient. Although variable, a seasonal trend towards $\delta^{15}N_{NO3}$ and $\delta^{15}N_{NH4}$ enrichment may be observed, which would be consistent with anammox reaction.

The reactive loss of nitrate, irrespective of ammonium, can also be accounted for by denitrification, considering the shallow water table at this site, which often leads to low DO levels and anoxic conditions (Figure 5.37). The reaction starts following partial nitrification of NH_4^+ to NO_3^- in the unsaturated zone. As previously described, the nitrification of NH_4^+ to NO_3^- derives approximately two O atoms from oxygen in the water molecules and one O atom from dissolved O_2, resulting in no significant ^{18}O fractionation *[Clark and Fritz, 1997]*. Unsaturated samples have an $\delta^{18}O_{-H2O}$ value of approximately -10.1‰, while soil O_2 $\delta^{18}O$, that of atmospheric (O_2 $\delta^{18}O$ is +23.5 ‰), resulting in $\delta^{18}O_{NO3}$ from partial nitrification of approximately 2.8‰. As seen in Figure 5.36, lysimeter $\delta^{18}O_{NO3}$ values ranges from -3.7 to 4.5‰, showing some variability around this value.

Initial dilution and crop uptake of nitrogen appear to be occurring in the unsaturated zone (lysimeters data) (Figure 5.37), followed by denitrification in the upper saturated zone (Figure 5.33) sampled by the tile drains, which only flow seasonally. A two-fold attenuation in the tile drains, results in strong enrichment in the piezometers. Deeper piezometers (P3-1B and P3-2B) do not reflect the same enrichment as the shallow piezometers (P3-1A and P3-2A). $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ values from P3-2A (Figures 5.36 and 5.37) show the greatest enrichment with values ranging between 9.5 and 21.3‰ and 17.2 to 47.8‰, respectively. Enrichment values ($\varepsilon^{18}O_{NO3}$ = -3.82‰, $\varepsilon^{15}N_{NO3}$ = -8.3‰) in piezometer P3-2A were

calculated. Although these values differ from those determined for denitrification by *Böttcher et al. [1990]*, they may be influenced by any possible anammox reaction in these groundwaters.

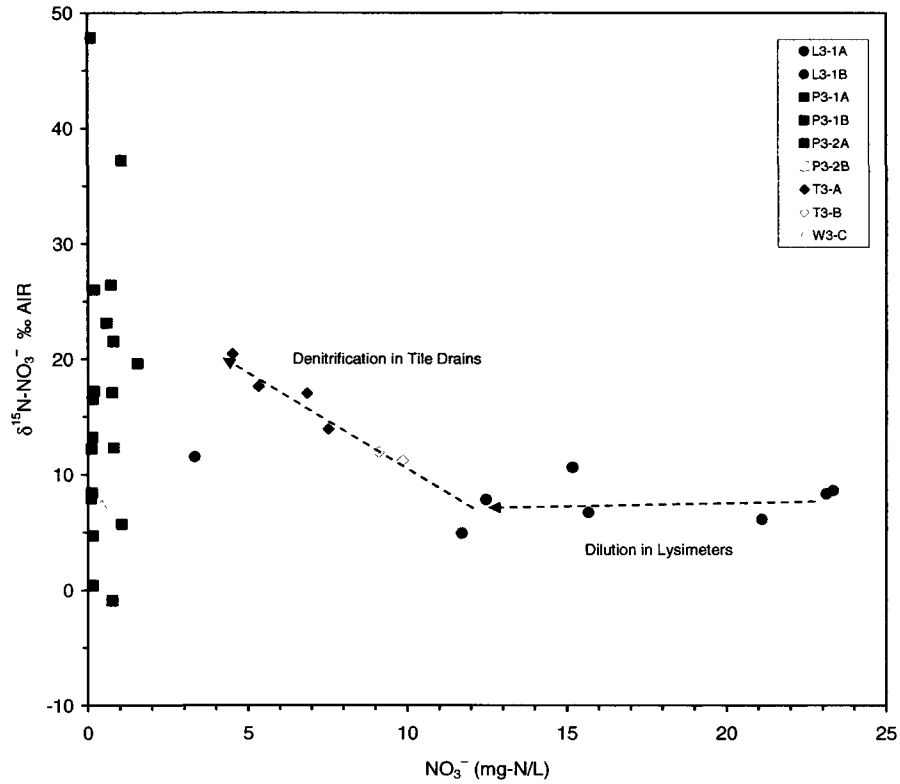

Figure 5.37: Site 3 – $\delta^{15}N_{NO3}$ vs. NO_3 plot. Shows dilution in the lysimeters, followed by denitrification in the tile drains.

5.5.6. Summary and Conclusions

Unsaturated zone results show a systematic bias towards enriched $\delta^{18}O$ and $\delta^{2}H$ reflecting a dominance of summer infiltration. Consistent with other sites, the long term monitoring of shallow groundwater shows attenuation with trends that are similar through time and which are offset from the well data by up to 1‰ for $\delta^{18}O$. Of note are the muted but discernable shifts for piezometer groundwaters during the winter months, followed by the uniform increase for all groundwaters in the spring, all of which follow the isotope trends in precipitation. This is accounted for by two-component mixing involving regional groundwaters and a component derived from infiltration through the fields. These findings correspond with observations of vertical hydraulic gradients, where recharge conditions were

recorded at mid-field piezometers and groundwater discharge conditions persisted in piezometers along the river.

The vertical profiles of nitrate and ammonium concentrations and isotopes essentially show similar unsaturated zone and shallow groundwater conditions as those at Site 2. The presence of NH_4^+ in the unsaturated zone at very low concentrations along with slightly increased concentrations in piezometers, coupled with the presence of NO_3^- in the unsaturated zone and presence of NO_3^- at very low concentrations in shallow groundwater, suggests that soil water NH_4^+ is quantitatively converted to NO_3^- as a result of the oxidizing environment in the lysimeters. One significant physical difference between the two sites is that the unsaturated zone is much shallower at Site 3, compared to that of Site 2, with a more rapid shift with depth to anoxic conditions. As a consequence, incomplete oxidation of NH_4^+ in the soils allows infiltration of both NO_3^- and NH_4^+ to the deeper groundwaters sampled by the piezometers.

The unusual combination of both NO_3^- and NH_4^+ present in the piezometer samples, along with trends toward enrichments in ^{15}N, demonstrating that reactive attenuation of both NO_3^- and NH_4^+ is occurring. Denitrification can account for the strong enrichment observed for the NO_3^-, while fractionation due to sorption during transport from the surface imparts only a minor to negligible enrichment on the ^{15}N of ammonium.

To account for the coupled loss of NH_4^+ and NO_3^- in shallow groundwaters, accompanied by the preferential accumulation of ^{15}N in both residual solutes, it is possible that biologically-mediated anammox reactions, whereby oxidation of NH_4^+ is facilitated using NO_3^- as the terminal electron acceptor exists. Although variable, a trend towards $\delta^{15}N_{NO3}$ and $\delta^{15}N_{NH4}$ enrichment is observed in one piezometer.

In contrast, bedrock groundwater from the wells show little or no measureable concentrations of NO_3^- and NH_4^+, suggesting reactive loss by anammox and denitrifying bacteria, or that groundwaters are of a regional rather than local source, which is supported by low E_H values.

6.0 CONCLUSIONS

This study shows that the use of stable isotope analysis, together with geochemistry, can effectively help distinguish between reactive processes and mixing during the attenuation of nitrogen species in groundwaters from an agricultural watershed. These methods were used to complete the primary objective, which was to evaluate subsurface nitrogen pathways, transformations, attenuation processes and their seasonal variations within the Raisin River agricultural watershed of eastern Ontario.

Conclusions developed here help provide insight into attenuation processes affecting nitrogen species, demonstrates the importance of multi-isotope investigations, and illustrates the heterogeneity of seemingly similar hydrogeologic environments.

6.1 Recharge Environment

Measurements of soil water and groundwater $\delta^{18}O$ and $\delta^{2}H$ results show that basin wide recharge of the overburden and bedrock aquifers occurs in the fall when precipitation totals are significant and photosynthetic transpiration declines, and in the spring prior to resumption of plant transpiration when ground ice has thawed permitting precipitation to infiltrate. Recharge pathways through the unsaturated zone occur in a strong mixing environment, where soil reservoirs of older water attenuate the seasonal isotope signals of newly infiltrating precipitation.

The seasonal isotopic signal showed further attenuation in piezometers of the Surficial Aquitard, and the highest levels of attenuation with respect to the meteoric signal in the Bedrock Aquifer. However, two-source mixing (direct infiltration and regional groundwater) was observed in several depth profiles, with varying mixing ratios. In addition, variability of the isotopic signal in deeper groundwater, indicative of rapid infiltration, was observed following heavy precipitation and winter thaw events, suggesting preferential recharge pathways to the Bedrock Aquifer exist.

The abundance of wormholes suggests the significance of macro-porosity in these sediments aiding the infiltration and contributing to the transmission of any meteoric signal and potential contaminants to the water table, thus providing the shift in trends observed in

the temporal monitoring. However, these variations were more prevalent in shallow groundwaters, while deeper groundwaters showed more seasonal attenuation.

In addition, unlike in previous investigation conducted in the area, there was no clear isotopic differentiation of infiltration through cultivated corridors where corn is grown versus naturally forested vegetation which is typically representative of regional groundwater. Although regional sources were found to be significant, local precipitation was found to be the major contributor to shallow groundwater and local bedrock groundwater, and thus suggesting that a C_4 ^{13}C signal would be prevalent in the local recharge environment, which was not readily observed.

6.2 Nitrogen Dynamics

Nitrate from both shallow and Bedrock Aquifer groundwater in the non-cultivated Background Site generally had low concentrations of <1 mg-N/L, while Bedrock Aquifer NO_3^- concentration in the agricultural sites were on average also low; however, elevated concentrations were observed, although still below drinking water standards (10 mg-N/L), which corresponds to observations from previous studies.

The geochemistry of soil water and shallow groundwater indicate they are impacted by nitrogen originating from synthetic fertilizers and manures, and the transport of leachate through soils is mitigated by reactive attenuation. While total NO_3^- and NH_4^+ concentrations of nitrogen in the unsaturated zone, as sampled in the lysimeters and tile drains reached over 30 mg-N/L, concentrations in groundwater were typically < 10 mg-N/L. Observations of shallow groundwater, typically from the Surficial Aquitard, suggest the presence and concentrations of NO_3^- and NH_4^+ may be dependent on the type of fertilizer applied at the surface. The presence and attenuation of NO_3^- and NH_4^+ concentrations were not consistent in soil water and groundwater and varied between the three agricultural sites; however, there was no one dominant attenuation process throughout, nor were NO_3^- and NH_4^+ concentrations elevated in the underlying Bedrock Aquifer. As such, results from this investigation suggest that the use of urea and manure fertilizers have only limited impacts on nitrate concentrations in underlying Bedrock Aquifer.

Findings indicate the urea only site (Site 1) has possibly longer retention of NH_4 in soil water, low concentrations of NH_4^+ but the presence of moderately higher NO_3^-

concentrations (up to 20 mg-N/L) in shallow groundwater of the Surficial Aquitard. The infiltration of nitrified NO_3^- appears to be followed by some level of denitrification, resulting in bedrock aquifer NO_3^- concentrations below 5 mg-N/L. Observations from the agricultural site where liquid manure was the dominant fertilization method (Site 2), suggest the chronic loading of NH_4^+ in the subsurface. There is possibly less retention of NH_4^+ in soil water (> 20 mg-N/L), resulting in the infiltration of NH_4^+ (2 mg-N/L in piezometers), while NO_3^- concentrations in shallow groundwater are below detection. Lastly, the mixed application at Site 3 shows the presence of both NO_3^- and NH_4^+ at similar concentration in shallow groundwater, with nitrogen attenuation by dilution, denitrification and potentially anammox.

Assuming similar geologic conditions at all sites, these results indicate that reactive losses of nitrogen together with crop uptake, appear to be major sinks for surface applied nitrogen, which greatly limit the total nitrogen flux that is reaching the underlying Bedrock Aquifer. Also, there does not appear to be any significant difference in groundwater NO_3^- and NH_4^+ concentrations between farming practices that utilize manure as a fertilizer, and those that solely rely on urea. Meanwhile, the ^{15}N and ^{18}O values of the Bedrock Aquifer nitrogen species could not be determined because concentrations were below quantifiable limits of the analytical methods.

Furthermore, seasonal variations of nitrogen species were not readily observed, likely because of the limited duration of the time series investigation. This suggests that multi-year investigations may be required to properly evaluate the presence of seasonal trends.

Study provides insight into heterogeneity of attenuation process in seemingly similar hydrogeologic environments. Overall, agricultural activities do not appear to be adversely impacting the underlying Bedrock Aquifer; however, poor well seals on domestic wells provide a contaminant pathway to the Bedrock Aquifer, and represent the principle threat to regional water quality.

6.3 Recommendations

This investigation has identified a variety of nitrogen transformation processes in soil water and groundwater influenced by agricultural practices. However, because only select nitrogen compound and isotopes were analyzed, a complete evaluation of the subsurface nitrogen cycle was not possible. Should additional investigations be conducted to evaluate

the subsurface attenuation of nitrogen species, it is recommended that additional techniques be used to identify the concentration and isotopic value of these nitrogen compounds. The installation of passive diffusion gas samplers for the analysis of N_20 and N_2 dissolved gas concentrations and isotopic values would allow the identification of end-member isotopic signatures following denitrification and anammox reactions.

Furthermore, the use of multi-level passive water samplers to conduct profile analysis at small (10-30cm) intervals *[Ronen et al., 1987]*, would provide insight into transformation processes right at the water table interface, as it fluctuates seasonally, and would eliminate the need to pump large quantities of groundwater from aquifers/aquitards with low hydraulic conductivities.

The use of $^3H/^3He$ groundwater age dating could be used to identify young groundwaters (<5 years), would help define the groundwater depth profile below the water table to better link recent farming practices with observed processes on neighbouring field.

On a technical level, it is recommended that in the future, soil cores be collected in place of using suction lysimeters. The oxidation of ammonium ions to nitrate in the suction lysimeters has shown to be a limitation in the interpretation of nitrogen species loading to the groundwater table. Lastly, the phylogenetic analysis of 16S ribosomal RNA gene sequences would conclusively show whether these bacteria are responsible for the anammox process.

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Appendix A
Climate Data - Environment Canada

Table A1: Climate Normals for Cornwall Ontario Station (6101874), for the period (1971 - 2000) *[Environment Canada(a)]*

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	Code
Temperature														
Daily Average (°C)	8 8	7 3	1 3	6 5	13 9	18 7	21 6	20 4	15 5	9 1	2 6	4 9	7 2	A
Standard Deviation	3	2 9	2 4	1 8	1 7	1 2	1	1 1	1 2	1 6	1 6	3 2	0 9	A
Daily Maximum (°C)	-4 6	3 1	3	11 3	19 3	23 9	26 7	25 3	20 2	13 2	5 9	1 3	11 7	A
Daily Minimum (°C)	12 9	-11 4	5 5	1 7	8 5	13 4	16 4	15 4	10 8	4 9	0 8	8 5	2 7	A
Extreme Maximum (°C)	18	18	26	30 5	33	35	35 6	36 5	34 5	28 5	23 9	20		
Date (yyyy/dd)	1996/19	2000/27	1998/31	1990/27	1999/31	1964/30	1955/22+	2001/08	1999/04	1991/05	1961/03+	2001/05		
Extreme Minimum (°C)	-43 3	-35 6	25	15	5 6	0 6	3 3	1 7	6 1	8 3	20	33 3		
Date (yyyy/dd)	1957/15	1951/10	1989/07	1954/03+	1952/05+	1953/04	1952/30	1957/22+	1951/30	1956/26	1951/06	1951/28+		
Precipitation														
Rainfall (mm)	27 3	20	34 3	69 6	82 8	88	92 6	93 2	102 4	81	69 5	34 1	794 8	A
Snowfall (cm)	54 5	43	33 1	11 3	0	0	0	0	0	1 4	17	46 7	207 1	A
Precipitation (mm)	81 7	63	67 5	81	82 9	88	92 6	93 2	102 4	82 4	86 5	80 8	1002	A
Extreme Daily Rainfall (mm)	37 5	37 6	39 1	33 8	46 8	58 9	73	70 9	110 4	60	46 4	35		
Date (yyyy/dd)	1978/08	1961/25	1973/17	1990/03	2000/08	1969/23	1977/17	1962/20	1979/14	1995/05	2000/26	1982/15		
Extreme Daily Snowfall (cm)	53 3	33 8	38 1	35 6	8 9	0	0	0	0	14 4	36 1	35 5		
Date (yyyy/dd)	1966/30	1972/03	1971/04	1975/03	1963/10	1951/01+	1951/01+	1951/01+	1951/01+	1988/22	1975/14	1993/21		
Extreme Daily Precipitation (mm)	53 3	37 6	42 4	41 7	46 8	58 9	73	70 9	110 4	60	46 4	35 5		
Date (yyyy/dd)	1966/30	1961/25	1973/17	2000/08	2000/08	1969/23	1977/17	1962/20	1979/14	1995/05	2000/26	1993/21		
Extreme Snow Depth (cm)	48	56	34	30	0	0	0	0	0	0	19	40		
Date (yyyy/dd)	1999/16	2000/16+	1998/24	2001/01	1983/01+	1983/01+	1983/01+	1983/01+	1983/01+	1983/01+	1997/17+	1995/21+		
Days with Maximum Temperature														
<= 0 °C	21 9	19 6	10 2	0 83	0	0	0	0	0	0	4 8	17 8	75 1	A
> 0 °C	9 1	8 7	20 8	29 2	31	30	31	31	30	31	25 2	13 2	290 2	A
> 10 °C	0 48	0 43	4 3	15 9	29 5	30	31	31	29 5	20 9	6 1	1 2	200 5	A
> 20 °C	0	0	0 38	2 7	13 2	23 9	29 9	28 2	14 2	3 2	0 27	0	115 9	A
> 30 °C	0	0	0	0 03	0 47	2 1	4	2 4	0 43	0	0	0	9 4	A
> 35 °C	0	0	0	0	0	0	0	0 03	0	0	0	0	0 03	A
Days with Minimum Temperature														
> 0 °C	1 5	1 4	5 9	18 2	30 5	30	31	31	29 7	25 5	13 1	2 8	220 6	A
<= 2 °C	30 6	27 8	28 7	17	1 9	0 1	0	0	0 83	9 8	22 4	29 9	169 1	A
<= 0 °C	29 6	26 9	25 1	11 8	0 47	0	0	0	0 33	5 5	16 9	28 2	144 7	A
< 2 °C	27 9	24 7	19 9	5 8	0 03	0	0	0	0	1 5	10 6	24	114 3	A
< 10 °C	18 8	16 6	7 2	0 33	0	0	0	0	0	0	1 1	11 9	55 9	A
< -20 °C	5 5	3 5	0 34	0	0	0	0	0	0	0	0	1 8	11 2	A
< - 30 °C	0 14	0 07	0	0	0	0	0	0	0	0	0	0	0 21	A

Table A1: Climate Normals for Cornwall Ontario Station (6101874), for the period (1971 - 2000) *[Environment Canada(a)]*

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	Code
Days with Rainfall														
>= 0.2 mm	3.6	3.5	6	10.6	12.9	11.9	10.9	11.2	12.2	11.8	11.3	5.1	111	A
>= 5 mm	1.6	1.6	2.3	5	5.4	5.6	5.7	5.4	6	5	4.4	2.3	50.6	A
>= 10 mm	0.87	0.6	1.1	2.5	2.8	3.2	3.1	3.3	3.6	2.6	2.4	1.2	27.4	A
>= 25 mm	0.3	0.07	0.1	0.27	0.33	0.53	0.73	0.83	0.67	0.43	0.4	0.17	4.8	A
Days With Snowfall														
>= 0.2 cm	12	9.1	6.7	2	0.03	0	0	0	0	0.4	4	10.4	44.5	A
>= 5 cm	4	2.8	2.4	0.63	0	0	0	0	0	0.1	1.3	3.1	14.3	A
>= 10 cm	1.4	1.4	0.77	0.37	0	0	0	0	0	0.03	0.63	1.4	6	A
>= 25 cm	0.07	0.1	0.1	0.07	0	0	0	0	0	0	0.03	0.13	0.5	A
Days with Precipitation														
>= 0.2 mm	14.6	11.5	11.6	11.8	12.9	11.9	10.9	11.2	12.2	12.1	14.2	14.4	149.5	A
>= 5 mm	5.8	4.5	4.7	5.7	5.4	5.6	5.7	5.4	6	5	5.7	5.5	65.1	A
>= 10 mm	2.2	2.1	1.8	2.9	2.9	3.2	3.1	3.3	3.6	2.6	3	2.7	33.6	A
>= 25 mm	0.37	0.17	0.27	0.4	0.33	0.53	0.73	0.83	0.67	0.43	0.5	0.33	5.6	A
Degree Days														
Above 24 °C	0	0	0	0	0.2	3.3	9.5	5.8	0.9	0	0	0	19.8	A
Above 18 °C	0	0	0	1.3	14.8	57.3	115.3	87.7	22.9	1.5	0	0	300.7	A
Above 15 °C	0	0	0.2	4.8	41.4	121.7	203.3	168.3	59.1	7.5	0.3	0	606.5	A
Above 10 °C	0	0.1	2.3	23.6	134.4	261.2	357.8	321.3	170.3	45.9	5.4	0.1	1322.3	A
Above 5 °C	1	1.1	15.1	84.6	276.8	410.7	512.8	476.3	315.5	139.6	31.5	2.9	2267.8	A
Above 0 °C	10.4	11.1	58.9	201.6	431	560.7	667.8	631.3	465.5	282.4	107.4	22.7	3450.7	A
Below 0 °C	275.5	224.5	96.4	6.8	0	0	0	0	0	0.2	30.2	174.8	808.4	A
Below 5 °C	421.2	355.9	207.6	39.7	0.8	0	0	0	0.1	12.4	104.2	310.1	1451.9	A
Below 10 °C	575.2	496.3	349.9	128.8	13.4	0.5	0	0	4.8	73.7	228.1	462.3	2332.8	A
Below 15 °C	730.2	637.6	502.7	259.9	75.4	11	0.5	2	43.6	190.3	373	617.1	3443.5	A
Below 18 °C	823.2	722.5	595.5	346.5	141.9	36.6	5.5	14.4	97.5	277.3	462.7	710.1	4233.5	A

Codes

A No more than 3 consecutive or 5 total missing years between 1971 to 2000

Table A2: Climate Normals for Ottawa Ontario Station (6105976), for the period (1971 - 2000) *[Environment Canada(a)]*

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	Code
Temperature														
Daily Average (°C)	10 5	8 6	-2 4	6	13 6	18 4	21	19 7	14 7	8 2	1 5	6 6	6 3	A
Standard Deviation	2 9	2 7	2 5	1 9	1 8	1 3	1 1	1 1	1 2	1 6	1 7	3 3	0 8	A
Daily Maximum (°C)	-6 1	3 9	2 1	10 9	19 1	23 8	26 4	25	19 7	12 6	4 9	-2 9	11	A
Daily Minimum (°C)	14 8	13 2	7	1 1	8	13	15 5	14 3	9 7	3 7	1 9	10 3	1 5	A
Extreme Maximum (°C)	11 7	12 2	25 6	31 2	35	36 7	37 8	37 8	36 7	29 4	23 3	16 1		
Date (yyyy/dd)	1932/14	1953/21	1945/28+	1990/27	1921/21	1921/22	1913/04+	1917/01+	1931/11	1891/03+	1961/03	1951/07		
Extreme Minimum (°C)	37 8	38 3	36 7	20 6	7 2	0	3 3	1 7	4 4	-12 8	23 9	38 9		
Date (yyyy/dd)	1925/19	1934/17	1938/04	1923/01	1902/10+	1910/04	1942/10	1934/30+	1947/28	1933/26	1925/30	1933/29		
Precipitation														
Rainfall (mm)	22 9	16 1	33 6	59 7	80 9	91 2	88 9	87 6	86 8	76 2	60 5	28 8	733 2	A
Snowfall (cm)	48 7	41 2	32 1	7 5	0 2	0	0	0	0	3	18	52 2	202 7	A
Precipitation (mm)	64 2	51 6	64 9	67 7	81	91 2	88 9	87 6	86 8	79 1	77	74 1	914 2	A
Extreme Daily Rainfall (mm)	40 1	38 4	41 8	48 3	75 9	77 5	74 2	90 4	93 2	58 4	49	73 2		
Date (yyyy/dd)	1995/15	1997/21	1980/21	1956/15	1916/17	1946/17	1899/11	1943/23	1942/09	1995/05	1907/07	1933/31		
Extreme Daily Snowfall (cm)	55 9	45 7	48 3	33	19 1	0	0	0	0	21 6	53 3	37 6		
Date (yyyy/dd)	1894/29	1895/08	1947/02	1970/02	1907/04	1890/01+	1890/01+	1890/01+	1890/01+	1933/24	1912/25	1973/20		
Extreme Daily Precipitation (mm)	55 9	45 7	48 8	48 3	75 9	77 5	74 2	90 4	93 2	58 4	53 3	73 2		
Date (yyyy/dd)	1894/29	1895/08	1962/12	1956/15	1916/17	1946/17	1899/11	1943/23	1942/09	1995/05	1912/25	1933/31		
Extreme Snow Depth (cm)	53	97	89	66	8	0	0	0	0	18	30	51		
Date (yyyy/dd)	1971/30+	1971/24+	1971/12	1971/01	1963/11	1961/01+	1961/01+	1961/01+	1961/01+	1997/27	1995/28	1970/25+		
Days with Maximum Temperature														
<= 0 °C	23 3	19 8	10 9	0 87	0	0	0	0	0	0	5 8	19 1	79 7	A
> 0 °C	7 7	8 5	20 1	29 1	31	30	31	31	30	31	24 2	11 9	285 5	A
> 10 °C	0 03	0 13	3	15 3	29 5	30	31	31	29 5	20 5	5 4	0 37	195 6	A
> 20 °C	0	0	0 13	2 6	12 8	24 1	29 8	27 4	13 6	2 6	0 07	0	113 2	A
> 30 °C	0	0	0	0 03	0 73	2 3	4 3	2 5	0 5	0	0	0	10 3	A
> 35 °C	0	0	0	0	0	0 03	0	0 03	0	0	0	0	0 06	A
Days with Minimum Temperature														
> 0 °C	0 97	1 1	4 5	17 5	30 3	30	31	31	29 5	23 6	10 5	1 8	211 9	A
<= 2 °C	30 9	27 9	29 5	18 5	2 5	0 07	0	0	1 5	12 3	24 3	30 4	177 9	A
<= 0 °C	30	27 2	26 5	12 5	0 67	0	0	0	0 5	7 4	19 5	29 2	153 4	A
< -2 °C	29	25 6	21 9	7	0 17	0	0	0	0 03	2 7	13 1	26 2	125 7	A
< 10 °C	21 8	18 7	10	0 37	0	0	0	0	0	0	1 9	15 2	67 9	A
< -20 °C	8 6	5 9	0 97	0	0	0	0	0	0	0	0	3 4	18 9	A
< - 30 °C	0 5	0 07	0	0	0	0	0	0	0	0	0	0 1	0 67	A

Table A2 Climate Normals for Ottawa Ontario Station (6105976), for the period (1971 - 2000) *[Environment Canada(a)]*

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	Code
Days with Rainfall														
>= 0.2 mm	3.9	3.3	6.3	10.8	13.4	12.9	12.4	12	14.1	13.7	10.7	5.1	118.5	A
>= 5 mm	1.5	1.1	2.1	4	5.3	5.2	5.1	4.9	5.3	4.7	3.7	2.1	45	A
>= 10 mm	0.73	0.47	1	1.9	2.7	3.1	3.1	2.6	2.8	2.3	1.9	1.1	23.9	A
>= 25 mm	0.23	0.07	0.2	0.3	0.37	0.8	0.7	0.83	0.63	0.47	0.4	0	5	A
Days With Snowfall														
>= 0.2 cm	14.8	10.6	8.2	2.7	0.17	0	0	0	0	1.1	5.5	13.4	56.6	A
>= 5 cm	3.4	2.7	2.6	0.37	0	0	0	0	0	0.1	1.2	3.6	13.9	A
>= 10 cm	0.8	0.93	0.83	0.17	0	0	0	0	0	0.07	0.4	1.4	4.6	A
>= 25 cm	0	0.13	0	0	0	0	0	0	0	0	0.03	0.07	0.23	A
Days with Precipitation														
>= 0.2 mm	16.6	12.2	12.4	12.4	13.4	12.9	12.4	12	14.1	14.2	14.7	16.1	163.4	A
>= 5 mm	4.3	3	4.3	4.6	5.3	5.2	5.1	4.9	5.3	4.9	4.7	5.2	57	A
>= 10 mm	1.4	1.5	1.9	2.2	2.7	3.1	3.1	2.6	2.8	2.4	2.4	2.3	28.5	A
>= 25 mm	0.23	0.17	0.23	0.3	0.37	0.8	0.7	0.83	0.63	0.47	0.43	0.1	5.3	A
Degree Days														
Above 24 °C	0	0	0	0	0.2	2.7	6.9	3.2	0.5	0	0	0	13.4	A
Above 18 °C	0	0	0	0.9	13	51	99.8	71.6	16.4	0.5	0	0	253	A
Above 15 °C	0	0	0	3.8	37.3	114.2	186.1	147.7	46.2	3.4	0	0	538.6	A
Above 10 °C	0	0	0.6	19.8	125.9	253.7	340.6	299.7	148.4	31.6	2.7	0	1222.8	A
Above 5 °C	0.1	0.3	8	76	266.3	403.2	495.6	454.7	291.1	115.3	21.1	0.8	2132.4	A
Above 0 °C	4.7	6.9	43.7	188.6	420.7	553.2	650.6	609.7	441	254.2	85.7	12.1	3270.9	A
Below 0 °C	329.8	249.1	118.9	8.5	0	0	0	0	0	0.3	39.8	217.5	963.9	A
Below 5 °C	480.2	383.8	238.2	46	0.7	0	0	0	0.1	16.5	125.2	361.2	1651.7	A
Below 10 °C	635.1	524.9	385.8	139.7	15.2	0.5	0	0	7.4	87.7	256.8	515.4	2568.5	A
Below 15 °C	790.1	666.2	540.2	273.7	81.6	1.1	0.5	3	55.3	214.5	404.1	670.4	3710.6	A
Below 18 °C	883.1	751	633.2	360.8	150.3	37.8	7.2	20	115.4	304.6	494.1	763.4	4520.8	A

Codes

A No more than 3 consecutive or 5 total missing years between 1971 to 2000

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
7/1/2005	31	21	26	1.4			1.4
7/2/2005	24	14	19				
7/3/2005	28	14	21				
7/4/2005	31	18.5	24.8	1.2			1.2
7/5/2005	28	21	24.5	7.8			7.8
7/6/2005	24.5	17.5	21				
7/7/2005	25.5	14	19.8				
7/8/2005	25.5	16	20.8	1.4			1.4
7/9/2005	22	18	20	1.8			1.8
7/10/2005	31.5	17.5	24.5	2.2			2.2
7/11/2005	34	21	27.5				
7/12/2005	33	22	27.5	0.8			0.8
7/13/2005	27.5	19.5	23.5	30			30
7/14/2005	29	19.5	24.3				
7/15/2005	30	17	23.5				
7/16/2005	31	18	24.5				
7/17/2005	29	23	26	9.2			9.2
7/18/2005	32	24	28				
7/19/2005	30.5	24	27.3	12.6			12.6
7/20/2005	27.5	19.5	23.5				
7/21/2005	30.5	19	24.8				
7/22/2005	28	21	24.5				
7/23/2005	26.5	15	20.8				
7/24/2005	27	14	20.5	0.8			0.8
7/25/2005	32.5	21	26.8				
7/26/2005	26.5	20	23.3	1			1
7/27/2005	20	18	19	2.6			2.6
7/28/2005	24.5	12	18.3				
7/29/2005	26	14.5	20.3				
7/30/2005	26	12.5	19.3				
7/31/2005	27	13	20				
8/1/2005	29	19	24				
8/2/2005	32	19	25.5	12.2			12.2
8/3/2005	29.5	20.5	25	3.2			3.2
8/4/2005	32.5	21.5	27	3			3
8/5/2005	29	23	26				
8/6/2005	28	15	21.5				
8/7/2005	30	17	23.5				
8/8/2005	31	19	25				
8/9/2005	30	21	25.5				
8/10/2005	31	23.5	27.3	2.6			2.6
8/11/2005	28	20	24				
8/12/2005	25	19	22	6.8			6.8
8/13/2005	28	20	24				
8/14/2005	23	20	21.5	1			1
8/15/2005	28	17	22.5				
8/16/2005	28	17.5	22.8				
8/17/2005	24	17	20.5				

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
8/18/2005	21	10	15.5	1			1
8/19/2005	22	11	16.5	13.8			13.8
8/20/2005	23	19	21	1			1
8/21/2005	27.5	20	23.8				
8/22/2005	23	14	18.5				
8/23/2005	21	14	17.5				
8/24/2005	23	11	17				
8/25/2005	28	13.5	20.8				
8/26/2005	28	15	21.5				
8/27/2005	31	16	23.5	6.2			6.2
8/28/2005	28	20	24				
8/29/2005	29	18.5	23.8				
8/30/2005	26.5	18.5	22.5	9.9			9.9
8/31/2005	22	19	20.5	82			82
9/1/2005	26	18	22				
9/2/2005	26.5	18	22.3	12			12
9/3/2005	25	16	20.5				
9/4/2005	21	14	17.5				
9/5/2005	24	10	17				
9/6/2005	26.5	11	18.8				
9/7/2005	27	15	21				
9/8/2005	21	17	19	46			46
9/9/2005	21.5	11.5	16.5				
9/10/2005	19	7	13				
9/11/2005	23.5	9.5	16.5				
9/12/2005	29	19	24				
9/13/2005	30	21	25.5				
9/14/2005	29.5	19	24.3				
9/15/2005	26.5	19	22.8				
9/16/2005	21	16	18.5	25			25
9/17/2005	17	15	16	15.1			15.1
9/18/2005	22	15	18.5				
9/19/2005	24	16	20				
9/20/2005	25	18	21.5				
9/21/2005	26	13	19.5				
9/22/2005	25.5	17.5	21.5	6			6
9/23/2005	19.5	13	16.3				
9/24/2005	17.5	6	11.8				
9/25/2005	20.5	10	15.3	7.4			7.4
9/26/2005	20.5	18	19.3	16			16
9/27/2005	19	9.5	14.3				
9/28/2005	23	12	17.5				
9/29/2005	19.5	10	14.8	15.4			15.4
9/30/2005	15	6	10.5				
10/1/2005	22.5	8	15.3				
10/2/2005	25.5	11	18.3				
10/3/2005	27	12	19.5				
10/4/2005	28	16	22				

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
10/5/2005	27	16.5	21.8				
10/6/2005	28	16	22				
10/7/2005	20	12	16	51.6			51.6
10/8/2005	11	6	8.5	7.6			7.6
10/9/2005	10.5	6	8.3				
10/10/2005	11	8.5	9.8	2			2
10/11/2005	13	10	11.5				
10/12/2005	13	8	10.5	6			6
10/13/2005	11	9	10	61			61
10/14/2005	15	10.5	12.8	8.8			8.8
10/15/2005	15	11.5	13.3	4.6			4.6
10/16/2005	12.5	9	10.8	2			2
10/17/2005	10.5	8	9.3	1			1
10/18/2005	12.5	6.5	9.5	2.4			2.4
10/19/2005	13.5	8.5	11	7.5			7.5
10/20/2005	11	3.5	7.3				
10/21/2005	10	-1	4.5				
10/22/2005	8.5	-1	3.8	10			10
10/23/2005	8	5.5	6.8	23.4			23.4
10/24/2005	8	5	6.5	3.6			3.6
10/25/2005	7	4	5.5	23.8			23.8
10/26/2005	5.5	2	3.8	4.6			4.6
10/27/2005	5	3	4				
10/28/2005	6	3	4.5				
10/29/2005	9.5	-2	3.8				
10/30/2005	15	4	9.5				
10/31/2005	16	8.5	12.3	1			1
11/1/2005	19	10.5	14.8	4			4
11/2/2005	8	3	5.5				
11/3/2005	17	3	10				
11/4/2005	6.5	4	5.3				
11/5/2005	13.5	0.5	7	8.6			8.6
11/6/2005	13.5	4.5	9	8.4			8.4
11/7/2005	11	8.5	9.8	0.6			0.6
11/8/2005	8.5	5.5	7				
11/9/2005	11.5	-3	4.3	18			18
11/10/2005	6.5	2	4.3				
11/11/2005	3.5	-1.5	1				
11/12/2005	12.5	-3	4.8				
11/13/2005	19	1	10				
11/14/2005	10	6	8				
11/15/2005	5.5	0	2.8	22.6			22.6
11/16/2005	19.5	1.5	10.5	6.2			6.2
11/17/2005	3.5	1.5	2.5				
11/18/2005	0	-6	-3				
11/19/2005	6	-4.5	0.8				
11/20/2005	9	0	4.5				
11/21/2005	9	8	8.5				

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
11/22/2005	5	-0.5	2.3	1			1
11/23/2005	-5	-8	-6.5				
11/24/2005	0	-8	-4		8	7.52	7.52
11/25/2005	-3	-11	-7				
11/26/2005	-2	-8	-5		1	0.94	0.94
11/27/2005	0.5	-7	-3.3	3			3
11/28/2005	15.5	-2.5	6.5	1			1
11/29/2005	20.5	4	12.3	21.6			21.6
11/30/2005	7.5	5	6.3				
12/1/2005	3.5	1.5	2.5				
12/2/2005	1	-7	-3		2	1.88	1.88
12/3/2005	-2	-5.5	-3.8				
12/4/2005	-1	-4	-2.5		2	1.88	1.88
12/5/2005	1	-2	-0.5				
12/6/2005	-1	-7	-4				
12/7/2005	-7.5	-9	-8.3				
12/8/2005	-3.5	-11.5	-7.5				
12/9/2005	0	-9	-4.5		5	4.7	4.7
12/10/2005	1	-6	-2.5				
12/11/2005	0	-3	-1.5		6	5.64	5.64
12/12/2005	-9	-14.5	-11.8		2	1.88	1.88
12/13/2005	-10	-18	-14				
12/14/2005	-10	-19	-14.5				
12/15/2005	-2	-18	-10	1	4	3.76	4.76
12/16/2005	-1	-10	-5.5		16	15.04	15.04
12/17/2005	1	-4.5	-1.8				
12/18/2005	0	-6.5	-3.3		1	0.94	0.94
12/19/2005	-3	-7	-5				
12/20/2005	-2.5	-6	-4.3		2	1.88	1.88
12/21/2005	-4	-19	-11.5		2	1.88	1.88
12/22/2005	1.5	-14	-6.3		3.5	3.29	3.29
12/23/2005	3	-1.5	0.8	5			5
12/24/2005	3	0.5	1.8				
12/25/2005	1.5	1	1.3				
12/26/2005	-2.5	-3	-2.8	8	2	1.88	9.88
12/27/2005	-2	-10	-6				
12/28/2005	-0.5	-6	-3.3	5			5
12/29/2005	2	-2	0				
12/30/2005	-7	-10	-8.5				
12/31/2005	-11.5	-16	-13.8				
1/1/2006	-7	-13	-10				
1/2/2006	-5	-11	-8				
1/3/2006	-5	-10	-7.5				
1/4/2006	-1.5	-11	-6.3		9	8.46	8.46
1/5/2006	0.5	-7	-3.3		7	6.58	6.58
1/6/2006	-4	-9.5	-6.8				
1/7/2006	-8.5	-16.5	-12.5				
1/8/2006	-3.5	-12.5	-8		3	2.82	2.82

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Temp Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
1/9/2006	-0.5	-9	-4.8		9	8.46	8.46
1/10/2006	2	-6.5	-2.3				
1/11/2006	3	-1.5	0.8	6			6
1/12/2006	4	1	2.5				
1/13/2006	13.5	-4.5	4.5	5			5
1/14/2006	5.5	-4	0.8	12	4.5	4.23	16.23
1/15/2006	-14	-17	-15.5				
1/16/2006	-11	-19	-15				
1/17/2006	7	-15	-4	8			8
1/18/2006	7	-6	0.5	22			22
1/19/2006	2.5	-2.5	0		2	1.88	1.88
1/20/2006	8	-1	3.5	2		0	2
1/21/2006	2	-1	0.5	6.6	3	2.82	9.42
1/22/2006	-2	-12	-7				
1/23/2006	-1	-8.5	-4.8				
1/24/2006	4	-5	-0.5		3	2.82	2.82
1/25/2006	2	0.5	1.3		5	4.7	4.7
1/26/2006	-9	-11	-10		1	0.94	0.94
1/27/2006	3.5	-15	-5.8				
1/28/2006	6	0	3				
1/29/2006	-1	-4.5	-2.8	4	2.5	2.35	6.35
1/30/2006	-2.5	-6	-4.3				
1/31/2006	0	-5	-2.5	0.6	2.5	2.35	2.95
2/1/2006	-1	-3	-2				
2/2/2006	3	-3	0	3.8			3.8
2/3/2006	6	-1	2.5	14			14
2/4/2006	6	2	4	6			6
2/5/2006	6.5	1	3.8	1.2			1.2
2/6/2006	-3.5	-7	-5.3		2	1.88	1.88
2/7/2006	-6	-9	-7.5				
2/8/2006	-7.5	-12	-9.8				
2/9/2006	-9	-14.5	-11.8				
2/10/2006	-8.5	-17.5	-13				
2/11/2006	-4.5	-16.5	-10.5				
2/12/2006	-6	-14	-10				
2/13/2006	-2	-11	-6.5				
2/14/2006	3	-4.5	-0.8		3.5	3.29	3.29
2/15/2006	8.5	-3	2.8			0	
2/16/2006	-2	-8.5	-5.3	12	5	4.7	16.7
2/17/2006	6.5	-11.5	-2.5		1	0.94	0.94
2/18/2006	-13	-17	-15				
2/19/2006	-4	-17	-10.5				
2/20/2006	-2	-9	-5.5				
2/21/2006	0.5	-6	-2.8		3	2.82	2.82
2/22/2006	3	-7	-2		6	5.64	5.64
2/23/2006	3	-3	0				
2/24/2006	-5	-8	-6.5				
2/25/2006	-11	-13.5	-12.3		23	21.62	21.62

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Temp Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
2/26/2006	-10	-14.5	-12.3				
2/27/2006	-10	-19	-14.5				
2/28/2006	-7.5	-15.5	-11.5				
3/1/2006	-5.5	-16	-10.8				
3/2/2006	-1	-7.5	-4.3				
3/3/2006	-5.5	-12.5	-9		1	0.94	0.94
3/4/2006	0.5	-9.5	-4.5				
3/5/2006	-1	-7.5	-4.3				
3/6/2006	-1	-10	-5.5				
3/7/2006	-2.5	-11	-6.8				
3/8/2006	0.5	-11.5	-5.5				
3/9/2006	3	-4	-0.5				
3/10/2006	13.5	1	7.3	8			8
3/11/2006	10	3	6.5				
3/12/2006	9.5	-1	4.3	4			4
3/13/2006	11	1.5	6.3	7.3			7.3
3/14/2006	7	1.5	4.3				
3/15/2006	-1	-4.5	-2.8				
3/16/2006	-0.5	-7.5	-4				
3/17/2006	-3	-8.5	-5.8				
3/18/2006	-5	-8.5	-6.8		1	0.94	0.94
3/19/2006	-2.5	-7.5	-5				
3/20/2006	-3	-9.5	-6.3				
3/21/2006	-0.5	-6.5	-3.5		1	0.94	0.94
3/22/2006	2	-3.5	-0.8				
3/23/2006	9	-1	4				
3/24/2006	8.5	1	4.8				
3/25/2006	9	1.5	5.3				
3/26/2006	9	1.5	5.3				
3/27/2006	7.5	-1	3.3				
3/28/2006	13	-3	5				
3/29/2006	14	-1	6.5				
3/30/2006	16	2	9				
3/31/2006	24	3	13.5				
4/1/2006	14	9	11.5	7.4			7.4
4/2/2006	11	0	5.5				
4/3/2006	11	0.5	5.8	9.2			9.2
4/4/2006	4	-1	1.5	7	6	5.64	12.64
4/5/2006	4	-2.5	0.8				
4/6/2006	9	1	5				
4/7/2006	7.5	4	5.8	8.4			8.4
4/8/2006	5	-4.5	0.3				
4/9/2006	10.5	-3	3.8				
4/10/2006	14.5	0.5	7.5				
4/11/2006	19	2.5	10.8				
4/12/2006	25	4	14.5				
4/13/2006	13.5	9.5	11.5				
4/14/2006	17	0.5	8.8	1.8			1.8

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
4/15/2006	17	11	14				
4/16/2006	11	4.5	7.8				
4/17/2006	14	5.5	9.8				
4/18/2006	20.5	5	12.8				
4/19/2006	23	6	14.5				
4/20/2006	20	7	13.5				
4/21/2006	20	5	12.5				
4/22/2006	15.5	7	11.3	12.2			12.2
4/23/2006	8	5.5	6.8	4.2			4.2
4/24/2006	8.5	6	7.3	6.2			6.2
4/25/2006	8.5	4.5	6.5	3.8			3.8
4/26/2006	11.5	0	5.8				
4/27/2006	10	-1	4.5				
4/28/2006	13	-2	5.5				
4/29/2006	16	-1	7.5				
4/30/2006	21	1.5	11.3				
5/1/2006	24	6	15				
5/2/2006	15.5	9.5	12.5	4.3			4.3
5/3/2006	14	7	10.5				
5/4/2006	26	6	16				
5/5/2006	20	9.5	14.8				
5/6/2006	10.5	7.5	9	9.4			9.4
5/7/2006	15	0	7.5				
5/8/2006	23	5	14				
5/9/2006	24	8	16				
5/10/2006	23.5	12	17.8				
5/11/2006	25.5	10.5	18				
5/12/2006	16	15	15.5	18			18
5/13/2006	16	12	14				
5/14/2006	14.5	11	12.8	8.9			8.9
5/15/2006	18.5	11	14.8	2.6			2.6
5/16/2006	18.5	11	14.8	2			2
5/17/2006	14.5	11	12.8	11			11
5/18/2006	18	13	15.5	21.7			21.7
5/19/2006	14	10.5	12.3	18.3			18.3
5/20/2006	10.5	9	9.8	10.1			10.1
5/21/2006	12.5	7	9.8	3			3
5/22/2006	10.5	4	7.3				
5/23/2006	15	7	11				
5/24/2006	21.5	7.5	14.5				
5/25/2006	26.5	11.5	19				
5/26/2006	22.5	14.5	18.5	0.6			0.6
5/27/2006	23.5	15.5	19.5				
5/28/2006	26.5	12	19.3	4			4
5/29/2006	29	15.5	22.3				
5/30/2006	28	19	23.5				
5/31/2006	31.5	17	24.3	12			12
6/1/2006	20.5	16.5	18.5	16			16

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Temp Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
6/2/2006	24	12	18	1.4			1.4
6/3/2006	15	14	14.5	13.6			13.6
6/4/2006	19.5	12.5	16				
6/5/2006	26.5	10.3	18.4				
6/6/2006	28.6	12.8	20.7				
6/7/2006	24.5	14	19.3	1			1
6/8/2006	17	14	15.5	2.4			2.4
6/9/2006	ND	ND	ND	ND	ND	ND	ND
6/10/2006	11	9	10	13.9			13.9
6/11/2006	14.5	7.4	11				
6/12/2006	ND	ND	ND	ND	ND	ND	ND
6/13/2006	22	11.5	16.8				
6/14/2006	25	13.6	19.3				
6/15/2006	25	11.5	18.3				
6/16/2006	28.5	14.5	21.5	1.4			1.4
6/17/2006	27	15.5	21.3				
6/18/2006	32	21	26.5				
6/19/2006	27	20.5	23.8	1.5			1.5
6/20/2006	24	18	21	1.9			1.9
6/21/2006	25	11	18	0.2			0.2
6/22/2006	28	17	22.5	1.6			1.6
6/23/2006	23	17.5	20.3				
6/24/2006	26	11.5	18.8				
6/25/2006	28.5	12.5	20.5				
6/26/2006	24.5	12.5	18.5	0.2			0.2
6/27/2006	29.5	20	24.8	28.2			28.2
6/28/2006	28	20	24				
6/29/2006	27.5	19.5	23.5				
6/30/2006	ND	ND	ND	ND	ND	ND	ND
7/1/2006	25.5	13.5	19.5	25.2			25.2
7/2/2006	29.5	17.5	23.5				
7/3/2006	29.5	14.5	22				
7/4/2006	28.5	21	24.8				
7/5/2006	ND	ND	ND	ND	ND	ND	ND
7/6/2006	23.5	14.5	19				
7/7/2006	28	14.5	21.3				
7/8/2006	28	16.5	22.3				
7/9/2006	28.5	16.5	22.5				
7/10/2006	30	18	24				
7/11/2006	ND	ND	ND	ND	ND	ND	ND
7/12/2006	23.5	18	20.8	2			2
7/13/2006	30	18	24				
7/14/2006	31.5	20	25.8				
7/15/2006	29	21	25	7			7
7/16/2006	32.5	20	26.3				
7/17/2006	ND	ND	ND	ND	ND	ND	ND
7/18/2006	ND	ND	ND	ND	ND	ND	ND
7/19/2006	29.5	15	22.3				

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow , cm	Total Snow (as rain) mm	Total Precipitation mm
7/20/2006	32.5	17	24.8	7			7
7/21/2006	28	20	24				
7/22/2006	ND	ND	ND	ND	ND	ND	ND
7/23/2006	26.5	16	21.3				
7/24/2006	ND	ND	ND	ND	ND	ND	ND
7/25/2006	ND	ND	ND	ND	ND	ND	ND
7/26/2006	30.5	19	24.8				
7/27/2006	30	22	26				
7/28/2006	ND	ND	ND	ND	ND	ND	ND
7/29/2006	30	21	25.5	2.6			2.6
7/30/2006	25	14	19.5				
7/31/2006	30.5	18	24.3	60			60
8/1/2006	34.5	22	28.3	5.6			5.6
8/2/2006	ND	ND	ND	ND	ND	ND	ND
8/3/2006	28	17.5	22.8	1			1
8/4/2006	30	19.5	24.8				
8/5/2006	24.5	15	19.8				
8/6/2006	28.5	14	21.3				
8/7/2006	30.5	21.5	26	7			7
8/8/2006	24.5	15.5	20				
8/9/2006	26.5	13.5	20				
8/10/2006	23	17	20	8.4			8.4
8/11/2006	21.5	11	16.3				
8/12/2006	21	11.5	16.3				
8/13/2006	ND	ND	ND	ND	ND	ND	ND
8/14/2006	ND	ND	ND	ND	ND	ND	ND
8/15/2006	25	17	21	1			1
8/16/2006	26	17	21.5				
8/17/2006	27	14	20.5				
8/18/2006	30	18.5	24.3				
8/19/2006	28	21	24.5	3.6			3.6
8/20/2006	20.5	16	18.3	1			1
8/21/2006	25.5	14.5	20				
8/22/2006	25.5	15.5	20.5				
8/23/2006	ND	ND	ND	ND	ND	ND	ND
8/24/2006	ND	ND	ND	ND	ND	ND	ND
8/25/2006	ND	ND	ND	ND	ND	ND	ND
8/26/2006	23.5	8.5	16				
8/27/2006	21.5	15.5	18.5	5.2			5.2
8/28/2006	24	17	20.5				
8/29/2006	25	15.5	20.3				
8/30/2006	20.5	14.5	17.5				
8/31/2006	22	7.5	14.8				
9/1/2006	ND	ND	ND	ND	ND	ND	ND
9/2/2006	ND	ND	ND	ND	ND	ND	ND
9/3/2006	19	12.5	15.8	4.4			4.4
9/4/2006	18.5	15.5	17	1.4			1.4
9/5/2006	20	16	18				

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
9/6/2006	19	15	17				
9/7/2006	23	13	18				
9/8/2006	26.5	14	20.3				
9/9/2006	18	14.5	16.3	1			1
9/10/2006	17.5	8.5	13				
9/11/2006	19	5	12				
9/12/2006	ND	ND	ND	ND	ND	ND	ND
9/13/2006	15	11.5	13.3	5.1			5.1
9/14/2006	18.5	14.5	16.5	13.2			13.2
9/15/2006	20	16	18				
9/16/2006	21	14	17.5				
9/17/2006	ND	ND	ND	ND	ND	ND	ND
9/18/2006	ND	ND	ND	ND	ND	ND	ND
9/19/2006	20	15.5	17.8	6.8			6.8
9/20/2006	ND	ND	ND	ND	ND	ND	ND
9/21/2006	17.5	6.5	12				
9/22/2006	ND	ND	ND	ND	ND	ND	ND
9/23/2006	ND	ND	ND	ND	ND	ND	ND
9/24/2006	23	16	19.5	3			3
9/25/2006	16	6	11	1			1
9/26/2006	17	10.5	13.8				
9/27/2006	23.5	8	15.8				
9/28/2006	19	13	16	36.6			36.6
9/29/2006	10.5	8.5	9.5	1			1
9/30/2006	17	4	10.5	3			3
10/1/2006	15.5	11.5	13.5	6.6			6.6
10/2/2006	18	11.5	14.8				
10/3/2006	18	9	13.5	1.6			1.6
10/4/2006	ND	ND	ND	ND	ND	ND	ND
10/5/2006	12.5	4	8.3				
10/6/2006	15	2	8.5				
10/7/2006	17	1	9				
10/8/2006	21.5	5.5	13.5				
10/9/2006	ND	ND	ND	ND	ND	ND	ND
10/10/2006	ND	ND	ND	ND	ND	ND	ND
10/11/2006	19	8.5	13.8	1.8			1.8
10/12/2006	17	10	13.5	4			4
10/13/2006	9.5	2	5.8				
10/14/2006	8	5	6.5	2.2			2.2
10/15/2006	11	2.5	6.8				
10/16/2006	14.5	3.5	9				
10/17/2006	13.5	4.5	9	25.2			25.2
10/18/2006	ND	ND	ND	ND	ND	ND	ND
10/19/2006	ND	ND	ND	ND	ND	ND	ND
10/20/2006	7	1	4	24.2			24.2
10/21/2006	ND	ND	ND	ND	ND	ND	ND
10/22/2006	ND	ND	ND	ND	ND	ND	ND
10/23/2006	6.5	3.5	5	3			3

Table A3: Daily Climate Data for Station 6101874 (Cornwall, Ontario), for the period (August 2005 - October 2006) *[Environment Canada(b)]*

Date	Temp Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
10/24/2006	6.5	4	5.3				
10/25/2006	7.5	4.5	6				
10/26/2006	ND	ND	ND	ND	ND	ND	ND
10/27/2006	7.5	1	4.3	14			14
10/28/2006	9.5	3.5	6.5	21.6			21.6
10/29/2006	ND	ND	ND	ND	ND	ND	ND
10/30/2006	10.5	4	7.3				
10/31/2006	13.5	1	7.3	4.4			4.4
11/1/2006	10	3.5	6.8				
11/2/2006	6.5	2	4.3				
11/3/2006	5	-1.5	1.8				
11/4/2006	4.5	-3	0.8				
11/5/2006	13	0.5	6.8				
11/6/2006	ND	ND	ND	ND	ND	ND	ND
11/7/2006	12	1	6.5	8			8
11/8/2006	9.5	7	8.3	7.2			7.2
11/9/2006	ND	ND	ND	ND	ND	ND	ND
11/10/2006	7.5	5	6.3				
11/11/2006	5.5	2.5	4	23.2			23.2
11/12/2006	4	2.5	3.3	3			3
11/13/2006	8	4	6	8.4			8.4
11/14/2006	8.5	7	7.8	5.2			5.2
11/15/2006	ND	ND	ND	ND	ND	ND	ND
11/16/2006	19	7.5	13.3	14.4			14.4
11/17/2006	13	7	10				
11/18/2006	5	2.5	3.8				
11/19/2006	2	1	1.5				
11/20/2006	1.5	-1	0.3				
11/21/2006	3.5	-1.5	1				
11/22/2006	6	-3	1.5				
11/23/2006	4.5	-2	1.3				
11/24/2006	6	-3	1.5				
11/25/2006	8.5	-4	2.3				
11/26/2006	11	-2	4.5	2			2
11/27/2006	6.5	4.5	5.5	7.6			7.6
11/28/2006	2	0.5	1.3	0.4			0.4
11/29/2006	16.5	1	8.8				
11/30/2006	19.5	9	14.3	23.4			23.4

Notes: ND = No Data Available

Table A4: Monthly Climate Data for Station 6101874, for the period (August 2005 - October 2006).

Date	Max °C	Temp Min °C	Mean °C	Total Rain mm	Total Snow cm	Total Snow (as rain) mm	Total Precipitation mm
2005-08	27.1	17.7	22.4	142.7			142.7
2005-09	23	14	18.5	142.9			142.9
2005-10	14.1	7.3	10.7	220.9			220.9
2005-11	8.4	0.2	4.3	95	9	8.5	103.5
2005-12	-2	-7.9	-5	19	47.5	44.7	63.7
2006-01	-0.2	-7.8	-4	66.2	51.5	48.4	114.6
2006-02	-2.4	-9.4	-5.9	37	43.5	40.9	77.9
2006-03	4.4	-4.4	0	19.3	3	2.8	22.1
2006-04	13.4	2.8	8.2	60.2	6	5.6	65.8
2006-05	19.6	10.2	14.9	125.9			125.9
2006-06	24.1	14.4	19.3	83.3			83.3
2006-07	28.7	17.6	23.2	103.8			103.8
2006-08	25.5	15.6	20.6	32.8			32.8
2006-09	19.0	11.7	15.4	76.5			76.5
2006-10	12.7	4.7	8.7	108.6			108.6

Appendix B
Laboratory Methods

Protocol for Denitrifier Method – $\delta^{15}N$ & $\delta^{18}O$ in NO_3^-

Using Aureofaciens Bacteria
Prepares 96 bacteria vials & 7 DDI H_2O Blanks
(Based on Sigma et al., 2001, and Casciotti et al., 2002)

I. Required Equipment, Materials and Supplies

See Appendix.

II. Preparation of Supplies

TO BE DONE PRIOR TO STARTING

1. Prepare all glassware for sterilizing;

2. Follow cleaning procedure to thoroughly sterilize the glassware:
   i. Wash all glassware with soap;
   ii. Soak in 10% HCl for a few days;
   iii. Rinse with DDI H_2O and soak in DDI H_2O for a few days;
   iv. Final rinse x 3 with DDI H_2O, then dry;
   v. Place all glassware in a Muffle Furnace (500°C) for 4 hours;

3. Wrap new tooth picks, 5mL, 2mL, and 0.2mL pipette tips in aluminium foil, place in beaker, then send to autoclave (dry cycle 20 minutes);

III. Preparation of TSB (Tryptic Soy Broth [Soybean-Casein Digest Medium])

DAY 1

1. Weight the following materials using analytical balance;

Materials for 2100 ml DDI	(Required Amount) mass (g)
TSB	63
K_2HPO_4 (dibasic)	10.5
$(NH_4)_2SO_4$	2.1
KNO_3	2.1

2. Add 2100mL DDI H_2O into a 2.5L volumetric beaker;

3. Add above listed materials into the beaker;

4. Stir thoroughly and transfer 130mL of solution into 16 (160mL) serum bottles using sterilized graduated cylinder;

5. Cap each serum bottles with a sterile grey butyl septum (I-shaped inner face, not O-shaped), then seal with crimper using aluminium seal;

6. Label each bottle with suitable paper labels (safe for autoclave);

7. Autoclave (wet cycle 85 minutes);

8. After autoclave, store 16 serum bottles at room temp until needed;

IV. Preparation of TSA + NO_3^- plates (Tryptic Soy Agar + KNO_3)

DAY 1

Materials	(Required Amount) mass (g)
TSA	10.0
KNO_3	0.25

1. Add 250 DDI H_2O into a 500mL volumetric flask;

2. Add the materials (mass indicated above) into the flask, stir until everything dissolves, then cover with aluminium foil;

3. Send to autoclave (wet cycle 20minutes), ONLY ONCE Nutrient Broth has been prepared;

V. Preparation of Nutrient Broth

DAY 1

1. Weigh 1.6g of Nutrient Broth, and place in Pyrex 250mL (orange cap) medical bottle;

2. Add 200mL DDI H_2O;

3. Seal bottle with lid and shake the solution until it is completely dissolved, then loosen the lid;

4. Autoclave (wet cycle 20 minutes);

5. Close bottle lid tightly after autoclaving;

6. Place bottle in fridge until needed;

VI. Transfer TSA+ NO3 into Petri-dishes.

DAY 1

Immediately after autoclave (wet cycle 20minutes) of TSA + KNO_3 complete;

1. Check viscosity of TSA, should NOT be solid;

If dissolved TSA is not transferred into Petri-dishes immediately after autoclaving, it will solidify. If so, before transferring them into Petri-dishes, reheat until it dissolves.

2. Take one (sealed and sterilized) plate (Petri-dish, small side down), remove the lid (dissolved TSA solution), at an angle of 45 degrees, carefully pour a couple millilitres of medium until the plate is completely coated with a thin layer, replace the plate lid. This step should be done carefully, but quickly enough to minimize contamination by other bacteria from airborne sources;

3. Repeat above step until approximately 30 plates are coated. Stack plates next to the Bunsen burner. It takes approximately 20 minutes for them to solidify. When they are solidifying, the heat from the Bunsen burner will encourage all the water vapour to evaporate from the plate;

If while pouring the medium it starts to solidify (gets clumpy), reheat the medium on a hot plate. Make sure to not shake it while it is solidifying;

4. Cut (width-wise) strips of Parafilm while waiting for the medium to solidify. After the plates have solidified wrap the edge with Parafilm, leave no gaps along the edges of the plates;

5. Discard plates that have too much condensation on the inside;

6. Store plates with solidified medium in the fridge (-4°C);

VII. Procedure for Bacterial Incubation:

DAY 2

1. Remove cryocane holder from cryostorage dewar, remove one cryotube from 1 cryocane. Replace crycane and cryocane holder immediately back into dewar, and close lid;

2. Open cryotube screw cap, using an autoclaved toothpick, remove a dollop of the frozen (-170°C) cells (bacteria) from cryotube, and spread immediately onto 2 of the 30 Petri-dishes with TSA, and label both plates as (Bacteria-Stock). Replace cryotube immediately back into cryocane and dewar;

3. Use flamed loop to streak cells **(allow the loop to cool before streaking the plate)**;

4. Transfer bacteria from plates (Bacteria-Stock) onto an additional10 plates (with TSA), label all 10 dishes as (Bacteria#1);

5. Incubate all 10 Petri-dishes (Bacteria#1) at a temperature of 26°C for 3 days;

DAY 5

1. Following incubation, transfer 10 best single colonies by flamed loop from any of the 10 incubated plates onto 10 new plates (with TSA) labelled (Bacteria#2);

2. Incubate all 10 plates (Bacteria#2) at a temperature of 26°C for 3 days;

3. All 10 plates labelled (Bacteria#1) can be disposed;

DAY 8

1. Clean work bench with germicide, light Bunsen burner;

2. Prepare necessary materials:
   i. 7 x 14mL Polystyrene Round-Bottom test tubes (17 x 100mm style);
   ii. Remove Nutrient Broth bottle from fridge;
   iii. Sterilized pipettes (5mL) and pipettor;

3. Transfer 5mL of nutrient broth into each of 7 Polystyrene tubes (pre-cleaned by placing the mouth of the tube near the flame). Replace remaining nutrient broth in fridge immediately;

4. Following incubation, transfer a single colony by flamed loop from plate (Bacteria#2) to a 5mL broth;

5. Use flamed loop to transfer the best single colony from any of the 10 plates labelled (Bacteria#2) into the 7 tubes (Choose 7 best single colonies). Place the flamed loop completely into the broth and stir it so that all the bacteria gets into the broth. Clean flamed loop on Bunsen burner between each tube and allow to cool;

6. After completing all 7 test tubes, close tube with cap and wrap cap with Parafilm, place on shaker table, and leave overnight;

DAY 9

1. The following day, if the test tube broth become cloudy, it is successful, if the broth is not cloudy, the inoculation step failed;

2. Using a sterile 1mL syringe and needle, inject 0.8mL of cloudy broth from the 7 test tubes into each of the 16 (160mL) serum bottles (each bottle contains 130mL TSB);

3. Wrap Parafilm overtop of crimp seal;

4. Place all 16 (160mL) bottles on shaker table and stir for 7 days at room temperature;

DAY 15

1. On day 6 of stirring, prepare 6.06 M $(NH_4)_2SO_4$ solution:
   i. Weight 36 g of $(NH_4)_2SO_4$;
   ii. Add 90mL DDI H_2O into a 250mL medical bottle (orange lid) and shake well;
   iii. Store in fridge when complete;

DAY 16

1. After one week of incubation, take all 16 (160mL) serum bottle (containing 0.8mL bacteria and 130mL TSB) from the shaker, if all the solutions are cloudy, the inoculation was successful, if they are clear, it indicates there was no bacteria growth. Label the serum bottles #1 - #16;

2. Prepare 16 (14mL) sterile Polystyrene Round-Bottom tubes (17 x 100mm style), label them #1 - #16;

3. Prepare an additional 3 (14mL) Polystyrene Round-Bottom tubes, label them "Sulfanilamide", "NED" and "Antifoam", and pipette 5mL of each reagent into each respective tube;

4. Nitrite test:
   iv. Open each of the 16 160mL serum bottles;
   v. Pipette 5mL from each serum bottles and add to respective 14mL tube;
   vi. Add 100µL of Sulfanilamide Reagent (1% w/v in 10%v/v Hydrochloric Acid)(Solution #1) into each tube;
   vii. Add 100µL of Naphthylethylenediamine Dihydrochloride (NED) solution (0.1%w/v aqueous solution) (Solution #2) into each tube;
   viii. If the solution colour in the serum bottles does not change, it means that the bacterial culture is good, if the solution colour become red or pink, it means the bacterial culture is no good;

5. Add 100µL of Antifoam to each of the 16 (160mL) serum bottles, shake them until the bubbles disappear;

6. Prepare 48 sterile 50mL centrifuge test tubes, labelled #1 - #16 (3 tubes per number, since 3 are taken from each serum bottle);

7. From each of the 16 (160mL) serum bottles, transfer 40mL into each of the 3 respectively labelled centrifuge tubes (serum bottles now only contain 125mL since 5mL was transferred to the 14mL test tubes - divided by 3 equals ~40mL);

8. Send all 48 centrifuge test tubes (40mL solution in each) to CAREG building (Room 419) for centrifuging (7500 rotations/min, 12mins each run, at 18°C);

9. After centrifuging, transfer the supernatant (LIQUID) from the centrifuge tubes back into each respectively labelled 160mL serum bottle. Three centrifuge tubes per one serum bottle. Leave the precipitate in the centrifuge tubes;

10. From all 16 (160mL) serum bottles, transfer 4mL of liquid back to each respectively labelled centrifuge test tube which contains the precipitate. (The solution in the centrifuge tube should be 10 times that of the initial 40mL solution);

11. Place all centrifuge tubes on a vortex shaker for a few seconds to ensure the 4mL solution is well mixed with the precipitate;

12. Take the stirred solutions (4mL in each centrifuge tube) and transfer contents of 10 centrifuge tubes into 1 tube. 4 centrifuge tubes will contain 40mL solution, while 1 centrifuge tube will contain 32mL;

13. Using pipettor, add 0.1mL 6.06 M $(NH_4)_2SO_4$ solution into each tube containing 40mL of concentrated solution. For the tube containing 32mL ass 0.08mL 6.06M $(NH_4)_2SO_4$. The objective is to obtain a 15nM concentration in each tube;

14. Use a 2mL pipette tip (autoclaved) and pipettor to transfer 2mL of the mixed solution from the 5 centrifuge tubes into sterile 20mL glass vials, repeat procedure until a total of 96 glass 20mL vials complete;

15. Seal each 20mL vial with PTFE/Silicone or butyl septum, and crimp with aluminium seal;

16. Invert vials and place in Styrofoam rack overnight;

VIII. IRMS Sample Preparation and Analysis

DAY 17

1. Revert vials, and touch each on Vortex shaker for approximately 3 seconds;

2. Insert outlet needle (3" 23G) in each 20mL vial. Do not insert into liquid;

3. Place each vial on multi-needle flush system and flush with helium at 30-60mL/min for 6-12 hours. The inlet needles should terminate in the liquid, resulting in continuous bubbling;

4. Check the helium flow rate from each outlet needle using Intelligent flow meter, (30 second constant flow rate), adjust master flow rate (needle valve) if required);

5. Check multi-needle flush system periodically to ensure bubbles continue during entire flushing period;

6. Prepare N15 (internal laboratory) and N3 (IAEA) standards while bacteria vials flushing. Standards should be prepared at concentrations similar to samples being analysed;

7. Replace chemical trap contents on Precon and flush with helium for 3+ hours;

8. Remove outlet needles, then remove vials from multi-needle flush system (remove one outlet needle at a time, followed by removal of vial from multi-needle flush system);

9. Prepare disposal syringes and needles and glass 100µL micro-syringe (for volumes < 0.1mL). Rinse micro-syringe using DDI H_2O between sample injections. Carefully suck and release water 3~5 times;

10. Inject desired nmole volume (20nmoles ideal) of sample and/or standard into bacteria vials (as per concentration requirements). The amount of sample transferred into the vial should not exceed 10ml. If the sample volume is to exceed 1.5mL, an outlet needle needs to be inserted (cautiously) to allow excess helium gas to escape. Ensure that positive pressure is always present in the vial while outlet needle in place;

Injection volume (mL) = [nmoles target of N_2O) / Nitrate concentration (µM]

11. Invert vials in Styrofoam rack and leave overnight;

12. Prepare 12mL of 10N NaOH solution and place in 14mL sterile test tube;

13. Transfer 5 mL of Antifoam B solution into 14mL sterile test tube;

DAY 18

1. The following morning, add 0.1mL of 10N NaOH (using 1mL disposable syringe) into each 20mL vial;

2. Add 3 drops of Antifoam B (using 1mL disposable syringe) into each 20mL vial;

3. Lightly shake vials to mix bacteria and solutions, and place vials into autosampler rack and prepare PreCon / IRMS for N_20 analysis;

4. ISODAT SEQUENCE
    i. AS Sample = peak Position
    ii. AS Method = Internal No.9
    iii. Identification 1 = (enter vial contents, i.e. Blank/std or sample lab ID)
    iv. Identification 2 = nothing entered
    v. Method = Precon+Pal\N2O-Autosampler.met

5. Start sequence, add liquid nitrogen every 6 hours to dewar, replace vials in rack every 12 hours;

APPENDIX: Required Equipment, Materials and Supplies

1. Lab Equipment:
   i. DDI H_2O supply
   ii. Muffle Furnace;
   iii. Incubator;
   iv. Shaker Table (capable of holding 32 (160mL) serum bottles;
   v. Pipettor;
   vi. Manual crimp tool (20mm);
   vii. Bunsen burner;
   viii. Flame loop;
   ix. Multi-needle flush system (capable of holding 103 (20mL) vials;
   x. Microbalance;
   xi. Autosampler / PreCon / CFIRMS setup;
   xii. Autoclave

2. Reagents:
   i. DDI H_2O
   ii. TSA;
   iii. TSB;
   iv. KNO_3 (for medium prep & N15 internal laboratory isotope standard)
   v. HCl (for glassware sterilizing);
   vi. Germicide;
   vii. 10N NaOH;
   viii. Antifoam;
   ix. IAEA-N3 isotope standard;

3. Disposable Supplies:
   i. Sterile plastic Petri dishes;
   ii. Latex gloves;
   iii. PTFE/Silicone or butyl septum (20mm);
   iv. Aluminum crimp caps (20mm);
   v. 1 inch 23G needles (He flush inlet, and Antifoam and NaOH injections);
   vi. 3 inch 23G needles (He flush outlet);
   vii. 1mL sterile syringes;
   viii. Tooth picks;
   ix. 5mL, 2mL and 0.5mL pipette tips;
   x. 50mL high-speed centrifuge tubes;
   xi. 14mL polystyrene test tubes;

4. Glassware:
   i. 16 × (160mL) serum bottles;
   ii. 103 × (20mL) serum vials;
   iii. 1 × (200mL) graduated cylinder;
   iv. 1 × (500mL) volumetric flask
   v. 2 × (250mL) volumetric flask (isotope standard preparation);

Protocol for Ammonium Diffusion – $\delta^{15}N$ in NH_4^+

Using H_2SO_4

(Based on Sebilo et al., 2004; and Schleppi et al., 2006; and Holmes et al., 1998)

I. Required Equipment, Materials and Supplies

See Appendix.

TO BE DONE PRIOR TO DAY 1

II. Preparation of Supplies

1. Prepare all glassware for sterilizing;

2. Follow cleaning procedure to thoroughly sterilize all glassware:
   i. Wash all glassware with soap;
   ii. Rinse in DDI H_2O;
   iii. Soak in 0.5N HCl for a few days;
   iv. Rinse with DDI H_2O and soak in DDI H_2O for a few days;
   v. Final rinse x 3 with DDI H_2O, then dry;
   vi. Place all glassware in a Muffle Furnace (400°C) for 4 hours;
   vii. Cover glassware with aluminium foil paper and store in large plastic container until use;

3. Clean, acidify and autoclave all necessary equipment;

TO BE DONE PRIOR TO DAY 1

III. Quartz Filter Preparation

1. Place aluminium foil paper in workspace area and wipe with 95% ethanol, wait till it dries;

2. Wipe forceps and scissors with ethanol, wait until it dries;

4. Keep an open jar of concentrated H_2SO_4 near the work site;

3. Cut quartz filters to appropriate dimensions (0.5x 1.5cm);
   i. Cut the full disk (47mm) in half;
   ii. Cut 5mm wide strips;
   iii. Cut appropriate length (15mm);
   iv. Use template to cut additional filters;

6. Cut one quartz filter (0.5x1.5cm) for each filter pack necessary;

7. Manipulate the quartz filters gently using forceps and latex gloves, they rip easily;

8. Place the cut filters in a glass watch and wrap with aluminium foil paper (both glass watch and aluminium foil paper should be wiped with ethanol then dried before use);

9. Calcinate the filters at 450°C for 5 hours (burns off any potential carbon);

10. Keep the filters in the glass watch wrapped in aluminium foil until ready to use;

DAY 1

IV. Filter Pack Preparation

1. Place aluminium foil paper in workspace and wipe with 95% ethanol, wait until dry;

2. Wipe forceps and scissors with ethanol, wait until dry;

3. Cut 47mm Mitex PTFE filters in half (alternatively use a 2 x 3 cm pre-cut filter);

4. Pre-fold the filters and press firmly, as illustrated in Figure 1, but using half disks;

5. Open the filter pack (undo the folds) with forceps and insert the quartz filter on the bottom of the fold;

6. Transfer 20 µL of H_2SO_4 on to the quartz filters using a micropipette;
   i. Place drops of acid side by side along the filter to avoid that the Quartz filter becomes oversaturated in one area;
   ii. Ensure the acid side is always facing up in the filter pack;

7. Close the PTFE filter (following the previously made folds) and press gently to ensure that the package is properly closed;

8. Cut 2-3cm (length) strips of Teflon tape and wrap it around the PTFE filter to better hold the filter pack together;

9. Place filter packs into small glass vials and cap;

10. Store the vials in desiccator with a small open vial of H_2SO_4 until ready to use;

The 'Ammonium Diffusion' Method

STEP 1:
Add 3 × 10 µL of H_2SO_4 on the glass fibre filter.
Place the glass fibre filter on the hydrophobic filter, below the centre line of the hydrophobic filter.
Fold one half the hydrophobic filter over the glass fibre filter without touching the glass fibre filter. Use tweezers to remove the air between the halves of the hydrophobic filter and seal the folded filter by applying mild pressure.

STEP 2:
Fold the lower half of the hydrophobic filter towards the centre line. remove air, and seal by applying mild pressure.

STEP 3:
Fold the left and right hand sides of the filter and seal. The filter pack is ready and should not open during the incubation.

STEP 4:
Place the filter into the incubation bottle.

STEP 5:
Add 2 mL of NaOH solution and/or the Devarda reagent. Close immediately.
The sides with folds are in contact with the solution. If not, shake the bottle gently.

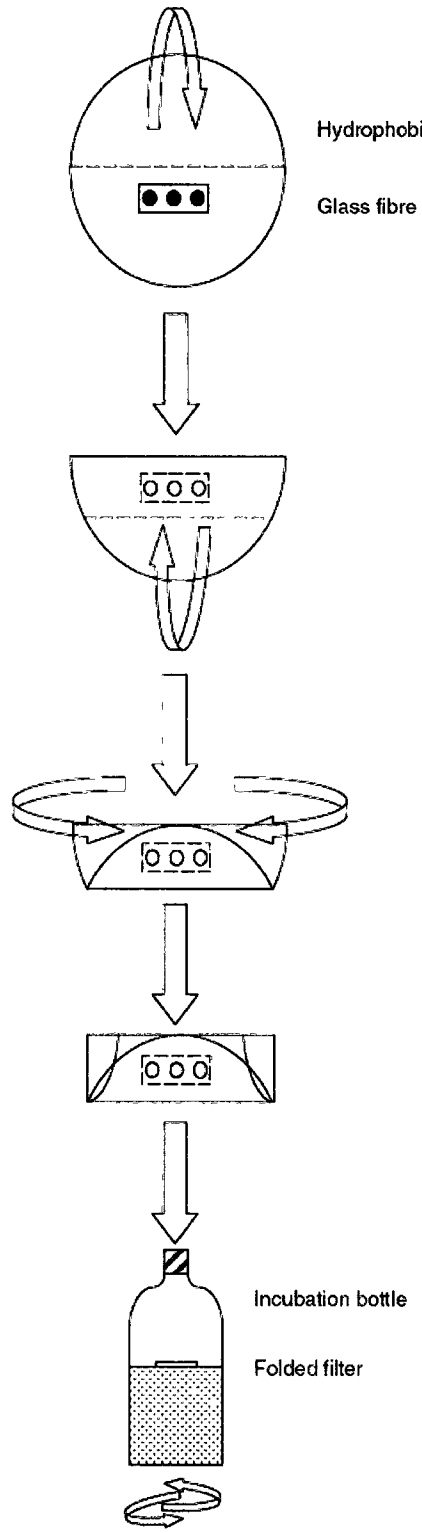


Fig. 1. Detailed preparation of the filter pack and the incubation solution.

DAY 1

V. Standard Preparation (for Ammonium Analysis)

1. Half fill 1L volumetric flask with DDI H_2O (cover with Parafilm);
2. Weigh out target amount of ammonium sulphate standard on microbalance (record the weight, enter onto spread sheet as actual standard concentration);
3. Place ammonium sulphate in the volumetric flask and top up with DDI H_2O (cover with Parafilm);
4. Shake volumetric flask to completely dissolve ammonium sulphate;

DAY 1

VI. Incubation Preparation

1. Start defrosting samples approximately 4 hours prior to beginning incubation step;
2. Place 150mL beaker on laboratory balance (ensure adequate capacity) and tare;
3. Pour desired volume of sample (between 25 and 150mL) into the graduated beaker (based on sample ammonium concentration, the desired nitrogen concentration is between 50 and 150µg-N) and note the weight;
4. Remove foil from 200mL serum bottle and pour the sample from the graduated beaker into it;
5. After having poured the sample into the bottle re-weigh the graduated beaker (this allows us to determine the exact weight, and therefore volume of sample used);
6. Add appropriate amount of DDI H_2O to bring total volume to 100mL (alternatively 150mL if low concentrations), if necessary;
7. Mark sample ID on bottle with permanent marker;
8. To insert the filter pack;
   i. Tilt the bottle sideways until the liquid is horizontal and near the opening of the bottle;
   ii. Gently rest the filter pack (acid side up) on the liquid - when you take the filter pack with the forceps, make sure you only pinch the side folds (ie. avoid pressing in the middle where the Quartz filter/acid is located);
   iii. Slowly re-tilt the bottle to its original upright position and always make sure that the acid side is facing up (i.e. more bulgy side, because the side folds are also facing up);
9. Place butyl septum on the bottle and seal with aluminium crimp cap;

10. Repeat steps 2-9 for each sample (30 samples, 4 standards and 2 blanks per batch)

11. To inject 5N NaOH;
    i. Use 10mL syringe to insert 2mL of 5N NaOH in each bottle;
    ii. Penetrate the butyl septum with the syringe;
    iii. Tilt the bottle a bit sideways and aim on the opposite side of the filter pack to avoid getting NaOH on it;
    iv. Always apply pressure on the syringe to avoid losses of ammonia gas created in the head space of the bottle;
    v. Wipe any excess of NaOH on the butyl septum with a Kimwipe;
    vi. Repeat step i. to v. for all samples and standards;

DAY 1

VII. Incubation Set-up

1. Place 36 bottles on the shaker table platform;

2. Start the shaker table (medium speed) and place the incubator box over top;

3. Start 40 watt light bulb and fan inside box (fan for air circulation);

4. Incubate and shake samples for desired length of time (7 to 10 days);

5. Check incubation every few days. Temperature should be between 35°C and 40°C;

DAY 8

VIII. Following Incubation Period

1. Remove bottles from the incubator box and remove the crimp caps;

2. Keep an open jar of concentrated H_2SO_4 near the work site;

3. Tilt the bottle sideways until the liquid gets near the opening of the bottle and gently make the liquid go back and fourth, this motion will make the filter pack approach the opening;

4. Pinch the filter pack on the side with the forceps and remove from the bottle;

5. Place the filter packs into segregated plastic tray;

6. Place the plastic tray in a desiccator with an open jar of H_2SO_4, leave for 2 days;

DAY 10

IX. Freeze Drying

1. Remove the plastic container from the desiccator and place a Kimwipe between samples and the plastic cover;

2. Place tray in a freezer (-30°C deep freezer) with an open container of H_2SO_4 beside it; leave in freezer for 1 day;

DAY 11

X. Freeze Drying

1. Remove plastic tray from freezer, place the tray in a freeze-drier set to -50°C (check freeze-drier operational procedures), leave for 24 hrs;

DAY 12

2. After 48 hrs, remove tray from freeze-drier and place each filter pack into individual glass vial, then place in desiccator with an open jar of H_2SO_4 until ready for analysis (if analysis is to be done immediately following freeze-drier removal, skip placement of filter packs into desiccator and begin with next step immediately);

XI. Isotope Analysis

1. Take the filter packs (one at a time) out of the plastic container, unfold the Mitex filter;

2. Place the quartz filter into a silver cup (10x10mm) and make sure that is it lying flat at the bottom of the cup, you may need to fold it onto itself;

3. Use the forceps to fold the silver cup as many times as possible, ensure it doesn't rip. Repeat for every sample and standard and place silver cup into new plastic segregated tray;

4. Prepare EA (Sulfanilic Acid) and isotope standards (C-54, C-55, C-56, C-59 and N-2), check CFIRMS linearity and load cups into EA carousel;

5. Enter Lab ID's into EA software and IRMS software (Isodat)

6. Begin analysis;

DAY 13

7. Process Isodat results and transfer EA and Isodat data files to Paul;

APPENDIX: Required Equipment, Materials and Supplies

1. Lab Equipment:
   i. DDI H_2O supply;
   ii. Muffle Furnace;
   iii. Incubated shaker table (capable of holding 36 - 200mL serum bottles);
   iv. Pipettor;
   v. Manual crimp tool (20mm);
   vi. Microbalance;
   vii. Desiccators;
   viii. Autoclave;
   ix. EA / CFIRMS setup;

2. Reagents:
   i. DDI H_2O;
   ii. 8N H_2SO_4 (ACS Grade);
   iii. H_2SO_4 (ACS Grade);
   iv. 95% ethanol (for aluminium foil paper, forceps, and scissors sterilizing);
   v. 0.5N HCl (for glassware sterilizing);
   vi. 5N NaOH; (ACS grade);
   vii. $(NH_4)_2SO_4$ (ACS Grade) (for standards);
   viii. IAEA-N2 isotope standard;
   ix. Sulfanilic Acid (SA) standard (for EA calibration)

3. Disposable Supplies:
   i. Latex gloves;
   ii. Butyl septum (20mm);
   iii. Aluminium crimp caps (20mm);
   iv. Aluminium foil paper;
   v. Hydrophobic filters ('Mitex', PTFE, 47mm diameter, 10μm pore size, Millipore);
   vi. Quartz filters (alternatively APFD Millipore Glass Fibre);
   vii. 10mL sterile syringes (for NaOH injections);
   viii. 0.5mL pipette tips (for sulphuric scid);

4. Glassware:
   i. 36 × (200mL) serum bottles;
   ii. 18 × (150mL) graduated beaker;
   iii. 2 × (1000mL) volumetric flask;
   iv. 1 × (250mL) volumetric flask;

Appendix C
Precipitation Data

Table C1: Event Weighted $\delta^{18}O$ and $\delta^{2}H$ Values from Stations M2, M5 and M6.

Date	M2			M5			M6		
dd/mm/yyyy	Total Precip mm	$\delta^{18}O$ (VSMOW) ‰	$\delta^{2}H$ (VSMOW) ‰	Total Precip mm	$\delta^{18}O$ (VSMOW) ‰	$\delta^{2}H$ (VSMOW) ‰	Total Precip mm	$\delta^{18}O$ (VSMOW) ‰	$\delta^{2}H$ (VSMOW) ‰
8/2/2005	17 2	-7 49	-58 6	7 4	-9 9	-73 7	11 5	-7 5	-56 4
8/10/2005	5 8			4 5	-4 0	-27 7	4 5	-4 7	-34 6
8/12/2005	5 7	-4 7	-30 6	7 9			6 4	-4 0	-30 2
8/19/2005	15 3	-7 42	-50 4				6 4	-7 0	-46 0
8/20/2005		-7 3	-49 0						
8/27/2005	8 4	-4 78	-27 8	11 3	-5 1	-29 6	9 2	-5 1	-27 4
8/31/2005	84 9	-10 31	-71 4	84 9			79 6	-10 2	-73 7
9/2/2005	2 3	-7 92	-67 5	8 5					
9/7/2005		-6 27	-45 1						
9/8/2005	17 0	-6 51	-50 2	18 7			44 6	-5 8	-32 5
9/17/2005	5 7	-5 84	-44 6	15 8	-6 2	-45 2	19 1	-5 7	-35 7
9/22/2005	10 2	-3 72	-27 3	9 9	-3 8	-18 9			
9/26/2005	20 4	-5 74	-42 4	18 7	-6 0	-38 6	31 5	-11 5	-82 0
9/29/2005	11 9	-6 78	-54 4				11 6	-8 0	-53 6
10/7/2005	54 3	-9 35	-71 8	56 6	-9 0	-71 8	14 3	-7 3	-74 8
10/12/2005	8 5	-9 4	-62 9	5 8	-10 7	-72 3	31 8	-10 9	-75 2
10/17/2005	1 7	-12 3	-91 2						
10/22/2005	6 2	-15 8	-117 2	9 6	-17 8	-129 5	8 0	-19 2	-143 7
10/24/2005				2 4	-19 7	-151 7			
11/1/2005	4 0	-8 93	-61 6				4 8	-8 8	-57 4
11/5/2005	10 2	-7 69	-47 3	6 2	-12 6	-91 3			
11/9/2005				30 6	-9 1	-61 1			
11/16/2005					-9 3	-57 9			
1/19/2006		-14 77	-102 6		-11 7	-76 0			
1/27/2006		-20 21	-152 6						
1/31/2006		-16 57	-121 9		-16 6	-120 6			
2/18/2006		-24 11	-183 7						
2/25/2006		-20 08	-147 9						
3/14/2006	12 4	-9 23	-84 5						
4/1/2006				6 1	-9 2	-61 5			
4/4/2006				15 9	-12 5	-84 8			
4/8/2006		-9 01	-94 7						
4/14/2006	1 2	-7 4	-78 6	0 5	-8 3	-56 9			
4/22/2006	17 0	-8 6	-76 6	15 8	-7 8	-49 5			
4/24/2006	3 4	-10 7	-84 4	6 2	-11 3	-75 5	19 1	-15 6	
5/2/2006				5 7	-13 1	-96 3			
5/5/2006	9 6	-16 08	-132 0	11 9	-16 2	-123 9		-16 4	-125 8
5/11/2006	38 5	-6 81	-55 9	24 9	-7 5	-52 5			
5/13/2006	7 9	-4 7	-43 6	10 8	-5 2	-36 0			
5/16/2006	4 2	-13 4	-95 3	4 6				-13 86	-106 79
5/19/2006	14 1	-13 33	-94 9	22 6	-13 2	-96 0			
5/28/2006								-4 5	
5/31/2006	6 2	-5 96	-33 8	38 5	-5 7	-35 5		-6 1	
6/2/2006	12 4	-10 21	-73 2		-8 7	-63 4		-9 9	
6/9/2006	8 2	-11 7	-77 8	12 4	-12 2	-90 8		-12 5	
6/14/2006	1 7	-4 62	-29 0					-6 2	
6/20/2006		-6 36	-47 6					-5 4	

Table C1: Event Weighted $\delta^{18}O$ and $\delta^{2}H$ Values from Stations M2, M5 and M6.

Date	M2			M5			M6		
dd/mm/yyyy	Total Precip mm	$\delta^{18}O$ (VSMOW) ‰	$\delta^{2}H$ (VSMOW) ‰	Total Precip mm	$\delta^{18}O$ (VSMOW) ‰	$\delta^{2}H$ (VSMOW) ‰	Total Precip mm	$\delta^{18}O$ (VSMOW) ‰	$\delta^{2}H$ (VSMOW) ‰
6/26/2006	26 6	-7 82	-52 8	4 6	-8 6	-65 3		-7 73	
6/30/2006	43 9	-16 37	-112 2	51 5	-7 3	-54 0		-10 02	
7/1/2006		-5 16	-27 0						
7/8/2006		-4 18	-28 5						
7/15/2006		-6 02	-37 1		-6 1	-45 1		-7 4	
7/20/2006		-4 49		20 0	-3 7			-3 5	
7/24/2006		-4 49		13 6	-8 3			-7 92	
7/28/2006				57 2	-9 2				
7/31/2006	53 5	-10 01		22 1	-5 6			-6 27	
8/2/2006	11 3	-5 85							
8/6/2006		-6 12							
8/9/2006	7 1	-13 47					8 0	-14 2	
8/20/2006							8 9	-7 8	
8/26/2006	6 2	-4 45							
9/3/2006		-6 71			-8 1				
9/8/2006	1 00	-8 1							
9/12/2006		-5 09							
9/15/2006		-8 27							
9/18/2006					-6 6		8 9	-6 1	
9/23/2006	11 3	-6 42		15 3	-6 4		15 9	-7 2	
9/29/2006	36 2			36 8	-12 7	0 0	31 8	-14 1	
10/4/2006								-11 18	
10/17/2006	29 4	-15 68							
10/19/2006	29 4	-19 24							
10/22/2006	19 5	-16 5					31 8	-19 0	
10/27/2006	16 4	-19 0			-19 5		25 5	-20 4	
10/31/2006		-6 89							

Appendix D
Isotope and Geochemistry Results and Statistics

Table D1: Background Site - Field Parameters, Analytical Results and Statistics.

Site ID			P9-1A														
Type			Piezometer														
Depth			1 8 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	1 19	0 53	0 14	0 08	0 50	0 00	0 48	0 04	0 31	0 10	0 75	0 93	1 12	1 59	0 24
Temp (°C)	-	0 1	16 0	17 3	13 8	8 9	7 0	6 1	2 5	4 8	7 0	10 9	15 0	13 4	19 0	15 9	10 6
pH	-	0 01	6 8	6 9	6 9	7 2	7 2	7 2	7 3	7 1	7 2	7 3	7 2	7 2	7 2	7 1	7 1
SpC (µS/cm)	-	1	1999	1985	922	1327	1880	-	1544	1311	1153	982	768	945	946	881	1249
DO (mg/L)	0 01	0 01	-	-	-	-	-		-	-	-	-	-	3 2	-	3 2	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	646	391	599	399	274
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	142	148	156	146	150	162	126	135	128	143	147	143	153	136	156
Na^{+} (mg/L)	1 0	-	8 6	6 5	5 3	5 1	4 9	5 4	4 0	4 1	4 1	4 7	4 9	5 1	5 5	4 9	5 1
Mg^{2+} (mg/L)	1 0	-	31	30	32	32	32	33	26	27	28	31	30	31	32	30	33
K^{+} (mg/L)	1 0	-	3 9	2 4	2 1	1 8	1 9	1 6	1 2	1 3	1 3	1 4	1 7	2 0	2 0	2 2	1 8
Total P (mg/L)	0 001	0 002	-	0 020	0 58	-	0 77	0 15	0 31	0 24	0 65	0 65	0 26	0 89	0 32	0 062	0 047
NH_4^{+} (mg-N/L)	0 001	0 003	-	0 022	-	0 004	0 004	0 008	0 003	-	0 003	-	0 011	0 013	-	-	-
Cl (mg/L)	1 0	-	32	28	25	28	25	26	27	28	27	32	36	40	38	39	40
SO_4^{2} (mg/L)	1 0	-	97	102	102	106	95	108	102	106	99	102	102	97	102	87	-
NO_3 (mg-N/L)	0 001	0 002	0 67	1 0	1 3	1 4	0 89	1 0	0 86	0 80	0 63	0 56	0 54	0 44	0 38	0 21	0 80
HCO_3 (mg/L)	3 9	-	310	229	387	459	421	449	299	427	391	429	427	401	524	409	386
Calculations																	
pCO_2 (atm)	-	-	-1 35	-1 57	-1 37	-1 61	-1 59	-1 60	-1 93	-1 57	-1 65	-1 70	-1 60	-1 67	-1 44	-1 55	-1 59
$SI_{calcite}$	-	-	0 692	0 714	1 110	2 008	1 519	1 775	1 192	1 206	1 300	2 304	2 247	2 137	2 868	1 821	1 619
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	12 4	-	10 7	-	14 3	-	15 3	17 0	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	3 7	-	5 7	-	6 6	-	6 5	7 9	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	85	59	101	107	102	107	69	105	93	97	98	91	121	96	92
DOC (ppmC)	1 0	0 1	-	2 2	4 4	1 2	1 8	1 8	3 1	2 8	1 7	3 3	4 9	3 0	1 1	3 7	1 9
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-14 3	-15 6	-16 1	-15 9	-15 8	-16 8	-	16 7	-16 2	-15 8	-15 4	-15 6	-16 1	-16 3	-15 4
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-25 8	-22 4	-21 6	-26 8	-25 4	-27 3	-26 9	-27 4	-26 9	-26 8	-26 8	-26 5	-26 9	-27 1
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-10 6	-10 9	-10 7	-10 5	-10 5	-10 5	-10 4	-	-10 1	-9 9	-10 2	-10 2	-10 5	-10 2
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-75 3	-78 4	-76 5	-77 9	-75 8	-76 4	-75 2	-	-68 7	-	-65 5	-	-	-

Table D1: Background Site - Field Parameters, Analytical Results and Statistics.

Site ID	P9-1A																					
Type	Piezometer																					
Depth	1 8 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 00	0 20	0 75	1 19	4	0 52	0 62	0 08	1 59	5	0 32	0 28	0 00	0 50	3	0 15	0 14	0 04	0 31	3	0 53	0 49	0 00	1 59	15
Temp (°C)	15 9	2 4	13 4	19 0	4	13 3	3 5	8 9	17 3	5	5 2	2 4	2 5	7 0	3	7 6	3 1	4 8	10 9	3	11 2	5 0	2 5	19 0	15
pH	7 1	0 2	6 8	7 2	4	7 1	0 1	6 9	7 2	5	7 2	0 1	7 2	7 3	3	7 2	0 1	7 1	7 3	3	7 1	0 1	6 8	7 3	15
SpC (µS/cm)	1164	562	768	1999	4	1273	444	881	1985	5	1712	237	1544	1880	2	1149	165	982	1311	3	1278	423	768	1999	14
DO (mg/L)	3 2	-	3 2	3 2	1	3 2	-	3 2	3 2	1	-	-	-	-	-	-	-	-	-	-	3 2	0 01	3 2	3 2	2
Eh (mV)	546	136	391	646	3	336	88	274	399	2	-	-	-	-	-	-	-	-	-	-	462	156	274	646	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	146	5 0	142	153	4	148	8 4	136	156	5	146	18	126	162	3	135	7 8	128	143	3	145	10	126	162	15
Na^{+} (mg/L)	6 0	1 7	4 9	8 6	4	5 4	0 65	4 9	6 5	5	4 8	0 69	4 0	5 4	3	4 3	0 32	4 1	4 7	3	5 2	1 1	4 0	8 6	15
Mg^{2+} (mg/L)	31	0 67	30	32	4	31	1 1	30	33	5	30	3 6	26	33	3	29	1 9	27	31	3	31	2 0	26	33	15
K^{+} (mg/L)	2 4	1 0	1 7	3 9	4	2 1	0 27	1 8	2 4	5	1 6	0 35	1 2	1 9	3	1 3	0 10	1 3	1 4	3	1 9	0 66	1 2	3 9	15
Total P (mg/L)	0 49	0 35	0 26	0 89	3	0 18	0 27	0 020	0 58	4	0 41	0 32	0 15	0 77	3	0 52	0 24	0 24	0 65	3	0 38	0 29	0 020	0 89	13
NH_4^{+} (mg-N/L)	0 012	0 002	0 011	0 013	2	0 013	0 013	0 004	0 022	2	0 005	0 003	0 003	0 008	3	0 003	-	0 003	0 003	1	0 008	0 007	0 003	0 022	8
Cl (mg/L)	37	3 5	32	40	4	32	7 1	25	40	5	26	1 2	25	27	3	29	2 8	27	32	3	31	5 8	25	40	15
SO_4^{2} (mg/L)	100	2 8	97	102	4	99	8 5	87	106	4	101	6 5	95	108	3	102	3 5	99	106	3	100	5 4	87	108	14
NO_3 (mg-N/L)	0 51	0 13	0 38	0 67	4	0 94	0 47	0 21	1 38	5	0 92	0 08	0 86	1 00	3	0 66	0 12	0 56	0 80	3	0 76	0 33	0 21	1 38	15
HCO_3 (mg/L)	415	88	310	524	4	374	86	229	459	5	390	80	299	449	3	416	21	391	429	3	397	72	229	524	15
Calculations																									
pCO_2 (atm)	-1 51	0 15	-1 67	-1 35	4	-1 54	0 10	-1 61	-1 37	5	-1 71	0 19	-1 93	-1 59	3	-1 64	0 07	-1 70	-1 57	3	-1 59	0 14	-1 93	-1 35	15
$SI_{calcite}$	1 986	0 921	0 692	2 868	4	1 455	0 533	0 714	2 008	5	1 495	0 292	1 192	1 775	3	1 603	0 608	1 206	2 304	3	1 634	0 616	0 692	2 868	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	17 0	-	17 0	17 0	1	12 4	-	12 4	12 4	1	10 7	-	10 7	10 7	1	14 8	0 7	14 3	15 3	2	13 9	2 5	10 7	17 0	5
$\delta^{18}O_{NO3}$ (‰)	7 9	-	7 9	7 9	1	3 7	-	3 7	3 7	1	5 7	-	5 7	5 7	1	6 6	0 1	6 5	6 6	2	6 1	1 5	3 7	7 9	5
Carbon																									
DIC (ppmC)	99	16	85	121	4	91	19	59	107	5	93	21	69	107	3	99	6	93	105	3	95	15	59	121	15
DOC (ppmC)	3 0	1 9	1 1	4 9	3	2 7	1 3	1 2	4 4	5	2 2	0 8	1 8	3 1	3	2 6	0 8	1 7	3 3	3	2 6	1 2	1 1	4 9	14
$\delta^{13}C_{DIC}$ (‰)	-15 3	0 8	-16 1	-14 3	4	-15 8	0 4	-16 3	-15 4	5	-16 3	0 7	-16 8	-15 8	2	-16 2	0 4	-16 7	-15 8	3	-15 9	0 6	-16 8	-14 3	14
$\delta^{13}C_{DOC}$ (‰)	-26 7	0 2	-26 8	-26 5	3	-24 8	2 6	-27 1	-21 6	5	-26 5	1 0	-27 3	-25 4	3	-27 1	0 3	-27 4	-26 9	3	-26 0	1 8	-27 4	-21 6	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 1	0 2	-10 2	-9 9	3	-10 6	0 3	-10 9	-10 2	5	-10 5	0 0	-10 5	-10 5	3	-10 3	0 2	-10 4	-10 1	2	-10 4	0 3	-10 9	-9 9	13
$\delta^{2}H_{H2O}$ (‰)	-65 5	-	-65 5	-65 5	1	76 7	1 6	-78 4	-75 3	3	-76 7	1 1	-77 9	-75 8	3	-71 9	4 6	-75 2	-68 7	2	-74 4	4 4	-78 4	-65 5	9

Table D1: Background Site - Field Parameters, Analytical Results and Statistics.

Site ID			W9-A														
Type			Overburden Well														
Depth			6 6 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr 06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	4 069	2 509	3 376	2 764	2 174	1 194	2 209	1 439	1 944	0 439	3 066	2 352	4 839	3 362	2 862
Temp (°C)	-	0 1	12 5	12 1	12 7	10 8	9 9	8 7	7 7	7 6	7 0	8 6	10 0	12 0	13 6	12 4	12 5
pH	-	0 01	6 9	6 8	7 0	7 1	6 9	7 0	7 1	7 2	7 6	7 0	6 8	6 9	6 8	6 9	6 8
SpC (µS/cm)	-	1	-	1762	1163	1600	1744	1688	1703	1140	1245	1169	964	1135	1229	1302	1308
DO (mg/L)	0 01	0 01	-	-	-	-	-	0 2	0 8	0 5	0 3	-	0 4	0 1	0 3	0 3	-
Eh (mV)	-	1	-	-	-	-	-	-	209	132	288	-	933	200	946	259	312
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	214	214	204	208	193	216	158	166	161	188	173	194	174	186	188
Na^{+} (mg/L)	1 0	-	24	24	22	22	15	19	13	14	12	18	41	20	34	20	20
Mg^{2+} (mg/L)	1 0	-	30	33	33	36	24	24	18	20	14	24	18	28	24	36	31
K^{+} (mg/L)	1 0	-	5 4	5 3	5 1	5 3	4 0	4 9	3 3	3 7	3 0	3 8	4 1	4 6	3 9	3 9	4 8
Total P (mg/L)	0 001	0 002	0 020	0 008	<0 65	<0 65	0 093	0 016	0 023	0 024	0 023	0 022	0 053	0 034	0 027	0 032	0 098
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	-	0 11	0 043	0 081	0 035	0 066	0 016	0 036	0 011	0 087	-	-	-
Cl (mg/L)	1 0	-	22	21	20	20	15	18	19	19	16	21	51	22	39	19	22
SO_4^{2} (mg/L)	1 0	-	-	91	107	110	72	91	87	95	60	90	55	95	71	89	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	0 30	<0 001	0 14	<0 001	0 24	<0 001	0 21
HCO_3 (mg/L)	3 9	-	591	361	720	735	551	732	293	645	695	591	529	603	714	980	473
Calculations																	
pCO_2 (atm)	-	-	-1 18	-1 30	-1 14	-1 28	-1 16	-1 20	-1 68	-1 41	-1 80	-1 25	-1 17	-1 16	-0 97	-0 95	-1 18
$SI_{calcite}$	-	-	2 024	0 986	2 533	3 357	1 363	2 664	1 027	2 600	7 103	1 761	1 170	1 772	1 560	2 667	1 202
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	7 9	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-2 3	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	156	101	185	178	154	187	72	155	148	155	149	161	203	261	133
DOC (ppmC)	1 0	0 1	6 9	4 2	9 3	6 2	5 7	6 6	8 1	4 7	4 5	6 6	8 8	6 3	4 1	11 1	4 0
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-13 0	-14 3	-14 3	-14 5	-15 3	-16 2	-	-15 2	-16 1	-15 4	-15 7	-15 0	-15 7	-14 9	-14 6
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-24 0	-22 6	-24 0	-23 3	-27 1	-26 8	-	-27 0	-27 0	-26 8	-26 8	-26 9	-26 7	-27 0	-27 1
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 8	-10 3	-10 4	-10 4	-9 5	-9 9	-10 6	-10 6	-	-10 5	-10 3	-10 7	-10 5	-10 4	-10 5
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-74 2	-74 9	-70 5	-73 4	-69 3	-70 9	-76 3	-82 8	-	-74 6	-	-67 1	-	-	-

Table D1: Background Site - Field Parameters, Analytical Results and Statistics.

Site ID	W9-A																					
Type	Overburden Well																					
Depth	6 6 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	3 58	1 09	2 35	4 84	4	2 97	0 38	2 51	3 38	5	1 86	0 58	1 19	2 21	3	1 27	0 77	0 44	1 94	3	2 57	1 12	0 44	4 84	15
Temp (°C)	12 0	1 5	10 0	13 6	4	12 1	0 8	10 8	12 7	5	8 8	1 1	7 7	9 9	3	7 7	0 8	7 0	8 6	3	10 5	2 2	7 0	13 6	15
pH	6 9	0 1	6 8	6 9	4	6 9	0 1	6 8	7 1	5	7 0	0 1	6 9	7 1	3	7 2	0 3	7 0	7 6	3	7 0	0 2	6 8	7 6	15
SpC (µS/cm)	1109	135	964	1229	3	1427	246	1163	1762	5	1712	29	1688	1744	3	1185	54	1140	1245	3	1368	272	964	1762	14
DO (mg/L)	0 2	0 1	0 1	0 4	3	0 3	-	0 3	0 3	1	0 5	0 4	0 2	0 8	2	0 4	0 2	0 3	0 5	2	0 3	0 21	0 1	0 8	8
Eh (mV)	693	427	200	946	3	286	37	259	312	2	209		209	209	1	210	110	132	288	2	410	332	132	946	8
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	189	20	173	214	4	200	12	186	214	5	189	29	158	216	3	172	15	161	188	3	189	20	158	216	15
Na^{+} (mg/L)	29 9	9 3	20 5	41 0	4	21 4	1 7	19 7	23 8	5	15 9	3 0	13 2	19 1	3	14 9	2 9	12 4	18 1	3	21 2	7 6	12 4	41 0	15
Mg^{2+} (mg/L)	25	5 4	18	30	4	34	2 1	31	36	5	22	3 7	18	24	3	19	5 0	14	24	3	26	6 8	14	36	15
K^{+} (mg/L)	4 5	0 66	3 9	5 4	4	4 9	0 57	3 9	5 3	5	4 1	0 8	3 3	4 9	3	3 5	0 43	3 0	3 8	3	4 3	0 77	3 0	5 4	15
Total P (mg/L)	0 033	0 014	0 020	0 053	4	0 046	0 046	0 008	0 098	3	0 044	0 042	0 016	0 093	3	0 023	0 001	0 022	0 024	3	0 036	0 028	0 008	0 098	13
NH_4^{+} (mg-N/L)	0 049	0 053	0 011	0 087	2	0 107	-	0 107	0 107	1	0 053	0 025	0 035	0 081	3	0 040	0 025	0 016	0 066	3	0 054	0 033	0 011	0 107	9
Cl (mg/L)	34	14	22	51	4	20	1 0	19	22	5	17	2 0	15	19	3	19	2 5	16	21	3	23	9 5	15	51	15
SO_4^{2} (mg/L)	73	20	55	95	3	99	11	89	110	4	83	10	72	91	3	82	19	60	95	3	86	16 7	55	110	13
NO_3 (mg-N/L)	0 19	0 07	0 14	0 24	2	0 21	-	0 21	0 21	1	-	-	-	-	-	0 30	-	0 30	0 30	1	0 22	0 07	0 14	0 30	4
HCO_3 (mg/L)	609	77	529	714	4	654	243	361	980	5	525	220	293	732	3	644	52	591	695	3	614	167	293	980	15
Calculations																									
pCO_2 (atm)	-1 12	0 10	-1 18	-0 97	4	-1 17	0 14	-1 30	-0 95	5	-1 35	0 29	-1 68	-1 16	3	-1 49	0 28	-1 80	-1 25	3	-1 26	0 23	-1 80	-0 95	15
$SI_{calcite}$	1 631	0 361	1 170	2 024	4	2 149	1 016	0 986	3 357	5	1 685	0 865	1 027	2 664	3	3 821	2 873	1 761	7 103	3	2 253	1 523	0 986	7 103	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	7 9	-	7 9	7 9	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7 9	-	7 9	7 9	1
$\delta^{18}O_{NO3}$ (‰)	-2 3	-	-2 3	-2 3	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-2 3	-	-2 3	-2 3	1
Carbon																									
DIC (ppmC)	167	24	149	203	4	172	61	101	261	5	138	59	72	187	3	153	4	148	155	3	160	43	72	261	15
DOC (ppmC)	6 6	1 9	4 1	8 8	4	7 0	3 1	4 0	11 1	5	6 8	1 2	5 7	8 1	3	5 3	1 1	4 5	6 6	3	6 5	2 1	4 0	11 1	15
$\delta^{13}C_{DIC}$ (‰)	-14 8	1 2	-15 7	-13 0	4	-14 5	0 2	-14 9	-14 3	5	-15 8	0 6	-16 2	-15 3	2	-15 6	0 5	-16 1	-15 2	3	-15 0	0 8	-16 2	-13 0	14
$\delta^{13}C_{DOC}$ (‰)	-26 1	1 4	-26 9	-24 0	4	-24 8	2 1	-27 1	-22 6	5	-27 0	0 2	-27 1	-26 8	2	-26 9	0 1	-27 0	-26 8	3	-25 9	1 6	-27 1	-22 6	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 6	0 2	-10 8	-10 3	4	-10 4	0 1	-10 5	-10 3	5	-10 0	0 6	-10 6	-9 5	3	-10 6	0 0	-10 6	-10 5	2	-10 4	0 3	-10 8	-9 5	14
$\delta^{2}H_{H2O}$ (‰)	-70 7	5 0	-74 2	-67 1	2	-72 9	2 2	-74 9	-70 5	3	72 2	3 7	-76 3	-69 3	3	-78 7	5 8	-82 8	-74 6	2	-73 4	4 4	-82 8	-67 1	10

Table D1: Background Site - Field Parameters, Analytical Results and Statistics

Site ID			W9-B														
Type			Bedrock Well														
Depth			17 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	2 439	1 994	1 821	1 621	1 471	1 161	1 401	1 091	1 146	1 118	2 663	2 038	2 368	1 976	1 521
Temp (°C)	-	0 1	12 5	12 3	12 0	9 9	10 5	9 3	9 0	10 2	12 4	10 4	11 0	10 9	12 4	12 6	10 6
pH	-	0 01	6 8	6 4	7 3	7 2	7 0	7 2	7 2	6 9	7 0	7 0	7 3	7 2	7 1	7 3	7 2
SpC (µS/cm)	-	1	-	1932	869	1249	1438	1265	1605	1295	1106	981	764	821	957	882	998
DO (mg/L)	0 01	0 01	-	-	-	-	0 1	0 2	0 3	0 2	-	-	0 1	0 2	0 1	0 2	-
Eh (mV)	-	1	-	-	-	-	-	-	119	162	-	-	197	157	366	172	108
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	114	105	126	139	126	131	126	111	117	135	130	120	103	104	99
Na^{+} (mg/L)	1 0	-	9	9	11	12	12	11	15	9	12	13	17	11	11	8	12
Mg^{2+} (mg/L)	1 0	-	38	37	41	39	36	39	32	33	33	39	37	39	40	35	39
K^{+} (mg/L)	1 0	-	2 4	2 4	2 5	2 9	2 9	2 8	2 5	2 3	2 4	2 9	2 6	2 7	2 6	2 3	2 8
Total P (mg/L)	0 001	0 002	0 010	0 019	0 016	<0 65	<0 65	0 055	0 021	0 030	0 17	0 042	0 24	0 048	0 063	0 039	0 042
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 057	0 075	0 063	0 057	0 071	-	0 061	0 059	0 041	0 093	-	-	
Cl (mg/L)	1 0	-	10	10	12	11	13	11	19	12	15	13	19	10	9 4	8 2	10
SO_4^{2} (mg/L)	1 0	-	68	73	73	63	72	70	81	77	78	82	66	64	49	62	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	0 013
HCO_3 (mg/L)	3 9	-	342	166	541	525	471	347	312	421	507	463	498	462	580	605	357
Calculations																	
pCO_2 (atm)	-	-	-1 31	-1 23	-1 60	-1 48	-1 35	-1 72	-1 72	-1 35	-1 36	-1 36	-1 60	-1 61	-1 38	-1 52	-1 72
$SI_{calcite}$	-	-	0 550	0 101	2 702	1 932	1 081	1 400	1 081	0 772	1 312	1 132	2 266	1 880	1 590	2 430	1 237
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	97	69	122	125	122	81	74	112	126	119	114	107	140	137	83
DOC (ppmC)	1 0	0 1	2 8	1 4	5 9	3 6	2 3	2 6	5 7	3 0	2 7	4 4	5 5	3 8	1 7	5 7	2 4
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-13 5	-14 2	-14 7	-14 2	-14 1	-14 4	-7 8	14 4	-14 0	-14 3	-13 5	-14 5	-15 0	-14 5	-14 9
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-23 2	-26 2	-22 6	-23 0	-26 9	-26 7	-27 1	-27 2	-27 3	-27 1	-27 9	-27 5	-31 4	-27 8	-30 2
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 4	-10 4	-10 4	-10 4	-10 2	-10 4	-10 2	-10 3	-	-8 4	-	-10 3	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-73 1	-75 9	-69 1	-73 7	-75 2	75 1	-74 1	-71 6	-	-67 8	-	-64 1	-	-	-

Table D1: Background Site - Field Parameters, Analytical Results and Statistics.

Site ID	W9-B																						
Type	Bedrock Well																						
Depth	17 5 mbgs																						
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	2 38	0 26	2 04	2 66	4	1 79	0 21	1 52	1 99	5	1 34	0 16	1 16	1 47	3	1 12	0 03	1 09	1 15	3	1 72	0 51	1 09	2 66	15
Temp (°C)	11 7	0 9	10 9	12 5	4	11 5	1 2	9 9	12 6	5	9 6	0 8	9 0	10 5	3	11 0	1 2	10 2	12 4	3	11 1	1 2	9 0	12 6	15
pH	7 1	0 2	6 8	7 3	4	7 1	0 4	6 4	7 3	5	7 1	0 1	7 0	7 2	3	7 0	0 1	6 9	7 0	3	7 1	0 2	6 4	7 3	15
SpC (µS/cm)	847	99	764	957	3	1186	444	869	1932	5	1436	170	1265	1605	3	1127	158	981	1295	3	1155	333	764	1932	14
DO (mg/L)	0 2	0 1	0 1	0 2	3	0 2	-	0 2	0 2	1	0 2	0 1	0 1	0 3	3	0 2	-	0 2	0 2	1	0 2	0 1	0 1	0 3	8
Eh (mV)	240	111	157	366	3	140	45	108	172	2	119	-	119	119	1	162	-	162	162	1	183	86	108	366	7
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	117	11	103	130	4	114	17	99	139	5	128	3 1	126	131	3	121	12	111	135	3	119	13	99	139	15
Na^{+} (mg/L)	12	3 4	9 1	17	4	10 3	1 9	8 1	12 3	5	13	2 2	11	15 3	3	11	1 7	9 3	13	3	11	2 3	8 1	17	15
Mg^{2+} (mg/L)	39	1 2	37	40	4	38	2 3	35	41	5	36	3 6	32	39	3	35	3 5	33	39	3	37	2 8	32	41	15
K^{+} (mg/L)	2 6	0 14	2 4	2 7	4	2 6	0 28	2 3	2 9	5	2 7	0 21	2 5	2 9	3	2 5	0 32	2 3	2 9	3	2 6	0 23	2 3	2 9	15
Total P (mg/L)	0 090	0 10	0 010	0 24	4	0 03	0 01	0 02	0 04	4	0 038	0 025	0 021	0 055	2	0 081	0 079	0 030	0 172	3	0 061	0 067	0 010	0 24	13
NH_4^{+} (mg-N/L)	0 067	0 037	0 041	0 093	2	0 066	-	0 057	0 075	2	0 064	0 007	0 057	0 071	3	0 060	0 001	0 059	0 061	2	0 064	0 015	0 041	0 093	9
Cl (mg/L)	12	4 4	9 4	19	4	10	1 4	8 2	12	5	14	4 3	11	19	3	13	1 6	12	15	3	12	3 2	8 2	19	15
SO_4^{2} (mg/L)	62	8 5	49	68	4	68	6 4	62	73	4	74	5 9	70	81	3	79	2 7	77	82	3	70	8 8	49	82	14
NO_3 (mg-N/L)	-	-	-	-	-	0 013	-	0 013	0 013	1	-	-	-	-	-	-	-	-	-	-	0 013	-	0 013	0 013	1
HCO_3 (mg/L)	471	99	342	580	4	439	178	166	605	5	377	84	312	471	3	464	43	421	507	3	440	117	166	605	15
Calculations																									
pCO_2 (atm)	-1 48	0 15	-1 61	-1 31	4	-1 51	0 18	-1 72	-1 23	5	-1 60	0 22	-1 72	-1 35	3	-1 35	0 01	-1 36	-1 35	3	-1 49	0 17	-1 72	-1 23	15
$SI_{calcite}$	1 57	0 73	0 55	2 27	4	1 68	1 04	0 10	2 70	5	1 19	0 18	1 08	1 40	3	1 07	0 28	0 77	1 31	3	1 431	0 715	0 101	2 702	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	114	18	97	140	4	107	30	69	137	5	92	26	74	122	3	119	7	112	126	3	108	23	69	140	15
DOC (ppmC)	3 4	1 6	1 7	5 5	4	3 8	2 0	1 4	5 9	5	3 5	1 9	2 3	5 7	3	3 3	0 9	2 7	4 4	3	3 5	1 5	1 4	5 9	15
$\delta^{13}C_{DIC}$ (‰)	-14 1	0 8	-15 0	-13 5	4	-14 5	0 3	-14 9	-14 2	5	-12 1	3 7	-14 4	-7 8	3	-14 3	0 2	-14 4	-14 0	3	-13 9	1 7	-15 0	-7 8	15
$\delta^{13}C_{DOC}$ (‰)	-27 5	3 3	-31 4	-23 2	4	-25 9	3 2	-30 2	-22 6	5	-26 9	0 2	-27 1	-26 7	3	-27 2	0 1	-27 3	-27 1	3	-26 8	2 4	-31 4	-22 6	15
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 4	0 1	-10 4	-10 3	2	-10 4	0 0	-10 4	-10 4	3	-10 3	0 1	-10 4	-10 2	3	-9 3	1 3	-10 3	-8 4	2	-10 1	0 6	-10 4	-8 4	10
$\delta^{2}H_{H2O}$ (‰)	-68 6	6 4	-73 1	-64 1	2	-72 9	3 5	-75 9	-69 1	3	-74 8	0 6	-75 2	-74 1	3	-69 7	2 7	-71 6	-67 8	2	-72 0	3 8	-75 9	-64 1	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID																	
Type																	
Depth																	
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	17 6	17 8	12 3	6 5	-	-	-	-	8 6	18 2	20 2	26 7	24 8	18 6	16 8
pH	-	0 01	7 1	7 3	7 2	7 2	-	-		-	7 7	7 5	7 0	7 1	6 9	7 0	7 1
SpC (µS/cm)	-	1	-	1477	787	1019	-	-	-	-	372	239	333	-	-	-	500
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	261
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	74	-	72	76	-	-	-	-	37	30	41	53	49	50	41
Na^{+} (mg/L)	1 0	-	15	-	16	14	-	-	-	-	4	4	8	10	9	10	8
Mg^{2+} (mg/L)	1 0	-	28	-	28	28	-	-	-	-	12	10	15	20	17	19	15
K^{+} (mg/L)	1 0	-	1 1	-	0 69	<1 0	-	-	-	-	0 59	1 1	0 9	0 7	0 8	0 6	0 4
Total P (mg/L)	0 001	0 002	<0 65	<0 65	-	<0 65	-	-	-	-	0 94	0 046	0 017	0 022	0 043	0 016	0 033
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 073	0 015	-	-	-	-	0 022	0 035	0 054	0 018	-		
Cl (mg/L)	1 0	-	30	58	-	39	-	-	-	-	24	11	8 8	6 6	4 7	3 9	2 3
SO_4^{2} (mg/L)	1 0	-	57	85	-	83	-	-	-	-	17	21	26	25	20	24	-
NO_3 (mg-N/L)	0 001	0 002	3 9	<0 001	<0 001	2 0	-	-	-	-	2 3	6 1	5 0	7 5	15	8 1	1 8
HCO_3 (mg/L)	3 9	-	-	161	241	239	-	-	-	-	126	125	148	206	165	187	170
Calculations																	
pCO_2 (atm)	-	-	-	-2 06	-1 90	-1 90	-	-	-	-	2 69	-2 36	-1 86	-1 77	-1 60	-1 75	-1 91
$SI_{calcite}$	-	-	-	-	0 730	0 549	-	-	-	-	0 590	0 356	0 226	0 594	0 224	0 303	0 286
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	5 0	-	-	-	-	-	6 5	5 9	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-0 7	-	-	-	-	-	-4 2	-3 9	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	36	55	56	-	-	-	-	26	27	36	47	43	46	40
DOC (ppmC)	1 0	0 1	-	6 9	4 8	4 1	-	-	-	-	11	25	8 1	5 5	4 4	5 2	3 1
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-7 4	-8 7	-9 4	-	-	-	-	-12 9	-13 3	-11 9	-13 7	-14 8	-13 8	-13 1
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-26 2	-21 5	-21 9	-	-	-	-	-25 7	-26 8	-23 7	-26 2	-25 5	-25 9	-25 1
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-9 6	-8 8	-	-	-	-10 0	-	-10 4	-	-10 7	-	-9 6	-9 1
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-66 9	-63 0	-	-	-	-70 4	-	-75 1		-79 8	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	L1-1A																								
Type	Lysimeter																								
Depth	0 3 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	22 3	4 2	17 6	26 7	4	14 4	5 0	6 5	18 6	5	-	-	-	-	-	13 4	6 8	8 6	18 2	2	17 1	6 1	6 5	26 7	11
pH	7 0	0 1	6 9	7 1	4	7 2	0 1	7 0	7 3	5	-	-	-	-	-	7 6	0 2	7 5	7 7	2	7 2	0 2	6 9	7 7	11
SpC (µS/cm)	333	-	333	333	1	946	413	500	1477	4	-	-	-	-	-	305	94	239	372	2	675	448	239	1477	7
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Eh (mV)	-	-	-	-	-	261	-	261	261	1	-	-	-	-	-	-	-	-	-	-	261	-	261	261	1
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	54	14	41	74	4	60	17	41	76	4	-	-	-	-	-	33	4 7	30	37	2	52	16	30	76	10
Na^{+} (mg/L)	10 5	3 0	7 8	14 8	4	12 1	3 6	8 2	15 7	4	-	-	-	-	-	4 3	0 11	4 2	4 4	2	9 9	4 1	4 2	15 7	10
Mg^{2+} (mg/L)	20	5 4	15	28	4	23	6 7	15	28	4	-	-	-	-	-	11	1 4	10	12	2	19	6 6	10	28	10
K^{+} (mg/L)	0 86	0 17	0 71	1 09	4	0 56	0 13	0 43	0 69	3	-	-	-	-	-	0 86	0 37	0 59	1 12	2	0 76	0 23	0 43	1 1	9
Total P (mg/L)	0 027	0 014	0 017	0 043	3	0 024	0 012	0 016	0 033	2	-	-	-	-	-	0 491	0 629	0 046	0 936	2	0 159	0 343	0 016	0 936	7
NH_4^{+} (mg-N/L)	0 036	0 025	0 018	0 054	2	0 044	0 041	0 015	0 073	2	-	-	-	-	-	0 029	0 010	0 022	0 035	2	0 036	0 023	0 015	0 073	6
Cl (mg/L)	12	12	4 7	30	4	26	27	2 3	58	4	-	-	-	-	-	17	9 1	11	24	2	19	18 5	2 3	58	10
SO_4^{2} (mg/L)	32	17	20	57	4	64	35	24	85	3	-	-		-	-	19	2 9	17	21	2	40	27 8	17	85	9
NO_3 (mg-N/L)	7 7	4 8	3 9	15	4	4 0	3 6	1 8	8 1	3	-	-	-	-	-	4 21	2 6	2 3	6 1	2	5 7	4 0	1 8	15	9
HCO_3 (mg/L)	173	30	148	206	3	199	38	161	241	5	-	-	-	-	-	126	1	125	126	2	177	41	125	241	10
Calculations																									
pCO_2 (atm)	-1 74	0 13	-1 86	-1 60	3	-1 90	0 11	-2 06	-1 75	5	-	-	-	-	-	-2 53	0 23	-2 69	-2 36	2	-1 98	0 32	-2 69	-1 60	10
$SI_{calcite}$	0 348	0 213	0 224	0 594	3	0 467	0 213	0 286	0 730	4	-	-	-	-	-	0 473	0 166	0 356	0 590	2	0 429	0 188	0 224	0 730	9
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
$\delta^{15}N_{NO3}$ (‰)	5 9	-	5 9	5 9	1	5 0	-	5 0	5 0	1	-	-	-	-	-	6 5	-	6 5	6 5	1	5 8	0 8	5 0	6 5	3
$\delta^{18}O_{NO3}$ (‰)	-3 9	-	-3 9	-3 9	1	-0 7	-	-0 7	-0 7	1	-	-	-	-	-	-4 2	-	-4 2	-4 2	1	-2 9	1 9	-4 2	-0 7	3
Carbon																									
DIC (ppmC)	42	6	36	47	3	47	9	36	56	5	-	-	-	-	-	27	0	26	27	2	41	10	26	56	10
DOC (ppmC)	6 0	1 9	4 4	8 1	3	4 8	1 4	3 1	6 9	5	-	-	-	-	-	18 3	10 2	11 1	25 5	2	7 9	6 6	3 1	25 5	10
$\delta^{13}C_{DIC}$ (‰)	-13 5	1 5	-14 8	-11 9	3	-10 5	2 8	-13 8	-7 4	5	-	-	-	-	-	-13 1	0 3	-13 3	-12 9	2	-11 9	2 5	-14 8	-7 4	10
$\delta^{13}C_{DOC}$ (‰)	-25 1	1 3	-26 2	-23 7	3	-24 1	2 3	-26 2	-21 5	5	-	-	-	-	-	-26 2	0 7	-26 8	-25 7	2	-24 8	1 9	-26 8	-21 5	10
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 7	-	-10 7	-10 7	1	-9 3	0 4	-9 6	-8 8	4	-	-	-	-	-	-10 2	0 3	-10 4	-10 0	2	-9 7	0 7	-10 7	-8 8	7
$\delta^{2}H_{H2O}$ (‰)	-79 8	-	-79 8	-79 8	1	-65 0	2 8	-66 9	-63 0	2	-	-	-	-	-	-72 7	3 3	-75 1	-70 4	2	-71 0	6 6	-79 8	-63 0	5

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID			L1-1B														
Type			Lysimeter														
Depth			0 9 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	17 5	16 5	12 3	6 9	4 1	3 2	4 6	-	5 7	11 4	18 0	22 0	21 0	15 2	12 2
pH	-	0 01	7 1	7 3	7 4	7 1	6 9	7 3	7 1		7 1	7 0	7 0	6 9	6 8	6 9	6 9
SpC (µS/cm)	-	1	1518	1488	713	1017	1431	1149	880	-	392	419	368	426	487	-	649
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	3 9	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	411	233	-	296
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	87	90	80	86	79	72	62	-	42	46	48	55	61	63	55
Na^{+} (mg/L)	1 0	-	12	12	11	11	10	9 0	8 0	-	6 1	6 7	7 1	8 4	10	10	9 1
Mg^{2+} (mg/L)	1 0	-	30	31	28	28	27	25	22	-	15	17	17	19	21	22	19
K^{+} (mg/L)	1 0	-	<1 0	<1 0	0 51	<1 0	0 96	0 37	0 38	-	0 40	0 39	0 40	0 42	0 50	0 59	0 45
Total P (mg/L)	0 001	0 002	0 0001	0 008	0 005	<0 65	0 024	<0 65	0 023	<0 11	0 023	0 029	<0 65	0 033	0 031	0 033	0 038
NH_4^{+} (mg-N/L)	0 001	0 003	-	0 005	0 068	0 014	0 004	0 004	-	-	0 019	0 027	0 025	0 008	-	-	-
Cl (mg/L)	1 0	-	41	40	-	39	42	35	34	18	18	17	17	16	16	14	13
SO_4^{2} (mg/L)	1 0	-	36	35	-	33	34	33	32	18	25	20	25	28	29	26	-
NO_3 (mg-N/L)	0 001	0 002	9 3	1 9	-	0 88	1 8	1 6	2 0	2 1	2 4	2 2	3 2	3 7	4 9	5 5	5 8
HCO_3 (mg/L)	3 9	-	275	258	336	327	253	197	160	-	153	160	181	191	220	192	188
Calculations																	
pCO_2 (atm)	-	-	-1 62	1 87	-1 95	-1 67	-1 55	-2 04	-1 97	-	-1 98	-1 83	-1 70	-1 60	-1 47	-1 59	-1 67
$SI_{calcite}$	-	-	0 735	1 125	1 754	0 699	0 264	0 437	0 232	-	0 164	0 180	0 241	0 287	0 293	0 232	0 207
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		4 7	-	-	5 6	-	6 3	-	5 0	-	6 4	6 8	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		1 6	-	-	1 8	-	3 3	-	5 6	-	0 7	-0 3	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	66	58	73	80	72	46	40	-	38	41	46	49	59	52	50
DOC (ppmC)	1 0	0 1	-	2 1	3 8	2 6	1 9	2 2	3 8	-	5 4	6 0	6 9	3 6	2 0	3 8	2 7
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-13 6	-9 5	-10 3	-10 2	-10 8	-11 1	-11 7	-	-13 1	-12 7	-11 9	-12 9	-13 5	-13 2	-13 2
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-33 3	-19 8	-19 8	-24 6	-24 3	-25 0	-	-27 2	-26 9	-26 7	-26 2	-26 2	-25 6	-25 8
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 0	-10 7	-10 7	-10 7	-10 4	-10 1	-10 0	10 7		-7 4	-9 4	-11 0	-10 4	-10 6	-10 8
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-77 4	-76 3	-74 7	-75 7	-77 1	-72 3	-70 2	-70 5	-	-64 1	-	-84 3	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	L1-1B																								
Type	Lysimeter																								
Depth	0 9 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	19 6	2 2	17 5	22 0	4	12 6	3 7	6 9	16 5	5	4 0	0 7	3 2	4 6	3	8 6	4 0	5 7	11 4	2	12 2	6 4	3 2	22 0	14
pH	6 9	0 1	6 8	7 1	4	7 1	0 2	6 9	7 4	5	7 1	0 2	6 9	7 3	3	7 0	0 1	7 0	7 1	2	7 0	0 2	6 8	7 4	14
SpC (µS/cm)	700	548	368	1518	4	967	383	649	1488	4	1153	276	880	1431	3	405	20	392	419	2	841	439	368	1518	13
DO (mg/L)	3 9	-	3 9	3 9	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3 9	-	3 9	3 9	1
Eh (mV)	322	126	233	411	2	296	-	296	296	1	-	-	-	-	-	-	-	-	-	-	313	90	233	411	3
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	63	17	48	87	4	75	15	55	90	5	71	8 8	62	79	3	44	3 2	42	46	2	66	16	42	90	14
Na^{+} (mg/L)	9 2	2 0	7 1	11 7	4	10 5	1 1	9 1	11 9	5	8 9	0 90	8 0	9 8	3	6 4	0 45	6 1	6 7	2	9 2	1 8	6 1	11 9	14
Mg^{2+} (mg/L)	22	5 7	17	30	4	26	5 1	19	31	5	25	2 8	22	27	3	16	1 3	15	17	2	23	5 3	15	31	14
K^{+} (mg/L)	0 44	0 05	0 40	0 5	3	0 52	0 07	0 45	0 59	3	0 57	0 34	0 37	1 0	3	0 4	0 01	0 39	0 40	2	0 49	0 17	0 37	1 0	11
Total P (mg/L)	0 022	0 019	0 000	0 033	3	0 021	0 017	0 005	0 038	4	0 023	0 000	0 023	0 024	2	0 026	0 004	0 023	0 029	2	0 023	0 013	0 000	0 038	11
NH_4^{+} (mg-N/L)	0 016	0 012	0 008	0 025	2	0 029	0 034	0 005	0 068	3	0 004	0 000	0 004	0 004	2	0 023	0 006	0 019	0 027	2	0 019	0 020	0 004	0 068	9
Cl (mg/L)	22	13	16	41	4	26	15	13	40	4	37	3 9	34	42	3	18	0 67	17	18	3	26	12	13	42	14
SO_4^{2} (mg/L)	30	4 4	25	36	4	31	4 7	26	35	3	33	0 7	32	34	3	21	3 3	18	25	3	29	5 6	18	36	13
NO_3 (mg-N/L)	5 3	2 8	3 2	9 31	4	3 5	2 5	0 9	5 8	4	1 8	0 19	1 6	2 0	3	2 2	0 12	2 1	2 4	3	3 4	2 3	0 88	9 3	14
HCO_3 (mg/L)	217	42	181	275	4	260	71	188	336	5	203	47	160	253	3	157	5	153	160	2	221	60	153	336	14
Calculations																									
pCO_2 (atm)	-1 60	0 10	-1 70	-1 47	4	-1 75	0 15	-1 95	-1 59	5	-1 85	0 26	-2 04	-1 55	3	-1 90	0 11	-1 98	-1 83	2	-1 75	0 18	-2 04	-1 47	14
$SI_{calcite}$	0 389	0 232	0 241	0 735	4	0 804	0 652	0 207	1 754	5	0 311	0 110	0 232	0 437	3	0 172	0 011	0 164	0 180	2	0 489	0 457	0 164	1 754	14
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	5 8	1 5	4 7	6 8	2	5 6	-	5 6	5 6	1	6 3	-	6 3	6 3	1	5 7	1 0	5 0	6 4	2	5 8	0 8	4 7	6 8	6
$\delta^{18}O_{NO3}$ (‰)	0 7	1 3	-0 3	1 6	2	1 8	-	1 8	1 8	1	3 3	-	3 3	3 3	1	3 2	3 5	0 7	5 6	2	2 1	2 1	-0 3	5 6	6
Carbon																									
DIC (ppmC)	55	9	46	66	4	63	13	50	80	5	53	17	40	72	3	39	2	38	41	2	55	13	38	80	14
DOC (ppmC)	4 2	2 5	2 0	6 9	3	3 0	0 8	2 1	3 8	5	2 7	1 0	1 9	3 8	3	5 7	0 5	5 4	6 0	2	3 6	1 6	1 9	6 9	13
$\delta^{13}C_{DIC}$ (‰)	-13 0	0 8	-13 6	-11 9	4	-11 3	1 8	-13 2	-9 5	5	-11 2	0 5	-11 7	-10 8	3	-12 9	0 3	-13 1	-12 7	2	-12 0	1 4	-13 6	-9 5	14
$\delta^{13}C_{DOC}$ (‰)	-26 4	0 3	-26 7	-26 2	3	-24 9	5 6	-33 3	-19 8	5	-24 6	0 3	-25 0	-24 3	3	-27 1	0 2	-27 2	-26 9	2	-25 5	3 4	-33 3	-19 8	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 4	0 8	-11 0	-9 4	4	-10 7	0 0	-10 8	-10 6	5	-10 2	0 2	-10 4	-10 0	3	-9 1	2 3	-10 7	-7 4	2	-10 3	0 9	-11 0	-7 4	14
$\delta^{2}H_{H2O}$ (‰)	-80 9	4 9	-84 3	-77 4	2	-75 6	0 8	-76 3	-74 7	3	-73 2	3 5	-77 1	-70 2	3	-67 3	4 5	-70 5	-64 1	2	-74 3	5 4	-84 3	-64 1	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID			L1-1C														
Type			Lysimeter														
Depth			1 8 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	15 8	17	12 2	7 3	5 1	5 8	5 4	4 7	8	9	17	19 2	20	14 9	10 4
pH	-	0 01	7 5	7 4	7 9	7 1	7 0	7 2	7 2	7 5	7 7	7 0	7 3	7 0	7 1	7 4	7 1
SpC (µS/cm)	-	1	1392	1654	892	1175	1669	1453	996	-	835	772	570	589	686	799	998
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	2 4	-	1 4	2 5	
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	403	414	384	302
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	92	99	93	100	98	98	72	59	74	83	81	86	92	96	87
Na^{+} (mg/L)	1 0	-	11	11	12	15	12	11	18	16	14	14	12	13	12	11	11
Mg^{2+} (mg/L)	1 0	-	34	38	34	34	34	35	25	20	25	29	28	29	32	34	31
K^{+} (mg/L)	1 0	-	2 1	2 4	2 1	1 7	1 3	1 2	1 1	1 7	1 3	1 3	1 2	1 3	1 8	2 0	1 7
Total P (mg/L)	0 001	0 002	0 008	<0 65	0 007	<0 65	0 038	<0 11	0 025	<0 11	0 022	0 18	0 029	0 032	0 042	0 032	0 055
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 043	0 007	0 012	0 012	0 002	0 033	0 021	0 043	0 019	0 005	-	-	-
Cl (mg/L)	1 0	-	36	37	-	32	44	37	37	33	35	35	30	30	29	29	25
SO_4^{2} (mg/L)	1 0	-	17	18	-	26	27	23	30	23	28	27	26	27	26	23	-
NO_3 (mg-N/L)	0 001	0 002	3 3	4 0	-	2 4	3 4	3 7	3 9	2 4	1 8	3 3	5 9	2 6	3 6	4 5	4 0
HCO_3 (mg/L)	3 9	-	351	136	451	389	317	252	278	239	335	273	345	301	405	394	291
Calculations																	
pCO_2 (atm)	-	-	-1 97	-2 23	-2 28	-1 59	-1 53	-1 85	-1 86	-2 19	-2 21	-1 59	-1 74	-1 56	-1 47	-1 78	-1 69
$SI_{calcite}$	-	-	2 527	0 819	7 335	0 946	0 489	0 670	0 625	0 803	2 346	0 441	1 384	0 832	1 307	2 056	0 712
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		7 0	-	-	6 3	-	-	-	8 2	2 0	7 6	8 2	-	-	-	9 5
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		3 9	-	-	1 0	-	-	-	2 0	1 8	-2 1	-6 9	-	-	-	-1 0
Carbon																	
DIC (ppmC)	1 0	0 1	75	30	92	95	85	60	65	52	70	71	78	73	96	87	70
DOC (ppmC)	1 0	0 1	-	1 5	5 1	3 7	1 8	2 2	16	19	5 6	8 0	9 3	5 9	1 4	4 6	3 0
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-14 2	-15 2	-14 8	-12 7	-12 7	-13 8	-17 0	-13 0	-12 4	-13 1	-12 1	-12 9	-13 3	-14 2	-13 1
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-28 4	-22 6	-21 8	-25 6	-25 5	-27 3	-28 0	-26 9	-27 2	-26 8	-26 6	-26 2	-26 2	-26 1
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 6	-10 4	-10 2	-10 2	-10 4	-10 4	-10 1	-10 4	-	-10 3	-10 5	-10 8	-10 5	-10 6	-10 6
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-76 2	-75 1	-69 7	-71 8	-73 8	-74 7	-72 0	-68 3	-	-71 2	-	-78 9	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	L1-1C																								
Type	Lysimeter																								
Depth	1 8 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	18 0	1 9	15 8	20 0	4	12 4	3 8	7 3	17 0	5	5 4	0 4	5 1	5 8	3	7 2	2 3	4 7	9 0	3	11 5	5 5	4 7	20 0	15
pH	7 2	0 2	7 0	7 5	4	7 4	0 3	7 1	7 9	5	7 1	0 1	7 0	7 2	3	7 4	0 4	7 0	7 7	3	7 3	0 3	7 0	7 9	15
SpC (µS/cm)	809	392	570	1392	4	1104	338	799	1654	5	1373	344	996	1669	3	803	45	772	835	2	1034	376	570	1669	14
DO (mg/L)	1 9	0 7	1 4	2 4	2	2 5	-	2 5	2 5	1	-	-	-	-	-	-	-	-	-	-	2 1	0 62	1 4	2 5	3
Eh (mV)	408	7	403	414	2	343	57	302	384	2	-	-	-	-	-	-	-	-	-	-	376	50	302	414	4
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	88	5 0	81	92	4	95	5 1	87	100	5	90	15	72	98	3	72	12	59	83	3	87	12	59	100	15
Na^{+} (mg/L)	11 9	0 98	11 0	13 3	4	12 1	1 6	11 0	14 9	5	13 4	3 9	10 6	17 8	3	14 7	1 1	13 8	15 9	3	12 8	2 1	10 6	17 8	15
Mg^{2+} (mg/L)	31	2 8	28	34	4	34	2 7	31	38	5	31	5 5	25	35	3	25	4 4	20	29	3	31	4 8	20	38	15
K^{+} (mg/L)	1 6	0 4	1 2	2 1	4	2 0	0 3	1 7	2 4	5	1 2	0 11	1 1	1 3	3	1 4	0 26	1 3	1 7	3	1 6	0 41	1 1	2 4	15
Total P (mg/L)	0 028	0 015	0 008	0 042	4	0 031	0 024	0 007	0 055	3	0 031	0 009	0 025	0 038	2	0 100	0 109	0 022	0 177	2	0 042	0 047	0 007	0 177	11
NH_4^{+} (mg-N/L)	0 012	0 010	0 005	0 019	2	0 025	0 026	0 007	0 043	2	0 008	0 006	0 002	0 012	3	0 032	0 011	0 021	0 043	3	0 020	0 015	0 002	0 043	10
Cl (mg/L)	31	3 1	29	36	4	31	5 0	25	37	4	40	3 7	37	44	3	34	1 5	33	35	3	33	4 8	25	44	14
SO_4^{2} (mg/L)	24	4 6	17	27	4	22	4 3	18	26	3	26	3 2	23	30	3	26	2 5	23	28	3	25	3 7	17	30	13
NO_3 (mg-N/L)	3 8	1 4	2 6	5 85	4	3 7	0 94	2 4	4 5	4	3 7	0 21	3 4	3 9	3	2 5	0 74	1 8	3 3	3	3 5	1 02	1 8	5 9	14
HCO_3 (mg/L)	351	43	301	405	4	332	124	136	451	5	282	33	252	317	3	282	49	239	335	3	317	79	136	451	15
Calculations																									
pCO_2 (atm)	-1 69	0 22	-1 97	-1 47	4	-1 92	0 32	-2 28	-1 59	5	-1 75	0 19	-1 86	-1 53	3	-2 00	0 35	-2 21	-1 59	3	-1 84	0 28	-2 28	-1 47	15
$SI_{calcite}$	1 513	0 719	0 832	2 527	4	2 373	2 825	0 712	7 335	5	0 595	0 094	0 489	0 670	3	1 197	1 012	0 441	2 346	3	1 553	1 733	0 441	7 335	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-		-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	7 6	0 8	7 0	8 2	2	7 9	2 3	6 3	9 5	2	-	-	-	-	-	5 9	3 4	2 0	8 2	3	7 0	2 4	2 0	9 5	7
$\delta^{18}O_{NO3}$ (‰)	-1 5	7 6	-6 9	3 9	2	0 0	1 4	-1 0	1 0	2	-	-	-	-	-	0 6	2 3	-2 1	2 0	3	-0 2	3 6	-6 9	3 9	7
Carbon																									
DIC (ppmC)	80	11	73	96	4	75	27	30	95	5	70	13	60	85	3	64	11	52	71	3	73	17	30	96	15
DOC (ppmC)	5 5	3 9	1 4	9 3	3	3 6	1 4	1 5	5 1	5	6 7	8 2	1 8	16 1	3	11 0	7 3	5 6	19 3	3	6 3	5 4	1 4	19 3	14
$\delta^{13}C_{DIC}$ (‰)	-13 1	0 9	-14 2	-12 1	4	-14 0	1 1	-15 2	-12 7	5	-14 5	2 2	-17 0	-12 7	3	-12 8	0 4	-13 1	-12 4	3	-13 6	1 3	-17 0	-12 1	15
$\delta^{13}C_{DOC}$ (‰)	-26 5	0 3	-26 8	-26 2	3	-25 0	2 8	-28 4	-21 8	5	-26 1	1 0	-27 3	-25 5	3	-27 4	0 6	-28 0	-26 9	3	-26 1	1 8	-28 4	-21 8	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 6	0 1	-10 8	-10 5	4	-10 4	0 2	-10 6	-10 2	5	-10 3	0 1	-10 4	-10 1	3	-10 4	0 1	-10 4	-10 3	2	-10 4	0 2	-10 8	-10 1	14
$\delta^{2}H_{H2O}$ (‰)	-77 6	1 9	-78 9	-76 2	2	-72 2	2 7	-75 1	-69 7	3	-73 5	1 4	74 7	-72 0	3	-69 8	2 1	-71 2	-68 3	2	-73 2	3 2	-78 9	-68 3	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID			T1-A														
Type			Tile Drain														
Depth			1 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	-	-	13 3	9 8	-	4 6	1 8		6 4	9 3	-	-	-	-	10 8
pH	-	0 01	-	-	7 7	7 0	-	7 3	7 0	-	7 2	7 1	-	-	-	-	7 1
SpC (µS/cm)	-	1	-	-	492	679	-	941	919	-	747	561	-	-	-	-	744
DO (mg/L)	0 01	0 01	-	-	-	-	-	11 4	7 4	-	-	-	-	-	-	-	-
Eh (mV)	-	1	-	-	-	-	-	-	415	-	-	-	-	-	-	-	254
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	-	47	63	-	63	67	-	67	66	-	-	-	-	65
Na^{+} (mg/L)	1 0	-	-	-	8 3	8 3	-	8 6	5 4	-	7 2	8 8	-	-	-	-	9 5
Mg^{2+} (mg/L)	1 0	-	-	-	13	16	-	21	14	-	18	20	-	-	-	-	20
K^{+} (mg/L)	1 0	-	-	-	3 2	1 0	-	0 68	0 70	-	0 65	1 1	-	-	-	-	1 0
Total P (mg/L)	0 001	0 002	-	-	0 073	<0 65	0 028	0 71	0 017	-	0 022	0 038	-	-	-	-	0 034
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 006	0 004	-	0 004		-	0 007	-	-	-	-	-	-
Cl (mg/L)	1 0	-	-	-	19	23	-	31	20	-	27	25	-	-	-	-	27
SO_4^{2} (mg/L)	1 0	-	-	-	13	16	-	17	18	-	24	36	-	-	-	-	-
NO_3 (mg-N/L)	0 001	0 002	-	-	6 9	8 2	-	9 2	6 5	-	6 7	10	-	-	-	-	8 9
HCO_3 (mg/L)	3 9	-	-	-	179	181	-	148	116	-	214	201	-	-	-	-	189
Calculations																	
pCO_2 (atm)	-	-	-	-	-2 51	-1 79	-	-2 15	-2 02	-	-1 90	-1 83	-	-	-	-	-1 87
$SI_{calcite}$	-	-	-	-	1 206	0 259	-	0 311	0 136	-	0 412	0 346	-	-	-	-	0 367
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	5 4	-	-	-	-	-	5 8	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	2 3	-	-	-	-	-	1 5	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	-	37	46	-	35	31	-	51	50	-	-	-	-	46
DOC (ppmC)	1 0	0 1	-	-	6 1	1 4	-	1 3	3 1	-	1 7	2 6	-	-	-	-	2 3
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-11 1	-11 8	-	-11 4	-13 0	-	-12 6	-12 2	-	-	-	-	-9 8
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-25 4	-21 6	-	-23 8	-26 2	-	-26 0	-24 9	-	-	-	-	-24 8
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-10 8	-10 7	-	-10 7	-11 0	-11 6	-	-10 4	-	-	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-76 2	-76 9	-	-77 2	-79 3	-79 4	-	-76 1	-	-	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID																									
Type																									
Depth																									
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	-	-	-	-	11 3	1 8	9 8	13 3	3	3 2	2 0	1 8	4 6	2	7 9	2 1	6 4	9 3	2	8 0	3 9	1 8	13 3	7
pH	-	-	-	-	-	7 3	0 4	7 0	7 7	3	7 1	0 2	7 0	7 3	2	7 1	0 1	7 1	7 2	2	7 2	0 3	7 0	7 7	7
SpC (µS/cm)	-	-	-	-	-	638	130	492	744	3	930	15	919	941	2	654	131	561	747	2	726	167	492	941	7
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	9 4	2 9	7 4	11 4	2	-	-	-	-	-	9 4	2 86	7 4	11 4	2
Eh (mV)	-	-	-	-	-	254	-	254	254	1	415	-	415	415	1	-	-	-	-	-	334	113	254	415	2
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	-	-	-	-	-	58	10	47	65	3	65	3 0	63	67	2	67	0 7	66	67	2	63	7 1	47	67	7
Na^{+} (mg/L)	-	-	-	-	-	8 7	0 71	8 3	9 5	3	7 0	2 2	5 4	8 6	2	8 0	1 2	7 2	8 8	2	8 0	1 3	5 4	9 5	7
Mg^{2+} (mg/L)	-	-	-	-	-	17	3 5	13	20	3	17	5 4	14	21	2	19	0 9	18	20	2	17	3 2	13	21	7
K^{+} (mg/L)	-	-	-	-	-	1 7	1 3	1 0	3 2	3	0 7	0 0	0 7	0 7	2	0 9	0 3	0 6	1 1	2	1 2	0 91	0 6	3 2	7
Total P (mg/L)	-	-	-	-	-	0 054	0 027	0 034	0 073	2	0 253	0 398	0 017	0 712	3	0 030	0 011	0 022	0 038	2	0 132	0 256	0 017	0 712	7
NH_4^{+} (mg-N/L)	-	-	-	-	-	0 005	0 002	0 004	0 006	2	0 004	-	0 004	0 004	1	0 007	-	0 007	0 007	1	0 005	0 002	0 004	0 007	4
Cl (mg/L)	-	-	-	-	-	23	3 7	19	27	3	25	8 1	20	31	2	26	1 4	25	27	2	25	4 2	19	31	7
SO_4^{2} (mg/L)	-	-	-	-	-	14	2 0	13	16	2	18	0 57	17	18	2	30	8 2	24	36	2	21	8 4	13	36	6
NO_3 (mg-N/L)	-	-	-	-	-	8 0	1 0	6 9	8 9	3	7 9	1 9	6 5	9 2	2	8 6	2 6	6 7	10 4	2	8 1	1 5	6 5	10 4	7
HCO_3 (mg/L)	-	-	-	-	-	183	5 6	179	189	3	132	23	116	148	2	207	9 0	201	214	2	176	33	116	214	7
Calculations																									
pCO_2 (atm)	-	-	-	-	-	-2 06	0 40	-2 51	-1 79	3	-2 09	0 09	-2 15	-2 02	2	-1 86	0 05	-1 90	-1 83	2	-2 01	0 25	-2 51	-1 79	7
$SI_{calcite}$	-	-	-	-	-	0 611	0 519	0 259	1 206	3	0 223	0 124	0 136	0 311	2	0 379	0 047	0 346	0 412	2	0 434	0 352	0 136	1 206	7
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	5 4	-	5 4	5 4	1	-	-	-	-	-	5 8	-	5 8	5 8	1	5 6	0 3	5 4	5 8	2
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	2 3	-	2 3	2 3	1	-	-	-	-	-	1 5	-	1 5	1 5	1	1 9	0 6	1 5	2 3	2
Carbon																									
DIC (ppmC)	-	-	-	-	-	43	5	37	46	3	33	3	31	35	2	50	1	50	51	2	42	8	31	51	7
DOC (ppmC)	-	-	-	-	-	3 3	2 5	1 4	6 1	3	2 2	1 3	1 3	3 1	2	2 1	0 6	1 7	2 6	2	2 7	1 7	1 3	6 1	7
$\delta^{13}C_{DIC}$ (‰)	-	-	-	-	-	-10 9	1 0	-11 8	-9 8	3	-12 2	1 1	-13 0	-11 4	2	-12 4	0 3	-12 6	-12 2	2	-11 7	1 1	-13 0	-9 8	7
$\delta^{13}C_{DOC}$ (‰)	-	-	-	-	-	-23 9	2 1	-25 4	-21 6	3	-25 0	1 7	-26 2	-23 8	2	-25 5	0 8	-26 0	-24 9	2	-24 7	1 6	-26 2	-21 6	7
Water																									
$\delta^{18}O_{H2O}$ (‰)	-	-	-	-	-	-10 8	0 1	-10 8	-10 7	2	-10 8	0 2	-11 0	-10 7	2	-11 0	0 8	-11 6	-10 4	2	-10 9	0 4	-11 6	-10 4	6
$\delta^{2}H_{H2O}$ (‰)	-	-	-	-	-	-76 6	0 5	-76 9	-76 2	2	-78 2	1 4	-79 3	-77 2	2	-77 8	2 3	-79 4	-76 1	2	-77 5	1 5	-79 4	-76 1	6

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID								T1-B									
Type								Tile Drain									
Depth								1 8 mbgs									
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	-	-	-	9 2	6 8	4 3	3 3	3 6	5 0	9 5	13 2	-	-	-	10 6
pH	-	0 01	-	-	-	7 1	7 3	7 0	7 4	6 9	7 2	7 0	6 8	-	-	-	6 8
SpC (µS/cm)	-	1	-	-	-	744	1101	935	858	342	774	638	454	-	-	-	691
DO (mg/L)	0 01	0 01	-	-	-	-	8 9	11 7	-	7 5	-	-	-	-	-	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	294	-	-	-	-	-	-	280
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	-	-	62	71	58	54	33	57	50	57	-	-	-	57
Na^{+} (mg/L)	1 0	-	-	-	-	12	11	10	8 8	5 2	9 2	10	11	-	-	-	12
Mg^{2+} (mg/L)	1 0	-	-	-	-	20	25	21	20	11	21	18	19	-	-	-	21
K^{+} (mg/L)	1 0	-	-	-	-	1 0	1 2	0 7	0 57	3 9	0 59	1 1	0 84	-	-	-	0 82
Total P (mg/L)	0 001	0 002	-	-	-	<0 65	0 040	0 045	0 014	0 066	0 021	0 035	0 031	-	-	-	0 042
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 009	0 004	0 004	0 004	-	0 15	0 008	0 095	0 003	-	-	-	-
Cl (mg/L)	1 0	-	-	-	-	22	26	30	30	20	31	25	25	-	-	-	23
SO_4^{2} (mg/L)	1 0	-	-	-	-	36	27	39	33	19	39	20	33	-	-	-	
NO_3 (mg-N/L)	0 001	0 002	-	-	-	8 0	5 1	10	7 7	4 7	8 1	10	7 7	-	-	-	12
HCO_3 (mg/L)	3 9	-	-	-	-	173	270	113	194	110	194	154	194	-	-	-	117
Calculations																	
pCO_2 (atm)	-	-	-	-	-	-1 94	-1 98	-2 02	-2 16	-1 92	-1 96	-1 90	-1 57	-	-	-	-1 79
$SI_{calcite}$	-	-	-	-	-	0 310	0 817	0 123	0 436	0 054	0 309	0 193	0 186	-	-	-	0 103
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	5 8	-	-	4 9	-	-	4 1	8 1	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	25 9	-	-	25 4	-	-	0 2	0 6	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	-	-	42	61	30	44	32	47	39	54	-	-	-	33
DOC (ppmC)	1 0	0 1	-	-	-	2 1	1 8	2 2	2 6	5 7	1 9	2 8	3 7	-	-	-	1 7
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-	-13 0	-13 6	-13 4	-13 7	-13 4	-13 6	-13 6	-13 7	-	-	-	-12 7
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-	-22 7	-25 7	-24 8	-25 0	-19 7	-25 8	-24 2	-25 2	-	-	-	-24 2
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-	-10 2	-10 7	-10 4	-10 8	-11 5	-	-10 5	-	-	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-	-72 7	-77 7	-75 1	-77 2	-79 8	-	-74 8	-	-	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	T1-B																								
Type	Tile Drain																								
Depth	1 8 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	13 2	-	13 2	13 2	1	9 9	1 0	9 2	10 6	2	4 8	1 8	3 3	6 8	3	6 0	3 1	3 6	9 5	3	7 3	3 5	3 3	13 2	9
pH	6 8	-	6 8	6 8	1	7 0	0 2	6 8	7 1	2	7 2	0 2	7 0	7 4	3	7 0	0 1	6 9	7 2	3	7 1	0 2	6 8	7 4	9
SpC (µS/cm)	454	-	454	454	1	718	38	691	744	2	964	124	858	1101	3	585	221	342	774	3	726	233	342	1101	9
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	10 3	2 0	8 9	11 7	2	7 5	-	7 5	7 5	1	9 4	2 14	7 5	11 7	3
Eh (mV)	-	-	-	-	-	280	-	280	280	1	-	-	-	-	-	294	-	294	294	1	287	9	280	294	2
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	57	-	57	57	1	60	3 2	57	62	2	61	9 1	54	71	3	47	13	33	57	3	55	10	33	71	9
Na^{+} (mg/L)	10 8	-	10 8	10 8	1	11 8	0 09	11 7	11 8	2	10 0	1 1	8 8	10 9	3	8 2	2 6	5 2	10 1	3	9 9	2 0	5 2	11 8	9
Mg^{2+} (mg/L)	19	-	19	19	1	20	0 5	20	21	2	22	2 8	20	25	3	17	5 1	11	21	3	19	3 7	11	25	9
K^{+} (mg/L)	0 8	-	0 84	0 84	1	0 9	0 2	0 8	1 0	2	0 8	0 3	0 6	1 2	3	1 9	1 8	0 6	3 9	3	1 2	1 05	0 6	3 9	9
Total P (mg/L)	0 03	-	0 031	0 031	1	0 042	-	0 042	0 042	1	0 033	0 017	0 014	0 045	3	0 041	0 023	0 021	0 066	3	0 037	0 016	0 014	0 066	8
NH_4^{+} (mg-N/L)	0 003	-	0 003	0 003	1	0 006	0 003	0 004	0 009	2	0 004	0 000	0 004	0 004	2	0 083	0 070	0 008	0 145	3	0 034	0 055	0 003	0 145	8
Cl (mg/L)	25	-	25	25	1	23	0 32	22	23	2	29	2 3	26	30	3	25	5 6	20	31	3	26	4 0	20	31	9
SO_4^{2} (mg/L)	33	-	33	33	1	36	-	36	36	1	33	6 3	27	39	3	26	11	19	39	3	31	7 8	19	39	8
NO_3 (mg-N/L)	7 73	-	7 7	7 7	1	9 9	2 7	8 0	12	2	7 5	2 2	5 1	9 6	3	7 5	2 6	4 7	9 8	3	8 1	2 2	4 7	12	9
HCO_3 (mg/L)	194	-	194	194	1	145	40	117	173	2	192	78	113	270	3	152	42	110	194	3	169	52	110	270	9
Calculations																									
pCO_2 (atm)	-1 57	-	-1 57	-1 57	1	-1 86	0 10	-1 94	-1 79	2	-2 05	0 10	-2 16	-1 98	3	-1 93	0 03	-1 96	-1 90	3	-1 92	0 16	-2 16	-1 57	9
$SI_{calcite}$	0 186	-	0 186	0 186	1	0 206	0 146	0 103	0 310	2	0 458	0 348	0 123	0 817	3	0 185	0 127	0 054	0 309	3	0 281	0 234	0 054	0 817	9
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	8 1	-	8 1	8 1	1	5 8	-	5 8	5 8	1	4 9	-	4 9	4 9	1	4 1	-	4 1	4 1	1	5 7	1 7	4 1	8 1	4
$\delta^{18}O_{NO3}$ (‰)	0 6	-	0 6	0 6	1	25 9	-	25 9	25 9	1	25 4	-	25 4	25 4	1	0 2	-	0 2	0 2	1	13 0	14 6	0 2	25 9	4
Carbon																									
DIC (ppmC)	54	-	54	54	1	38	6	33	42	2	45	15	30	61	3	39	8	32	47	3	42	10	30	61	9
DOC (ppmC)	3 7	-	3 7	3 7	1	1 9	0 3	1 7	2 1	2	2 2	0 4	1 8	2 6	3	3 5	2 0	1 9	5 7	3	2 7	1 3	1 7	5 7	9
$\delta^{13}C_{DIC}$ (‰)	-13 7	-	-13 7	-13 7	1	-12 9	0 2	-13 0	-12 7	2	-13 5	0 2	-13 7	-13 4	3	-13 5	0 1	-13 6	-13 4	3	-13 4	0 3	13 7	-12 7	9
$\delta^{13}C_{DOC}$ (‰)	-25 2	-	-25 2	-25 2	1	-23 4	1 0	-24 2	-22 7	2	-25 1	0 5	-25 7	-24 8	3	-23 3	3 2	-25 8	-19 7	3	-24 1	1 9	-25 8	-19 7	9
Water																									
$\delta^{18}O_{H2O}$ (‰)	-	-	-	-	-	-10 2	-	-10 2	-10 2	1	-10 6	0 2	-10 8	-10 4	3	-11 0	0 7	-11 5	-10 5	2	-10 7	0 4	-11 5	-10 2	6
$\delta^{2}H_{H2O}$ (‰)	-	-	-	-	-	-72 7	-	-72 7	-72 7	1	-76 7	1 4	-77 7	-75 1	3	-77 3	3 5	-79 8	-74 8	2	-76 2	2 5	-79 8	-72 7	6

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID			P1-1B														
Type			Piezometer														
Depth			3 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	2 72	2 98	1 94	0 65	1 14	1 07	0 92	1 14	0 77	0 48	1 10	1 54	1 75	2 61	0 66
Temp (°C)	-	0 1	13 7	15 5	11 1	9 0	5 6	8 8	6 9	9 8	12 4	10 8	13 8	15 0	16 6	12 4	9 9
pH	-	0 01	7 9	7 6	7 8	7 1	7 4	7 1	7 7	7 5	7 7	7 0	7 6	7 7	7 5	7 7	7 5
SpC (µS/cm)	-	1	1424	1063	818	931	1349	1043	936	765	722	703	560	644	700	759	976
DO (mg/L)	0 01	0 01		-	-	-	-	-	-	-	-	-	3 6	-	2 9	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	456	430	428	394	296
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	76	85	75	81	79	84	73	72	73	80	81	83	82	80	84
Na^{+} (mg/L)	1 0	-	11	11	11	11	10	11	9 0	8 8	8 8	10	10	10	11	10	10
Mg^{2+} (mg/L)	1 0	-	29	32	29	30	29	31	26	26	27	30	30	31	31	30	31
K^{+} (mg/L)	1 0	-	3 7	3 9	3 6	3 4	3 1	3 4	2 7	2 8	2 5	2 8	2 9	3 0	3 3	3 4	3 3
Total P (mg/L)	0 001	0 002	<0 65	0 023	<0 38	<0 65	0 019	<0 11	0 018	0 017	0 022	0 053	0 031	0 029	0 043	0 010	0 052
NH_4^{+} (mg-N/L)	0 001	0 003	-	0 064	0 060	0 004	0 004	0 004	-	-	-	0 006	0 010	0 006	-	-	-
Cl (mg/L)	1 0	-	15	13	17	18	19	19	19	20	21	21	22	20	21	20	22
SO_4^{2} (mg/L)	1 0	-	22	21	22	21	20	22	20	22	21	20	20	21	23	23	-
NO_3 (mg-N/L)	0 001	0 002	2 2	1 6	2 9	3 4	3 2	3 3	3 5	3 7	4 1	3 6	3 9	3 4	3 7	3 0	4 0
HCO_3 (mg/L)	3 9	-	334	262	346	321	317	210	211	340	338	287	356	341	422	346	322
Calculations																	
pCO_2 (atm)	-	-	-2 37	-2 22	-2 32	-1 69	-1 97	-1 80	-2 40	-1 99	-2 25	-1 58	-2 07	-2 15	-1 90	-2 19	-2 05
$SI_{calcite}$	-	-	4 493	2 357	3 747	0 734	1 143	0 420	1 392	1 549	3 157	0 505	2 723	3 275	2 953	3 136	1 863
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-		-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		8 1	-	-	7 7	-	7 5	-	8 2	-	-	7 7	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		4 9	-	-	4 6	-	5 3	-	5 0	-	-	3 7	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	68	55	71	77	71	52	45	74	70	73	75	71	90	72	69
DOC (ppmC)	1 0	0 1	-	1 8	2 8	1 6	1 1	1 7	2 0	1 8	1 3	2 0	4 8	2 5	1 5	3 6	1 5
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-16 3	-16 3	-17 0	-16 8	-15 7	-16 7	17 4	16 9	-17 0	-16 9	-16 5	-16 6	-17 1	-17 1	-16 6
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-24 7	-23 1	-21 7	-26 2	-26 0	-25 2	-26 5	-26 5	-25 7	-26 3	-26 3	-26 8	-26 2	-25 3
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 0	-10 9	-10 9	-10 7	-10 9	-10 8	-11 0	-10 8	-	-10 6	-10 9	-10 9	-10 8	-11 1	-10 9
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-78 3	-78 8	-77 4	-74 4	-77 1	-76 6	-78 9	-72 7	-	-74 3	-	-75 8	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	P1-1B																					
Type	Piezometer																					
Depth	3 5 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 78	0 69	1 10	2 72	4	1 77	1 08	0 65	2 98	5	1 05	0 12	0 92	1 14	3	0 80	0 33	0 48	1 14	3	1 43	0 80	0 48	2 98	15
Temp (°C)	14 8	1 4	13 7	16 6	4	11 6	2 5	9 0	15 5	5	7 1	1 6	5 6	8 8	3	11 0	1 3	9 8	12 4	3	11 4	3 2	5 6	16 6	15
pH	7 7	0 1	7 5	7 9	4	7 6	0 3	7 1	7 8	5	7 4	0 3	7 1	7 7	3	7 4	0 4	7 0	7 7	3	7 5	0 3	7 0	7 9	15
SpC (µS/cm)	832	399	560	1424	4	909	122	759	1063	5	1109	215	936	1349	3	730	32	703	765	3	893	249	560	1424	15
DO (mg/L)	3 2	0 5	2 9	3 6	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3 2	0 53	2 9	3 6	2
Eh (mV)	438	16	428	456	3	345	69	296	394	2	-	-	-	-	-	-	-	-	-	-	401	63	296	456	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	81	3 4	76	83	4	81	3 7	75	85	5	78	5 8	73	84	3	75	4 5	72	80	3	79	4 4	72	85	15
Na^{+} (mg/L)	10 4	0 64	9 7	11 1	4	10 7	0 42	10 2	11 2	5	9 9	0 82	9 0	10 6	3	9 2	0 62	8 8	9 9	3	10 2	0 81	8 8	11 2	15
Mg^{2+} (mg/L)	30	1 3	29	31	4	30	1 2	29	32	5	29	2 1	26	31	3	28	2 1	26	30	3	29	1 7	26	32	15
K^{+} (mg/L)	3 2	0 35	2 9	3 7	4	3 5	0 22	3 3	3 9	5	3 1	0 34	2 7	3 4	3	2 7	0 13	2 5	2 8	3	3 2	0 39	2 5	3 9	15
Total P (mg/L)	0 034	0 007	0 029	0 043	3	0 028	0 021	0 010	0 052	3	0 018	0 001	0 018	0 019	2	0 030	0 019	0 017	0 053	3	0 029	0 014	0 010	0 053	11
NH_4^{+} (mg-N/L)	0 008	0 003	0 006	0 010	2	0 042	0 034	0 004	0 064	3	0 004	0 000	0 004	0 004	2	0 006	-	0 006	0 006	1	0 020	0 026	0 004	0 064	8
Cl (mg/L)	19	3 3	15	22	4	18	3 4	13	22	5	19	0 27	19	19	3	21	0 45	20	21	3	19	2 6	13	22	15
SO_4^{2} (mg/L)	21	1 1	20	23	4	22	0 7	21	23	4	20	1 1	20	22	3	21	0 9	20	22	3	21	1 0	20	23	14
NO_3 (mg-N/L)	3 3	0 78	2 2	3 9	4	3 0	0 86	1 6	4 0	5	3 3	0 18	3 2	3 5	3	3 8	0 26	3 6	4 1	3	3 3	0 66	1 6	4 1	15
HCO_3 (mg/L)	363	40	334	422	4	319	34	262	346	5	246	62	210	317	3	322	30	287	340	3	317	55	210	422	15
Calculations																									
pCO_2 (atm)	-2 12	0 19	-2 37	-1 90	4	-2 09	0 24	-2 32	-1 69	5	-2 06	0 31	-2 40	-1 80	3	-1 94	0 33	-2 25	-1 58	3	-2 06	0 24	-2 40	-1 58	15
$SI_{calcite}$	3 361	0 788	2 723	4 493	4	2 368	1 164	0 734	3 747	5	0 985	0 505	0 420	1 392	3	1 737	1 336	0 505	3 157	3	2 230	1 252	0 420	4 493	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	7 9	0 3	7 7	8 1	2	7 7	-	7 7	7 7	1	7 5	-	7 5	7 5	1	8 2	-	8 2	8 2	1	7 8	0 3	7 5	8 2	5
$\delta^{18}O_{NO3}$ (‰)	4 3	0 8	3 7	4 9	2	4 6	-	4 6	4 6	1	5 3	-	5 3	5 3	1	5 0	-	5 0	5 0	1	4 7	0 6	3 7	5 3	5
Carbon																									
DIC (ppmC)	76	10	68	90	4	69	8	55	77	5	56	13	45	71	3	72	2	70	74	3	69	11	45	90	15
DOC (ppmC)	2 9	1 7	1 5	4 8	3	2 3	0 9	1 5	3 6	5	1 6	0 5	1 1	2 0	3	1 7	0 3	1 3	2 0	3	2 1	1 0	1 1	4 8	14
$\delta^{13}C_{DIC}$ (‰)	-16 6	0 3	-17 1	-16 3	4	-16 7	0 3	-17 1	-16 3	5	-16 6	0 8	17 4	-15 7	3	-16 9	0 1	-17 0	-16 9	3	-16 7	0 4	-17 4	-15 7	15
$\delta^{13}C_{DOC}$ (‰)	-26 5	0 3	-26 8	-26 3	3	-24 2	1 8	-26 2	-21 7	5	-25 8	0 5	-26 2	-25 2	3	-26 2	0 5	-26 5	-25 7	3	-25 5	1 4	-26 8	-21 7	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 9	0 1	-11 0	-10 8	4	-10 9	0 1	-11 1	-10 7	5	-10 9	0 1	-11 0	-10 8	3	-10 7	0 1	-10 8	-10 6	2	-10 9	0 1	-11 1	-10 6	14
$\delta^{2}H_{H2O}$ (‰)	-77 1	1 8	-78 3	-75 8	2	-76 9	2 2	-78 8	-74 4	3	-77 5	1 2	-78 9	-76 6	3	-73 5	1 1	-74 3	-72 7	2	-76 4	2 1	-78 9	-72 7	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID																	
Type																	
Depth																	
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	4 425	4 213	2 745	1 435	1 733	1 888	1 451	2 013	1 743	1 643	1 571	1 951	1 904	2 861	0 475
Temp (°C)	-	0 1	12 1	15 8	11 6	8 1	4 8	9 6	7 7	10 1	11 6	11 4	13 6	14 3	17 0	11 9	8 7
pH	-	0 01	7 7	7 3	7 9	7 2	7 4	7 1	7 9	7 6	7 4	7 0	7 8	7 7	7 7	7 8	7 4
SpC (µS/cm)	-	1	1190	1070	704	946	1081	923	705	572	581	545	440	508	534	599	994
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	2 6	-	2 2	-	-
Eh (mV)	-	1	-	-	-	-		-	-	-	-	-	461	229	409	391	305
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	58	58	61	76	57	61	54	53	54	58	59	59	60	58	82
Na^{+} (mg/L)	1 0	-	11	11	10	12	10	10	9 0	9 0	9 2	10	10	10	11	10	11
Mg^{2+} (mg/L)	1 0	-	23	24	24	28	22	23	21	20	21	23	22	24	24	23	30
K^{+} (mg/L)	1 0	-	4 8	4 7	4 5	3 9	3 9	4 4	3 6	3 7	3 6	3 8	3 8	3 9	4 1	3 9	3 2
Total P (mg/L)	0 001	0 002	0 10	0 13	0 077	<0 65	0 13	<0 11	0 13	0 13	0 13	0 21	0 17	0 19	0 20	0 19	0 093
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 20	0 18	0 28	0 12	0 006	-	0 006	0 004	0 010	-	-	-	-
Cl (mg/L)	1 0	-	5 8	3 7	8 7	13	6 0	3 5	4 6	6 3	3 8	3 5	4 0	2 9	3 3	3 0	16
SO_4^{2} (mg/L)	1 0	-	8 2	5 3	11	12	6 7	5 0	4 9	4 8	4 9	4 4	4 7	3 1	4 3	3 3	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	1 3	2 0	0 30	0 33	0 62	0 50	0 50	0 49	0 43	0 32	0 45	<0 001	3 7
HCO_3 (mg/L)	3 9	-	296	202	321	328	290	189	301	301	283	246	314	298	348	306	347
Calculations																	
pCO_2 (atm)	-	-	-2 26	-1 99	-2 45	-1 74	-1 96	-1 89	-2 45	-2 19	-2 04	-1 64	-2 34	-2 22	-2 13	-2 40	-1 87
$SI_{calcite}$	-	-	2 055	0 620	3 749	0 799	0 697	0 339	2 519	1 525	1 039	0 334	3 013	2 131	2 739	2 994	1 297
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-		-	-	-	-	-		-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	8 6	-	-	-	7 0	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-0 4	-	-	-	3 1	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	61 6	45 3	65 3	77 2	65 6	45 7	61 7	63 4	61 4	62 8	64 5	62 1	72 4	62 7	77 6
DOC (ppmC)	1 0	0 1	-	1 5	4 4	2 1	1 7	1 7	2 1	2 5	1 5	2 6	3 0	2 3	1 3	3 4	1 8
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-15 62	-15 86	-16 68	-15 98	-16 19	-16 12	-	-16 51	-16 21	-16 29	-16 09	-16 38	-16 43	-16 87	-14 56
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-24 86	-24 54	-21 88	-26 32	-26 30	-26 48	-27 00	-26 73	-26 72	-26 52	-27 13	-26 96	-27 10	-26 19
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 04	-11 00	-11 02	-10 86	-10 82	-10 91	-10 77	-11 08	-	-10 89	-11 06	-11 06	-11 01	-11 14	-10 81
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-78 80	-77 40	-73 80	-78 80	-77 70	-78 40	-77 60	-74 40	-	-75 41	-	-75 90	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	P1-1C																					
Type	Piezometer																					
Depth	5 0 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	2 46	1 32	1 57	4 42	4	2 35	1 44	0 47	4 21	5	1 69	0 22	1 45	1 89	3	1 80	0 19	1 64	2 01	3	2 14	1 04	0 47	4 42	15
Temp (°C)	14 3	2 1	12 1	17 0	4	11 2	3 1	8 1	15 8	5	7 4	2 4	4 8	9 6	3	11 0	0 8	10 1	11 6	3	11 2	3 2	4 8	17 0	15
pH	7 7	0 1	7 7	7 8	4	7 5	0 3	7 2	7 9	5	7 4	0 4	7 1	7 9	3	7 4	0 3	7 0	7 6	3	7 5	0 3	7 0	7 9	15
SpC (µS/cm)	668	350	440	1190	4	863	201	599	1070	5	903	189	705	1081	3	566	19	545	581	3	759	248	440	1190	15
DO (mg/L)	2 4	0 3	2 2	2 6	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2 4	0 28	2 2	2 6	2
Eh (mV)	366	122	229	461	3	348	61	305	391	2	-	-	-	-	-	-	-	-	-	-	359	92	229	461	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	59	0 79	58	60	4	67	11	58	82	5	57	3 8	54	61	3	55	2 9	53	58	3	61	7 9	53	82	15
Na^{+} (mg/L)	10 4	0 49	9 8	10 9	4	10 6	0 63	9 8	11 5	5	9 7	0 73	9 0	10 4	3	9 3	0 41	9 0	9 8	3	10 1	0 72	9 0	11 5	15
Mg^{2+} (mg/L)	23	0 68	22	24	4	26	2 8	23	30	5	22	1 4	21	23	3	21	1 4	20	23	3	24	2 5	20	30	15
K^{+} (mg/L)	4 2	0 42	3 8	4 8	4	4 0	0 56	3 2	4 7	5	3 9	0 42	3 6	4 4	3	3 7	0 08	3 6	3 8	3	4 0	0 43	3 2	4 8	15
Total P (mg/L)	0 164	0 046	0 098	0 196	4	0 121	0 049	0 077	0 189	4	0 127	0 000	0 127	0 127	2	0 156	0 050	0 125	0 214	3	0 143	0 044	0 077	0 214	13
NH_4^{+} (mg-N/L)	0 010	-	0 010	0 010	1	0 192	0 013	0 182	0 201	2	0 135	0 136	0 006	0 278	3	0 005	0 001	0 004	0 006	2	0 101	0 110	0 004	0 278	8
Cl (mg/L)	4 0	1 3	2 9	5 8	4	8 9	5 8	3 0	16	5	4 7	1 3	3 5	6 0	3	4 6	1 6	3 5	6 3	3	5 9	3 9	2 9	16	15
SO_4^{2} (mg/L)	5 1	2 2	3 1	8 2	4	7 8	4 1	3 3	12	4	5 5	1 0	4 9	6 7	3	4 7	0 25	4 4	4 9	3	5 9	2 6	3 1	12	14
NO_3 (mg-N/L)	0 40	0 07	0 32	0 45	3	2 32	1 26	1 26	3 7	3	0 42	0 18	0 30	0 62	3	0 50	0 004	0 49	0 50	3	0 91	1 0	0 30	3 7	12
HCO_3 (mg/L)	314	24	296	348	4	301	57	202	347	5	260	62	189	301	3	277	28	246	301	3	291	46	189	348	15
Calculations																									
pCO_2 (atm)	-2 24	0 08	-2 34	-2 13	4	-2 09	0 32	-2 45	-1 74	5	-2 10	0 31	-2 45	-1 89	3	-1 96	0 29	-2 19	-1 64	3	-2 10	0 26	-2 45	-1 64	15
$SI_{calcite}$	2 484	0 467	2 055	3 013	4	1 892	1 399	0 620	3 749	5	1 185	1 169	0 339	2 519	3	0 966	0 599	0 334	1 525	3	1 723	1 102	0 334	3 749	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	8 6	-	8 6	8 6	1	-	-	-	-	-	7 0	-	7 0	7 0	1	7 8	1 1	7 0	8 6	2
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-0 4	-	-0 4	-0 4	1	-	-	-	-	-	-3 1	-	-3 1	-3 1	1	-1 8	1 9	-3 1	-0 4	2
Carbon																									
DIC (ppmC)	65	5	62	72	4	66	13	45	78	5	58	11	46	66	3	63	1	61	63	3	63	9	45	78	15
DOC (ppmC)	2 2	0 9	1 3	3 0	3	2 6	1 2	1 5	4 4	5	1 8	0 2	1 7	2 1	3	2 2	0 6	1 5	2 6	3	2 3	0 9	1 3	4 4	14
$\delta^{13}C_{DIC}$ (‰)	-16 1	0 4	-16 4	-15 6	4	-16 0	0 9	-16 9	-14 6	5	-16 2	0 0	-16 2	-16 1	2	-16 3	0 2	-16 5	-16 2	3	-16 1	0 6	-16 9	-14 6	14
$\delta^{13}C_{DOC}$ (‰)	-26 9	0 3	-27 1	-26 5	3	-24 9	2 0	-27 1	-21 9	5	-26 4	0 1	-26 5	-26 3	3	-26 8	0 2	-27 0	-26 7	3	-26 1	1 4	-27 1	-21 9	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 0	0 0	-11 1	-11 0	4	-11 0	0 1	-11 1	-10 8	5	-10 8	0 1	-10 9	-10 8	3	-11 0	0 1	-11 1	-10 9	2	-11 0	0 1	-11 1	-10 8	14
$\delta^{2}H_{H2O}$ (‰)	-77 4	2 1	-78 8	-75 9	2	-76 7	2 6	-78 8	-73 8	3	-77 9	0 4	-78 4	-77 6	3	-74 9	0 7	-75 4	-74 4	2	-76 8	1 8	-78 8	-73 8	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID			P1-2B														
Type			Piezometer														
Depth			3 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	2 536	2 502	0 532	0 432	1 232	0 974	1 032	0 769	0 887	0 310	-	1 702	1 762	2 567	0 682
Temp (°C)	-	0 1	13 7	19 5	11 6	8 4	6 3	7 7	5 2	10 0	7 5	10 2	15 6	15 2	18 3	13 4	10 2
pH	-	0 01	7 9	7 8	8 0	7 2	7 4	7 3	7 8	7 5	7 6	7 0	7 7	7 6	7 5	7 7	7 6
SpC (µS/cm)	-	1	1424	965	628	748	990	857	718	572	649	552	444	496	492	585	754
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	1 8	2 4	2 0	0 9	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	352	169	397	128	143
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	56	59	56	58	56	60	53	54	54	57	59	59	60	59	60
Na^{+} (mg/L)	1 0	-	10	10	10	10	10	10	9	9	9	9	11	10	11	11	11
Mg^{2+} (mg/L)	1 0	-	22	22	21	21	21	22	20	20	20	22	22	22	23	22	22
K^{+} (mg/L)	1 0	-	2 0	2 2	1 8	1 7	2 4	1 7	1 4	1 6	1 4	1 3	1 4	1 6	1 8	1 9	1 6
Total P (mg/L)	0 001	0 002	0 007	0 008	1 1	<0 65	0 32	<0 11	1 8	1 2	2 8	1 4	0 73	2 3	0 045	0 73	1 3
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 13	0 14	0 07	0 018	0 026	0 044	0 004	0 051	0 050	0 085	-	-	-
Cl (mg/L)	1 0	-	14	13	13	6 4	5 2	15	15	16	15	15	16	16	16	15	15
SO_4^{2} (mg/L)	1 0	-	32	32	32	14	12	33	33	35	34	35	35	35	37	36	-
NO_3 (mg-N/L)	0 001	0 002	0 15	<0 001	<0 001	<0 001	<0 001	0 15	0 11	0 36	0 19	0 26	<0 001	0 22	0 44	<0 001	0 32
HCO_3 (mg/L)	3 9	-	238	149	253	224	223	159	169	237	227	191	247	230	270	246	229
Calculations																	
pCO_2 (atm)	-	-	-2 52	-2 61	-2 62	-1 91	-2 07	-2 13	-2 66	-2 22	-2 28	-1 77	-2 32	-2 24	-2 05	-2 32	-2 25
$SI_{calcite}$	-	-	2 491	1 695	3 238	0 444	0 568	0 374	1 118	1 018	0 940	0 247	1 977	1 396	1 424	1 772	1 152
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	10 9	-	9 0	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	7 1	-	5 7	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	49	30	51	53	50	37	35	51	48	49	51	49	58	51	49
DOC (ppmC)	1 0	0 1	-	1 1	2 6	1 9	1 5	1 4	1 6	1 8	1 9	2 3	2 3	2 2	1 2	2 7	1 6
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-14 9	-15 6	-15 8	-15 2	-15 3	-15 5	-16 1	-15 7	-15 5	-15 4	-15 0	-15 2	-15 3	-15 5	-15 6
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-24 2	-24 3	-22 9	-26 9	-26 1	-26 2	-26 7	-27 0	-26 5	-26 2	-26 8	-26 2	-26 4	-28 0
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 8	-10 7	-10 7	-10 6	-10 5	-10 7	-11 1	-10 7	-	-8 6	-10 9	-10 9	-10 7	-10 9	-10 8
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-76 2	-77 4	-73 4	-77 7	-78 6	-76 7	-78 6	-72 9	-	-67 5	-	-79 8	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	P1-2B																					
Type	Piezometer																					
Depth	3 5 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	2 00	0 47	1 70	2 54	3	1 34	1 09	0 43	2 57	5	1 08	0 14	0 97	1 23	3	0 66	0 30	0 31	0 89	3	1 28	0 80	0 31	2 57	14
Temp (°C)	15 7	1 9	13 7	18 3	4	12 6	4 3	8 4	19 5	5	6 4	1 3	5 2	7 7	3	9 2	1 5	7 5	10 2	3	11 5	4 3	5 2	19 5	15
pH	7 7	0 2	7 5	7 9	4	7 6	0 3	7 2	8 0	5	7 5	0 3	7 3	7 8	3	7 4	0 3	7 0	7 6	3	7 6	0 3	7 0	8 0	15
SpC (µS/cm)	714	474	444	1424	4	736	148	585	965	5	855	136	718	990	3	591	51	552	649	3	725	255	444	1424	15
DO (mg/L)	2 1	0 3	1 8	2 4	3	0 9	-	0 9	0 9	1	-	-	-	-	-	-	-	-	-	-	1 8	0 64	0 9	2 4	4
Eh (mV)	306	121	169	397	3	135	10	128	143	2	-	-	-	-	-	-	-	-	-	-	238	127	128	397	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	58	1 8	56	60	4	58	1 7	56	60	5	56	3 6	53	60	3	55	1 7	54	57	3	57	2 5	53	60	15
Na^{+} (mg/L)	10	0 41	9 9	10 8	4	10 4	0 21	10 2	10 6	5	9 6	0 77	8 7	10 2	3	9 0	0 26	8 7	9 2	3	10	0 72	8 7	10 8	15
Mg^{2+} (mg/L)	22	0 44	22	23	4	22	0 62	21	22	5	21	1 2	20	22	3	21	1 0	20	22	3	22	0 95	20	23	15
K^{+} (mg/L)	1 7	0 23	1 4	2 0	4	1 8	0 21	1 6	2 2	5	1 8	0 54	1 4	2 4	3	1 4	0 13	1 3	1 6	3	1 7	0 31	1 3	2 4	15
Total P (mg/L)	0 774	1 081	0 007	2 318	4	0 776	0 559	0 008	1 271	4	1 054	1 043	0 317	1 791	2	1 805	0 889	1 204	2 826	3	1 056	0 886	0 007	2 826	13
NH_4^{+} (mg-N/L)	0 067	0 025	0 050	0 085	2	0 137	0 007	0 132	0 142	2	0 037	0 026	0 018	0 066	3	0 033	0 025	0 004	0 051	3	0 062	0 046	0 004	0 142	10
Cl (mg/L)	15	1	14	16	4	13	4	6	15	5	12	6	5	15	3	15	0	15	16	3	14	3 3	5	16	15
SO_4^{2} (mg/L)	35	2	32	37	4	28	10	14	36	4	26	12	12	33	3	34	0	34	35	3	31	7 9	12	37	14
NO_3 (mg-N/L)	0 27	0 15	0 15	0 44	3	0 32	-	0 32	0 32	1	0 13	0 02	0 11	0 15	2	0 27	0 09	0 19	0 36	3	0 24	0 11	0 11	0 44	9
HCO_3 (mg/L)	246	17	230	270	4	220	42	149	253	5	184	35	159	223	3	218	24	191	237	3	220	36	149	270	15
Calculations																									
pCO_2 (atm)	-2 28	0 19	-2 52	-2 05	4	-2 34	0 29	-2 62	-1 91	5	-2 29	0 32	-2 66	-2 07	3	-2 09	0 28	-2 28	-1 77	3	-2 26	0 26	-2 66	-1 77	15
$SI_{calcite}$	1 822	0 520	1 396	2 491	4	1 660	1 030	0 444	3 238	5	0 687	0 386	0 374	1 118	3	0 735	0 424	0 247	1 018	3	1 324	0 825	0 247	3 238	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10 0	1 3	9 0	10 9	2	10 0	1 3	9 0	10 9	2
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6 4	1 0	5 7	7 1	2	6 4	1 0	5 7	7 1	2
Carbon																									
DIC (ppmC)	51	4	49	58	4	47	9	30	53	5	41	8	35	50	3	49	1	48	51	3	47	7	30	58	15
DOC (ppmC)	1 9	0 6	1 2	2 3	3	2 0	0 7	1 1	2 7	5	1 5	0 1	1 4	1 6	3	2 0	0 3	1 8	2 3	3	1 9	0 5	1 1	2 7	14
$\delta^{13}C_{DIC}$ (‰)	-15 1	0 2	-15 3	-14 9	4	-15 5	0 2	-15 8	-15 2	5	-15 6	0 4	-16 1	-15 3	3	-15 5	0 2	-15 7	-15 4	3	-15 4	0 3	-16 1	-14 9	15
$\delta^{13}C_{DOC}$ (‰)	-26 4	0 3	-26 8	-26 2	3	-25 1	2 0	-28 0	-22 9	5	-26 4	0 4	-26 9	-26 1	3	-26 7	0 2	-27 0	-26 5	3	-26 0	1 3	-28 0	-22 9	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 8	0 1	-10 9	-10 7	4	-10 8	0 1	-10 9	-10 6	5	-10 8	0 3	-11 1	-10 5	3	-9 6	1 5	-10 7	-8 6	2	-10 6	0 6	-11 1	-8 6	14
$\delta^{2}H_{H2O}$ (‰)	-78 0	2 5	-79 8	-76 2	2	-76 2	2 4	-77 7	-73 4	3	-78 0	1 1	-78 6	-76 7	3	-70 2	3 8	-72 9	-67 5	2	-75 9	3 7	-79 8	-67 5	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID			W1 A														
Type			Bedrock Well														
Depth			14 3 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	7 554	7 534	5 844	6 864	7 224	7 322	7 054	5 704	7 029	5 564	7 256	7 424	7 399	7 616	7 119
Temp (°C)	-	0 1	10 5	10 9	10 2	10 1	10 7	9 4	8 8	10 5	10 0	10 4	11 0	10 1	13 1	11 6	10 3
pH	-	0 01	7 4	7 3	7 4	7 1	7 0	7 2	6 5	7 2	7 1	7 0	6 8	7 0	6 9	7 1	7 1
SpC (µS/cm)	-	1	-	1837	956	1004	1123	1076	994	813	790	789	620	732	883	792	1139
DO (mg/L)	0 01	0 01	-	-	-	-	4 2	4 1	5 7	3 8	-	-	4 4	3 2	-	2 8	-
Eh (mV)	-	1	-	-	-	-	-	-	348	348	-	-	665	445	440	373	337
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	104	123	135	119	107	107	91	86	99	115	118	121	126	110	133
Na^{+} (mg/L)	1 0	-	5 5	9 9	5 0	9 0	12	13	8 8	7 8	7 0	5 7	6 0	6 1	5 3	9 5	8 3
Mg^{2+} (mg/L)	1 0	-	9 8	11	8 8	9 0	8 7	9 7	7 3	6 6	7 2	7 6	8 5	9 8	10	9 9	10
K^{+} (mg/L)	1 0	-	9 1	26	29	24	25	25	16	25	11	21	13	14	11	5 6	26
Total P (mg/L)	0 001	0 002	0 11	0 066	<0 65	<0 65	0 053	0 085	0 041	0 19	0 049	0 32	0 049	0 063	0 062	0 041	0 12
NH_4^{+} (mg-N/L)	0 001	0 003		-	0 015	0 014	0 024	0 021	0 018	0 034	0 01	0 009	0 006	0 003	-	-	-
Cl (mg/L)	1 0	-	11	14	12	10	-	11	12	18	12	13	11	12	8 0	7 8	15
SO_4^{2} (mg/L)	1 0	-	29	27	18	19	-	26	23	20	22	17	18	21	18	21	-
NO_3 (mg-N/L)	0 001	0 002	4 6	9 7	14	7 8	-	6 8	8 1	8 9	6 3	8 3	4 9	5 2	4 0	2 7	9 2
HCO_3 (mg/L)	3 9	-	335	346	458	366	340	202	139	275	316	310	300	340	424	522	363
Calculations																	
pCO_2 (atm)	-	-	-1 87	-1 79	-1 79	-1 54	-1 54	-1 99	-1 43	-1 78	-1 65	-1 54	-1 39	-1 53	-1 34	-1 44	-1 55
$SI_{calcite}$	-	-	1 705	1 729	3 147	1 027	0 848	0 801	0 091	0 786	0 862	0 747	0 516	0 889	1 052	1 617	1 158
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		10 6	-	-	10 9	-	-	-	11 4	-	-	13 4	13 2	-	-	13 5
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		5 1	-	-	0 4	-	-	-	2 2	-	-	7 4	1 5	-	-	0 9
Carbon																	
DIC (ppmC)	1 0	0 1	75	78	101	91	86	47	53	65	77	80	85	86	110	125	90
DOC (ppmC)	1 0	0 1	3 1	4 7	9 1	4 7	3 7	3 6	5 9	7 4	3 0	5 8	5 4	3 9	1 7	4 9	4 6
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-14 3	-15 1	-16 8	-16 1	-16 3	-15 9	-16 0	-16 3	-16 0	-16 8	-16 0	-16 4	16 2	-15 8	-16 5
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-25 3	-27 2	-30 6	-24 9	-27 6	-27 5	-27 6	-27 7	-27 5	-27 4	-27 4	-27 5	-27 5	-27 4	-27 9
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 6	-11 1	-10 1	-10 8	-10 7	-10 8	-10 8	-11 2	-	-10 7	-10 8	-11 0	-10 7	-11 0	-10 6
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-85 1	-80 2	-69 9	-78 0	-81 9	-78 1	-76 3	-76 3	-	-75 4	-	-75 9	-	-	

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID																						
Type																						
Depth																						
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	7 41	0 12	7 26	7 55	4	7 00	0 71	5 84	7 62	5	7 20	0 14	7 05	7 32	3	6 10	0 81	5 56	7 03	3	6 97	0 69	5 56	7 62	15
Temp (°C)	11 2	1 3	10 1	13 1	4	10 6	0 6	10 1	11 6	5	9 6	1 0	8 8	10 7	3	10 3	0 3	10 0	10 5	3	10 5	1 0	8 8	13 1	15
pH	7 0	0 2	6 8	7 4	4	7 2	0 2	7 1	7 4	5	6 9	0 4	6 5	7 2	3	7 1	0 1	7 0	7 2	3	7 1	0 2	6 5	7 4	15
SpC (µS/cm)	745	132	620	883	3	1146	406	792	1837	5	1064	65	994	1123	3	797	14	789	813	3	968	294	620	1837	14
DO (mg/L)	3 8	0 9	3 2	4 4	2	2 8	-	2 8	2 8	1	4 6	0 9	4 1	5 7	3	3 8	-	3 8	3 8	1	4 0	0 93	2 8	5 7	7
Eh (mV)	516	129	440	665	3	355	26	337	373	2	348	-	348	348	1	348	-	348	348	1	422	116	337	665	7
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	117	9 4	104	126	4	124	10	110	135	5	102	9 2	91	107	3	100	15	86	115	3	113	14	86	135	15
Na^{+} (mg/L)	5 7	0 4	5 3	6 1	4	8 4	2 0	5 0	9 9	5	11 1	2 0	8 8	12 8	3	6 8	1 1	5 7	7 8	3	7 9	2 4	5 0	12 8	15
Mg^{2+} (mg/L)	10	0 70	8 5	10	4	10	0 88	8 8	11	5	8 6	1 2	7 3	10	3	7 1	0 53	6 6	7 6	3	8 9	1 3	6 6	11	15
K^{+} (mg/L)	11 9	2 2	9 1	14 2	4	22 0	9 4	5 6	28 7	5	22 1	4 9	16 4	25 1	3	18 7	7 3	10 6	24 9	3	18 7	7 54	5 6	28 7	15
Total P (mg/L)	0 071	0 028	0 049	0 113	4	0 075	0 039	0 041	0 118	3	0 060	0 023	0 041	0 085	3	0 187	0 134	0 049	0 317	3	0 096	0 079	0 041	0 317	13
NH_4^{+} (mg-N/L)	0 005	0 003	0 003	0 006	2	0 015	0 001	0 014	0 015	2	0 021	0 003	0 018	0 024	3	0 018	0 014	0 009	0 034	3	0 016	0 009	0 003	0 034	10
Cl (mg/L)	10	1 6	8 0	12	4	12	3 0	7 8	15	5	12	0 8	11	12	2	14	3 3	12	18	3	12	2 7	7 8	18	14
SO_4^{2} (mg/L)	22	4 9	18	29	4	22	3 9	18	27	4	24	2 3	23	26	2	20	2 8	17	22	3	22	3 7	17	29	13
NO_3 (mg-N/L)	4 7	0 54	4 0	5 2	4	8 7	4 1	2 7	14 2	5	7 5	0 90	6 8	8 1	2	7 8	1 32	6 3	8 9	3	7 2	2 9	2 7	14 2	14
HCO_3 (mg/L)	350	53	300	424	4	411	76	346	522	5	227	103	139	340	3	301	22	275	316	3	336	93	139	522	15
Calculations																									
pCO_2 (atm)	-1 53	0 24	-1 87	-1 34	4	-1 62	0 16	-1 79	-1 44	5	-1 65	0 30	-1 99	-1 43	3	-1 66	0 12	-1 78	-1 54	3	-1 61	0 19	-1 99	-1 34	15
$SI_{calcite}$	1 040	0 496	0 516	1 705	4	1 735	0 843	1 027	3 147	5	0 580	0 424	0 091	0 848	3	0 799	0 058	0 747	0 862	3	1 132	0 710	0 091	3 147	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	12 4	1 6	10 6	13 4	3	12 2	1 8	10 9	13 5	2	-	-	-	-	-	11 4	-	11 4	11 4	1	12 2	1 3	10 6	13 5	6
$\delta^{18}O_{NO3}$ (‰)	4 7	3 0	1 5	7 4	3	0 7	0 4	0 4	0 9	2	-	-	-	-	-	2 2	-	2 2	2 2	1	2 9	2 7	0 4	7 4	6
Carbon																									
DIC (ppmC)	89	15	75	110	4	97	18	78	125	5	62	21	47	86	3	74	8	65	80	3	83	20	47	125	15
DOC (ppmC)	3 5	1 6	1 7	5 4	4	5 6	1 9	4 6	9 1	5	4 4	1 3	3 6	5 9	3	5 4	2 2	3 0	7 4	3	4 8	1 8	1 7	9 1	15
$\delta^{13}C_{DIC}$ (‰)	-15 7	0 9	-16 4	-14 3	4	-16 1	0 6	-16 8	-15 1	5	-16 1	0 2	-16 3	-15 9	3	-16 4	0 4	-16 8	-16 0	3	-16 0	0 6	-16 8	-14 3	15
$\delta^{13}C_{DOC}$ (‰)	-26 9	1 1	-27 5	-25 3	4	-27 6	2 0	-30 6	-24 9	5	-27 5	0 1	-27 6	-27 5	3	-27 5	0 2	-27 7	-27 4	3	-27 4	1 2	-30 6	-24 9	15
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 0	0 4	-11 6	-10 7	4	-10 7	0 4	-11 1	-10 1	5	-10 7	0 0	-10 8	-10 7	3	-11 0	0 3	-11 2	-10 7	2	-10 9	0 3	-11 6	-10 1	14
$\delta^{2}H_{H2O}$ (‰)	-80 5	6 5	-85 1	-75 9	2	-76 0	5 4	-80 2	-69 9	3	-78 8	2 9	-81 9	-76 3	3	-75 8	0 7	-76 3	-75 4	2	-77 7	4 1	-85 1	-69 9	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID			W1-B														
Type			Bedrock Well														
Depth			21 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	5 814	5 921	5 131	4 246	4 821	5 129	4 176	4 127	4 449	3 666	5 039	5 484	5 391	5 856	4 456
Temp (°C)	-	0 1	10 1	9 4	8 6	8 3	10 0	8 7	8 5	9 9	10 4	9 4	11 4	9 9	9 7	9 9	9 1
pH	-	0 01	7 2	7 6	8 2	7 3	7 6	7 0	7 2	7 4	7 7	7 0	7 6	7 6	7 3	7 5	7 3
SpC (µS/cm)	-	1	-	1866	1074	1147	1379	1204	1091	1050	1003	1022	755	777	1008	1012	1270
DO (mg/L)	0 01	0 01	-	-	-	-	0 3	0 6	0 8	1 0	-	-	0 5	0 4	0 4	0 4	-
Eh (mV)	-	1	-	-	-	-	-	-	392	310	-	-	390	382	-	349	308
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	<1 0	<1 0	<1 0	5 0	<1 0	0 2	0 3	1 7	0 2	0 2	0 2	0 2	0 2	0 2	0 4
Na^{+} (mg/L)	1 0	-	10	10	4 2	2 2	7 9	1 7	5 4	3 2	5 3	3 0	3 5	4 9	5 5	1 6	2 6
Mg^{2+} (mg/L)	1 0	-	<1 0	<1 0	<1 0	<1 0	<1 0	0 037	0 039	0 087	0 032	0 027	0 035	0 035	0 034	0 042	0 103
K^{+} (mg/L)	1 0	-	230	232	233	245	219	235	206	212	214	220	226	234	233	218	245
Total P (mg/L)	0 001	0 002	<0 65	0 009	0 011	<0 65	0 038	0 017	0 018	0 021	0 021	0 023	0 018	0 018	0 017	0 017	0 023
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 007	0 004	0 005	0 008	0 002	0 058	-	-	0 002	-	-	-	-
Cl (mg/L)	1 0	-	13	13	12	13	12	12	12	12	12	11	11	11	11	12	13
SO_4^{2} (mg/L)	1 0	-	41	42	45	44	43	40	40	41	42	42	39	39	39	41	-
NO_3 (mg-N/L)	0 001	0 002	1 1	0 90	0 88	1 4	1 0	0 92	1 3	1 4	1 0	1 5	0 81	1 0	1 1	1 1	1 7
HCO_3 (mg/L)	3 9	-	250	280	348	298	308	200	260	277	300	241	301	291	313	440	277
Calculations																	
pCO_2 (atm)	-	-	-1 89	-2 21	-2 68	-1 88	-2 18	-1 71	-1 83	-1 99	-2 25	-1 70	-2 12	-2 17	-1 85	-1 94	-1 95
$SI_{calcite}$	-	-	-		-	0 063	-	0 001	0 003	0 026	0 006	0 001	0 006	0 004	0 003	0 008	0 005
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	4 3	-	-	9 2	-	-	9 1	9 5	-	-	8 2
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	25 3	-	-	4 3	-	-	4 2	2 8	-	-	3 0
Carbon																	
DIC (ppmC)	1 0	0 1	58	59	70	68	65	53	61	61	63	61	64	62	71	94	62
DOC (ppmC)	1 0	0 1	1 6	2 4	3 3	1 3	1 2	1 4	2 2	2 0	1 5	1 5	3 4	2 0	0 9	3 8	1 6
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-12 7	-13 1	-13 5	-13 0	-13 1	-13 1	-11 7	-13 0	-13 5	-13 0	-13 2	-13 5	-13 4	-13 7	-13 1
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-21 6	-22 5	-22 5	-20 1	-26 5	-26 1	-26 6	-26 7	27 4	-26 3	-27 0	-26 8	-27 3	-27 1	-26 7
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 6	-11 3	-11 4	-11 5	-11 3	-11 1	-11 2	-11 0	-	-8 5	-10 9	-11 0	-11 1	-11 3	-11 1
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-82 8	-82 0	-80 9	-79 9	-81 5	-81 0	-80 1	-76 7	-	-67 2	-	-76 4	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	W1-B																						
Type	Bedrock Well																						
Depth	21 mbgs																						
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	5 43	0 32	5 04	5 81	4	5 12	0 77	4 25	5 92	5	4 71	0 49	4 18	5 13	3	4 08	0 39	3 67	4 45	3	4 91	0 71	3 67	5 92	15
Temp (°C)	10 3	0 8	9 7	11 4	4	9 1	0 6	8 3	9 9	5	9 1	0 8	8 5	10 0	3	9 9	0 5	9 4	10 4	3	9 6	0 8	8 3	11 4	15
pH	7 4	0 2	7 2	7 6	4	7 6	0 3	7 3	8 2	5	7 3	0 3	7 0	7 6	3	7 4	0 3	7 0	7 7	3	7 4	0 3	7 0	8 2	15
SpC (µS/cm)	847	140	755	1008	3	1274	345	1012	1866	5	1225	145	1091	1379	3	1025	24	1003	1050	3	1118	272	755	1866	14
DO (mg/L)	0 4	0 0	0 4	0 5	3	0 4	-	0 4	0 4	1	0 6	0 2	0 3	0 8	3	1 0	-	1 0	1 0	1	0 6	0 22	0 3	1 0	8
Eh (mV)	386	6	382	390	2	329	29	308	349	2	392	-	392	392	1	310	-	310	310	1	355	39	308	392	6
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	0 21	0 034	0 17	0 24	3	1 9	2 7	0 24	5 0	3	0 24	0 054	0 200	0 28	2	0 68	0 86	0 18	1 7	3	0 79	1 5	0 17	5 0	11
Na^{+} (mg/L)	6 0	2 8	3 5	9 9	4	4 0	3 2	1 6	9 6	5	5 0	3 1	1 7	7 9	3	3 8	1 3	3 0	5 3	3	4 7	2 7	1 6	9 9	15
Mg^{2+} (mg/L)	0 035	0 001	0 034	0 035	3	0 1	0 043	0 042	0 10	2	0 038	0 002	0 037	0 039	2	0 048	0 033	0 027	0 087	3	0 047	0 026	0 027	0 103	10
K^{+} (mg/L)	230 6	3 5	226 2	234 1	4	234 7	11 0	218 3	245 0	5	219 9	14 2	206 1	234 5	3	215 5	4 1	212 5	220 1	3	226 8	11 51	206 1	245 0	15
Total P (mg/L)	0 018	0 001	0 017	0 018	3	0 015	0 006	0 009	0 023	4	0 024	0 012	0 017	0 038	3	0 022	0 001	0 021	0 023	3	0 019	0 007	0 009	0 038	13
NH_4^{+} (mg-N/L)	0 002	-	0 002	0 002	1	0 006	0 003	0 004	0 007	2	0 005	0 003	0 002	0 008	3	0 058	-	0 058	0 058	1	0 012	0 020	0 002	0 058	7
Cl (mg/L)	12	1 1	11	13	4	12	0 54	12	13	5	12	0 33	12	12	3	12	0 57	11	12	3	12	0 71	11	13	15
SO_4^{2} (mg/L)	39	0 83	39	41	4	43	2 0	41	45	4	41	1 9	40	43	3	41	0 70	41	42	3	41	1 9	39	45	14
NO_3 (mg-N/L)	1 0	0 14	0 81	1 1	4	1 2	0 34	0 88	1 7	5	1 1	0 18	0 92	1 3	3	1 3	0 27	1 0	1 5	3	1 2	0 26	0 81	1 7	15
HCO_3 (mg/L)	289	28	250	313	4	328	68	277	440	5	256	54	200	308	3	273	30	241	300	3	292	54	200	440	15
Calculations																									
pCO_2 (atm)	-2 01	0 16	-2 17	-1 85	4	-2 13	0 33	-2 68	-1 88	5	-1 91	0 25	-2 18	-1 71	3	1 98	0 28	-2 25	-1 70	3	-2 02	0 25	-2 68	-1 70	15
$SI_{calcite}$	0 004	0 001	0 003	0 006	3	0 025	0 033	0 005	0 063	3	0 002	0 001	0 001	0 003	2	0 011	0 013	0 001	0 026	3	0 011	0 018	0 001	0 063	11
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	9 3	0 3	9 1	9 5	2	8 2	-	8 2	8 2	1	4 3	-	4 3	4 3	1	9 2	-	9 2	9 2	1	8 1	2 2	4 3	9 5	5
$\delta^{18}O_{NO3}$ (‰)	3 5	1 0	2 8	4 2	2	3 0	-	3 0	3 0	1	25 3	-	25 3	25 3	1	4 3	-	4 3	4 3	1	7 9	9 7	2 8	25 3	5
Carbon																									
DIC (ppmC)	64	6	58	71	4	71	14	59	94	5	60	6	53	65	3	62	1	61	63	3	65	9	53	94	15
DOC (ppmC)	2 0	1 0	0 9	3 4	4	2 5	1 1	1 3	3 8	5	1 6	0 5	1 2	2 2	3	1 6	0 3	1 5	2 0	3	2 0	0 9	0 9	3 8	15
$\delta^{13}C_{DIC}$ (‰)	-13 2	0 3	-13 5	-12 7	4	-13 3	0 3	-13 7	-13 0	5	-12 6	0 8	-13 1	-11 7	3	-13 2	0 3	-13 5	-13 0	3	-13 1	0 5	-13 7	-11 7	15
$\delta^{13}C_{DOC}$ (‰)	-25 7	2 7	-27 3	-21 6	4	-23 8	3 0	-27 1	-20 1	5	-26 4	0 3	-26 6	-26 1	3	-26 8	0 5	-27 4	-26 3	3	-25 4	2 4	-27 4	-20 1	15
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 2	0 3	-11 6	-10 9	4	-11 3	0 1	-11 5	-11 1	5	-11 2	0 1	-11 3	-11 1	3	-9 8	1 8	-11 0	-8 5	2	-11 0	0 8	-11 6	-8 5	14
$\delta^{2}H_{H2O}$ (‰)	-79 6	4 5	-82 8	-76 4	2	-80 9	1 1	-82 0	-79 9	3	-80 9	0 7	-81 5	-80 1	3	-72 0	6 7	-76 7	-67 2	2	-78 9	4 6	-82 8	-67 2	10

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID				W1-C													
Type				Bedrock Well													
Depth				14 8 mbgs													
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	4 930	4 032	3 430	3 968	4 043	3 630	4 191	3 702	2 792	4 240	4 535	4 488	4 855	3 795
Temp (°C)	-	0 1	-	10 6	10 0	-	12 0	9 1	8 6	10 5	11 4	10 5	15 2	11 4	12 1	10 8	10 4
pH	-	0 01	-	7 4	7 8	-	7 2	6 8	7 2	7 4	7 0	7 0	7 5	7 4	7 2	7 4	7 3
SpC (µS/cm)	-	1	-	1455	741	-	907	884	898	784	697	686	542	654	783	816	884
DO (mg/L)	0 01	0 01	-	-	-	-	0 7	0 1	0 1	0 4	0 3	-	0 5	0 2	0 9	0 2	-
Eh (mV)	-	1	-	-	-	-	-	-	83	332	-	-	411	252	-	-	140
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	90	86	-	86	88	77	83	80	85	92	94	95	93	94
Na^{+} (mg/L)	1 0	-	-	10	11	-	11	11	9 2	11	10	11	11	11	11	11	11
Mg^{2+} (mg/L)	1 0	-	-	18	17	-	17	18	15	17	16	18	18	19	19	19	19
K^{+} (mg/L)	1 0	-	-	2 5	2 4	-	2 6	2 7	2 4	2 7	2 3	2 6	2 8	3 7	3 2	4 5	3 5
Total P (mg/L)	0 001	0 002	-	0 013	0 024	-	0 019	0 044	0 018	0 027	0 027	0 030	0 031	0 034	0 062	0 043	0 053
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 067	-	0 049	0 062	0 052	0 076	0 045	0 046	0 064	0 47	0 41	1 1	0 31
Cl (mg/L)	1 0	-	-	13	12	-	14	12	14	15	14	13	15	19	17	21	16
SO_4^{2} (mg/L)	1 0	-	-	41	41	-	38	39	38	40	40	40	39	35	30	35	-
NO_3 (mg-N/L)	0 001	0 002	-	<0 001	<0 001	-	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	-	236	358	-	295	179	186	318	262	264	323	315	434	502	280
Calculations																	
pCO_2 (atm)	-	-	-	-2 04	-2 27	-	-1 73	-1 60	-2 02	-1 94	-1 62	-1 63	-2 02	-1 98	-1 63	-1 78	-1 88
$SI_{calcite}$	-	-	-	1 090	3 946	-	0 858	0 215	0 520	1 425	0 481	0 507	2 424	1 780	1 572	2 662	1 115
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	52	74	-	70	52	43	70	67	67	69	69	100	110	64
DOC (ppmC)	1 0	0 1	-	1 4	4 2	-	1 3	1 9	2 3	3 0	1 7	2 7	4 9	3 5	2 5	6 4	2 3
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-14 0	-14 2	-	-14 0	-14 1	-16 0	-14 2	14 4	-14 1	-14 0	-14 7	-14 7	-15 2	-14 6
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-25 9	-22 7	-	-26 5	-26 5	-26 7	-27 3	-27 4	-26 9	-26 9	-27 4	-27 3	-27 3	-27 4
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-11 3	-11 5	-	-11 4	-11 4	-11 5	-11 3	-	-9 5	-11 0	-11 5	-11 5	-11 7	-11 4
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-79 1	-82 4	-	83 6	-83 9	-83 2	-79 0	-	-72 0	-	-79 3	-	-	-

Table D2: Site 1 - Field Parameters, Analytical Results and Statistics.

Site ID	W1-C																					
Type	Bedrock Well																					
Depth	14 8 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	4 42	0 16	4 24	4 54	3	4 21	0 66	3 43	4 93	5	3 88	0 22	3 63	4 04	3	3 56	0 71	2 79	4 19	3	4 05	0 57	2 79	4 93	14
Temp (°C)	12 9	2 0	11 4	15 2	3	10 5	0 3	10 0	10 8	4	9 9	1 8	8 6	12 0	3	10 8	0 5	10 5	11 4	3	11 0	1 6	8 6	15 2	13
pH	7 4	0 1	7 2	7 5	3	7 5	0 2	7 3	7 8	4	7 1	0 2	6 8	7 2	3	7 1	0 2	7 0	7 4	3	7 3	0 3	6 8	7 8	13
SpC (µS/cm)	660	121	542	783	3	974	326	741	1455	4	896	12	884	907	3	722	54	686	784	3	826	218	542	1455	13
DO (mg/L)	0 6	0 3	0 2	0 9	3	0 2	-	0 2	0 2	1	0 3	0 4	0 1	0 7	3	0 3	0 0	0 3	0 4	2	0 4	0 28	0 1	0 9	9
Eh (mV)	331	113	252	411	2	140	-	140	140	1	83	-	83	83	1	332	-	332	332	1	244	135	83	411	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	94	1 2	92	95	3	91	3 6	86	94	4	84	6 2	77	88	3	83	2 5	80	85	3	88	5 7	77	95	13
Na^{+} (mg/L)	11	0 12	11 2	11	3	11	0 23	10 4	11	4	10	0 91	9 2	11	3	10	0 52	9 9	11	3	11	0 60	9 2	11	13
Mg^{2+} (mg/L)	19	1 0	18	19	3	18	0 85	17	19	4	17	1 4	15	18	3	17	1 2	16	18	3	18	1 3	15	19	13
K^{+} (mg/L)	3 2	0 43	2 8	3 7	3	3 2	1 0	2 4	4 5	4	2 6	0 15	2 4	2 7	3	2 5	0 2	2 3	2 7	3	2 9	0 62	2 3	4 5	13
Total P (mg/L)	0 042	0 017	0 031	0 062	3	0 033	0 018	0 013	0 053	4	0 027	0 015	0 018	0 044	3	0 028	0 002	0 027	0 030	3	0 033	0 014	0 013	0 062	13
NH_4^{+} (mg-N/L)	0 316	0 220	0 064	0 475	3	0 498	0 549	0 067	1 116	3	0 054	0 007	0 049	0 062	3	0 055	0 017	0 045	0 076	3	0 231	0 319	0 045	1 116	12
Cl (mg/L)	17	2 1	15	19	3	15	4 0	12	21	4	13	1 0	12	14	3	14	0 67	13	15	3	15	2 6	12	21	13
SO_4^{2} (mg/L)	35	4 2	30	39	3	39	3 7	35	41	3	39	0 67	38	39	3	40	0 21	40	40	3	38	3 2	30	41	12
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HCO_3 (mg/L)	357	66	315	434	3	344	117	236	502	4	220	65	179	295	3	281	32	262	318	3	304	90	179	502	13
Calculations																									
pCO_2 (atm)	-1 88	0 21	-2 02	-1 63	3	-1 99	0 22	-2 27	-1 78	4	-1 78	0 21	-2 02	-1 60	3	-1 73	0 18	-1 94	-1 62	3	-1 86	0 21	-2 27	-1 60	13
$SI_{calcite}$	1 926	0 444	1 572	2 424	3	2 203	1 375	1 090	3 946	4	0 531	0 322	0 215	0 858	3	0 804	0 538	0 481	1 425	3	1 430	1 064	0 215	3 946	13
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	79	18	69	100	3	75	25	52	110	4	55	13	43	70	3	68	2	67	70	3	70	18	43	110	13
DOC (ppmC)	3 6	1 2	2 5	4 9	3	3 5	2 2	1 4	6 4	4	1 9	0 5	1 3	2 3	3	2 5	0 7	1 7	3 0	3	2 9	1 5	1 3	6 4	13
$\delta^{13}C_{DIC}$ (‰)	-14 5	0 4	-14 7	-14 0	3	-14 5	0 5	-15 2	-14 0	4	-14 7	1 1	-16 0	-14 0	3	-14 2	0 2	-14 4	-14 1	3	-14 5	0 6	-16 0	-14 0	13
$\delta^{13}C_{DOC}$ (‰)	-27 2	0 3	-27 4	-26 9	3	-25 8	2 2	-27 4	-22 7	4	-26 6	0 1	-26 7	-26 5	3	-27 2	0 2	-27 4	-26 9	3	-26 6	1 3	-27 4	-22 7	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 3	0 3	-11 5	-11 0	3	-11 5	0 2	-11 7	-11 3	4	-11 4	0 0	-11 5	-11 4	3	-10 4	1 3	-11 3	-9 5	2	-11 2	0 6	-11 7	-9 5	12
$\delta^{2}H_{H2O}$ (‰)	-79 3	-	-79 3	-79 3	1	-80 8	2 3	-82 4	-79 1	2	-83 6	0 4	-83 9	-83 2	3	-75 5	4 9	-79 0	-72 0	2	-80 3	4 0	-83 9	-72 0	8

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			L2-1A														
Type			Lysimeter														
Depth			0 3 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	-	15 6	12 8	4 9	-	-	-	-	11 6	16 4	21 3	25 5	-	-	-
pH	-	0 01	-	7 4	7 5	7 3	-	-	-	-	6 6	7 2	7 1	6 9	-	-	-
SpC (µS/cm)	-	1	-	-	568	916	-	-	-	-	455	374	-	-	-	-	-
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Eh (mV)	-	1													-	-	-
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	50	46	46	58	-	-	-	-	34	32	31	35	-	-	-
Na^{+} (mg/L)	1 0	-	16	17	17	17	-	-	-	-	18	22	23	24	-	-	-
Mg^{2+} (mg/L)	1 0	-	12	11	12	15	-	-	-	-	7 6	7 3	7 3	8 4	-	-	-
K^{+} (mg/L)	1 0	-	3 6	3 0	2 8	2 5	-	-	-	-	2 7	2 8	2 9	3 5	-	-	-
Total P (mg/L)	0 001	0 002	<0 65	<0 65	0 033	<0 65	-	-	-	-	0 026	0 035	0 048	<0 65	-	-	-
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 080	0 013	-	-	-	-	0 034	0 054	0 374	0 104	-	-	-
Cl (mg/L)	1 0	-	25	22	-	11	-	-	-	-	12	11	9 5	9 4	-	-	-
SO_4^{2} (mg/L)	1 0	-	24	23	-	26	-	-	-	-	31	29	31	34	-	-	-
NO_3 (mg-N/L)	0 001	0 002	35	33	-	35	-	-	-	-	26	24	26	31	-	-	-
HCO_3 (mg/L)	3 9	-	-	17	61	90	-	-	-	-	42	42	50	14	-	-	-
Calculations																	
pCO_2 (atm)	-	-	-	-3 18	-2 70	-2 42	-	-	-	-	-2 04	-2 61	-2 35	-2 66	-	-	-
$SI_{calcite}$	-	-	-	0 054	0 220	0 194	-	-	-	-	0 015	0 071	0 066	0 015	-	-	-
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	5 7	-	-	-	-	10 1	-	10 8	7 2	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	1 4	-	-	-	-	1 9	-	0 3	0 9	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	3 7	13	21	-	-	-	-	14	10	12	3 7	-	-	-
DOC (ppmC)	1 0	0 1	-	3 1	10	10	-	-	-	-	16	16	16	15	-	-	-
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-15 0	-15 5	-16 4	-	-	-	-	-15 0	-14 4	-16 6	-15 8	-	-	-
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-25 5	-25 9	-25 8	-	-	-	-	-25 5	-25 3	-25 9	-25 9	-	-	-
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-9 79	-9 6	-9 4	-8 6	-	-	-	-	-	-9 2	-	-9 8	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-68 1	-68 5	-64 2	-62 5	-	-	-	-	-	-66 4	-	-70 1	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	L2-1A																								
Type	Lysimeter																								
Depth	0 3 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	23 4	3 0	21 3	25 5	2	11 1	5 5	4 9	15 6	3	-	-	-	-	-	14 0	3 4	11 6	16 4	2	15 4	6 7	4 9	25 5	7
pH	7 0	0 1	6 9	7 1	2	7 4	0 1	7 3	7 5	3	-	-	-	-	-	6 9	0 4	6 6	7 2	2	7 1	0 3	6 6	7 5	7
SpC (µS/cm)	-	-	-	-	-	742	246	568	916	2	-	-	-	-	-	414	57	374	455	2	578	239	374	916	4
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Eh (mV)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	39	10	31	50	3	50	7 1	46	58	3	-	-	-	-	-	33	1 0	32	34	2	41	10	31	58	8
Na^{+} (mg/L)	20 9	4 1	16 3	23 6	3	16 8	0 43	16 5	17 3	3	-	-		-	-	20 0	2 2	18 5	21 6	2	19 2	3 1	16 3	23 6	8
Mg^{2+} (mg/L)	9 3	2 5	7 3	12	3	13	2 1	11	15	3	-	-		-	-	7 4	0 17	7 3	7 6	2	10	2 9	7 3	15	8
K^{+} (mg/L)	3 4	0 40	2 9	3 6	3	2 8	0 24	2 5	3 0	3	-	-	-	-	-	2 8	0 037	2 7	2 8	2	3 0	0 39	2 5	3 6	8
Total P (mg/L)	0 048	-	0 048	0 048	1	0 033	-	0 033	0 033	1	-	-	-	-	-	0 031	0 007	0 026	0 035	2	0 036	0 009	0 026	0 048	4
NH_4^{+} (mg-N/L)	0 239	0 191	0 104	0 374	2	0 046	0 048	0 013	0 080	2	-	-	-	-	-	0 044	0 015	0 034	0 054	2	0 110	0 133	0 013	0 374	6
Cl (mg/L)	15	8 9	9 4	25	3	16	7 7	11	22	2	-	-	-	-	-	11	0 93	11	12	2	14	6 4	9 4	25	7
SO_4^{2} (mg/L)	30	5 5	24	34	3	24	2 2	23	26	2	-	-	-	-	-	30	1 6	29	31	2	28	4 2	23	34	7
NO_3 (mg-N/L)	31	5	26	35	3	34	2	33	35	2	-	-	-	-	-	25	0 74	24	26	2	30	5	24	35	7
HCO_3 (mg/L)	32	25	14	50	2	56	37	17	90	3	-	-	-	-	-	42	0 44	42	42	2	45	26	14	90	7
Calculations																									
pCO_2 (atm)	-2 51	0 22	-2 66	-2 35	2	-2 77	0 38	-3 18	-2 42	3	-	-	-	-	-	-2 33	0 40	-2 61	-2 04	2	-2 57	0 35	-3 18	-2 04	7
$SI_{calcite}$	0 040	0 036	0 015	0 066	2	0 156	0 089	0 054	0 220	3	-	-	-	-	-	0 043	0 039	0 015	0 071	2	0 091	0 083	0 015	0 220	7
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	9 0	2 5	7 2	10 8	2	5 7	-	5 7	5 7	1	-	-	-	-	-	10 1	-	10 1	10 1	1	8 5	2 4	5 7	10 8	4
$\delta^{18}O_{NO3}$ (‰)	0 6	0 4	0 3	0 9	2	1 4	-	1 4	1 4	1	-	-	-	-	-	1 9	-	1 9	1 9	1	1 1	0 7	0 3	1 9	4
Carbon																									
DIC (ppmC)	8	6	4	12	2	13	8	4	21	3	-	-	-	-	-	12	3	10	14	2	11	6	4	21	7
DOC (ppmC)	15 3	0 8	14 7	15 9	2	7 8	4 1	3 1	10 3	3	-	-	-	-	-	16 0	0 3	15 8	16 2	2	12 3	4 8	3 1	16 2	7
$\delta^{13}C_{DIC}$ (‰)	-16 2	0 6	-16 6	-15 8	2	-15 6	0 7	-16 4	-15 0	3	-	-	-	-	-	-14 7	0 4	-15 0	-14 4	2	-15 5	0 8	-16 6	-14 4	7
$\delta^{13}C_{DOC}$ (‰)	-25 9	0 0	-25 9	-25 9	2	-25 8	0 2	-25 9	-25 5	3	-	-	-	-	-	-25 4	0 1	-25 5	-25 3	2	-25 7	0 3	-25 9	-25 3	7
Water																									
$\delta^{18}O_{H2O}$ (‰)	-9 8	0 0	-9 8	-9 8	2	-9 2	0 6	-9 6	-8 6	3	-	-	-	-	-	-9 2	-	-9 2	-9 2	1	-9 4	0 5	-9 8	-8 6	6
$\delta^{2}H_{H2O}$ (‰)	-69 1	1 4	-70 1	-68 1	2	-65 1	3 1	-68 5	-62 5	3	-	-	-	-	-	-66 4	-	-66 4	-66 4	1	-66 6	2 9	-70 1	-62 5	6

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			L2-1B														
Type			Lysimeter														
Depth			0 9 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	18 3	19 8	13 7	6 9	4 0	3 8	0 2	-	10 9	13 2	20 0	24 7	21 1	16 0	8 6
pH	-	0 01	7 0	7 0	7 4	7 2	6 5	6 8	6 8	-	6 5	7 0	6 1	6 1	6 2	6 2	6 3
SpC (µS/cm)	-	1	904	888	540	695	2018	846	940	-	556	476	410	-	404	440	616
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	3 9	4 1	
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	-	401	422	295
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	41	40	41	41	41	41	39	-	39	41	41	44	39	35	33
Na^{+} (mg/L)	1 0	-	17	17	17	17	15	14	13	-	13	14	15	16	17	15	15
Mg^{2+} (mg/L)	1 0	-	14	15	15	15	16	15	15	-	15	16	15	16	14	13	13
K^{+} (mg/L)	1 0	-	0 90	1 0	1 0	0 83	0 90	0 67	0 54	-	0 65	0 66	0 74	0 87	0 93	0 83	0 73
Total P (mg/L)	0 001	0 002	<0 65	0 007	0 007	<0 65	0 026	<0 11	0 051	-	0 041	0 050	0 023	0 032	0 044	0 028	0 034
NH_4^{+} (mg-N/L)	0 001	0 003	-		0 051	0 007	0 004	0 017	0 005	-	0 012	0 044	0 013	0 008	-	-	-
Cl (mg/L)	1 0	-	30	29	-	27	26	25	24		20	20	19	19	18	17	17
SO_4^{2} (mg/L)	1 0	-	17	15	-	18	17	18	18	-	23	23	24	23	21	23	-
NO_3 (mg-N/L)	0 001	0 002	28	31	-	31	31	27	31	-	30	31	31	31	28	26	25
HCO_3 (mg/L)	3 9	-	49	36	129	139	60	83	59	-	76	78	45	52	49	45	38
Calculations																	
pCO_2 (atm)	-	-	-2 34	-2 46	-2 33	-2 10	-1 82	-1 97	-2 08	-	-1 70	-2 16	-1 41	-1 34	-1 50	-1 55	-1 76
$SI_{calcite}$	-	-	0 067	0 052	0 386	0 180	0 016	0 042	0 022	-	0 025	0 088	0 007	0 011	0 010	0 007	0 006
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		6 5	-	-	7 1	-	6 4	8 4	-	8 3	-	6 5	-	-	-	9 3
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		0 1	-	-	2 9	-	0 0	1 3	-	0 3	-	0 1	-	-	-	1 2
Carbon																	
DIC (ppmC)	1 0	0 1	12	8 8	28	33	24	25	19	-	28	19	28	29	24	24	20
DOC (ppmC)	1 0	0 1	-	1 4	3 7	3 6	2 5	3 0	4 5	-	3 0	3 1	4 1	3 3	1 7	3 0	2 6
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-14 2	-16 2	-16 6	-15 8	-16 8	-16 3	-16 6	-	-17 3	-16 2	-15 8	-16 4	-16 6	-16 5	-16 1
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-26 3	-26 1	-25 5	-25 8	-26 1	26 2	-	-26 2	-25 7	-26 2	-25 2	-26 0	-25 8	-25 6
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 6	-10 9	-10 5	-10 4	-9 8	-9 6	-9 7	-	-	-8 0	-	-9 7	-9 4	-9 4	-9 5
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-75 9	-74 1	-75 5	-72 5	-71 5	-69 2	-70 7	-	-	-59 0	-	-70 7	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	L2-1B																								
Type	Lysimeter																								
Depth	0 9 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	21 0	2 7	18 3	24 7	4	13 0	5 3	6 9	19 8	5	2 7	2 1	0 2	4 0	3	12 1	1 6	10 9	13 2	2	12 9	7 5	0 2	24 7	14
pH	6 3	0 5	6 1	7 0	4	6 8	0 6	6 2	7 4	5	6 7	0 2	6 5	6 8	3	6 8	0 3	6 5	7 0	2	6 6	0 4	6 1	7 4	14
SpC (µS/cm)	573	287	404	904	3	636	169	440	888	5	1268	652	846	2018	3	516	57	476	556	2	749	429	404	2018	13
DO (mg/L)	3 9	-	3 9	3 9	1	4 1	-	4 1	4 1	1	-	-	-	-	-	-	-	-	-	-	4 0	0 14	3 9	4 1	2
Eh (mV)	401	-	401	401	1	359	90	295	422	2	-	-	-	-		-	-	-	-	-	373	68	295	422	3
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	41	2 1	39	44	4	38	3 9	33	41	5	41	1 2	39	41	3	40	1 3	39	41	2	40	2 8	33	44	14
Na^{+} (mg/L)	16	0 85	15	17	4	16	0 93	15	17	5	14	1 2	13	15	3	13	1 0	13	14	2	15	1 4	13	17	14
Mg^{2+} (mg/L)	15	0 7	14	16	4	14	1 2	13	15	5	15	0 36	15	16	3	15	0 70	15	16	2	15	0 94	13	16	14
K^{+} (mg/L)	0 86	0 08	0 74	0 9	4	0 87	0 11	0 73	1 0	5	0 70	0 18	0 54	0 90	3	0 66	0 00	0 65	0 66	2	0 80	0 14	0 54	1 0	14
Total P (mg/L)	0 033	0 010	0 023	0 044	3	0 019	0 014	0 007	0 034	4	0 039	0 018	0 026	0 051	2	0 045	0 007	0 041	0 050	2	0 031	0 015	0 007	0 051	11
NH_4^{+} (mg-N/L)	0 011	0 003	0 008	0 013	2	0 029	0 030	0 007	0 051	2	0 009	0 007	0 004	0 017	3	0 028	0 022	0 012	0 044	2	0 018	0 017	0 004	0 051	9
Cl (mg/L)	21	5 5	18	30	4	23	6 4	17	29	4	25	1 1	24	26	3	20	0 58	20	20	2	22	4 6	17	30	13
SO_4^{2} (mg/L)	21	2 9	17	24	4	19	3 9	15	23	3	17	0 33	17	18	3	23	0 10	23	23	2	20	3 1	15	24	12
NO_3 (mg-N/L)	29	2 0	28	31	4	28	3 3	25	31	4	30	2 6	27	31	3	30	0 65	30	31	2	29	2 4	25	31	13
HCO_3 (mg/L)	49	2 7	45	52	4	77	52	36	139	5	67	14	59	83	3	77	1 1	76	78	2	67	32	36	139	14
Calculations																									
pCO_2 (atm)	-1 64	0 47	-2 34	-1 34	4	-2 04	0 38	-2 46	-1 55	5	-1 95	0 13	-2 08	-1 82	3	-1 93	0 33	-2 16	-1 70	2	-1 89	0 37	-2 46	-1 34	14
$SI_{calcite}$	0 024	0 029	0 007	0 067	4	0 126	0 162	0 006	0 386	5	0 026	0 014	0 016	0 042	3	0 056	0 044	0 025	0 088	2	0 066	0 104	0 006	0 386	14
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	6 5	0 0	6 5	6 5	2	8 2	1 6	7 1	9 3	2	7 4	1 4	6 4	8 4	2	8 3	-	8 3	8 3	1	7 5	1 2	6 4	9 3	7
$\delta^{18}O_{NO3}$ (‰)	0 1	0 0	0 1	0 1	2	2 1	1 2	1 2	2 9	2	0 7	0 9	0 0	1 3	2	0 3	-	0 3	0 3	1	0 8	1 1	0 0	2 9	7
Carbon																									
DIC (ppmC)	23	8	12	29	4	23	9	9	33	5	23	3	19	25	3	24	6	19	28	2	23	7	9	33	14
DOC (ppmC)	3 0	1 2	1 7	4 1	3	2 8	0 9	1 4	3 7	5	3 3	1 1	2 5	4 5	3	3 1	0 1	3 0	3 1	2	3 0	0 9	1 4	4 5	13
$\delta^{13}C_{DIC}$ (‰)	-15 8	1 1	-16 6	-14 2	4	-16 3	0 3	-16 6	-15 8	5	-16 6	0 2	-16 8	-16 3	3	-16 8	0 8	-17 3	-16 2	2	-16 3	0 7	-17 3	-14 2	14
$\delta^{13}C_{DOC}$ (‰)	-25 8	0 5	-26 2	-25 2	3	-25 9	0 4	-26 3	-25 5	5	-26 0	0 2	-26 2	-25 8	3	-26 0	0 4	-26 2	-25 7	2	-25 9	0 3	-26 3	-25 2	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-9 9	0 6	-10 6	-9 4	3	-10 1	0 7	-10 9	-9 4	5	-9 7	0 1	-9 8	-9 6	3	-8 0	-	-8 0	-8 0	1	-9 8	0 8	-10 9	-8 0	12
$\delta^{2}H_{H2O}$ (‰)	-73 3	3 7	-75 9	-70 7	2	-74 0	1 5	-75 5	-72 5	3	-70 5	1 2	-71 5	-69 2	3	-59 0	-	-59 0	-59 0	1	-71 0	5 0	-75 9	-59 0	9

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			L2-1C														
Type			Lysimeter														
Depth			1 8 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-		-		-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	17 9	17 8	12 8	7 5	4 7	-	-	-	11	11	17	25 1	21 5	19	10 7
pH	-	0 01	7 1	7 4	7 2	7 4	7 37	-	-	-	7 8	7 0	7 5	8 0	7 6	7 7	7 6
SpC (µS/cm)	-	1	1503	1543	883	1040	1424	-	-	-	685	672	547	-	595	631	949
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	3 5	2 0	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	-	379	397	267
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	77	79	78	76	71	-	-	-	57	67	68	71	73	73	74
Na^{+} (mg/L)	1 0	-	24	25	24	22	20	-	-	-	19	15	16	17	19	19	20
Mg^{2+} (mg/L)	1 0	-	34	36	35	32	31	-	-	-	23	29	29	31	31	31	32
K^{+} (mg/L)	1 0	-	4 3	4 7	4 6	4 3	3 6	-	-	-	3 0	2 2	2 6	2 9	3 2	3 2	3 2
Total P (mg/L)	0 001	0 002	<0 65	0 010	0 007	<0 65	<0 65	0 56	-	-	<0 11	0 028	0 032	0 019	0 13	0 020	0 027
NH_4^{+} (mg-N/L)	0 001	0 003	-	0 010	0 061	0 009	0 015	-	-	-	0 37	0 029	-	0 013	-	-	-
Cl (mg/L)	1 0	-	31	32	-	30	20	-	-	-	26	24	27	27	-	28	27
SO_4^{2} (mg/L)	1 0	-	45	51	-	44	25	-	-	-	28	24	29	31	-	34	-
NO_3 (mg-N/L)	0 001	0 002	0 67	0 42	-	2 4	1 1	-	-	-	14	14	12	8 5	-	3 3	3 1
HCO_3 (mg/L)	3 9	-	323	187	352	348	271	-	-	-	217	191	267	277	370	305	311
Calculations																	
pCO_2 (atm)	-	-	-1 64	-2 15	-1 72	-1 94	-2 01	-	-	-	-2 50	-1 80	-2 09	-2 53	-2 05	-2 22	-2 18
$SI_{calcite}$	-	-	0 946	1 053	1 096	1 329	0 806	-	-	-	1 723	0 316	1 580	7 102	3 705	3 229	2 124
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	6 7	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		9 4	-	-	9 0	-	-	-	-	-	8 1	8 1	-	-	-	6 9
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		1 9	-	-	2 5	-	-	-	-	-	1 4	0 8	-	-	-	6 4
Carbon																	
DIC (ppmC)	1 0	0 1	75 21	40	81	77	61 03	-	-	-	45	48	57	56	77	63	65
DOC (ppmC)	1 0	0 1	-	1 6	4 4	3 1	4 3	-	-	-	13	11	6 4	6 0	4 5	6 5	4 2
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-13 6	-14 4	-13 6	-13 4	-14 3	-	-	-	-13 4	-14 1	-13 7	-14 3	-14 6	-15 0	-14 7
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-25 5	-22 6	-22 4	-27 1	-	-	-	-27 8	-28 0	-28 2	-28 6	-28 5	-28 1	-28 0
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 2	-11 1	-11 2	-11 1	-10 9	-	-	-	-	-10 5	-	-11 1	-10 2	-10 9	-10 9
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-80 2	-80 5	-75 1	-75 2	-78 8	-	-	-	-	-69 7	-	-80 8	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	L2-1C																								
Type	Lysimeter																								
Depth	1 8 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	20 4	3 7	17 0	25 1	4	13 6	4 8	7 5	19 0	5	4 7	-	4 7	4 7	1	11 0	0 0	11 0	11 0	2	14 7	6 0	4 7	25 1	12
pH	7 6	0 4	7 1	8 0	4	7 5	0 2	7 2	7 7	5	7 4	-	7 4	7 4	1	7 4	0 5	7 0	7 8	2	7 5	0 3	7 0	8 0	12
SpC (µS/cm)	881	539	547	1503	3	1009	335	631	1543	5	1424	-	1424	1424	1	678	10	672	685	2	952	379	547	1543	11
DO (mg/L)	3 5	-	3 5	3 5	1	2 0	-	2 0	2 0	1	-	-	-	-	-	-	-	-	-	-	2 8	1 07	2 0	3 5	2
Eh (mV)	379	-	379	379	1	332	92	267	397	2	-	-	-	-	-	-	-	-	-	-	348	70	267	397	3
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	72	3 9	68	77	4	76	2 5	73	79	5	71	-	71	71	1	62	7 3	57	67	2	72	6 1	57	79	12
Na^{+} (mg/L)	19	3 4	16	24	4	22	2 8	19	25	5	20	-	20	20	1	17	3 1	15	19	2	20	3 3	15	25	12
Mg^{2+} (mg/L)	31	1 9	29	34	4	33	2 0	31	36	5	31	-	31	31	1	26	4 3	23	29	2	31	3 3	23	36	12
K^{+} (mg/L)	3 2	0 71	2 6	4 3	4	4 0	0 72	3 2	4 7	5	3 6	-	3 6	3 6	1	2 6	0 55	2 2	3 0	2	3 5	0 80	2 2	4 7	12
Total P (mg/L)	0 060	0 060	0 019	0 129	3	0 016	0 009	0 007	0 027	4	0 562	-	0 562	0 562	1	0 028	-	0 028	0 028	1	0 093	0 180	0 007	0 562	9
NH_4^{+} (mg N/L)	0 013	-	0 013	0 013	1	0 027	0 030	0 009	0 061	3	0 015	-	0 015	0 015	1	0 198	0 239	0 029	0 367	2	0 072	0 131	0 009	0 367	7
Cl (mg/L)	28	2 3	27	31	3	29	2 0	27	32	4	20	-	20	20	1	25	1 2	24	26	2	27	3 4	20	32	10
SO_4^{2} (mg/L)	35	8 7	29	45	3	43	8 8	34	51	3	25	-	25	25	1	26	2 9	24	28	2	34	9 8	24	51	9
NO_3 (mg-N/L)	7 0	5 8	0 67	12	3	2 3	1 3	0 42	3 3	4	1 1	-	1 1	1 1	1	14	0 007	14	14	2	6 0	5 6	0 42	14	10
HCO_3 (mg/L)	309	47	267	370	4	301	67	187	352	5	271	-	271	271	1	204	18	191	217	2	285	62	187	370	12
Calculations																									
pCO_2 (atm)	-2 08	0 36	-2 53	-1 64	4	-2 04	0 21	-2 22	-1 72	5	-2 01	-	-2 01	-2 01	1	-2 15	0 49	-2 50	-1 80	2	-2 07	0 27	-2 53	-1 64	12
$SI_{calcite}$	3 333	2 776	0 946	7 102	4	1 766	0 924	1 053	3 229	5	0 806	-	0 806	0 806	1	1 020	0 995	0 316	1 723	2	2 084	1 863	0 316	7 102	12
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-		-	-	-	-	-	6 7	-	6 7	6 7	1	6 7	-	6 7	6 7	1
$\delta^{15}N_{NO3}$ (‰)	8 8	0 9	8 1	9 4	2	8 0	1 5	6 9	9 0	2	-	-	-	-	-	8 1	-	8 1	8 1	1	8 3	1 0	6 9	9 4	5
$\delta^{18}O_{NO3}$ (‰)	1 4	0 8	0 8	1 9	2	4 5	2 8	2 5	6 4	2	-	-	-	-	-	1 4	-	1 4	1 4	1	2 6	2 2	0 8	6 4	5
Carbon																									
DIC (ppmC)	66	11	56	77	4	65	16	40	81	5	61	-	61	61	1	46	2	45	48	2	62	14	40	81	12
DOC (ppmC)	5 6	1 0	4 5	6 4	3	4 0	1 8	1 6	6 5	5	4 3	-	4 3	4 3	1	11 9	1 7	10 7	13 1	2	5 9	3 3	1 6	13 1	11
$\delta^{13}C_{DIC}$ (‰)	-14 0	0 5	-14 6	-13 6	4	-14 2	0 7	-15 0	-13 4	5	-14 3	-	-14 3	-14 3	1	-13 7	0 5	-14 1	-13 4	2	-14 1	0 5	-15 0	-13 4	12
$\delta^{13}C_{DOC}$ (‰)	-28 4	0 2	-28 6	-28 2	3	-25 3	2 8	-28 1	-22 4	5	-27 1	-	-27 1	-27 1	1	-27 9	0 1	-28 0	-27 8	2	-26 8	2 3	-28 6	-22 4	11
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 8	0 5	-11 2	-10 2	3	-11 0	0 1	-11 2	-10 9	5	-10 9	-	-10 9	-10 9	1	-10 5	-	-10 5	-10 5	1	-10 9	0 3	-11 2	-10 2	10
$\delta^{2}H_{H2O}$ (‰)	-80 5	0 4	-80 8	-80 2	2	-76 9	3 1	-80 5	-75 1	3	-78 8	-	-78 8	-78 8	1	69 7	-	-69 7	-69 7	1	-77 2	4 1	-80 8	-69 7	7

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			T2-A															
Type			Tile Drain															
Depth			1 0 mbgs															
Season			Summer	Fall			Winter			Spring			Summer			Fall		
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06	
Field																		
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Temp (°C)	-	0 1	-	-	10 3	8 6	-	2 8	1 7	3 5	6 0	10 3	-	-	-	-	10 0	
pH	-	0 01	-	-	6 8	6 7	-	6 4	6 8	7 3	7 5	6 9	-	-	-	-	7 2	
SpC (µS/cm)	-	1	-	-	-	2253	-	2774	2634	2419	2003	1388	-	-	-	-	1083	
DO (mg/L)	0 01	0 01	-	-	-	-	-	9 1	-	-	-	-	-	-	-	-	-	
Eh (mV)	-	1	-	-	-	-	-	-	356	-	-	-	-	-	-	-	233	
Major Ions and Nutrients																		
Ca^{2+} (mg/L)	1 0	-	-	-	223	165	-	142	117	131	124	113	-	-	-	-	128	
Na^{+} (mg/L)	1 0	-	-	-	239	161	-	120	108	118	103	105	-	-	-	-	158	
Mg^{2+} (mg/L)	1 0	-	-	-	54	42	-	37	30	33	34	29	-	-	-	-	34	
K^{+} (mg/L)	1 0	-	-	-	2 9	2 3	-	2 0	1 9	2 0	2 0	1 9	-	-	-	-	3 4	
Total P (mg/L)	0 001	0 002	-	-	0 020	<0 65	0 025	0 40	0 029	0 019	0 023	0 038	-	-	-	-	0 076	
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 005	0 014	-	0 010	0 003	0 014	0 018	0 007	-	-	-	-	-	
Cl (mg/L)	1 0	-	-	-	640	260	-	322	325	359	325	254	-	-	-	-	79	
SO_4^{2} (mg/L)	1 0	-	-	-	45	21	-	28	27	25	29	25	-	-	-	-	-	
NO_3 (mg-N/L)	0 001	0 002	-	-	4 1	2 3	-	3 9	2 7	2 3	3 5	4 9	-	-	-	-	8 8	
HCO_3 (mg/L)	3 9	-	-	-	299	280	-	88	164	312	335	263	-	-	-	-	-	
Calculations																		
pCO_2 (atm)	-	-	-	-	-1 32	-1 31	-	-1 58	-1 71	-1 85	-2 08	-1 52	-	-	-	-	-	
$SI_{calcite}$	-	-	-	-	0 555	0 380	-	0 048	0 182	1 037	2 221	0 441	-	-	-	-	-	
Nitrogen Isotopes																		
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	7 3	-	-	-	-	-	3 8	-	-	-	-	3 5	
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	2 4	-	-	-	-	-	24 8	-	-	-	-	24 6	
Carbon																		
DIC (ppmC)	1 0	0 1	-	-	90	89	-	39	49	73	72	71	-	-	-	-	-	
DOC (ppmC)	1 0	0 1	-	-	6 0	2 8	-	3 5	4 8	3 6	2 2	4 6	-	-	-	-	5 0	
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-11 5	-11 4	-	-11 6	-11 9	-11 5	-11 6	-11 7	-	-	-	-	-12 7	
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-22 3	-22 2	-	-25 5	-26 6	-25 6	-25 6	-24 4	-	-	-	-	-26 0	
Water																		
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-10 9	-10 1	-	-10 0	-11 1	-11 0	-	-10 7	-	-	-	-	-	
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-80 2	-71 5	-	-72 4	-78 7	-74 1	-	-75 2	-	-	-	-	-	

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID						T2-A																			
Type						Tile Drain																			
Depth						1 0 mbgs																			
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	-	-	-	-	9 6	0 9	8 6	10 3	3	2 3	0 8	1 7	2 8	2	6 6	3 4	3 5	10 3	3	6 7	3 6	1 7	10 3	8
pH	-	-	-	-	-	6 9	0 3	6 7	7 2	3	6 6	0 3	6 4	6 8	2	7 2	0 3	6 9	7 5	3	7 0	0 4	6 4	7 5	8
SpC (µS/cm)	-	-	-	-	-	1668	828	1083	2253	2	2704	99	2634	2774	2	1937	519	1388	2419	3	2079	634	1083	2774	7
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	9 1	-	9 1	9 1	1	-	-	-	-	-	9 1	-	9 1	9 1	1
Eh (mV)	-	-	-	-	-	233	-	233	233	1	356	-	356	356	1	-	-	-	-	-	294	87	233	356	2
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	-	-	-	-	-	172	48	128	223	3	130	18	117	142	2	123	8 9	113	131	3	143	36	113	223	8
Na^{+} (mg/L)	-	-	-	-	-	186	46	158	239	3	114	8 5	108	120	2	109	7 9	103	118	3	139	46	103	239	8
Mg^{2+} (mg/L)	-	-	-	-	-	43	10	34	54	3	34	5 1	30	37	2	32	2 6	29	34	3	37	8 0	29	54	8
K^{+} (mg/L)	-	-	-	-	-	2 8	0 59	2 3	3 4	3	1 9	0 052	1 9	2 0	2	2 0	0 030	1 9	2 0	3	2 3	0 56	1 9	3 4	8
Total P (mg/L)	-	-	-	-	-	0 048	0 040	0 020	0 076	2	0 151	0 215	0 025	0 400	3	0 027	0 010	0 019	0 038	3	0 079	0 131	0 019	0 400	8
NH_4^{+} (mg-N/L)	-	-	-	-	-	0 009	0 007	0 005	0 014	2	0 006	0 005	0 003	0 010	2	0 013	0 006	0 007	0 018	3	0 010	0 006	0 003	0 018	7
Cl (mg/L)	-	-	-	-	-	327	286	79	640	3	324	1 6	322	325	2	313	54	254	359	3	321	156	79	640	8
SO_4^{2} (mg/L)	-	-	-	-	-	33	17	21	45	2	27	0 6	27	28	2	26	2 2	25	29	3	28	7 9	21	45	7
NO_3 (mg-N/L)	-	-	-	-	-	5 1	3 4	2 3	8 8	3	3 3	0 79	2 7	3 9	2	3 6	1 3	2 3	4 9	3	4 1	2 1	2 3	8 8	8
HCO_3 (mg/L)	-	-	-	-	-	289	14	280	299	2	126	54	88	164	2	304	37	263	335	3	249	90	88	335	7
Calculations																									
pCO_2 (atm)	-	-	-	-	-	-1 32	0 01	-1 32	-1 31	2	-1 65	0 09	-1 71	-1 58	2	-1 82	0 28	-2 08	-1 52	3	-1 63	0 28	-2 08	-1 31	7
$SI_{calcite}$	-	-	-	-	-	0 467	0 124	0 380	0 555	2	0 115	0 095	0 048	0 182	2	1 233	0 906	0 441	2 221	3	0 695	0 743	0 048	2 221	7
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	5 4	2 7	3 5	7 3	2	-	-	-	-	-	3 8	-	3 8	3 8	1	4 9	2 1	3 5	7 3	3
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	13 5	15 7	2 4	24 6	2	-	-	-	-	-	24 8	-	24 8	24 8	1	17 3	12 9	2 4	24 8	3
Carbon																									
DIC (ppmC)	-	-	-	-	-	89	0 7	89	90	2	44	7	39	49	2	72	0 9	71	73	3	69	19	39	90	7
DOC (ppmC)	-	-	-	-	-	4 6	1 7	2 8	6 0	3	4 2	0 9	3 5	4 8	2	3 4	1 2	2 2	4 6	3	4 1	1 3	2 2	6 0	8
$\delta^{13}C_{DIC}$ (‰)	-	-	-	-	-	-11 9	0 7	-12 7	-11 4	3	-11 7	0 2	-11 9	-11 6	2	-11 6	0 1	-11 7	-11 5	3	-11 7	0 4	-12 7	-11 4	8
$\delta^{13}C_{DOC}$ (‰)	-	-	-	-	-	-23 5	2 1	-26 0	-22 2	3	-26 0	0 8	-26 6	-25 5	2	-25 2	0 7	-25 6	-24 4	3	-24 8	1 7	-26 6	-22 2	8
Water																									
$\delta^{18}O_{H2O}$ (‰)	-	-	-	-	-	-10 5	0 5	-10 9	-10 1	2	-10 5	0 8	-11 1	-10 0	2	-10 9	0 2	-11 0	-10 7	2	-10 6	0 5	-11 1	-10 0	6
$\delta^{2}H_{H2O}$ (‰)	-	-	-	-	-	-75 9	6 2	-80 2	-71 5	2	-75 6	4 5	-78 7	-72 4	2	-74 6	0 7	-75 2	-74 1	2	-75 3	3 5	-80 2	-71 5	6

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			T2-B														
Type			Tile Drain														
Depth			1 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	-	-	8 3	9 1	-	3 9	1 0	3 1	6 0	8 1	-	-	-	-	9 6
pH	-	0 01	-	-	6 9	6 8	-	7 5	7 5	7 5	7 5	7 5	-	-	-	-	7 0
SpC (µS/cm)	-	1	-	-	-	1032	-	1517	1588	706	909	-	-	-	-	-	2123
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	9 1	-	-	-	-	-	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	316	-	-	-	-	-	-	217
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	-	141	82	-	78	71	31	69	54	-	-	-	-	78
Na^{+} (mg/L)	1 0	-	-	-	116	35	-	34	31	28	23	24	-	-	-	-	33
Mg^{2+} (mg/L)	1 0	-	-	-	39	26	-	24	24	10	23	17	-	-	-	-	25
K^{+} (mg/L)	1 0	-	-	-	1 8	0 94	-	1 2	0 85	2 8	0 78	1 7	-	-	-	-	1 4
Total P (mg/L)	0 001	0 002	-	-	0 055	<0 65	0 026	0 21	0 059	0 19	0 022	0 071	-	-	-	-	0 21
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 004	0 004	-	0 013	-	0 20	0 013	0 007	-	-	-	-	-
Cl (mg/L)	1 0	-	-	-	326	94	-	70	100	76	70	53	-	-	-	-	315
SO_4^{2} (mg/L)	1 0	-	-	-	36	27	-	22	22	12	24	17	-	-	-	-	-
NO_3 (mg-N/L)	0 001	0 002	-	-	4 4	9 4	-	5 4	6 2	2 4	8 3	6 7	-	-	-	-	3 3
HCO_3 (mg/L)	3 9	-	-	-	288	183	-	120	213	98	241	176	-	-	-	-	194
Calculations																	
pCO_2 (atm)	-	-	-	-	-1 47	-1 55	-	-2 49	-2 21	-2 61	-2 23	-2 28	-	-	-	-	-1 79
$SI_{calcite}$	-	-	-	-	0 496	0 177	-	0 504	0 652	0 190	1 071	0 580	-	-	-	-	0 314
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	6 5	-	5 1	-	4 9	-	6 7	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-1 0	-	2 7	-	8 4	-	1 0	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	-	80	55	-	26	47	21	52	38		-	-	-	49
DOC (ppmC)	1 0	0 1	-	-	7 1	2 2	-	3 4	4 3	4 1	2 7	5 9	-	-	-	-	3 4
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-11 1	-11 6	-	-11 8	-11 6	-12 8	-11 4	-12 1	-	-	-	-	-
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-24 0	-23 1	-	-24 2	-26 2	-21 4	-25 7	-21 4	-	-	-	-	-24 9
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-10 6	-10 3	-	-10 1	-11 0	-11 1	-	-10 7	-	-	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-69 9	-71 4	-	-73 3	-77 7	-75 9	-	-78 7	-	-	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	T2-B																							
Type	Tile Drain																							
Depth	1 5 mbgs																							
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	-	-	-	-	9 0	0 7	8 3	9 6	3	2 5	2 1	1 0	3 9	2	5 7	2 5	3 1	8 1	3	6 1	3 2	1 0	9 6	8
pH	-	-	-	-	-	6 9	0 1	6 8	7 0	3	7 5	0 0	7 5	7 5	2	7 5	0 0	7 5	7 5	3	7 3	0 3	6 8	7 5	8
SpC (µS/cm)	-	-	-	-	-	1577	772	1032	2123	2	1553	50	1517	1588	2	807	144	706	909	2	1313	526	706	2123	6
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9 1	-	9 1	9 1	1	9 1	-	9 1	9 1	1
Eh (mV)	-	-	-	-	-	217	-	217	217	1	-	-	-	-	-	316	-	316	316	1	267	70	217	316	2
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	-	-	-	-	-	100	35	78	141	3	74	4 8	71	78	2	51	19	31	69	3	75	31	31	141	8
Na^{+} (mg/L)	-	-	-	-	-	61	47	33	116	3	32	2 0	31	34	2	25	2 7	23	28	3	40	31	23	116	8
Mg^{2+} (mg/L)	-	-	-	-	-	30	7 8	25	39	3	24	0 21	24	24	2	17	6 6	10	23	3	23	8 2	10	39	8
K^{+} (mg/L)	-	-	-	-	-	1 4	0 43	0 94	1 8	3	1 0	0 23	0 9	1 2	2	1 7	1 0	0 78	2 8	3	1 4	0 66	0 78	2 8	8
Total P (mg/L)	-	-	-	-	-	0 134	0 111	0 055	0 212	2	0 099	0 098	0 026	0 210	3	0 093	0 085	0 022	0 187	3	0 105	0 083	0 022	0 212	8
NH_4^{+} (mg-N/L)	-	-	-	-	-	0 004	0 000	0 004	0 004	2	0 013	-	0 013	0 013	1	0 073	0 109	0 007	0 198	3	0 040	0 078	0 004	0 198	6
Cl (mg/L)	-	-	-	-	-	245	131	94	326	3	85	21	70	100	2	67	12	53	76	3	138	113	53	326	8
SO_4^{2} (mg/L)	-	-	-	-	-	31	6 5	27	36	2	22	0 23	22	22	2	18	6 2	12	24	3	23	7 6	12	36	7
NO_3 (mg-N/L)	-	-	-	-	-	5 7	3 24	3 3	9 4	3	5 8	0 55	5 4	6 2	2	5 8	3 0	2 4	8 3	3	5 8	2 4	2 4	9 4	8
HCO_3 (mg/L)	-	-	-	-	-	222	58	183	288	3	167	65	120	213	2	172	71	98	241	3	189	61	98	288	8
Calculations																									
pCO_2 (atm)	-	-	-	-	-	-1 60	0 16	-1 79	-1 47	3	-2 35	0 19	-2 49	-2 21	2	-2 37	0 21	-2 61	-2 23	3	-2 08	0 42	-2 61	-1 47	8
$SI_{calcite}$	-	-	-	-	-	0 329	0 160	0 177	0 496	3	0 578	0 105	0 504	0 652	2	0 613	0 441	0 190	1 071	3	0 498	0 290	0 177	1 071	8
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	6 5	-	6 5	6 5	1	5 1	-	5 1	5 1	1	5 8	1 3	4 9	6 7	2	5 8	0 9	4 9	6 7	4
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-1 0	-	-1 0	-1 0	1	2 7	-	2 7	2 7	1	4 7	5 2	1 0	8 4	2	2 8	4 0	-1 0	8 4	4
Carbon																									
DIC (ppmC)	-	-	-	-	-	61	17	49	80	3	37	15	26	47	2	37	15	21	52	3	46	18	21	80	8
DOC (ppmC)	-	-	-	-	-	4 3	2 6	2 2	7 1	3	3 9	0 6	3 4	4 3	2	4 2	1 6	2 7	5 9	3	4 1	1 6	2 2	7 1	8
$\delta^{13}C_{DIC}$ (‰)	-	-	-	-	-	-11 4	0 4	-11 6	-11 1	2	-11 7	0 1	-11 8	-11 6	2	-12 1	0 7	-12 8	-11 4	3	-11 8	0 6	-12 8	-11 1	7
$\delta^{13}C_{DOC}$ (‰)	-	-	-	-	-	-24 0	0 9	-24 9	-23 1	3	-25 2	1 4	-26 2	-24 2	2	-22 8	2 5	-25 7	-21 4	3	-23 9	1 8	-26 2	-21 4	8
Water																									
$\delta^{18}O_{H2O}$ (‰)	-	-	-	-	-	-10 4	0 2	-10 6	-10 3	2	-10 6	0 7	-11 0	-10 1	2	-10 9	0 3	-11 1	-10 7	2	-10 6	0 4	-11 1	-10 1	6
$\delta^{2}H_{H2O}$ (‰)	-	-	-	-	-	-70 7	1 1	-71 4	-69 9	2	-75 5	3 1	-77 7	-73 3	2	-77 3	2 0	-78 7	-75 9	2	-74 5	3 5	-78 7	-69 9	6

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			P2-1B														
Type			Piezometer														
Depth			5 1 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	2 341	2 431	2 136	1 423	1 305	1 469	1 181	1 568	1 111	0 981	1 086	1 453	1 368	1 920	1 676
Temp (°C)	-	0 1	11 9	14 2	10 5	8 5	6 9	4 9	6 4	9 0	11 5	11 0	13 0	14 9	14 1	13 2	10 1
pH	-	0 01	7 8	8 0	8 0	7 1	7 5	7 4	8 0	7 9	7 9	7 0	7 6	7 9	7 8	7 9	7 9
SpC (µS/cm)	-	1	1980	1938	1066	1074	1664	1519	1410	1014	978	905	749	820	656	987	1236
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	2 0	-	1 1	0 6	-
Eh (mV)	-	1	-	-	-	-	-	-	-			-	123	-	238	174	80
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	24	27	21	23	23	23	19	19	20	24	24	23	24	23	22
Na^{+} (mg/L)	1 0	-	144	142	130	136	125	149	113	120	114	124	119	132	135	138	159
Mg^{2+} (mg/L)	1 0	-	22	24	21	21	21	22	17	18	18	21	21	22	23	22	22
K^{+} (mg/L)	1 0	-	13	12	11	11	11	12	9 5	10	9 4	10	10	11	11	11	12
Total P (mg/L)	0 001	0 002	1 8	1 7	-	1 2	1 6	2 0	1 7	1 8	1 4	1 5	1 4	1 5	1 7	1 9	2 2
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	2 5	2 2	2 7	2 8	2 6	2 6	2 4	2 2	2 3	2 5	2 5	3 0	2 8
Cl (mg/L)	1 0	-	23	22	23	21	20	22	22	11	22	19	20	20	22	24	22
SO_4^{2} (mg/L)	1 0	-	<1 0	<1 0	0 52	<1 0	<1 0	<1 0	<1 0	3 6	<1 0	<1 0	<1 0	<1 0	<1 0	<1 0	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	481	362	496	415	483	297	326	512	492	394	491	493	624	526	506
Calculations																	
pCO_2 (atm)	-	-	-2 19	-2 47	-2 39	-1 54	-1 90	-2 01	-2 50	-2 29	-2 26	-1 49	-1 98	-2 24	-2 05	-2 23	-2 25
$SI_{calcite}$	-	-	1 761	2 396	2 478	0 243	0 715	0 316	1 104	1 808	1 784	0 235	1 212	2 310	2 278	2 334	1 884
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		2 9	10 1	2 5	5 4	10 5	4 2	6 2	5 1	9 1	-	4 3	5 5	7 1	4 8	5 0
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	11 9	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-10 8	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	99	73	100	101	104	66	67	104	100	98	103	100	128	107	103
DOC (ppmC)	1 0	0 1	-	5 2	8 4	6 8	6 2	7 8	10 5	7 2	5 0	7 2	9 4	7 2	4 3	8 7	6 8
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-9 2	-10 7	-11 1	-11 4	-12 5	-13 8	-13 3	-11 7	-10 7	-11 5	-12 2	-12 4	-13 5	-11 7	-12 5
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-28 3	-33 4	-25 8	-28 3	-31 5	-30 8	-27 6	-31 2	-26 8	-26 6	-26 3	-26 4	-26 9	-27 1
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-9 7	-9 6	-9 7	-9 6	-9 6	-9 5	-9 8	-9 6	-	-9 7	-9 1	-10 0	-9 7	-9 8	-9 8
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-69 8	-66 8	-71 1	-68 7	-67 9	-67 6	-69 8	-70 6	-	-63 8	-	-72 4	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	P2-1B																								
Type	Piezometer																								
Depth	5 1 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 56	0 54	1 09	2 34	4	1 92	0 39	1 42	2 43	5	1 32	0 14	1 18	1 47	3	1 22	0 31	0 98	1 57	3	1 56	0 45	0 98	2 43	15
Temp (°C)	13 5	1 3	11 9	14 9	4	11 3	2 3	8 5	14 2	5	6 1	1 0	4 9	6 9	3	10 5	1 3	9 0	11 5	3	10 7	3 0	4 9	14 9	15
pH	7 8	0 1	7 6	7 9	4	7 8	0 4	7 1	8 0	5	7 6	0 3	7 4	8 0	3	7 6	0 5	7 0	7 9	3	7 7	0 3	7 0	8 0	15
SpC (µS/cm)	1051	623	656	1980	4	1260	389	987	1938	5	1531	127	1410	1664	3	966	56	905	1014	3	1200	415	656	1980	15
DO (mg/L)	1 6	0 6	1 1	2 0	2	0 6	-	0 6	0 6	1	-	-	-	-	-	-	-	-	-	-	1 3	0 69	0 6	2 0	3
Eh (mV)	180	81	123	238	2	127	67	80	174	2	-	-	-	-	-	-	-	-	-	-	154	68	80	238	4
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	24	0 66	23	24	4	23	2 1	21	27	5	22	2 2	19	23	3	21	2 8	19	24	3	23	2 0	19	27	15
Na^{+} (mg/L)	132 5	10 3	118 7	143 5	4	141 0	10 9	130 0	159 0	5	129 0	18 2	112 9	148 7	3	119 4	5 1	114 0	124 2	3	132 0	13 1	112 9	159 0	15
Mg^{2+} (mg/L)	22	0 89	21	23	4	22	1 3	21	24	5	20	2 5	17	22	3	19	1 9	18	21	3	21	1 8	17	24	15
K^{+} (mg/L)	10 9	1 1	9 9	12 5	4	11 3	0 6	10 8	12 0	5	10 6	1 1	9 5	11 7	3	9 8	0 4	9 4	10 0	3	10 8	0 94	9 4	12 5	15
Total P (mg/L)	1 606	0 194	1 415	1 834	4	1 744	0 448	1 154	2 212	4	1 771	0 222	1 603	2 022	3	1 572	0 210	1 424	1 813	3	1 673	0 277	1 154	2 212	14
NH_4^{+} (mg-N/L)	2 466	0 118	2 330	2 539	3	2 600	0 349	2 176	2 959	4	2 698	0 081	2 606	2 758	3	2 398	0 227	2 180	2 633	3	2 545	0 237	2 176	2 959	13
Cl (mg/L)	21	1 5	20	23	4	23	1 1	21	24	5	21	1 2	20	22	3	17	5 6	11	22	3	21	3 1	11	24	15
SO_4^{2} (mg/L)	-	-	-	-	-	0 52	-	0 52	0 52	1	-	-	-	-	-	3 6	-	3 6	3 6	1	2 1	2 2	0 52	3 6	2
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	-			-	-	-	-	-	-	-	-	-	-	-	-
HCO_3 (mg/L)	522	68	481	624	4	461	70	362	526	5	369	100	297	483	3	466	63	394	512	3	460	85	297	624	15
Calculations																									
pCO_2 (atm)	-2 11	0 12	-2 24	-1 98	4	-2 18	0 37	-2 47	-1 54	5	-2 14	0 32	-2 50	-1 90	3	-2 01	0 45	-2 29	-1 49	3	-2 12	0 30	-2 50	-1 49	15
$SI_{calcite}$	1 890	0 517	1 212	2 310	4	1 867	0 936	0 243	2 478	5	0 711	0 394	0 316	1 104	3	1 276	0 901	0 235	1 808	3	1 524	0 825	0 235	2 478	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	4 9	1 8	2 9	7 1	4	5 6	2 8	2 5	10 1	5	6 9	3 2	4 2	10 5	3	7 1	2 8	5 1	9 1	2	5 9	2 5	2 5	10 5	14
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	11 9	-	11 9	11 9	1	-	-	-	-	-	11 9	-	11 9	11 9	1
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-10 8	-	-10 8	-10 8	1	-	-	-	-	-	-10 8	-	-10 8	-10 8	1
Carbon																									
DIC (ppmC)	107	14	99	128	4	97	14	73	107	5	79	22	66	104	3	101	3	98	104	3	97	16	66	128	15
DOC (ppmC)	7 0	2 6	4 3	9 4	3	7 2	1 4	5 2	8 7	5	8 2	2 1	6 2	10 5	3	6 5	1 3	5 0	7 2	3	7 2	1 7	4 3	10 5	14
$\delta^{13}C_{DIC}$ (‰)	-11 8	1 8	-13 5	-9 2	4	-11 5	0 7	-12 5	-10 7	5	-13 2	0 6	-13 8	-12 5	3	-11 3	0 5	-11 7	-10 7	3	-11 9	1 2	-13 8	-9 2	15
$\delta^{13}C_{DOC}$ (‰)	-26 4	0 2	-26 6	-26 3	3	-28 3	3 0	-33 4	-25 8	5	-30 2	1 6	-31 5	-28 3	3	-28 5	2 3	-31 2	-26 8	3	-28 3	2 4	-33 4	-25 8	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-9 6	0 4	-10 0	-9 1	4	-9 7	0 1	-9 8	-9 6	5	-9 7	0 2	-9 8	-9 5	3	-9 7	0 1	-9 7	-9 6	2	-9 7	0 2	-10 0	-9 1	14
$\delta^{2}H_{H2O}$ (‰)	-71 1	1 8	-72 4	-69 8	2	-68 9	2 2	-71 1	-66 8	3	-68 4	1 2	-69 8	-67 6	3	-67 2	4 8	-70 6	-63 8	2	-68 8	2 5	-72 4	-63 8	10

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			P2-2B														
Type			Piezometer														
Depth			3 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	2 393	1 962	0 308	0 361	0 992	0 592	0 782	0 952	0 447	0 152	1 046	1 987	1 897	2 487	0 517
Temp (°C)	-	0 1	15 4	19 5	12 1	9 7	6 3	6 7	3 0	7 9	15 0	13 6	16 0	16 9	16 8	15 5	9 6
pH	-	0 01	7 7	7 7	7 9	7 0	7 6	7 6	8 0	7 6	7 7	7 5	7 5	7 6	7 6	7 9	7 7
SpC (µS/cm)	-	1	1436	1291	783	932	1323	1111	1203	798	693	668	560	668	715	631	991
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	1 0	1 1	0 7	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	81	121	205	123	110
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	53	55	51	52	52	55	44	46	49	53	56	51	52	49	54
Na^{+} (mg/L)	1 0	-	42	42	42	42	41	44	35	36	33	40	38	43	46	43	44
Mg^{2+} (mg/L)	1 0	-	30	31	29	29	28	31	25	26	28	31	30	30	31	30	31
K^{+} (mg/L)	1 0	-	7 4	7 1	6 9	6 7	6 5	7 3	5 4	5 7	5 1	5 9	5 8	6 6	7 1	6 9	7 0
Total P (mg/L)	0 001	0 002	0 24	0 28	0 64	<0 65	0 57	<0 11	0 48	0 43	0 52	0 59	0 56	0 47	0 56	0 55	0 55
NH_4^{+} (mg-N/L)	0 001	0 003	0 76	1 2	1 4	1 3	1 3	1 4	1 3	1 2	1 1	1 1	1 2	1 3	1 4	1 4	1 3
Cl (mg/L)	1 0	-	12	12	12	8	13	12	10	11	13	12	14	13	11	10	12
SO_4^{2} (mg/L)	1 0	-	4 4	4 1	3 8	2 7	4 9	6 9	2 3	3 4	5 0	3 7	4 3	4 9	3 2	1 7	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	375	365	372	332	391	277	270	396	392	391	410	402	499	415	385
Calculations																	
pCO_2 (atm)	-	-	-2 16	-2 13	-2 37	-1 53	-2 09	-2 17	-2 69	-2 10	-2 09	1 94	-1 94	-2 03	-1 89	-2 27	-2 12
$SI_{calcite}$	-	-	2 666	2 969	3 505	0 376	1 584	1 046	2 279	1 617	2 289	1 587	2 068	2 346	2 598	3 858	1 975
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		9 9	9 1	4 1	5 0	8 1	5 4	5 3	2 8	2 0	3 5	3 3	6 3	13 5	6 8	7 0
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	78	75	76	85	83	59	55	83	82	84	87	84	105	85	81
DOC (ppmC)	1 0	0 1	-	3 2	4 2	3 2	1 7	2 6	2 9	2 8	1 9	3 5	7 2	4 0	1 6	4 9	2 2
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-13 7	14 5	-15 6	-15 3	-15 1	-15 5	-14 9	-15 0	-15 6	-14 9	-14 9	-15 1	-15 4	-15 5	-15 2
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-25 2	-23 8	-22 9	-27 8	-31 9	-30 0	-28 4	-28 0	-27 1	-27 4	-27 4	-27 3	-27 2	-27 0
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 4	-10 2	-10 4	-10 3	-10 2	-10 2	-10 5	-10 4	-	-10 4	-9 9	-10 5	-10 4	-10 4	-10 5
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-75 8	-74 0	-73 5	-77 4	-74 3	-74 8	-75 0	-72 2	-	-70 2	-	-73 7	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	P2-2B																								
Type	Piezometer																								
Depth	3 5 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 83	0 57	1 05	2 39	4	1 13	1 02	0 31	2 49	5	0 79	0 20	0 59	0 99	3	0 52	0 40	0 15	0 95	3	1 13	0 80	0 15	2 49	15
Temp (°C)	16 3	0 7	15 4	16 9	4	13 3	4 2	9 6	19 5	5	5 3	2 0	3 0	6 7	3	12 2	3 8	7 9	15 0	3	12 3	4 8	3 0	19 5	15
pH	7 6	0 1	7 5	7 7	4	7 6	0 4	7 0	7 9	5	7 7	0 3	7 6	8 0	3	7 6	0 1	7 5	7 7	3	7 6	0 2	7 0	8 0	15
SpC (µS/cm)	845	399	560	1436	4	926	247	631	1291	5	1212	106	1111	1323	3	720	69	668	798	3	920	287	560	1436	15
DO (mg/L)	1 1	0 1	1 0	1 1	2	0 7	-	0 7	0 7	1	-	-	-	-	-	-	-	-	-	-	0 9	0 24	0 7	1 1	3
Eh (mV)	136	63	81	205	3	116	9	110	123	2	-	-	-	-	-	-	-	-	-	-	128	46	81	205	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	53	2 2	51	56	4	52	2 6	49	55	5	50	5 9	44	55	3	49	3 5	46	53	3	51	3 4	44	56	15
Na^{+} (mg/L)	43	3 3	38	46	4	43	0 9	42	44	5	40	4 3	35	44	3	36	3 3	33	40	3	41	3 6	33	46	15
Mg^{2+} (mg/L)	31	0 5	30	31	4	30	1 2	29	31	5	28	3 0	25	31	3	28	2 3	26	31	3	29	1 9	25	31	15
K^{+} (mg/L)	6 7	0 7	5 8	7 4	4	6 9	0 2	6 7	7 1	5	6 4	1 0	5 4	7 3	3	5 6	0 4	5 1	5 9	3	6 5	0 72	5 1	7 4	15
Total P (mg/L)	0 46	0 15	0 24	0 56	4	0 51	0 15	0 28	0 64	4	0 53	0 062	0 48	0 57	2	0 51	0 080	0 43	0 59	3	0 50	0 12	0 24	0 64	13
NH_4^{+} (mg-N/L)	1 2	0 28	0 76	1 4	4	1 3	0 092	1 2	1 4	5	1 3	0 056	1 3	1 4	3	1 1	0 07	1 1	1 2	3	1 2	0 17	0 76	1 4	15
Cl (mg/L)	12	1 3	11	14	4	11	1 8	8 1	12	5	12	1 5	10	13	3	12	1 0	11	13	3	12	1 5	8 1	14	15
SO_4^{2} (mg/L)	4 2	0 70	3 2	4 9	4	3 1	1 1	1 7	4 1	4	4 7	2 3	2 3	6 9	3	4 0	0 84	3 4	5 0	3	3 9	1 3	1 7	6 9	14
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HCO_3 (mg/L)	422	54	375	499	4	374	30	332	415	5	313	68	270	391	3	393	2	391	396	3	378	55	270	499	15
Calculations																									
pCO_2 (atm)	-2 00	0 12	-2 16	-1 89	4	-2 08	0 33	-2 37	-1 53	5	-2 32	0 33	-2 69	-2 09	3	-2 04	0 09	-2 10	-1 94	3	-2 10	0 25	-2 69	-1 53	15
$SI_{calcite}$	2 419	0 272	2 068	2 666	4	2 537	1 402	0 376	3 858	5	1 636	0 618	1 046	2 279	3	1 831	0 396	1 587	2 289	3	2 184	0 897	0 376	3 858	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	8 2	4 4	3 3	13 5	4	6 4	1 9	4 1	9 1	5	6 3	1 6	5 3	8 1	3	2 7	0 7	2 0	3 5	3	6 1	3 1	2 0	13 5	15
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	88	12	78	105	4	80	5	75	85	5	66	15	55	83	3	83	1	82	84	3	80	12	55	105	15
DOC (ppmC)	4 3	2 8	1 6	7 2	3	3 5	1 0	2 2	4 9	5	2 4	0 6	1 7	2 9	3	2 7	0 8	1 9	3 5	3	3 3	1 5	1 6	7 2	14
$\delta^{13}C_{DIC}$ (‰)	-14 8	0 7	-15 4	-13 7	4	-15 2	0 4	-15 6	-14 5	5	-15 1	0 3	-15 5	-14 9	3	-15 2	0 3	-15 6	-14 9	3	-15 1	0 5	-15 6	-13 7	15
$\delta^{13}C_{DOC}$ (‰)	-27 4	0 1	-27 4	-27 3	3	-25 2	1 9	-27 2	-22 9	5	-29 9	2 0	-31 9	-27 8	3	-27 8	0 6	-28 4	-27 1	3	-27 2	2 3	-31 9	-22 9	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 3	0 3	-10 5	-9 9	4	-10 4	0 1	-10 5	-10 2	5	-10 3	0 1	-10 5	-10 2	3	-10 4	0 0	-10 4	-10 4	2	-10 3	0 2	-10 5	-9 9	14
$\delta^{2}H_{H2O}$ (‰)	-74 8	1 5	-75 8	-73 7	2	-75 0	2 1	-77 4	-73 5	3	-74 7	0 4	-75 0	-74 3	3	-71 2	1 4	-72 2	-70 2	2	-74 1	2 0	-77 4	-70 2	10

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID																	
Type																	
Depth																	
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	2 960	2 605	2 810	2 700	2 635	2 418	2 673	2 475	2 940	2 900	3 170	3 620	2 825
Temp (°C)	-	0 1	-	-	11 1	9 5	10 4	10 0	8 4	11 2	12 0	11 5	10 5	10 7	10 8	10 9	10 4
pH	-	0 01	-	-	7 4	7 6	7 7	7 8	7 3	7 8	8 0	7 4	7 9	7 9	7 7	7 9	7 8
SpC (µS/cm)	-	1	-	-	734	860	989	855	913	7	684	670	551	638	761	759	883
DO (mg/L)	0 01	0 01	-	-	-	-	3 4	4 5	4 7	4 6	-	-	5 3	5 2	-	2 8	-
Eh (mV)	-	1	-	-	-	-	-	-	267	229	-	-	306	156	240	-	122
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	-	64	68	66	66	57	60	60	64	67	66	67	63	68
Na^{+} (mg/L)	1 0	-	-	-	29	28	29	29	25	26	25	29	30	33	31	30	32
Mg^{2+} (mg/L)	1 0	-	-	-	22	22	23	22	19	20	20	22	21	22	23	21	23
K^{+} (mg/L)	1 0	-	-	-	3 4	3 4	3 4	5 3	2 9	3 1	2 9	3 2	3 5	3 7	3 5	3 3	3 5
Total P (mg/L)	0 001	0 002	-	-	0 045	-	0 020	0 030	0 028	0 051	0 021	0 051	0 051	0 041	0 059	0 042	0 056
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 34	0 34	0 15	0 13	0 10	0 12	0 11	0 25	0 29	0 32	0 33	0 31	0 34
Cl (mg/L)	1 0	-	-	-	17	18	19	11	18	18	18	20	22	22	21	20	19
SO_4^{2} (mg/L)	1 0	-	-	-	28	29	30	19	29	29	31	30	30	31	32	31	-
NO_3 (mg-N/L)	0 001	0 002	-	-	<0 001	<0 001	0 17	<0 001	0 49	0 29	0 75	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	-	-	333	313	311	235	165	307	314	294	327	321	427	466	293
Calculations																	
pCO_2 (atm)	-	-	-	-	-1 92	-2 19	-2 26	-2 43	-2 15	-2 34	-2 52	-1 94	-2 41	-2 40	-2 13	-2 29	-2 33
$SI_{calcite}$	-	-	-	-	1 203	1 940	2 259	1 960	0 416	2 545	4 215	1 002	3 649	3 387	3 211	5 215	2 520
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	4 0	5 4	-	-	-	-	-	-	-	0 3	1 2	2 9	0 2
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	-	73	66	65	49	37	63	64	65	67	66	89	95	61
DOC (ppmC)	1 0	0 1	-	-	2 4	1 7	1 1	1 3	2 3	2 0	1 5	1 8	2 5	2 6	0 87	4 2	1 5
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-13 6	-13 2	-12 9	-12 9	-13 6	-13 2	-13 1	-13 2	-12 9	-13 0	-13 4	-13 3	-13 4
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-23 1	-20 5	-26 9	-26 0	-25 9	-27 0	-27 2	-26 9	-26 4	-27 5	-27 2	-27 0	-28 5
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-11 4	-11 4	-11 3	-11 4	-11 4	-11 3	-	-11 2	-	-11 4	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-78 6	-81 7	-83 3	-81 5	-82 4	-79 2	-	-78 0	-	-75 5	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	W2-F																						
Type	Overburden Well																						
Depth	3 0 mbgs																						
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	3 00	0 15	2 90	3 17	3	3 00	0 44	2 61	3 62	4	2 72	0 09	2 64	2 81	3	2 52	0 13	2 42	2 67	3	2 83	0 32	2 42	3 62	13
Temp (°C)	10 7	0 2	10 5	10 8	3	10 5	0 7	9 5	11 1	4	9 6	1 1	8 4	10 4	3	11 6	0 4	11 2	12 0	3	10 6	0 9	8 4	12 0	13
pH	7 8	0 1	7 7	7 9	3	7 7	0 2	7 4	7 9	4	7 6	0 2	7 3	7 8	3	7 7	0 3	7 4	8 0	3	7 7	0 2	7 3	8 0	13
SpC (µS/cm)	650	106	551	761	3	809	74	734	883	4	919	68	855	989	3	454	387	7	684	3	716	246	7	989	13
DO (mg/L)	5 3	0 1	5 2	5 3	2	2 8	-	2 8	2 8	1	4 2	0 7	3 4	4 7	3	4 6	-	4 6	4 6	1	4 4	0 93	2 8	5 3	7
Eh (mV)	234	75	156	306	3	122	-	122	122	1	267	-	267	267	1	229	-	229	229	1	220	69	122	306	6
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	67	0 8	66	67	3	66	2 8	63	68	4	63	5 1	57	66	3	61	2 4	60	64	3	64	3 4	57	68	13
Na^{+} (mg/L)	31	1 2	30	33	3	30	1 6	28	32	4	27	2 3	25	29	3	27	1 9	25	29	3	29	2 4	25	33	13
Mg^{2+} (mg/L)	22	0 92	21	23	3	22	0 71	21	23	4	21	1 9	19	23	3	20	1 1	20	22	3	21	1 3	19	23	13
K^{+} (mg/L)	3 6	0 12	3 5	3 7	3	3 4	0 07	3 3	3 5	4	3 9	1 2	2 9	5 3	3	3 1	0 13	2 9	3 2	3	3 5	0 59	2 9	5 3	13
Total P (mg/L)	0 050	0 009	0 041	0 059	3	0 048	0 008	0 042	0 056	3	0 026	0 005	0 020	0 030	3	0 041	0 018	0 021	0 051	3	0 041	0 014	0 020	0 059	12
NH_4^{+} (mg-N/L)	0 31	0 024	0 29	0 33	3	0 33	0 015	0 31	0 34	4	0 13	0 028	0 096	0 151	3	0 16	0 081	0 108	0 25	3	0 24	0 10	0 096	0 34	13
Cl (mg/L)	22	0 59	21	22	3	18	1 3	17	20	4	16	4 1	11	19	3	19	0 94	18	20	3	19	2 7	11	22	13
SO_4^{2} (mg/L)	31	0 83	30	32	3	29	1 2	28	31	3	26	6 1	19	30	3	30	1 0	29	31	3	29	3 5	19	32	12
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	0 33	0 23	0 17	0 49	2	0 52	0 33	0 29	0 75	2	0 43	0 26	0 17	0 75	4
HCO_3 (mg/L)	358	59	321	427	3	351	78	293	466	4	237	73	165	311	3	305	10	294	314	3	316	74	165	466	13
Calculations																									
pCO_2 (atm)	-2 31	0 16	-2 41	-2 13	3	-2 18	0 18	-2 33	-1 92	4	-2 28	0 14	-2 43	-2 15	3	-2 26	0 30	-2 52	-1 94	3	-2 25	0 18	-2 52	-1 92	13
$SI_{calcite}$	3 416	0 221	3 211	3 649	3	2 719	1 749	1 203	5 215	4	1 545	0 989	0 416	2 259	3	2 587	1 607	1 002	4 215	3	2 579	1 347	0 416	5 215	13
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	0 8	0 6	0 3	1 2	2	3 1	2 2	0 2	5 4	4	-	-	-	-	-	-	-	-	-	-	2 3	2 1	0 2	5 4	6
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	74	13	66	89	3	74	15	61	95	4	50	14	37	65	3	64	1	63	65	3	66	15	37	95	13
DOC (ppmC)	2 0	1 0	0 9	2 6	3	2 5	1 2	1 5	4 2	4	1 6	0 7	1 1	2 3	3	1 8	0 3	1 5	2 0	3	2 0	0 9	0 9	4 2	13
$\delta^{13}C_{DIC}$ (‰)	-13 1	0 3	-13 4	-12 9	3	-13 4	0 2	-13 6	-13 2	4	-13 1	0 4	-13 6	-12 9	3	-13 1	0 0	-13 2	-13 1	3	-13 2	0 2	-13 6	-12 9	13
$\delta^{13}C_{DOC}$ (‰)	-27 0	0 6	-27 5	-26 4	3	-24 8	3 7	-28 5	-20 5	4	-26 3	0 5	-26 9	-25 9	3	-27 0	0 1	-27 2	-26 9	3	-26 2	2 1	-28 5	-20 5	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 4	-	-11 4	-11 4	1	-11 4	0 0	-11 4	-11 4	2	-11 4	0 1	-11 4	-11 3	3	-11 2	0 1	-11 3	-11 2	2	-11 3	0 1	-11 4	-11 2	8
$\delta^{2}H_{H2O}$ (‰)	-75 5	-	-75 5	-75 5	1	-80 2	2 2	-81 7	-78 6	2	-82 4	0 9	-83 3	-81 5	3	78 6	0 9	-79 2	-78 0	2	-80 0	2 6	-83 3	-75 5	8

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			W2-A														
Type			Bedrock Well														
Depth			15 4 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	2 015	2 200	1 157	0 210	0 440	0 195	0 265	0 259	0 075	0 035	0 737	1 275	0 990	1 883	0 735
Temp (°C)	-	0 1	12 3	11 2	10 2	7 5	10 0	8 2	8 5	9 2	10 0	11 5	11 0	11 2	15 0	12 3	9 0
pH	-	0 01	7 4	7 1	7 5	7 1	7 1	7 1	7 2	7 0	7 3	7 0	7 2	7 2	7 1	7 3	7 1
SpC (µS/cm)	-	1	-	2030	1029	1296	1383	1234	1075	930	843	769	602	769	806	870	1226
DO (mg/L)	0 01	0 01	-	-	-	-	0 1	-	0 1	2 0	0 3	-	0 2	0 0	0 2	0 1	-
Eh (mV)	-	1	-	-	-	-	-	-	88	206	118	-	144	149	209	174	143
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	108	105	105	119	108	98	80	85	84	89	94	94	96	93	111
Na^{+} (mg/L)	1 0	-	18	18	21	17	15	15	11	12	13	13	14	14	15	15	18
Mg^{2+} (mg/L)	1 0	-	32	32	32	32	30	28	22	24	24	25	25	27	28	27	32
K^{+} (mg/L)	1 0	-	11	11	11	10	9 4	8 8	6 8	7 8	8 0	7 4	8 4	9 3	9 4	9 5	11
Total P (mg/L)	0 001	0 002	<0 65	<0 65	0 032	<0 65	0 032	0 015	0 039	0 038	0 023	0 029	0 024	0 024	0 031	0 024	0 030
NH_4^{+} (mg-N/L)	0 001	0 003	1 1	1 0	1 1	1 0	1 0	0 80	0 73	0 82	0 84	0 77	0 87	1 1	1 1	1 4	1 4
Cl (mg/L)	1 0	-	27	29	37	35	28	10	20	21	20	18	19	20	21	23	29
SO_4^{2} (mg/L)	1 0	-	35	34	44	41	30	14	31	32	33	30	31	30	32	33	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	394	271	536	442	418	267	289	337	407	335	371	376	513	604	376
Calculations																	
pCO_2 (atm)	-	-	-1 79	-1 74	-1 78	-1 56	-1 49	-1 75	-1 79	-1 53	-1 76	-1 53	-1 64	-1 68	-1 40	-1 53	-1 61
$SI_{calcite}$	-	-	2 078	0 824	3 203	1 299	1 039	0 690	0 736	0 593	1 500	0 670	1 087	1 239	1 421	2 263	1 103
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		4 5	6 9	6 7	6 8	7 5	7 4	6 4	8 0	6 1	7 5	8 3	7 6	4 7	-	4 4
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	87	65	116	107	104	65	68	86	91	84	88	87	123	137	91
DOC (ppmC)	1 0	0 1	4 2	3 2	6 7	2 7	3 4	3 1	4 7	3 8	2 4	4 1	5 3	4 7	2 0	6 7	3 9
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-12 6	-13 6	-13 9	-14 1	-13 9	-13 9	-14 3	-14 0	-13 5	-14 2	-13 3	-13 7	-13 8	-13 7	-13 7
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-24 4	-25 4	-23 3	-22 2	-26 6	-26 2	-27 0	-26 7	-26 8	-26 7	-26 8	-26 9	-26 8	-26 5	-26 9
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 2	-11 0	-10 9	-11 2	-11 2	-11 1	-11 4	-11 2	-	-11 1	-	-11 3	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-79 0	-78 6	-76 7	-80 4	-82 3	-80 8	-81 6	79 0	-	-77 4	-	-80 3	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	W2-A																								
Type	Bedrock Well																								
Depth	15 4 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 25	0 55	0 74	2 01	4	1 24	0 82	0 21	2 20	5	0 30	0 13	0 19	0 44	3	0 12	0 12	0 03	0 26	3	0 83	0 73	0 03	2 20	15
Temp (°C)	12 4	1 8	11 0	15 0	4	10 0	1 9	7 5	12 3	5	8 9	1 0	8 2	10 0	3	10 2	1 2	9 2	11 5	3	10 5	1 9	7 5	15 0	15
pH	7 2	0 1	7 1	7 4	4	7 2	0 1	7 1	7 5	5	7 1	0 1	7 1	7 2	3	7 1	0 2	7 0	7 3	3	7 2	0 1	7 0	7 5	15
SpC (µS/cm)	726	109	602	806	3	1290	446	870	2030	5	1231	154	1075	1383	3	848	81	769	930	3	1062	362	602	2030	14
DO (mg/L)	0 1	0 1	0 0	0 2	3	0 1	-	0 1	0 1	1	0 1	0 0	0 1	0 1	2	1 2	1 2	0 3	2 0	2	0 4	0 66	0 0	2 0	8
Eh (mV)	167	36	144	209	3	159	22	143	174	2	88	-	88	88	1	162	63	118	206	2	154	41	88	209	8
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	98	6 8	94	108	4	107	9 5	93	119	5	95	14	80	108	3	86	2 4	84	89	3	98	11	80	119	15
Na^{+} (mg/L)	15	2 0	14	18	4	18	2 4	15	21	5	14	2 1	11	15	3	13	0 4	12	13	3	15	2 7	11	21	15
Mg^{2+} (mg/L)	28	3 0	25	32	4	31	2 4	27	32	5	27	4 1	22	30	3	24	0 9	24	25	3	28	3 6	22	32	15
K^{+} (mg/L)	9 6	1 2	8 4	11 3	4	10 5	1 0	9 5	11 5	5	8 3	1 4	6 8	9 4	3	7 7	0 3	7 4	8 0	3	9 3	1 46	6 8	11 5	15
Total P (mg/L)	0 027	0 004	0 024	0 031	3	0 029	0 004	0 024	0 032	3	0 029	0 012	0 015	0 039	3	0 030	0 008	0 023	0 038	3	0 029	0 007	0 015	0 039	12
NH_4^{+} (mg-N/L)	1 0	0 10	0 87	1 1	4	1 2	0 19	1 0	1 4	5	0 83	0 13	0 73	0 97	3	0 81	0 035	0 77	0 84	3	1 00	0 20	0 73	1 4	15
Cl (mg/L)	22	3 7	19	27	4	31	5 6	23	37	5	19	9 0	10	28	3	20	1 4	18	21	3	24	7 1	10	37	15
SO_4^{2} (mg/L)	32	2 0	30	35	4	38	5 1	33	44	4	25	9 5	14	31	3	31	1 5	30	33	3	32	6 7	14	44	14
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HCO_3 (mg/L)	414	67	371	513	4	446	131	271	604	5	325	81	267	418	3	360	41	335	407	3	396	97	267	604	15
Calculations																									
pCO_2 (atm)	-1 63	0 17	-1 79	-1 40	4	-1 64	0 11	-1 78	-1 53	5	-1 68	0 16	-1 79	-1 49	3	-1 61	0 14	-1 76	-1 53	3	-1 64	0 13	-1 79	-1 40	15
$SI_{calcite}$	1 5	0 44	1 1	2 1	4	1 7	0 98	0 82	3 2	5	0 82	0 19	0 69	1 0	3	0 92	0 50	0 59	1 5	3	1 3	0 72	0 59	3 2	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	6 3	2 0	4 5	8 3	4	6 2	1 2	4 4	6 9	4	7 1	0 6	6 4	7 5	3	7 2	1 0	6 1	8 0	3	6 6	1 3	4 4	8 3	14
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	96	18	87	123	4	103	27	65	137	5	79	21	65	104	3	87	4	84	91	3	93	21	65	137	15
DOC (ppmC)	4 0	1 4	2 0	5 3	4	4 6	1 9	2 7	6 7	5	3 7	0 9	3 1	4 7	3	3 4	0 9	2 4	4 1	3	4 1	1 4	2 0	6 7	15
$\delta^{13}C_{DIC}$ (‰)	-13 3	0 5	-13 8	-12 6	4	-13 8	0 2	-14 1	-13 6	5	-14 1	0 2	-14 3	-13 9	3	-13 9	0 4	-14 2	-13 5	3	-13 8	0 4	-14 3	-12 6	15
$\delta^{13}C_{DOC}$ (‰)	-26 2	1 2	-26 9	-24 4	4	-24 9	2 0	-26 9	-22 2	5	-26 6	0 4	-27 0	-26 2	3	-26 8	0 1	-26 8	-26 7	3	-25 9	1 5	-27 0	-22 2	15
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 3	0 0	-11 3	-11 2	2	-11 1	0 1	-11 2	-10 9	3	-11 2	0 1	-11 4	-11 1	3	-11 1	0 0	-11 2	-11 1	2	-11 2	0 1	-11 4	-10 9	10
$\delta^{2}H_{H2O}$ (‰)	-79 7	0 9	-80 3	-79 0	2	-78 6	1 9	-80 4	-76 7	3	-81 6	0 8	-82 3	-80 8	3	-78 2	1 1	-79 0	-77 4	2	-79 6	1 8	-82 3	-76 7	10

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID									W2-B								
Type									Bedrock Well								
Depth									14 3 mbgs								
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	12 3	11 1	10 7	9 5	9 7	9 9	8 6	10 4	11 5	13 0	10 0	14 3	11 2	10 3	10 4
pH	-	0 01	7 8	7 7	7 9	7 6	7 5	7 7	7 7	7 3	7 7	7 3	7 5	7 7	7 5	7 9	7 6
SpC (µS/cm)	-	1		1521	787	1005	1403	951	1191	855	803	702	716	659	858	781	949
DO (mg/L)	0 01	0 01	-	-	-	-	0 3	0 3	2 0	0 2	0 4	-	0 1	-	0 1	0 3	-
Eh (mV)	-	1	-	-	-	-	-	-	328	189	209	-	285	-	247	204	133
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	56	52	53	74	88	61	82	57	67	67	82	67	72	53	58
Na^{+} (mg/L)	1 0	-	37	40	37	31	37	35	34	29	30	31	32	33	34	36	38
Mg^{2+} (mg/L)	1 0	-	27	27	26	30	32	27	30	25	27	29	29	29	29	26	28
K^{+} (mg/L)	1 0	-	6 0	6 3	5 9	5 5	5 5	5 7	4 9	5 1	4 9	5 1	5 1	5 4	5 3	5 6	6 1
Total P (mg/L)	0 001	0 002	0 11	0 12	0 12	<0 65	0 053	0 090	0 15	0 10	0 068	0 12	0 066	0 10	0 10	0 16	0 16
NH_4^{+} (mg-N/L)	0 001	0 003	0 54	0 39	0 58	0 48	0 33	0 56	0 28	0 48	0 36	0 42	0 31	0 41	0 48	0 63	0 48
Cl (mg/L)	1 0	-	25	24	23	33	79	25	79	25	31	29	49	27	26	22	21
SO_4^{2} (mg/L)	1 0	-	49	38	47	80	70	56	71	60	76	68	75	69	68	48	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	0 33	<0 001	0 41	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	290	182	352	309	342	317	213	277	321	286	322	323	429	448	284
Calculations																	
pCO_2 (atm)	-	-	-2 33	-2 52	-2 40	-2 20	-2 05	-2 27	-2 41	-1 94	-2 22	-1 90	-2 01	-2 19	-1 94	-2 28	-2 24
$SI_{calcite}$	-	-	2 142	1 164	3 284	2 036	2 016	2 151	1 642	0 742	2 329	0 944	1 588	2 462	2 230	3 822	1 621
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	5 9	4 2	-	6 7	5 9	7 0	3 6	5 9	-	-	6 1	5 2	4 4
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	18 9	-	17 0	-	-	-	21 3	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	7 6	-	7 3	-	-	-	14 2	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	60	38	72	65	73	66	45	62	67	64	70	67	92	92	60
DOC (ppmC)	1 0	0 1	2 3	91 0	3 8	1 1	1 4	1 9	2 6	2 7	1 3	2 6	4 8	3 4	1 0	4 4	2 3
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-14 2	-14 8	-14 5	-13 8	-13 6	-14 5	-14 4	-14 4	-13 7	-14 2	-13 8	-14 2	-14 5	-14 9	-14 6
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-21 3	-25 2	-23 3	-22 0	-26 8	-	-27 1	-26 8	-26 3	-26 5	-27 2	-27 2	-26 9	-26 9	-27 5
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 9	-10 8	-10 8	-11 1	-11 1	-10 8	-11 2	-11 0	-	-10 7	-	-10 9	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-75 0	-76 5	-79 6	-79 7	-81 1	-76 4	-80 3	-78 2	-	-75 4	-	-72 3	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	W2-B																								
Type	Bedrock Well																								
Depth	14 3 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	12 0	1 8	10 0	14 3	4	10 4	0 6	9 5	11 1	5	9 4	0 7	8 6	9 9	3	11 6	1 3	10 4	13 0	3	10 9	1 5	8 6	14 3	15
pH	7 6	0 1	7 5	7 8	4	7 8	0 1	7 6	7 9	5	7 6	0 1	7 5	7 7	3	7 4	0 2	7 3	7 7	3	7 6	0 2	7 3	7 9	15
SpC (µS/cm)	744	102	659	858	3	1009	303	781	1521	5	1182	226	951	1403	3	787	78	702	855	3	941	261	659	1521	14
DO (mg/L)	0 1	0 0	0 1	0 1	2	0 3	-	0 3	0 3	1	0 9	1 0	0 3	2 0	3	0 3	0 1	0 2	0 4	2	0 5	0 64	0 1	2 0	8
Eh (mV)	266	27	247	285	2	169	50	133	204	2	328	-	328	328	1	199	14	189	209	2	228	64	133	328	7
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	69	11	56	82	4	58	9 5	52	74	5	77	14	61	88	3	64	5 9	57	67	3	66	12	52	88	15
Na^{+} (mg/L)	34	2 2	32	37	4	36	3 2	31	40	5	35	1 7	34	37	3	30	0 8	29	31	3	34	3 1	29	40	15
Mg^{2+} (mg/L)	29	1 0	27	29	4	27	1 7	26	30	5	30	2 7	27	32	3	27	1 9	25	29	3	28	2 0	25	32	15
K^{+} (mg/L)	5 5	0 39	5 1	6 0	4	5 9	0 33	5 5	6 3	5	5 4	0 41	4 9	5 7	3	5 0	0 09	4 9	5 1	3	5 5	0 43	4 9	6 3	15
Total P (mg/L)	0 095	0 020	0 066	0 109	4	0 139	0 020	0 120	0 157	4	0 098	0 050	0 053	0 152	3	0 095	0 026	0 068	0 120	3	0 11	0 033	0 053	0 16	14
NH_4^{+} (mg-N/L)	0 44	0 099	0 31	0 54	4	0 51	0 097	0 39	0 63	5	0 39	0 146	0 28	0 56	3	0 42	0 056	0 36	0 48	3	0 45	0 10	0 28	0 63	15
Cl (mg/L)	32	11	25	49	4	25	4 8	21	33	5	61	31	25	79	3	28	2 9	25	31	3	35	19 1	21	79	15
SO_4^{2} (mg/L)	65	11	49	75	4	53	19	38	80	4	65	8 3	56	71	3	68	7 9	60	76	3	63	13 0	38	80	14
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	0 37	0 06	0 33	0 41	2	-	-	-	-	-	0 37	0 06	0 33	0 41	2
HCO_3 (mg/L)	341	61	290	429	4	315	97	182	448	5	291	69	213	342	3	295	24	277	321	3	313	68	182	448	15
Calculations																									
pCO_2 (atm)	-2 12	0 17	-2 33	-1 94	4	-2 33	0 13	-2 52	-2 20	5	-2 24	0 18	-2 41	-2 05	3	-2 02	0 18	-2 22	-1 90	3	-2 19	0 19	-2 52	-1 90	15
$SI_{calcite}$	2 106	0 370	1 588	2 462	4	2 385	1 126	1 164	3 822	5	1 936	0 264	1 642	2 151	3	1 338	0 864	0 742	2 329	3	2 011	0 812	0 742	3 822	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	6 1	-	6 1	6 1	1	4 9	0 8	4 2	5 9	4	6 3	0 5	5 9	6 7	2	5 5	1 7	3 6	7 0	3	5 5	1 1	3 6	7 0	10
$\delta^{15}N_{NO3}$ (‰)	21 3	-	21 3	21 3	1	-	-	-	-	-	18 0	1 3	17 0	18 9	2	-	-	-	-	-	19 1	2 2	17 0	21 3	3
$\delta^{18}O_{NO3}$ (‰)	14 2	-	14 2	14 2	1	-	-	-	-	-	7 5	0 2	7 3	7 6	2	-	-	-	-	-	9 7	3 9	7 3	14 2	3
Carbon																									
DIC (ppmC)	72	14	60	92	4	65	20	38	92	5	61	15	45	73	3	64	3	62	67	3	66	14	38	92	15
DOC (ppmC)	2 9	1 6	1 0	4 8	4	20 5	39 4	1 1	91 0	5	2 0	0 6	1 4	2 6	3	2 2	0 8	1 3	2 7	3	8 4	22 9	1 0	91 0	15
$\delta^{13}C_{DIC}$ (‰)	-14 2	0 3	-14 5	-13 8	4	-14 5	0 4	-14 9	-13 8	5	-14 2	0 5	-14 5	-13 6	3	-14 1	0 4	-14 4	-13 7	3	-14 3	0 4	-14 9	-13 6	15
$\delta^{13}C_{DOC}$ (‰)	-25 7	2 9	-27 2	-21 3	4	-25 0	2 3	-27 5	-22 0	5	-26 9	0 3	-27 1	-26 8	2	-26 5	0 2	-26 8	-26 3	3	-25 8	2 0	-27 5	-21 3	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 9	0 0	-10 9	-10 9	2	-10 9	0 2	-11 1	-10 8	3	-11 0	0 2	-11 2	-10 8	3	-10 8	0 2	-11 0	-10 7	2	-10 9	0 2	-11 2	-10 7	10
$\delta^{2}H_{H2O}$ (‰)	-73 7	1 9	-75 0	-72 3	2	-78 6	1 8	-79 7	-76 5	3	-79 3	2 5	-81 1	-76 4	3	-76 8	2 0	-78 2	-75 4	2	-77 4	2 8	-81 1	-72 3	10

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID			W2-C														
Type			Bedrock Well														
Depth			18 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	3 265	-	2 461	1 745	1 900	1 725	2 535	1 795	1 513	1 235	1 960	2 504	2 368	3 142	1 985
Temp (°C)	-	0 1	9 8	-	9 6	8 7	8 9	9 8	8 4	9 4	9 0	9 4	11 0	9 7	11 8	9 5	8 5
pH	-	0 01	7 0	-	7 1	7 0	7 0	6 9	6 8	6 7	6 9	6 9	6 7	7 0	6 8	7 0	6 9
SpC (µS/cm)	-	1	-	-	2171	2256	-	2203	3067	2156	2037	2099	2738	2947	2363	2410	2513
DO (mg/L)	0 01	0 01	-	-	-	-	-	0 1	0 1	0 1	0 6	-	0 4	0 1	0 1	0 2	-
Eh (mV)	-	1	-	-	-	-	-	-	58	52	52	-	82	314	215	166	134
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	159	-	134	142	124	126	91	103	95	119	119	124	121	130	117
Na^{+} (mg/L)	1 0	-	24	-	24	20	18	19	15	15	16	20	21	30	21	22	20
Mg^{2+} (mg/L)	1 0	-	54	-	54	47	39	42	33	33	37	47	49	81	49	51	43
K^{+} (mg/L)	1 0	-	136	-	176	125	124	129	127	109	125	150	200	383	177	170	154
Total P (mg/L)	0 001	0 002	0 10	-	0 051	<0 65	0 073	0 090	0 093	0 070	0 059	0 11	0 20	0 21	0 15	0 11	0 093
NH_4^{+} (mg-N/L)	0 001	0 003	42	-	46	31	34	33	12	11	12	12	13	15	42	50	42
Cl (mg/L)	1 0	-	85	-	62	70	28	59	85	77	75	75	159	160	87	95	70
SO_4^{2} (mg/L)	1 0	-	28	-	25	44	17	32	44	43	51	45	31	32	43	38	-
NO_3 (mg-N/L)	0 001	0 002	0 50	-	0 65	0 34	0 15	0 16	0 71	0 61	0 40	0 60	<0 001	0 30	0 46	0 49	0 87
HCO_3 (mg/L)	3 9	-	786	-	1044	858	742	355	503	721	749	864	892	1604	1214	1559	733
Calculations																	
pCO_2 (atm)	-	-	-1 18	-	-1 09	-1 12	-1 22	-1 40	-1 14	-0 94	-1 05	-1 05	-0 80	-0 87	-0 80	-0 87	-1 12
$SI_{calcite}$	-	-	2 176	-	2 634	1 991	1 718	0 662	0 497	0 736	0 918	1 501	0 918	2 950	1 764	3 164	1 243
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		4 8	-	5 7	5 1	7 1	5 7	4 0	5 3	7 6	4 2	4 9	6 0	6 1	6 6	4 7
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	5 4	-	-	-	21 2	-	19 7	-	-	2 5	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	2 3	-	-	-	10 4	-	5 9	-	-	25 4	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	199	-	259	220	188	96	149	219	208	229	277	406	337	396	196
DOC (ppmC)	1 0	0 1	23 0	-	24 1	14 0	10 9	12 4	16 9	18 7	13 8	22 1	26 3	43 4	11 7	37 2	15 0
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-2 8	-	-1 9	-5 0	-2 4	-4 1	-2 4	-3 2	-1 8	-0 7	2 2	6 2	-0 4	-2 5	-3 2
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-21 2	-	-22 2	-22 4	-25 8	-25 1	-25 9	-26 0	-26 0	-25 8	-25 8	-	-25 8	-25 6	-25 7
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 3	-	-10 9	-10 8	-10 7	-10 9	-10 8	-10 6	-	-10 7	-10 2	-10 3	-10 7	-10 6	-10 5
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-82 6	-	-73 5	-77 3	-75 4	-75 1	-77 9	-72 6	-	-71 4	-	-64 1	-	-	-

Table D3: Site 2 - Field Parameters, Analytical Results and Statistics.

Site ID	W2-C																					
Type	Bedrock Well																					
Depth	18 5 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	2 52	0 55	1 96	3 27	4	2 33	0 62	1 75	3 14	4	2 05	0 43	1 73	2 54	3	1 51	0 28	1 24	1 80	3	2 15	0 59	1 24	3 27	14
Temp (°C)	10 6	1 0	9 7	11 8	4	9 1	0 6	8 5	9 6	4	9 0	0 7	8 4	9 8	3	9 3	0 2	9 0	9 4	3	9 5	0 9	8 4	11 8	14
pH	6 9	0 2	6 7	7 0	4	7 0	0 1	6 9	7 1	4	6 9	0 1	6 8	7 0	3	6 8	0 1	6 7	6 9	3	6 9	0 1	6 7	7 1	14
SpC (µS/cm)	2683	296	2363	2947	3	2337	153	2171	2513	4	2635	611	2203	3067	2	2098	59	2037	2156	3	2413	339	2037	3067	12
DO (mg/L)	0 2	0 2	0 1	0 4	3	0 2	-	0 2	0 2	1	0 1	0 0	0 1	0 1	2	0 3	0 3	0 1	0 6	2	0 2	0 18	0 1	0 6	8
Eh (mV)	204	116	82	314	3	150	23	134	166	2	58	-	58	58	1	52	0	52	52	2	134	94	52	314	8
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	131	19	119	159	4	131	10	117	142	4	114	20	91	126	3	106	12	95	119	3	122	18	91	159	14
Na^{+} (mg/L)	24	4 3	21	30	4	21	1 8	20	24	4	17	1 7	15	19	3	17	2 6	15	20	3	20	3 9	15	30	14
Mg^{2+} (mg/L)	58	15	49	81	4	49	5 2	43	54	4	38	4 6	33	42	3	39	7 3	33	47	3	47	12 1	33	81	14
K^{+} (mg/L)	224	109	136	383	4	156	23	125	176	4	127	2 5	124	129	3	128	21	109	150	3	163	68	109	383	14
Total P (mg/L)	0 17	0 047	0 10	0 21	4	0 084	0 030	0 051	0 11	3	0 085	0 011	0 073	0 093	3	0 081	0 028	0 059	0 11	3	0 11	0 049	0 051	0 21	13
NH_4^{+} (mg-N/L)	28	16	13	42	4	42	8 2	31	50	4	26	12	12	34	3	12	0 577	11	12	3	28	15	11	50	14
Cl (mg/L)	123	43	85	160	4	74	14	62	95	4	57	28	28	85	3	75	1 3	75	77	3	85	35 6	28	160	14
SO_4^{2} (mg/L)	33	6 6	28	43	4	36	9 4	25	44	3	31	14	17	44	3	46	3 9	43	51	3	36	9 7	17	51	13
NO_3 (mg-N/L)	0 42	0 10	0 30	0 50	3	0 59	0 23	0 34	0 87	4	0 34	0 32	0 15	0 71	3	0 54	0 12	0 40	0 61	3	0 48	0 21	0 15	0 87	13
HCO_3 (mg/L)	1124	368	786	1604	4	1048	363	733	1559	4	533	195	355	742	3	778	76	721	864	3	902	354	355	1604	14
Calculations																									
pCO_2 (atm)	-0 91	0 18	-1 18	-0 80	4	-1 05	0 12	-1 12	-0 87	4	-1 25	0 14	-1 40	-1 14	3	-1 01	0 07	-1 05	-0 94	3	-1 05	0 17	-1 40	-0 80	14
$SI_{calcite}$	1 952	0 847	0 918	2 950	4	2 258	0 829	1 243	3 164	4	0 959	0 663	0 497	1 718	3	1 052	0 399	0 736	1 501	3	1 634	0 866	0 497	3 164	14
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	5 4	0 7	4 8	6 1	4	5 5	0 8	4 7	6 6	4	5 6	1 5	4 0	7 1	3	5 7	1 7	4 2	7 6	3	5 5	1 1	4 0	7 6	14
$\delta^{15}N_{NO3}$ (‰)	2 5	-	2 5	2 5	1	5 4	-	5 4	5 4	1	-	-	-	-	-	20 5	1 1	19 7	21 2	2	12 2	9 6	2 5	21 2	4
$\delta^{18}O_{NO3}$ (‰)	25 4	-	25 4	25 4	1	2 3	-	2 3	2 3	1	-	-	-	-	-	8 2	3 2	5 9	10 4	2	11 0	10 2	2 3	25 4	4
Carbon																									
DIC (ppmC)	305	88	199	406	4	268	89	196	396	4	144	46	96	188	3	219	11	208	229	3	241	88	96	406	14
DOC (ppmC)	26 1	13 1	11 7	43 4	4	22 5	10 8	14 0	37 2	4	13 4	3 1	10 9	16 9	3	18 2	4 2	13 8	22 1	3	20 7	9 7	10 9	43 4	14
$\delta^{13}C_{DIC}$ (‰)	1 3	3 8	-2 8	6 2	4	-3 1	1 3	-5 0	-1 9	4	-2 9	1 0	-4 1	-2 4	3	-1 9	1 2	-3 2	-0 7	3	-1 6	2 8	-5 0	6 2	14
$\delta^{13}C_{DOC}$ (‰)	-24 3	2 7	-25 8	-21 2	3	-24 0	1 9	-25 7	-22 2	4	-25 6	0 5	-25 9	-25 1	3	-25 9	0 1	-26 0	-25 8	3	-24 9	1 7	-26 0	-21 2	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 6	0 5	-11 3	-10 2	4	-10 7	0 2	-10 9	-10 5	4	-10 8	0 1	-10 9	-10 7	3	-10 7	0 1	-10 7	-10 6	2	-10 7	0 3	-11 3	-10 2	13
$\delta^{2}H_{H2O}$ (‰)	-73 4	13 1	-82 6	-64 1	2	-75 4	2 7	-77 3	-73 5	2	-76 1	1 5	-77 9	75 1	3	-72 0	0 9	-72 6	-71 4	2	-74 4	5 1	-82 6	-64 1	9

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID									L3-1A								
Type									Lysimeter								
Depth									0 3 mbgs								
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	-	-	13 0		-	-	-	-	-	17 4	23 1	28 2	27 2	-	-
pH	-	0 01	-	-	7 4	-	-	-	-	-	-	7 0	7 4	7 4	7 4	-	-
SpC (µS/cm)	-	1	-	-	444	-	-	-	-	-	-	425	-	-	-	-	-
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	-	44	-	-	-	-	-	-	47	52	54	24	-	-
Na^{+} (mg/L)	1 0	-	-	-	10	-	-	-	-	-	-	18	17	18	15	-	-
Mg^{2+} (mg/L)	1 0	-	-	-	10	-	-	-	-	-	-	11	12	13	5 6	-	-
K^{+} (mg/L)	1 0	-	-	-	2 7		-	-	-	-	-	1 4	1 2	1 2	1 3	-	-
Total P (mg/L)	0 001	0 002	-	-	<0 65	-	-	-		-	-	<0 65	0 29	<0 65	-	-	-
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	-	-	-	-	-	-	-	0 056	0 023	0 040	-	-	-
Cl (mg/L)	1 0	-	-	-	7		-	-	-	-	-	39	28	20	-	-	-
SO_4^{2} (mg/L)	1 0	-	-	-	25	-	-	-	-	-	-	28	25	25	-	-	-
NO_3 (mg-N/L)	0 001	0 002	-	-	12	-	-		-	-	-	12	15	17	-	-	-
HCO_3 (mg/L)	3 9	-	-	-	113		-	-	-	-	-	113	188	114	148	-	-
Calculations																	
pCO_2 (atm)	-	-	-	-	-2 37	-	-	-	-	-	-	-1 98	-2 06	-2 33	-2 20	-	-
$SI_{calcite}$	-	-	-	-	0 327	-	-	-	-	-	-	0 170	0 797	0 752	0 440	-	-
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-		-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	7 8	-	-	-	-	-	-	4 9	10 6	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	2 3	-	-	-	-	-	-	-3 7	0 2	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	-	25	-	-	-	-	-	30	28	41	24	32	88	-
DOC (ppmC)	1 0	0 1	-	-	19	-	-	-	-	-	37	17	18	11	25	-	-
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-11 3	-	-	-	-	-	-9 3	-11 4	-13 7	-12 4	-12 5	-12 3	-
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-24 6	-	-	-	-	-	-22 0	-23 3	-24 2	-24 3	-24 0	-	-
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-9 3	-	-	-	-	-	-	-10 6	-9 8	-10 7	-9 0	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-70 2	-	-	-	-	-	-	-73 7	-	-75 2	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	L3-1A																								
Type	Lysimeter																								
Depth	0 3 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	26 2	2 7	23 1	28 2	3	13 0	-	13 0	13 0	1	-	-		-	-	17 4	-	17 4	17 4	1	21 8	6 5	13 0	28 2	5
pH	7 4	0 0	7 4	7 4	3	7 4	-	7 4	7 4	1	-	-		-	-	7 0	-	7 0	7 0	1	7 3	0 2	7 0	7 4	5
SpC (µS/cm)	-	-	-	-	-	444	-	444	444	1	-	-	-	-	-	425	-	425	425	1	435	13	425	444	2
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Eh (mV)	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	44	17	24	54	3	44	-	44	44	1	-		-	-	-	47	-	47	47	1	44	12	24	54	5
Na^{+} (mg/L)	16	1 5	15	18	3	10	-	10	10	1	-	-	-	-	-	18	-	18	18	1	15	3 1	10	18	5
Mg^{2+} (mg/L)	10	4 1	5 6	13	3	10	-	10	10	1	-		-	-	-	11	-	11	11	1	10	2 9	5 6	13	5
K^{+} (mg/L)	1 2	0 05	1 2	1 3	3	2 7	-	2 7	2 7	1	-	-	-	-	-	1 4	-	1 4	1 4	1	1 6	0 63	1 2	2 7	5
Total P (mg/L)	0 29	-	0 29	0 29	1	-	-	-	-	-	-	-	-		-	-	-	-	-	-	0 29	-	0 29	0 29	1
NH_4^{+} (mg-N/L)	0 031	0 012	0 023	0 040	2	-	-	-	-	-	-	-		-	-	0 056	-	0 056	0 056	1	0 039	0 016	0 023	0 056	3
Cl (mg/L)	24	5 7	20	28	2	7 1	-	7 1	7 1	1	-	-	-	-	-	39	-	39	39	1	24	13 5	7 1	39	4
SO_4^{2} (mg/L)	25	0 7	25	25	2	25	-	25	25	1	-	-	-	-	-	28	-	28	28	1	26	1 6	25	28	4
NO_3 (mg-N/L)	16	1 0	15	17	2	12	-	12	12	1	-	-	-	-	-	12	-	12	12	1	14	2 31	12	17	4
HCO_3 (mg/L)	150	37	114	188	3	113	-	113	113	1	-	-	-	-	-	113	-	113	113	1	135	33	113	188	5
Calculations																									
pCO_2 (atm)	-2 2	0 14	-2 3	-2 1	3	-2 4	-	-2 4	-2 4	1	-	-	-	-	-	-2 0	-	-2 0	-2 0	1	-2 2	0 17	-2 4	-2 0	5
$SI_{calcite}$	0 66	0 195	0 44	0 80	3	0 33	-	0 33	0 33	1	-	-	-	-	-	0 17	-	0 17	0 17	1	0 50	0 27	0 17	0 80	5
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	11	-	11	11	1	7 8	-	7 8	7 8	1	-	-	-	-	-	4 9	-	4 9	4 9	1	7 8	2 9	4 9	11	3
$\delta^{18}O_{NO3}$ (‰)	0 2	-	0 2	0 2	1	2 3	-	2 3	2 3	1	-	-	-	-	-	-3 7	-	-3 7	-3 7	1	-0 4	3 0	-3 7	2 3	3
Carbon																									
DIC (ppmC)	32	8	24	41	3	57	45	25	88	2	-		-	-	-	29	2	28	30	2	38	23	24	88	7
DOC (ppmC)	18 0	7 0	11 2	25 2	3	19 4	-	19 4	19 4	1	-	-	-	-	-	27 0	14 6	16 7	37 3	2	21 3	9 1	11 2	37 3	6
$\delta^{13}C_{DIC}$ (‰)	-12 8	0 7	-13 7	-12 4	3	-11 8	0 7	-12 3	-11 3	2	-		-	-	-	-10 3	1 4	-11 4	-9 3	2	-11 8	1 4	-13 7	-9 3	7
$\delta^{13}C_{DOC}$ (‰)	-24 2	0 1	-24 3	-24 0	3	24 6	-	-24 6	-24 6	1	-	-	-	-	-	-22 7	1 0	-23 3	-22 0	2	-23 7	1 0	-24 6	-22 0	6
Water																									
$\delta^{18}O_{H2O}$ (‰)	-9 8	0 9	-10 7	-9 0	3	-9 3	-	-9 3	-9 3	1	-	-	-	-	-	-10 6	-	-10 6	-10 6	1	-9 9	0 8	-10 7	-9 0	5
$\delta^{2}H_{H2O}$ (‰)	-75 2	-	-75 2	-75 2	1	-70 2	-	-70 2	-70 2	1	-	-	-	-	-	-73 7	-	-73 7	-73 7	1	-73 0	2 6	-75 2	-70 2	3

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			L3-1B														
Type			Lysimeter														
Depth			1 8 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Temp (°C)	-	0 1	19 7	16 7	13	7 2	6 3	-	-	-	-	15 4	17	23 4	19 4	-	9 5
pH	-	0 01	7 7	7 3	7 5	7 3	7 31	-	-	-	-	7 5	7 1	7 2	7 1	-	7 1
SpC (µS/cm)	-	1	1357	-	892	1192	-	-	-	-	-	687	669	-	697	-	984
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	3 4	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	426	417	-	260
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	90	89	94	95	95	-	-	-	74	90	95	108	103	101	80
Na^{+} (mg/L)	1 0	-	18	33	18	16	15	-	-	-	12	15	16	17	18	17	15
Mg^{2+} (mg/L)	1 0	-	32	51	34	33	34	-	-	-	28	33	34	39	38	37	30
K^{+} (mg/L)	1 0	-	1 4	8 0	<1 0	<1 0	<1 0	-	-	-	0 55	0 25	0 25	0 58	0 36	0 46	0 22
Total P (mg/L)	0 001	0 002	<0 65	0 27	0 008	<0 65	<0 65	0 016	-	-	<0 11	0 043	0 030	0 090	0 047	0 047	0 028
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 081	0 004	0 007	-	-	-	-	0 031	0 041	0 029	-	-	
Cl (mg/L)	1 0	-	9 1	12	-	7 3	6 9	-	-	-	-	23	28	32	33	32	26
SO_4^{2} (mg/L)	1 0	-	21	26	-	21	19	-	-	-	-	19	19	21	19	20	-
NO_3 (mg-N/L)	0 001	0 002	23	0 53	-	21	23	-	-	-	-	17	16	15	11	5 9	3 3
HCO_3 (mg/L)	3 9	-	233	342	400	379	354	-	-	-	-	346	346	378	495	-	313
Calculations																	
pCO_2 (atm)	-	-	-2 37	-1 82	-1 93	-1 75	-1 83	-	-	-	-	-1 98	-1 55	-1 64	-1 37	-	-1 65
$SI_{calcite}$	-	-	3 408	1 698	2 684	1 206	1 226	-	-	-	-	2 422	1 010	2 252	1 604	-	0 653
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		8 3	-	-	6 1	8 6	-	-	-	-	-	6 7	-	-	-	11 5
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		1 0	-	-	4 5	1 9	-	-	-	-	-	-0 7	-	-	-	3 9
Carbon																	
DIC (ppmC)	1 0	0 1	48	75	86	88	81	-	-	-	-	74	83	84	118	-	77
DOC (ppmC)	1 0	0 1	-	2 6	6 8	4 7	2 8	-	-	-	-	5 1	7 1	5 3	2 8	5 2	2 9
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-9 08	-17 2	-12 0	-	-11 9	-	-	-	-	-11 8	-11 6	-12 1	-13 2	-	-11 8
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-25 1	-25 9	-21 6	-26 6	-	-	-	-	-24 6	-25 6	-25 9	-25 2	-26 2	-25 3
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-10 5	-9 9	-9 9	-9 8	-	-	-10 0	-	-8 5	-9 8	-9 9	-9 7	-9 8	-9 9
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-75 7	-67 1	-72 4	-72 6	-	-	-72 3	-	-65 5	-	-73 7	-		-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	L3-1B																								
Type	Lysimeter																								
Depth	1 8 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	19 9	2 6	17 0	23 4	4	11 6	4 2	7 2	16 7	4	6 3	-	6 3	6 3	1	15 4	-	15 4	15 4	1	14 8	5 7	6 3	23 4	10
pH	7 3	0 3	7 1	7 7	4	7 3	0 2	7 1	7 5	4	7 3	-	7 3	7 3	1	7 5	-	7 5	7 5	1	7 3	0 2	7 1	7 7	10
SpC (µS/cm)	907	389	669	1357	3	1023	154	892	1192	3	-	-	-	-	-	687	-	687	687	1	925	270	669	1357	7
DO (mg/L)	3 4	-	3 4	3 4	1	-	-	-	-	-		-	-	-	-	-	-	-	-	-	3 4	-	3 4	3 4	1
Eh (mV)	422	6	417	426	2	260	-	260	260	1	-	-		-	-	-	-	-	-	-	368	93	260	426	3
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	99	8 1	90	108	4	92	7 6	80	101	5	95	-	95	95	1	82	11	74	90	2	93	9 3	74	108	12
Na^{+} (mg/L)	17	1 2	16	18	4	20	7 3	15	33	5	15	-	15	15	1	14	2 0	12	15	2	18	5 1	12	33	12
Mg^{2+} (mg/L)	36	3 4	32	39	4	37	8 0	30	51	5	34	-	34	34	1	31	3 8	28	33	2	35	5 8	28	51	12
K^{+} (mg/L)	0 65	0 53	0 25	1 4	4	2 9	4 4	0 22	8 0	3		-	-	-	-	0 40	0 21	0 25	0 55	2	1 3	2 5	0 22	8 0	9
Total P (mg/L)	0 056	0 031	0 030	0 090	3	0 087	0 12	0 008	0 27	4	0 016	-	0 016	0 016	1	0 043	-	0 043	0 043	1	0 064	0 079	0 008	0 27	9
NH_4^{+} (mg-N/L)	0 035	0 009	0 029	0 041	2	0 042	0 055	0 004	0 081	2	0 007	-	0 007	0 007	1	0 031	-	0 031	0 031	1	0 032	0 028	0 004	0 081	6
Cl (mg/L)	26	11	9	33	4	19	11	7	32	4	7	-	7	7	1	23	-	23	23	1	21	10 9	7	33	10
SO_4^{2} (mg/L)	20	1	19	21	4	22	3	20	26	3	19	-	19	19	1	19	-	19	19	1	21	2 2	19	26	9
NO_3 (mg-N/L)	16	5 040	11	23	4	7 71	9 190	0 53	21	4	23	-	23	23	1	17	-	17	17	1	14	8 157	0 53	23	10
HCO_3 (mg/L)	363	107	233	495	4	359	38	313	400	4	354	-	354	354	1	346	-	346	346	1	359	66	233	495	10
Calculations																									
pCO_2 (atm)	-1 73	0 44	-2 37	-1 37	4	-1 79	0 12	-1 93	-1 65	4	-1 83	-	-1 83	-1 83	1	-1 98	-	-1 98	-1 98	1	-1 79	0 27	-2 37	-1 37	10
$SI_{calcite}$	2 069	1 027	1 010	3 408	4	1 560	0 862	0 653	2 684	4	1 226	-	1 226	1 226	1	2 422	-	2 422	2 422	1	1 816	0 858	0 653	3 408	10
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	7 5	1 1	6 7	8 3	2	8 8	3 8	6 1	11 5	2	8 6	-	8 6	8 6	1	-	-	-	-	-	8 2	2 1	6 1	11 5	5
$\delta^{18}O_{NO3}$ (‰)	0 2	1 2	-0 7	1 0	2	4 2	0 4	3 9	4 5	2	1 9	-	1 9	1 9	1	-	-	-	-	-	2 1	2 1	-0 7	4 5	5
Carbon																									
DIC (ppmC)	83	29	48	118	4	81	6	75	88	4	81	-	81	81	1	74	-	74	74	1	81	17	48	118	10
DOC (ppmC)	5 1	2 1	2 8	7 1	3	4 4	1 7	2 6	6 8	5	2 8	-	2 8	2 8	1	5 1	-	5 1	5 1	1	4 5	1 7	2 6	7 1	10
$\delta^{13}C_{DIC}$ (‰)	-11 5	1 7	-13 2	-9 1	4	-13 6	3 1	-17 2	-11 8	3	-11 9	-	-11 9	-11 9	1	-11 8	-	-11 8	-11 8	1	-12 3	2 1	-17 2	-9 1	9
$\delta^{13}C_{DOC}$ (‰)	-25 5	0 3	-25 9	-25 2	3	-24 8	1 8	-26 2	-21 6	5	-26 6	-	-26 6	-26 6	1	-24 6	-	-24 6	-24 6	1	-25 2	1 4	-26 6	-21 6	10
Water																									
$\delta^{18}O_{H2O}$ (‰)	-9 8	0 1	-9 9	-9 7	3	-10 0	0 3	-10 5	-9 8	5	-9 8	-	-9 8	-9 8	1	-9 2	1 0	-10 0	-8 5	2	-9 8	0 5	-10 5	-8 5	11
$\delta^{2}H_{H2O}$ (‰)	-73 7	-	-73 7	-73 7	1	-71 7	4 3	-75 7	-67 1	3	-72 6	-	-72 6	-72 6	1	-68 9	4 8	-72 3	-65 5	2	-71 3	3 7	-75 7	-65 5	7

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			T3-A															
Type			Tile Drain															
Depth			1 0 mbgs															
Season			Summer	Fall			Winter			Spring			Summer			Fall		
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06	
Field																		
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Temp (°C)	-	0 1	-	-	9 1	-	8 5	-	3 0	-	5 0	10 0	12 0	-	-	-	10 6	
pH	-	0 01	-	-	7 1	-	7 0	-	6 3	-	6 3	6 9	7 3	-	-	-	7 2	
SpC (µS/cm)	-	1	-	-	-	-	1548	-	1296	-	1013	973	703	-	-	-	1200	
DO (mg/L)	0 01	0 01	-	-	-	-	6 1	-	-	-		-	-	-	-	-	-	
Eh (mV)	-	1	-	-	-		-	-	-	-	-	-	298	-	-	-	231	
Major Ions and Nutrients																		
Ca^{2+} (mg/L)	1 0	-	-	-	76	-	84	-	74	-	85	80	85	-	-	-	93	
Na^{+} (mg/L)	1 0	-	-	-	25	-	28	-	26	-	34	32	28	-	-	-	35	
Mg^{2+} (mg/L)	1 0	-	-	-	28	-	31	-	27	-	31	29	30	-	-	-	34	
K^{+} (mg/L)	1 0	-	-	-	2 1	-	1 7	-	1 4	-	1 5	1 6	1 9	-	-	-	2 0	
Total P (mg/L)	0 001	0 002	-	-	0 068	-	0 051	0 076	<0 11	-	0 038	0 075	0 067	-	-	-	0 076	
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 004	-	0 013	-		-	0 010	0 012	0 006	-	-	-	-	
Cl (mg/L)	1 0	-	-	-	38	-	58	-	64	-	106	89	51	-	-	-	87	
SO_4^{2} (mg/L)	1 0	-	-	-	22	-	26	-	25	-	27	26	24	-	-	-	-	
NO_3 (mg-N/L)	0 001	0 002	-	-	7 5	-	8 3	-	6 2	-	5 0	5 3	6 9	-	-	-	4 5	
HCO_3 (mg/L)	3 9	-		-	330	-	295	-	115	-	149	266	334	-	-	-	305	
Calculations																		
pCO_2 (atm)	-	-	-	-	-1 59	-	-1 61	-	-1 31	-	-1 24	-1 56	-1 79	-	-	-	-1 76	
$SI_{calcite}$	-	-	-	-	0 575	-	0 511	-	0 028	-	0 048	0 380	1 178	-	-	-	0 941	
Nitrogen Isotopes																		
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-		-	-	-	-	-	-	-	
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	13 9	-	-	-	-	-	-	17 6	17 0	-	-	-	20 4	
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	7 4	-	-	-	-	-	-	8 2	7 1	-	-	-	9 2	
Carbon																		
DIC (ppmC)	1 0	0 1	-	-	82	-	75	-	64	-	74	70	76	-	-	-	71	
DOC (ppmC)	1 0	0 1	-	-	5 3	-	2 1	-	3 4	-	2 0	3 3	4 3	-	-	-	2 3	
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-13 2	-	-13 2	-	-8 1	-	-14 3	-14 1	-12 2	-	-	-	-14 0	
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-23 5	-	-25 5	-	-26 2	-	-26 3	-25 7	-25 7	-	-	-	-26 3	
Water																		
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-10 0	-	-10 1	-	-10 6	-	-	-10 3	-	-	-	-	-	
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-67 3	-	-75 0	-	-74 3			-75 4	-	-	-	-	-	

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	T3-A																								
Type	Tile Drain																								
Depth	1 0 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	12 0	-	12 0	12 0	1	9 9	1 1	9 1	10 6	2	5 8	3 9	3 0	8 5	2	7 5	3 5	5 0	10 0	2	8 3	3 2	3 0	12 0	7
pH	7 3	-	7 3	7 3	1	7 1	0 1	7 1	7 2	2	6 7	0 5	6 3	7 0	2	6 6	0 4	6 3	6 9	2	6 9	0 4	6 3	7 3	7
SpC (µS/cm)	703	-	703	703	1	1200	-	1200	1200	1	1422	179	1296	1548	2	993	28	973	1013	2	1122	293	703	1548	6
DO (mg/L)	-	-	-	-	-	-	-	-	-	-	6 1	-	6 1	6 1	1	-	-	-	-	-	6 1	-	6 1	6 1	1
Eh (mV)	298		298	298	1	231	-	231	231	1	-	-	-	-	-	-	-	-	-	-	265	47	231	298	2
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	85	-	85	85	1	85	12	76	93	2	79	7 3	74	84	2	82	3 4	80	85	2	82	6 5	74	93	7
Na^{+} (mg/L)	28	-	28	28	1	30	7 1	25	35	2	27	1 1	26	28	2	33	1 4	32	34	2	30	4 0	25	35	7
Mg^{2+} (mg/L)	30	-	30	30	1	31	4 1	28	34	2	29	2 9	27	31	2	30	1 6	29	31	2	30	2 3	27	34	7
K^{+} (mg/L)	1 9	-	1 9	1 9	1	2 0	0 09	2 0	2 1	2	1 5	0 21	1 4	1 7	2	1 5	0 034	1 5	1 6	2	1 7	0 27	1 4	2 1	7
Total P (mg/L)	0 067	-	0 067	0 067	1	0 072	0 005	0 068	0 076	2	0 063	0 018	0 051	0 076	2	0 057	0 026	0 038	0 075	2	0 064	0 015	0 038	0 076	7
NH_4^{+} (mg-N/L)	0 006	-	0 006	0 006	1	0 004	-	0 004	0 004	1	0 013	-	0 013	0 013	1	0 011	0 002	0 010	0 012	2	0 009	0 004	0 004	0 013	5
Cl (mg/L)	51	-	51	51	1	63	34	38	87	2	61	4	58	64	2	97	12	89	106	2	70	24 1	38	106	7
SO_4^{2} (mg/L)	24	-	24	24	1	22	-	22	22	1	26	0 3	25	26	2	27	1	26	27	2	25	1 9	22	27	6
NO_3 (mg-N/L)	6 9	-	6 9	6 9	1	6 0	2 1	4 5	7 5	2	7 2	1 5	6 2	8 3	2	5 1	0 27	5 0	5 3	2	6 2	1 4	4 5	8 3	7
HCO_3 (mg/L)	334	-	334	334	1	317	18	305	330	2	205	127	115	295	2	207	83	149	266	2	256	88	115	334	7
Calculations																									
pCO_2 (atm)	-1 79	-	-1 79	-1 79	1	-1 68	0 12	-1 76	-1 59	2	-1 46	0 21	1 61	-1 31	2	-1 40	0 23	-1 56	-1 24	2	-1 55	0 21	-1 79	-1 24	7
$SI_{calcite}$	1 178	-	1 178	1 178	1	0 758	0 259	0 575	0 941	2	0 270	0 341	0 028	0 511	2	0 214	0 235	0 048	0 380	2	0 523	0 428	0 028	1 178	7
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-		-	-	-
$\delta^{15}N_{NO3}$ (‰)	17 0	-	17 0	17 0	1	17 2	4 6	13 9	20 4	2	-	-	-	-	-	17 6	-	17 6	17 6	1	17 2	2 7	13 9	20 4	4
$\delta^{18}O_{NO3}$ (‰)	7 1	-	7 1	7 1	1	8 3	1 3	7 4	9 2	2	-	-	-		-	8 2	-	8 2	8 2	1	8 0	0 9	7 1	9 2	4
Carbon																									
DIC (ppmC)	76	-	76	76	1	77	8	71	82	2	69	8	64	75	2	72	2	70	74	2	73	6	64	82	7
DOC (ppmC)	4 3	-	4 3	4 3	1	3 8	2 1	2 3	5 3	2	2 7	1 0	2 1	3 4	2	2 6	0 9	2 0	3 3	2	3 2	1 2	2 0	5 3	7
$\delta^{13}C_{DIC}$ (‰)	-12 2	-	-12 2	-12 2	1	-13 6	0 5	-14 0	-13 2	2	-10 7	3 6	-13 2	-8 1	2	-14 2	0 1	-14 3	-14 1	2	-12 7	2 2	-14 3	-8 1	7
$\delta^{13}C_{DOC}$ (‰)	-25 7	-	-25 7	-25 7	1	-24 9	2 0	-26 3	-23 5	2	-25 9	0 5	-26 2	-25 5	2	-26 0	0 5	-26 3	-25 7	2	-25 6	1 0	-26 3	-23 5	7
Water																									
$\delta^{18}O_{H2O}$ (‰)	-	-	-	-	-	-10 0	-	-10 0	-10 0	1	-10 3	0 3	-10 6	-10 1	2	-10 3	-	-10 3	-10 3	1	-10 2	0 3	-10 6	-10 0	4
$\delta^{2}H_{H2O}$ (‰)	-	-	-	-	-	-67 3	-	-67 3	-67 3	1	-74 7	0 5	-75 0	-74 3	2	-75 4	-	-75 4	-75 4	1	-73 0	3 8	-75 4	-67 3	4

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			T3-B															
Type			Tile Drain															
Depth			1 3 mbgs															
Season			Summer	Fall			Winter			Spring			Summer			Fall		
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06	
Field																		
W L (mbgs)	-	0 001		-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Temp (°C)	-	0 1	-	-	6 2	-	7 9	-	3 5	-	6 0	10 1	14 0	-	-	-	10 7	
pH	-	0 01	-	-	7 2	-	7 3	-	6 8	-	7 0	7 1	7 1	-	-	-	7 1	
SpC (µS/cm)	-	1	-	-	-	-	1109	-	869	-	751	633	499	-	-	-	805	
DO (mg/L)	0 01	0 01	-	-	-	-	5 0	-	-	-	-	-	6 2	-	-	-	-	
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	373	-	-	-	275	
Major Ions and Nutrients																		
Ca^{2+} (mg/L)	1 0	-	-	-	69	-	78	-	66	-	67	67	75	-	-	-	81	
Na^{+} (mg/L)	1 0	-	-	-	11	-	6 7	-	5 3	-	5 9	6 7	6 7	-	-	-	8 2	
Mg^{2+} (mg/L)	1 0	-	-	-	14	-	13	-	11	-	12	12	12	-	-	-	15	
K^{+} (mg/L)	1 0	-	-	-	4 7	-	19	-	17		17	13	16	-	-	-	13	
Total P (mg/L)	0 001	0 002	-	-	0 037	-	0 036	0 014	<0 11	-	0 022	0 031	0 026	-	-	-	0 030	
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 008	-	0 009	-	0 003	-	0 005	-	-	-	-	-	-	
Cl (mg/L)	1 0	-	-	-	6 4	-	6 1	-	5 9	-	6 6	6 2	6 4	-	-	-	5 8	
SO_4^{2} (mg/L)	1 0	-	-	-	20	-	27	-	25	-	25	21	21	-	-	-	-	
NO_3 (mg-N/L)	0 001	0 002	-	-	16	-	6 9	-	5 8	-	7 9	9 9	9 1	-	-	-	9 5	
HCO_3 (mg/L)	3 9	-	-	-	227	-	280	-	199	-	219	221	247	-	-	-	227	
Calculations																		
pCO_2 (atm)	-	-	-	-	-1 93	-	-1 88	-	-1 62	-	-1 70	-1 76	-1 78	-	-	-	-1 82	
$SI_{calcite}$	-	-	-	-	0 513	-	0 830	-	0 165	-	0 274	0 379	0 665	-	-	-	0 573	
Nitrogen Isotopes																		
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-		-	-		-	-	-	-	-	-	-	-	
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-		-	11 2	11 9	-	-	-	-	
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	5 2	3 3	-	-	-	-	
Carbon																		
DIC (ppmC)	1 0	0 1	-	-	53	-	64	-	59	-	58	55	58	-	-	-	54	
DOC (ppmC)	1 0	0 1	-	-	4 6	-	2 8	-	5 0	-	2 7	3 4	3 9	-	-	-	3 1	
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-13 3	-	-14 6	-	-	-	-14 9	-14 2	-13 9	-	-	-	-14 2	
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	23 9	-	-26 8	-	-27 2	-	-27 1	-26 4	-26 7	-	-	-	-27 7	
Water																		
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-10 0	-	-10 4	-	-10 9	-10 8	-	-10 4	-	-	-	-	-	
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-70 1	-	-74 0	-	-77 5	-80 2	-	-75 1	-	-	-	-	-	

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	T3-B																								
Type	Tile Drain																								
Depth	1 3 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	-	-		-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	14 0	-	14 0	14 0	1	8 5	3 2	6 2	10 7	2	5 7	3 1	3 5	7 9	2	8 1	2 9	6 0	10 1	2	8 3	3 5	3 5	14 0	7
pH	7 1	-	7 1	7 1	1	7 2	0 1	7 1	7 2	2	7 1	0 3	6 8	7 3	2	7 0	0 1	7 0	7 1	2	7 1	0 1	6 8	7 3	7
SpC (µS/cm)	499	-	499	499	1	805	-	805	805	1	989	170	869	1109	2	692	83	633	751	2	778	209	499	1109	6
DO (mg/L)	6 2	-	6 2	6 2	1	-	-	-	-	-	5 0	-	5 0	5 0	1	-	-	-	-	-	5 6	0 86	5 0	6 2	2
Eh (mV)	373	-	373	373	1	275	-	275	275	1	-	-	-	-	-	-	-	-	-	-	324	69	275	373	2
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	75	-	75	75	1	75	8 3	69	81	2	72	8 5	66	78	2	67	0 47	67	67	2	72	6 1	66	81	7
Na^{+} (mg/L)	6 7	-	6 7	6 7	1	9 5	1 8	8 2	10 7	2	6 0	1 0	5 3	6 7	2	6 3	0 57	5 9	6 7	2	7 2	1 8	5 3	10 7	7
Mg^{2+} (mg/L)	12	-	12	12	1	14	0 75	14	15	2	12	1 4	11	13	2	12	0 002	12	12	2	13	1 1	11	15	7
K^{+} (mg/L)	15 6	-	15 6	15 6	1	9 0	6 1	4 7	13 3	2	17 6	1 6	16 5	18 7	2	15 3	2 8	13 3	17 2	2	14 2	4 65	4 7	18 7	7
Total P (mg/L)	0 026	-	0 026	0 026	1	0 034	0 005	0 030	0 037	2	0 025	0 016	0 014	0 036	2	0 026	0 007	0 022	0 031	2	0 028	0 008	0 014	0 037	7
NH_4^{+} (mg-N/L)	-	-	-	-	-	0 008	-	0 008	0 008	1	0 006	0 004	0 003	0 009	2	0 005	-	0 005	0 005	1	0 006	0 003	0 003	0 009	4
Cl (mg/L)	6 4	-	6 4	6 4	1	6 1	0 40	5 8	6 4	2	6 0	0 17	5 9	6 1	2	6 4	0 30	6 2	6 6	2	6 2	0 28	5 8	6 6	7
SO_4^{2} (mg/L)	21	-	21	21	1	20	-	20	20	1	26	1 6	25	27	2	23	2 5	21	25	2	23	2 9	20	27	6
NO_3 (mg-N/L)	9 1	-	9 1	9 1	1	13	4 7	9 5	16	2	6 4	0 77	5 8	6 9	2	8 9	1 4	7 9	9 9	2	9 3	3 4	5 8	16	7
HCO_3 (mg/L)	247	-	247	247	1	227	0 084	227	227	2	239	57	199	280	2	220	1 2	219	221	2	232	25	199	280	7
Calculations																									
pCO_2 (atm)	-1 78	-	-1 78	-1 78	1	-1 88	0 08	-1 93	-1 82	2	-1 75	0 19	-1 88	-1 62	2	-1 73	0 04	-1 76	-1 70	2	-1 79	0 11	-1 93	-1 62	7
$SI_{calcite}$	0 665	-	0 665	0 665	1	0 543	0 042	0 513	0 573	2	0 497	0 470	0 165	0 830	2	0 327	0 074	0 274	0 379	2	0 485	0 230	0 165	0 830	7
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	11 9	-	11 9	11 9	1	-	-	-	-	-	-	-	-	-	-	11 2	-	11 2	11 2	1	11 6	0 5	11 2	11 9	2
$\delta^{18}O_{NO3}$ (‰)	3 3	-	3 3	3 3	1	-	-	-	-	-	-	-	-	-	-	5 2	-	5 2	5 2	1	4 3	1 3	3 3	5 2	2
Carbon																									
DIC (ppmC)	58	-	58	58	1	54	1	53	54	2	62	4	59	64	2	57	2	55	58	2	57	4	53	64	7
DOC (ppmC)	3 9	-	3 9	3 9	1	3 9	1 1	3 1	4 6	2	3 9	1 5	2 8	5 0	2	3 1	0 5	2 7	3 4	2	3 7	0 9	2 7	5 0	7
$\delta^{13}C_{DIC}$ (‰)	-13 9	-	-13 9	-13 9	1	-13 8	0 6	-14 2	-13 3	2	-14 6	-	-14 6	-14 6	1	-14 6	0 5	-14 9	-14 2	2	-14 2	0 5	-14 9	-13 3	6
$\delta^{13}C_{DOC}$ (‰)	-26 7	-	-26 7	-26 7	1	-25 8	2 7	-27 7	-23 9	2	-27 0	0 2	-27 2	-26 8	2	-26 7	0 4	-27 1	-26 4	2	-26 5	1 2	-27 7	-23 9	7
Water																									
$\delta^{18}O_{H2O}$ (‰)	-	-	-	-	-	-10 0	-	-10 0	-10 0	1	-10 6	0 4	-10 9	-10 4	2	-10 6	0 3	-10 8	-10 4	2	-10 5	0 4	-10 9	-10 0	5
$\delta^{2}H_{H2O}$ (‰)	-	-	-		-	-70 1	-	-70 1	-70 1	1	-75 7	2 4	-77 5	-74 0	2	-77 7	3 6	-80 2	-75 1	2	-75 4	3 8	-80 2	-70 1	5

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			P3-1A														
Type			Piezometer														
Depth			3 3 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	1 494	1 352	0 540	0 762	1 052	1 042	0 935	1 008	0 992	0 902	1 024	1 140	1 167	1 457	0 611
Temp (°C)	-	0 1	14 2	13 5	12 5	7 8	6 3	5 3	6 5	8 4	11 9	10 2	17 0	19 4	14 6	15 0	10 6
pH	-	0 01	7 3	7 8	7 3	7 5	7 2	7 2	7 7	7 5	7 3	7 1	7 4	7 6	7 3	7 6	7 5
SpC (µS/cm)	-	1	1922	1909	1015	1172	1553	1493	1342	1043	912	899	719	904	1408	917	1214
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	1 6	-	1 0	2 4	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	322	372	307	502	82
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	85	88	76	82	82	87	69	72	72	82	85	83	85	83	86
Na^{+} (mg/L)	1 0	-	34	34	34	35	34	36	28	27	29	34	32	34	35	34	35
Mg^{2+} (mg/L)	1 0	-	49	49	45	46	46	48	37	38	40	46	45	48	49	49	49
K^{+} (mg/L)	1 0	-	8 2	8 9	8 3	8 4	8 0	8 9	6 7	6 6	6 6	7 2	7 1	7 8	7 9	8 2	8 4
Total P (mg/L)	0 001	0 002	<0 65	<0 65	<0 65	<0 65	0 28	0 41	0 43	0 25	0 26	0 34	0 32	0 37	0 66	0 20	0 61
NH_4^{+} (mg-N/L)	0 001	0 003	0 45	-	0 86	0 92	1 0	0 78	0 7	0 63	0 64	0 71	0 55	0 71	0 76	1 8	1 4
Cl (mg/L)	1 0	-	12	13	11	12	14	11	12	12	12	14	13	-	13	13	13
SO_4^{2} (mg/L)	1 0	-	25	29	23	26	28	20	23	24	26	28	28	-	29	24	-
NO_3 (mg-N/L)	0 001	0 002	0 15	1 1	0 23	0 11	3 2	0 36	0 81	0 39	0 22	1 6	0 96	-	0 76	0 23	0 12
HCO_3 (mg/L)	3 9	-	465	447	497	-	502	455	142	512	490	474	551	540	637	543	515
Calculations																	
pCO_2 (atm)	-	-	-1 66	-2 16	-1 62	-	-1 59	-1 57	-2 65	-1 81	-1 68	-1 49	-1 69	-1 83	-1 54	-1 89	-1 80
$SI_{calcite}$	-	-	1 818	5 294	1 584	-	1 179	0 935	1 042	2 041	1 634	1 026	3 017	4 491	2 557	4 216	2 596
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	17 5	11 2	9 3	7 3	6 5	11 2	10 6	9 9	8 6	9 7	10 1	5 8	8 2	6 9
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		13 2	-	-	7 9	-	-	12 3	-	-	19 6	-	-	17 1	-	12 2
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		8 1	-	-	4 6	-	-	8 7	-	-	6 0	-	-	10 6	-	14 2
Carbon																	
DIC (ppmC)	1 0	0 1	104	92	112	-	118	111	30	111	109	114	119	114	141	114	112
DOC (ppmC)	1 0	0 1	-	3 7	7 2	4 4	2 6	3 4	4 7	3 5	3 0	5 0	7 2	5 9	2 4	7 3	4 5
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-16 5	-16 6	-17 7	-17 5	-17 1	-17 4	-18 4	-17 6	-17 5	-17 4	-16 9	-17 6	-17 5	-17 4	-17 7
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-24 9	-25 9	-23 9	-25 8	-25 9	-26 2	-26 3	-26 2	-26 1	-26 9	-26 3	-26 3	-26 6	-27 1
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 5	-10 6	-10 6	-10 4	-10 5	-10 5	-10 8	-10 5	-	-10 6	-	-10 8	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-76 3	-76 2	-76 8	-78 0	-75 7	-73 1	-79 0	-75 2	-	-72 2	-	-74 1	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	P3-1A																					
Type	Piezometer																					
Depth	3 3 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 21	0 20	1 02	1 49	4	0 94	0 43	0 54	1 46	5	1 01	0 06	0 94	1 05	3	0 97	0 06	0 90	1 01	3	1 03	0 27	0 54	1 49	15
Temp (°C)	16 3	2 4	14 2	19 4	4	11 9	2 8	7 8	15 0	5	6 0	0 6	5 3	6 5	3	10 2	1 8	8 4	11 9	3	11 5	4 2	5 3	19 4	15
pH	7 4	0 1	7 3	7 6	4	7 5	0 2	7 3	7 8	5	7 4	0 3	7 2	7 7	3	7 3	0 2	7 1	7 5	3	7 4	0 2	7 1	7 8	15
SpC (µS/cm)	1239	541	719	1922	4	1246	390	917	1909	5	1462	109	1342	1553	3	951	80	899	1043	3	1228	370	719	1922	15
DO (mg/L)	1 3	0 4	1 0	1 6	2	2 4	-	2 4	2 4	1	-	-	-		-	-	-	-	-	-	1 6	0 69	1 0	2 4	3
Eh (mV)	334	34	307	372	3	292	297	82	502	2	-	-	-	-	-	-	-	-	-	-	317	152	82	502	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	84	1 2	83	85	4	83	4 5	76	88	5	79	9 3	69	87	3	75	6 1	72	82	3	81	6 0	69	88	15
Na^{+} (mg/L)	34	1 3	32	35	4	34	0 8	34	35	5	32	4 2	28	36	3	30	3 4	27	34	3	33	2 7	27	36	15
Mg^{2+} (mg/L)	48	2 1	45	49	4	47	2 0	45	49	5	44	6 2	37	48	3	41	4 2	38	46	3	46	4 2	37	49	15
K^{+} (mg/L)	7 7	0 47	7 1	8 2	4	8 4	0 28	8 2	8 9	5	7 9	1 1	6 7	8 9	3	6 8	0 37	6 6	7 2	3	7 8	0 80	6 6	8 9	15
Total P (mg/L)	0 452	0 184	0 319	0 662	3	0 401	0 289	0 197	0 606	2	0 373	0 084	0 276	0 430	3	0 282	0 048	0 252	0 337	3	0 375	0 147	0 197	0 662	11
NH_4^{+} (mg-N/L)	0 616	0 144	0 449	0 762	4	1 232	0 426	0 859	1 766	4	0 836	0 162	0 709	1 019	3	0 660	0 047	0 627	0 714	3	0 849	0 348	0 449	1 766	14
Cl (mg/L)	13	1 1	12	13	3	12	0 9	11	13	5	12	1 3	11	14	3	12	1 0	12	14	3	12	0 93	11	14	14
SO_4^{2} (mg/L)	27	2 2	25	29	3	25	2 4	23	29	4	24	3 9	20	28	3	26	1 9	24	28	3	26	2 6	20	29	13
NO_3 (mg-N/L)	0 63	0 42	0 15	0 96	3	0 36	0 41	0 11	1 1	5	1 4	1 5	0 36	3 2	3	0 72	0 73	0 22	1 6	3	0 72	0 82	0 11	3 2	14
HCO_3 (mg/L)	548	70	465	637	4	500	40	447	543	4	367	196	142	502	3	492	19	474	512	3	484	110	142	637	14
Calculations																									
pCO_2 (atm)	-1 68	0 12	-1 83	-1 54	4	-1 87	0 23	-2 16	-1 62	4	-1 94	0 62	-2 65	-1 57	3	-1 66	0 16	-1 81	-1 49	3	-1 78	0 30	-2 65	-1 49	14
$SI_{calcite}$	2 971	1 127	1 818	4 491	4	3 422	1 653	1 584	5 294	4	1 052	0 122	0 935	1 179	3	1 567	0 511	1 026	2 041	3	2 388	1 403	0 935	5 294	14
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	8 5	2 4	5 8	10 1	3	10 6	4 2	6 9	17 5	5	8 3	2 5	6 5	11 2	3	9 7	1 0	8 6	10 6	3	9 5	2 9	5 8	17 5	14
$\delta^{15}N_{NO3}$ (‰)	15 2	2 8	13 2	17 1	2	10 1	3 0	7 9	12 2	2	12 3	-	12 3	12 3	1	19 6	-	19 6	19 6	1	13 7	4 1	7 9	19 6	6
$\delta^{18}O_{NO3}$ (‰)	9 4	1 8	8 1	10 6	2	9 4	6 8	4 6	14 2	2	8 7	-	8 7	8 7	1	6 0	-	6 0	6 0	1	8 7	3 4	4 6	14 2	6
Carbon																									
DIC (ppmC)	120	16	104	141	4	107	10	92	114	4	86	49	30	118	3	112	3	109	114	3	107	25	30	141	14
DOC (ppmC)	5 2	2 5	2 4	7 2	3	5 4	1 7	3 7	7 3	5	3 5	1 0	2 6	4 7	3	3 8	1 0	3 0	5 0	3	4 6	1 7	2 4	7 3	14
$\delta^{13}C_{DIC}$ (‰)	-17 1	0 5	-17 6	-16 5	4	-17 4	0 5	-17 7	-16 6	5	-17 6	0 7	-18 4	-17 1	3	17 5	0 1	-17 6	-17 4	3	-17 4	0 5	-18 4	-16 5	15
$\delta^{13}C_{DOC}$ (‰)	-26 5	0 4	-26 9	-26 3	3	-25 7	1 3	-27 1	-23 9	5	-26 0	0 2	-26 2	-25 8	3	-26 2	0 1	-26 3	-26 1	3	-26 0	0 8	-27 1	-23 9	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 7	0 2	-10 8	-10 5	2	-10 6	0 1	-10 6	-10 4	3	-10 6	0 2	-10 8	-10 5	3	-10 5	0 1	-10 6	-10 5	2	-10 6	0 1	-10 8	-10 4	10
$\delta^{2}H_{H2O}$ (‰)	-75 2	1 6	-76 3	-74 1	2	-77 0	0 9	-78 0	-76 2	3	-75 9	3 0	-79 0	-73 1	3	-73 7	2 1	-75 2	-72 2	2	-75 7	2 1	-79 0	-72 2	10

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			P3-1B														
Type			Piezometer														
Depth			4 3 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	1 420	1 461	0 816	0 851	1 066	1 136	0 895	1 147	1 021	0 996	1 061	1 173	1 108	1 501	0 724
Temp (°C)	-	0 1	13 6	13 4	12 5	7 3	6 8	6 3	6 0	10 2	13 0	12 0	17 0	17 8	13 6	13 9	9 1
pH	-	0 01	7 5	7 7	7 7	7 3	7 3	7 3	7 5	7 6	7 5	7 3	7 7	7 6	7 6	7 6	7 6
SpC (µS/cm)	-	1	1903	1966	970	1192	1597	1425	1365	968	868	839	722	813	797	929	1245
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	0 7	0 7	0 7	0 6	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-		-	356	752	194	179	45
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	68	77	77	73	72	76	60	63	62	72	73	73	75	73	77
Na^{+} (mg/L)	1 0	-	35	40	38	38	37	40	31	32	33	38	37	37	38	37	37
Mg^{2+} (mg/L)	1 0	-	42	50	49	45	44	47	36	38	39	46	44	48	48	48	48
K^{+} (mg/L)	1 0	-	8 4	10	9 6	9 3	9 3	10	7 7	8 2	8 0	8 6	8 8	8 8	9 1	9 1	9 3
Total P (mg/L)	0 001	0 002	<0 65	<0 65	<0 65	<0 65	0 45	0 63	0 40	0 39	0 38	0 54	0 54	0 61	0 58	0 43	1 0
NH_4^{+} (mg-N/L)	0 001	0 003		-	1 1	1 0	0 78	0 041	0 79	0 82	0 81	1 0	1 0	1 0	1 1	1 3	1 3
Cl (mg/L)	1 0	-	6 4	6 7	5 6	6 7	6 7	6 2	5 7	6 3	6 5	6 5	6 7	6 5	6 8	6 5	7 0
SO_4^{2} (mg/L)	1 0	-	10	8 6	8 2	12	8 8	10	8 8	9 1	10	8 8	10	10	10	7 8	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	0 76	1 1	0 17	0 13	<0 001	<0 001	0 17	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	512	408	541	492	502	254	355	541	513	497	580	528	652	537	536
Calculations																	
pCO_2 (atm)	-	-	-1 86	-2 08	-2 03	-1 69	-1 70	-1 97	-2 06	-1 91	-1 81	-1 60	-1 92	-1 86	-1 78	-1 88	-1 93
$SI_{calcite}$	-	-	2 811	3 258	4 753	1 378	1 390	0 716	1 381	2 730	2 204	1 385	5 092	3 766	3 944	3 435	3 169
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		10 4	8 9	5 6	5 9	6 9	-	13 4	9 3	18 7	9 1	7 8	8 4	9 5	3 2	7 2
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-0 9	5 7	0 4	8 4	-	-	4 7	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-1 9	-0 1	8 3	10 4	-	-	16 9	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	109	85	112	111	113	58	76	115	110	113	120	111	138	113	114
DOC (ppmC)	1 0	0 1	-	4 5	6 4	4 5	3 5	3 6	5 7	3 8	3 3	5 9	8 7	3 9	2 7	6 4	3 7
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-16 7	-17 3	-17 7	-17 2	-17 1	-17 0	-17 5	-17 6	-17 6	-17 2	-16 9	-17 4	-17 5	-17 7	-17 6
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-24 8	-25 3	-25 1	-26 8	-26 3	-26 3	-26 6	-26 4	-26 4	-26 9	-26 3	-26 2	-26 3	-26 6
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 1	-10 0	-10 1	-10 1	-10 0	-10 0	-10 2	-10 0	-	-9 9	-	-10 2	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-70 0	-70 3	-66 4	-73 4	-72 2	-71 5	-74 1	-73 3	-	-69 8	-	-69 0	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	P3-1B																					
Type	Piezometer																					
Depth	4 3 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 19	0 16	1 06	1 42	4	1 1	0 38	0 72	1 50	5	1 03	0 12	0 90	1 14	3	1 06	0 08	1 00	1 15	3	1 09	0 23	0 72	1 50	15
Temp (°C)	15 5	2 2	13 6	17 8	4	11 2	2 9	7 3	13 9	5	6 4	0 4	6 0	6 8	3	11 7	1 4	10 2	13 0	3	11 5	3 7	6 0	17 8	15
pH	7 6	0 06	7 5	7 7	4	7 6	0 2	7 3	7 7	5	7 4	0 1	7 3	7 5	3	7 4	0 2	7 3	7 6	3	7 5	0 1	7 3	7 7	15
SpC (µS/cm)	1059	564	722	1903	4	1261	418	929	1966	5	1462	121	1365	1597	3	892	68	839	968	3	1173	403	722	1966	15
DO (mg/L)	0 7	0 01	0 7	0 7	3	0 6	-	0 6	0 6	1	-	-	-	-	-	-	-	-	-	-	0 7	0 04	0 6	0 7	4
Eh (mV)	434	287	194	752	3	112	94	45	179	2	-	-	-	-	-	-	-		-	-	305	273	45	752	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	72	2 8	68	75	4	75	2 0	73	77	5	69	7 9	60	76	3	66	5 6	62	72	3	71	5 5	60	77	15
Na^{+} (mg/L)	37	1 5	35	38	4	38	1 1	37	40	5	36	4 8	31	40	3	34	3	32	38	3	37	2 7	31	40	15
Mg^{2+} (mg/L)	46	3 0	42	48	4	48	1 8	45	50	5	42	5 8	36	47	3	41	4 3	38	46	3	45	4 3	36	50	15
K^{+} (mg/L)	8 8	0 26	8 4	9 1	4	9 5	0 50	9 1	10 4	5	9 0	1 2	7 7	10	3	8 3	0 34	8 0	8 6	3	9 0	0 73	7 7	10 4	15
Total P (mg/L)	0 576	0 037	0 537	0 611	3	0 716	0 398	0 434	0 998	2	0 493	0 124	0 398	0 633	3	0 439	0 087	0 385	0 540	3	0 542	0 176	0 385	0 998	11
NH_4^{+} (mg-N/L)	1 016	0 075	0 972	1 102	3	1 147	0 140	0 994	1 266	4	0 536	0 429	0 041	0 788	3	0 860	0 079	0 808	0 950	3	0 910	0 308	0 041	1 266	13
Cl (mg/L)	6 6	0 17	6 4	6 8	4	6 5	0 56	5 6	7 0	5	6 2	0 49	5 7	6 7	3	6 4	0 08	6 3	6 5	3	6 5	0 39	5 6	7 0	15
SO_4^{2} (mg/L)	10	0 40	10	10	4	9 1	1 7	7 8	12	4	9 1	0 63	8 8	10	3	9 3	0 58	8 8	10	3	9 4	0 99	7 8	12	14
NO_3 (mg-N/L)	0 17	-	0 17	0 17	1	-	-	-	-	-	0 66	0 45	0 17	1 1	3	0 13	-	0 13	0 13	1	0 46	0 43	0 13	1 1	5
HCO_3 (mg/L)	568	63	512	652	4	503	57	408	541	5	370	125	254	502	3	517	22	497	541	3	496	95	254	652	15
Calculations																									
pCO_2 (atm)	-1 86	0 06	-1 92	-1 78	4	-1 92	0 15	-2 08	-1 69	5	-1 91	0 19	-2 06	-1 70	3	-1 77	0 16	-1 91	-1 60	3	-1 87	0 14	-2 08	-1 60	15
$SI_{calcite}$	3 903	0 935	2 811	5 092	4	3 199	1 203	1 378	4 753	5	1 162	0 386	0 716	1 390	3	2 107	0 678	1 385	2 730	3	2 761	1 330	0 716	5 092	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	9 0	1 2	7 8	10 4	4	6 2	2 1	3 2	8 9	5	10 2	4 6	6 9	13 4	2	12 4	5 5	9 1	18 7	3	8 9	3 7	3 2	18 7	14
$\delta^{15}N_{NO3}$ (‰)	4 7	-	4 7	4 7	1	-	-	-	-	-	1 7	3 5	-0 9	5 7	3	8 4	-	8 4	8 4	1	3 7	3 8	-0 9	8 4	5
$\delta^{18}O_{NO3}$ (‰)	16 9	-	16 9	16 9	1	-	-	-	-	-	2 1	5 4	-1 9	8 3	3	10 4	-	10 4	10 4	1	6 7	7 8	-1 9	16 9	5
Carbon																									
DIC (ppmC)	119	13	109	138	4	107	12	85	114	5	83	28	58	113	3	113	2	110	115	3	107	19	58	138	15
DOC (ppmC)	5 1	3 1	2 7	8 7	3	5 1	1 2	3 7	6 4	5	4 2	1 3	3 5	5 7	3	4 3	1 4	3 3	5 9	3	4 7	1 6	2 7	8 7	14
$\delta^{13}C_{DIC}$ (‰)	-17 1	0 4	-17 5	-16 7	4	-17 5	0 2	-17 7	-17 2	5	-17 2	0 3	-17 5	-17 0	3	-17 5	0 2	-17 6	-17 2	3	-17 3	0 3	-17 7	-16 7	15
$\delta^{13}C_{DOC}$ (‰)	-26 5	0 4	-26 9	-26 2	3	-25 6	0 8	-26 6	-24 8	5	-26 5	0 3	-26 8	-26 3	3	-26 5	0 1	-26 6	-26 4	3	-26 2	0 7	-26 9	-24 8	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 2	0 0	-10 2	-10 1	2	-10 0	0 0	-10 1	-10 0	3	-10 1	0 1	-10 2	-10 0	3	-10 0	0 1	-10 0	-9 9	2	-10 1	0 1	-10 2	-9 9	10
$\delta^{2}H_{H2O}$ (‰)	-69 5	0 7	-70 0	-69 0	2	-70 0	3 5	-73 4	-66 4	3	-72 6	1 3	-74 1	-71 5	3	-71 5	2 5	-73 3	-69 8	2	-71 0	2 4	-74 1	-66 4	10

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			P3-1C														
Type			Piezometer														
Depth			6 4 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	1 400	1 481	1 091	0 841	0 916	-	1 111	0 769	0 923	1 011	0 966	1 096	0 993	1 397	0 973
Temp (°C)	-	0 1	12 6	12 3	12 2	7 4	7 3	-	4 6	10 1	11 0	11 4	17 0	14 4	13 0	12 8	9 2
pH	-	0 01	7 8	7 9	7 6	7 5	7 5	-	8 0	7 8	7 5	7 3	7 8	7 8	7 8	7 9	7 9
SpC (µS/cm)	-	1	1778	1798	904	1107	1668	-	1316	896	801	798	690	850	749	879	1126
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	0 5	0 8	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	53	145	127	125	60
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	50	50	50	46	47	-	42	42	42	48	49	49	50	48	51
Na^{+} (mg/L)	1 0	-	47	47	48	47	47	-	40	41	41	48	48	49	50	46	49
Mg^{2+} (mg/L)	1 0	-	45	47	47	42	43	-	37	37	38	44	42	46	47	46	47
K^{+} (mg/L)	1 0	-	12	12	12	12	12	-	10	11	11	12	12	12	12	12	13
Total P (mg/L)	0 001	0 002	<0 65	<0 65	<0 65	<0 65	1 0	-	0 72	0 82	0 87	0 90	0 84	0 92	0 82	0 57	0 86
NH_4^{+} (mg-N/L)	0 001	0 003	0 89	-	1 5	1 4	1 5	-	1 5	1 5	1 5	1 5	1 6	1 5	1 5	1 5	1 7
Cl (mg/L)	1 0	-	3 3	3 3	3 4	3 3	3 5	-	3 2	3 6	3 4	3 5	3 6	3 4	3 5	3 5	3 5
SO_4^{2} (mg/L)	1 0	-	<1 0	0 84	0 45	<1 0	<1 0	-	1 0	0 8	<1 0	0 39	<1 0	<1 0	<1 0	<1 0	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	<0 001	-	1 1	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	476	463	497	476	478	-	-	489	456	462	525	491	626	502	477
Calculations																	
pCO_2 (atm)	-	-	-2 12	-2 31	-1 98	-1 91	-1 86	-	-	-2 20	1 90	-1 72	-2 11	-2 18	-2 03	-2 24	-2 27
$SI_{calcite}$	-	-	3 109	4 519	2 392	1 383	1 293	-	-	3 003	1 352	1 071	4 370	4 015	4 313	4 420	3 799
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		5 9	7 2	5 3	7 3	3 3		7 1	4 7	9 4	6 2	7 8	9 0	7 2	8 6	7 8
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	98	94	104	103	104	-	-	100	98	103	108	100	129	102	98
DOC (ppmC)	1 0	0 1	-	5 5	7 4	6 2	4 2	-	8 3	4 7	4 6	7 4	9 8	6 9	3 8	7 4	4 9
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-16 6	-17 1	-17 4	-17 1	-16 9	-	-	-17 5	-17 4	-17 0	-16 8	-17 2	-17 1	-17 5	-17 2
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-26 4	-28 4	-25 6	-25 7	-	-27 0	-26 6	-25 8	-25 7	-26 1	-25 8	-25 7	-25 7	-26 1
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-9 9	-9 9	-9 9	-9 9	-9 8	-	-10 1	-9 8	-	-9 9	-	-10 0	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-73 4	-70 7	-69 0	-73 3	-72 4	-	-73 6	67 6	-	-68 6	-	-69 8	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	P3-1C																				
Type	Piezometer																				
Depth	6 4 mbgs																				
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 11	0 20	0 97	1 40	4	1 16	0 27	0 84	1 48	5	1 01	0 14	0 92	1 11	2	0 90	0 12	0 77	1 01	3	1 07	0 22	0 77	1 48	14
Temp (°C)	14 3	2 0	12 6	17 0	4	10 8	2 4	7 4	12 8	5	6 0	1 9	4 6	7 3	2	10 8	0 7	10 1	11 4	3	11 1	3 2	4 6	17 0	14
pH	7 8	0 0	7 8	7 8	4	7 8	0 2	7 5	7 9	5	7 8	0 4	7 5	8 0	2	7 6	0 3	7 3	7 8	3	7 7	0 2	7 3	8 0	14
SpC (µS/cm)	1017	512	690	1778	4	1163	373	879	1798	5	1492	249	1316	1668	2	832	55	798	896	3	1097	390	690	1798	14
DO (mg/L)	0 5	-	0 5	0 5	1	0 8	-	0 8	0 8	1	-	-	-	-	-	-	-	-	-	-	0 6	0 16	0 5	0 8	2
Eh (mV)	108	49	53	145	3	93	46	60	125	2	-	-	-	-	-	-	-	-	-	-	102	42	53	145	5
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	49	0 71	49	50	4	49	2 0	46	51	5	45	3 4	42	47	2	44	3 7	42	48	3	47	3 3	42	51	14
Na^{+} (mg/L)	49	1 4	47	50	4	48	1 1	46	49	5	44	4 3	40	47	2	43	3 8	41	48	3	46	3 2	40	50	14
Mg^{2+} (mg/L)	45	2 0	42	47	4	46	2 0	42	47	5	40	4 4	37	43	2	39	3 8	37	44	3	43	3 8	37	47	14
K^{+} (mg/L)	12	0 19	12	12	4	12	0 40	12	13	5	11	0 91	10	12	2	11	0 50	11	12	3	12	0 66	10	13	14
Total P (mg/L)	0 86	0 052	0 82	0 92	3	0 71	0 21	0 57	0 86	2	0 87	0 21	0 72	1 0	2	0 86	0 038	0 82	0 90	3	0 83	0 12	0 57	1 0	10
NH_4^{+} (mg-N/L)	1 37	0 32	0 89	1 55	4	1 55	0 13	1 42	1 74	4	1 54	0 012	1 53	1 55	2	1 49	0 016	1 5	1 50	3	1 5	0 19	0 89	1 7	13
Cl (mg/L)	3 4	0 14	3 3	3 6	4	3 4	0 10	3 3	3 5	5	3 3	0 21	3 2	3 5	2	3 5	0 11	3 4	3 6	3	3 4	0 13	3 2	3 6	14
SO_4^{2} (mg/L)	-	-	-	-	-	0 65	0 27	0 45	0 84	2	1 0	-	1 0	1 0	1	0 60	0 30	0 4	0 8	2	0 70	0 27	0 39	1 0	5
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	1 1	-	1 1	1 1	1	-	-	-	-	-	1 1	-	1 1	1 1	1
HCO_3 (mg/L)	530	67	476	626	4	483	16	463	502	5	478	-	478	478	1	469	17	456	489	3	494	44	456	626	13
Calculations																									
pCO_2 (atm)	-2 11	0 06	-2 18	-2 03	4	-2 14	0 18	-2 31	-1 91	5	-1 86	-	-1 86	-1 86	1	-1 94	0 24	-2 20	-1 72	3	-2 06	0 18	-2 31	-1 72	13
$SI_{calcite}$	3 952	0 583	3 109	4 370	4	3 303	1 368	1 383	4 519	5	1 293	-	1 293	1 293	1	1 808	1 044	1 071	3 003	3	3 003	1 352	1 071	4 519	13
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	7 4	1 3	5 9	9 0	4	7 2	1 2	5 3	8 6	5	5 2	2 6	3 3	7 1	2	6 8	2 4	4 7	9 4	3	6 9	1 7	3 3	9 4	14
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	109	14	98	129	4	100	4	94	104	5	104	-	104	104	1	100	3	98	103	3	103	8	94	129	13
DOC (ppmC)	6 8	3 0	3 8	9 8	3	6 3	1 1	4 9	7 4	5	6 2	2 9	4 2	8 3	2	5 6	1 6	4 6	7 4	3	6 2	1 8	3 8	9 8	13
$\delta^{13}C_{DIC}$ (‰)	-16 9	0 3	-17 2	-16 6	4	-17 3	0 2	-17 5	-17 1	5	-16 9	-	-16 9	-16 9	1	-17 3	0 3	-17 5	-17 0	3	-17 1	0 3	-17 5	-16 6	13
$\delta^{13}C_{DOC}$ (‰)	-25 9	0 2	-26 1	-25 7	3	-26 4	1 1	-28 4	-25 6	5	-26 4	0 9	27 0	-25 7	2	-26 1	0 5	-26 6	-25 7	3	-26 2	0 8	-28 4	-25 6	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 0	0 1	-10 0	-9 9	2	-9 9	0 0	-9 9	-9 9	3	-9 9	0 3	-10 1	-9 8	2	-9 8	0 1	-9 9	-9 8	2	-9 9	0 1	-10 1	-9 8	9
$\delta^{2}H_{H2O}$ (‰)	-71 6	2 5	-73 4	-69 8	2	-71 0	2 2	-73 3	-69 0	3	-73 0	0 8	-73 6	-72 4	2	-68 1	0 7	-68 6	-67 6	2	-70 9	2 3	-73 6	-67 6	9

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			P3-2A														
Type			Piezometer														
Depth			3 2 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	1 959	1 647	1 019	0 912	1 341	1 292	1 122	1 027	1 253	1 277	1 416	1 565	1 619	1 912	0 934
Temp (°C)	-	0 1	13 0	13 5	11 1	8 3	8 6	8 5	6 4	9 0	10 0	11 0	15 0	17 1	16 6	14 0	11 1
pH	-	0 01	7 3	7 7	7 7	7 5	7 5	7 6	7 6	7 4	7 6	7 3	7 3	7 6	7 3	7 5	7 5
SpC (µS/cm)	-	1	1369	1425	686	896	1172	969	996	714	727	662	541	592	654	640	862
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	1 1	0 9	1 4	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	272	378	187	103
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	71	75	69	71	69	75	62	64	64	72	72	71	74	72	74
Na^{+} (mg/L)	1 0	-	18	17	17	17	17	18	14	14	15	17	17	17	18	16	17
Mg^{2+} (mg/L)	1 0	-	27	28	26	27	26	27	22	23	24	26	26	27	28	27	27
K^{+} (mg/L)	1 0	-	3 5	3 5	3 2	3 3	3 6	3 5	2 4	2 6	2 5	2 9	2 8	3 0	3 2	3 0	3 1
Total P (mg/L)	0 001	0 002	0 11	0 16	0 13	<0 65	0 17	0 19	0 19	0 11	0 11	0 17	0 34	0 21	0 27	0 23	0 26
NH_4^{+} (mg-N/L)	0 001	0 003	-	0 13	0 11	0 08	0 47	0 15	-	0 004	-	0 084	0 12	0 37	-	0 28	0 20
Cl (mg/L)	1 0	-	19	18	18	19	18	11	18	18	18	17	18	18	19	19	18
SO_4^{2} (mg/L)	1 0	-	29	29	30	30	23	16	27	29	28	26	27	27	28	27	-
NO_3 (mg-N/L)	0 001	0 002	0 18	0 21	0 15	0 22	0 30	0 46	0 80	0 73	0 52	0 90	1 1	0 60	0 39	0 36	0 12
HCO_3 (mg/L)	3 9	-	289	266	324	333	333	271	158	298	310	297	322	336	387	331	303
Calculations																	
pCO_2 (atm)	-	-	-1 83	-2 27	-2 27	-2 07	-2 06	-2 21	-2 44	-1 99	-2 18	-1 82	-1 78	-2 13	-1 70	-2 03	-2 07
$SI_{calcite}$	-	-	0 878	2 226	2 690	1 628	1 571	1 608	0 732	1 048	1 814	0 858	1 090	2 875	1 434	1 947	1 661
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	12 9	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		16 5	17 2	-	26 0	-	-	21 5	26 4	-	-	37 2	23 1	-	-	47 8
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		17 8	9 5		10 1	-	-	11 9	11 9	-	-	14 8	8 6	-	-	21 3
Carbon																	
DIC (ppmC)	1 0	0 1	66	56	67	71	72	58	34	66	65	68	73	70	87	70	65
DOC (ppmC)	1 0	0 1	-	2 3	3 8	2 4	2 3	2 6	3 3	2 5	1 8	3 1	6 1	3 6	0 71	3 9	2 2
$\delta^{13}C_{DIC}$ (‰)	-	0 2	14 9	-15 6	-15 6	-15 3	-15 0	-14 6	-15 6	-15 3	-16 0	-15 4	-15 1	-15 9	-16 1	-16 0	-15 8
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-24 8	-23 8	-23 5	-26 5	-25 9	-26 6	-26 6	-26 7	-26 5	-27 1	-26 5	-26 5	-26 7	-26 9
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 5	-10 3	-10 7	-10 5	-10 5	-10 5	-10 7	-10 3	-	-9 5	-	-10 5	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-76 4	-73 2	-77 0	-78 6	-74 7	-73 0	-76 6	-72 2	-	-67 1	-	-79 7	-	-	

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	P3-2A																					
Type	Piezometer																					
Depth	3 2 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 64	0 23	1 42	1 96	4	1 28	0 46	0 91	1 91	5	1 25	0 11	1 12	1 34	3	1 19	0 14	1 03	1 28	3	1 35	0 33	0 91	1 96	15
Temp (°C)	15 4	1 8	13 0	17 1	4	11 6	2 3	8 3	14 0	5	7 8	1 2	6 4	8 6	3	10 0	1 0	9 0	11 0	3	11 5	3 2	6 4	17 1	15
pH	7 4	0 2	7 3	7 6	4	7 6	0 1	7 5	7 7	5	7 6	0 0	7 5	7 6	3	7 4	0 2	7 3	7 6	3	7 5	0 2	7 3	7 7	15
SpC (µS/cm)	789	390	541	1369	4	902	313	640	1425	5	1046	111	969	1172	3	701	34	662	727	3	860	278	541	1425	15
DO (mg/L)	1 0	0 1	0 9	1 1	2	1 4	-	1 4	1 4	1	-	-	-	-	-	-	-	-	-	-	1 1	0 22	0 9	1 4	3
Eh (mV)	325	75	272	378	2	145	59	103	187	2	-	-	-	-	-		-	-	-	-	235	118	103	378	4
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	72	1 7	71	74	4	72	2 5	69	75	5	69	6 6	62	75	3	67	4 5	64	72	3	70	4 0	62	75	15
Na^{+} (mg/L)	17	0 72	17	18	4	17	0 53	16	17	5	16	1 8	14	18	3	15	1 4	14	17	3	17	1 2	14	18	15
Mg^{2+} (mg/L)	27	1 0	26	28	4	27	0 8	26	28	5	25	2 3	22	27	3	24	1 7	23	26	3	26	1 7	22	28	15
K^{+} (mg/L)	3 2	0 30	2 8	3 5	4	3 2	0 17	3 0	3 5	5	3 2	0 67	2 4	3 6	3	2 6	0 21	2 5	2 9	3	3 1	0 39	2 4	3 6	15
Total P (mg/L)	0 23	0 097	0 11	0 34	4	0 20	0 059	0 13	0 26	4	0 182	0 015	0 17	0 19	3	0 13	0 036	0 11	0 17	3	0 19	0 068	0 11	0 34	14
NH_4^{+} (mg-N/L)	0 24	0 18	0 12	0 37	2	0 16	0 080	0 081	0 28	5	0 312	0 23	0 15	0 47	2	0 044	0 056	0 004	0 084	2	0 18	0 14	0 004	0 47	11
Cl (mg/L)	18	0 44	18	19	4	18	0 38	18	19	5	16	4 4	11	18	3	18	0 50	17	18	3	18	2 0	11	19	15
SO_4^{2} (mg/L)	28	1 0	27	29	4	29	1 1	27	30	4	22	5 5	16	27	3	28	1 3	26	29	3	27	3 5	16	30	14
NO_3 (mg-N/L)	0 56	0 38	0 18	1 06	4	0 21	0 09	0 12	0 36	5	0 52	0 25	0 30	0 80	3	0 71	0 19	0 52	0 90	3	0 47	0 29	0 12	1 1	15
HCO_3 (mg/L)	333	41	289	387	4	311	28	266	333	5	254	89	158	333	3	302	7 0	297	310	3	304	50	158	387	15
Calculations																									
pCO_2 (atm)	-1 86	0 19	-2 13	-1 70	4	-2 14	0 12	-2 27	-2 03	5	-2 23	0 19	-2 44	-2 06	3	-2 00	0 18	-2 18	-1 82	3	-2 06	0 21	-2 44	-1 70	15
$SI_{calcite}$	1 569	0 900	0 878	2 875	4	2 030	0 441	1 628	2 690	5	1 304	0 495	0 732	1 608	3	1 240	0 506	0 858	1 814	3	1 604	0 643	0 732	2 875	15
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	12 9	-	12 9	12 9	1	-	-	-	-	-	-	-	-	-		-	-	-	-	-	12 9	-	12 9	12 9	1
$\delta^{15}N_{NO3}$ (‰)	25 6	10 6	16 5	37 2	3	30 3	15 8	17 2	47 8	3	21 5	-	21 5	21 5	1	26 4	-	26 4	26 4	1	27 0	10 6	16 5	47 8	8
$\delta^{18}O_{NO3}$ (‰)	13 7	4 7	8 6	17 8	3	13 6	6 6	9 5	21 3	3	11 9	-	11 9	11 9	1	11 9	-	11 9	11 9	1	13 2	4 4	8 6	21 3	8
Carbon																									
DIC (ppmC)	74	9	66	87	4	66	6	56	71	5	54	19	34	72	3	66	1	65	68	3	66	11	34	87	15
DOC (ppmC)	3 5	2 7	0 7	6 1	3	2 9	0 9	2 2	3 9	5	2 7	0 5	2 3	3 3	3	2 5	0 7	1 8	3 1	3	2 9	1 3	0 7	6 1	14
$\delta^{13}C_{DIC}$ (‰)	-15 5	0 6	-16 1	-14 9	4	-15 6	0 3	-16 0	-15 3	5	-15 0	0 5	-15 6	-14 6	3	-15 5	0 4	-16 0	-15 3	3	-15 5	0 4	-16 1	-14 6	15
$\delta^{13}C_{DOC}$ (‰)	-26 7	0 3	-27 1	-26 5	3	-25 2	1 6	-26 9	-23 5	5	-26 3	0 4	-26 6	-25 9	3	-26 6	0 1	-26 7	-26 5	3	-26 0	1 1	-27 1	-23 5	14
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 5	0 0	-10 5	-10 5	2	-10 5	0 2	-10 7	-10 3	3	-10 6	0 1	-10 7	-10 5	3	-9 9	0 6	-10 3	-9 5	2	-10 4	0 3	-10 7	-9 5	10
$\delta^{2}H_{H2O}$ (‰)	-78 1	2 3	-79 7	-76 4	2	-76 3	2 8	-78 6	-73 2	3	-74 8	1 8	-76 6	-73 0	3	-69 7	3 6	-72 2	-67 1	2	-74 8	3 7	-79 7	-67 1	10

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			P3-2B														
Type			Piezometer														
Depth			4 8 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	1 941	1 608	1 183	0 962	1 127	0 763	0 763	0 866	0 993	1 183	1 192	1 346	1 303	1 728	1 025
Temp (°C)	-	0 1	11 5	11 6	10 7	7 6	7 2	6 1	6 8	9 9	12 0	12 0	12 0	14 5	14 3	12 9	10 6
pH	-	0 01	7 3	7 9	7 9	7 6	7 4	7 2	7 6	7 7	7 0	7 4	7 5	7 7	7 7	7 8	7 2
SpC (µS/cm)	-	1	1307	1300	626	816	1162	1620	856	635	594	568	511	547	646	643	797
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	0 9	1 2	0 5	-	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	-	-	-	280	236	251	82
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	55	56	55	58	56	-	49	52	52	57	58	56	59	55	58
Na^{+} (mg/L)	1 0	-	19	19	20	21	19	-	17	18	18	20	20	20	22	18	20
Mg^{2+} (mg/L)	1 0	-	25	25	24	25	25	-	22	23	23	25	25	26	27	25	26
K^{+} (mg/L)	1 0	-	4 6	4 9	4 6	4 7	4 6	-	4 2	4 4	4 3	4 5	4 5	4 7	5 3	4 4	4 8
Total P (mg/L)	0 001	0 002	<0 65	<0 65	0 44	<0 65	<0 65	0 35	<0 65	0 30	0 29	0 42	<0 65	0 47	0 50	0 32	0 42
NH_4^{+} (mg-N/L)	0 001	0 003	0 34	-	0 31	0 35	0 41	-	0 074	0 10	0 12	0 30	0 21	0 33	0 40	0 35	0 38
Cl (mg/L)	1 0	-	6 6	7 8	7 8	8 0	8 8	-	7 6	7 2	7 8	7 3	7 6	7 0	7 3	6 9	7 2
SO_4^{2} (mg/L)	1 0	-	24	23	26	27	25	-	24	24	25	23	24	24	24	24	-
NO_3 (mg-N/L)	0 001	0 002	<0 001	<0 001	<0 001	<0 001	<0 001	-	0 47	0 27	<0 001	0 004	<0 001	<0 001	<0 001	<0 001	0 15
HCO_3 (mg/L)	3 9	-	268	219	308	313	295	-	130	301	248	292	317	304	348	305	273
Calculations																	
pCO_2 (atm)	-	-	-1 93	-2 62	-2 45	-2 13	-1 95	-	-2 55	-2 31	-1 69	-2 02	-1 99	-2 28	-2 14	-2 34	-1 85
$SI_{calcite}$	-	-	0 716	2 450	2 980	1 340	0 763	-	0 535	1 907	0 348	1 102	1 230	2 398	2 347	2 560	0 637
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		11 1	9 1	8 1	-	8 2	-	-	-	-	-	-	14 9	8 9	5 8	6 2
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	2 1	2 3	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-1 3	0 0	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	60	45	63	67	66	-	28	62	61	63	69	63	73	63	63
DOC (ppmC)	1 0	0 1	-	2 8	5 0	2 3	2 3	-	4 1	2 1	2 2	3 6	5 3	2 0	2 3	3 4	2 2
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-14 0	-14 5	-15 0	-14 4	-14 3	-	-14 5	-14 2	-14 7	-14 1	-14 0	-14 4	-14 4	-14 5	-14 4
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-25 9	-24 6	-22 8	-26 1	-	-25 7	-26 7	26 7	-27 0	-26 8	-26 7	-26 6	-26 7	-26 6
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-10 8	-10 6	-10 8	-10 7	-10 7	-	-10 8	-10 7	-	-10 6	-	-10 7	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-78 7	-77 2	-76 4	-80 2	-77 8	-	-77 4	-72 4	-	-72 1	-	-80 4	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	P3-2B																					
Type	Piezometer																					
Depth	4 8 mbgs																					
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 45	0 34	1 19	1 94	4	1 30	0 35	0 96	1 73	5	0 88	0 21	0 76	1 13	3	1 01	0 16	0 87	1 18	3	1 20	0 34	0 76	1 94	15
Temp (°C)	13 1	1 5	11 5	14 5	4	10 7	2 0	7 6	12 9	5	6 7	0 6	6 1	7 2	3	11 3	1 2	9 9	12 0	3	10 6	2 6	6 1	14 5	15
pH	7 5	0 2	7 3	7 7	4	7 7	0 3	7 2	7 9	5	7 4	0 2	7 2	7 6	3	7 4	0 3	7 0	7 7	3	7 5	0 3	7 0	7 9	15
SpC (µS/cm)	753	374	511	1307	4	836	273	626	1300	5	1213	384	856	1620	3	599	34	568	635	3	842	342	511	1620	15
DO (mg/L)	0 9	0 3	0 5	1 2	3	-	-	-	-	-		-	-	-	-		-	-	-	-	0 9	0 35	0 5	1 2	3
Eh (mV)	258	31	236	280	2	167	119	82	251	2	-	-		-	-	-	-	-	-	-	212	88	82	280	4
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	57	1 7	55	59	4	57	1 8	55	58	5	53	4 7	49	56	2	53	3 0	52	57	3	56	2 9	49	59	14
Na^{+} (mg/L)	20	1 3	19	22	4	19	0 88	18	21	5	18	1 3	17	19	2	18	1 4	18	20	3	19	1 3	17	22	14
Mg^{2+} (mg/L)	26	1 1	25	27	4	25	0 74	24	26	5	23	2 1	22	25	2	24	1 3	23	25	3	25	1 4	22	27	14
K^{+} (mg/L)	4 8	0 37	4 5	5 3	4	4 7	0 21	4 4	4 9	5	4 4	0 31	4 2	4 6	2	4 4	0 12	4 3	4 5	3	4 6	0 28	4 2	5 3	14
Total P (mg/L)	0 48	0 023	0 47	0 50	2	0 39	0 065	0 32	0 44	3	0 35	-	0 35	0 35	1	0 34	0 072	0 29	0 42	3	0 39	0 076	0 29	0 50	9
NH_4^{+} (mg-N/L)	0 32	0 081	0 21	0 40	4	0 35	0 028	0 31	0 38	4	0 24	0 24	0 074	0 41	2	0 17	0 111	0 095	0 30	3	0 28	0 12	0 074	0 41	13
Cl (mg/L)	7 1	0 42	6 6	7 6	4	7 6	0 46	6 9	8 0	5	8 2	0 84	7 6	8 8	2	7 4	0 35	7 2	7 8	3	7 5	0 54	6 6	8 8	14
SO_4^{2} (mg/L)	24	0 32	24	24	4	25	1 53	23	27	4	25	0 24	24	25	2	24	0 98	23	25	3	24	1 0	23	27	13
NO_3 (mg-N/L)	-	-	-	-	-	0 15	-	0 15	0 15	1	0 47	-	0 47	0 47	1	0 13	0 19	0 004	0 27	2	0 22	0 20	0 004	0 47	4
HCO_3 (mg/L)	309	33	268	348	4	284	39	219	313	5	212	117	130	295	2	280	28	248	301	3	280	54	130	348	14
Calculations																									
pCO_2 (atm)	-2 08	0 16	-2 28	-1 93	4	-2 28	0 30	-2 62	-1 85	5	-2 25	0 42	-2 55	-1 95	2	-2 01	0 31	-2 31	-1 69	3	-2 16	0 27	-2 62	-1 69	14
$SI_{calcite}$	1 673	0 835	0 716	2 398	4	1 993	0 971	0 637	2 980	5	0 649	0 162	0 535	0 763	2	1 119	0 780	0 348	1 907	3	1 522	0 891	0 348	2 980	14
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	11 6	3 0	8 9	14 9	3	7 3	1 5	5 8	9 1	4	8 2	-	8 2	8 2	1	-	-	-	-	-	9 0	2 9	5 8	14 9	8
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	2 1	-	2 1	2 1	1	2 3	-	2 3	2 3	1	2 2	0 1	2 1	2 3	2
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-1 3	-	-1 3	-1 3	1	0 0	-	0 0	0 0	1	-0 7	0 9	-1 3	0 0	2
Carbon																									
DIC (ppmC)	66	6	60	73	4	60	9	45	67	5	47	27	28	66	2	62	1	61	63	3	60	11	28	73	14
DOC (ppmC)	3 2	1 8	2 0	5 3	3	3 1	1 1	2 2	5 0	5	3 2	1 3	2 3	4 1	2	2 6	0 9	2 1	3 6	3	3 1	1 2	2 0	5 3	13
$\delta^{13}C_{DIC}$ (‰)	-14 2	0 2	-14 4	-14 0	4	-14 5	0 2	-15 0	-14 4	5	-14 4	0 2	-14 5	-14 3	2	-14 3	0 3	-14 7	-14 1	3	-14 4	0 3	-15 0	-14 0	14
$\delta^{13}C_{DOC}$ (‰)	-26 7	0 1	-26 8	-26 6	3	-25 3	1 6	-26 7	-22 8	5	-25 9	0 3	-26 1	-25 7	2	-26 8	0 2	-27 0	-26 7	3	-26 1	1 2	-27 0	-22 8	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 8	0 1	-10 8	-10 7	2	-10 7	0 1	-10 8	-10 6	3	-10 7	0 1	-10 8	-10 7	2	-10 6	0 0	-10 7	-10 6	2	-10 7	0 1	-10 8	-10 6	9
$\delta^{2}H_{H2O}$ (‰)	-79 6	1 2	-80 4	-78 7	2	-77 9	2 0	-80 2	-76 4	3	-77 6	0 3	-77 8	-77 4	2	-72 3	0 2	-72 4	-72 1	2	-77 0	3 0	-80 4	-72 1	9

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			W3-C														
Type			Overburden Well														
Depth			2 3 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	0 555	0 665	0 610	0 635	0 700	0 548	0 454	0 888	1 110	1 029	1 089	0 695
Temp (°C)	-	0 1	-	-	-	9 3	6 1	4 0	3 6	4 1	4 0	11 5	12 0	14 6	16 6	14 3	10 0
pH	-	0 01	-	-	-	7 4	7 4	7 0	7 0	7 1	7 4	7 2	7 0	6 9	6 8	7 0	7 1
SpC (µS/cm)	-	1	-	-	-	1086	1442	1504	1362	1348	1211	815	760	896	913	934	1221
DO (mg/L)	0 01	0 01	-	-	-		1 3	1 1	0 7	0 2	0 9	-	0 4	0 4	0 5	0 5	-
Eh (mV)	-	1	-	-	-	-	-	502	348	226	-	-	337	395	468	224	297
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	-	-	119	121	128	109	116	115	118	128	94	54	132	134
Na^{+} (mg/L)	1 0	-	-	-	-	12	12	12	10	11	11	11	13	10	7	14	14
Mg^{2+} (mg/L)	1 0	-	-	-	-	21	23	24	21	23	23	23	24	16	9	25	25
K^{+} (mg/L)	1 0	-	-	-	-	2 2	1 0	1 4	0 7	0 7	0 6	0 8	0 9	2 8	3 7	1 1	1 7
Total P (mg/L)	0 001	0 002	-	-	-	<0 65	0 029	0 034	0 018	0 028	0 023	0 035	0 019	0 017	0 025	0 021	0 027
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	-	0 004	0 004	0 007	-	0 006	0 002	0 005	0 01	0 023	-	-	
Cl (mg/L)	1 0	-	-	-	-	63	40	33	75	79	79	73	83	76	21	89	85
SO_4^{2} (mg/L)	1 0	-	-	-	-	33	28	25	39	37	39	37	40	36	14	40	-
NO_3 (mg-N/L)	0 001	0 002	-	-	-	0 39	<0 001	<0 001	<0 001	<0 001	<0 001	0 45	<0 001	0 56	1 35	<0 001	0 29
HCO_3 (mg/L)	3 9	-	-	-	-	334	375	299	263	350	384	337	366	213	153	541	306
Calculations																	
pCO_2 (atm)	-	-	-	-	-	-1 90	-1 86	-1 57	-1 70	-1 61	-1 85	-1 73	-1 51	-1 59	-1 63	-1 27	-1 65
$SI_{calcite}$	-	-	-	-	-	1 842	1 831	0 588	0 515	0 797	1 634	1 374	1 071	0 392	0 158	1 485	0 994
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	7 3	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-		-	-	-	-	-	5 5	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	-	-	74	84	80	68	88	87	78	91	56	42	137	75
DOC (ppmC)	1 0	0 1	-	-	-	0 89	1 4	2 1	3 1	2 3	2 0	2 8	4 1	3 0	1 2	4 2	2 0
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-	-16 3	-16 4	-17 0	-7 0	-17 9	-17 6	-17 8	-17 4	-15 5	-13 7	-17 5	-16 7
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-	-22 8	-27 1	-27 3	-27 4	-27 2	-26 6	-27 2	-27 3	-27 2	-27 5	-27 5	-27 5
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-	-10 9	-10 8	-11 1	-11 1	-10 7	-	-10 9	-	-10 7	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-	-77 1	-75 8	-78 3	-78 5	-74 5	-	-74 4	-	-84 9	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	W3-C																						
Type	Overburden Well																						
Depth	2 3 mbgs																						
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	1 01	0 11	0 89	1 11	3	0 78	0 28	0 55	1 09	3	0 64	0 03	0 61	0 66	3	0 57	0 12	0 45	0 70	3	0 75	0 22	0 45	1 11	12
Temp (°C)	14 4	2 3	12 0	16 6	3	11 2	2 7	9 3	14 3	3	4 6	1 3	3 6	6 1	3	6 5	4 3	4 0	11 5	3	9 2	4 7	3 6	16 6	12
pH	6 9	0 1	6 8	7 0	3	7 1	0 2	7 0	7 4	3	7 1	0 2	7 0	7 4	3	7 2	0 1	7 1	7 4	3	7 1	0 2	6 8	7 4	12
SpC (µS/cm)	856	84	760	913	3	1080	144	934	1221	3	1436	71	1362	1504	3	1125	277	815	1348	3	1124	258	760	1504	12
DO (mg/L)	0 4	0 1	0 4	0 5	3	0 5	-	0 5	0 5	1	1 0	0 3	0 7	1 3	3	0 6	0 5	0 2	0 9	2	0 7	0 38	0 2	1 3	9
Eh (mV)	400	65	337	468	3	261	51	224	297	2	425	109	348	502	2	226	-	226	226	1	350	102	224	502	8
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	92	37	54	128	3	128	8 4	119	134	3	119	10	109	128	3	116	1 5	115	118	3	114	22	54	134	12
Na^{+} (mg/L)	9 7	3 1	6 6	13	3	13	1 2	12	14	3	11	1 2	10	12	3	11	0 52	11	11	3	11	2 0	6 6	14	12
Mg^{2+} (mg/L)	16	7 5	8 7	24	3	24	2 3	21	25	3	23	1 9	21	24	3	23	0 29	23	23	3	21	4 7	8 7	25	12
K^{+} (mg/L)	2 5	1 4	0 93	3 7	3	1 7	0 55	1 1	2 2	3	1 0	0 35	0 68	1 4	3	0 7	0 12	0 62	0 8	3	1 5	0 98	0 62	3 7	12
Total P (mg/L)	0 020	0 005	0 017	0 025	3	0 024	0 004	0 021	0 027	2	0 027	0 008	0 018	0 034	3	0 029	0 006	0 023	0 035	3	0 025	0 006	0 017	0 035	11
NH_4^{+} (mg-N/L)	0 017	0 009	0 010	0 023	2	0 004	-	0 004	0 004	1	0 005	0 002	0 004	0 007	2	0 004	0 002	0 002	0 006	3	0 008	0 007	0 002	0 023	8
Cl (mg/L)	60	34	21	83	3	79	14	63	89	3	50	23	33	75	3	77	3 6	73	79	3	66	22	21	89	12
SO_4^{2} (mg/L)	30	14	14	40	3	37	4 8	33	40	2	31	7 0	25	39	3	38	1 1	37	39	3	33	8 2	14	40	11
NO_3 (mg-N/L)	0 96	0 56	0 56	1 35	2	0 34	0 07	0 29	0 39	2	-		-	-	-	0 45	-	0 45	0 45	1	0 61	0 43	0 29	1 35	5
HCO_3 (mg/L)	244	110	153	366	3	393	128	306	541	3	312	57	263	375	3	357	24	337	384	3	327	96	153	541	12
Calculations																									
pCO_2 (atm)	-1 58	0 06	-1 63	-1 51	3	-1 60	0 32	-1 90	-1 27	3	-1 71	0 14	-1 86	-1 57	3	-1 73	0 12	-1 85	-1 61	3	-1 66	0 17	-1 90	-1 27	12
$SI_{calcite}$	0 540	0 474	0 158	1 071	3	1 440	0 426	0 994	1 842	3	0 978	0 739	0 515	1 831	3	1 268	0 428	0 797	1 634	3	1 057	0 577	0 158	1 842	12
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-		-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7 3	-	7 3	7 3	1	7 3	-	7 3	7 3	1
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5 5	-	5 5	5 5	1	5 5	-	5 5	5 5	1
Carbon																									
DIC (ppmC)	63	25	42	91	3	95	36	74	137	3	78	8	68	84	3	84	6	78	88	3	80	23	42	137	12
DOC (ppmC)	2 8	1 5	1 2	4 1	3	2 4	1 7	0 9	4 2	3	2 2	0 9	1 4	3 1	3	2 4	0 4	2 0	2 8	3	2 4	1 1	0 9	4 2	12
$\delta^{13}C_{DIC}$ (‰)	-15 5	1 9	-17 4	-13 7	3	-16 8	0 6	-17 5	-16 3	3	-13 5	5 6	-17 0	-7 0	3	-17 7	0 1	-17 9	-17 6	3	-15 9	3 1	-17 9	-7 0	12
$\delta^{13}C_{DOC}$ (‰)	-27 3	0 2	-27 5	-27 2	3	-25 9	2 7	-27 5	-22 8	3	-27 3	0 1	-27 4	-27 1	3	-27 0	0 3	-27 2	-26 6	3	-26 9	1 3	-27 5	-22 8	12
Water																									
$\delta^{18}O_{H2O}$ (‰)	-10 7	-	-10 7	-10 7	1	-10 9	-	-10 9	-10 9	1	-11 0	0 2	-11 1	-10 8	3	-10 8	0 1	-10 9	-10 7	2	-10 9	0 1	-11 1	-10 7	7
$\delta^{2}H_{H2O}$ (‰)	-84 9	-	-84 9	-84 9	1	-77 1	-	-77 1	-77 1	1	-77 5	1 5	-78 5	-75 8	3	-74 4	0 1	-74 5	-74 4	2	-77 6	3 6	-84 9	-74 4	7

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID			W3 B														
Type			Bedrock Well														
Depth			16 5 mbgs														
Season			Summer	Fall			Winter			Spring			Summer			Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	4 393	-	3 519	3 479	3 746	3 702	3 704	3 769	3 619	3 471	3 867	4 177	4 128	4 582	3 733
Temp (°C)	-	0 1	10 5	-	10 5	10 2	9 9	8 9	9 5	10 3	11 7	13 3	10 7	11 0	11 7	10 7	10 2
pH	-	0 01	7 5	-	7 7	7 5	7 3	-	7 7	7 5	7 5	7 2	7 6	7 5	7 3	7 7	7 5
SpC (µS/cm)	-	1	-	-	773	851	1088	-	819	823	719	631	531	617	736	687	881
DO (mg/L)	0 01	0 01	-	-	-	-	0 5	0 6	0 2	0 1	0 4	-	0 7	0 1	0 2	0 3	-
Eh (mV)	-	1	-	-	-	-	-	-	49	54	92	-	270	171	336	178	147
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	68	-	72	77	73	-	66	68	69	73	74	73	74	61	77
Na^{+} (mg/L)	1 0	-	13	-	15	15	15	-	13	14	14	14	13	13	13	14	17
Mg^{2+} (mg/L)	1 0	-	27	-	26	26	26	-	23	24	24	26	25	26	26	23	27
K^{+} (mg/L)	1 0	-	2 8	-	2 9	3 0	2 8	-	2 6	2 7	2 8	2 9	3 0	3 0	3 0	2 6	3 1
Total P (mg/L)	0 001	0 002	<0 65	-	0 008	<0 65	0 024	0 023	<0 65	0 017	0 022	0 027	0 033	0 018	0 027	0 014	0 020
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	0 092	0 10	1 3	-	0 093	0 10	0 090	0 088	0 086	0 091	-	-	-
Cl (mg/L)	1 0	-	12	-	24	23	22	-	23	24	23	21	18	16	16	8	18
SO_4^{2} (mg/L)	1 0	-	55	-	54	53	48	-	53	51	54	52	53	53	54	46	
NO_3 (mg-N/L)	0 001	0 002	0 000	-	<0 001	<0 001	<0 001	-	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001	<0 001
HCO_3 (mg/L)	3 9	-	269	-	325	305	293	-	121	289	297	265	305	284	350	418	265
Calculations																	
pCO_2 (atm)	-	-	-2 14	-	-2 19	-2 07	-1 92	-	-2 65	-2 10	-2 10	-1 82	-2 20	-2 07	-1 83	-2 08	-2 10
$SI_{calcite}$	-	-	1 327	-	2 269	1 582	1 004	-	0 845	1 387	1 578	0 759	2 160	1 388	1 242	2 525	1 333
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-		-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	58	-	68	66	66	-	25	62	63	61	64	61	78	88	57
DOC (ppmC)	1 0	0 1	0 8	-	3 6	0 6	2 0	-	2 3	2 1	1 5	1 9	2 8	2 0	1 1	3 8	1 8
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-12 5	-	-14 0	-13 7	-13 6	-	-14 2	-13 8	13 4	-13 5	-13 1	-13 5	-13 5	-13 4	-13 4
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-24 7	-	-22 0	-22 8	-25 0	-	-27 1	-26 6	-27 3	-27 5	-26 1	-27 5	-27 2	-27 7	-28 7
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-11 1	-	-10 9	-11 0	-10 8	-	-11 1	-10 9	-	-10 9	-	-11 0	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-82 0	-	-76 2	-77 3	-78 0	-	-78 4	-77 2	-	-76 6	-	-75 6	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	W3-B																						
Type	Bedrock Well																						
Depth	16 5 mbgs																						
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	4 14	0 22	3 87	4 39	4	3 83	0 51	3 48	4 58	4	3 72	0 02	3 70	3 75	3	3 62	0 15	3 47	3 77	3	3 85	0 34	3 47	4 58	14
Temp (°C)	11 0	0 5	10 5	11 7	4	10 4	0 2	10 2	10 7	4	9 4	0 5	8 9	9 9	3	11 8	1 5	10 3	13 3	3	10 7	1 1	8 9	13 3	14
pH	7 5	0 1	7 3	7 6	4	7 6	0 1	7 5	7 7	4	7 5	0 2	7 3	7 7	2	7 4	0 2	7 2	7 5	3	7 5	0 1	7 2	7 7	13
SpC (µS/cm)	628	103	531	736	3	798	87	687	881	4	954	190	819	1088	2	724	96	631	823	3	763	146	531	1088	12
DO (mg/L)	0 3	0 3	0 1	0 7	3	0 3	-	0 3	0 3	1	0 4	0 2	0 2	0 6	3	0 2	0 2	0 1	0 4	2	0 3	0 21	0 1	0 7	9
Eh (mV)	259	83	171	336	3	162	22	147	178	2	49		49	49	1	73	27	54	92	2	162	101	49	336	8
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	72	2 9	68	74	4	72	7 3	61	77	4	70	5 2	66	73	2	70	2 7	68	73	3	71	4 5	61	77	13
Na^{+} (mg/L)	13	0 22	13	13	4	15	1 1	14	17	4	14	1 4	13	15	2	14	0 20	14	14	3	14	1 2	13	17	13
Mg^{2+} (mg/L)	26	0 84	25	27	4	26	1 8	23	27	4	24	2 1	23	26	2	25	1 1	24	26	3	25	1 4	23	27	13
K^{+} (mg/L)	2 9	0 10	2 8	3 0	4	2 9	0 21	2 6	3 1	4	2 7	0 14	2 6	2 8	2	2 8	0 09	2 7	2 9	3	2 9	0 15	2 6	3 1	13
Total P (mg/L)	0 026	0 007	0 018	0 033	3	0 014	0 006	0 008	0 020	3	0 023	0 001	0 023	0 024	2	0 022	0 005	0 017	0 027	3	0 021	0 007	0 008	0 033	11
NH_4^{+} (mg-N/L)	0 088	0 004	0 086	0 091	2	0 096	0 006	0 092	0 100	2	0 69	0 84	0 093	1 3	2	0 092	0 005	0 088	0 098	3	0 22	0 40	0 086	1 3	9
Cl (mg/L)	15	2 4	12	18	4	18	7 4	7 7	24	4	23	0 2	22	23	2	23	1 9	21	24	3	19	5 1	7 7	24	13
SO_4^{2} (mg/L)	54	1 1	53	55	4	51	4 4	46	54	3	51	3 0	48	53	2	52	1 2	51	54	3	52	2 6	46	55	12
NO_3 (mg-N/L)	0 000	-	0 000	0 000	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0 000	-	0 000	0 000	1
HCO_3 (mg/L)	302	35	269	350	4	328	65	265	418	4	207	122	121	293	2	284	17	265	297	3	291	66	121	418	13
Calculations																									
pCO_2 (atm)	-2 06	0 16	-2 20	-1 83	4	-2 11	0 06	-2 19	-2 07	4	-2 29	0 51	-2 65	-1 92	2	-2 01	0 16	-2 10	-1 82	3	-2 10	0 21	-2 65	-1 82	13
$SI_{calcite}$	1 529	0 425	1 242	2 160	4	1 927	0 562	1 333	2 525	4	0 925	0 112	0 845	1 004	2	1 241	0 428	0 759	1 578	3	1 492	0 537	0 759	2 525	13
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	65	9	58	78	4	70	13	57	88	4	45	28	25	66	2	62	1	61	63	3	63	14	25	88	13
DOC (ppmC)	1 7	0 9	0 8	2 8	4	2 5	1 5	0 6	3 8	4	2 2	0 2	2 0	2 3	2	1 8	0 3	1 5	2 1	3	2 0	1 0	0 6	3 8	13
$\delta^{13}C_{DIC}$ (‰)	-13 1	0 5	-13 5	-12 5	4	-13 6	0 3	-14 0	-13 4	4	-13 9	0 4	-14 2	-13 6	2	-13 6	0 2	-13 8	-13 4	3	-13 5	0 4	-14 2	-12 5	13
$\delta^{13}C_{DOC}$ (‰)	-26 4	1 3	-27 5	-24 7	4	-25 3	3 4	-28 7	-22 0	4	-26 0	1 5	-27 1	-25 0	2	-27 1	0 5	-27 5	-26 6	3	-26 2	2 0	-28 7	-22 0	13
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 1	0 1	-11 1	-11 0	2	-11 0	0 1	-11 0	-10 9	2	-11 0	0 2	-11 1	-10 8	2	-10 9	0 0	-10 9	-10 9	2	-11 0	0 1	-11 1	-10 8	8
$\delta^{2}H_{H2O}$ (‰)	-78 8	4 5	-82 0	-75 6	2	-76 8	0 8	-77 3	-76 2	2	-78 2	0 3	-78 4	-78 0	2	-76 9	0 5	-77 2	-76 6	2	-77 7	2 0	-82 0	-75 6	8

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID									W3-D							
Type									Bedrock Well							
Depth									14 5 mbgs							
Season			Summer	Fall			Winter			Spring			Summer		Fall	
Variable / Units	DL	QL	Aug-05	Sep-05	Oct-05	Nov-05	Dec-05	Jan-06	Feb-06	Mar-06	Apr-06	May-06	Jun-06	Jul-06	Aug-06	Sep-06	Oct-06
Field																	
W L (mbgs)	-	0 001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temp (°C)	-	0 1	-	-	-	9 3	11 3	9 8	9 8	10 6	11 0	-	12 4	14 1	10 7	10 9	
pH	-	0 01	-	-	-	7 3	7 4	7 4	7 5	7 4	7 6	-	7 6	7 5	7 3	7 5	-
SpC (µS/cm)	-	1	-	-	-	1481	1548	1412	1320	1222	1159	-	-	1025	1299	1090	-
DO (mg/L)	0 01	0 01	-	-	-	-	-	-	-	-	-	-	-	-	-	1 5	-
Eh (mV)	-	1	-	-	-	-	-	-	-	-	320	-	-	193	375	276	-
Major Ions and Nutrients																	
Ca^{2+} (mg/L)	1 0	-	-	-	-	106	100	103	90	95	94	-	100	100	102	91	-
Na^{+} (mg/L)	1 0	-	-	-	-	51	48	48	44	45	49	-	47	47	50	36	-
Mg^{2+} (mg/L)	1 0	-	-	-	-	40	39	39	34	36	37	-	37	39	40	36	-
K^{+} (mg/L)	1 0	-	-	-	-	3 1	2 9	3 3	2 7	2 9	3 0	-	3 1	3 3	3 3	3 0	-
Total P (mg/L)	0 001	0 002	-		-	<0 65	0 036	0 036	0 062	0 024	0 023	-	0 031	0 03	0 039	0 023	-
NH_4^{+} (mg-N/L)	0 001	0 003	-	-	-	0 022	0 036	0 028	0 017	0 029	0 024	-	0 028	0 024			-
Cl (mg/L)	1 0	-	-	-	-	150	64	108	144	142	143	-	136	127	129	103	-
SO_4^{2} (mg/L)	1 0	-	-	-	-	57	29	44	52	55	57	-	54	55	54	54	-
NO_3 (mg-N/L)	0 001	0 002	-	-	-	<0 001	<0 001	<0 001	<0 001	0 20	<0 001	-	<0 001	<0 001	<0 001	<0 001	-
HCO_3 (mg/L)	3 9	-	-	-	-	322	321	291	156	328	341	-	359	324	437	492	-
Calculations																	
pCO_2 (atm)	-	-	-	-	-	-1 86	-1 95	-1 97	2 38	-1 89	-2 12	-	-2 03	-1 97	-1 72	-1 86	-
$SI_{calcite}$	-	-	-	-	-	1 297	1 727	1 400	0 932	1 415	2 595	-	2 684	2 045	1 771	2 818	-
Nitrogen Isotopes																	
$\delta^{15}N_{NH4}$ (‰)	0 7 mg-N/L		-	-	-	-	-		-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	0 124 mg-N/L		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbon																	
DIC (ppmC)	1 0	0 1	-	-	-	73	70	64	33	73	72	-	76	70	98	106	-
DOC (ppmC)	1 0	0 1	-	-	-	0 1	0 6	1 6	2 2	1 8	1 8	-	3 3	2 5	0 6	4 0	-
$\delta^{13}C_{DIC}$ (‰)	-	0 2	-	-	-	-13 9	-13 5	-13 5	-14 1	-13 7	-13 8	-	-13 3	-13 7	-13 8	-13 9	-
$\delta^{13}C_{DOC}$ (‰)	-	0 2	-	-	-	-19 5	-26 4	-27 0	-27 4	-27 4	-25 8	-	-25 8	-27 5	-27 6	-27 5	-
Water																	
$\delta^{18}O_{H2O}$ (‰)	-	0 15	-	-	-	-11 1	-10 9	-11 0	-11 1	-11 0	-	-	-	-11 0	-	-	-
$\delta^{2}H_{H2O}$ (‰)	-	2 0	-	-	-	-79 4	-76 7	78 1	-80 6	75 7	-	-	-	-71 2	-	-	-

Table D4: Site 3 - Field Parameters, Analytical Results and Statistics.

Site ID	W3-D																								
Type	Bedrock Well																								
Depth	14 5 mbgs																								
Season	Summer					Fall					Winter					Spring					Total				
Variable / Units	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n	Mean	σ	Min	Max	n
Field																									
W L (mbgs)	-	-	-	-	0	-	-	-	-	0	-	-	-	-	0	-	-	-	-	0	-	-	-	-	0
Temp (°C)	12 4	1 7	10 7	14 1	3	10 1	1 1	9 3	10 9	2	10 3	0 9	9 8	11 3	3	10 8	0 3	10 6	11 0	2	11 0	1 4	9 3	14 1	10
pH	7 4	0 1	7 3	7 6	3	7 4	0 1	7 3	7 5	2	7 4	0 1	7 4	7 5	3	7 5	0 2	7 4	7 6	2	7 4	0 1	7 3	7 6	10
SpC (µS/cm)	1162	193	1025	1299	2	1285	276	1090	1481	2	1427	115	1320	1548	3	1191	45	1159	1222	2	1284	177	1025	1548	9
DO (mg/L)	-	-	-	-	-	1 5	-	1 5	1 5	1	-		-	-	-	-	-	-	-	-	1 5	-	1 5	1 5	1
Eh (mV)	284	129	193	375	2	276	-	276	276	1	-		-	-	-	320	######	320	320	1	291	77	193	375	4
Major Ions and Nutrients																									
Ca^{2+} (mg/L)	101	1 3	100	102	3	98	11	91	106	2	98	7 0	90	103	3	94	0 59	94	95	2	98	5 5	90	106	10
Na^{+} (mg/L)	48	1 6	47	50	3	44	11	36	51	2	47	2 4	44	48	3	47	3 0	45	49	2	47	4 4	36	51	10
Mg^{2+} (mg/L)	39	1 7	37	40	3	38	2 5	36	40	2	37	2 5	34	39	3	36	1 0	36	37	2	38	1 9	34	40	10
K^{+} (mg/L)	3 2	0 11	3 1	3 3	3	3 0	0 05	3 0	3 1	2	3 0	0 31	2 7	3 3	3	2 9	0 09	2 9	3 0	2	3 0	0 20	2 7	3 3	10
Total P (mg/L)	0 034	0 004	0 031	0 039	3	0 023	-	0 023	0 023	1	0 045	0 015	0 036	0 062	3	0 023	0 001	0 023	0 024	2	0 034	0 012	0 023	0 062	9
NH_4^{+} (mg-N/L)	0 026	0 003	0 024	0 028	2	0 022	-	0 022	0 022	1	0 027	0 009	0 017	0 036	3	0 027	0 003	0 024	0 029	2	0 026	0 006	0 017	0 036	8
Cl (mg/L)	131	4 5	127	136	3	126	33	103	150	2	105	40	64	144	3	143	0 53	142	143	2	125	26 3	64	150	10
SO_4^{2} (mg/L)	54	0 51	54	55	3	56	2 0	54	57	2	42	12	29	52	3	56	1 8	55	57	2	51	8 6	29	57	10
NO_3 (mg-N/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0 20	-	0 20	0 20	1	0 20	-	0 20	0 20	1
HCO_3 (mg/L)	373	58	324	437	3	407	120	322	492	2	256	88	156	321	3	335	9	328	341	2	337	88	156	492	10
Calculations																									
pCO_2 (atm)	-1 91	0 17	-2 03	-1 72	3	-1 86	0 00	-1 86	-1 86	2	-2 10	0 24	-2 38	-1 95	3	-2 01	0 16	-2 12	-1 89	2	-1 97	0 18	-2 38	-1 72	10
$SI_{calcite}$	2 166	0 468	1 771	2 684	3	2 058	1 075	1 297	2 818	2	1 353	0 400	0 932	1 727	3	2 005	0 834	1 415	2 595	2	1 868	0 648	0 932	2 818	10
Nitrogen Isotopes																									
$\delta^{15}N_{NH4}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{15}N_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}O_{NO3}$ (‰)	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Carbon																									
DIC (ppmC)	81	15	70	98	3	89	23	73	106	2	56	20	33	70	3	72	1	72	73	2	74	19	33	106	10
DOC (ppmC)	2 1	1 4	0 6	3 3	3	2 0	2 7	0 1	4 0	2	1 5	0 8	0 6	2 2	3	1 8	0 0	1 8	1 8	2	1 8	1 2	0 1	4 0	10
$\delta^{13}C_{DIC}$ (‰)	-13 6	0 3	-13 8	-13 3	3	-13 9	0 0	-13 9	-13 9	2	-13 7	0 3	-14 1	-13 5	3	-13 7	0 1	-13 8	-13 7	2	-13 7	0 2	-14 1	-13 3	10
$\delta^{13}C_{DOC}$ (‰)	-27 0	1 0	-27 6	-25 8	3	-23 5	5 7	-27 5	-19 5	2	-26 9	0 5	-27 4	-26 4	3	-26 6	1 2	-27 4	-25 8	2	-26 2	2 5	-27 6	-19 5	10
Water																									
$\delta^{18}O_{H2O}$ (‰)	-11 0	-	-11 0	-11 0	1	-11 1	-	-11 1	-11 1	1	-11 0	0 1	-11 1	-10 9	3	-11 0	-	-11 0	-11 0	1	-11 0	0 1	-11 1	-10 9	6
$\delta^{2}H_{H2O}$ (‰)	-71 2	-	-71 2	-71 2	1	-79 4	-	-79 4	-79 4	1	-78 5	2 0	-80 6	-76 7	3	-75 7	-	-75 7	-75 7	1	-77 0	3 3	-80 6	-71 2	6

Appendix E
River Disharge Data - Environment Canada

Table E1: Daily and Average Monthly Discharge Data for Raisin River at Williamstown, Ontario, for the period (August 2005 - October 2006) *[Environment Canada(c)]*

Date	Discharge	Date	Discharge	Date	Discharge	Date	Discharge	Date	Discharge
dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)
8/1/2005	0.137	9/1/2005	0.330	10/1/2005	1.103	11/1/2005	6.620	12/1/2005	25.494
8/2/2005	0.119	9/2/2005	0.249	10/2/2005	1.036	11/2/2005	6.183	12/2/2005	18.725
8/3/2005	0.119	9/3/2005	0.483	10/3/2005	0.801	11/3/2005	5.643	12/3/2005	13.157
8/4/2005	0.109	9/4/2005	0.359	10/4/2005	0.621	11/4/2005	5.006	12/4/2005	8.954
8/5/2005	0.104	9/5/2005	0.237	10/5/2005	0.517	11/5/2005	4.434	12/5/2005	6.870
8/6/2005	0.110	9/6/2005	0.183	10/6/2005	0.469	11/6/2005	4.394	12/6/2005	5.415
8/7/2005	0.109	9/7/2005	0.146	10/7/2005	0.782	11/7/2005	6.248	12/7/2005	4.322
8/8/2005	0.089	9/8/2005	0.145	10/8/2005	15.632	11/8/2005	7.142	12/8/2005	3.430
8/9/2005	0.074	9/9/2005	0.256	10/9/2005	19.333	11/9/2005	6.002	12/9/2005	3.065
8/10/2005	0.066	9/10/2005	0.259	10/10/2005	13.031	11/10/2005	13.974	12/10/2005	2.787
8/11/2005	0.065	9/11/2005	0.298	10/11/2005	8.022	11/11/2005	16.023	12/11/2005	2.667
8/12/2005	0.068	9/12/2005	0.323	10/12/2005	5.796	11/12/2005	11.048	12/12/2005	2.522
8/13/2005	0.081	9/13/2005	0.237	10/13/2005	10.815	11/13/2005	8.047	12/13/2005	1.900
8/14/2005	0.082	9/14/2005	0.165	10/14/2005	49.285	11/14/2005	6.668	12/14/2005	1.730
8/15/2005	0.077	9/15/2005	0.116	10/15/2005	50.693	11/15/2005	5.800	12/15/2005	1.700
8/16/2005	0.073	9/16/2005	0.091	10/16/2005	41.271	11/16/2005	17.231	12/16/2005	1.750
8/17/2005	0.065	9/17/2005	0.159	10/17/2005	26.896	11/17/2005	26.396	12/17/2005	1.770
8/18/2005	0.056	9/18/2005	0.279	10/18/2005	15.820	11/18/2005	20.834	12/18/2005	1.770
8/19/2005	0.057	9/19/2005	0.321	10/19/2005	11.378	11/19/2005	13.499	12/19/2005	1.760
8/20/2005	0.076	9/20/2005	0.302	10/20/2005	10.118	11/20/2005	9.707	12/20/2005	1.720
8/21/2005	0.079	9/21/2005	0.295	10/21/2005	8.659	11/21/2005	8.222	12/21/2005	1.710
8/22/2005	0.071	9/22/2005	0.239	10/22/2005	7.020	11/22/2005	7.334	12/22/2005	1.700
8/23/2005	0.060	9/23/2005	0.230	10/23/2005	6.496	11/23/2005	6.295	12/23/2005	1.720
8/24/2005	0.051	9/24/2005	0.195	10/24/2005	9.032	11/24/2005	5.089	12/24/2005	1.800
8/25/2005	0.046	9/25/2005	0.149	10/25/2005	11.447	11/25/2005	4.017	12/25/2005	1.930
8/26/2005	0.040	9/26/2005	0.170	10/26/2005	24.857	11/26/2005	3.597	12/26/2005	2.250
8/27/2005	0.036	9/27/2005	0.491	10/27/2005	27.302	11/27/2005	3.421	12/27/2005	3.000
8/28/2005	0.051	9/28/2005	0.723	10/28/2005	19.885	11/28/2005	3.393	12/28/2005	3.480
8/29/2005	0.045	9/29/2005	0.830	10/29/2005	12.797	11/29/2005	5.306	12/29/2005	3.500
8/30/2005	0.035	9/30/2005	1.046	10/30/2005	9.430	11/30/2005	22.326	12/30/2005	3.380
8/31/2005	0.171	10/1/2005	1.103	10/31/2005	7.494			12/31/2005	3.220
Aug 2005	0.078	Sep 2005	0.336	Oct 2005	13.801	Nov 2005	8.997	Dec 2005	4.490

Table E1: Daily and Average Monthly Discharge Data for Raisin River at Williamstown, Ontario, for the period (August 2005 - October 2006) *[Environment Canada(c)]*

Date	Discharge	Date	Discharge	Date	Discharge	Date	Discharge	Date	Discharge
dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)
1/1/2006	3.347	2/1/2006	5.618	3/1/2006	2.099	4/1/2006	20.407	5/1/2006	3.486
1/2/2006	2.873	2/2/2006	5.118	3/2/2006	2.039	4/2/2006	22.916	5/2/2006	2.945
1/3/2006	2.570	2/3/2006	6.385	3/3/2006	1.948	4/3/2006	17.987	5/3/2006	2.714
1/4/2006	2.329	2/4/2006	17.324	3/4/2006	1.850	4/4/2006	20.647	5/4/2006	2.610
1/5/2006	2.330	2/5/2006	31.143	3/5/2006	1.798	4/5/2006	24.639	5/5/2006	2.523
1/6/2006	2.284	2/6/2006	34.933	3/6/2006	1.737	4/6/2006	19.423	5/6/2006	2.568
1/7/2006	2.107	2/7/2006	26.977	3/7/2006	1.682	4/7/2006	14.839	5/7/2006	3.827
1/8/2006	2.085	2/8/2006	18.670	3/8/2006	1.601	4/8/2006	15.769	5/8/2006	3.938
1/9/2006	2.070	2/9/2006	12.839	3/9/2006	1.607	4/9/2006	13.273	5/9/2006	3.145
1/10/2006	2.003	2/10/2006	8.947	3/10/2006	5.069	4/10/2006	10.290	5/10/2006	2.544
1/11/2006	2.012	2/11/2006	6.501	3/11/2006	22.979	4/11/2006	8.499	5/11/2006	2.169
1/12/2006	3.452	2/12/2006	4.992	3/12/2006	29.107	4/12/2006	7.276	5/12/2006	2.075
1/13/2006	5.739	2/13/2006	4.157	3/13/2006	30.420	4/13/2006	6.639	5/13/2006	8.792
1/14/2006	8.670	2/14/2006	3.633	3/14/2006	30.420	4/14/2006	6.314	5/14/2006	12.484
1/15/2006	11.859	2/15/2006	3.379	3/15/2006	30.420	4/15/2006	5.769	5/15/2006	10.762
1/16/2006	11.269	2/16/2006	3.388	3/16/2006	27.256	4/16/2006	5.339	5/16/2006	9.960
1/17/2006	9.088	2/17/2006	3.559	3/17/2006	17.770	4/17/2006	4.983	5/17/2006	8.444
1/18/2006	15.104	2/18/2006	4.616	3/18/2006	11.803	4/18/2006	4.545	5/18/2006	15.500
1/19/2006	29.228	2/19/2006	5.063	3/19/2006	8.329	4/19/2006	3.944	5/19/2006	37.546
1/20/2006	30.876	2/20/2006	4.355	3/20/2006	6.467	4/20/2006	3.427	5/20/2006	52.465
1/21/2006	33.224	2/21/2006	3.661	3/21/2006	4.932	4/21/2006	2.932	5/21/2006	52.375
1/22/2006	30.723	2/22/2006	3.183	3/22/2006	4.403	4/22/2006	2.677	5/22/2006	41.771
1/23/2006	26.843	2/23/2006	2.955	3/23/2006	4.783	4/23/2006	3.685	5/23/2006	24.464
1/24/2006	20.742	2/24/2006	2.785	3/24/2006	9.257	4/24/2006	5.984	5/24/2006	13.469
1/25/2006	15.828	2/25/2006	2.565	3/25/2006	13.240	4/25/2006	7.971	5/25/2006	8.841
1/26/2006	12.266	2/26/2006	2.574	3/26/2006	17.269	4/26/2006	8.404	5/26/2006	6.671
1/27/2006	10.779	2/27/2006	2.404	3/27/2006	20.181	4/27/2006	7.387	5/27/2006	5.456
1/28/2006	8.514	2/28/2006	2.241	3/28/2006	20.425	4/28/2006	6.300	5/28/2006	4.514
1/29/2006	7.668			3/29/2006	19.891	4/29/2006	5.328	5/29/2006	3.749
1/30/2006	6.906			3/30/2006	18.976	4/30/2006	4.188	5/30/2006	3.308
1/31/2006	6.316			3/31/2006	18.411			5/31/2006	2.888
Jan 2006	10.681	Feb 2006	8.356	Mar 2006	12.522	Apr 2006	9.726	May 2006	11.548

Table E1: Daily and Average Monthly Discharge Data for Raisin River at Williamstown, Ontario, for the period (August 2005 - October 2006) *[Environment Canada(c)]*

Date	Discharge	Date	Discharge	Date	Discharge	Date	Discharge	Date	Discharge
dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)	dd/mm/yyyy	(m^3/sec)
6/1/2006	7.934	7/1/2006	1.738	8/1/2006	7.421	9/1/2006	0.112	10/1/2006	1.202
6/2/2006	13.112	7/2/2006	4.991	8/2/2006	15.968	9/2/2006	0.095	10/2/2006	1.112
6/3/2006	9.312	7/3/2006	7.618	8/3/2006	15.471	9/3/2006	0.115	10/3/2006	1.262
6/4/2006	9.852	7/4/2006	5.037	8/4/2006	9.490	9/4/2006	0.121	10/4/2006	1.273
6/5/2006	8.421	7/5/2006	3.143	8/5/2006	5.420	9/5/2006	0.117	10/5/2006	0.955
6/6/2006	6.030	7/6/2006	2.391	8/6/2006	3.493	9/6/2006	0.135	10/6/2006	1.053
6/7/2006	4.431	7/7/2006	1.851	8/7/2006	2.397	9/7/2006	0.151	10/7/2006	0.807
6/8/2006	3.505	7/8/2006	1.399	8/8/2006	1.793	9/8/2006	0.154	10/8/2006	0.727
6/9/2006	3.123	7/9/2006	1.099	8/9/2006	1.567	9/9/2006	0.135	10/9/2006	0.620
6/10/2006	3.429	7/10/2006	0.872	8/10/2006	1.339	9/10/2006	0.105	10/10/2006	0.574
6/11/2006	4.993	7/11/2006	0.682	8/11/2006	1.086	9/11/2006	0.084	10/11/2006	0.505
6/12/2006	5.596	7/12/2006	0.584	8/12/2006	0.908	9/12/2006	0.073	10/12/2006	0.504
6/13/2006	5.350	7/13/2006	0.531	8/13/2006	0.768	9/13/2006	0.070	10/13/2006	0.552
6/14/2006	4.225	7/14/2006	0.456	8/14/2006	0.671	9/14/2006	0.091	10/14/2006	0.606
6/15/2006	3.355	7/15/2006	0.450	8/15/2006	0.605	9/15/2006	0.114	10/15/2006	0.572
6/16/2006	2.650	7/16/2006	0.575	8/16/2006	0.543	9/16/2006	0.116	10/16/2006	0.537
6/17/2006	2.155	7/17/2006	1.037	8/17/2006	0.462	9/17/2006	0.110	10/17/2006	0.587
6/18/2006	1.945	7/18/2006	1.299	8/18/2006	0.437	9/18/2006	0.108	10/18/2006	2.067
6/19/2006	1.828	7/19/2006	0.892	8/19/2006	0.395	9/19/2006	0.121	10/19/2006	3.959
6/20/2006	1.640	7/20/2006	0.617	8/20/2006	0.386	9/20/2006	0.119	10/20/2006	4.227
6/21/2006	1.465	7/21/2006	0.580	8/21/2006	0.412	9/21/2006	0.102	10/21/2006	9.528
6/22/2006	1.360	7/22/2006	0.523	8/22/2006	0.370	9/22/2006	0.091	10/22/2006	9.870
6/23/2006	1.224	7/23/2006	0.481	8/23/2006	0.318	9/23/2006	0.094	10/23/2006	13.154
6/24/2006	1.175	7/24/2006	0.423	8/24/2006	0.334	9/24/2006	0.119	10/24/2006	13.994
6/25/2006	1.038	7/25/2006	0.566	8/25/2006	0.338	9/25/2006	0.138	10/25/2006	10.273
6/26/2006	0.926	7/26/2006	5.357	8/26/2006	0.262	9/26/2006	0.135	10/26/2006	7.273
6/27/2006	0.755	7/27/2006	6.953	8/27/2006	0.226	9/27/2006	0.145	10/27/2006	5.587
6/28/2006	1.757	7/28/2006	3.973	8/28/2006	0.219	9/28/2006	0.169	10/28/2006	9.445
6/29/2006	1.984	7/29/2006	3.175	8/29/2006	0.193	9/29/2006	0.673	10/29/2006	23.066
6/30/2006	1.681	7/30/2006	5.453	8/30/2006	0.159	9/30/2006	1.076	10/30/2006	19.972
		7/31/2006	2.785	8/31/2006	0.130			10/31/2006	13.387
Jun 2006	3.875	Jul 2006	2.178	Aug 2006	2.374	Sep 2006	0.166	Oct 2006	5.137

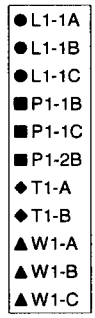
Appendix F
Sample Symbol Legend

Symbol and Nomenclature Legend for Each Site

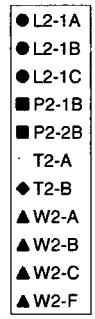
L = Lysimeter
T = Tile Drain
P = Piezometer
W = Well

Background Site

Site 1



Site 2



Site 3