Surface-subsurface hydrologic exchange and nutrient dynamics in a groundwater-fed stream, Bauman Creek, Ontario, Canada

by

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Authors Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of my thesis, including any required final revisions, as accepted by my examiners.

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Abstract

The stream-riparian-aquifer interface plays a major role in the regional flow of nutrients and contaminants due to a strong physical-chemical gradient that promotes the transformation, retention, elimination or release of biogenic elements. To better understand the effects of the near-stream zones on stream biogeochemistry, we conducted a field study on a small groundwater-fed stream located in the *rare* Charitable Research Reserve, Cambridge, Ontario, Canada. This study focused on monitoring the spatial distributions of nutrient elements in the riparian and hyporheic zones. Several piezometer nests were installed near stream to obtain data on the groundwater chemistry and sampled from May 2013 to May 2014. In addition to piezometer groundwater sampling, a series of passive (diffusion) water samplers, known as peepers, were installed along longitudinal and lateral transects centered on the stream during the Summer of 2013. Equilibrium time of peepers was determined in the laboratory to be ~28 days. The spatial and temporal variation in surface water and groundwater chemistry (carbon, nutrients) was observed between locations. Notably, groundwater upwelling along the stream resulted in distinctly different groundwater types and associated nitrate concentrations between small distances in the riparian zone (<4m). Notably, high concentrations of nitrate (13.5 mg/L N) were observed in deep groundwater and surface water. The flux of nitrate to the receiving Grand River ranged from 47 kg N d^{-1} in July and August to over 133 kg N d^{-1} in October. After the upstream source of the stream surface water concentrations of nutrients (nitrate, ammonium, sulfate and carbon) did not significantly change before the stream outlet. Although reduction of nitrate and sulphate were reported in the riparian zone of the stream, this did not significantly influence the chemistry of the adjacent stream water. Also, minimal retention in the hyporheic zones limited reduction of reactive compounds (NO_3^- and SO_4^{-2}) within the stream channel. This study suggests dissolved organic carbon (DOC) and residence time of water in the hyporheic zone and in surface water limited denitrification.

Acknowledgements

I would like to send a giant thank-you to Dr. Fereidoun Rezanezhad, because if not for him as my co-supervisor I would have never been able to finish. He has been a continual source of encouragement and knowledge throughout my time at the University of Waterloo. Also, I would like to acknowledge Dr. Philippe Van Cappellen for the opportunity to complete my MSc. with the Ecohydrology Group at the University of Waterloo

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Table of Contents

List of Figures

List of Tables

1. Introduction

Predicting the movement and export of nutrients is centered on our ability to understand the underlying chemical, biogeochemical and physical processes controlling the fate and transport of nutrients. Of particular significance in a watershed are the riparian and hyporheic zones along rivers and streams. These zones have the ability to act as important filters protecting both groundwater and surface water from contaminated runoff, pollutants and erosion. The biogeochemical and hydrological processes in these zones also play a major role in the local flow of nutrients (Baker et al., 2000; Boulton et al., 2010; Findlay, 1995; Heppell et al., 2014; Kasahara and Hill, 2007; Naimen and Decamps, 1997). The spatial variability and temporal trends of biogeochemical activity of these interfaces and how they impact stream chemistry is limited (Bernal et al., 2014; Dent et al., 2007).

With the use of hydrologic tracers, Triska et al. (1989) defined the hyporheic zone as the interstitial water in the streambed that contains 10% to 98% surface water. Broadly, Valett et al. (1993) described the hyporheic zone as the subsurface area interacting with surface water. This ecotone between surface water and groundwater can differ both spatially and temporally depending on topography, hydrology, hydraulic head, oxygen concentrations and substrate porosity (Findlay, 1995; Triska et al., 1989; Valett et al., 1993; Vervier et al., 1992). In addition to this groundwater-surface water (GW-SW) interface within the streambed, the riparian zone is also a significant area of GW-SW exchange extending along the terrestrial margins of a river/stream (**Figure 1-1**). Riparian soils and vegetation have been shown to influence the retention and release of many solutes to and from surface water; of particular significance are nitrogen, labile carbon and phosphorus (Bernal et al., 2014; Dent et al., 2007; Kasahara and Hill, 2007; Hill et al., 1998). Energy, biota and water flows bi-directionally through these zones creating highly reactive regions characterized by strong redox gradients that transform the chemical and thus physical characteristics of the river/stream (Naiman and Decamps, 1997; McClain et al., 2003).

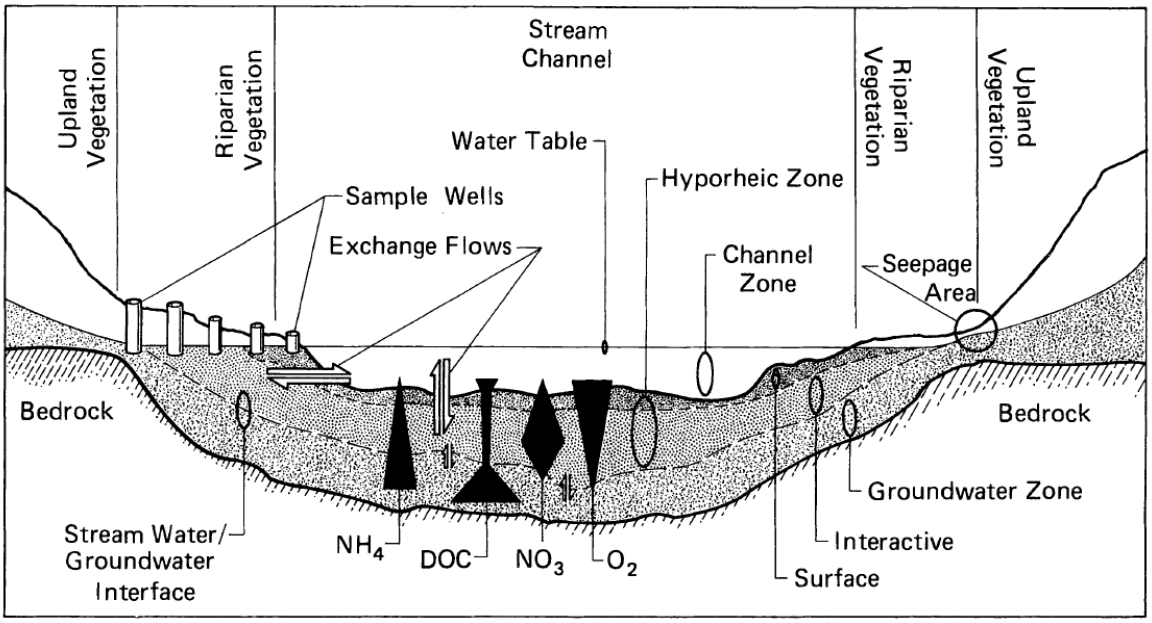

Figure 1-1. Conceptual depiction of the interaction between groundwater and surface water of a lotic system from Triska *et al.*, (1989). Depth profiles of characteristic concentrations gradients of ammonium (NH_4^+), dissolved organic carbon (DOC), nitrate (NO_3^-) and oxygen (O_2) in the hyporheic zone are shown.

Oxygen is the most energetically favourable electron acceptor (-120 kJ) and therefore is consumed rapidly in riparian soils, hyporheic soils and adjacent surface waters (Dooge, 2009; Duff and Triska, 2000) (**Figure 1-1** and **Table 1-1**). After the depletion of oxygen, there is a predictable cascade of electron acceptors consumed. This sequence follows the thermodynamic yield of free energy that can be acquired from available electron acceptors (O_2, NO_3^-, Mn_4^+, Fe_3^+, SO_4^{2-}) and electron donors (DOC, CH_4^+, NH_4^+, H_2) (Dooge, 2009). For example, as oxygen decreases in the soil profile the processes of denitrification and sulphate reduction become more energetically favourable and therefore more prevalent (see **Table 1-1**) (Groffman et al., 2005; Hill, 2010). However, in natural environments the consumption of electron acceptors does not always follow this idealized sequence. Anaerobic and aerobic redox processes have been shown to occur simultaneously and depending on environmental factors, bacteria can utilize more than one metabolic pathway (Duff and Triska, 2000; Triska et al., 1998). Furthermore, substrate

availability can result in denitrifying bacteria competing for nitrate with other soil fauna and riparian/hyporheic vegetation (Naiman and Decamps, 1997; Pinay et al., 2003).

Nitrogen is an essential and often limiting nutrient in aquatic ecosystems although excess amounts of nitrate can become toxic to aquatic organisms and negatively impact ecosystem health through processes such as eutrophication (Eddy, 2005; Kuwabara et al., 2012). This is of particular importance in agriculturally dominated areas where fertilizers and animal waste can contaminate nearby surface water and increase eutrophication events (Bouwman et al., 2013). Nitrogen can exist in groundwater and surface water in a wide range of oxidation states ranging from -3 (ammonium) to +5 (nitrate). Denitrification has been identified as the major mechanism removing nitrogen from wetlands and denitrification rates are governed by nitrate supply, redox state and organic carbon availability (Boulton et al., 2010; Duff and Triska 2000; Groffman et al., 2005). This process involves the reduction of oxidized nitrogen anions (nitrate and nitrite) to dinitrogen gas and occurs at higher rates under low-oxygen conditions (Duff and Triska, 2000; Galloway et al., 2004). In contrast, nitrification is the oxidation of ammonium by chemolithotrophic bacteria using carbon dioxide and often occurs under high oxygen conditions (Galloway et al., 2004).

Carbon in the form of dissolved organic carbon (DOC) has been identified as the limiting variable in subsurface metabolism of nitrogen within riparian forest soils (Bravo and Hill, 2012; Pinay et al., 1994). DOC in surface water can be supplied from upwelling groundwater or from decomposing particulate organic matter from allochthonous sources (Findlay et al., 2003; Groffman et al., 2005; Hill, 2010).The depth of flow paths under the riparian and hyporheic zones can significantly influence the supply of DOC and thus nitrogen removal in aquatic systems; this is particularly important in groundwater fed streams (Groffman et al., 2005; Shabaga and Hill, 2010). Surface-subsurface exchange of nutrients has been shown to not only significantly influence denitrification in the hyporheic zone (Shabaga and Hill, 2010) but also the supply of electron donors that are essential for all microbially mediated redox reactions (Baker et al., 2000).

Table 1-1. List of redox reactions and associated energies calculated per mole of organic carbon (CH_2O) for reduction reactions and per mole of oxygen (O_2) for oxidation reactions. Change in Gibbs free energy calculated using $\Delta G_0' = \Delta G_0 - RT \ln[H^+]^p$ at standard conditions (Adapted from Dooge, 2009).

Process	Electron Donor	Electron Acceptor	Free Energy (kJ) $\Delta G_0'$
Reduction Processes			
Aerobic respiration	Organic Carbon	O_2	-120.0
Denitrification	Organic Carbon	NO_3^-	-113.9
Sulphate Reduction	Organic Carbon	SO_4^{2-}	-25.0
Methanogenesis	Organic Carbon	CO_2	-19.2
Oxidation Processes			
Methane Oxidation	Oxygen	CH_4	-97.7
Sulphide Oxidation	Oxygen	HS^-	-95.0
Nitrification	Oxygen	NH_4^+	-41.4

Streams are not homogenous conduits but dynamic entities (Dent et al., 2007). The biogeochemical processes in small headwater streams have the ability to influence the nutrient concentrations and distribution within the larger basin. For example, Peterson et al. (2001) reported that small streams in North America exhibit the highest rate of inorganic nitrogen uptake and transformation due to the high residence time of water in smaller streams and the large streambed to water ratio. The high residence time of water creates an environment where it can move into and out of the hyporheic and riparian zones numerous times. Furthermore, due to the small basin area of headwater streams they are sensitive and respond quickly to anthropogenic stressors including land-use changes, climate change and excess nutrient inputs (McClain et al., 2003; Peterson et al. 2001; Vitousek et al., 1997). In perennial headwater streams supplied by groundwater these physiochemical relationships become more ecologically important because stable water temperatures, supply of nutrients and stream flows provide a refuge for invertebrates and fishes (Burkholder et al., 2008; Fowler and Scarsbrook, 2002). Due to all these characteristics, small perennial headwater streams are ideal locations for researching lateral and longitudinal surface-subsurface solute movements (Bernal et al., 2014).

1.1. Thesis Objectives

In this study, we monitored the spatial distributions of a series of selected nutrient elements and key biogeochemical redox indicators in the riparian and hyporheic zones of a small, groundwater-fed stream over the course of one year. The hypothesis of this study was to use the spatio-temporal patterns to unravel the key biogeochemical transformations affecting nutrient speciation and fluxes within the riparian and hyporheic zones and establish their response to seasonal variations in stream hydrology and geochemistry. This was completed through a laboratory experiment and subsequent field study. The objectives of this thesis are outlined as follows:

1. Determine the effectiveness and preparation techniques of passive (diffusion) water samplers known as "peepers" to collect high spatial resolution of groundwater quality parameters.

2. Investigate the distributions of water quality parameters (chemical and physical) within the surface water and groundwater (riparian and hyporheic zones) of a small groundwater-fed stream.

3. Understand the hydrogeochemistry of a groundwater-fed stream to explain the critical factors that lead to the observed spatial and temporal signature of the pore water chemistry.

2. Materials and Methods

2.1 Laboratory Tank Experiment: Testing Peeper Sampling Devices

The following experiment was conducted to test the equilibrium time and efficacy of diffusion equilibrium sampling devices. Also, a comparison between these devices, piezometers and MicroRhizon™ samplers was completed.

Peat soil samples were collected from Beverly Swamp, a forested riparian wetland located northwest of Hamilton, Ontario, Canada. The soil was homogenized and transferred into a Plexiglass™ experimental tank built to the dimensions shown in **Figure 2-1**. Approximately 2.5cm of washed gravel covered with Nitex mesh (1mm) was placed in the bottom of the tank before the addition of the soil to facilitate water flow and prevent clogging of tubing.

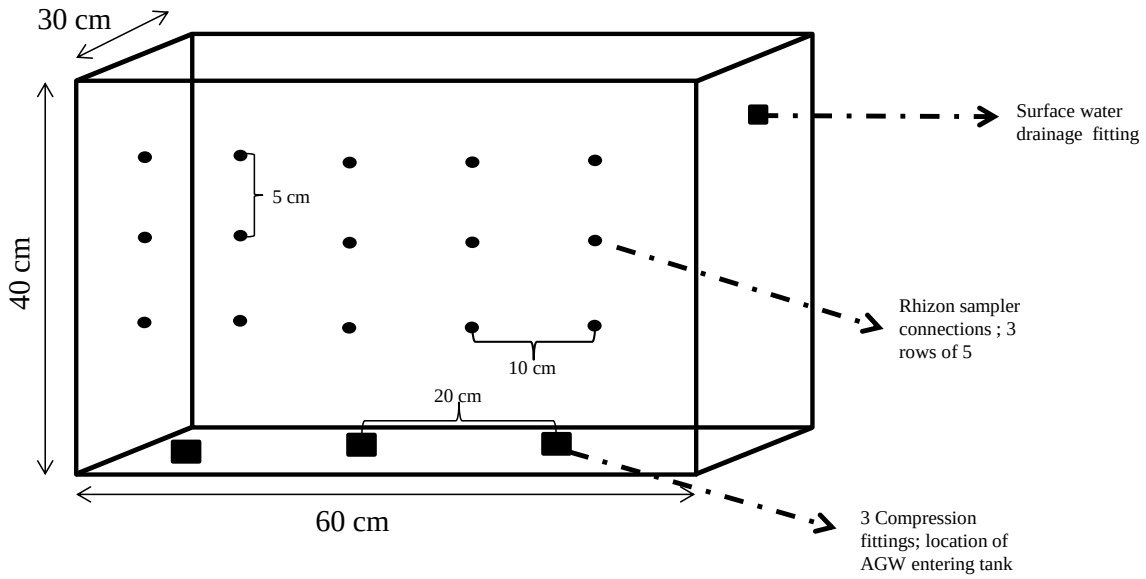

Figure 2-1. Tank experimental set-up used to compare sampling devices and effectiveness of peeper design before field deployment.

This laboratory experiment was designed to simulate field conditions of groundwater (GW) upwelling through the soil to surface water (SW). To achieve this, the tank was saturated with artificial groundwater (AGW) containing $CaCl_2$ (1.7 mM), $NaHCO_3$ (1.0 mM), KBr (0.5mM) and $MgSO_4$ (0.5 mM) using a peristaltic pump (Gilson's Minipuls) that pumped AGW into the bottom of the tank and allowed water to discharge from the top. The pump was maintained at a constant flow rate for the duration of the experiment (120 ml h^{-1}). The AGW reflected the aqueous chemistry of the Beverly Swamp field site and had a final ionic strength of 0.11 mM l^{-1}. AGW was prepared with ultra-pure Mili-Q® (18MΩ) water in autoclaved containers and purged with nitrogen gas for ~2 hrs before use. Anoxic conditions were maintained after purging via a nitrogen filled bag attached to the top of the AGW container. Gas tight tubing (Viton® tubing, Cole-Parmer) was utilized to pump the AGW into the tank. The experiment ran for 28 days at room temperature (22 ± 2 °C).

Outflow samples were collected every 12 hours and analysed for Bromide (as conservative flow tracer), dissolved oxygen and pH. Bromide concentrations were measured using a Portable Br^- Probe (Fischer Scientific Orion Model 290A) and confirmed later with Ion Chromatography (IC, Dionex ICS-5000). Dissolved oxygen, pH (Thermo Scientific Orion 5 Star pH meter) and bromide concentrations were measured daily to ensure DO < 2mg l^{-1} and a pH of 7. Testing and comparison of sampling devices was conducted after the tank was saturated with AGW which was measured by the breakthrough curve of bromide. After this time, three mini-piezometers, 15 micro-rhizon samplers and 5 passive (diffusion) water samplers known as "peepers" were installed in the tank. Specific protocols associated with peeper preparation and cleaning can be found in Section 2.1.1. The mini- piezometers were constructed from stainless steel with a terminal 1cm screen (**Figure 2-2c**). Three mini-piezometers were inserted at -4 cm, -9 cm and -14 cm; this corresponded to the depth of the micro-rhizon ports and specific cells of the peepers. Micro-rhizon samplers (CSS5 MicroRhizon™ samplers, Eijkelkamp, Netherlands, #19.21.23F) (**Figure 2-2d**) were inserted into the ports fitted to the front of the tank. The 10cm length porous tube of

the micro-rhizon samplers was inserted into the front panel of the tank and was attached to an external polyethylene tube that contained a terminal lure-lock fitting cap that could be removed during sampling.

The pore water samples were extracted by micro-rhizon samplers directly into the analysis vials through a needle delivering the sample in a septum-sealed vial. A vacuum pump (Soil Measurement Systems, LLC, USA, #CL-042) set at -100 mbar was used to extract pore water through the micro-rhizon samplers. Four Plexiglass™ peepers (**Figure 2-2a,b**) were carefully inserted vertically into the soil aligning with the micro-rhizon ports and piezometers. Once every week for 4 weeks one peeper, all mini-piezometers and the three micro-rhizons directly in front of the peeper were sampled.

2.1.1. Peeper Design and Preparation

Peeper sampling devices are based on diffusive equilibrium between the ambient interstitial pore water and the water within the peeper sampling cells. The samplers constructed for this experiment are modified versions of the original "peeper" design first presented by Hesslein (1976). Peepers were constructed from a Plexiglass™ body (20 cm × 10 cm) fitted with a Plexiglass ™ face plate (20cm×10cm) with small stain-less steel screws (**Figure 2-3a,b**). Each peeper contained 15 vertically aligned sample cells spaced at 1cm intervals. The cell volume, *V*, was 4 cm^3 (40 mm×10 mm×10 mm).

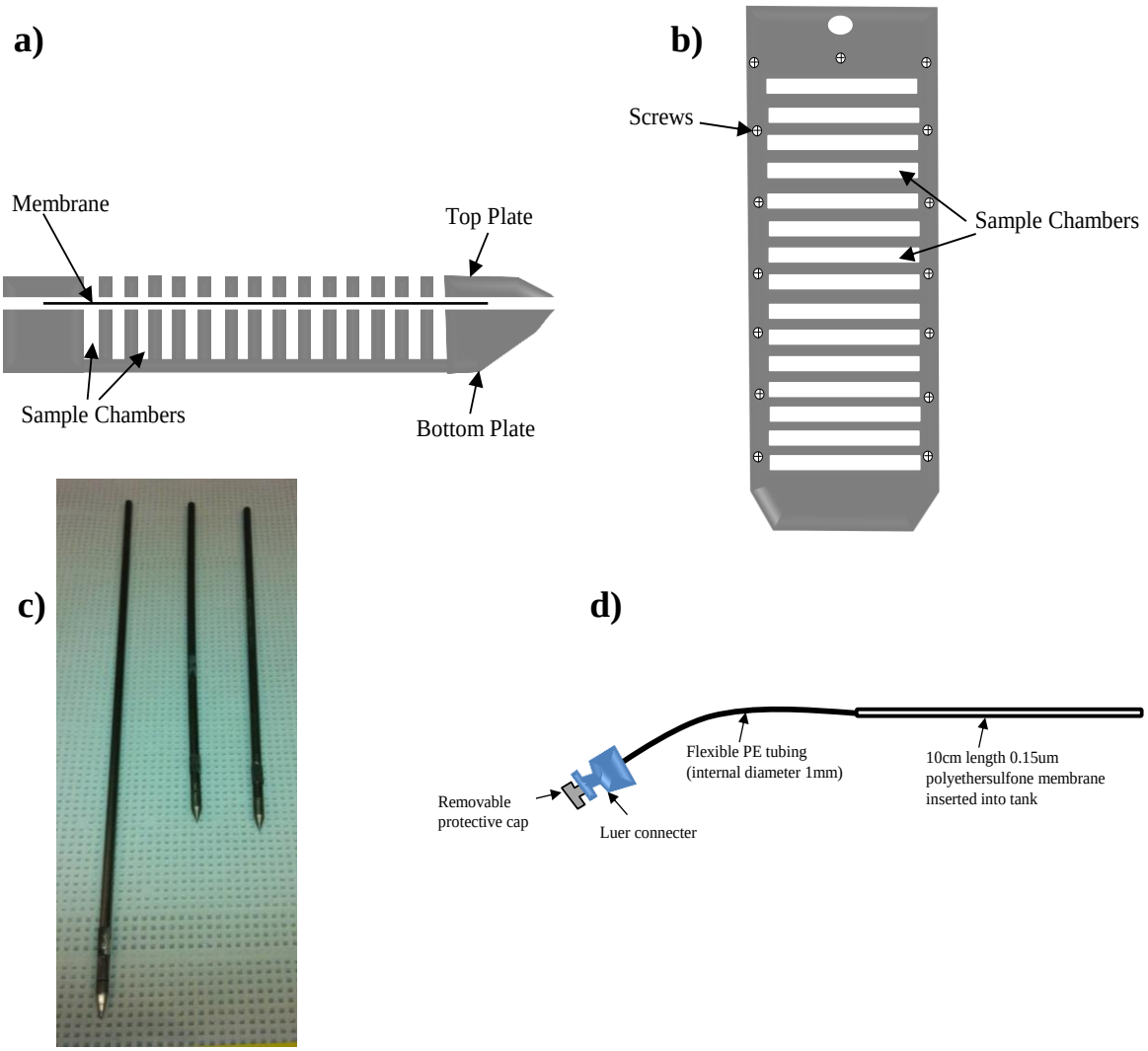

Figure 2-2. a)Schematic cross-section of the Plexiglass™ peeper design. b) Peeper design as viewed from the front showing screws holding the front plate to the back plate. c) Mini-piezometers. d) Micro-rhizon sampling devices.

All peeper samplers were washed with an alkaline washing detergent (Extran®) to eliminate any potential grease and debris from handling/manufacturing. After this initial cleaning they were soaked in 10% (v/v) nitric acid to remove any trace metals. Following a thorough rinsing with Mili-Q®, the peepers were then assembled within a water-bath to ensure all cells were completely filled with water and to minimize air bubbles. In theory, the water in the sampling cells will exchange with the soil pore water in the field until equilibrium is reached. Assembly consisted of placing a 0.2 µm polysulfone membrane (Gelman HT-200 polysulfone membrane, Pall Corporation) between the base and face plate of the peeper and secured in place with stainless steel screws. After assembly, the peepers were placed in air-tight Plexiglass™ boxes (**Figure 2-4**). These boxes were then purged for 30 minutes per day for 7 days with nitrogen gas to de-oxygenate the cell water; this process is crucial in preventing dissolved oxygen from influencing sediment biogeochemistry during field deployment.

Peepers were inserted into the soil with minimal disturbance to surrounding soil. The peepers were pulled out from the soil and were quickly rinsed with Milli-Q and sampled using syringes equipped with 19-guage needles. Peepers were always sampled from the bottom (anoxic) to top (oxic) end.

Figure 2-3. Plexiglass™ boxes containing peeper sampling devices. One-way gas valves built into the boxes were used to purge them with nitrogen gas before the peepers were inserting into the soil.

2.2 Field Study Site

Field sampling was conducted on a small groundwater-fed stream located in the *rare* Charitable Research Reserve, Cambridge, Ontario, Canada. This stream, Bauman Creek, is a narrow (~1 m width) first order tributary of the Grand River watershed with a length of ~980 m and catchment size of ~2 km^2 (**Figure 2-4**). Bedrock in this region is dominated by dolostone (Cruickston Charitable Research Reserve, 2002). The bedrock is overlaid with loamy soils in the upper watershed (dominated by agricultural land-use) and swampy peat soils in the lower watershed adjacent to Bauman Creek (dominated by deciduous-mixed forests) (CH2M Gore and Storrie Ltd, 1997). The channel substrate in the upstream region of Bauman Creek contains heavily embedded fine sand and silt and ~500 m downstream the streambed becomes mostly gravel and sand.

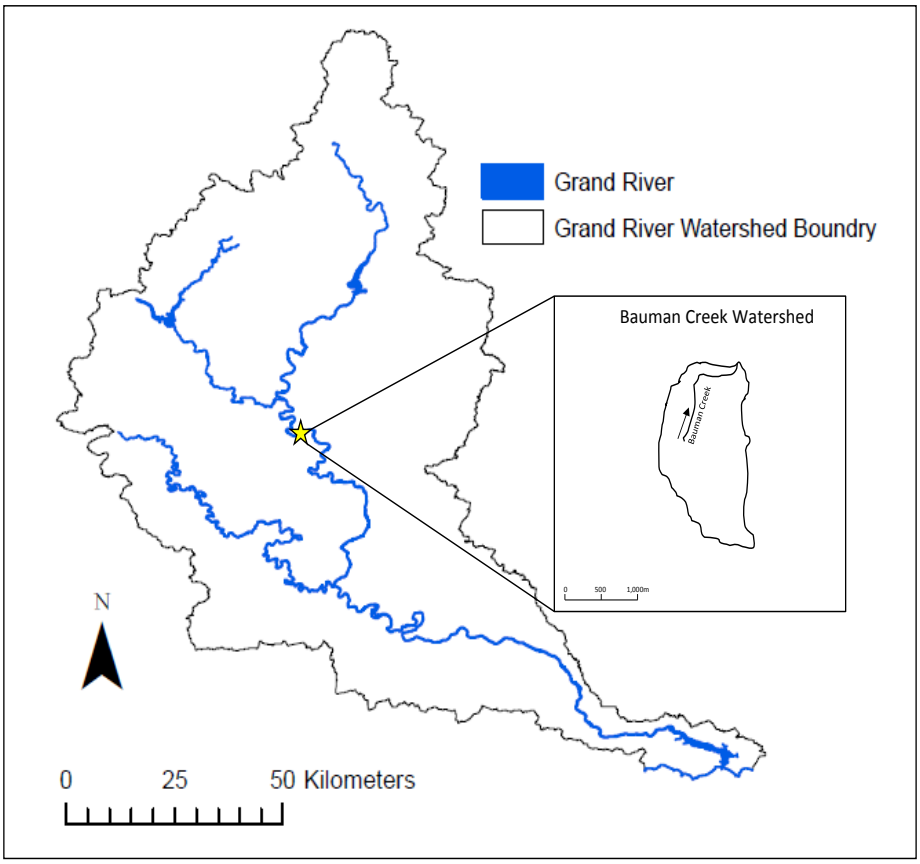

Figure 2-4. Location of Bauman Creek within the Grand River Watershed in Southern Ontario, Canada.

2.3 Groundwater and Surface Water Sampling

Four piezometer nests, each consisting of three piezometers were installed (using a hand auger) within the left riparian zone at sampling locations 1 (Source), 2 (Upstream), 3 (Midstream) and 4 (Downstream) (shown in **Figure 2-5**). Piezometers were constructed from polyvinylchloride (PVC) with an interior diameter of 5 cm and the terminal 5 cm covered with Nitex mesh to prevent clogging. Piezometers installed at the Source location were installed 80 cm, 60 cm and 30 cm below surface level. Piezometers at the Upstream location were inserted 100 cm, 60 cm and 30 cm below surface level. Piezometers at the Midstream location were installed 90 cm, 60 cm and 30 cm below surface level. Depths of piezometers at these locations were often limited by an impermeable clay/gravel layer at ~100 cm. Due to a confining layer located at the Downstream location, piezometers could only be installed at 60 cm, 40 cm and 25 cm deep. All piezometers were purged and allowed to fill before samples were collected. Sampling of piezometers during July 2013 at the Upstream location can be seen in **Figure 2-7**.

Surface water grab samples were collected from the middle of the stream (stream depth ~30cm) adjacent to each piezometer nest; two additional samples were also collected further downstream towards the outlet. Sampling took place on a bi-weekly basis from May to November 2013, with additional sampling taking place in February and April 2014. Stream flow rates were recorded using a handheld device (Global Water Instrumentation, Digital Water Velocity Probe FP11) at each surface water site during sampling.

In order to measure the groundwater/soil temperature profile throughout the field season, a soil temperature profile probe (Hoskin Scientific Ltd.) was inserted at the Midstream location. This temperature profile probe contained six highly accurate temperature sensors located 5cm, 10cm, 20cm, 30cm, 50cm and 100cm from the top of the probe. The data was collected on a data logger (DL6, Delta-T Devices) every hour from May 2013 to June 2014. Data was retrieved from the data logger once per month.

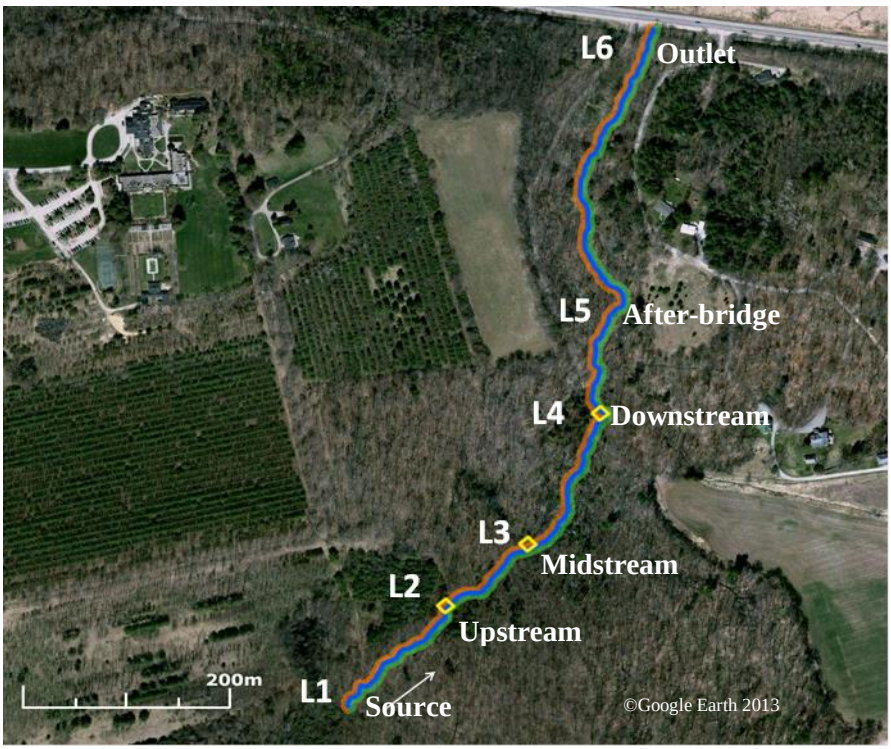

Figure 2-5. Satellite image (Google Earth, 2013) of Bauman Creek study area and water quality monitoring locations. Piezometer nests were located in the left bank riparian zone at Locations marked Source, Upstream, Midstream and Downstream. Surface water samples were collected from all locations from Source to the Outlet.

To obtain a centimetre-scale resolution of groundwater quality, peepers were installed along longitudinal and lateral transects centered on the stream (**Figure 2-6**). Large peepers containing 40 vertically aligned sample cells were deployed in the left and right banks (riparian zone) and a smaller peeper containing 15 sampling cells was inserted into the streambed (hyporheic zone). For details on peeper preparation please refer to Section 2.1.1. Each peeper was pushed into the soil/sediment with minimal disturbance to surrounding soil and vegetation (see **Figure 2-8a**). Peepers were deployed in transects at the Upstream, Midstream and Downstream locations (**Figure 2-6**). The sampling point labelled "After-Bridge" is located after a small organic bridge displaying a significant amount of accumulated organic matter and debris. Peepers were installed in the beginning of May 2013 and were sampled for four months. Water samples were collected from peepers after a period of ~28 days with

sterile 20 ml syringes equipped with 19-gauge needles. **Figure 2-8b** depicts a peeper removed from the sediment before being rinsed and sampled. Once peepers were removed and sampled, new prepared peepers from the lab were inserted in the soil at the same location. All groundwater and surface water samples were immediately filtered (0.45 µm Whatman® Nylon Filters) and sub-sampled into acid-washed/ Mili-Q® rinsed containers and were transferred to laboratory on ice for water quality analysis.

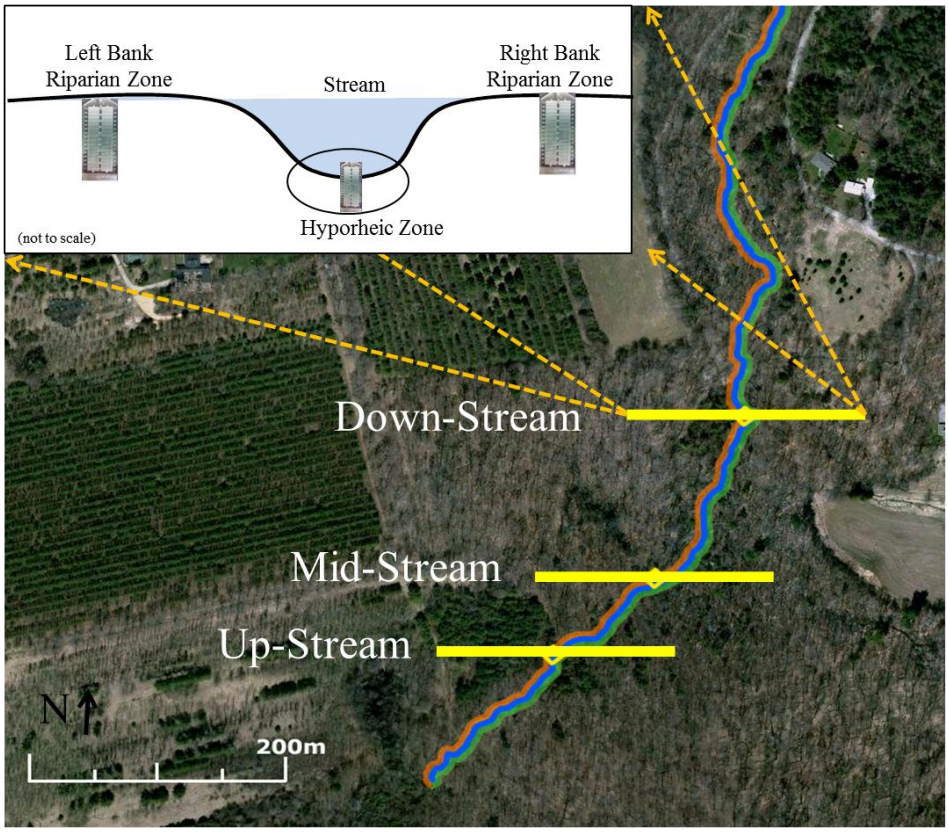

Figure 2-6. Peeper sampling locations and peeper field placement (Modified from Google Earth, 2013).

Figure 2-7. Piezometer nest located at Midstream location showing piezometer placement and dense skunk cabbage understory (July, 2013).

Figure 2-8. a) Deployment of peeper sampling devices into the riparian sediment. b) Removal of peeper from sediment after 28 days.

2.4. Groundwater and Surface Water Level Monitoring

To monitor the groundwater level, wells containing water level data loggers (Solinst, 3001 LT Levelogger Junior, M5/F15, #110241) were installed adjacent to all four piezometer nests, including an additional well installed within the streambed at the Downstream location. Pressure readings from the loggers were calibrated for variations in barometric pressure using a Solinst Barrologger placed at the site and against bi-monthly manual water level readings.

2.5. Pore water Analysis

Groundwater and surface water samples were immediately analyzed in the field for dissolved oxygen, conductivity, oxidation-reduction potential (Eh), pH and temperature using a portable multi-parameter probe (YSI™ Pro20). Water samples preserved in the field with HNO_3 were analyzed for a suite of cations (Fe, Ca, Mg, K, Na, S and Si) using Inductively Coupled Plasma Optical Emission Spectrometry (Thermo iCAP 6200 Duo ICP-OES). An additional subsample was preserved with HCl (< 2 pH) and placed in coloured glass bottles for dissolved organic carbon (DOC) analysis using Shimadzu TOC-LCPH/CPN. Also, 1ml of water samples was filtered through a 0.2µm membrane filter (Thermo Scientific Polysulfone filter) for analysis of nitrate (NO_3^-), chloride (Cl^-) and sulfate (SO_4^{2-}) by Ion Chromatography (IC, Dionex ICS-5000). Silica (SiO_2), ammonium (NH_4^+) and total alkalinity ($CaCO_3^-$) concentrations were determined using a continuous flow injection analyzer (LaChat QuikChem 8500 Series 2 FIA System). Samples for these solutes were not preserved but were analyzed in the laboratory as soon as possible. Furthermore, field blanks were collected and analyzed alongside other samples.

3. Results and Discussion

3.1 Laboratory Tank Experiment

Subsurface-surface exchange of solutes was investigated by injecting an artificial groundwater (AGW) containing a bromide (Br^-) conservative tracer into a simulated groundwater-fed tank system. Saturation of the tank with AGW was determined using the breakthrough curve of Br^- and was predicted as follows:

V= Soil Sample Volume = (60 × 30 × 22 cm) = 39600 cm^3

Q= flow rate or pore water velocity = 120 ml h^{-1}

Φ: Porosity for homogenized peat soil = 0.70

P= Pore volume

$$P = \frac{vt}{L} = \frac{Qt}{\phi V}$$

t: time to reach to one pore volume, P=1

t = 231 h = 9.62 days

K_{sat}= Saturated hydraulic conductivity = 0.0484 cm s^{-1}

Ksat and porosity were measured in the laboratory using standard procedures presented by Klute and Dirksen (1986). The saturated hydraulic conductivity (Ksat) was determined using the constant head method. Soil porosity was determined gravimetrically after drying approximately 20g of fresh soil at 80˚C for a minimum of 48h. The measured breakthrough curve for Br^-, normalized against inflow concentration (C_0) is shown in **Figure 3-1**. As predicted, the maximum concentration was reached after a period of approximately 10 days (see **Figure 3-1)**.

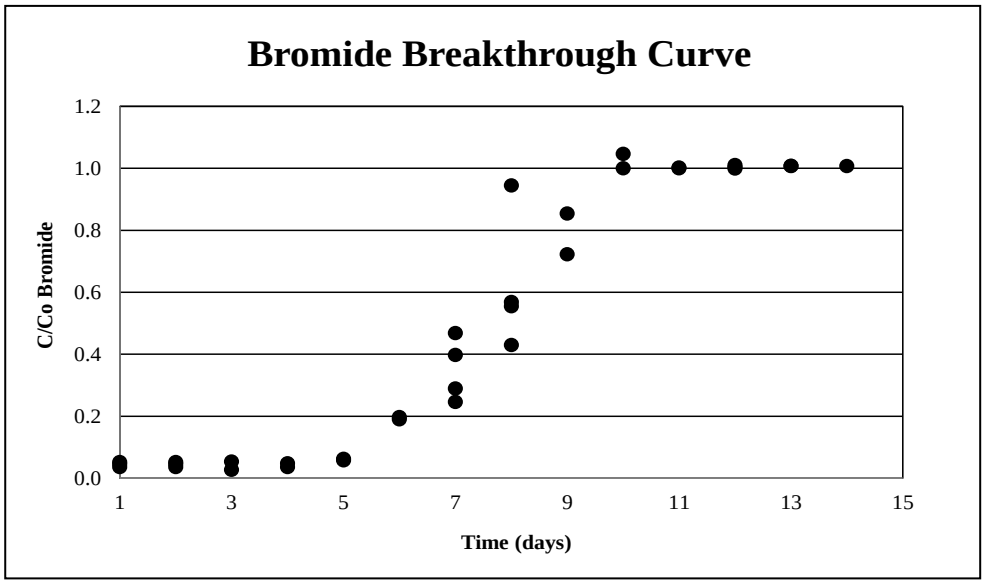

Figure 3-1. Bromide breakthrough curve for the laboratory tank experiment using portable bromide probe.

Peepers, micro-rhizons and piezometers were sampled weekly and the results for Br^- are shown in **Figure 3-2**. **Figure 3-3** displays depth profiles of the weekly sampled peepers. Piezometer and peeper values closely resembled each for other all weeks. Micro-rhizon samples displayed a significant difference compared to the other two samplers. This variation suggests an unexpected preferential flow of the AGW around the inside edges of the tank where the micro-rhizons were located. Due to this preferential flow, the tracer concentration in the peepers and piezometers that were inserted in the interior of the tank did not reach the concentration of the input solution (40 mg l^{-1}) (**Figure 3-1**). While this preferential flow makes micro-rhizon sample comparisons unusable, the assessment of peeper vertical resolution and procedural effectiveness could still be completed.

Quality assurance measures were completed prior to placing all sampling devices in the tank to confirm peepers deployed were free from contamination. Quality assurance samples were collected after the peeper components were cleaned and purged with nitrogen gas. All blank samples were free of detectable anions, suggesting the cleaning and purging system was effective before field deployment.

After the first week of sampling the samples showed a noisy depth profile indicating the cells have not fully equilibrated with the surrounding pore water. After the third week of sampling, Br^- concentrations within the sample cells appeared to remain constant and representative of the soil pore water; the soil also appeared to have settled at this point after the initial disturbance from the peeper insertion. Therefore, equilibrium of the peepers with the pore water appeared to occur after the third week (see **Figure 3-3**). After laboratory pre-investigation of peeper technique and equilibrium time, it was determined that the most suitable incubation period would be ~28 days (3 to 4 weeks).

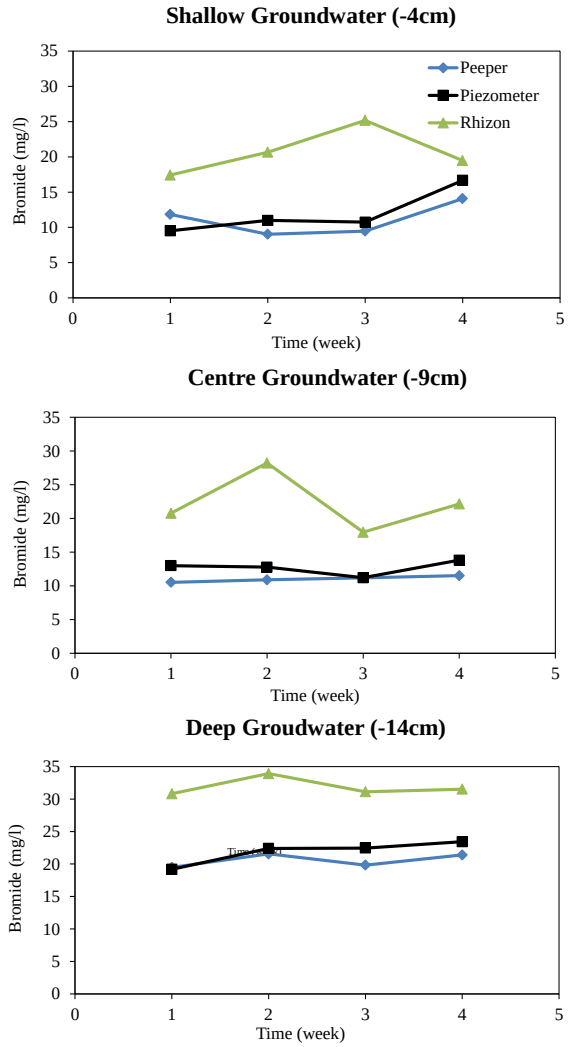

Figure 3-2. Bromide concentrations sampled from piezometers, peepers and micro-rhizons. A comparison of all three sampling methods for the upper , middle and lower peeper depths in tank experiment.

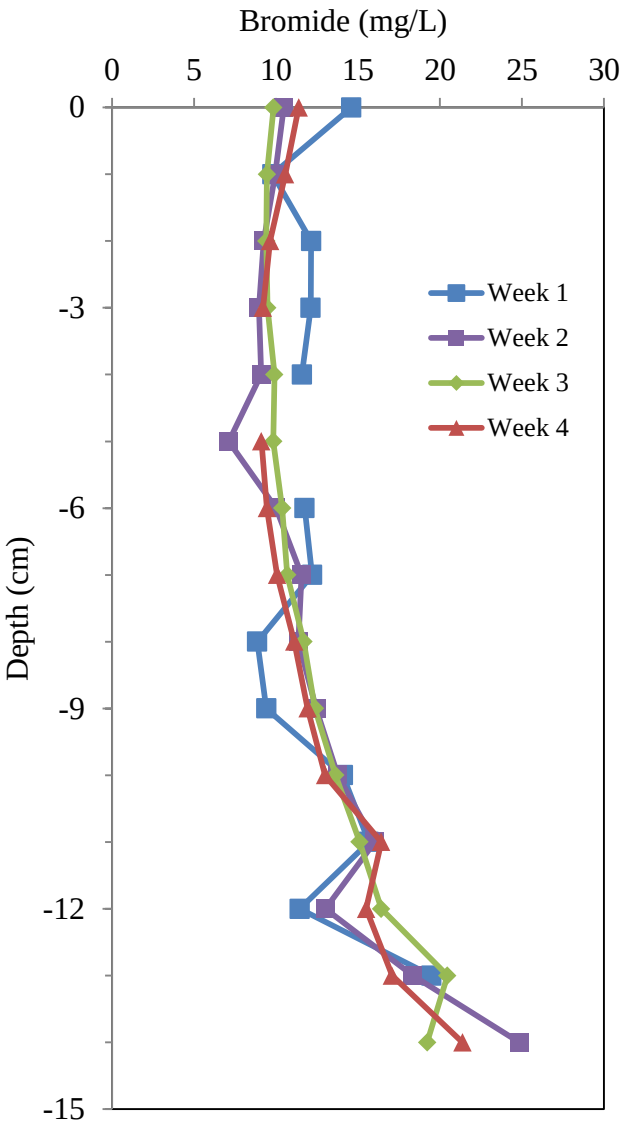

Figure 3-3. Bromide concentration depth profile measured from peepers incubated from 1 to 4 weeks in tank experiment.

The Hesselein (1976) style sampling devices known as "peepers" were designed and built for this study. These sampling devices allow for the collection of high-resolution nutrient data at the centimetre-scale. The equilibrium time for peepers was first presented by Brandl and Haselman (1991) to be controlled by the design factor, f [cm], where $f=V/A$. V is the volume of the sampling chamber and A is the exchangeable area of the membrane of each chamber. This value allows for the calculation of an incubation time; larger f values correlating to longer incubation times. The design factor (f) for the peepers used in this study was 0.68cm. Using the design factor, the equilibrium time for each chemical species of interest can be calculated based on the following equation:

$$C_i / C_o = 1 - \exp(-2 / f \cdot k^M \cdot t) \quad (1)$$

where k^M is the coefficient for a chemical species to permeate the membrane, C_i is the concentration of the chemical species inside the peeper chamber, C_o is the concentration of the species outside the chamber at the time of sampling, and t is the incubation period (Brandl and Haselman, 1981). Equation 1 can accurately estimate equilibrium time within a water column; once peepers are placed in the soil, equilibrium times can drastically change and have been reported to be anywhere from 1-5 weeks (Carignan, 1984; Hesslein, 1972; Stelxzer and Bartsch, 2012).

Diffusion equilibrium samplers have been extensively used in lotic systems but research focusing on lentic systems, such as streams and rivers, is lacking (Carignan, 1994; Hoffman et al., 2013; Passeport et al., 2014). Although the design factor (f) ensures the size of the peeper cells are not the limiting factor influencing the equilibrium time, there are many other factors still pertinent to equilibrium times of peepers used in riverine systems. Equilibrium times need to be adjusted in areas with higher subsurface flow rates and changing redox conditions (Johnston et al., 2000; Teasdale et al., 1995). The k^M and the growth of microbial biofilms on different membranes can influence the movement of solutes into sampling cells (Carignan, 1984). Also, the soil matrix, disturbance to the soil during deployment and

adsorption-diffusion dynamics of a chemical species will influence the movement and concentration of solutes to the sampling cells (Teasdale et al., 1995; Webster et al., 1998). For the aforementioned reasons, this study tested the design and manufactured integrity of the samplers within a simulated groundwater-fed system.

This laboratory study successfully confirmed the preparation and sampling procedure of the peeper sampling devices before their use in the field. While piezometers provide more sample volume (~200ml) in the field than peepers (~8ml), piezometers are not able to capture the steep redox gradient in the first several centimetres of soil (Hill and Lymburner, 1998). Peepers provide high resolution data at a centimeter scale that is not possible with piezometers. Piezometer sampling represents a "snap-shot" look at the solute composition of the groundwater and can often be influenced by exposure to oxygen; in contrast, peepers are placed in the soil for several weeks to equilibrate to the groundwater. All sampling devices have their list of pros and cons but the most important aspect of sampling is the proper interpretation of results based on sampling methods utilized.

3.2. Field Study

3.2.1. Temperature

Soil temperature was recorded using a soil temperature profile probe that was inserted at the Midstream location (refer to **Figure 2-5** for image of sampling locations). **Figure 3-5** (a, b) illustrates characteristic temperature profiles of a gaining and losing stream; the similarity of the temperature profile observed at the Midstream location (**Firgure 3-5, c**) and the temperature profile of a gaining reach confirms groundwater upwelling at Bauman Creek.

The greatest difference between deep groundwater and shallow groundwater/surface water was observed during the warmest part of the summer (July) and during the coldest months of winter (January/February) (see **Figure 3-4**). After a depth of -45cm below surface level the groundwater temperature did not significantly change over the course of the year (average 8.1 ±0.2) (**Figure 3-5, c**).

Since Bauman Creek is groundwater-fed, surface water temperatures are moderated from the upwelling groundwater. Shallow soil temperatures e exhibited similar values to adjacent surface waters and neither froze, even during the cold winter season (see-5cm depth in **Figure 3-4**). This can significantly influence the ecology of the stream and watershed insect and fish community structures (Moldan and Cerny, 1994). The thermal refuge created by the upwelling groundwater provided a corridor for Brook Trout in Bauman Creek as far upstream as the Midstream location during the summer months. Temperature is an important variable influencing ecosystem processes of both surface water and groundwater and temperature-dependant microbial processes (Jones and Mulholland, 1999).

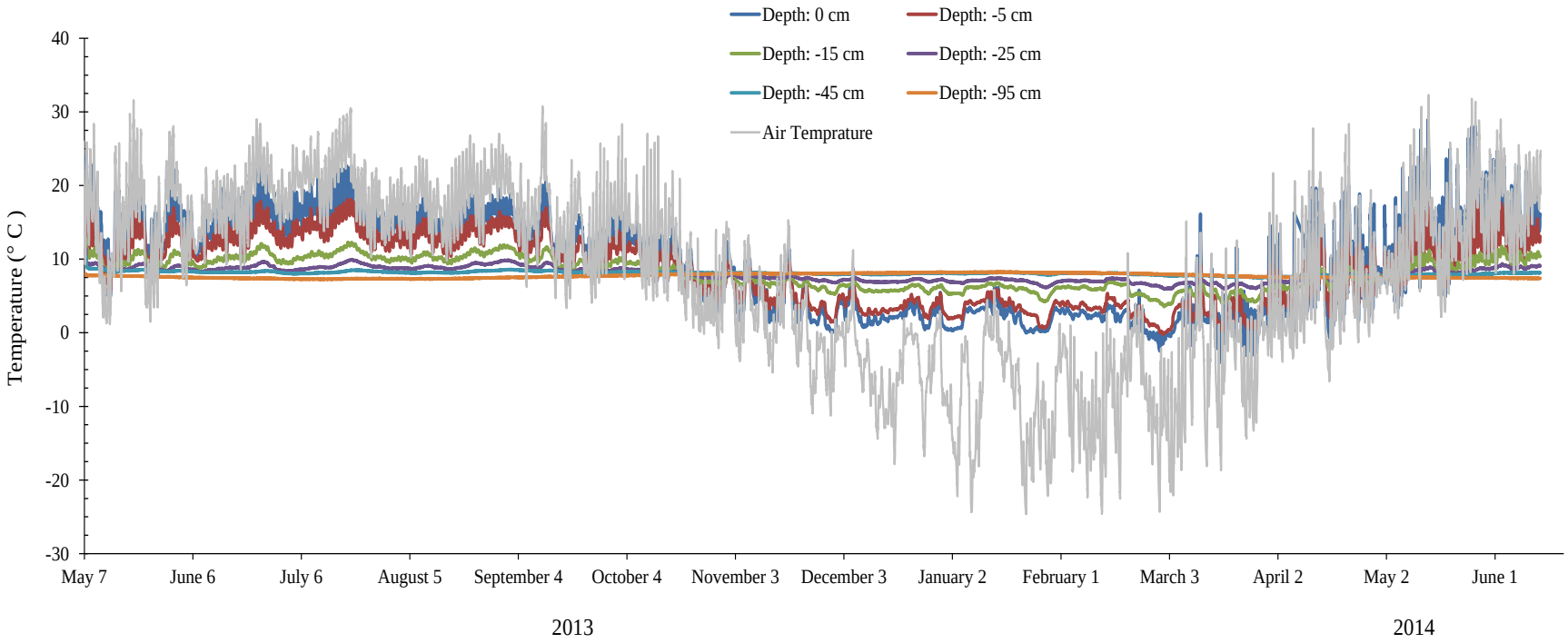

Figure 3-4. Groundwater temperature at Bauman Creek field site. Air temperature was recorded at the site using the Solinst Barrologger. Soil temperature was collected using Hoskin Scientific soil temperature profile probe.

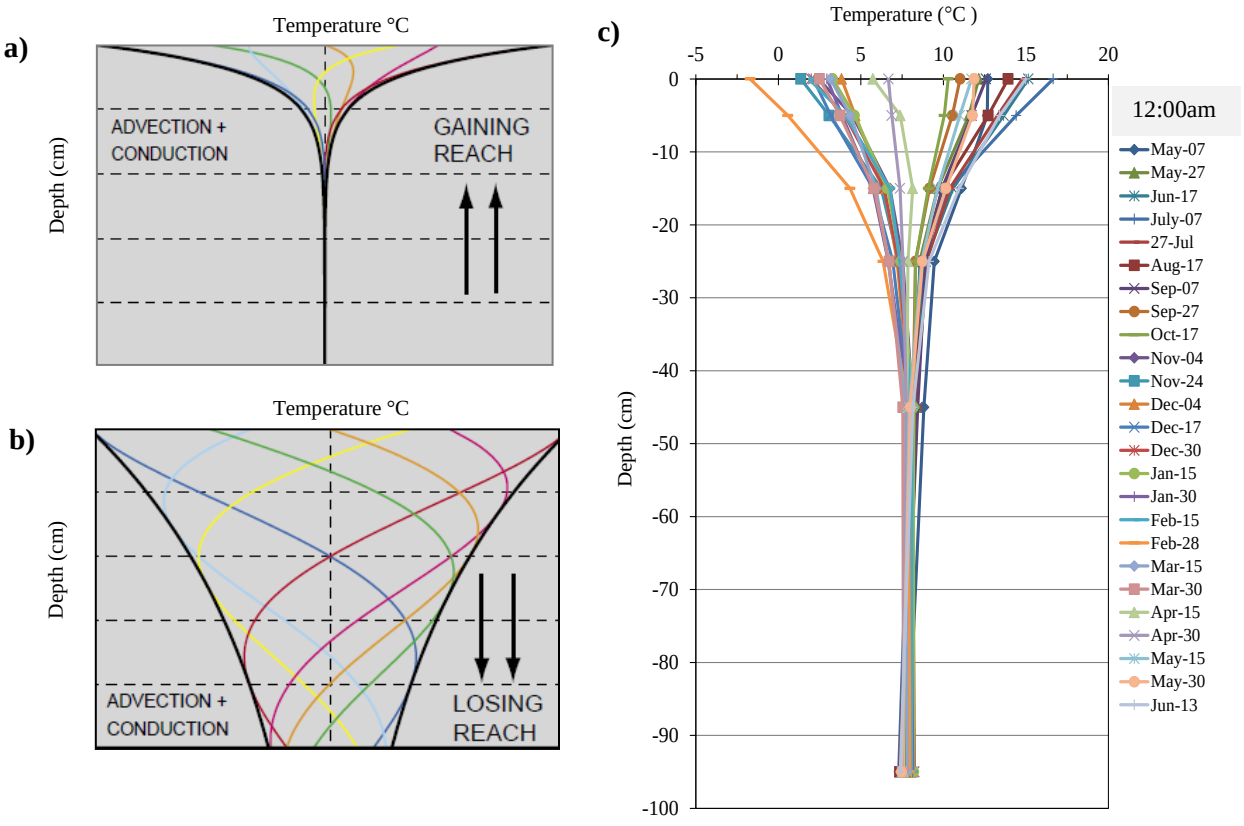

Figure 3-5. a-b) Characteristic temperature profiles for a losing and gaining stream, respectively (Stonestrom and Constantz , 2004). c) Temperature profile data to a depth of 95cm below soil surface. This field data from the Midstream location reflects the gaining stream as shown in (a) and thus confirming groundwater upwelling at Bauman Creek. The subset of data was from 12:00am on each day presented (May 2013 to June 2014).

3.2.2. Surface Water and Piezometer Groundwater Geochemistry

The water table for all four groundwater sampling locations were above the shallowest water sampled (>-30cm). Water table graphs can be found in Appendix A, **Figure A-15 (a-e)**. The Downstream location (location 4) showed a water table above the soil surface level for all seasons. At the Midstream location a water table above the sediment surface was observed throughout the summer and fall of 2013 with a slightly decreased during the spring of 2014.

Surface water samples were collected approximately bi-weekly between May 2013 to December 2013 with an additional sampling in February and April 2014. Surface water samples were collected from six locations and groundwater samples were collected from four piezometer nests. Four piezometer nests, each consisting of three piezometers were installed within the left bank riparian zone at sampling locations 1 (Source), 2 (Upstream), 3 (Midstream) and 4 (Downstream) (see **Figure 2-5**). The groundwater upwelling at Bauman Creek resulted in saturated soils extending into the riparian zones throughout the summer and fall seasons; piezometers were installed in this saturated region. Surface water samples and deep groundwater samples retrieved from the piezometers is shown in **Figure 3-6 (a-h)**. Deep groundwater at the Source, Upstream, Midstream and Downstream locations were -80cm, -100cm, -90cm and -65cm, respectively.

Bauman Creek watershed is underlain by dolostone bedrock, the weathering and dissolution of this carbonate rock resulted in water rich in Ca^{2+}, Mg^{2+} and HCO_3^-. These major ions accounted for the majority of the ionic chemistry in both groundwater and surface water at Bauman Creek and resulted in very hard water throughout the summer and winter months (250-300 mg l^{-1} Alkalinity as $CaCO_3$). Alkalinity buffers stream water from significant changes in pH (Jones and Mulholland, 1999). Although, over a distance of less than a kilometer, surface water in Bauman Creek increased from an average pH of 7.3±0.09 (Source) to pH 8.2±0.07 (Outlet) (**Appendix B, B-6**). The pH changes were concomitant with a decrease in HCO_3^- from 357 mg l^{-1} at the Source to 334 mg l^{-1} at the Outlet. Over the same distance the log [P_{CO2}] decreased from -2.05 to -3.04. Groundwater saturated with CO_2 discharging at the Source

location would explain the pH, concentration of CO_2 and changes in major ions as the surface water flows downstream (Jones and Mulholland, 1999). The following equation shows how the increase in pH occurs due to the consumption of H^+ and HCO_3^- as CO_2 degasses from the surface water (to equilibrating with the atmospheric CO_2).

$$CO_{2\,(g)} + H_20 \leftrightarrow H_2CO_{3\,(aq)} \leftrightarrow H^+ + HCO_{3\,(aq)}^-$$

As the partial pressure of CO_2 decreased downstream, dissolved oxygen (DO) concentrations at Bauman Creek increased. The lowest saturation of DO was observed at the Source (5.3±1.8 mg l^{-1}) location but increased downstream (9.0±2.4 mg l^{-1}). As surface water moved downstream, water temperature (**Appendex B, B-1** and **B-2**) and mixing effects (stream flow rates) increased which resulted in higher concentrations of DO (Moldan and Cerny, 1994). Furthermore, the temporal trend of DO in surface water negatively correlated with temperature; higher DO values recorded in the fall and winter months compared to the summer months.

The riparian groundwater chemistry at the Downstream location was more sensitive to weather events compared to the other locations. This was reflected in the large changes in water table levels. The groundwater in this area was unique in that it showed large variations in alkalinity, calcium and magnesium trends. As groundwater table fluctuated in response to incoming groundwater these compounds were flushed and released from the soil resulting in the observed trends.

Surface water nitrate values did not follow a normal distribution and therefore an ANOVA test based on ranks with a subsequent Tukeys test was completed to compare means between locations. There was a significant difference between the Source location compared to all other locations downstream ($P<0.05$) (**Figure 3-6, b and f**). Surface water nitrate values were relatively low at the stream Source location but increased and remained statistically similar from the Upstream location to the Outlet ($P>0.05$). (**Figure 3-6, b**). Ammonium was not detected in stream surface water and remained low (<300ug l^{-1}) in all deep groundwater samples. Nitrate and sulfate concentrations in surface water

negatively correlated to DOC concentrations. DOC remained low (median 2.9mg l^{-1}) at all locations after the Source and thus minimal reduction of nitrate at these locations. Overall, There was a significant difference between the Source location for nitrate, sulfate and DOC compared to all other locations downstream locations ($P<0.05$) (**Figure 3-6)**.

Deep groundwater upwelling at the stream Source suggests denitrification occurring -30 to -60cm below the sediment surface before discharging into the surface water (**Appendix A, Figure A-7, a**). When chloride is used as a conservative tracer (NO_3^-/Cl^-), changes in nitrate suggest nitrate removal is not due to dilution but removed through denitrification. The riparian groundwater at -30cm depth exhibited a similar chemical signature to the adjacent surface water suggesting lateral groundwater movement from this depth into the adjacent stream (refer to Appendix A for additional groundwater graphs).

Groundwater at the Midstream location showed a high and stable upwelling of nitrogen rich water (**Figure 3-6, f**). The deep groundwater (-90cm) nitrate averaged 57.5 mg l^{-1} (±7.1) and the shallow water (-30cm) average was 57.9 mg l^{-1} (±6.7), for the sampling year at this piezometer nest (**Appendix A, A-7, c**). DOC results displayed a negative correlation with nitrate and sulphate aside from an outlier on May 7 (DOC average of 28.70 mg l^{-1}) the DOC remained low (<5 mg l^{-1}) in the deep and shallow groundwater throughout the summer, fall and winter months (**Figure 3-6, h**). Due to the low DOC and high nitrate in the groundwater at this location, it suggests DOC is the limiting factor influencing the riparian soil to remove nitrate through denitrification. Stelzer and Bartsch (2012) reported similar results where nitrate saturation due to high loading of nitrate in groundwater overwhelmed the ability of the sediment to remove nitrogen from the system.

The anaerobic microbial process of denitrification reduces nitrate in the presence of organic matter and is the primary process of nitrate removal in small catchments, such as Bauman Creek (Peterson et al., 2001). A simplified equation of nitrate reduction is as follows:

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

Previous reports have suggested for the efficient removal of nitrogen by denitrification in stream waters a concentration of <1 mg N l^{-1} is needed (Mulholland et al., 2009). Above this concentration could result in depletion of biologically available DOC, limiting denitrification rates and subsequently the ability of the stream to reduce nitrate loading to downstream locations (Mulholland et al., 2009). The Midstream location at Bauman Creek displayed the highest groundwater nitrogen concentrations compared to the other piezometer locations (Source, Upstream and Downstream).

Flow rate (velocity) was measured using a hand held meter at all surface water sampling locations. The characteristic width of the stream was ~1m and depth was ~30cm. The average stream flow at the Source, Upstream, Midstream, Downstream, After-bridge and Outlet locations were 0.1 ms^{-1}, 0.1ms^{-1} 0.1 ms^{-1}, 0.2 ms^{-1}, 0.3 ms^{-1} and 0.7 ms^{-1}, respectively. Stream flow displayed minimal seasonal changes with only slightly higher flow rates at the Outlet during September (0.9 ms^{-1}) and October (1.1 ms^{-1}). Upwelling groundwater provided a constant base flow at the Source, Upstream or Midstream locations where water velocity was maintained between 0.1 to 0.2 ms^{-1}. Stream velocity and thus discharge from a watershed influences water residence times and thus uptake and release of nutrients to receiving waters. The following equation (2) utilizes flow values (m s^{-1}) to calculate discharge (m^3 s^{-1}) and concentration values (mg l^{-1}) to estimate the mass flux of nitrate leaving the Bauman Creek watershed:

$$\text{Mass Flux} = (\text{discharge}) \times (\text{concentration}) \qquad (2)$$

Mass flux of nitrate at the Outlet location ranged from 0.24 kg N ha^{-1} d^{-1} (as nitrogen) in July and August to 0.77 kg N $ha^{-1}d^{-1}$ in October 2013when discharge was the highest. The lowest flux of 0.21 kg N ha^{-1} d^{-1} was observed in April of 2014. There was a 27% difference in the nitrate flux at the Outlet over the course of the sampling year.

Characteristic back-of-the-envelope calculations of nitrate loading from Bauman Creek reveal loadings of 136 kg N $ha^{-1}yr^{-1}$. Historically, CH2M Gore and Storrie (1997) reported nitrate values of 25.5 mg l^{-1} as NO_3^- in February of 1994 and 8.9 mg l^{-1} as NO_3^- during the summer of 1994. This translates into discharge values ranging from below detection limit to 112 kg N $ha^{-1}yr^{-1}$. The range of values reported by CH2M Gore and Storrie (1997) are considerably lower than the values found in this study. To determine how nitrate fluxes change on a longer time scale, there is a need for further monitoring at Bauman Creek.

From the upper reaches of the Grand River to the mouth, nitrate concentrations increase from below the detection limit (<0.001 mg/L) in the Boston/Mackenzie Creek watersheds to 13 mgl^{-1} close the mouth at Dunnville (Loomer and Cooke, 2011). In the middle reach of the Grand River near the confluence of the Speed River, a couple kilometers north of Bauman Creek, nitrate values are 14.2 mg l^{-1}(Loomer and Cooke, 2011). The concentration of water discharging into the Grand River from Bauman Creek ranged from 15.9mg l^{-1}(April 2014) to 60.5mg l^{-1} (May 2013). All nitrate concentrations found in this study from the outlet of Bauman Creek were higher than the values observed in receiving Grand River.

Overall, water quality decreases down the Grand River as headwaters drain from mostly forested areas through agricultural landscapes and heavily populated urban areas. Land use within a watershed can have a substantial impact on water quality; agricultural watersheds characteristically discharging more N and P compared to urban or forested watersheds (Peterson et al., 2008). Chesapeake Bay region reported mass fluxes from agricultural dominated landscapes to range from 70->885 kg ha^{-1} yr^{-1}, forested areas ranges from 10-130 kg ha^{-1} yr^{-1} and urban areas ranged from 103-269 kg ha^{-1} yr^{-1} (Vyhnálek, 1994). Peterson et al. (2008) compiled data on small streams (<100 l s^{-1}) in upper Michigan State and reported

loadings of 12 kg N d^{-1} from agricultural watersheds, 15kg d^{-1} from urban watersheds and 0.22 kg N d^{-1} of nitrate flux from forest covered watersheds. Depending on the percentage land cover, fertilizer applications and management practices within a watershed change these values can double or triple (Dauer et al., 2000; Peterson et al., 2008). Although Bauman Creek watershed has a large forested riparian zone and over 50% of the watershed is forest covered, the chemical composition of the water does not reflect forested areas. Small headwater streams are often over-looked but have the potential to act as non-point sources of pollution. Small streams are often seen as sinks and filters for excess nutrients but Bauman Creek was observed to discharge a significant amount of nitrate from this seemingly pristine forested watershed. More research is needed on the long-term trends in nitrate fluxes from Bauman Creek as well as to determine the source of groundwater upwelling in this area. Identifying areas of tile drainage in the region and isotope analysis of groundwater would aid in identifying groundwater sources.

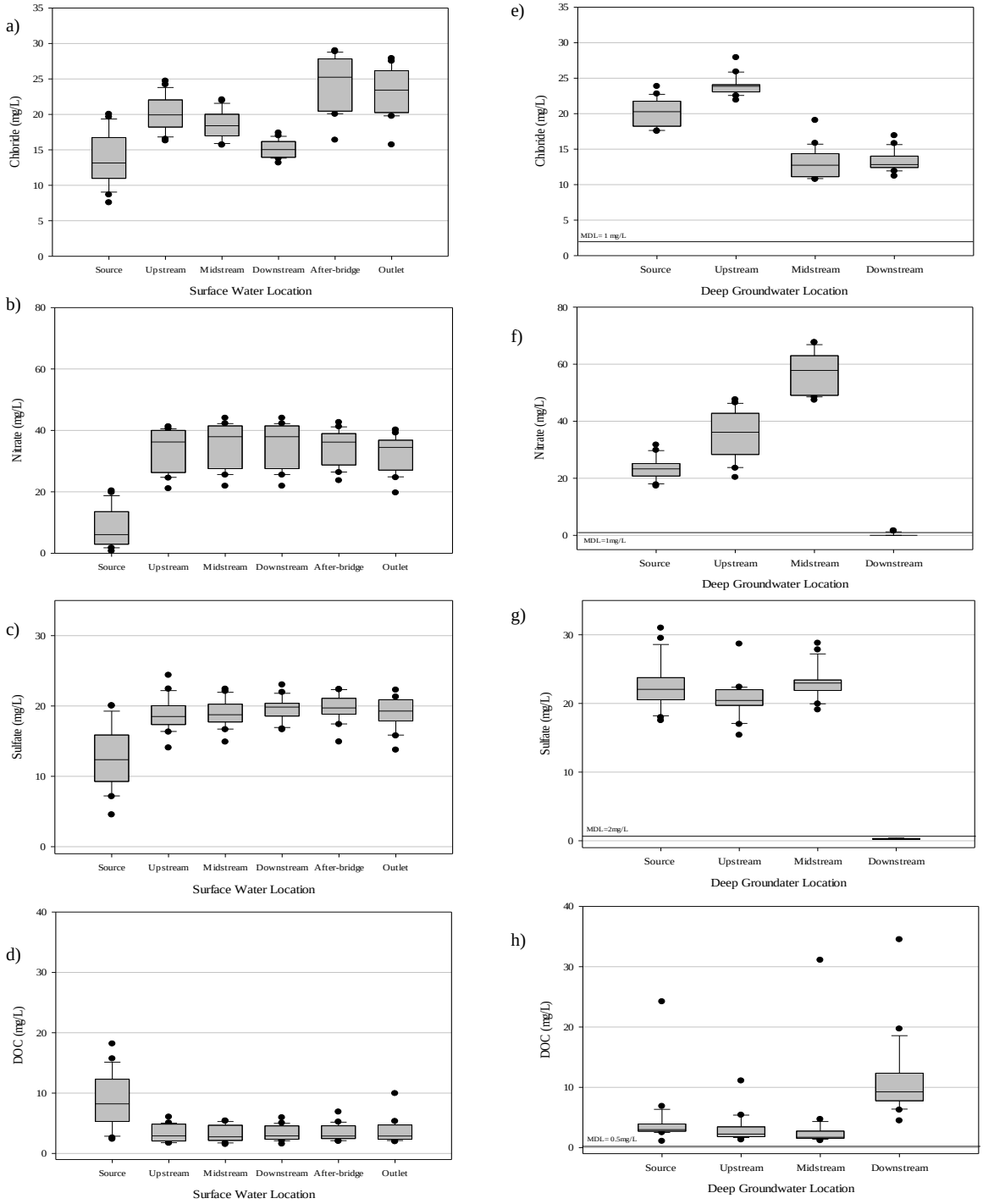

Figure 3-6. a-d) Box- plots illustrating surface water chloride, nitrate, sulphate and DOC concentrations from Bauman Creek between Summer 2013 Winter 2014. All boxes have lines representing the lower quartile, median, and upper quartile and the whiskers represent the minimum and maximum values of the data. Outliers are indicated by circles. Box-plot comparison of surface water samples illustrate the significant difference of the upstream (Source) water chemistry compared to the relatively constant downstream locations. n=17 for each location. e-h). Deep groundwater concentrations from piezometer samples. Surface water and groundwater site locations are shown in Figure 2-6.

Deep groundwater nitrate and sulfate results at the Downstream location were consistently below the detection limit (**Figure 3-6, f-g**). Sulfate was not detected in deep groundwater between June 25th and November 19th. Sulfate increased again to 19.5 mg l^{-1} and 22.8 mg l^{-1} during the cold months of February and April 2014, respectively. Sulfate showed a strong negative correlation with temperature, where increased groundwater temperature resulted in low concentrations during the summer while colder fall and winter temperatures correlated to higher sulfate values. DOC values that ranged from 22.1 mg l^{-1} at the beginning of May 2013 then decreased to 3.9 mg l^{-1} during the first week of June and remained <5 mg l^{-1} for the remainder of the year. Data from the Downstream location highlights how riparian soils effectively removed nitrate and sulphate from groundwater during the summer months but this had no effect on adjacent or downstream stream concentrations.

The Downstream location was situated before a small bridge and substantial buildup of organic matter. This organic dam resulted in significant flooding in this area which reduced flow rates and water residence times. Inorganic matter from fallen organic debris (trees, leaves, branches) are important for the functioning of small headwater streams (Bilby and Liken, 1980; Smock et al., 1989) ensuring POM and DOM for macroinvertebrates, microorganisms and fish habitats. Essentially, organic build-up can act two-fold, increasing water residence time and providing organic matter and habitat for small invertebrates and fish. This small dam showed considerable flooding and highly saturated riparian soils throughout the summer resulting in reduced nitrate and sulphate concentrations in the groundwater. This could suggest an explanation to the maintained reducing conditions of the soil at this location. Bilby and Kinen (1980) in Hubbard Brook research site also found that these dams of organic matter significantly increased organic matter retention time and carbon processing to the stream and subsurface. The subsurface chemistry is in sharp contrast to the surface water which did not decrease in nitrate or sulphate and remained low in DOC at the Downstream location.

Refer to Appendix A and B for supplementary chemical and physical data collected from Bauman Creek.

3.2.3. Peeper Geochemistry

To better evaluate the spatial trends, peepers were placed in transect at the Upstream, Midstream and Downstream locations. Three peepers were placed at each location; one in the left bank, one in the streambed and one in the right bank. The Early Summer sampling period refers to samples collected on June 4th, Mid-Summer refers to samples collected July 31st and Late Summer samples were collected September 3rd (all in 2013).

Nitrate concentration in shallow riparian groundwater was lower than deeper groundwater (**Figure 3-7**). The only exception is the Upstream site in the right riparian bank and Midstream left bank where nitrate increased with depth (**Figure 3-7, l and m**). Chloride profiles throughout the summer season (Early, Mid and Late) remained stable and did not show significant changes and this suggests the decrease in nitrate concentrations in peepers is due to denitrification. Pore water nitrate at the Downstream location remained undetectable (<MDL) for the entirety of the summer season (**Figure 3-7 p and r**).

High concentrations of DOC are seen at the Downstream left bank during the Mid and Late Summer but this section of high DOC was below detection limit during the Early Summer (**Figure 3-7, y**). This increase in DOC occurs at the same depth that nitrate was observed to decrease below detection limit during the Mid and Late Summer (**Figure 3-7, p**). There is a similar hot spot of DOC observed in the Upstream location around -20cm depth but at a lower concentration and did not appear to influence nitrate concentrations. The results indicate that denitrification rates were temporally and spatially variable depending on DOC availability. The zone of -20cm signifies the end of the A soil horizon into the lower B horizon. These peaks in organic matter at this depth are most likely from the change in soil horizons and thus biological activity can created DOC hotspots; this division is also an area of POC deposition which would explain DOC accumulation at this depth (Vervier, 1992). Over the summer season, DOC in the riparian and hyporheic zones of the Upstream and Midstream locations remained relatively low

(<1mg l^{-1}). Similarly, DOC in the groundwater entering the stream through the hyporheic zone at the Source was quickly consumed and remained low in all downstream SW locations (<10 mg l^{-1}).

Many of the stabilized depth profiles at many locations shown in **Figure 3-7** indicate the riparian and hyporheic zones were limited in their ability to remove or reduce in amount of nitrogen in the system. This can be important in agricultural watersheds where nitrogen from fertilizers has entered deep groundwater streams (Shabaga and Hill, 2010). This is due to the limited availability of labile carbon (DOC) limiting factor in denitrification of upwelling groundwater (Groffman et al., 2005; Shabaga and Hill, 2010). Often organic carbon within riparian forest soils has been recorded as the limiting factor controlling denitrification (Bravo and Hill, 2012).Pore water data from this study reflects similar studies (Galloway et al., 2004) where higher rates of nitrogen removal in occurred in the Midsummer during the warmest part of the summer.

The nitrate profiles of the peepers shown in **Figure 3-7 (j-r)** suggest a strong redox gradient at this surface-subsurface interface which consumes oxygen and subsequently anaerobic metabolism of nitrate (Hedin et al., 1998). Shabaga and Hill (2007) reported that the dominate factor eliminating nitrate in the riparian zone of a southern Ontario stream was denitrification. Although reduction of nitrate and sulphate was observed in the riparian zone of Bauman Creek field site, once groundwater moved from the riparian and hyporheic zones to the surface water the low residence time of surface water results in relatively high nitrogen and DO (dissolved oxygen) and low ammonia and DOC concentrations and negligible transformation of these nutrients (Bravo and Hill, 2012; Pinay et al., 1994; Triska et al., 1993).

The hyporheic profiles for the Downstream location suggest some reduction of nitrate and subsequently reduction of sulphate, but this had no effect on surface water values at this location (**Figure 3-7**, **q and ai)**. DOC was consistently low in the hyporheic zone of all locations. The Upstream location results show hyporheic water and surface water concentrations were similar during the Early Summer (~26 mg l^{-1}) and Late Summer (33 mg l^{-1}) with a declining concentration gradient during Mid Summer. The Midstream location did not display any vertical gradient in nutrient concentrations over the summer

months and during Mid Summer the nitrate values of the hyporheic zone were 68% higher than surface water values. These results suggest the nitrate rich deep groundwater is by-passing the riparian zone and upwelling directly into surface water. Hyporheic transformations of reactive elements seem to be highly dependent on flow paths and water residence times in the stream. Similar results presented by Triska et al. (1993) and Hill and Lymbumer (1998) support the hypothesis that relatively high nitrogen and DO and low ammonia and DOC concentrations are characteristic of hyporheic zones with low residence times.

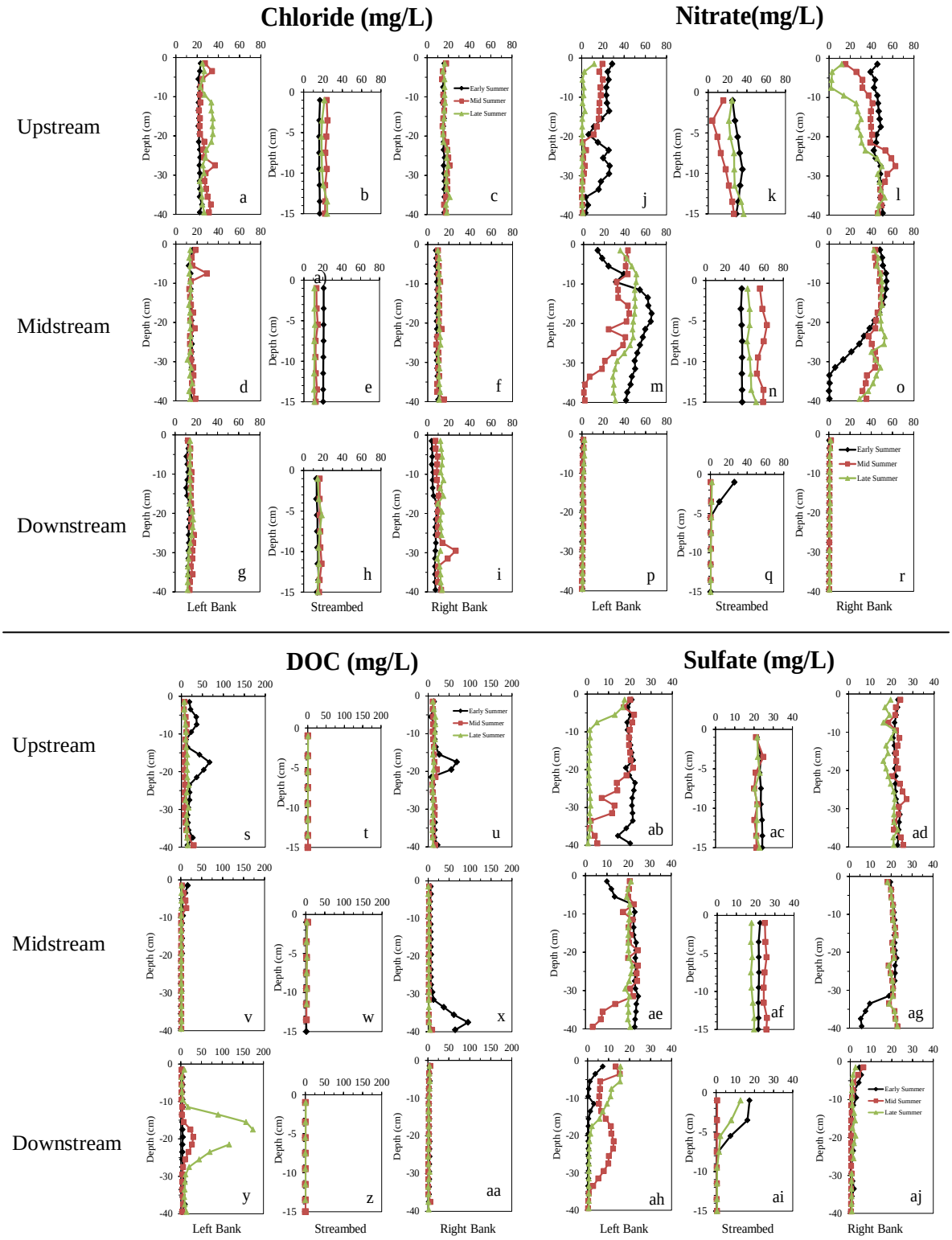

Figure 3-7 (a-aj). Peeper measured concentrations depth profiles for chloride, nitrate, DOC and sulfate. Peepers were sampled during Early-Summer (June 4th), Mid-Summer (July 31st) and Late-Summer (September 3rd) 2013.

4. Conclusion

Determine the effectiveness and preparation techniques of passive (diffusion) water samplers known as "peepers" to collect high spatial resolution of water quality parameters.

There are many factors to consider while sampling pore water chemistry. In order to obtain representative and useful sample results, effective samplers and proper sampling procedures is imperative. This study effectively used diffusion equilibrium samplers (peepers) in the laboratory to establish peeper sampling protocols and equilibrium times (~28days). This knowledge was then translated to the use of peepers in the field to collect high resolution chemical data to study surface-subsurface dynamics.

Investigate the distributions of water quality parameters (chemical and physical) within the surface water and groundwater (riparian and hyporheic zones) of a small groundwater-fed stream.

Riparian buffers are often been described as a sink of reactive elements such as nitrate; this study found groundwater flow paths and low residence times can result in these zones becoming a source of nitrate to receiving waters. Also, chronic high nitrate loading cannot be effectively removed by the riparian or hyporheic sediments without sufficient DOC availability. The ability of near stream zones to mitigate a chronic influx of nitrate is controlled by sufficient electron donors (DOC), groundwater flow paths and subsurface residence times.

The field site, Bauman Creek, is a forested catchment located within the *rare* Charitable Research Reserve in Southern Ontario. During the 2013-2014 sampling period many groundwater and surface water samples exceeded the Ministry of the Environment (MOE, 2003) safe drinking water limit of 44.3 mg l^{-1} of nitrate as well as the Canadian Council of Ministers of the Environment (CCME) Water Quality Guidelines for the Protection of Aquatic Life limit of 13 mg l^{-1} (CCME, 2014). It has been well documented that the legacy of nitrogen rich agricultural fertilizers in Southern Ontario can influence surface water and groundwater far beyond the original agricultural boundaries (Bravo and Hill, 2012;

Hill, 1978; Rudolph and Goss, 1997; Tan et al., 2002). For this reason, more research is needed at this location to identify the source of this nitrate rich groundwater. Further research should also include the potential impact of small headwater streams, such as Bauman Creek, has on the nitrate on the larger Grand River Watershed.

Understand the hydrogeochemistry of a groundwater-fed stream to explain the critical factors that lead to the observed spatial and temporal signature of the pore water chemistry.

The bi-directional exchange of water and solutes at this groundwater-surface water (GW-SW) interface often creates strong redox gradients that influence of biological and physical characteristics of stream and terrestrial systems. Pore water samples displayed a large variation in groundwater chemistry between not only two sampling locations but between peepers in the same location. Consequently, to better understanding this complex spatial and temporal heterogeneity of surface-subsurface exchanges sampling location and timing must be carefully considered.

Upstream to downstream differences of surface water in Bauman Creek displayed minor differences in NO_3^-, NH_4^+,DOC and SO_4^{-2} after the upstream source location which suggests minor retention and transformation of nutrients in this stream and hyporheic zones. In contrast, shallow and deep pore water showed considerable variation in reactive compounds over small distances (<4m between left and right bank). Riparian zone water residence times, seasonally persistent saturation and groundwater upwelling provided heterogeneous conditions for nitrate and sulphate reduction. Groundwater denitrification and sulfate reduction was limited by DOC over all seasons. Overall, this study at Bauman Creek will be invaluable to the creation and application of future nutrient models focusing on surface-subsurface interfaces and time-series data within the Grand River Watershed. This study also provides the first known comprehensive dataset on the groundwater and surface water chemistry of Bauman Creek.

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APPENDIX A – GROUNDWATER SUPPLEMENTARY INFORMATION

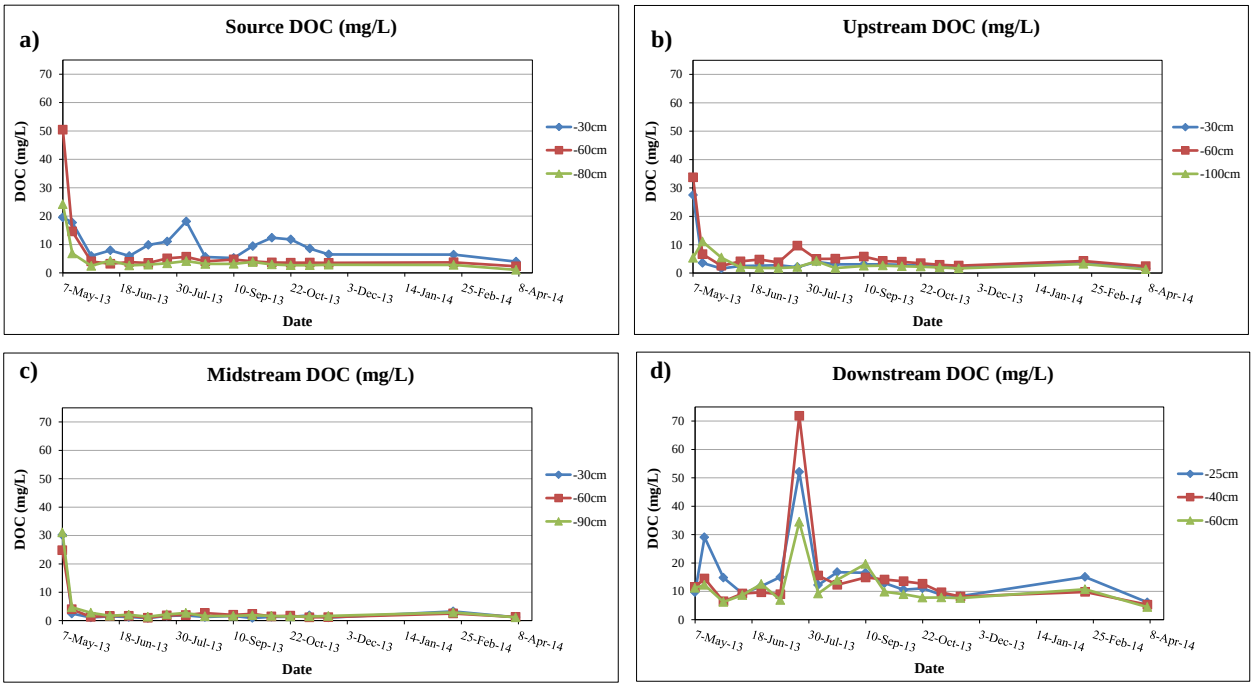


Figure A-1(a-d). Dissolved Organic Carbon (DOC) concentrations in groundwater from Bauman Creek Watershed (piezometers). Sites are as in **Figure 2-5**.

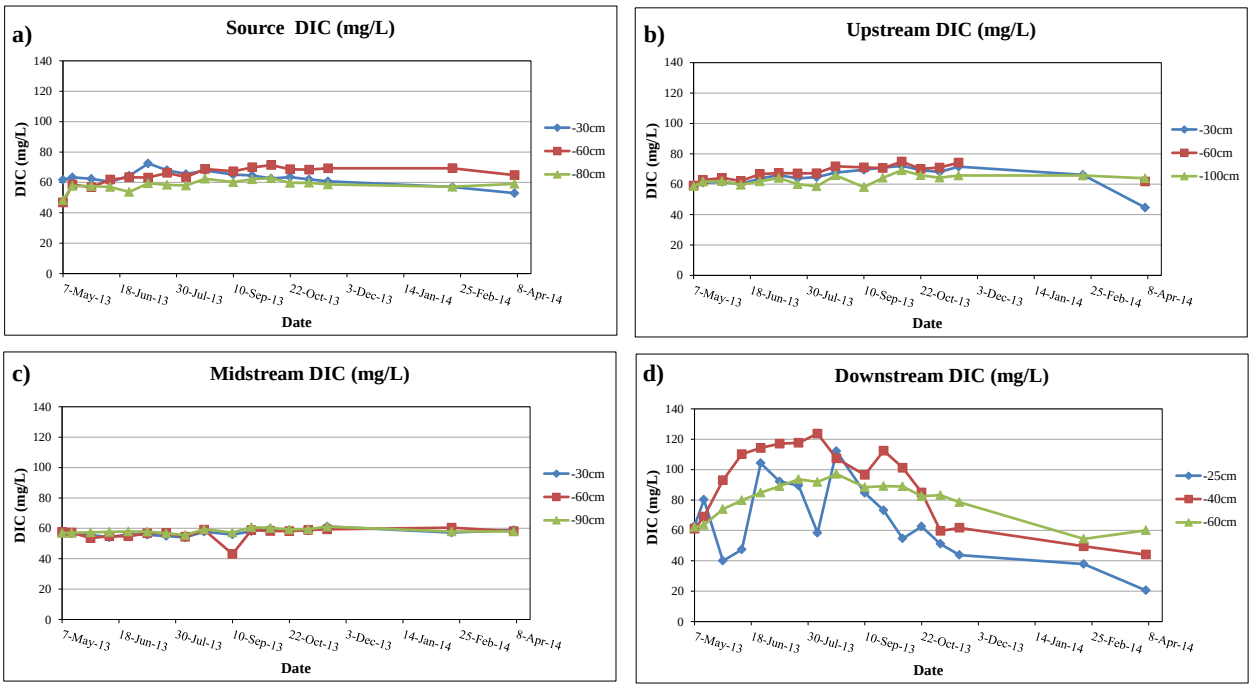


Figure A-2(a-d). Dissolved Inorganic Carbon (DIC) concentrations in groundwater from Bauman Creek Watershed (piezometers). Sites are as in **Figure 2-5**.

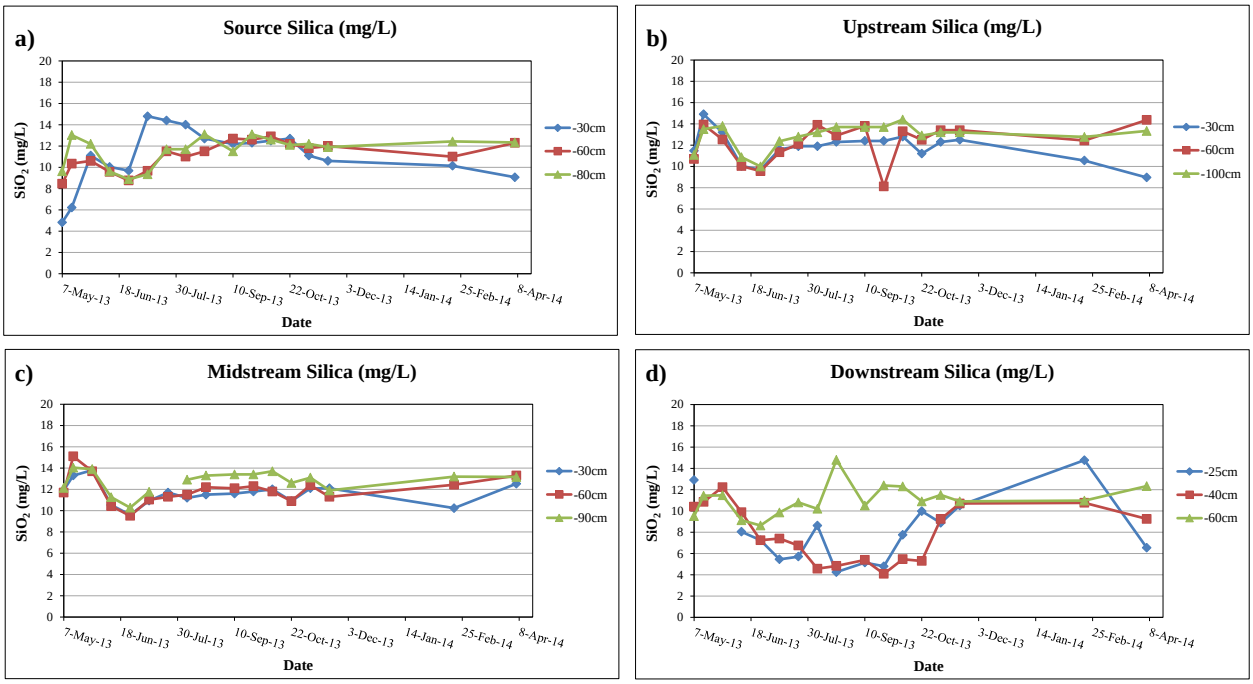


Figure A-3(a-d). Silica (SiO_2) concentrations in groundwater from Bauman Creek Watershed (piezometers). Sites are as in **Figure 2-5.**

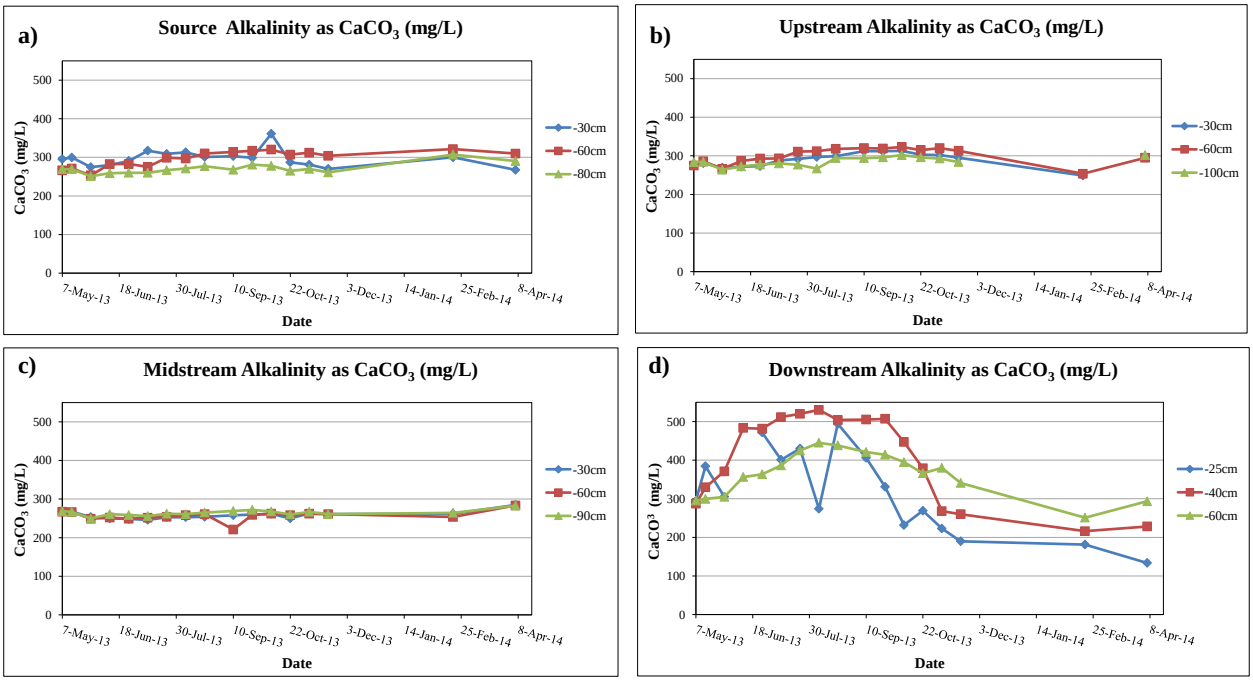


Figure A-4(a-d). Total Alkalinity expressed mg/L as CaO_3 in groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5**.

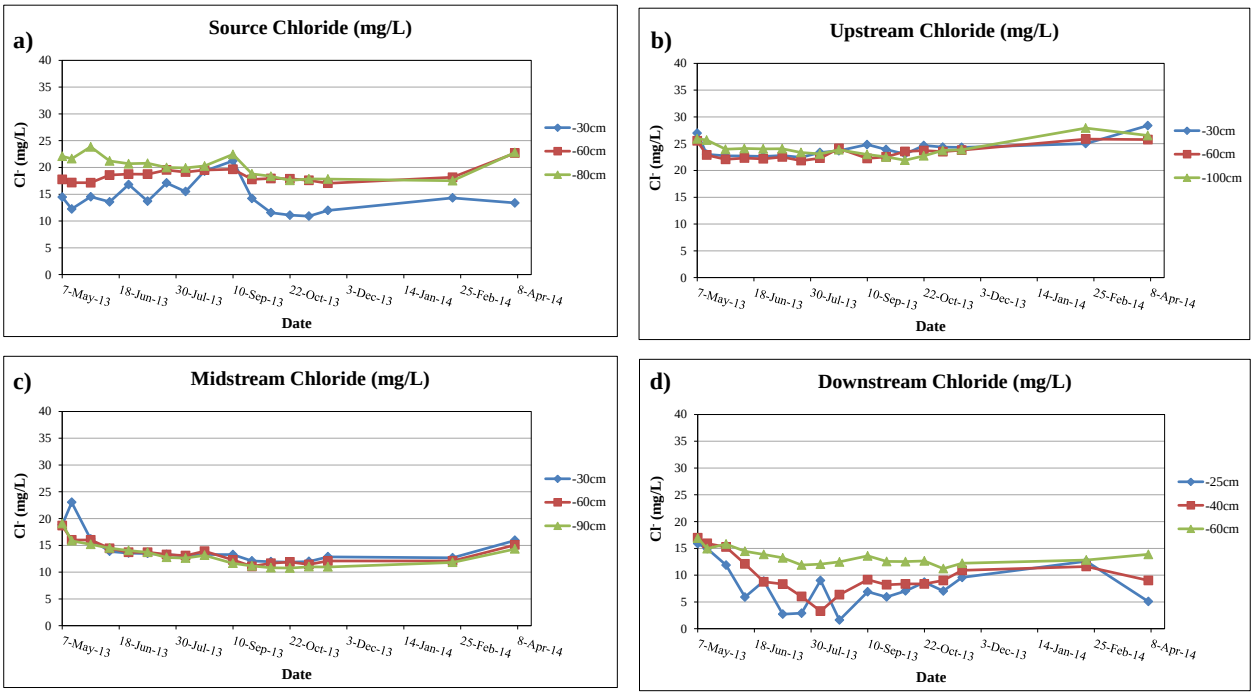


Figure A-5(a-d). Chloride (Cl^-) concentrations in groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5**.

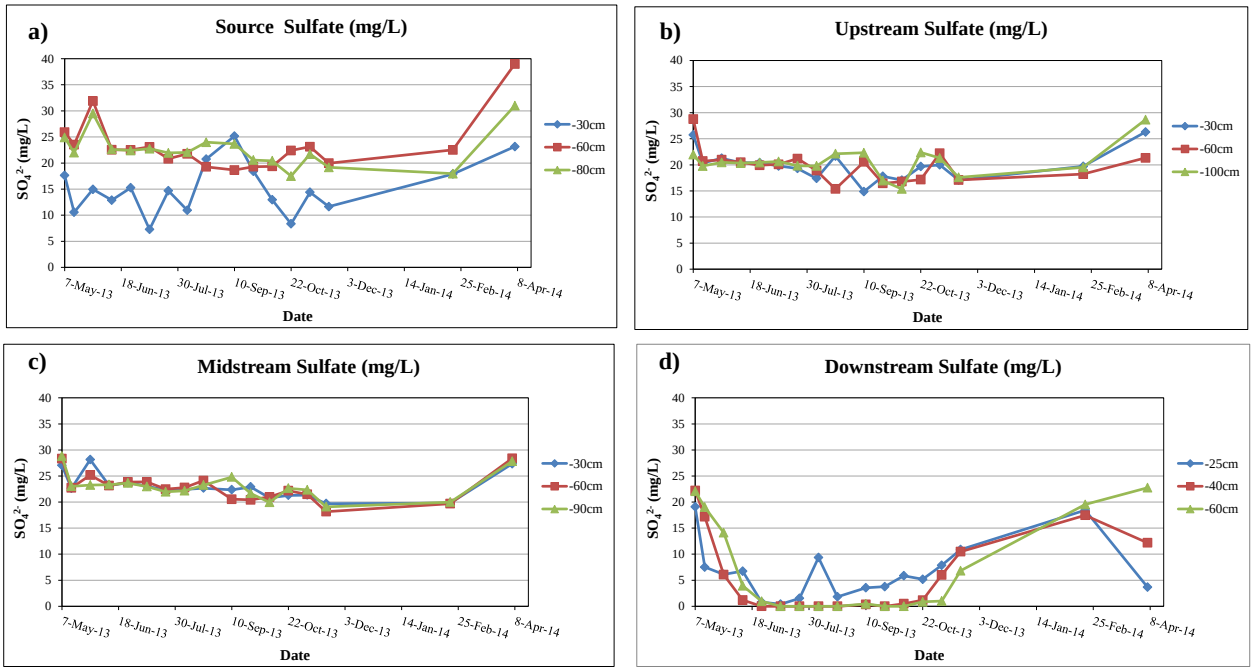


Figure A-6(a-d). Sulfate (SO_4^{2-}) concentrations in groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5**.

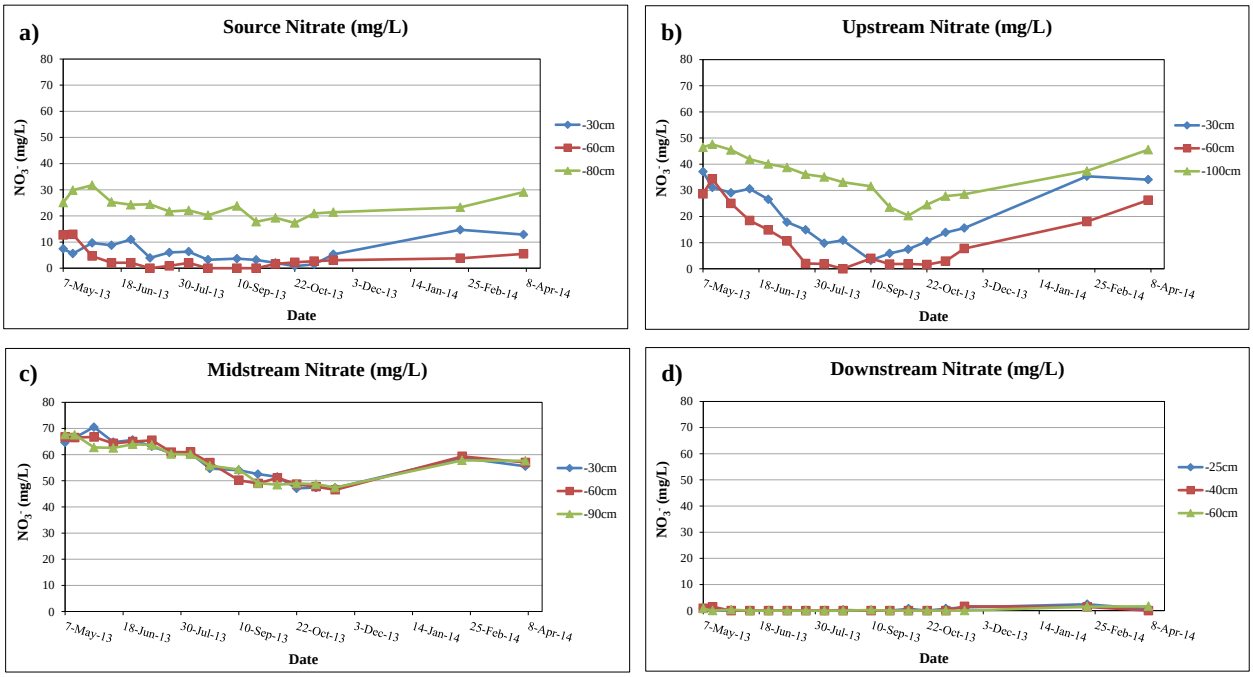


Figure A-7(a-d). Nitrate (NO_3^-) concentrations in groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-6**.

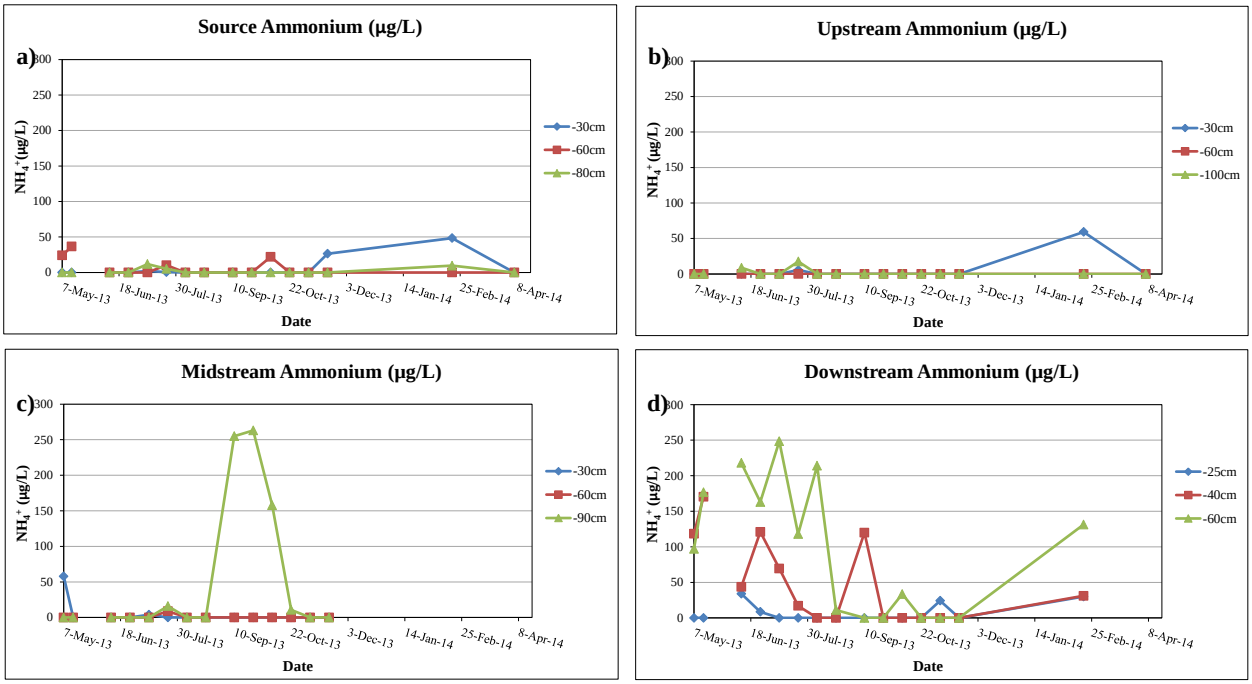


Figure A-8(a-d). Ammonium (NH_4^+) concentrations in groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5.**

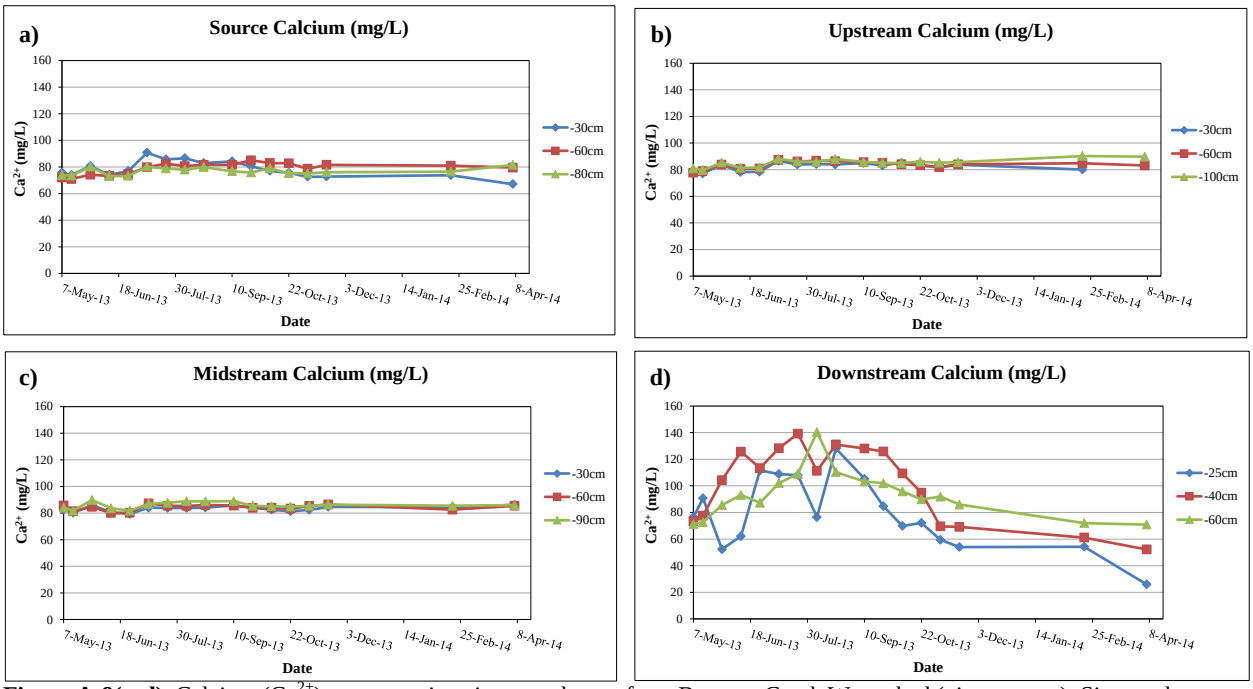


Figure A-9(a-d). Calcium (Ca^{2+}) concentrations in groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5**.

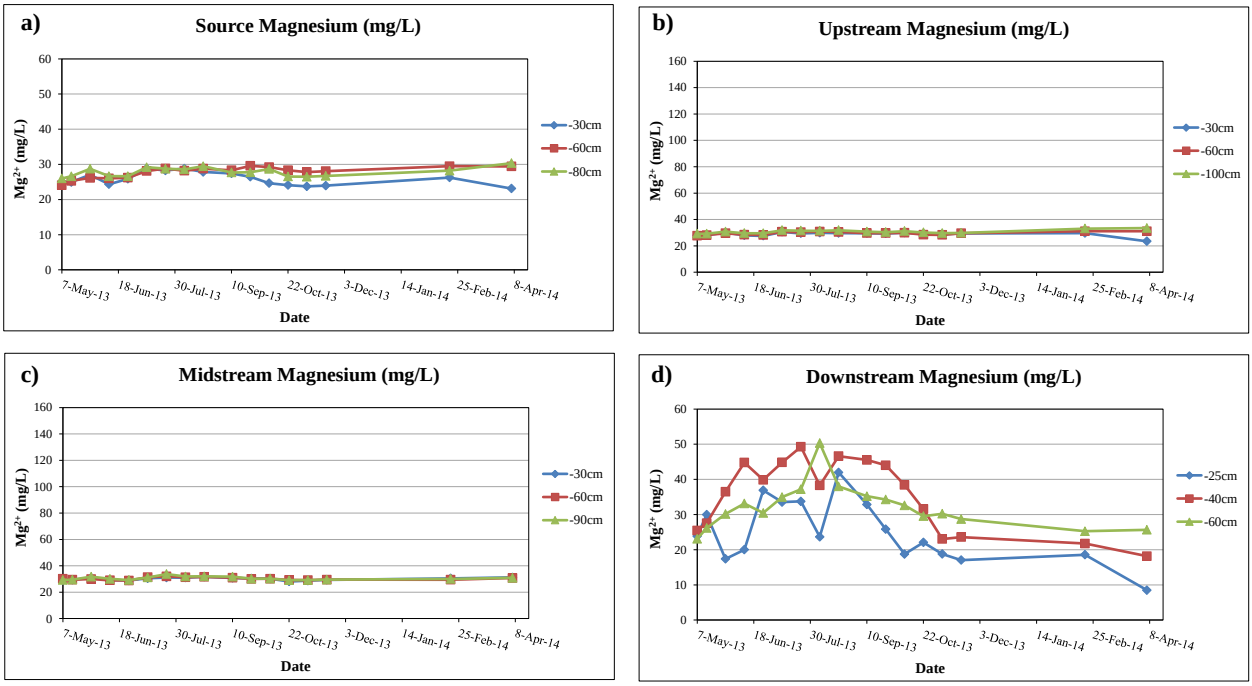


Figure A-10(a-d). Magnesium (Mg^{2+}) concentrations in shallow groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5.**

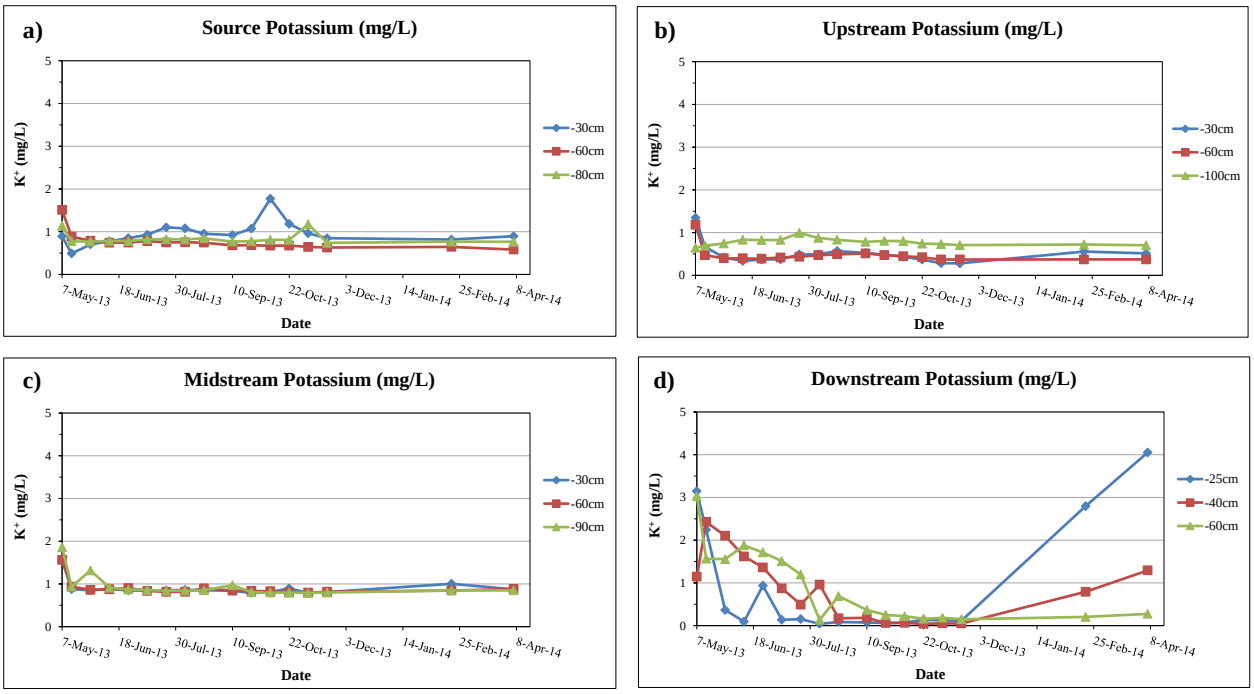


Figure A-11. (a-d) Potassium (K^+) concentrations in shallow groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5**.

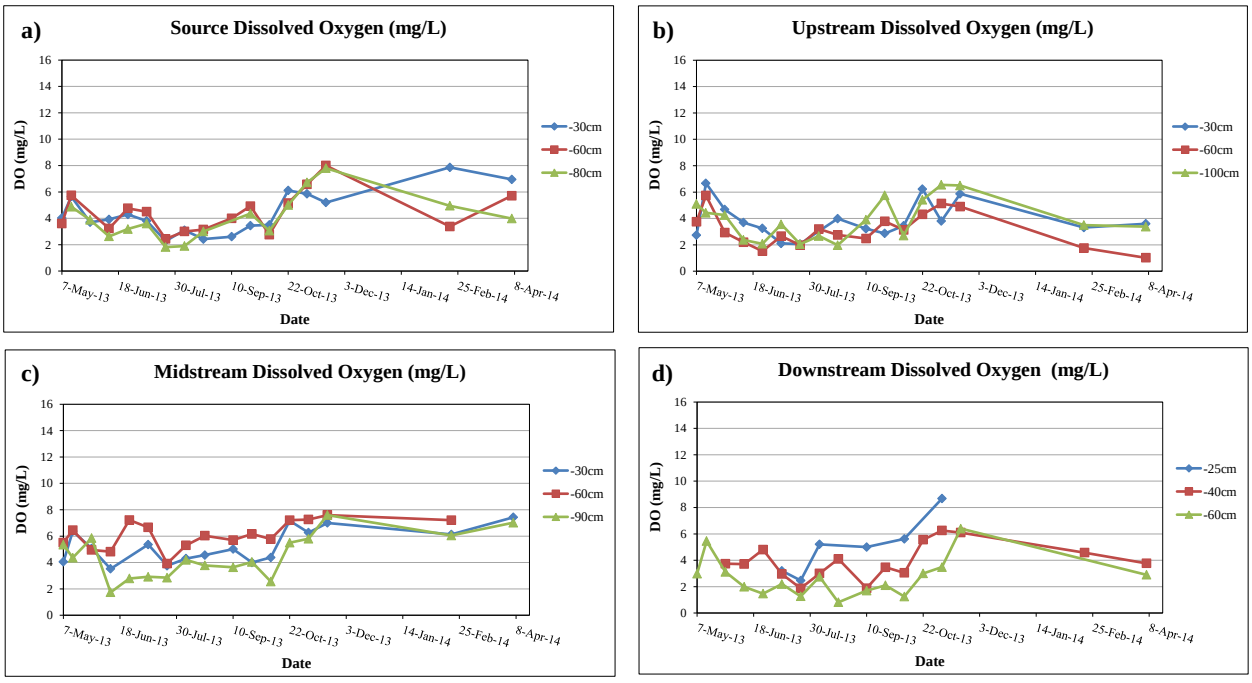


Figure A-12(a-d). Dissolved Oxygen (DO) in shallow groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5.**

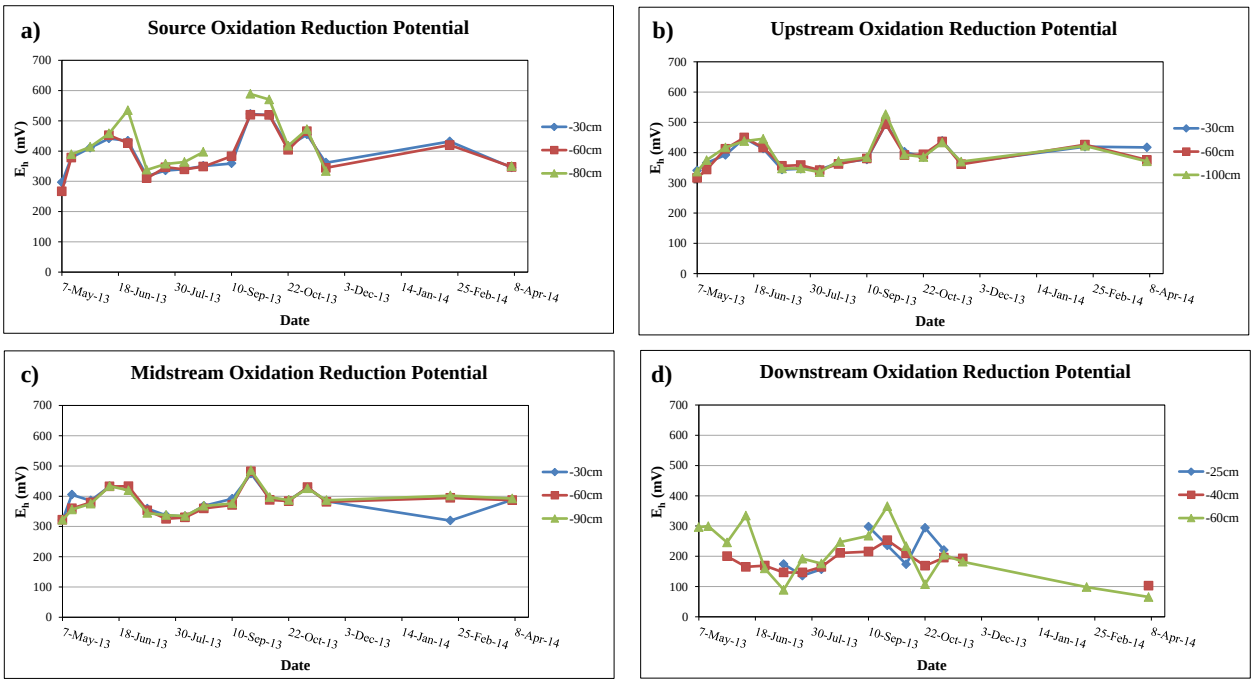


Figure A-13(a-d). Oxidation-Reduction Potential (E_h) of shallow groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5**.

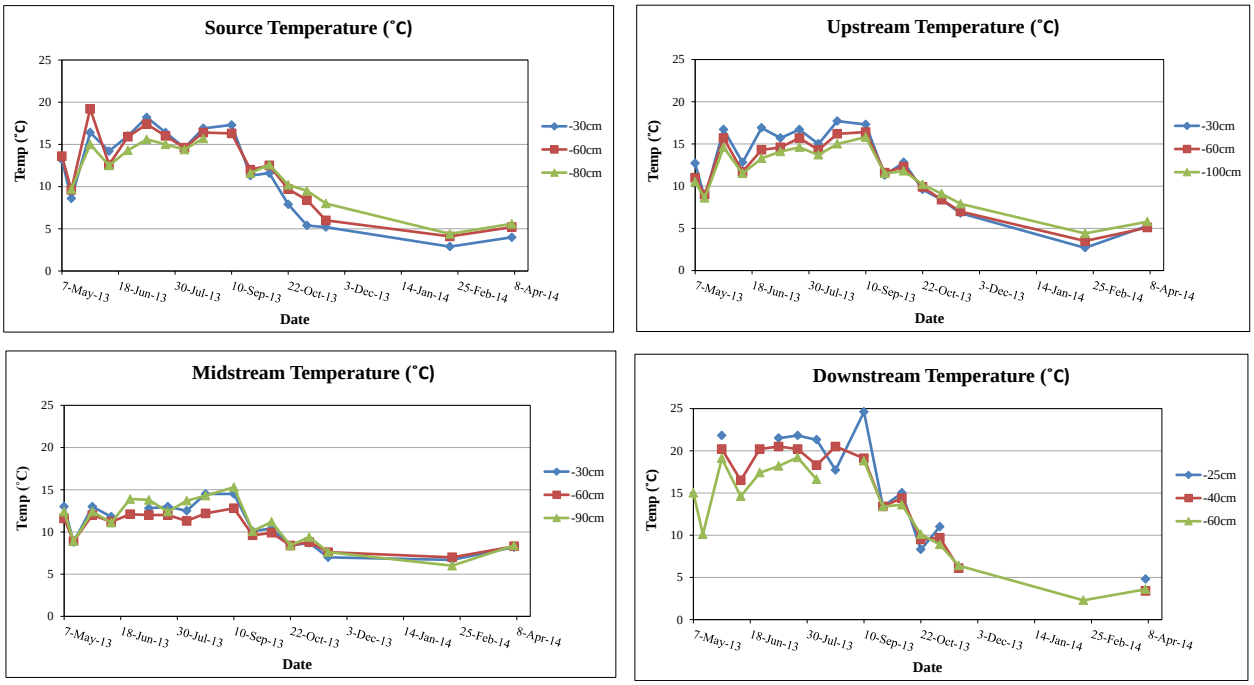
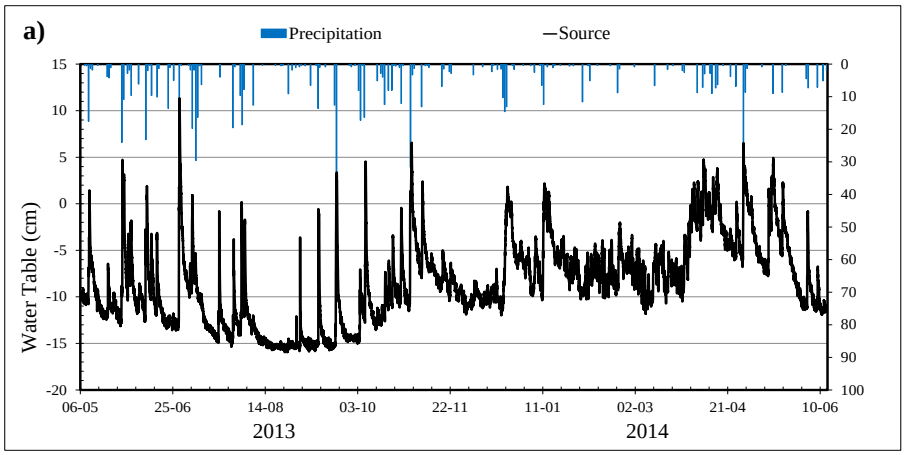
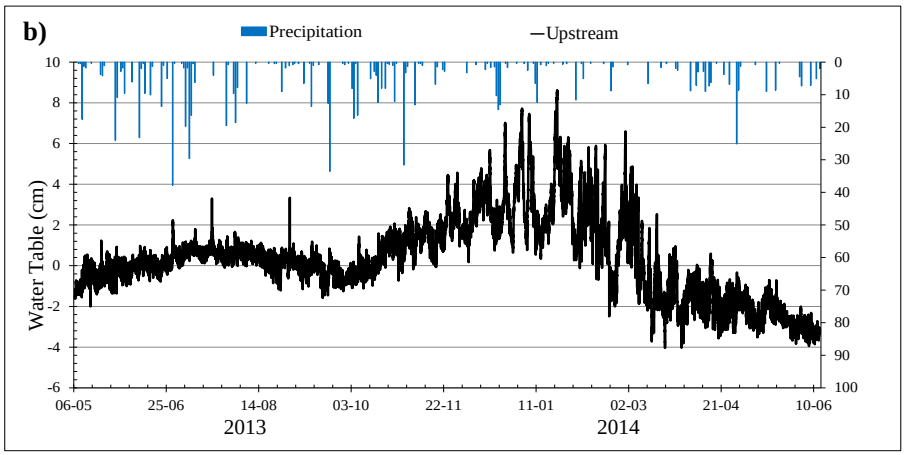
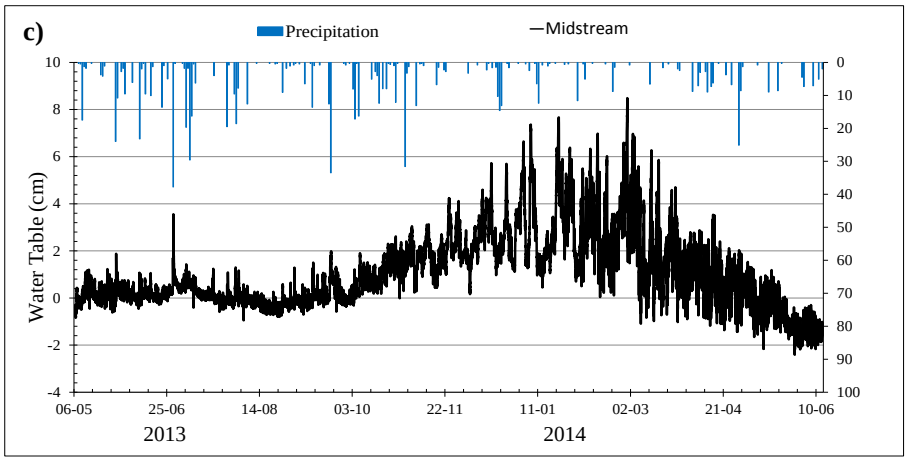
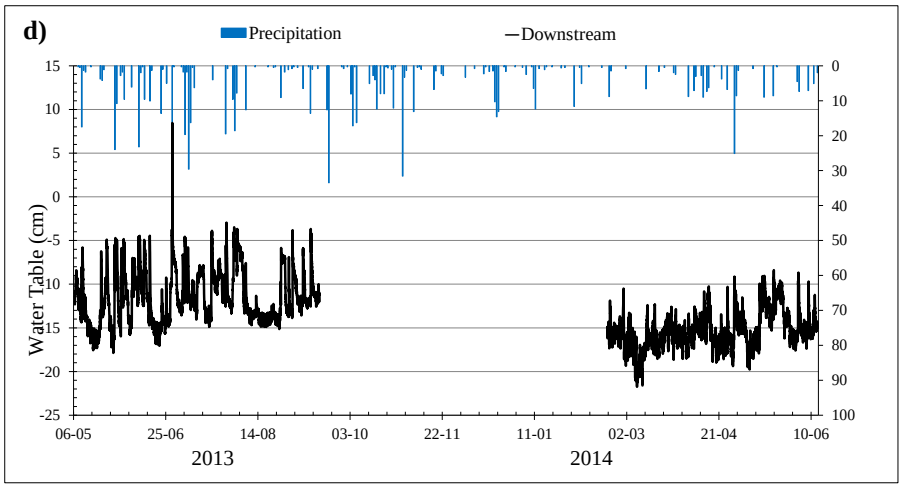


Figure A-14(a-d). Temperature (˚C) of shallow groundwater from Bauman Creek Watershed (piezometers). Site numbers are as in **Figure 2-5**.


a)
Precipitation
Source
Water Table (cm)
15
10
5
0
-5
-10
-15
-20
0
10
20
30
40
50
60
70
80
90
100
06-05
25-06
14-08
03-10
22-11
11-01
02-03
21-04
10-06
2013
2014


b)
Precipitation
Upstream
Water Table (cm)
10
8
6
4
2
0
-2
-4
-6
0
10
20
30
40
50
60
70
80
90
100
06-05
25-06
14-08
03-10
22-11
11-01
02-03
21-04
10-06
2013
2014


c)
Precipitation
Midstream
Water Table (cm)
10
8
6
4
2
0
-2
-4
0
10
20
30
40
50
60
70
80
90
100
06-05
25-06
14-08
03-10
22-11
11-01
02-03
21-04
10-06
2013
2014



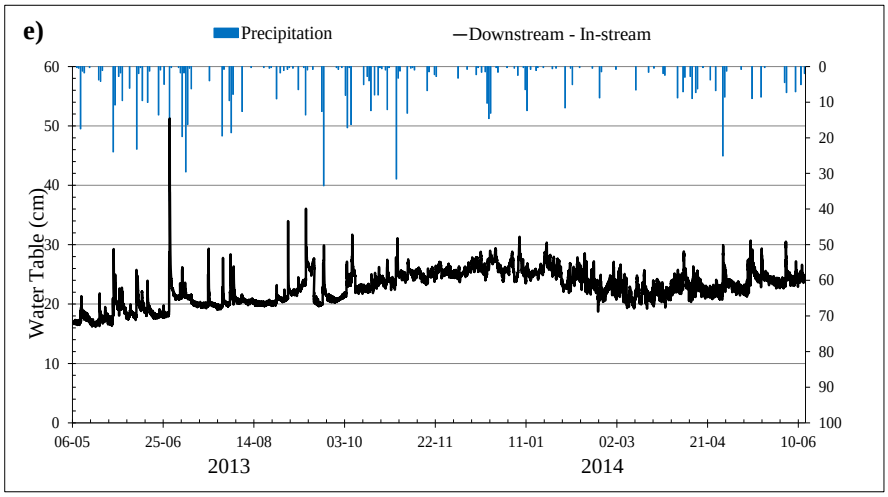


Figure A-15(a-e). Water table levels from four riparian zone sampling locations and one additional in-stream level logger at the Downstream location (e). Site numbers are as in **Figure 2-5.**

APPENDIX B – SURFACE WATER SUPPLEMENTARY INFORMATION

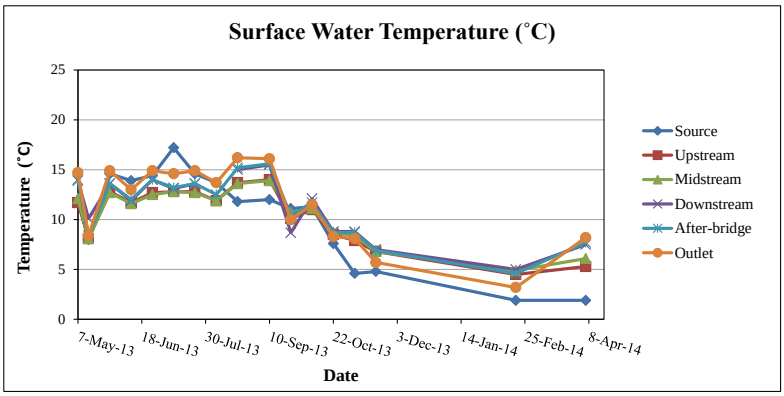


Figure B-1. Surface water temperatures.

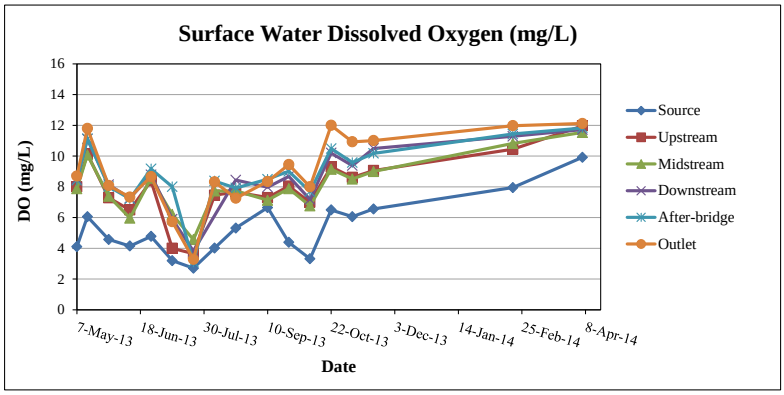


Figure B-2. Surface water dissolved oxygen.

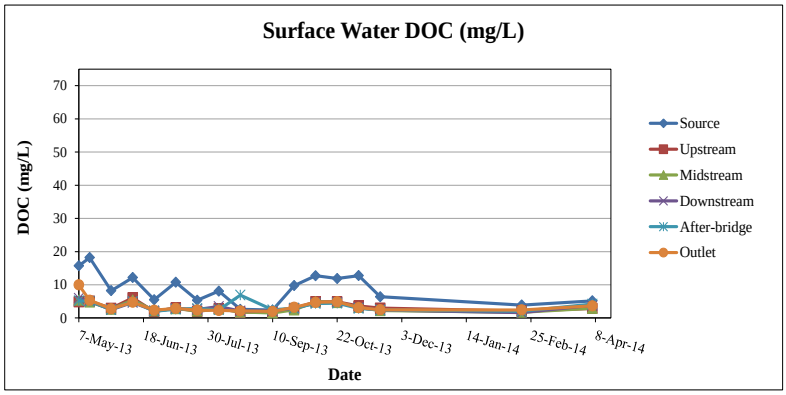


Figure B-3. Surface water dissolved organic carbon (DOC).

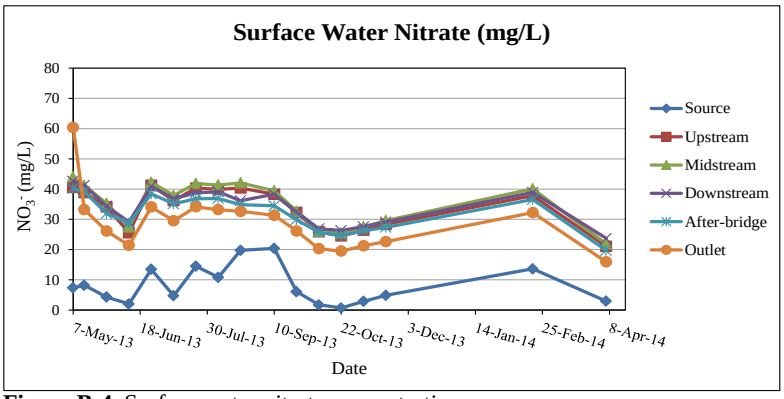


Figure B-4. Surface water nitrate concentrations.

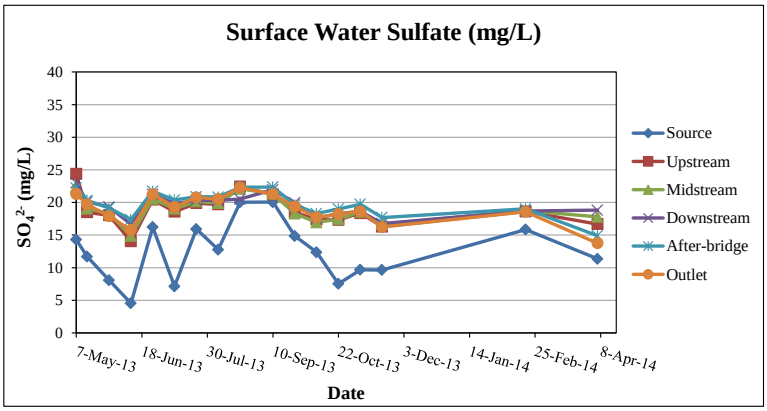


Figure B-5. Surface water sulfate concentrations.

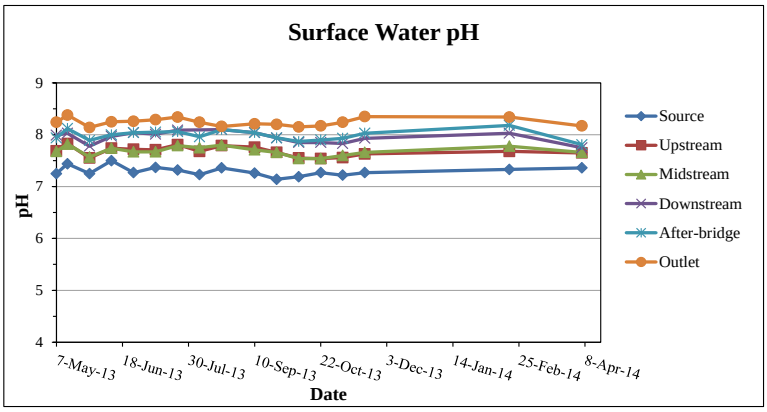


Figure B-6. Surface water pH.

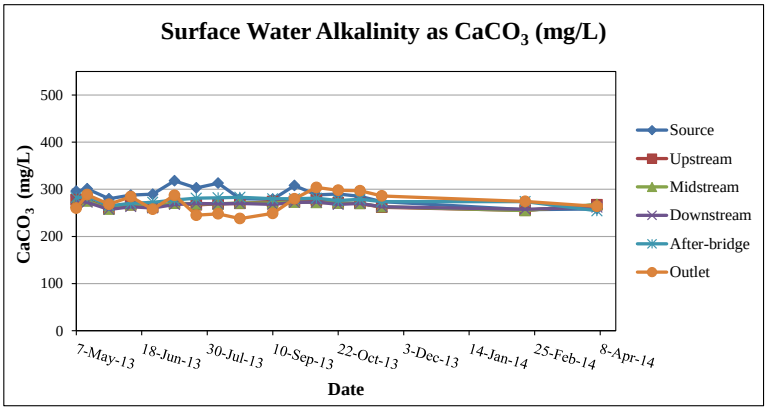


Figure B-7. Surface Water Alkalinity.

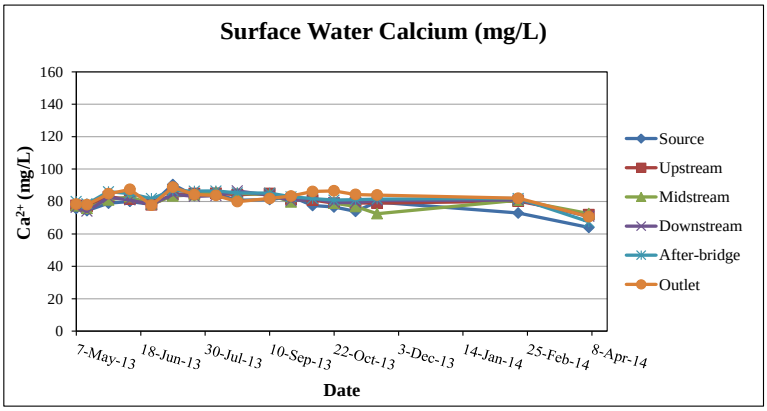


Figure B-8. Surface water calcium concentrations.

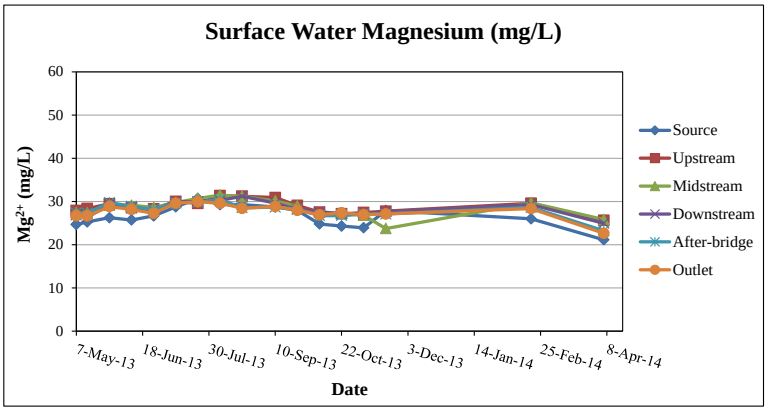


Figure B-9. Surface water magnesium concentrations.

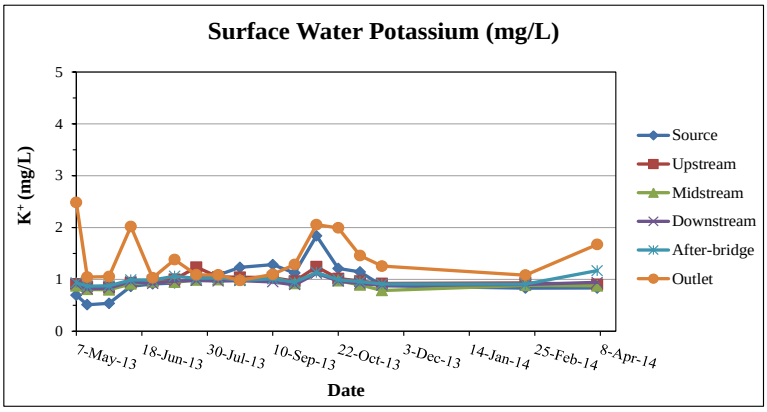


Figure B-10. Surface water potassium concentrations.

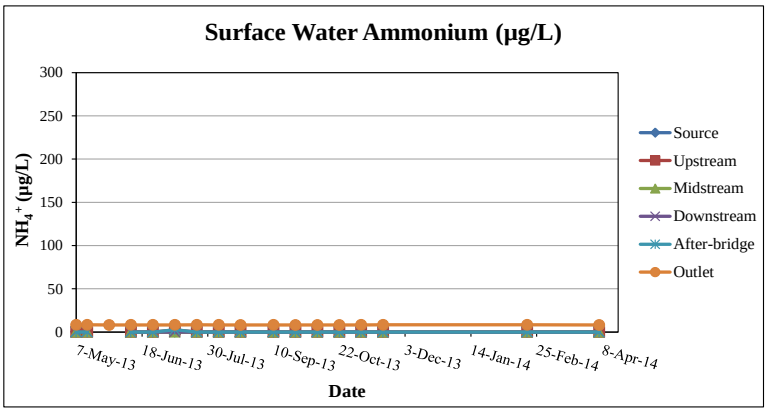


Figure B-11. Surface water ammonium concentrations.

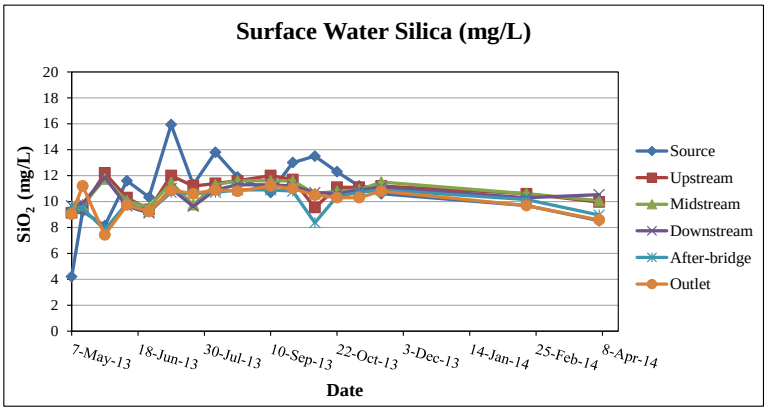


Figure B-12. Surface water silica concentrations.

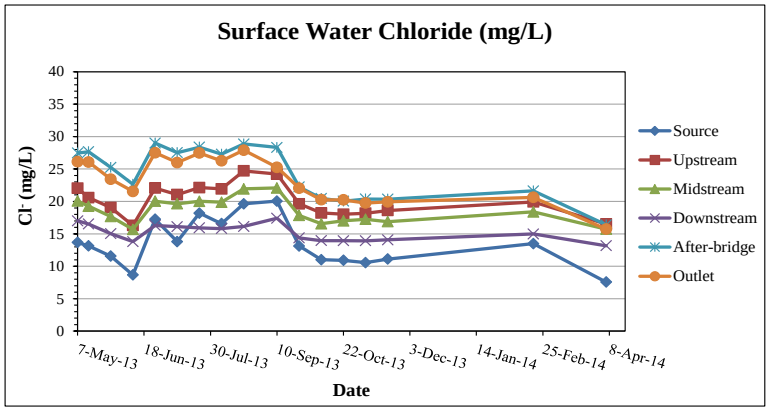


Figure B-13. Surface Water Chloride values

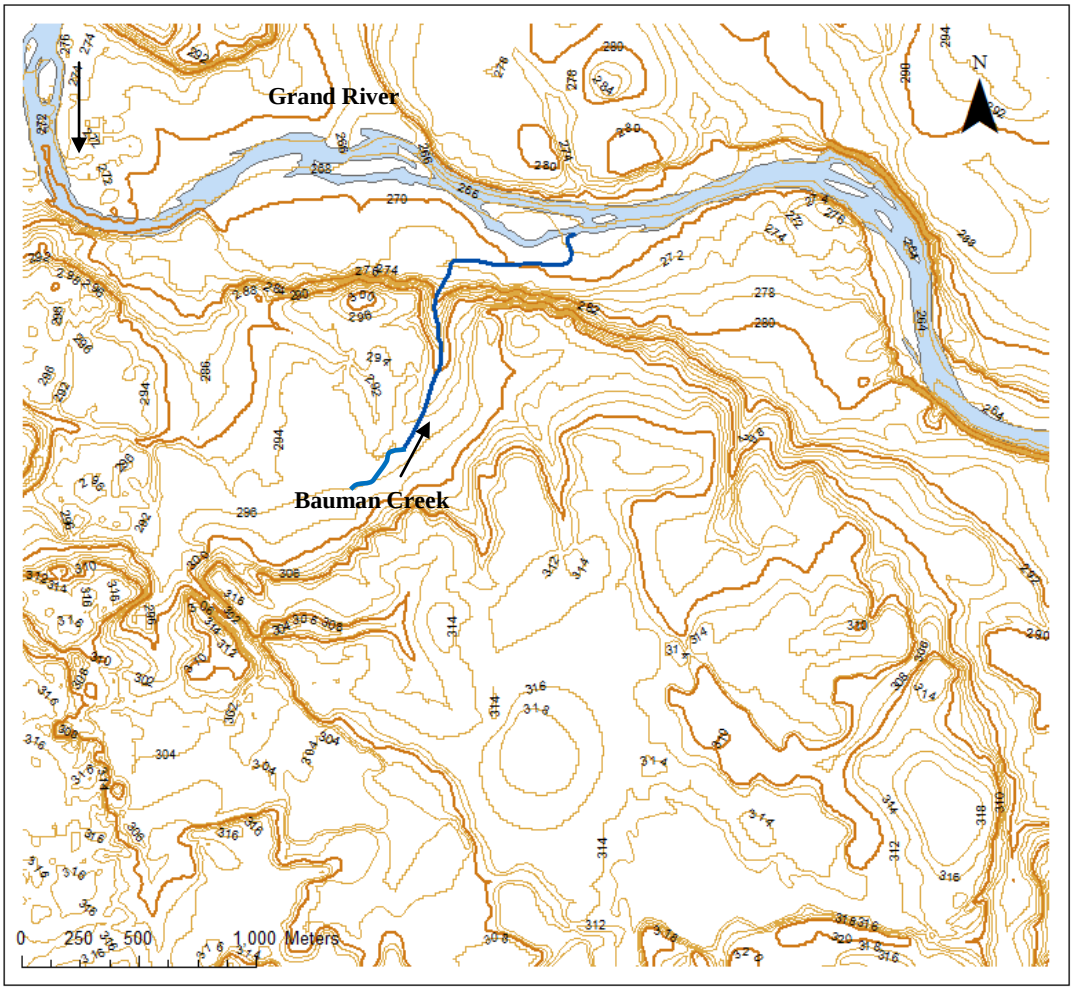


Figure B-14. Contour map (2m) of Bauman Creek field site, Cambridge Ontario.