Charaterization and Locating PCB-Contaminated Groundwater Entering a Stream Overlying Faulted and Folded Crystalline Rock

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CHARACTERIZING AND LOCATING PCB-CONTAMINATED GROUNDWATER ENTERING A STREAM OVERLYING FAULTED AND FOLDED CRYSSTALLINE ROCK

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Hydrogeology

by
David Hahn
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Accepted by:
Dr. Cindy M. Lee, Committee Chair
Dr. Lawrence Murdoch
Dr. James Castle
Abstract

Substantial research focused on Lake Hartwell and a major tributary, Twelvemile Creek, has provided information regarding surface transport, deposition, and biological interactions of PCBs. However, little is understood about the transport of PCBs in groundwater between the contamination site (Sangamo Weston Superfund Site in Pickens, SC) and Town Creek, a tributary to Twelvemile Creek located less than 500 m south of the contamination site. The objectives of this thesis were to 1) locate and measure groundwater influx to Town Creek, 2) determine the concentrations of PCBs in groundwater, 3) identify the colloids present in groundwater and surface water, 4) determine if colloids are adsorbing PCBs, and 5) characterize the basic geology and hydrogeology between Town Creek and the Sangamo Weston Site.

Locations of possible groundwater input to the stream were identified using distributed temperature sensing (DTS) fiber optics placed along ~230 m length of Town Creek down gradient of the Sangamo Weston site in September 2011. A follow up seepage meter and mini-piezometer test in the summer of 2012 was performed to confirm if the DTS was identifying groundwater. Polyethylene strips were used to adsorb dissolved PCBs in groundwater samples collected from two bedrock wells (701 and 702) north of Town Creek, and gas chromatography was employed to determine the concentrations. Colloids from surface and groundwater samples were filtered through 1 μ and 100 kDa filters, respectively, and characterized using FT-IR and SEM. The geology along the creek was mapped for lithology and structure, and hydrogeological data from the site were used to develop hydraulic head maps for both saprolite and bedrock wells.

Results from this research confirmed groundwater inflow between 185 and 210 m upstream of Reece Mill Bridge using seepage meter measurements, and identified a possible
location between 128 and 146 m upstream of the bridge with the DTS. Seepage meter measurements indicated an average flux into the stream of $7.63 \times 10^{-6}$ m/s and mini-piezometers confirmed upward flow into Town Creek. PCB concentrations in groundwater wells averaged 1800 ng/L in well 701 and 6535 ng/L in well 702. Colloid characterization recognized gibbsite, kaolinite, and iron (hydr)oxides in surface water, and montmorillonite and manganese (hydr)oxides in groundwater. The montmorillonite is likely an artifact of the well construction. Geologic mapping documented a thrust fault, folds, fractures, and igneous intrusions along the stream, with rock predominantly made up of gneiss. The head maps produced indicated that groundwater should flow down gradient from the Sangamo Weston site to the Town Creek study area through saprolite if isotropic and homogeneous hydraulic conductivities are assumed.

Head measurements from wells indicated flow towards the stream and seepage meter measurements confirmed flux into the stream consistent with other streams in the Piedmont. Groundwater data suggest that significant concentrations of PCBs are present at the site, and surface water PCB concentrations suggest that groundwater is entering the stream. However, groundwater colloid data may be skewed by the bentonite used during well installation. Initial study of colloid facilitated PCBs has found that adsorption does occur in the groundwater collected, but additional study is required to quantify concentrations.
Acknowledgments

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1 – Introduction

Study of the Sangamo Weston PCB Contamination Superfund Site, and its role in the pollution of the Twelvemile Creek watershed, has produced evidence that groundwater may play a significant role in the transport of polychlorinated biphenyls (PCBs). Recommendations by the Environmental Protection Agency (EPA) and other research to study the groundwater to surface water pathway of PCBs near their discharge point; have led to the need for additional study of the site (USEPA, 2004; Dang et al., 2010). The goal of this thesis is to determine the role of groundwater in the transport of dissolved and possibly colloid facilitated PCBs to surface water, and identify possible groundwater inputs to Town Creek in Pickens, SC.

Polychlorinated biphenyls are a group of anthropogenically produced chlorinated hydrocarbons, which have as many as 209 possible variations in chlorination referred to as congeners (UNEP, 1999). PCBs have a high degree of chemical stability, resistance to thermal breakdown and several oxidants, and are highly hydrophobic (USEPA, 1983). Their characteristics led to widespread use as coolants and lubricants prior to the United States ban in 1979 when they were classified as a persistent organic pollutant (POP) (USEPA, 1979). They are also capable of volatilization and transport through the atmosphere, which may result in wide scale transport and redistribution in the environment (UNEP, 1999).

Gneiss bedrock, saprolite, and soils underlying the Sangamo Weston site act to transport groundwater to the Twelvemile Creek watershed (USEPA, 2004; Garihan et al., 2008). The saprolite, formed from in situ weathering of gneiss and schist, is infiltrated by surface water that may transport contaminants into the subsurface through various flow paths (Buol, 2003). The underlying gneiss is cut by fractures that act as preferential flow paths for groundwater and contaminants. The weathering processes produce mobile inorganic particles on the scale of
micrometers to nanometers called colloids, which are capable of transporting organic contaminants (McCarthy and Zachara, 1989).

Groundwater discharge to Town Creek has not been directly measured at the study site but other streams in the Piedmont have produced valuable seepage flux data, and methods useful in determining vertical gradient. Seepage meters modified for use in streams were deployed in Twelvemile Creek and indicated an average seepage flux of 6.67x10^-6 m/s (Kelly, 2001). Additional seepage measurements in the Piedmont identified average seepage flux values of 4.45x10^-6 m/s in Eighteen Mile Creek (Gebhard, 2010). Murdoch and Kelly (2003) identified mini-piezometers attached to inverted U-manometers as systems capable of rapidly determining vertical gradient within stream sediments overlying rock.

The dominant colloids present in the groundwater near the Sangamo Weston study site are likely inorganic due to the low organic matter content in the soil (0.5 to 1.0%), saprolite (<0.02%), and gneiss/schist bedrock (USDA, 2010). Oxidation of feldspar from the weathering of gneiss has resulted in the formation of kaolinite/gibbsite-rich soils (Buol, 2003). Additionally, the warm wet climate and acidic soils (pH 5-5.5) in the Piedmont enhance the weathering of minerals in gneiss and schist to form manganese and iron (hydr)oxides (USDA, 2010; Buol, 2003).

The evaluation of the Town Creek and Sangamo Weston study site will provide information needed to determine the role of saprolite and fractured bedrock in the transport of PCBs by colloids. Further review of PCBs and their properties is important to this project and will be covered in the literature review. The Sangamo Weston site is within the Piedmont region of upstate South Carolina, and its geology must be critically evaluated to understand its role in colloidal transport.
2 – Literature Review

2.1 – History of the Sangamo Weston Site

The Sangamo Weston/Twelve Mile Creek/Lake Hartwell PCB Contamination Superfund Site in Pickens, SC, has been the site of remediation by contractors hired by Schlumberger, the property owner and responsible party. Two Operable Units (OU1 and OU2) were established by the EPA with OU1 addressing the land-based source areas at the Sangamo Weston Plant and six satellite disposal areas (USEPA, 2004). OU2 addresses the sediment, surface water, and biological migration pathways downstream of the Sangamo Weston Site. The reports (five-year reviews) associated with the OU reviews include information about the methods, findings, and conclusions, and are required by Superfund Law to be released every five years (USEPA, 2004). Identification of newfound issues or possible improvements is discussed and recommendations for additional research are listed. The most recent published review was conducted between October 2003 and August 2004 and specifically addressed PCBs present in sediments and aquatic biota (USEPA, 2004).

Sangamo Weston manufactured capacitors using dielectric fluids, which contained PCBs that reportedly enhanced performance and stability (USEPA, 1994). The PCBs used by the company were made up primarily of Aroclors 1254 (five Cl), 1242 (four Cl), and 1016 (three Cl), which are specific mixtures of PCBs. During production some of the waste containing PCBs was disposed of at the site in two wastewater lagoons that drained into Town Creek. According to EPA estimates, nearly 181,000 kg of PCBs was discharged to the stream between 1958 and 1977 (USEPA, 1994).

The Sangamo Weston site was added to the National Priorities List (NPL) in 1990 and remedial action began in 1993 (USEPA, 1994).
Weston site resulted in contaminated sediment removal, testing of sediment concentrations, and groundwater monitoring/sampling between the site and Town Creek using saprolite and bedrock wells (Figure 2.1). Additionally, baskets containing a freshwater clam, *Corbicula*, were placed along Town Creek and Twelvemile Creek to study bioaccumulation in sediment dwellers. The review in 2004 indicated that the majority of the sediment along Twelvemile Creek had reached the 1 mg/kg cleanup goal, but higher concentrations were still found in Town Creek (USEPA, 2004). The 2004 review also indicated that study of groundwater to surface water pathways would begin that year to determine if PCBs were being transported through groundwater to the stream.

Figure 2.1. Topographic and well map of the Sangamo Weston Site and Town Creek study site. Saprolite monitoring wells indicated by MW. Bedrock monitoring wells indicated by RW. Modified from TRC (2011).
Additional investigation of Town Creek near the contamination site using semipermeable membrane devices (SPMDs) suggested that groundwater is a likely source of additional input of PCBs. Dang et al. (2010) measured the enantiomeric fraction of dissolved PCBs collected by the SPMDs. These PCBs may be racemic, 50:50 mixtures of enantiomers, or nonracemic mixtures formed through biotransformation or metabolic processes. Dang et al. (2010) found two racemic PCBs in the SPMDs placed in Town Creek near the contamination site, suggesting that unaltered PCBs are entering the surface water. Additionally, these racemic PCBs were found in high concentrations unavailable in the atmosphere suggesting that groundwater is a probable source.

2.2 - PCB Chemistry, Transport, and Adsorption

PCBs are a class of compounds with a biphenyl structure made up of two benzene rings connected by a single bond, with variable degrees of chlorination (UNEP, 1999). The ten possible chlorination sites allow for up to 209 congeners to exist, with 50 commonly produced congeners (Figure 2.2). The large variability in chlorination affects the mass and chemical properties of each congener.

The density, mass per volume, of PCBs (>1.182 g/mL) is greater than water (1 g/mL) due to the high mass of the attached chlorines and carbon rings (UNEP, 1999). Compared to strong hydrogen bonding found in water due to the bipolarity (opposing charges of hydrogen and oxygen), PCBs have van der Waals bonds (1/10th the strength of H-bonds) in pure organic liquid (Schwarzenbach et al. 2003). The strong contrast in bond strength results in excess heat energy or enthalpy between water and PCBs, and systems in equilibrium prefer low values. The excess enthalpy produces low solubility for PCBs in water and low dissolved transport.
Vapor pressure is the pressure of a system at thermodynamic equilibrium that is used to determine the amount that will enter the gas phase. The bonds in the pure organic liquid form of PCBs result in vapor pressure values ranging from $10^{-4}$ to $10^{-12}$ atm at 25 °C (UNEP, 2010).

![Figure 2.2. The structure of a PCB molecule. Note that each position on the rings can be substituted with a chlorine at (i.e., each PCB molecule can contain up to ten chlorine atoms). Modified from UNEP (1999).](image)

The tendency of PCBs to resist shear or tensile stress gives them a high viscosity in their natural organic liquid phase (Pfafflin and Ziegler, 2006). Highly viscous compounds have increased resistance to flow, which is the result of intermolecular forces and the temperature within a system. PCBs at temperatures common in groundwater (14 °C) maintain strong forces between molecules, increasing their resistance to flow.

Low solubility and high viscosity in PCBs makes advection a slow process, resulting in long residence times (decades) within porous media. The low solubility of PCBs shifts the system towards equilibrium and separates them from water, while the higher density results in the accumulation at the bottom of saturated aquifers (Spitz and Moreno, 1996). These properties limit PCB transport through advection unless they are sorbed to a mobile colloid or solid.
Colloid adsorption occurs due to intermolecular forces and the strong hydrophobic characteristics of PCBs. PCBs separate from water to minimize the excess enthalpy, and often bond to mobile particles in groundwater. Sediments and colloids in porous media form van der Waals bonds with PCBs and decrease the enthalpy (Schwarzenbach et al., 2003). Colloids also undergo van der Waals adsorption to PCBs in a process called hydrophobic bonding (Figure 2.3), and readily transport them through groundwater (Qingyu et al., 2001).

![Figure 2.3. PCB transport via colloids. (1) Increase in ionic strength mobilizes colloids, (2) PCBs interact with colloids and form van der Waals bonds, (3) Adsorbed PCBs are transported with colloids. Modified from Ryan and Elimelech (1996).]

2.3 – Hydrogeological and Geologic Setting

The former Sangamo Weston plant site is located in the town of Pickens, SC, which lies in the northwest corner of the state in the Piedmont physiographic province. This region of gently rolling hills extends from central Alabama to New Jersey, and is bordered on the west by the Appalachian Mountains and on the east by the Atlantic Coastal Plains (USGS, 1990). Metamorphic and igneous rocks dominate the lithology in the Piedmont, with gneiss and schist common in northwestern SC (Figure 2.4). The bedrock is commonly overlain by to 10 to 15 m of saprolite and soil, with alluvium present in stream valleys (USGS, 1990).
The hydrogeology of the research site is similar to that in other sections of the Piedmont Province (Harned and Daniel, 1989) (Figure 2.5). Groundwater recharge occurs as water percolates into the unsaturated soils and saprolite overlying the bedrock. Water reaching the water table may be transported through saprolite or fractured rock. The hydraulic head generally decreases in the direction of streams where groundwater discharge occurs. Average groundwater discharge to streams has been found to range from $4.45 \times 10^{-6}$ to $6.67 \times 10^{-6}$ m/s in streams near the research site (Kelly, 2001; Gebhard, 2010). These streams are commonly shaped by faulting and contacts between rock units when saprolite and sediments are not present (Daniel and Sharpless, 1983).
Figure 2.5. Conceptual model of groundwater transport to streams in the Piedmont (Daniel and Sharpless, 1983).

The bedrock of the Piedmont often contains fractures that allow fluid flow and groundwater transport (McKay et al. 2002). These crystalline rocks commonly have high angle fractures that intersect, which increases water movement (USGS, 1990). Fracture density generally decrease with depth due to the sealing action of lithostatic pressure. Horizontal fractures, likely formed by stress-relief, may also be found in the crystalline rock of SC and act to transport groundwater (NRC, 1996).

The Sangamo Weston site and Town Creek are situated in a region of the Piedmont dominated by biotite; quartzo-feldspathic gneiss and amphibole; and migmatic, schistose, muscovite-biotite gneiss (Garihan et al., 2008). At the study site, Garihan et al. (2008) identified the Table Rock gneiss and Tallulah Falls Amphibolite formations contacting at a thrust fault (Figure 2.6). Tens of feet of saprolite overlie the metamorphic rock at the study site and tapers...
in the direction of Town Creek. Fine deposits of sand are prominent downstream of the site, and partially overlie the rock in Town Creek.

Figure 2.6. Geologic map of the Town Creek study area. The Sangamo Weston site and waste water lagoons are identified in the top left corner. Modified from Garihan et al. (2008).

2.4 – Colloid Formation

The sediments surrounding Town Creek are generally low in organic matter indicating the primary colloids responsible for PCB transport are likely inorganic (USDA, 2010). Gneiss and schist in the region contain quartz, potassium feldspar, amphiboles, biotite, and muscovite (Garihan et al., 2008). The potassium feldspar and mica found in the rock weathers to form
kaolinite in the saprolite (Figure 2.7). This microscopic weathering process, which progresses vertically from the bedrock, occurs as feldspar alters to gibbsite, gibbsite to halloysite, and halloysite to kaolinite (Buol, 2003). Continual erosion of kaolinite rich soils produces colloid sized particles capable of groundwater transport.

Figure 2.7. Effects of weathering on aluminosilicate minerals (Langmuir, 1997).

Iron/manganese (hydr)oxides may also be found at the study site due to the weathering of rock found at the study site. The warm and wet climate of South Carolina has dissolved biotite and released iron that was rapidly oxidized to ferric ($\text{Fe}^{3+}$) oxide (Buol, 2003). Water soluble ferrous ($\text{Fe}^{2+}$), is formed when ferric oxide is reduced during microbial respiration, resulting in leaching into subsurface sediment and groundwater. Similarly, manganese is weathered from metamorphic minerals and (hydr)oxides of both metals are produced.
2.5 – Colloid Mobilization and Transport

Changes in fluid chemistry play a significant role in the release and mobilization of colloids into fluid. Assuming that the chemistry within a system permits mobilization, the flow rate becomes a significant influence in both colloid interaction time with the matrix and the rate at which they flow. Both chemical and physical changes control interactions and the quantity of colloids in a groundwater system.

The mobilization of inorganic silicate colloids like kaolinite is often controlled by ionic strength (McCarthy and McKay, 2004; McCarthy and Zachara, 1989). Kaolinite suspension is frequently controlled by the concentration of cations like Na\(^{+}\) and Ca\(^{2+}\) in solution. Most clay and colloid sized particles have a net negative charge making them electrically attractive to cations in solution. Divalent cation like Ca\(^{2+}\) can bond to the surface of colloids and break the monovalent interlayer cation bonds between clays. The reaction may mobilize colloids into groundwater with high ionic strength (McCarthy and McKay, 2004).

Minerals that precipitate from groundwater may also act as colloids. Saturation of groundwater with compounds like iron (hydr)oxides may result in their precipitation within porous media (McKay et al., 2002). These minerals can then be mobilized by an increase in ionic strength and bond with contaminants. Dissolution of a cement material through changes in pH or ionic strength can also release colloids immobilized within the cement (McCarthy and Zachara, 1989).

Fractures within rock or saprolite provide zones of preferential flow and the potential for rapid transport of colloids under ideal conditions (McKay et al., 2002). Colloids flowing through fractures have less contact with matrix particles that may reduce transport rates via friction or adsorption, which increases both the range of colloid transport and the rate of transport. During
colloidal flow through fractures PCB adsorption may occur, allowing rapid transport of PCBs through groundwater (Qingyu et al., 2001) (Figure 2.8).

![Conceptual model of PCB and colloid interactions within an open fracture](image)

Figure 2.8. Conceptual model of PCB and colloid interactions within an open fracture.

### 2.6 – Distributed Temperature Sensing

Distributed temperature sensing (DTS) is a process using lengths of fiber optic cable up to tens of kilometers in length to identify fluctuations in temperature. Sensors connected to the fiber optics are capable of detecting temperature changes to a resolution of 0.01°C every meter (Selker et al., 2006). Such precise measurements allow characterization of processes involving both groundwater and surface water (Constanz, 1998; Selker et al., 1998; Suarez et al., 2011a). The capabilities of DTS allow for the detection of both abrupt and broad input of groundwater to streams.

The basic principles of DTS are dependent on the transfer of light energy through the fiber optic cable used. A light pulse emitted from a laser is sent through a single fiber of a duplex (two fiber optic cables in one wire) cable to an end point, which reflects the light back to the DTS through the second fiber optic. The majority of the light reflects back at the same wavelength, but some wavelengths are altered by temperature (Selker et al., 2006). The process, known as Raman-backscatter, produces longer wavelengths (Stokes backscatter) and shorter wavelengths (Anti-Stokes backscatter). The Anti-Stokes backscatter has an amplitude linearly
dependent on temperature, while the Stokes backscatter does not (Selker et al., 2006). By taking the ratio of Stokes/Anti-Stokes, the temperature can be determined for any point along the cable.

A study by Constanz (1998) of alpine streams indicated that the temperature could be affected by the input of groundwater when stream volumetric flow rate was low. Based on this work, Selker et al. (2006) studied a first-order stream using DTS to quantify both stream temperatures dynamics and groundwater inflow. The DTS detected four groundwater locations in the stream where the cable was near exposed vertical bedrock.

The stream research done by Constanz (1998) and Selker et al. (2006) indicated that Town Creek would be a good candidate for distributed temperature sensing. The low volumetric flow rate of Town Creek during summer months allowed the DTS to capture slight changes in stream temperature related to groundwater input. Additionally, the low volumetric flow rate decreased the chance of cable displacement along the stream. The ability of the system to detect abrupt changes in stream temperature related to groundwater input from exposed rock also indicated that it would work well, since large sections of the Town Creek study area overlie bedrock.

3 - Materials & Methods

The methods used for this research produced data regarding the transport of PCBs through groundwater to Town Creek from the Sangamo Weston Superfund site. A basic characterization of the geology and hydrogeology was completed to determine where groundwater would likely enter the stream from both the saprolite-bedrock interface and bedrock fractures. The dissolved fraction of PCBs in groundwater was measured from two wells, and previous research data from the surface water PCBs were considered. The colloids present in the
surface and groundwater were characterized, and the associated concentrations of PCBs were determined.

3.1 - Characterizing basic Geology and Hydrogeology

The geology and hydrogeology of the Town Creek study area were surveyed to determine where groundwater likely enters the stream. Characterization, measurement, and mapping of the rock along the stream bed were focused on determining how the geology could influence the formation of fractures. Additionally, information regarding the surface and subsurface geology and hydrogeology from well logs was provided by TRC (TRC Companies, Inc., Greenville, SC).

3.1.1 - Town Creek Geologic Mapping

Based on reconnaissance of Town Creek geology, it was determined that the ideal study area would extend approximately 250 m upstream of the bridge located at the corner of Reece Mill Road and Sangamo Road (Figure 3.1). This section of the stream was also ideal due to the surface water PCB data collected by Dang et al. (2012, unpublished), its proximity to several TRC wells, and its location downhill of the waste water lagoons. Surface sediments along the stream were visually characterized for major grain sizes (sand, pebble, cobble, and boulder, for example) using grade scale classification in areas where bedrock was not exposed (Wentworth, 1922). Bedrock exposed in the stream was also noted during the examination of the site. The process was repeated at approximately 7.5 m intervals upstream of the bridge and a simplified sediment cover map was developed along the stream.
Figure 3.1. Map of study area near Pickens, SC with four flow rate test locations. Google Maps (2012).

The 250 m stretch of stream used for the sediment map was then surveyed for structural geology. Strike and dip data for bedrock and plunge for folds were collected, and fracture location and orientations were noted. Measurements of rock and fold orientation were collected using Rocklogger v1.41 on a Motorola Droid X, and fracture orientation was determined using a compass.

A lithology examination of the bedrock along the stream study area was completed to characterize the rock present. A map of the site by Garihan et al. (2008) was consulted and used for comparison. Hand samples and in situ study of the rock was performed via visual investigation and under hand lens. Mineralogy and foliations were primarily used to determine the presence of metamorphic rock, while mineralogy and grain size was employed to characterize igneous rock. Contacts between the major metamorphic rocks were located, and igneous intrusions were noted. Using structural and lithology data collected along the stream, a geologic map of the stream study area was generated.
The mineralogy and rock type between Town Creek and the Sangamo Weston site were identified and compared to site maps (Garihan et al., 2008). Few exposures of bedrock between Town Creek and Sangamo Road were characterized due to overlying saprolite. Borehole logs from wells 701 and 702 taken by TRC were used to determine the likely rock types and how they relate to the exposed bedrock on the surface and in the stream (Appendix A; Appendix B).

Because the groundwater contribution to the stream is a major objective of this study, fractures noted during structural mapping were studied. Folds within the metamorphic rock and foliations that visually appeared to be open were closely inspected. A 3 ft x 5/32 in metal dowel rod was used to investigate cracks to determine if they were open or compacted with sediment/cement. Fractures that accepted the rod were noted for study with the DTS.

3.1.2 - Hydrogeology of the Study Site

During the remediation of the Sangamo Weston Superfund site, private consulting firms were contracted to monitor the remediation of the site. TRC was tasked with the installation of groundwater monitoring wells. These wells were used for collecting groundwater samples and determining groundwater flow direction and hydraulic gradient.

TRC well data logs and location maps were employed to generate a contour maps of head for saprolite monitoring wells and bedrocks wells (Appendix C). These maps were developed to include the location and water level of Town Creek and wells. Using the water level and ground surface elevation, the change in head was determined and likely flow directions were plotted on the maps.

3.2 - Locating Groundwater Input to Town Creek

Due to the difficulty associated with finding fractures in the stream bedrock, a Sensornet Oryx Field Deployable – Distributed Temperature Sensor (FD-DTS) (Sensornet Ltd.,
Hertfordshire, England) was acquired through the Center for Transformative Environmental Monitoring Programs (CTEMPs). CTEMPs is supported by the National Science Foundation and jointly operated by Oregon State University and University of Nevada, Reno (http://ctemps.org/). The FD-DTS was designed to measure temperature with a resolution of 0.01°C along a fiber optic cable with ~1 meter location accuracy, which can help identify groundwater flowing through fractures in a streambed (Selker et al., 2006), which is possible due to the difference in temperature between warm (>20°C) surface water and cool (~14.1°C, average from Well 701 and 702 in September 2011) groundwater in the summer months. Prior to deployment in September 2011, factors including the flow rate of Town Creek and groundwater temperature were determined to help in groundwater discharge identification.

3.2.1 - Preparation for FD-DTS Deployment

To determine the volumetric flow rate (Q) of Town Creek during the time of FD-DTS deployment, a Vernier Flow Rate Sensor was used in the stream. The sensor has a resolution of 0.0012 m/s and accuracy within 1% when doing measurements greater than 15 s (Vernier, 2010). During measurement, flow rates were collected for 30 s at 1 ft intervals across the stream width. Volumetric flow rates were taken at 30 and 120 m upstream of Reece Mill Bridge on June 30, 2011 (Figure 3.1). Two additional volumetric flow tests were done on July 17 and July 19 with one 25 m downstream of the Reece Mill Bridge and the other 75 m upstream of the bridge, respectively. The measured values for June were 0.27 m³/s and 0.25 m³/s, July 17 produced a value of 0.17 m³/s, and July 19 produced 0.11 m³/s. After discussing these values with CTEMPs personnel, it was determined that the DTS would work in Town Creek.

The temperature difference between surface and groundwater at the site was important to post FD-DTS deployment interpretation. While the FD-DTS was in the stream, temperature
measurements were taken in wells 701 and 702 using a Vernier Extra Long Temperature Probe with an accuracy of 0.2°C. The probe was lowered to the bottom of each well and allowed to stabilize for 60 seconds before measuring. Measurements indicated that groundwater temperature was between 14.1 and 14.2°C.

Prior to installing the distributed temperature sensor at Town Creek, the system was assembled and tested at Rich Laboratory to check for system errors. The weather stations were assembled and the software was checked to determine if the stations were functioning correctly. Additionally, 100 m of fiber optic cable were placed in shaded and hot areas and calibration baths were used. The solar panels for the system were installed and tested.

3.2.2 - Deployment of the FD-DTS

Equipment supplied by CTEMPs and Clemson University was used for the DTS system at Town Creek. Wireless eKo Pro Series (Crossbow Technology, Inc., Milpitas, CA) weather stations with precipitation, wind speed and direction, and humidity measurement capabilities were provided along with software for the DTS computer. Built into the DTS were two platinum resistance thermometers (PT100) for calibration of the cable with water baths. A 1000 m spool of duplex (two optical fibers) fiber-optic cable (AFL Communication, Spartanburg, SC) was sent by CTEMPs with modifications for use with the DTS. Four EverStart 24DC-6 (Johnson Controls Battery Group, Inc., Milwaukee, WI) batteries were used to power the system when solar energy was not available and at night.

The FD-DTS was installed along Town Creek in late August, 2011 (Figure 3.2). The DTS, three solar panels, fiber optic spool, and one weather station were placed along the southeast bank of Town Creek allowing the cable to enter the stream approximately 20 m upstream of Reece Mill Bridge. An additional weather station was placed along the northwest
bank of the stream approximately 225 m upstream of the bridge. The solar panels were arranged with a southward orientation to recharge the system batteries, but trees and overgrowth reduced exposure to sunlight. Two calibration coolers, one filled with ice water and one with river water, were placed near the fiber optic spool and 20 m of fiber optic cable were coiled and placed on plastic inserts to prevent the cable from touching the sides or bottom of the coolers. Each calibration bath was mixed using a bubbler to reduce temperature stratification. A path from the bank to stream was cleared to run the cable into Town Creek.

The fiber optic cable was placed in Town Creek for temperature sensing. The end of the cable was pulled 229 m upstream along the western bank and tied to a tree to hold it in place. To increase the chance of finding groundwater input, another 454 m of cable was deployed to double back along the first length (232 m) leaving another 222 m which was placed along the middle of the stream (Figure 3.3). The cable in the stream was anchored to the bottom by

Figure 3.2. DTS installation site along Town Creek. The DTS with solar panels (left) and weather station (foreground). The fiber optic spool can be seen to the right of the DTS.
placing rocks every few meters and on areas of tension. Exposed cable was marked with tape and noted as such for data analysis. The remaining cable in the calibration baths and on the spool was left in place for the duration of the test.

Figure 3.3. Simplified layout of the fiber optic cable along Town Creek. Numbers added to indicate different location of cable placement. Not to scale.

After placement of the cable, the DTS system was powered on and initialized to measure the temperature along the stream. The Oryx DTS User Manual v2 was followed to establish a double ended measurement using the cable provided with the system (Sensornet Ltd., 2007). The fiber optic cable in each cooler was calibrated to the PT 100 thermometers on the DTS after bubblers mixed the water for several minutes. Using the calibration bath adjustment curves, the cable in the stream was calibrated to reduce temperature errors to less than 0.1°C using methods outlined by Hausner et al. (2011) and Suarez et al. (2011a). The measurement times were set to take 60 seconds of temperature values with 60 seconds of standby to conserve battery power.
Measuring at this interval helps reduce error introduced by cloud cover and brief shading of the cable by overhanging trees. The DTS was set to run continually for the month of September with brief interruptions to add ice into the cold water bath and change batteries.

3.2.3 - FD-DTS Data Analysis

The data collected on the DTS computer were separated into stream temperature and weather station logs. Each 60 s measurement from the system was stored in an Excel file, which resulted in 16,388 temperature samples from the stream. The large data set was processed with MATLAB using code developed by Suarez et al. (2011a). To analyze the data, median stream temperature for the complete 60 s stream measurement was subtracted from each ~1 m sample interval. The difference in temperature between the stream median and ~1 m sample was used to locate cool locations.

The highest temperature variation (>3°C) were checked against locations noted during deployment as being exposed to the atmosphere. Locations that showed a drop in stream temperature during both day and night were noted for comparison to hydrogeology and geology data. Cool locations were considered possible locations for groundwater input, but other factors could cause stream temperature drops.

3.2.4 – Confirmation of Groundwater Influx

DTS temperature data collected along Town Creek indicated cool locations along the stream where groundwater may be flowing in during the summer. However, cooling does not definitively indicate groundwater input, so seepage meters were installed to verify, and if possible, quantify the seepage flux into Town Creek. Additionally, mini piezometers and oil manometers were installed in the stream to determine vertical flux orientation and stream flow rate. Finally, a map showing sections of the stream shaded by plants during September 2011 was
generated to aid in determining if cool locations could be dependent on the amount of plant life at the site.

The bed of Town Creek is predominantly covered with thin layers of gravel and sand overlying bedrock where rock is not directly exposed, making seepage meter tests difficult along the majority of the stream. However, in an effort to confirm locations identified by the DTS, three seepage tests were performed between 185 and 230 m upstream of Reece Mill Bridge and a fourth was done approximately 250 m upstream. At these locations tests were performed to determine the groundwater flux into Town Creek using specialized seepage meters and methods developed for stream measurements (Gebhard, 2010; Murdoch and Kelly, 2003).

Installation of seepage meters was performed carefully to reduce error in measurements. Each meter was submerged in water and air bubbles were removed from the collection bucket. The meters were then pushed into the stream sediment until the base of the carapace shields were even with the sediment surface. Air from the seepage bags was then removed and each bag was connected to a seepage meter with the flow valve in the closed position. A timer was then set and the flow valves were opened simultaneously. Water was allowed to collect in each bag for 900 seconds and then the flow valves were closed. Seepage bags were removed and water was collected in mason jars and immediately placed in a backpack for transport back to Rich Lab. A duplicate test for each location was then performed using the same seepage meter and seepage bag.

Water from each seepage test was measured volumetrically using a 500 mL graduated cylinder and then stored in the lab for future study. Test duplicates were averaged for each location and the groundwater volumetric flow rate (m³/s) was determined for the four locations. The seepage flux (q) for each location was calculated in m/s using:
\[ q = \frac{\Delta V}{\Delta T \times A} \]  

where \( \Delta V \) is the change in volume (m\(^3\)), \( \Delta T \) is the change in time (s), and \( A \) is the area of the seepage meter collection pan (m\(^2\)). Seepage flux values were recorded individually, and then averaged to get a generalized value across the length of Town Creek tested.

A manometer was also installed in the stream sediment and used to determine flow rate. A location of high flow was selected and the manometer was filled with water using a syringe. One end of the manometer tubing was tied in place to point upstream and the other end was pointed downstream. Oil was then injected into the tubing and the system was allowed to stabilize. The difference in head between the upstream tubing and downstream tubing was then measured with a ruler and the value was divided by ten to account for the oil amplifying the head difference. The value is the velocity head, which was then used to calculate the stream velocity \( v \) in m/s using:

\[ v = \sqrt{2\Delta h g} \]  

where \( \Delta h \) is the velocity head and \( g \) is gravity (m/s\(^2\)).

After the velocity head test, a mini-piezometer was attached to the manometer tubing and pushed into stream sediment. The remaining manometer tube was allowed to point downstream and oil was again injected into the manometer to amplify head. Head differences between the stream and the base of the mini-piezometer were measured on the manometer and the vertical hydraulic head was calculated with:

\[ \text{Vertical Gradient} = \frac{\Delta h}{L} \]  

where \( \Delta h \) is the change in head and \( L \) is the depth of the piezometer in sediment. Using the vertical head, the direction of groundwater flow was determined for the stream to confirm seepage and DTS measurements.
Three days after installing the DTS fiber optic cables in Town Creek photographs were taken along the stream. These images served to indicate where the cable was exposed to the atmosphere, where it was sitting on bedrock, and where it was placed on sediment. Additionally, these photos showed locations along the stream where plants shaded the cable and stream bed. Being that shaded sections of the stream could be cooler than locations in sunlight, a map indicating variations between the two was constructed for the site.

3.3 - Dissolved PCB Collection and Analysis

At the request of Clemson University and the EPA, access to wells installed in the bedrock was granted by TRC for collection of groundwater for PCB analysis. Two wells (identified as SPRW701 and SPRW702 by TRC) installed between the Sangamo Weston site and Town Creek were used for collection of sample water (Appendix A; Appendix B; Figure 2.1). Dissolved PCB concentrations in the wells were determined using methods from previous study of Town Creek (V.D. Dang, 2012, unpublished data).

3.3.1 - Collection of Groundwater for Dissolved PCB Analysis

Six 4 L amber jars were washed and rinsed multiple times with deionized (DI) water to prepare for collection. Three jars were labeled for collection from each well and capped for transportation to the site. Each well contained a down-hole pump to draw water into a high-density polyethylene (HDPE) tube. The tubes extended to a collection point near Sangamo Road where it was connected to polyvinyl chloride (PVC) pipe with a spigot (Figure 3.4).

One day before sampling, a TRC site manager operated the pumps to purge the system. On the sampling date, the TRC onsite manager connected a garden hose to each spigot and turned on the pumps individually for wells 701 and 702. Water from the hose was pumped into each amber jar until approximately 2/3 full and capped immediately. Once samples were
capped, they were placed under a blanket to reduce photodegradation of PCBs. The sample bottles were transported covered to Rich Laboratory within an hour of collection.

![Figure 3.4](image)

Figure 3.4. TRC collection point for groundwater wells 701 and 702.

3.3.2 - Collection of Dissolved PCBs on Polyethylene Strips

The groundwater samples collected from wells 701 and 702 were immediately prepared for collection of dissolved PCBs. Water was transferred between the three collection bottles from each well to get a similar volume in each amber jar. Single-layer polyethylene (PE) strips (Brentwood Plastics, Inc., St. Louis, MO) were used for collection due to their high diffusion, partitioning coefficient, and uptake of PCBs (Pascall et al., 2005; Gschwend, 2010). Prior to use, the PE strips were cut into 5 x 2.5 cm pieces and soaked for 24 hours in dichloromethane, hexane, and methanol (Fernandez et al., 2009). Three PE strips were suspended by copper wire in each of the six sample jars for collection (Figure 3.5). A single strip was removed at 10, 20, and 30 days from each jar to determine equilibrium between the dissolved PCBs and PE passive
samplers. All six jars were capped with aluminum foil and placed on a C10 Platform Shaker (New Brunswick Scientific, Enfield, CT) at 100 rpm to equilibrate the dissolved PCB concentrations.

![Image](image_url)

Figure 3.5. Polyethylene strip suspended by copper wire in groundwater sample.

### 3.3.3 - PCB Extraction from PEs

The six sample PEs from each ten day interval were processed immediately or stored at 7°C until analysis. A lab blank PE was added to detect any contamination during the extraction process. The six sample PEs and an additional blank were spiked with 100 µL recovery standard with PCBs 14 and 169 at a concentration of 2 mg/L after being placed in clean 50 mL beakers. After a five minute contact time with the recovery standards, 20 mL of dichloromethane (DCM) were added to each sample and both blanks before the beakers were covered with plastic paraffin film. Samples were cooled at 7°C for 24 hours to allow PCB extraction from the PEs via dialysis.
The samples were removed from the refrigerator and the DCM was pipetted into a corresponding flask, which was covered and cooled again. Another 20 mL of DCM were added to each sample before being refrigerated for an additional 24 hrs. Each sample was again rinsed and pipetted into the flasks, and the PEs were set aside to dry before being weighed. The flasks were placed under a manifold and condensed to 5 mL with high purity nitrogen gas.

A sodium sulfate drying column was used to remove any remaining water from the 5 mL extracts. A column with a 2.0 cm inner diameter was packed with fiberglass to plug and reduce any sodium sulfate loss. Ten grams of sodium sulfate were poured onto the fiberglass, and the column was rinsed with enough hexane to allow a few drops through. The extracts were then poured into each column and rinsed into a beaker to a volume of 20 mL with hexane. Extracts were condensed to 2 mL under the nitrogen manifold, brought to a volume of 10 mL with isooctane, and then condensed a final time to 2 mL. The final extracts were transferred to 2 mL vials and capped for storage at 7°C.

3.3.4 - Preparation for Gas Chromatograph

Sample and standard preparation for the gas chromatograph (GC) involved the use of a 500 µL sample vial inset in a new 2 mL vial. Six standards (mixtures of Aroclors 1016, 1254, and 1260 at 1:1:1 w:w:w) were used to calibrate retention times, and the samples were prepared for analysis. Each empty 500 µL vial had 5 µL of aldrin and PCB 204 at concentrations of 2 mg/L in isooctane added for internal standard calibration. The sample extracts and standards were added to the vial at 250 µL and crimped with PTFE/RR red seals for use in the GC.

3.3.5 - Sample Analysis using Gas Chromatography (GC)

Samples, standards, and blanks were tested using achiral methods based on previous investigation of Town Creek PCBs (Dang et al., 2010). A congener-specific analysis was
conducted with a HP 6890-GC with a RTX-5 column (Restek, Bellefonte, PA; 60m length, 0.25 mm diameter, and 0.25 µm film thickness) and a $^{63}$Ni electron capture detector. High purity helium and nitrogen (99.99% and 99.95%, respectively) were used as the carrier and make-up gas. The flow rate, anode, and nitrogen gas were conditioned sequentially at 2.0, 6.0, and 60 mL/min, respectively. Samples were processed with the injector at 215°C and the detector at 325°C using the program VIETPCB2. The GC conditions began with the initial oven temperature at 115°C for 2 min. The temperature was increased to 185°C at a rate of 5°C/min and in turn to 260°C at a rate of 2°C/min. It was held at 260°C for 15 min. The total run time for each sample was 82.5 minutes. Before and during sample analysis, isoctane was injected as a blank and used to rinse the GC syringe between injections.

The GC targeted 140 possible PCB congeners (with some coelution) during analysis of the dissolved PCB samples (Dang et al., 2010). The sum of all 140 congeners was determined and reported as the total PCBs for this sample set, and homolog specific concentrations were determined as well. No significant shift in PCB peak retention times (RT) was found during the analysis of these samples. However, peak concentrations exceeded the calibration curve limits, and possible water contamination was found during the first attempt to analyze the samples. This issue was resolved using the methods in section 3.3.6.

### 3.3.6 - Cleanup and Dilution of Dissolved PCB Samples

The remaining 1.75 mL of each sample was cleaned and diluted to improve GC detection. A glass pipet column was used with a fiberglass plug under 0.5 g sodium sulfate and 0.3 g alumina, respectively. The 1.75 mL from each sample was poured through the column and rinsed with 7 mL of isoctane to a final volume of 8.75 mL, which diluted the samples by a factor of five for use in the GC. Samples were again prepared and run on the GC. Peak values from the analysis
fell within the calibration for the GC and evidence indicated that the cleanup had removed any remaining water.

3.3.7 – Estimating Seepage Flux with PCB Concentrations

An estimate of seepage flux into the stream was determined using characteristics of Town Creek and PCB concentrations from the stream and groundwater. Stream PCB concentrations collected by Dang (Unpublished, 2012) in the winter of 2010 at 15 m and 240 m upstream of Reece Mill Bridge were employed to find seepage flux \( q \) in m/s using:

\[
q = \frac{Q_{in}(C_b - C_{in}) - Q_{in}}{wx}
\]

(4)

Where \( Q_{in} \) is stream volumetric flow rate \( (\text{m}^3/\text{s}) \), \( C_b \) is the groundwater PCB concentration \( (\text{ng/g}) \), \( C_{in} \) is the PCB concentration \( (\text{ng/g}) \) at 240 m upstream, \( C \) is the PCB concentration \( (\text{ng/g}) \) at 15 m upstream, \( w \) is the average stream width \( (\text{m}) \), and \( x \) is the distance \( (\text{m}) \) between \( C_{in} \) and \( C \) (Murdoch, 2009). The \( Q_{in} \) for Town Creek was estimated \( (0.35 \text{ m}^3/\text{s}) \) for winter 2010 using measurements taken in July 2011 and historical Twelvemile Creek measurements. An average stream width of 7.65 m was determined using values from July \( Q_{in} \) measurements.

3.4 – Colloid Collection and Characterization

Colloids were collected to help determine the mineralogy of particles that could be transporting PCBs. The total suspended solids (TSS) were measured for the samples. Large volumes from surface and groundwater were filtered and dried prior to characterization. Non-destructive methods of analysis, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) were used to characterize the inorganic colloids.
3.4.1 – Filtration of Colloid Facilitated PCBs

Samples for colloidal PCB analysis were collected using the same procedure outlined in section 3.3.1 and agitated on the C10 Platform Shaker until filtration. For the largest colloids, glass fiber filters (1 μ, 47 mm; Pall Corporation, Port Washington, NY) were selected for groundwater and surface water. An additional volume of groundwater that had been filtered through 0.45 μ filters was used to supplement the 1 μ colloids collected during colloid characterization. For the smallest (~10 nm) colloids, 100 kDa Regenerated Cellulose Ultrafiltration Membranes (Millipore Corporation, Billerica, MA) were selected. For removal of large particles, 300 mL Suction Filtration Funnels (Gelman Sciences, Inc., Ann Harbor, MI) were selected. A 500 mL pressure vessel pressurized with nitrogen gas was used with an Amicon 8050 Stirred Cell (Millipore Corporation, Billerica, MA) for fine particle collection.

Samples from Town Creek and wells 701 and 702 required filtering to remove large particles. Two 300 mL Gelman funnels were washed and rinsed thoroughly with DI water and allowed to dry prior to filtration. The 1 μ filters were placed on the base of the funnel and clamped between the top and bottom using magnets. To clean each filter, 200 mL of DI water was suction filtered into jars which were only used for this purpose. Sample water from the 4 L bottles was poured into both funnels and filtered under vacuum into clean jars. Filtered water was poured into clean 4 L amber bottles and capped between each filtration. Once all of the samples were filtered, new filters were used and the process was repeated. The filtered samples were capped and placed back on the platform table prior to additional filtration.

Preparation for collection of colloids on the 100 kDa filter required the pressure vessel, Amicon stirred cell, tubing, and collection containers to all be thoroughly washed and rinsed with DI water. Each filter was weighed and transferred to the stirred cell using Millipore filter
forceps. Approximately 300 mL of ultrapure Milli-Q water (Millipore Corporation, Billerica, MA) water was added to the pressure vessel, and the assembled system was pressurized to clean the filter. Once 250 mL of water were passed through the filter, the vessel and stirred cell were depressurized and the remaining Milli-Q water was removed. A sample of 1.5 L was added to the pressure vessel, and the system was again pressurized to filter the colloids. Additional water was used for groundwater colloids. The stirred cell was placed on a stir plate and mixed at 350 rpm. The water was filtered until the stirred cell was empty; the filter was removed, placed in an aluminum pan, and stored in a freezer for analysis. Filtered water was saved in a clean 4 L bottle and the equipment was cleaned between samples. The process was repeated for both groundwater and surface water samples for a total of four (two each) samples.

3.4.2 – Colloid Characterization

The colloids collected on 100 kDA filters were used in the characterization process. A Nicolet 6700 FT-IR Spectrometer (Thermo Scientific, Sunnyvale, CA) was used for the initial characterization due to its ability to quickly identify clay minerals. The FT-IR was setup to run 32 scans with a resolution range of 1 cm⁻¹, starting at an aperture of 80 and a gain of 8. The background signal was collected and then a piece of sample filter was added to cover the FT-IR crystal. The filter was pressed onto the crystal and analyzed to show the absorbance for wavelengths from 500 to 4000 cm⁻¹.

Scanning electron microscopy was used for elemental analysis of filtered particles and high powered imaging. A SU6600 Analytical VP FESEM (Hitachi High Technologies America, Inc., Pleasanton, CA) was used for both surface and groundwater samples. A 1x1 cm piece of each filter was cut and placed on double sided carbon tape and stuck to the SEM stub/holder for analysis. Additionally, a 1x1 cm piece of copper was taped to the stub/holder for calibration of
the SEM for elemental analysis. Each sample was then loaded individually into the SEM and the system was evacuated of air to a pressure of 30 Pa. The sample stage was raised to allow only 12 mm between the sample and base of the electron gun. The SEM was powered on and the sample was scanned.

The elemental analysis was conducted using INCA Microanalysis (Oxford Instruments PLC., Abingdon, Oxfordshire) calibrated to the copper standard. INCA was used to characterize particle clusters, coatings, and single particles on the filters. After elemental analysis, the SEM was used to take high powered images of filtered particles for use in characterization. Data and images were saved for comparison to FT-IR results.

4 – Results

4.1 - Geology and Hydrogeology

Sediment characterization along Town Creek found variations in sediment size and mineralogy. Biotite gneiss boulders and cobbles mixed with sand and gravel were dominant from Reece Mill Bridge to 150 m upstream. Between 150 and 185 m upstream of the bridge, micaceous quartz sand was found accumulating on eroded bedrock. From 185 to 210 m upstream, micaceous quartz sand dominated the stream with thicknesses approaching 1 m. The stream segment above 210 m to 250 m consisted of exposed bedrock with gneiss boulders and cobbles, and micaceous quartz sand. The changes in sediment size along the stream were plotted on a map and simplified to show sand, gravel, and cobble/boulder sized materials (Appendix D).

Study of the structural geology along Town Creek provided information regarding bedrock orientation and folding, along with faulting and fracturing. Strike and dip measurements collected along the stream were organized based on location upstream of Reece Mill Bridge.
(Table 4.1). Measurements of fold and plunge orientations were also collected along the stream. A thrust fault identified by Garhian et al. (2008) was indicated by a change from exposed gneiss to a thick layer of saprolite at 180 m upstream of the bridge. A map showing structural data was developed, and fractures visible along the stream were added to indicate orientation (Appendix E).

Characterization of stream bedrock found variations of lithology along the 250 m stretch of Town Creek typical of the Table Rock Gneiss (TRg) and Tallulah Falls Amphibolite (TFa) formation (Garihan et al., 2008). Within these two formations, nine total variations were identified along the stream and labeled based on initial occurrence upstream of Reece Mill Bridge (Table 4.1). The first exposed rock (R1) appeared from 69-113 m upstream of the bridge and was characterized as a gray, medium grained, biotite quartzo-feldspathic gneiss with occasional amphibolite banding. From 119 to 128 m upstream, quartz veins as wide as 30 cm appear with no other mineralogy changes from R1, and this variation was labeled R2. Present at 130 m, R3 had the same mineralogy as R1, but was separated by R2. Upstream at 137 to 152 m a submerged and eroded unit (R4) was found with mineralogy similar to R1, but with a meter wide quartzo-feldspathic igneous intrusion. Between 152 and 175 m a dark gray, medium grained, biotite quartzo-feldspathic gneiss (R5) with abundant amphibolite banding was found intruded by a meter wide pegmatitic quartz-K-feldspar vein along the northwest bank. The variations from R1 to R5 are all characteristic of the Table Rock gneiss (Garihan et al., 2008).

The variations in rock type upstream of R5 all appear to be characteristic of the Tallulah Falls Amphibolite formation (Table 4.1) (Garihan et al., 2008). Found at 210 m and again from 239-241 m upstream of the bridge, R6 was identified as a light brown to dark gray, garnetiferous, schistose, mica gneiss with dark amphibolite bands. Present around 219 m and later at 238 m,
R7 was characterized as a light gray, coarse grained, migmatic quartz gneiss. Continuing upstream, R8 was exposed at 224 m and again at 232 m and was described as a light gray, muscovite quartzo-feldspathic gneiss with indicator millimeter wide quartz veins and centimeter wide biotite veins. Centered at 229 m upstream was the heavily eroded R9, which was labeled as a dark brown to light orange, coarse grained migmatic quartz gneiss. Exposures of Table Rock Gneiss and Talullah Falls Amphibolite were plotted with structural data on the map presented in Appendix E.

Table 4.1. Structural geology orientation and rock types present along the Town Creek study area upstream of Reece Mill Bridge.

<table>
<thead>
<tr>
<th>Upstream (m)</th>
<th>Strike</th>
<th>Dip</th>
<th>Plunge</th>
<th>Rock #</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>N69°W</td>
<td>11°S</td>
<td>-</td>
<td>R1</td>
<td>exposed rock</td>
</tr>
<tr>
<td>76</td>
<td>N48°E</td>
<td>7°S</td>
<td>-</td>
<td>R1</td>
<td>exposed rock</td>
</tr>
<tr>
<td>84</td>
<td>N64°W</td>
<td>12°S</td>
<td>-</td>
<td>R1</td>
<td>submerged</td>
</tr>
<tr>
<td>99</td>
<td>N75°E</td>
<td>26°S</td>
<td>-</td>
<td>R1</td>
<td>exposed rock</td>
</tr>
<tr>
<td>101</td>
<td>N74°E</td>
<td>36°S</td>
<td>-</td>
<td>R1</td>
<td>exposed rock</td>
</tr>
<tr>
<td>107</td>
<td>N56°E</td>
<td>13°S</td>
<td>-</td>
<td>R1</td>
<td>exposed rock</td>
</tr>
<tr>
<td>113</td>
<td>-</td>
<td>-</td>
<td>58°SE</td>
<td>R1</td>
<td>fold</td>
</tr>
<tr>
<td>119</td>
<td>N75°E</td>
<td>60°S</td>
<td>-</td>
<td>R2</td>
<td>exposed rock</td>
</tr>
<tr>
<td>123</td>
<td>N72°E</td>
<td>52°S</td>
<td>-</td>
<td>R2</td>
<td>exposed rock</td>
</tr>
<tr>
<td>128</td>
<td>N89°W</td>
<td>79°S</td>
<td>-</td>
<td>R2</td>
<td>upturn</td>
</tr>
<tr>
<td>130</td>
<td>N56°W</td>
<td>20°S</td>
<td>-</td>
<td>R3</td>
<td>exposed rock</td>
</tr>
<tr>
<td>137</td>
<td>N42°W</td>
<td>-</td>
<td>-</td>
<td>R4</td>
<td>submerged</td>
</tr>
<tr>
<td>146</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>R4</td>
<td>poor exposure</td>
</tr>
<tr>
<td>152</td>
<td>N63°E</td>
<td>7°N</td>
<td>-</td>
<td>R5</td>
<td>uneven from erosion</td>
</tr>
<tr>
<td>152</td>
<td>N69°W</td>
<td>4°N</td>
<td>-</td>
<td>R5</td>
<td>uneven from erosion</td>
</tr>
<tr>
<td>168</td>
<td>N70°E</td>
<td>15°S</td>
<td>-</td>
<td>R5</td>
<td>exposed rock</td>
</tr>
<tr>
<td>175</td>
<td>N61°W</td>
<td>24°S</td>
<td>-</td>
<td>R5</td>
<td>exposed rock</td>
</tr>
<tr>
<td>180</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>R5</td>
<td>buried thrust fault</td>
</tr>
<tr>
<td>210</td>
<td>N13°W</td>
<td>14°N</td>
<td>-</td>
<td>R6</td>
<td>uneven from erosion</td>
</tr>
<tr>
<td>219</td>
<td>E-W</td>
<td>24°S</td>
<td>-</td>
<td>R7</td>
<td>exposed rock</td>
</tr>
<tr>
<td>224</td>
<td>N78°W</td>
<td>47°S</td>
<td>-</td>
<td>R8</td>
<td>exposed rock</td>
</tr>
<tr>
<td>229</td>
<td>N19°E</td>
<td>-</td>
<td>32°SE</td>
<td>R9</td>
<td>fold</td>
</tr>
<tr>
<td>232</td>
<td>N25°E</td>
<td>3°N</td>
<td>-</td>
<td>R8</td>
<td>uneven from erosion</td>
</tr>
<tr>
<td>238</td>
<td>N36°W</td>
<td>29°N</td>
<td>-</td>
<td>R7</td>
<td>exposed rock</td>
</tr>
</tbody>
</table>
The groundwater flow in saprolite and rock monitoring wells indicated flow towards Town Creek with slight variations between mediums. Saprolite wells indicated southern flow towards Town Creek west of the study area, while flow from north and northeast appeared to flow into the study area (Figure 4.1). Rock wells also indicated flow into the stream with southeastern flow west of the study area and southwestern flow between the stream and the Sangamo Weston site (Figure 4.2).

![Saprolite monitoring well head contour map with arrows indicating flow direction. Modified from TRC (2011).](image)
4.2 – DTS and Seepage Meter Confirmation

Data collected by the FD-DTS and processed using Matlab produced evidence of cooling in Town Creek. Due to the large data set, the measurements were split in half with September 1st through the 15th in the first set and September 15th to the 28th in the second. Power was lost to the system due to battery failure on September 4th at 14:25 UT and restored on September 7th at 12:32 UT. The variations found from subtracting the stream median temperature for each 60 second sample from each <1.1 m interval along the cable for the 60 measurement were plotted against time to show temperatures at each point in the stream throughout September (Figures 4.3 and 4.4).
Figure 4.3. Temperature variation along the stream from September 1\textsuperscript{st} - 15\textsuperscript{th}. Power was lost between September 4\textsuperscript{th} and 7\textsuperscript{th}.

Figure 4.4. Temperature variations along the stream from September 15\textsuperscript{th} – 28\textsuperscript{th}.
Groups of stream data were created to include: 1) sections of known cable exposure to the atmosphere, 2) lengths showing cooling during daylight hours that may indicate groundwater inflow, and 3) data that do not indicate a change from the median stream temperature. Data showing locations of possible groundwater inflow were organized in Tables 4.2 and 4.3. Locations with cooling beginning on September 1\textsuperscript{st} continued to show the daily cooling cycles until September 15\textsuperscript{th} in Table 4.2. Cooling beginning on September 8\textsuperscript{th} and continuing through the 15\textsuperscript{th} was also common in Table 4.2. Measurements shown in Table 4.3 indicate that cooling began on September 20\textsuperscript{th} and 21\textsuperscript{st} and continued until the system was shut down on the 28\textsuperscript{th}.

Table 4.2. Locations of cooling during daytime temperature measurement from September 1\textsuperscript{st} - 15\textsuperscript{th}. The first two columns correspond to Figure 4.2 measurement locations. GPS data was collected at points of cooling along the stream. Dates indicate the time when cooling was measured.

<table>
<thead>
<tr>
<th>DTS min (&lt;1.1 m)</th>
<th>DTS max (&lt;1.1 m)</th>
<th>GPS Location (UTM)</th>
<th>Beginning Time</th>
<th>End Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>81</td>
<td>17S 342581 3862284</td>
<td>09/01/2011 - 00:00</td>
<td>09/15/2011 - 18:55</td>
</tr>
<tr>
<td>179</td>
<td>183</td>
<td>17S 342628 3862358</td>
<td>09/01/2011 - 00:00</td>
<td>09/15/2011 - 18:55</td>
</tr>
<tr>
<td>207</td>
<td>213</td>
<td>17S 342628 3862359</td>
<td>09/01/2011 - 00:00</td>
<td>09/15/2011 - 18:55</td>
</tr>
<tr>
<td>340</td>
<td>344</td>
<td>17S 342573 3862280</td>
<td>09/01/2011 - 00:00</td>
<td>09/04/2011 - 14:21</td>
</tr>
</tbody>
</table>
Table 4.3. Locations of cooling during daytime temperature measurement from September 15th – 28th. The first two columns correspond to Figure 4.3 measurement locations. GPS data was collected at points of cooling along the stream. Dates indicate the time when cooling was measured.

<table>
<thead>
<tr>
<th>DTS min (&lt;1.1 m)</th>
<th>DTS max (&lt;1.1 m)</th>
<th>GPS Location (UTM)</th>
<th>Beginning Time</th>
<th>End Time</th>
</tr>
</thead>
</table>
Cooling along Town Creek during the September deployment was likely influenced by precipitation. Rain collected downstream of the site near Twelvemile Creek in Liberty, SC, by the USGS indicated two major precipitation events in September (Figure 4.5) (USGS, 2011). The first rain occurred from September 4th to the 7th with greater than an inch of rain falling across the area. The second precipitation event occurred between September 20th and the 24th with approximately 3.5 inches falling on the area (Figure 4.6). Light precipitation was also measured on the 26th with 0.2 inches collected. Plant material clogged in the two weather stations placed along Town Creek likely skewed precipitation measurements, so these data were excluded.
Figure 4.5. Precipitation data for September 2011 collected by USGS rain gauges downstream of the study site near Liberty, SC (USGS, 2011).
Figure 4.6. A section of the stream with increased cooling after the rain event indicated by the yellow line. Greatest cooling (blue) was indicated in the afternoon of each day.

The locations where cool water was identified (Table 4.3) were marked with GPS for seepage meter tests (Tables 4.2 and 4.3). After marking the cool points, it was found that the majority were grouped in two sections along the stream. The area between 185 and 210 m upstream of the bridge, which was noted as thick (~1 m) sand overlying the thrust fault, showed several locations of cooling during daylight hours. A second location between 128 and 146 m upstream of the bridge was found to have several cool locations. This section of the stream has several deep (>1 m) locations due to steeply dipping limbs of a fold (Figure 4.7).
Figure 4.7. Location of possible groundwater input between 128 and 146 m upstream of Reece Mill Bridge.

The four seepage tests performed along the upper section of Town Creek collected water in the seepage bags confirming groundwater influx to the stream. Seepage flux measurements ranged from $5.46 \times 10^{-7}$ to $1.99 \times 10^{-5}$ m/s, with an average flux of $7.63 \times 10^{-6}$ m/s (Table 4.4). Sites 1 and 4 were described as locations of minimal stream flow and sand greater than 0.5 m in thickness along the northwest bank of the stream. Site 2 was established on rock covered by a
thin (<0.25 m) layer of sand with minimal stream flow, and Site 3 was placed in a location with a thick (>0.5 m) layer of sand with a high flow velocity of 0.35 m/s as determined using the oil manometer.

Table 4.4. Volumetric flow rate and seepage flux measurements along Town Creek.

<table>
<thead>
<tr>
<th>Site</th>
<th>Location (UTM)</th>
<th>(Q_{\text{seepage}}) (m(^3)/s)</th>
<th>(q_{\text{seepage}}) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17S 342656 3862386</td>
<td>3.01E-07</td>
<td>5.95E-06</td>
</tr>
<tr>
<td>2</td>
<td>17S 342648 3862376</td>
<td>2.77E-08</td>
<td>5.46E-07</td>
</tr>
<tr>
<td>3</td>
<td>17S 342616 3862346</td>
<td>1.01E-06</td>
<td>1.99E-05</td>
</tr>
<tr>
<td>4</td>
<td>17S 342616 3862341</td>
<td>2.08E-07</td>
<td>4.11E-06</td>
</tr>
</tbody>
</table>

The oil manometer and piezometer test identified a vertical gradient and direction of flow in Town Creek. A head difference between the stream and sediment water indicated a vertical gradient of +0.012. Based on the positive value for vertical gradient, water is flowing from the sediment to the surface water indicating that Town Creek is a gaining stream in the study area.

A map of the study site showing shade was developed to identify where plant life may reduce the stream temperature as identified by the DTS (Appendix F). Pictures used to make the map indicated that the stream was mostly shaded from Reece Mill Bridge to 145 m upstream, with the exception of the first 15 m upstream of the bridge. Upstream of 145 m the southeastern half of the stream was generally shaded, while the northwestern half was exposed to sunlight.

4.3 – *Dissolved PCB Concentrations*

Gas chromatography data produced in this project for wells 701 and 702 identified concentrations in mass of PCBs per mass of PE sampler (ng/g) (Figure 4.8). To convert to the concentration in the groundwater, the mass of PCBs (ng) was divided by the volume of water in each 4 L amber sample jar to provide a normalized concentration (ng/L). The normalized
The corrected analyte concentration for the total PCB concentrations in GW was found for wells 701 and 702 at ten, twenty, and thirty days. These data, including standard deviation bars, are presented in Figure 4.9. The concentrations presented for well 701 at ten, twenty, and thirty days indicate that groundwater contains total dissolved PCB concentrations ranging from 1610 to 1935 ng/L. Groundwater from well 702 showed higher total dissolved concentrations for the ten day intervals of PCB collection on PEs with concentrations between 5952 and 7016 ng/L. Well 701 ten day intervals had standard deviation values between 104 and 175 ng/L, while well 702 ranged from 245 to 650 ng/L.

Figure 4.8. Total PCB concentration collected on PE samplers at ten day intervals. Error bars indicate standard deviation. Each sample was replicated three times with the exception of both day 30 samples, which each lost one sample during preparation.
Figure 4.9. Total Dissolved PCBs in groundwater samples at ten day intervals. Error bars indicate standard deviation. Each sample was replicated three times with the exception of both day 30 samples, which each lost one sample during preparation.

The percentage for dissolved PCB homologs were determined for wells 701 and 702 for each ten day interval. Well 701 data (Figure 4.10) indicate that homologs with two to five chlorines make up greater than 99% of PCBs present, while homologs with six to nine chlorines make up less than 1%. Similarly, data from well 702 also show homologs with two to five chlorines making up 99% and homologs with six to nine chlorines less than 1% (Figure 4.11). Of the eight homologs present, tetra chlorinated PCBs made up the greatest percentage (>40%) in well 701, while in well 702 tri and tetra homologs both represented nearly 40% of the PCBs present. Variability between ten, twenty, and thirty day intervals was greatest (~10%) between tri chlorinated PCBs in well 701, but most ten day intervals showed a difference of less than 5%.
Figure 4.10. Comparison of PCB homologs between ten day sample intervals in well 701. Error bars indicate standard deviation between samples. Each sample was replicated three times with the exception of both day 30 samples, which each lost one sample during preparation.

Figure 4.11. Comparison of PCB homologs between ten day sample intervals in well 702. Error bars indicate standard deviation between samples. Each sample was replicated three times with the exception of both day 30 samples, which each lost one sample during preparation.
Using the equation developed by Murdoch (2009), surface water PCB concentrations from Dang (Unpublished, 2012), and the average groundwater concentration (Figure 4.8), the groundwater flux into Town Creek was estimated using equation 5. The value determined over the 190 m stretch between surface water samples was $5.05 \times 10^{-6}$ m/s.

4.4 – Colloid Characterization

FT-IR analysis produced data suggesting that clay minerals are present in both the groundwater and surface water at the study site. Scans of colloids collected from the surface water on 100 kDa filters generated peaks characteristic of gibbsite and kaolinite from 3300 to 3700 cm$^{-1}$ and 800 to 1100 cm$^{-1}$ (Figures 4.12 and 4.13). Peaks were designated using information from White and Roth (1986), which was modified and reported as Table 4.5. Additionally, standards of kaolinite and gibbsite were compared to surface water samples, and confirmed the results.

Figure 4.12. FT-IR spectrum for colloids in surface water sample 1.
Figure 4.13. FT-IR spectrum for colloids in surface water sample 2.

Analysis of colloids collected from groundwater on the 100 kDa filters using the FT-IR produced peaks from 3000 to 3600 cm\(^{-1}\) and 1600 to 1700 cm\(^{-1}\), which were consistent with montmorillonite clay (Figures 4.14 and 4.15). However, peaks within the 900 to 1100 cm\(^{-1}\) range are more indicative of kaolinite and gibbsite. The peak formed between 2800 and 3000 cm\(^{-1}\) is likely residual filter, since filter blanks produced strong peaks in this range. This peak was only seen in groundwater samples, which suggests that surface water colloids completely coated the filter.

Table 4.5. Infrared absorption bands of clay minerals indicated in groundwater and surface water. Adapted from White and Roth (1986).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Wavelength (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>3695 3670 3650 3620 1108 1038 1012 940 915 700</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>3620 3400 1640 1100 1040 1020 915</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>3610 3525 3445 3395 1102 1030 975 800 745 670</td>
</tr>
</tbody>
</table>
The elemental analysis from the SU-6600 scanning electron microscope provided evidence of clay minerals and metals in particles collected from surface water on 1μ filters. The sections of 100kDa sample filters examined indicate a strong presence of carbon (17-20%) and oxygen (60-64%) by weight from the carbon tape used to hold the sample and atmospheric input during sample loading, respectively (Table 4.6). Scans of the filter found aluminum around 5-
6%, silicon at 3-4%, and iron from 7-9%. Trace percentages (<1%) of copper, titanium, and calcium were identified.

Table 4.6. Elemental percentages reported by elemental analysis of surface water colloids from SU-6600.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Cu</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.73</td>
<td>5.07</td>
<td>3.78</td>
<td>0.26</td>
<td>0</td>
<td>7.04</td>
<td>0.5</td>
<td>63.62</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>5.92</td>
<td>4.31</td>
<td>0.28</td>
<td>0.27</td>
<td>9.25</td>
<td>0.7</td>
<td>61.26</td>
</tr>
</tbody>
</table>

SEM scans of the groundwater filters indicate oxides and clay minerals. Due to the reduced suspended particles in the groundwater, lower percentages by mass were recorded compared to surface water samples. The 100 kDa filter used to collect colloids from groundwater passed through the 0.45 μ filter was scanned at both the middle and edge, since stirring while filtering resulted in particle accumulation around the outer rim. Elemental percentages based on filter location are categorized in Table 4.7. The data indicated that the particles were segregated to the edge of the filter and that clays (indicated by the Al, Na, and Si) and manganese are the likely colloids in the groundwater.

Table 4.7. Elemental percentages reported by elemental analysis of groundwater colloids from SU-6600.

<table>
<thead>
<tr>
<th>Filter Location</th>
<th>C</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Fe</th>
<th>O</th>
<th>Cl</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Edge</td>
<td>26.28</td>
<td>0.12</td>
<td>0.07</td>
<td>0.4</td>
<td>0.16</td>
<td>0.26</td>
<td>0.27</td>
<td>0.14</td>
<td>0</td>
<td>71.62</td>
<td>0.05</td>
<td>0.63</td>
</tr>
<tr>
<td>Inner Edge</td>
<td>26.71</td>
<td>0.09</td>
<td>0</td>
<td>0.35</td>
<td>0.07</td>
<td>0.17</td>
<td>0.15</td>
<td>0.08</td>
<td>0.1</td>
<td>72.13</td>
<td>0</td>
<td>0.17</td>
</tr>
<tr>
<td>Center A</td>
<td>27.08</td>
<td>0</td>
<td>0</td>
<td>0.19</td>
<td>0.05</td>
<td>0.07</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
<td>72.55</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Center B</td>
<td>27.05</td>
<td>0</td>
<td>0</td>
<td>0.22</td>
<td>0</td>
<td>0.1</td>
<td>0.07</td>
<td>0</td>
<td>0.06</td>
<td>72.5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
5 – Discussion

5.1 - Geology and Hydrogeology

The fractured and folded Table Rock gneiss and Tallulah Falls Amphibolite formation are exposed in Town Creek, and north of the stream at the Sangamo Weston site. Additionally, the thrust fault mapped in the stream by Garihan et al. (2008) is exposed between the two formations along Sangamo Road south of the former plant site. It can be interpreted that the folds and fractures continue between the stream and plant site. These fractures may act as conduits for contaminated groundwater to enter Town Creek.

The groundwater flow direction presented in Figures 4.1 and 4.2 suggests that groundwater north and northeast of the stream is flowing into Town Creek in both saprolite and bedrock. Groundwater transported through the saprolite between the lagoons/Sangamo site and Town Creek should flow into the stream assuming that flow is perpendicular to head contours. However, when assuming flow perpendicular to the head contours in bedrock, it appears that groundwater from the Sangamo Weston site and lagoons may flow to a section of Town Creek downstream of the Reece Mill Bridge. Flow directions determined from head data support claims by the EPA 5-Year Review (USEPA, 2004) and work by Dang et al. (2010) that PCBs may enter the stream through groundwater.

5.2 – Locating Groundwater

The DTS system used for this project identified areas with temperatures as low as 2°C below stream median. Based on the groundwater temperature measured at 14.1°C and the temperature of the surface water commonly measured at >20.0°C, it can be concluded that the temperature identified with the DTS is likely the result of groundwater inflow to the stream. As
noted in Tables 4.2 and 4.3 and Section 4.2, the cooling was dominant in two locations along the study portion of the stream.

The section of the stream between 185 and 210 m upstream of the bridge shows the most evidence of groundwater input to Town Creek. Four locations of cooling were indicated along the northern side of the stream and two more were found along the southern side. The stream bed here consists of sand overlying the thrust fault noted by Garihan et al. (2008), which may act as a conduit for groundwater transport to the stream. It should be noted that this section of the stream was not continuously shaded with water depth of 2 to 10 cm during September with exposed sand along much of the stream (Appendix D; Appendix F; Figure 5.1). This part of the stream is likely acting as a source of groundwater to Town Creek, but additional research is required to confirm this.

Figure 5.1. DTS cable installed ~190 m upstream of Reece Mill Bridge. This 10 m stretch of stream was found to have several cool spikes throughout the month.
Another area of cooling along the stream occurred between 128 and 146 m upstream of the bridge. This location was found to have an uneven streambed due to the folded gneiss at its base and was shaded by overhanging trees. No fractures could be visibly identified at this section of the stream, but the folding and foliations may contain active fractures. The strike of the gneiss is nearly perpendicular to stream flow resulting in multiple steps and uneven topography resulting in 1 m deep sections. These 1 m deep points along the stream were noted as being cooler in the DTS data, which makes it difficult to discern whether the temperature change is due to stream depth, shading, or groundwater.

Several factors influence surface water temperatures. Riparian vegetation commonly shades sections of the stream, which may decrease stream temperatures during portions of the day (Larson and Larson, 1996). However, most of temperature variation presented in Figures 4.3 and 4.4 does not show significant change in temperature throughout daylight hours caused by plant and tree shading. These observations do not discount the possibility of shading, but do suggest that a different factor may be the primary source of cooling.

Temperature measured along the stream may also be influenced by exposed rock versus sediment covered rock. The amphibolite-rich gneiss exposed along the stream has a lower albedo than the sand, which should result in greater solar radiation absorption by the rock and less by the sand (Gerrard, 1988). This zonal heating could increase the median stream temperature measured by the DTS, making sediment covered locations appear to be cooler. However, the majority of the stream bed is covered with sediment and much of the upstream cable was placed so that it did not lie directly on exposed rock.

The stream depth was noted as being a possible source of temperature change along the stream. Deeper water absorbs less solar radiation than shallow water, resulting in lower
temperatures at depth. Deep water could result in the cooling observed between 128 and 146 m upstream of the bridge; additional study of this area is needed. The effects of stream depth on temperature support the prediction that groundwater is coming in around 185 to 210 m upstream, since the stream was shallow and still produced strong cooling spikes during daily peak temperatures.

Input of precipitation during rain events noticeably changed the stream temperatures. Loss of power to the DTS did not allow measurement of precipitation in early September, but a second precipitation event later in the month was captured. When comparing Figure 4.4 with Figure 4.5, it is apparent that the precipitation beginning around September 19th rapidly changed the median stream temperature detected by the DTS. Multiple points of cooling began to appear on September 21st and could be the result of groundwater entering the stream.

Considering all of these potential sources of cooling in Town Creek supported the need for confirming groundwater flow using the seepage meters and manometers. All four of the seepage meters confirmed groundwater input to the stream with two of the meters placed between 185 and 210 m upstream of the bridge where the DTS indicated cooling. Additionally the mini piezometer test with the manometer indicated upward flow where the DTS identified cooling, which suggests that the cooling measured by the DTS between 185 and 210 m upstream of the bridge was likely due to groundwater entering the stream. Though direct confirmation of groundwater could not be performed with seepage meters and mini piezometers between 128 and 146 m upstream of the bridge, upstream measurements strongly suggest that the DTS is likely identifying groundwater in zones of cooling.
5.3 – Dissolved PCB Concentrations

The dissolved concentrations in wells 701 and 702 show that PCBs are in groundwater between the Sangamo Weston site and Town Creek. Water solubility of the three PCB Aroclors, 1016, 1242, and 1254 (0.42, 0.24 and 0.012 mg/L at 25°C, respectively) used at the Sangamo Weston facility, suggests that the measured dissolved concentrations found in the groundwater of the study site are possible (Avalos and Bradburg, 2004; USEPA, 1994). The high concentrations may be the result of accumulation in groundwater after discharge from the former waste lagoons north of the wells and from groundwater transport directly from Sangamo Weston. When comparing the two wells, 702 was found to have a greater concentration than 701, which may be the result of 702 being closer to a ditch noted by TRC staff as being the former location of lagoon outfall to the stream.

The high concentrations found in groundwater are likely contributing to PCBs found in Town Creek. Work by Dang (unpublished data, 2012) using PE samplers placed in the surface water of Town Creek found that PCB concentrations more than doubled (749 ng/g to 2110 ng/g) between 240 m and 15 m upstream of Reece Mill Bridge. Groundwater PE concentrations plotted in Figure 4.8 are more than 71x (702) and 19x (701) the concentration found at the point 15 m upstream of the bridge. The seepage flux estimated using groundwater and surface water measurements was 5.05x10^{-6} m/s, while the measured value was 7.63x10^{-6} m/s. Being that the seepage estimate was highly dependent on average groundwater PCB concentration as the input and that the estimate was close to the measured seepage value, one can suggest that the concentration of PCBs entering Town Creek along the 190m stretch is similar to that of the average groundwater PCB concentration.
The use of PE strips for PCB uptake worked well for my study due to their ease of use, but there are some limitations. It was noted by Pascall et al. (2005) that PE exhibits high PCB uptake, diffusion, and partitioning coefficient; however, this decreases with increased chlorination. The decreased uptake of PCBs with increasing chlorination does not significantly affect this test, since Aroclors 1254, 1242, and 1016 have five or fewer chlorines. The combined mass of congeners with six or more chlorines was less than 1% of the total mass found on the PEs.

The data found for 10, 20, and 30 day intervals of PEs in groundwater suggest that equilibrium is reached before day ten (Figure 4.9). The concentrations found over 10 day intervals for both wells remained similar and fell within the standard deviations. Methods used appear to allow rapid equilibrium, which allows for quick sample preparation and analysis. However, additional work is required to determine how quickly equilibrium can be reached using this method.

5.4 – Colloid Characterization

Characterization of the colloids collected from the surface water of Town Creek indicated the presence of kaolinite, gibbsite, and (hydr)oxides, which is consistent with other studies of colloids in the Piedmont (Buol, 2003; Grant, 1963; Price et al., 2005). When characterizing the groundwater colloids using FT-IR, it was found that montmorillonite was the dominant clay mineral, but minor peaks for kaolinite and gibbsite were noted. The bentonite used during well installation was largely made up of montmorillonite, which complicated the characterization process by largely masking other clays that might be present in the groundwater. However, during SEM elemental analysis significant percentages of manganese were identified in the
colloids collected from the groundwater. McKay et al. (2002) noted that manganese and iron (hydr)oxides are commonly found in saprolite and in filled fractures.

Finding mostly montmorillonite clays in the groundwater may have been the result of the pumping process. The pumps used by TRC staff were operated at high rates, which likely displaced montmorillonite near the base of the well. A minimum flow rate should have been used to reduce contamination and only collect colloids in the groundwater (Backhus et al., 1993). Bailers were also a viable option for careful water collection, but could not be used with wells 701 and 702.

The size of colloids influences their flow rate through porous and fractured media (Ryan and Elimelech, 1996). The wide range of colloid sizes (1 μm to ~10 nm) selected for this research was done to maximize the sample size for ease of characterization and to determine if colloid types change with size. As the size of colloids increases, less diffusion and interaction with fracture walls occurs, but gravity becomes more of an influence (Cumbie and McKay, 1999). Based on this information, the colloids collected should represent what might be found in the groundwater, fractured rock, and saprolite.

6 – Conclusions and Recommendations

The conclusions of this thesis suggest that PCBs are entering Town Creek through groundwater. Study of the geology along Town Creek found deformed and folded metamorphic rock, and confirmed a geologic contact noted as a thrust fault. Contour maps produced using well and stream water levels indicate that groundwater from the Sangamo Weston site and former waste water treatment lagoons should flow into section of Town Creek studied when flowing through saprolite. Based on bedrock well measurements, some groundwater from the Sangamo Weston site may flow to a point downstream of the study area. Additionally, two
locations of possible groundwater inflow were identified along the Town Creek study site using distributed temperature sensing, and one was confirmed using seepage measurements.

The reported groundwater dissolved PCB concentrations support proposals that groundwater is the source of PCBs along the Town Creek study site. Identification of colloidal kaolinite and gibbsite, along with iron and manganese (likely (hydr)oxides), suggests that PCB transport via adsorption to colloids may occur. Ongoing study has produced initial data showing greater PCB concentrations on groundwater colloids when compared to surface water colloids at the study site. Continuous study of the Sangamo Weston site and Town Creek will provide an understanding of contaminant transport through fractured crystalline rock, and improve the scientific methods for modeling PCBs in groundwater.

Recommendations for Town Creek site and surrounding area should include research along the stream and groundwater. Using water collected from the seepage meters, dissolved PCB concentrations should be determined and compared to groundwater and surface water data. The colloids should also be filtered and characterized for comparison with those collected in surface and groundwater. Filtered colloids should be studied for PCB concentrations to determine their role in adsorption.

Collaboration with the EPA and TRC should continue to allow further study of groundwater at the site. Additional groundwater collection should transpire at these wells for PCB concentrations and colloid collection. During collection of groundwater, pumps should be set to the lowest rate capable of removing groundwater in an effort to reduce displacement of matrix colloids. Groundwater PCB congeners should be used to trace the flow of groundwater into Town Creek by comparing to surface water and groundwater concentrations collected in this thesis and previous studies.
7 – Appendices
Appendix A – TRC Well Construction and Borehole Data for 701

WELL CONSTRUCTION DIAGRAM
Not To Scale

PROJECT: SANGAMO PLANT SITE, PICKENS, S.C.
PROJECT NO.: 7238.22
WELL NO.: SPRW-701
DATE INSTALLED: AUGUST 5, 2005
DRILLING CONTRACTOR: A. E. DRILLING SERVICES, INC.
RMT TECHNICIAN: D.O. MADISON
SOIL BORING LOG

Client: Sangamo Plant Site
Site: Pickens, SC
Geologist/Technician: Jon Brown
Driller (name/company): Cleve Sanders
Drill Rig Type: CME-550
Borehole Diameter (in.): 14.25/10

Boring Coordinates:
N: 692332.60 E: 1482321.00 Total Depth (ft.): 36.00
Datum Description:
Datum Elevation (ft.): 953.35 (LS)

Sample Interval % Recovery Sample Type Blow Counts FID (rpm) Stratigraphy
1 Silty sand (SM) - large rock fragments, gravel to cobble; light brown; moist; Drilled harder at 2'.
2
3 Silty sand (SM) - Weathered rock fragments; more dense rock, (feldspar, quartz, biotite)
Auger refusal at 3.5'
Gneiss, weathered; cuttings are silty sand, fine to coarse grained sand and rock fragments; high feldspar and quartz content, very pale orange; slightly moist
4
5 Gneiss, weathered; silty sand, fine to coarse sand; moderate brown (SYR 4/4); moist

6 Gneiss, weathered; cuttings are silty sand, fine to medium sand; micaceous; pale yellowish brown (10YR 6/2); rock fragments are medium grey (N5)
8.5-9.5 harder rock

7 Gneiss, weathered; cuttings are silty sand, with coarse sand and rock fragments; less dense section of weathered rock; moderate brown (SYR 4/4);
Gneiss; same content as above (high quartz content); fresh bedrock.

8

9 Gneiss; dense; high quartz content; light grey (N7)

10 Gneiss; more dense than above; medium to dark grey (N4); observed minor water when drill rod added at 19'

11 Gneiss; darker grey with high biotite content; drilled softer than above

12 Gneiss; abundant mica; dark grey

13 Gneiss; abundant mica; finer grains; dark grey

14

15

16

17

18

19

Greenville (ver. 9/1/97) Continued Next Page
### SOIL BORING LOG

**Client:** Sangamo Plant Site  
**Site:** Pickens, SC  
**Geologist/Technician:** Jon Brown  
**Driller (name/company):** Clive Sanders  
**Drill Rig Type:** CME-550  
**Drilling Method:** HSA/Air Rotary  
**Borehole Diameter (in.):** 14.25/10  

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**Boring Coordinates:**  
N: 692332.60  
E: 1482321.00  

**Sample Interval**  
**% Recovery**  
**Sample Type**  
**Blow Counts**  
**FID (rpm)**  
**Depth (feet)**  

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**LITHOLOGIC DESCRIPTION**

- Gneiss, abundant mica; fine grained; minerals are dark grey

- Gneiss; mineral fragments larger and more coarse, medium to light grey (N5)

- Gneiss; increased mica and dark mineral content; cuttings darker, dark grey (N3); more coarse than the above

- Gneiss; cuttings are coarse sand to gravel sized; high % of dark minerals, quartz and mica present; wet

- Gneiss; abundant dark minerals; more silt than previous section; wet; coarse rock fragments

- Gneiss; abundant mica and dark minerals; schistose; coarse fragments (gravel size); hard; wet

Boring terminated at 36' BLS

Borehole logged from drill cuttings
Appendix B – TRC Well Construction and Borehole Data for 702
### Soil Boring Log

**Client:** Sangamo Plant Site  

**Drilling Start Date:** 8-1-05  
**Drilling End Date:** 8-3-05  
**Page of:** 1

**Site:** Pickens, SC  
**Drilling Method:** HSA/Air Rotary  
**Project Number:** 71238.22

**Geologist/Technician:** Jon Brown  
**Driller (name/company):** Clete Sanders  
**Drill Rig Type:** CME-550  
**Borehole Diameter (in):** 14.25/10

**Boring Coordinates:**  
N: 692227.50  
E: 1482164.30  
**Total Depth (ft):** 45.70

**Datum Description:**  
**Datum Elevation (ft):** Checked by: Dan Madison

### Lithologic Description

- **Silty sand (ML):** fine grained sands; light brown; moist; saprolite

- **Silty sand (ML):** fine grained, clayey; light brown; moist; saprolite

- **Silty sand (ML):** mostly fine grained with some coarse grains; micaeous; moderate brown (SYE 5/4); some rock fragments, schistose (feldspar, mica); becomes more dense with depth; saprolite

- **Silty sand (ML):** mostly fine grained with some coarse grains; more micaeous minerals than above section; moderate brown; abundant rock fragments, schistose (feldspar, mica); Auger refusal at 10.5’

- **Gneiss, weathered:** micaeous; abundant feldspar, quartz;

- **Gneiss, weathered:** softer zone than above; moister than above

- **Gneiss, weathered:** more dense than above

- **Gneiss, weathered:** cuttings are silty sand, fine to medium grained, with abundant rock fragments; micaeous; light brown; moist

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*Note: The image contains a table and a diagram with findings from drilling operations.*

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*Continued Next Page*
SOIL BORING LOG

Client: Sangamo Plant Site
Site: Pickens, SC

Drilling Start Date: 8-1-05
Drilling Method: HSA/Air Rotary
Drilling End Date: 8-3-05
Project Number: 71238.22

Geologist/Technician: Jon Brown

Driller (name/company): Cleve Sanders
AE Drilling

Drill Rig Type: CME-550
Borehole Diameter (in.): 14.25/10

Boring Coordinates:
N: 692227.50
E: 1482154.30
Total Depth (ft.): 45.70
Measuring Point Elevation (ft.): 970.03 (LS)

Datum Description:
Datum Elevation (ft.): Checked by: Dan Madison

LITHOLOGIC DESCRIPTION

-21
-22
-23
-24
-25
-26
-27
-28
-29
-30
-31
-32
-33
-34
-35
-36
-37
-38
-39

Observed water when drill rod added at 31'
Gneiss, weathered, less dense than above
Geniss, weathered; cuttings have abundant rock fragments and coarse grained sands and silt; wet

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**SOIL BORING LOG**

**Client:** Sangamo Plant Site  
**Site:** Pickens, SC

**Geologist/Technician:** Jon Brown  
**Driller (name/company):** Cleo Sanders  
**Drill Rig Type:** CME-550

**Boring Coordinates:**

| N: 692227.50 | E: 1482164.30 | Total Depth (ft.): 45.70 |

**Datum Description:**

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**LITHOLOGIC DESCRIPTION**

- Guessed, weathered, (less weathered than previous cuttings); cuttings contain medium to coarse sand and silt; increased percent of feldspar and quartz; wet;  
  Dense layer at 44'  
  Dense layer at 45'  

- Boring terminated at 45.7' BLS  

Borehole logged from drill cuttings
### Appendix C – Summary of Groundwater Level Elevations

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</tbody>
</table>

\(^{(1)}\) Measured in feet.  
\(^{(2)}\) Measured in feet above msl.  
NM = Not Measured

Well data collected by TRC (2011).
Appendix D – Town Creek Sediment Map
Town Creek Sediment Key

Sand
Sand/Gravel
Sand/Boulders
Cobbles/Boulders
Bedrock
Registration Line
Appendix E – Town Creek Geology Map
## Town Creek Geology Key

<table>
<thead>
<tr>
<th>Feature</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tallulah Falls Formation</td>
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<tr>
<td>Table Rock Gneiss</td>
<td>![Symbol]</td>
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<tr>
<td>Submerged Bedrock</td>
<td>![Symbol]</td>
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<tr>
<td>Pegmatite Vein</td>
<td>![Symbol]</td>
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<tr>
<td>Foliation Orientation</td>
<td>![Symbol]</td>
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<tr>
<td>Sediment/Boulders</td>
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<tr>
<td>Strike &amp; Dip</td>
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<tr>
<td>Fold Axis &amp; Plunge Direction</td>
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<tr>
<td>Registration Line</td>
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</tr>
<tr>
<td>Surface Fracture</td>
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</tbody>
</table>
Appendix F – Shade Cover Map
Concrete
91 m -
107 m -
122 m -
Town Creek Shade Cover Key

Stream Bed

Shade

Registration Point
8 – References


Garihan, J. M.; Ranson, W. A.; and Clendenin, C. W. 2008. Geologic Quadrangle Map Pickens, SC. South Carolina Department of Natural Resources.


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United States Environmental Protection Agency. 1994. Sangamo Weston/Twelve Mile Creek/Lake Hartwell PCB Contamination Superfund Site - Operable Unit Two Pickens, Pickens County, South Carolina. SCD003354412.


