

ABSTRACT

BIRCH, ANDREW LIFUR. Evaluating the Subsurface Export of Municipal Wastewater at a Forested Land-Application Site. (Under the direction of Elizabeth Guthrie Nichols)

Municipal wastewater land application to managed forests is an important treatment and disposal practice globally and, particularly, in North Carolina, U.S.A. Concern for the ecological and human health risks of pharmaceuticals and personal care products in municipal wastewater continues to grow, but, the contribution of wastewater from land-application to surface waters through groundwater transport is uncertain and not well studied. This study evaluated the contribution of municipal wastewater to local hydrology at a 3,000 ha facility where primary-treated wastewater has been land-applied to a mixed hardwood, pine forest for 17 years. Stable isotopes of hydrogen (^2H) and oxygen (^{18}O), chloride concentrations, and specific conductance were used as environmental tracers, in combination with hydrometric measurements, to examine the contribution of irrigated wastewater to local surface waters and groundwater at small catchment scales using two hillslope transects and at the watershed scale. Data were collected to determine wastewater flowpaths from the time of application to discharge from the watershed. Stable isotopes, chloride concentrations, and specific conductance were shown to be effective tools to identify wastewater in groundwaters and surface waters across the site; significantly higher levels of these tracers were observed in waters under the influence of wastewater irrigation. A two-component, three-end member isotopic mixing model estimated that wastewater comprised on average 24% of the mean daily discharge ($13,853 \text{ m}^3/\text{day}$) at the watershed outlet.

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Evaluating the Subsurface Export of Municipal Wastewater at a Forested Land-Application Site.

by
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BIOGRAPHY

Andrew L. Birch was born August 20, 1990 in Weddington, North Carolina. After graduation from Charlotte Catholic High School, he enrolled at North Carolina State University to pursue a Bachelor of Science in Environmental Technology and Management. While an undergraduate, Andrew captained the nationally ranked NCSU men's rugby team and played in two Collegiate Rugby Championships. Through coursework and internships with Waterborne Environmental Inc. and Dr. Ryan Emanuel's research lab, he developed an interest in the hydrologic sciences. After graduation, and chose to pursue this interest by attending graduate school in the same department beginning in January of 2013. Andrew carries his lifelong love of water outside of the classroom as an avid fisherman, paddler, and boater.

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CHAPTER 1: INTRODUCTION

In the United States, the Clean Water Act (CWA) requires wastewater discharging entities to acquire an NPDES (National Pollutant Discharge Elimination System) permit to discharge treated wastewater onto land or into surface water systems (USEPA, 1972).

Increasingly strict water quality standards for surface waters and the difficulty in acquiring a NPDES permit for direct discharge have led to increases in both the cost and the complexity of maintaining compliant direct discharge systems. These issues, combined with financial incentives, have led municipalities to seek alternative means of wastewater disposal and treatment such as the land application of wastewater to forested or agricultural lands (Al-Jamal, *et al.* 2002). Land application is encouraged as an alternative to direct discharge systems because it promotes groundwater recharge and mitigates effluent nutrients by using biotic and abiotic processes within the plant–soil–water matrix to biologically and chemically treat wastewater constituents (Aulenbach and Clesceri, 1980, Hutchins, *et al.* 1985).

Applying wastewater to forested land allows for plant uptake of nutrients and contaminant mitigation via adsorption, ion exchange, abiotic degradation, and biodegradation, and land application recharges groundwater rather than releasing wastewater directly to surface waters (Hutchins, *et al.* 1985; Barton *et al.* 2005). This approach has been shown to be an effective practice for preventing the direct discharge of nutrients to surface water systems in well-designed and managed systems (Crites 1984, Hutchins, *et al.* 1985).

A growing global concern is the presence of various pharmaceuticals, personal care products, and other organic contaminants in surface waters. Many of these chemicals are not currently regulated and are considered emerging contaminants (Barnes, *et al.* 2008, Gross, *et*

al. 2004). In the United States, the U.S. Geological Survey found emerging contaminants in surface waters near wastewater treatment plants that directly discharged to streams and rivers (Kolpin *et al.* 2002). In Germany, 55 pharmaceuticals, 6 hormones, 9 metabolites, 6 biocides, and 1 flame retardant were found in the treated-discharges of 49 wastewater treatment plants and their receiving surface water systems (Ternes, *et al.* 2004). While these compounds have been observed leaving these surface water systems, few studies have evaluated the connectivity between the groundwater and local surface waters at municipal land application sites (Crites, 1984, Hutchins, *et al.* 1985, Sabourin, 2009). As water availability and water resource management become increasingly important to regional and local stakeholders, understanding these hydrologic systems becomes important to maintain healthy aquatic ecosystems and to avoid risk to human health via groundwater and surface water use.

Evaluating the effectiveness of land application as a treatment method for emerging contaminants requires a quantitative assessment of the hydrological system (Ruiz, *et al.* 2002). To determine the export of this wastewater offsite, changes in the local water cycle must be observed at the hillslope scale and entire watershed scale (Sliva and Williams, 2001). Watershed scale observation can estimate the total wastewater leaving the hydrological system to surface waters on and offsite while smaller hillslope scale data are needed to identify the relationship between observed water composition at the watershed outlet and the areas of wastewater application and consequent groundwater recharge.

Specific conductivity, chloride, and stable isotopes of water are useful tracers to identify different water sources in hydrologic studies, particularly wastewater sources (Kirchner, *et al.* 2010, Svensson, *et al.* 2012, Katz, *et al.* 2009, Ronkanen and Klove, 2007).

Specific conductance has been used in a number of studies to identify water sources within a catchment (Cox *et al* 2007, Gooseff and McGlynn 2005, Jencso. *et al.* 2010, Pilgrim, *et al.* 1979). Gasser *et al.* (2010) used chloride to quantify the presence of municipal wastewater in potable drinking water supplies, and Katz *et al.* (2009) used both chloride concentrations and stable water isotopes to identify sources of nutrient pollution in a karstic basin in northern Florida (U.S.A.). In the latter study, groundwater located down-gradient of a land application operation had more positive $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic values and higher chloride concentrations than other groundwater sources.

In North Carolina, 86 municipalities are permitted to land apply wastewater effluent, and fifty-six percent of these facilities land-apply to forested lands (Nielsen, 2011). At most of these operations, wastewater effluent is stored in large open air lagoons prior to land application. Under these conditions, evaporation positively enriches $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in lagoon waters compared to streams and rivers and provide a useful tracer of municipal wastewater in the hydrologic system. Chloride concentrations and specific conductance will likewise be greater in lagoon wastewaters than ambient surface water sources due to evaporation and the higher chloride content characteristic of municipal wastewater (Gasser, *et al.* 2010, Stewart, 1975, Vandenberg, *et al.* 2005).

To understand the potential fate and transport of the land applied wastewater effluent on forested lands, hydrometric data and environmental tracers were used to observe the flowpaths and off-site export of municipal wastewater at a 3,000 ha municipal land-application facility that applies primary-treated wastewater to a mixed hardwood, pine forest. The entire study area is a 4,351 ha watershed on the eastern coast of North Carolina.

The primary objectives of the study were to (1) assess total export of wastewater from the facility on a watershed scale and (2) to analyze the flowpaths from where the wastewater is land applied to where it discharges to the local surface water system. From March to December 2014, hydrometric and water quality sampling were conducted every two weeks for groundwater, surface water, wastewater, and precipitation to observe temporal changes in the composition of each source in response to wastewater irrigation volumes and natural rainfall volumes. These data provide insight into the sustainable practice of land application onto forested lands and the impact of this practice on the local hydrologic cycle and, ultimately, surface water quality.

CHAPTER 2: STUDY SITE

The municipal facility applies primary-treated municipal wastewater to approximately 989 ha of a mixed loblolly pine hardwood forest via ~1m tall irrigation risers organized in a block-grid system; land application began in 1998 with a potential capacity of 2,400 ha for irrigation. The risers are organized into 28 irrigation blocks, each of which independently applies wastewater at the discretion of the operators and as allowed by permit requirements for soil composition. Twenty-one of these irrigation blocks fall within the chosen 4,351 ha study watershed, which drains the majority of the site via Southwest Creek (SWC) (Figure 1). Land use is primarily forested (51%) with upland pine plantations, lowland hardwood wetlands (16%), natural mixed pine/hardwood stands and 217 ha of urban development (5%). Other land uses in the watershed are pasture (3%), shrub/scrub (8%) and cultivated crops (17%). Soils under irrigation are classified as either well-drained or moderately well-drained, with poor and very poor drainage classes dominating the non-irrigated perimeter of the watershed and lowland riparian zones (NRCS Web Soil Survey, 2015). Soils present in the watershed are dominated by sandy loam and fine sand textural classes. For the two hillslope transects (Figure 1), soils are dominated by Norfolk loamy fine sand with a porosity of 0.43. Slopes at transect A were more moderate (0-4.5%) than those at transect B (0-10%). Topography across the watershed is relatively flat with a mean surface slope of 1.65%, and only 0.39% of the watershed exceeding 10% slope. Elevations in the watershed range from 8.5 to 49 meters above sea level. The watershed receives a yearly average of 1,346 mm of rainfall (NC CRONOS Database Station NC-ON-59 - Jacksonville 6.9 NW).

Evapotranspiration for established loblolly pine plantations in coastal NC has been estimated

to be 1011 -1226 mm/year (Sun, G. *et al.* 2010).

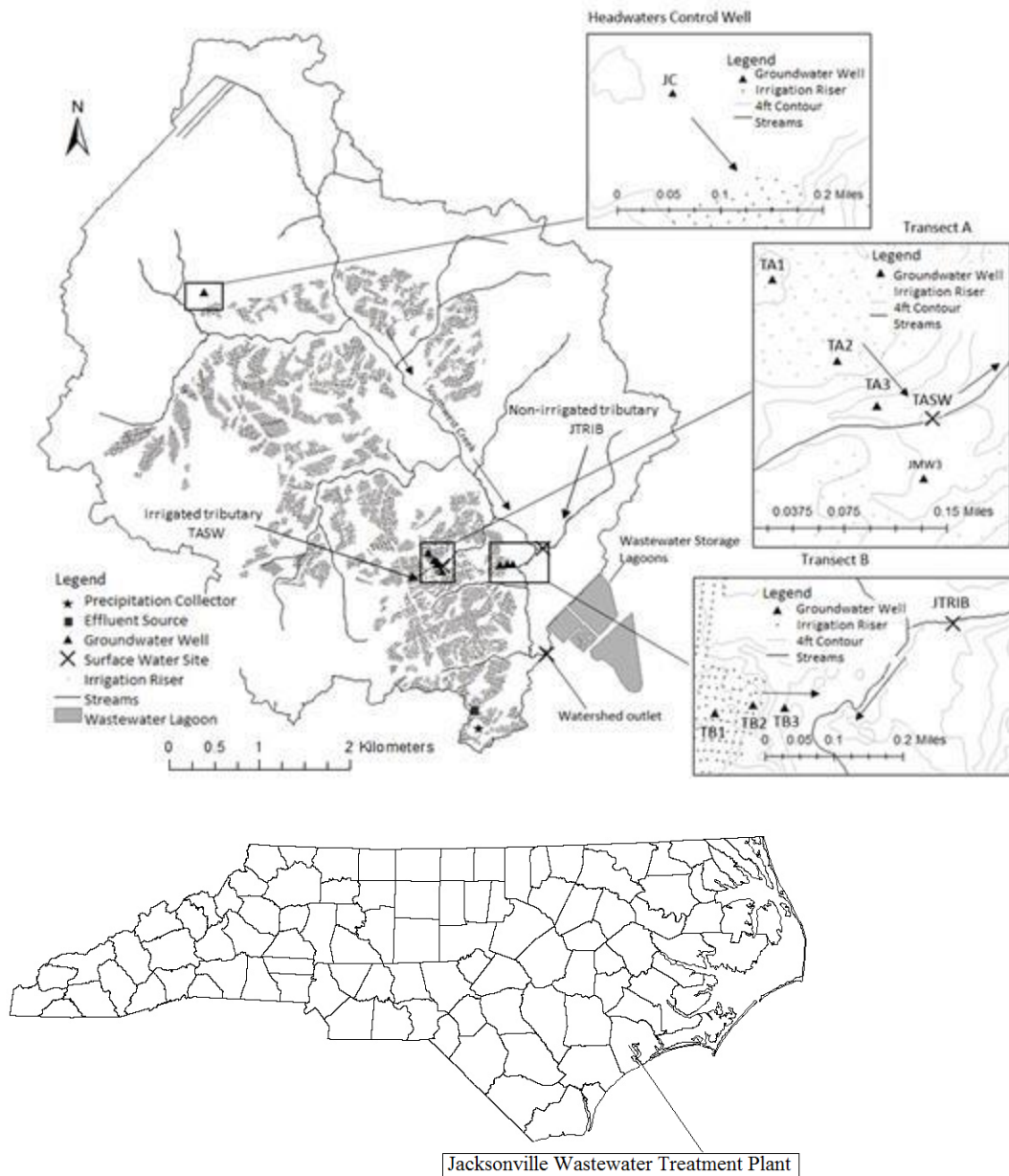


Figure 1: Geographic location and map of the study watershed showing sampling points, major hydrography, and wastewater irrigation areas.

CHAPTER 3: METHODS

Hydrometric and Water Quality Sample Collection

The watershed was gauged at the watershed outlet of Southwest creek (SWC) (Figure 1). Groundwater well transects were installed along two hillslopes transitioning between the upland pine plantations where the wastewater is applied to the lowland cypress wetlands where discharge occurs. Boreholes were augered by hand to a depth of 2-3 m and wells were capped at the bottom with 0.3 m of screening. After installation, boreholes were back filled with gravel pack and sealed at the surface with 20 cm of expanding bentonite clay to prevent infiltration directly into the well. Transects were aligned perpendicular to topographic contours. One of these transects (TA) connected a large area of irrigation to a small tributary while the second transect (TB) connects an upland irrigation area to the main stem of Southwest creek (SWC) (Figure 1). Two additional groundwater wells were monitored during the study period. Well JC was installed one month into the study in the headwaters of the watershed, up gradient of all irrigation activities as a reference well. Well MW3 was previously installed and operated by the WWTP, and was in an area free of irrigation. Daily precipitation and irrigation data, including volumetric and spatial distribution of irrigation were provided by the plant on a daily time step. These two wells were assumed to represent reservoir groundwater, or groundwater not altered chemically or isotopically by wastewater irrigation. Samples for water quality parameters were collected on a biweekly basis during the study period from March 2014 to December 2014 from 14 different locations in the watershed, including 1 precipitation collector, 3 surface water sites, 9 groundwater wells, and 1 wastewater effluent source (Figure 1). At each site, a sample was taken for ^{18}O and ^2H

stable isotopic analysis, chloride analysis, and specific conductance analysis. Stream samples were taken only where water was flowing and as close to the thalweg as possible. Nitrile gloves were worn for all sample collection events. Hydrometric measurements were made of groundwater level and stream discharge at each sampling event.

Samples for ^{18}O and ^2H isotopic analysis were collected in 20 ml disposable scintillation vials, capped without air bubbles, and stored at room temperature until analysis. Isotopic analysis was determined using a cavity ring-down mass spectrometer (model L2120- I, Picarro, Inc., Santa Clara, CA, USA) with a CTC Analytics LEAP technologies HTC PAL auto sampler (LEAP Technologies, Inc., Carrboro, NC, USA). Isotopic values are given as relative to VSMOW (Vienna Standard Mean Ocean Water)/ SLAP (Standard Light Antarctic Precipitation) and are calculated with the equation,

Equation 1.
$$\delta^{18}\text{O or } \delta^2\text{H} (\text{‰}) = \left(\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right) * 1000$$

where $R_{\text{sample}}/R_{\text{standard}}$ is the ratio of ^2H to ^1H atoms, or ^{18}O to ^{16}O of the sample divided by that of the reference standard. Raw instrument data was calibrated following the IAEA (International Atomic Energy Agency) published guidelines (Tanweer *et al* 2009).

Water samples for chloride and specific conductance were collected in pre-cleaned 500-1000 ml Nalgene bottles and put on ice in the field and refrigerated until analysis within a seven-day holding period. Specific conductance (SpC) was measured using a YSI Professional Plus series water quality sonde with a temperature correction following Method 120.1 (USEPA, 1982). For water sources known to have lower $[\text{Cl}^-]$ between 10 mg/L and 30 mg/L, a digital titration with silver nitrate was performed with a HACH digital titrator

following standard method 4500-Cl B. (NEMI, 1995). For some water sources known to have higher [Cl⁻] than 32 mg/L, HACH Quantitab titrator test strips were used to determine chloride concentrations.

A stilling well was installed at the watershed outlet at the start of the study period to continuously measure stage in 10 minute intervals. This well was constructed of 5 cm diameter PVC piping which was attached to an iron T-post driven deep into the thalweg of the stream and equipped with a 3 m long capacitance water level logger (Odyssey Water Level Recorder, Dataflow Systems Pty, Ltd, Christchurch, New Zealand). The stilling well was closed at the bottom, and slotted at 10cm intervals. At each biweekly sampling event, discharge was gauged at this site to establish a stream rating curve for Southwest Creek. Additional trips were made during high and low flow periods to measure extreme ends of the rating curve. For periods of low flow, salt dilution was used to make discharge measurements (Rantz *et al* 2013); for periods of moderate flow to high flow, a flow meter and wading rod were used (Rantz *et al* 2013).

To ensure groundwater samples were representative of water within the saturated zone surrounding each well, groundwater wells were purged three times the total well volume. Wells were equipped with 3m capacitance water level loggers to continuously monitor groundwater levels at 10 minute intervals in order to build a continuous time series of the hydraulic gradient ($\delta h/\delta L$) between the upland recharge zone and the riparian discharge zone. All capacitance water levels collected were compared to manually calculated water levels measured using a hand held water level meter (Geotech Environmental Equipment Inc, Denver, CO, USA). Continuous time series were combined with saturated hydraulic conductivity (K)

to estimate groundwater flow rate over time using Darcy's law,

Equation 2.
$$q = K \frac{\delta h}{\delta L}$$

where q is equal to Darcy flow, K is equal to hydraulic conductivity (cm/day), and $\delta h/\delta L$ is a unitless hydraulic gradient. A slug test was used to calculate K for each transect following Hooghoudt's method (1934). To calculate hydraulic head differences (δh), wells were surveyed according to the procedures compiled by Cunningham and Shalk (2011). Linear distances between wells (δL) were measured with a tape in the field.

Data Analysis

Isotopic and chemical mixing models using conservative tracers have been shown to be an effective means of identifying water sources in the environment (Burns, *et al* 2001, Genereux *et al* 1998, McGlynn, *et al* 1999). A two component, three end member mixing model (wastewater effluent and reservoir groundwater at the time of sampling, precipitation aggregated from the previous two weeks) was used to approximate the contributing fraction of wastewater irrigation to each sample collected during the study period. For each site where irrigation influence was suspected, a mixing model was created with three combinations of tracer components: $\delta^{18}\text{O}$ and $\delta^2\text{H}$, $\delta^{18}\text{O}$ and specific conductance and $\delta^2\text{H}$ and conductivity. Chloride concentrations were not used as mixing components due to concentrations in ground and surface water samples that exceeded concentrations in all three end members. Chloride was therefore used as a qualitative indicator of wastewater influence in surface and groundwaters. The following simultaneous equations describe the 2 component 3 end used, and are derived from those used by Burns *et al* (2001).

Chloride was therefore used as a qualitative indicator of wastewater influence in surface and groundwaters. The following simultaneous equations describe the 2 component 3 end used, and are derived from those used by Burns *et al* (2001).

Equation 3. $1 = f_{irr} + f_p + f_{res}$

$$A_{sample} = f_{irr}A_{irr} + f_pA_p + f_{res}A_{res}$$

$$B_{sample} = f_{irr}B_{irr} + f_pB_p + f_{res}B_{res}$$

$$C_{sample} = f_{irr}C_{irr} + f_pC_p + f_{res}C_{res}$$

Where f_{irr} is the calculated fraction of wastewater irrigation in the sample, f_p is the fraction of the previous two weeks precipitation in the sample, and f_{res} is the fraction of reservoir groundwater in the sample. A_i , B_i , and C_i are measured values of tracer A , B , and C for water source i . For some sample events, the sample concentration fell outside of the bounds of the three end members. These outliers were dealt with by forcing the fraction of the least contributing end member to equal 0 using the Pythagorean Theorem (Liu *et al* (2004). Where hydrometric data were available, these mixing fractions were converted to volumetric or one dimensional depth estimates of source contribution using the following equation,

Equation 4. $f_{irr}V_{total} + f_pV_{total} + f_{res}V_{total} = V_{total}$

$$V_i = f_iV_{total}$$

where V_{total} is the volume of water source for each sample, and V_i is the volumetric input of source i to that site.

Distributions of groundwater and surface water quality data were tested for normality using a Shapiro Wilk test. Surface water data were normally distributed; hence, a paired

Student's *t* test was used to determine significant differences between two sample means ($\alpha = 0.05$). Groundwater data were not normally distributed, and significance was determined using a Kruskal-Wallis test for wells receiving irrigation (TA2, TA3, TB1, TB2), non-irrigated wells (TA1, JC, MW3) and wells downgradient of irrigation (TA3, TB3) ($\alpha = 0.05$). A number of studies have addressed the inherent uncertainty in the use of stable isotope and geochemical mixing models (Joerin *et al.* 2002, Moore and Semmens 2008, Phillips and Gregg 2001). This uncertainty was quantified using a Gaussian error propagation proposed by Genereux (1998) for each mixing model.

Quality Assurance/ Quality Control

Field duplicates comprised 10% of total samples collected. A 100 ppm [Cl⁻] standard was analyzed before and after each set of samples to check for accuracy. Field precision error for chloride was less than 5% while the analytical error for accuracy and precision was less than 3% for chloride analyses. The YSI Professional was calibrated to a 1000 $\mu\text{S}/\text{cm}$ standard within 24 hours of use. Field precision error for specific conductance was less than 6% while laboratory analysis and precision error was less than 8%. For isotopic analysis, an analytical sample duplicate and a randomly placed check standard calibrated with VSMOW/SLAP were analyzed along with each sample run. During analysis, three calibrated standards were run before and after each set of nine samples to monitor and to minimize the effects of instrument drift during the run. Field precision for $\delta^{18}\text{O}$ was $\pm 0.09\text{‰}$ and $\pm 0.35\text{‰}$ for $\delta^2\text{H}$. Analytical accuracy was $\pm 0.24\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.54\text{‰}$ for $\delta^2\text{H}$. Analytical precision was $\pm 0.26\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.99\text{‰}$ for $\delta^2\text{H}$.

CHAPTER 4: RESULTS AND DISCUSSION

Infiltration of Wastewater to Shallow Groundwater

During the nine month study period, the hillslope catchment areas (TA1-TA3 and TB1-TB3) received similar amounts of wastewater irrigation (225 mm and 264 mm, respectively) and 1028 mm of precipitation (Table S-1 Supplemental Table – Hydrometric data). Using hydrometric data, a one-dimensional Darcian groundwater flow was estimated to range from 0.17 m/day to 0.26 m/day between wells TA2 and TA3 with a mean horizontal flow rate of 0.22 m/day. Flow between well TB2 and TB3 was estimated to range from 0.15 m/day to 0.22 m/day with a mean flow rate of 0.2 m/day.

Chloride, stable isotopes, and specific conductance were found to be indicative of wastewater in water samples collected from the land application area (Figure 2, Table S-2 Supplemental). The lowest specific conductance and isotope values were observed in precipitation and non-irrigated groundwater wells (JC, MW3, and TA1). Water samples for wastewater, irrigated groundwaters, and surface waters within the facility had greater chloride, specific conductivity, and $\delta^{18}\text{O}/\delta^2\text{H}$ values than water samples from areas without irrigation ($p < 0.05$; Figure 2). One exception was groundwater from well TB3 which was not significantly different than the reference well JC.

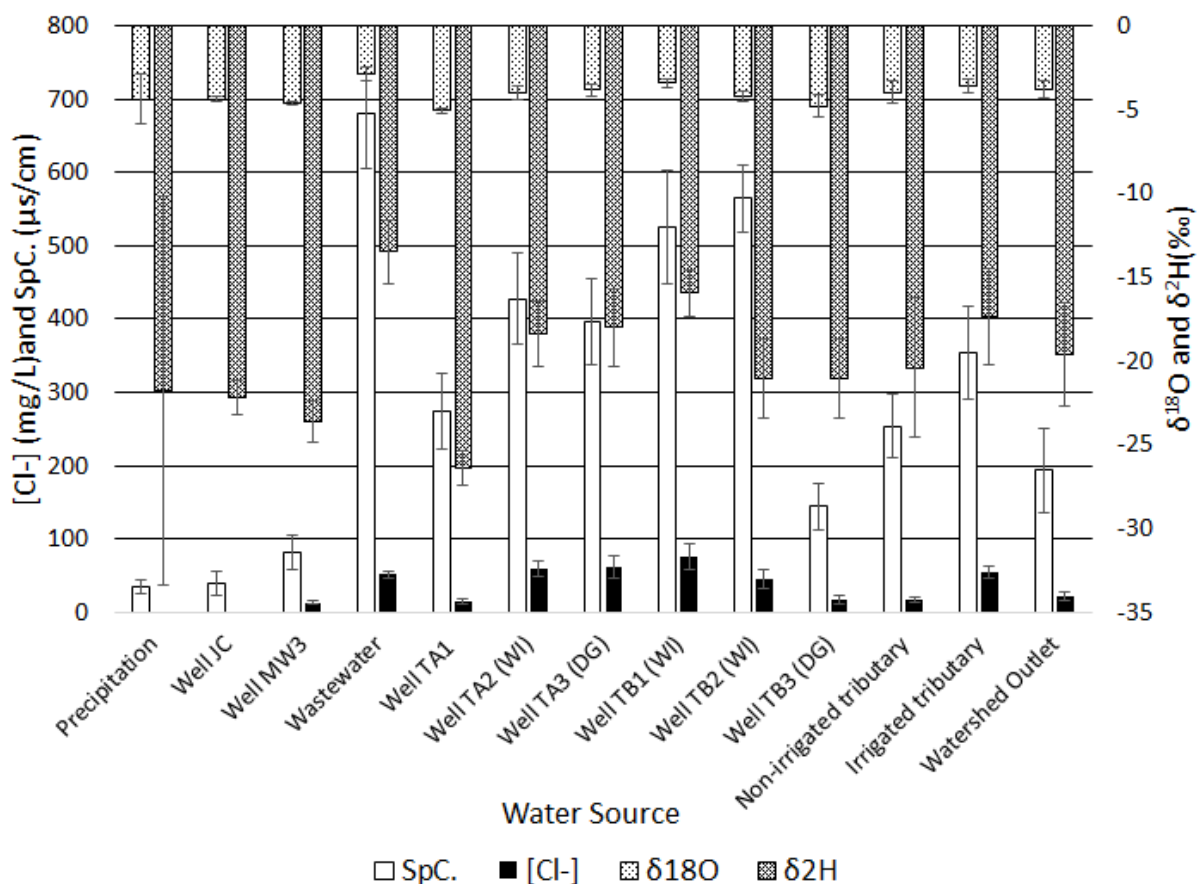


Figure 2: Mean values for the four tracers across all sample sites \pm one standard deviation. (NI) denoted groundwater that is not irrigated, (WI) indicates groundwater that is irrigated with wastewater, (DG) indicates water that is topographically down gradient of wastewater irrigation.

Wastewater had significantly higher specific conductivity than all other water sources, but chloride concentrations similar to irrigated groundwater wells. Specific conductance and chloride concentrations in wastewater were comparable to those found by Katz et al. (2009). Chloride concentrations in wells receiving irrigation frequently exceeded those of the wastewater effluent which prevents chloride's use as a mixing end member to model

contributing water sources to surface waters (Figure 3a). Fass *et al.* (2007) reported that plants can exclude chloride at the root/soil interface during transpiration, changing chloride concentrations in groundwater without affecting isotopic composition.

Isotopic values for wastewater, groundwater, and surface waters from the land application site did not align with the local meteoric water line and isotopic values for precipitation and non-irrigated groundwater and surface waters (Figure 3). The isotopic values for wastewater effluent form a local evaporation line with a difference in slope of 2.83. As shown in Figures 2 and 3, groundwater subjected to irrigation had $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values that were more positive than groundwater not impacted by irrigation.

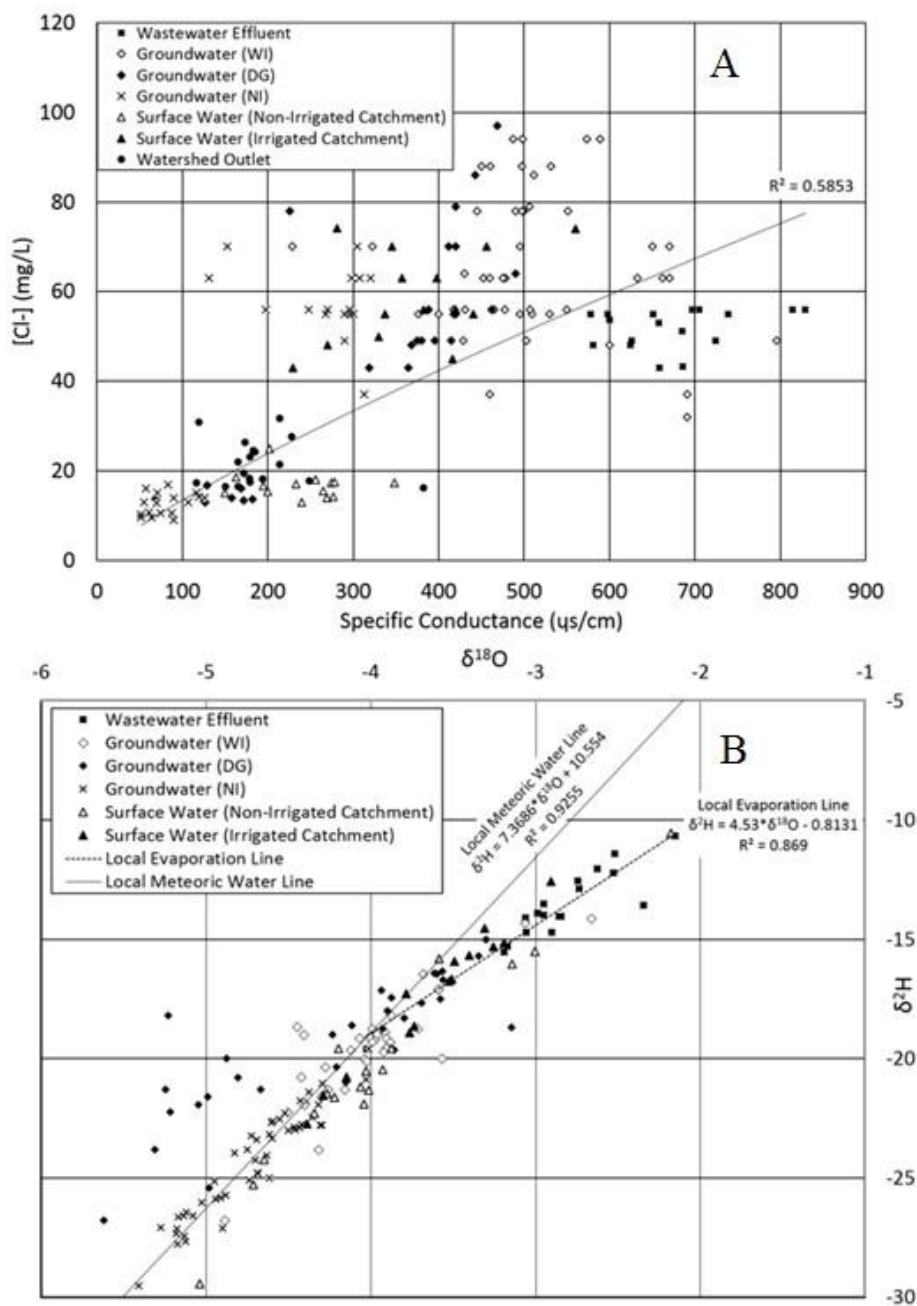


Figure 3: (A) $\delta^{18}O$ and δ^2H values for all samples a, volume weighted meteoric water line derived from precipitation samples, and a local evaporation line derived from isotopically enriched wastewater effluent (B) Chloride Concentrations and specific conductance for all samples collected.

Because the isotopic signature of wastewater can be traced in waters irrigated with wastewater and their receiving streams, a two component, three-source mixing model was used to estimate wastewater composition at all affected sites. Combining each isotopic tracer with specific conductance produced the most effective model with fewest outliers needing correction. For transect A, reservoir groundwater was given the tracer values of well TA1 which lies at the catchment boundary of the irrigated treatment catchment. TA1 received irrigation in the past, but was not irrigated during the study period. This could explain its higher mean chloride and specific conductance values relative to other non-irrigated groundwater sources although its mean isotopic composition did not differ ($p > 0.05$, Kruskal Wallis) from other non-irrigated groundwater sources. In fact, TA1 groundwater was the most isotopically depleted of all sampled water sources. For transect B, reservoir groundwater was represented by well MW3 which does not receive irrigation and is not directly down gradient of any irrigated areas. An assumption based on isotopic data was made that groundwater from these wells represented non-irrigated groundwater entering each hillslope.

Irrigation in agriculture has been shown by a number of studies to have an effect on groundwater composition and recharge (Böhlke 2001, Scanlon *et al.* 2005). Chen *et al.* (2006) found that wastewater irrigation altered the local pattern in water table change, eliminating seasonal variability present in non-irrigated sites. At transect A, the irrigated well TA2 showed considerable response in water table elevation to both precipitation and irrigation; each irrigation event raised water levels by ~200 mm (Figure 4). The mean wastewater irrigation fraction for well TA2 reflected this water table response and was 53%

using $\delta^2\text{H}$ and specific conductance and 50% using $\delta^{18}\text{O}$ and specific conductance. When converted to wastewater storage, wastewater depths ranged from 178 to 547 mm with a mean storage of 407 mm for TA2.

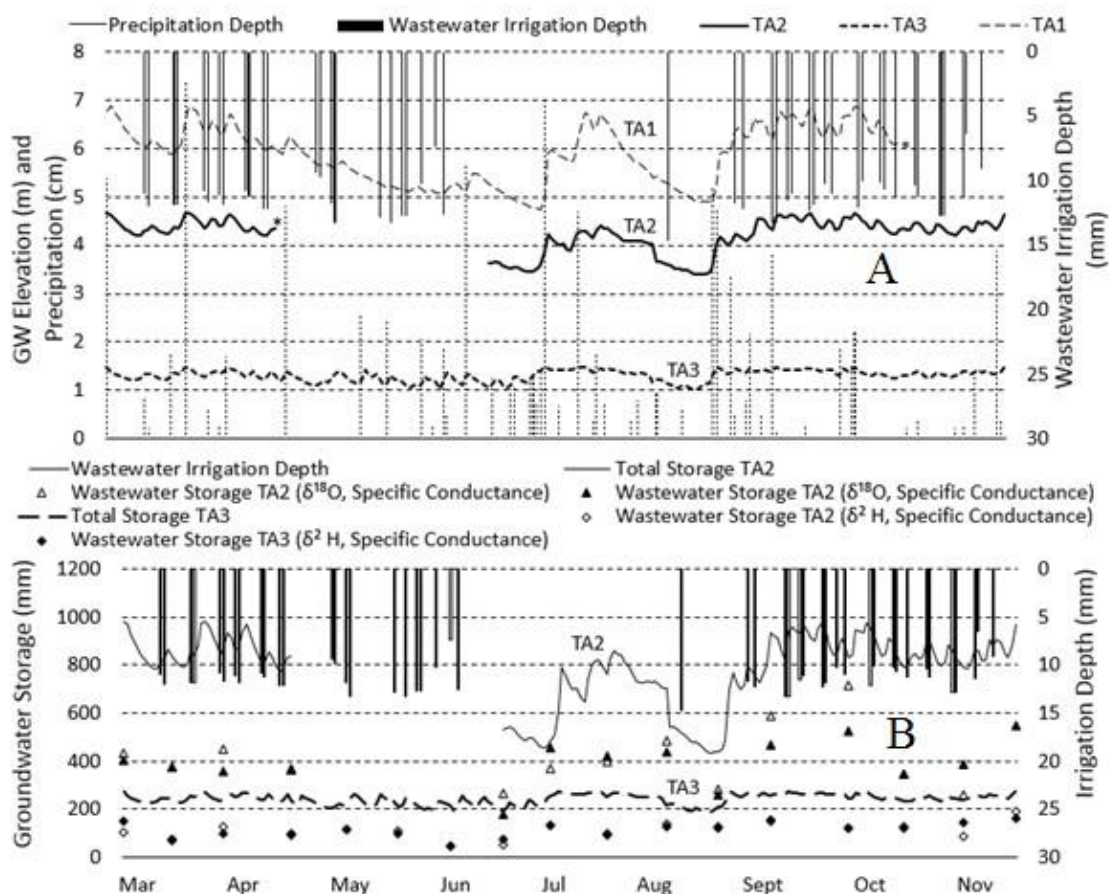


Figure 4: (A) Water table elevation in relation to an arbitrary datum at the bottom of well TA3 along with daily precipitation and wastewater irrigation to transect A. (B) Biweekly wastewater storage in TA2 and TA3, total daily storage in TA2 and TA3, and daily wastewater irrigation. The asterisk (*) denotes where no data were available due to equipment failure.

At well TA3, down gradient of well TA2, there was little water table response to irrigation, and fluxes were dominated by diurnal water table variations and large precipitation

events. The mean wastewater irrigation percentage for well TA3 was 47% using both $\delta^2\text{H}$ and specific conductance and $\delta^{18}\text{O}$ and specific conductance. The similar wastewater composition at TA3 to TA2 would indicate that a large portion of base flow leaving the hillslope is composed of wastewater, with little dilution by other water sources occurring before discharge. When converted to storage, TA3 contained wastewater depths ranging from 47-158 mm, with the lowest wastewater storage observed the summer months (Figure 4). As shown in Figure 4, storage of wastewater in TA3 was significantly less than the storage in TA2 which could indicate loss to evapotranspiration along its flow path. Riparian vegetation has been shown to have a great influence on groundwater level and base flow (Gribovszki *et al.* 2008, Emanuel *et al.* 2014). Attributing this to loss to evapotranspiration can be supported by the diurnal water table flux observed in this well which Gribovszki *et al.* (2008) used to estimate riparian evapotranspiration.

At hillslope transect B, irrigated well TB1 had a mean wastewater irrigation percentage of 76% using $\delta^2\text{H}$ and specific conductance and a mean percentage of 73% using $\delta^{18}\text{O}$ and specific conductance. This percentage was not converted to wastewater storage, as this well was installed by the plant operators and was not instrumented to measure water level. Well TB2 contained a mean wastewater percentage of 73% using $\delta^2\text{H}$ and specific conductance and a mean percentage of 72% using $\delta^{18}\text{O}$ and specific conductance. When converted to storage, well TB2 contained wastewater depths ranged from 58 mm to 960 mm with the lowest storage depths occurring in the early summer months (Figure 5).

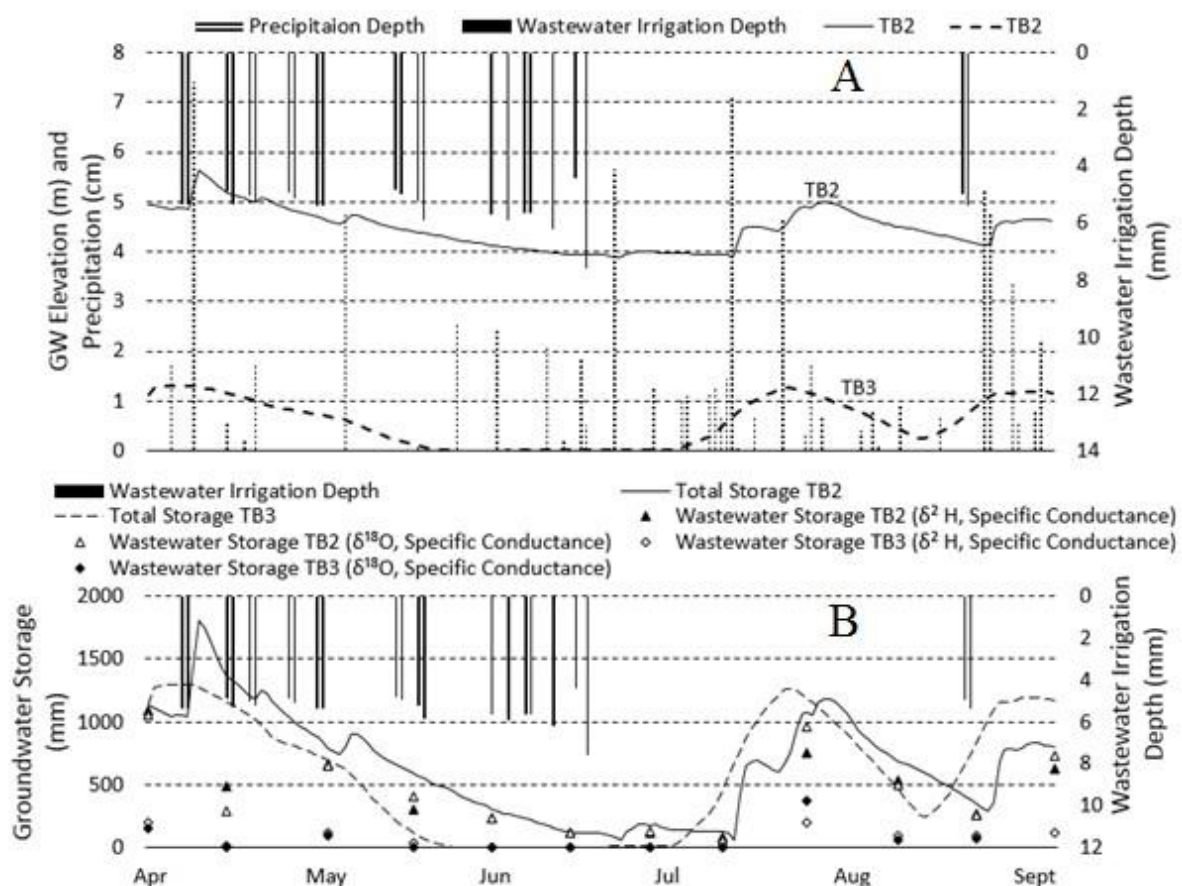


Figure 5: (A) Water table elevation in relation to an arbitrary datum at the bottom of well TB3 along with daily precipitation and wastewater irrigation to transect B. (B) Biweekly wastewater storage in TB2 and TB3, total daily storage in TB2 and TB3, and daily wastewater irrigation. The asterisk (*) denotes where no data were available due to equipment failure.

In contrast to TA2, irrigated well TB2 exhibited little to no water table response to irrigation events, despite receiving similar irrigation volumes (Figure 5). The lack of a water table response is interesting given that higher wastewater fractions and tracer values were observed for TB2. Hanson and May (2004) observed no influence of agricultural irrigation on water table elevation until irrigation exceeded estimated crop evapotranspiration. The

lack of water table response in TB2 could be a result of evapotranspiration exceeding the volume of wastewater directly applied to the well; thus, the more positive isotopic values and wastewater percentages observed in this well derive from irrigated groundwater up gradient of the well or residual wastewater in the subsurface. At well TA2, the mean depth to water during the study period was 589 mm, while mean depth to water in well TB2 was 851 mm.

The increased difference between the soil surface and the water table observed at transect B could also account for the lack of water table response to irrigation in this well. The wetting front generated from irrigation events may be completely retained within the vadose zone at this transect, with no wastewater reaching the water table during the event. A seasonal water table drop was observed in both wells TA2 and TB2; however, this drop was not influenced by irrigation events in TB3, as it was at TA2 (Figures 4,5).

Non-irrigated well TB3, which is down gradient of irrigated areas had a mean wastewater irrigation percentage of 11% using both using $\delta^2\text{H}$ and specific conductance and $\delta^{18}\text{O}$ and specific conductance. When converted to wastewater storage, well TB3 contained 0-197 mm of wastewater. During four sampling events during the summer, well TB3 was dry and samples could not be obtained. Percentages of wastewater and tracer values in TB3 were much lower than in TA3, despite similar landscape positions at the bottom of hillslopes receiving irrigation. Well TB3 was positioned 65.5 m from TB2, while TA3 was positioned 42.6 m from TA2. An additional difference between the two transects is in their riparian vegetation. The riparian area at transect A was dominated by loblolly pine, while the riparian area at transect B was hardwood dominated. These differences could further explain the

difference in observed connectivity between the two transects. This observation suggests that hydrologic connectivity between upland areas of irrigation and lowland discharge areas is strongly heterogeneous across the site and that the potential for wastewater-containing groundwater to contribute to stream flow varies with landscape position, riparian area, and proximity to irrigation. Such heterogeneity in response to landscape characteristics has been documented in multiple studies (Jencso *et al.* 2010, McGlynn and Seibert 2003).

While irrigation accounted for 22% of the blocks total water input, the mixing models indicated mean wastewater percentages of 53% and 50% in groundwater at wellTA2. Ideally, groundwater composition would reflect the input volumes more closely. One explanation is that large precipitation events are leaving the block largely through saturation excess overland flow before infiltration to shallow groundwater can occur. This could result in a disproportionate contribution to the biweekly precipitation tracer signal when considering how much of each event remains in the hydrologic system. Several studies observed that irrigation with wastewater effluent altered the runoff rate of irrigated soils (Agassi, *et al.* 2003, Mamedov, A.I. *et al.* 2000) and reduced infiltration and increased surface runoff in sandy soils (Lado *et al.* (2005). Such an alteration would prevent rainfall infiltration during heavy precipitation events thus limiting the contribution of precipitation to shallow groundwater composition. All land-applied wastewater that is not retained in the vadose zone or consumed in evapotranspiration, should infiltrate to groundwater if the facility is in compliance with its permitting. No overland flow was observed at the site during periods of irrigation.

Surface Water: Small Catchment Scale

An irrigated headwater catchment and a non-irrigated reference catchment within the Southwest creek watershed were used to observe the influence of this wastewater enriched groundwater on the composition of headwater streams draining irrigated areas. Wastewater irrigated catchment TASW contained portions of four irrigation blocks and received a total of 1180 mm of combined rainfall and wastewater irrigation during the study period (12.9% irrigation) and percentages of total biweekly hydrologic load supplied to the catchment by wastewater ranged from 3.10% to 62.5%. The non-irrigated reference catchment JTRIB received a total of 1028 mm of precipitation and no irrigation. Significantly higher specific conductance chloride levels and more positive $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ($p > 0.05$; Figure 2) were observed in surface water exiting the irrigated catchment TASW than in the reference catchment JTRIB. While samples from both catchment TASW and catchment JTRIB depart from the meteoric water line, samples from TASW depart more drastically and frequently, indicating wastewater influence on stream composition.

Because the wastewater's tracer signal could be detected in TASW, the same two component, three end member mixing model used for the groundwater transects was used to estimate the percentage of streamflow contributed by irrigation. Wastewater percentages estimated for TASW ranged from 28% to 77% using $\delta^2\text{H}$ and specific conductance, with a mean percentage of 55%. Wastewater percentages using $\delta^{18}\text{O}$ and specific conductance ranged from 22% to 76% with a mean percentage of 51%. These percentages are very similar to irrigated groundwater. During three sampling events, the stream (TASW) was dry. Data from transect A show an increase in hillslope groundwater storage and an increased hydraulic gradient between the uplands (TA2) and the riparian area (TA3) as a result of irrigation

(Figure 4). This would suggest an increase in baseflow-driven stream flow from this catchment as a result of wastewater irrigation. Headwater streams have been shown to be more sensitive to variations in hillslope processes and more sensitive to alterations in land use (Gomi *et al.* 2002). These small streams provide critical habitats for aquatic life, and the elevated wastewater composition in such streams has the potential to threaten their aquatic ecosystems (Meyer and Wallace, 2011).

Surface Water: Watershed Scale

At the watershed scale, total precipitation during the study period was 928 mm and total irrigation was 24.6 mm (6.8% irrigation). Total discharge from the Southwest creek watershed during the study period was 362 mm resulting in a runoff ratio of 0.38. Chloride concentrations, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ at the outlet of Southwest creek were significantly higher ($p < 0.05$) than in reference catchment JTRIB and in non-irrigated groundwater sources.

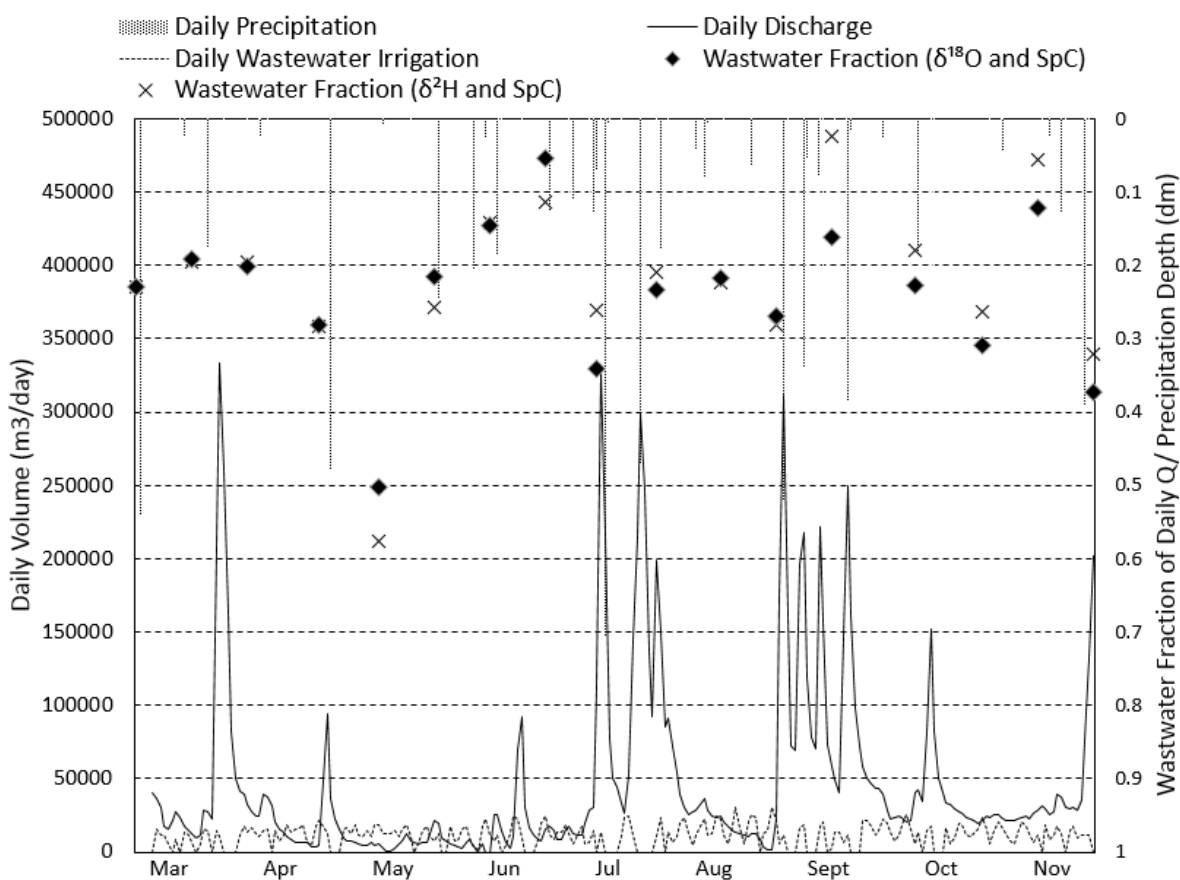


Figure 6: Daily Hydrograph for the study period showing daily watershed wastewater irrigation and precipitation, along with estimated fractions of discharge contributed by irrigation.

The mixing model estimated that wastewater percentages at the outlet ranged from 5% to 50% with a mean percentage of 24% using $\delta^{18}\text{O}$ and specific conductance, and ranged from 3% to 58% using $\delta^2\text{H}$ and specific conductance with a mean percentage of 23%. The highest wastewater percentages were observed during low flow conditions, indicating that flow during these periods could be highly driven by wastewater influenced baseflow (Figure 6, Figure 7). Given that Wastewater irrigation only accounts for 6.8% of the total hydrologic input over the study period, wastewater percentages in stream discharge ranging up to 58%

seem comparatively high. Basins receiving large amounts of agricultural irrigation have been shown to maintain irrigation driven, higher than normal flows during low flow periods. Kendy *et al.* (2006) found that excess irrigation in the Gallatin River Basin in Montana led to higher than natural flows during seasonal low flow periods. Similarly, Kustu *et al.* (2011) observed a link between irrigation in the high plains and increased summer streamflow in the Midwestern United States. Biweekly wastewater percentages were converted to volumetric wastewater discharge estimates based on the daily discharge during the sampling event. Estimated daily wastewater discharges ranged from 73.0 to 75,580 m³/day using $\delta^{18}\text{O}$ and specific conductance with a mean discharge of 13,853 m³/day, and ranged from 154 to 65,096 m³/day using $\delta^2\text{H}$ and specific conductance with a mean discharge of 11,623 m³/day of wastewater. These volumes are high relative to the mean daily wastewater irrigation volume during the study period was 11,052 m³/day. It is possible that this discrepancy is due to uncertainty in the mixing models or temporal variations in the discharge from the watershed when related to total irrigation volumes.

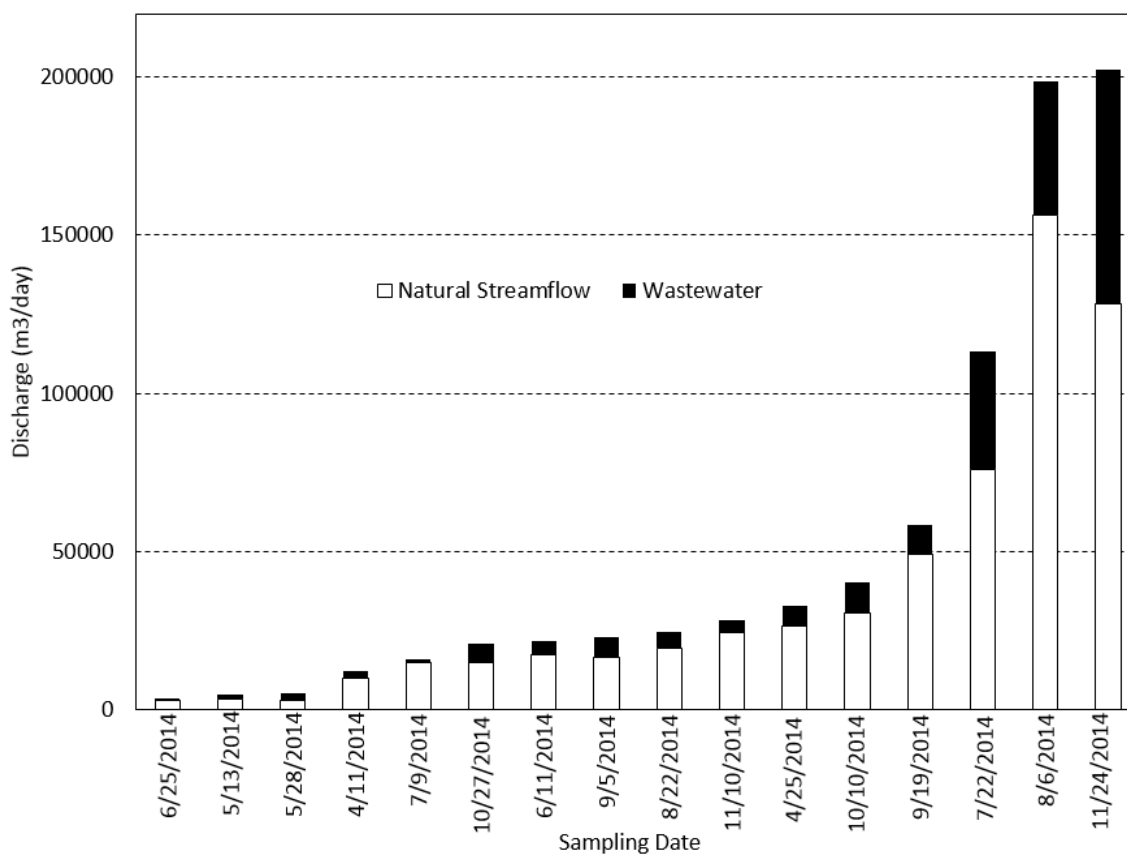


Figure 7: Wastewater composition of watershed discharge for each sampling event.

Uncertainty in Mixing Models

A number of studies have addressed the inherent uncertainty in the results of stable isotope and geochemical mixing models (Joerin *et al.* 2002, Moore and Semmens 2008, Phillips and Gregg 2001). Error for each model based on a Gaussian error propagation averaged 31% for all models used and ranged from 19% to 51%, with the highest uncertainty calculated at TB2 and TA2. This high level of uncertainty is a product of the temporal changes in tracer values of the end members used over the course of the period and is directly proportional to the degree of variability observed at each site. One contribution to the observed error is the

temporal variability of source signatures for precipitation and irrigation in surface waters and groundwater whether irrigated and non-irrigated groundwater.

CHAPTER 5: CONCLUSIONS

Specific conductance, chloride, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were used to evaluate the contribution of land-applied municipal wastewater to groundwater and surface waters in a mixed pine, hardwood forested watershed. These tracers were found to be more prevalent in water sources influenced by wastewater irrigation and proved effective in identifying wastewater flowpaths offsite. The composition of groundwater in irrigated areas ranged from 50 to 76% wastewater prior to discharge to surface waters. The headwater stream leaving a small irrigated catchment (TASW) was mostly wastewater during low precipitation periods, and tracer values indicated that wastewater was a major contributor to its total flow in comparison to a reference tributary without irrigation. Collectively, hydrometric data and the mixing-models provided an estimated mean daily wastewater discharge volume of 11,623 to 13,853 m^3/day from the watershed; wherein, water derived from wastewater irrigation comprised an estimated 23-24% of discharged surface flows from the watershed. The facility does not operate at full capacity and has additional areas to irrigate, and continued population growth will require more wastewater treatment and land-application in the future. If the phenomenon of land application becomes more popular as a way to comply with the clean water act, we could see more land-application across the country in the future. This study provides an initial baseline of how this land-application system to forested land contributes wastewater to the subsurface and watershed. A fundamental knowledge of the site's hydrological function is required to understand current and potential impacts of this waste treatment system on aquatic ecosystem health in the watershed with regards to the release of emerging contaminants.

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APPENDICES

Appendix A: Daily hydrometric data.

Appendix B: Water quality data.

Appendix A: Daily hydrometric data.

Date	Discharge (m ³ /day)	Precipitation (m ³ /day)	Irrigation (m ³ /day)
3/28/2014	320594	0	16715
3/29/2014	198300	2346823	0
3/30/2014	92497	0	0
3/31/2014	50089	0	0
4/1/2014	40214	0	0
4/2/2014	36858	0	15899
4/3/2014	30670	0	11735
4/4/2014	17451	0	11735
4/5/2014	15155	0	5678
4/6/2014	21137	0	0
4/7/2014	27265	0	8464
4/8/2014	23437	364734	0
4/9/2014	17829	98245	13049
4/10/2014	14468	0	10978
4/11/2014	12286	0	6814
4/12/2014	9846	0	0
4/13/2014	11619	0	5678
4/14/2014	28797	0	15899
4/15/2014	27291	772450	14509
4/16/2014	22871	0	0
4/17/2014	207408	0	14887
4/18/2014	333737	0	10221
4/19/2014	261064	3219974	0
4/20/2014	162749	0	0
4/21/2014	81821	0	0
4/22/2014	50177	0	0
4/23/2014	41158	0	11735
4/24/2014	39770	0	17230
4/25/2014	32891	252827	13601
4/26/2014	27544	0	16277
4/27/2014	24745	0	12844
4/28/2014	24593	106841	10529
4/29/2014	39013	0	14202
4/30/2014	36962	750345	15937

5/1/2014	31185	0	0
5/2/2014	20802	0	14006
5/3/2014	15695	0	7192
5/4/2014	13125	0	11735
5/5/2014	10524	0	18522
5/6/2014	8323	0	13823
5/7/2014	6791	0	15903
5/8/2014	6431	0	16731
5/9/2014	6693	0	18549
5/10/2014	6198	0	6814
5/11/2014	3359	0	4921
5/12/2014	3885	0	17034
5/13/2014	4923	0	21630
5/14/2014	48176	0	16986
5/15/2014	94322	0	12027
5/16/2014	36024	2085246	0
5/17/2014	22900	0	0
5/18/2014	15332	0	0
5/19/2014	9185	0	15097
5/20/2014	7655	0	16722
5/21/2014	7632	0	12154
5/22/2014	6121	0	18170
5/23/2014	5173	0	10978
5/24/2014	4178	0	10078
5/25/2014	4660	0	14171
5/26/2014	6439	0	9997
5/27/2014	4614	0	18170
5/28/2014	5306	0	18549
5/29/2014	2789	33158	12492
5/30/2014	397	0	12051
5/31/2014	16	0	12593
6/1/2014	2454	0	14385
6/2/2014	5497	0	10575
6/3/2014	7514	0	15225
6/4/2014	11985	0	18246
6/5/2014	7971	1121219	10762
6/6/2014	6698	0	0

6/7/2014	5931	0	4996
6/8/2014	6700	0	13999
6/9/2014	6442	0	17576
6/10/2014	12862	0	10421
6/11/2014	21813	0	6989
6/12/2014	19881	1075781	12022
6/13/2014	9875	0	0
6/14/2014	7118	0	0
6/15/2014	5513	0	17034
6/16/2014	4775	0	7192
6/17/2014	3323	0	7692
6/18/2014	2198	0	15126
6/19/2014	6010	0	17791
6/20/2014	8887	0	9085
6/21/2014	3391	900168	3944
6/22/2014	1339	0	0
6/23/2014	5420	0	17413
6/24/2014	-819	106841	21955
6/25/2014	-1912	0	10978
6/26/2014	25464	0	7724
6/27/2014	25777	801923	11173
6/28/2014	14754	225963	0
6/29/2014	6367	0	4542
6/30/2014	2779	0	12492
7/1/2014	10439	0	24228
7/2/2014	69091	0	22357
7/3/2014	92029	2457349	9754
7/4/2014	30008	0	0
7/5/2014	16623	0	0
7/6/2014	11141	0	0
7/7/2014	8303	0	8238
7/8/2014	7418	0	19602
7/9/2014	15752	0	24227
7/10/2014	17833	541575	11735
7/11/2014	13961	0	8257
7/12/2014	8678	0	13893
7/13/2014	8848	0	13249

7/14/2014	15667	0	18927
7/15/2014	17092	447014	12492
7/16/2014	12845	477715	5300
7/17/2014	11020	0	11735
7/18/2014	11572	0	17498
7/19/2014	19137	0	5449
7/20/2014	28173	504733	6814
7/21/2014	30502	551399	14763
7/22/2014	113268	311927	0
7/23/2014	328089	626311	13801
7/24/2014	215559	3076291	0
7/25/2014	76893	25789	0
7/26/2014	50643	0	0
7/27/2014	43917	0	0
7/28/2014	33088	294734	10460
7/29/2014	26319	0	23244
7/30/2014	52213	0	24189
7/31/2014	143725	0	11356
8/1/2014	215128	0	0
8/2/2014	299812	2039808	0
8/3/2014	246377	0	0
8/4/2014	137411	0	0
8/5/2014	91911	0	0
8/6/2014	198475	159648	10171
8/7/2014	150364	773678	23156
8/8/2014	85682	0	0
8/9/2014	91402	314383	13627
8/10/2014	72487	0	6435
8/11/2014	54330	0	10269
8/12/2014	39849	0	19504
8/13/2014	30170	0	23848
8/14/2014	25800	0	12113
8/15/2014	27489	0	4817
8/16/2014	28073	178069	11413
8/17/2014	32563	0	17791
8/18/2014	36397	345085	22334
8/19/2014	28771	33158	11735

8/20/2014	24740	0	12324
8/21/2014	23474	0	24314
8/22/2014	24524	0	22712
8/23/2014	19958	416312	11360
8/24/2014	17356	0	5236
8/25/2014	14251	0	16971
8/26/2014	13215	0	30283
8/27/2014	12038	0	16277
8/28/2014	11067	0	5279
8/29/2014	10960	0	20111
8/30/2014	12514	282454	24984
8/31/2014	12483	0	23465
9/1/2014	8833	0	0
9/2/2014	3041	0	12360
9/3/2014	1878	0	14006
9/4/2014	1099	0	30283
9/5/2014	22789	0	21935
9/6/2014	173963	0	5968
9/7/2014	311590	2263315	11356
9/8/2014	161001	2077878	0
9/9/2014	72734	0	0
9/10/2014	69319	0	0
9/11/2014	195473	0	16277
9/12/2014	217561	1473672	18058
9/13/2014	119393	232103	0
9/14/2014	78711	0	0
9/15/2014	70682	0	0
9/16/2014	221397	342629	17737
9/17/2014	157372	946834	20573
9/18/2014	73281	0	0
9/19/2014	58367	0	2227
9/20/2014	49812	227191	13249
9/21/2014	40361	0	13249
9/22/2014	146056	0	6814
9/23/2014	249579	1668934	11619
9/24/2014	161769	77368	0
9/25/2014	97779	0	0

9/26/2014	72330	0	0
9/27/2014	58101	0	21549
9/28/2014	50485	0	21577
9/29/2014	45956	0	17751
9/30/2014	42990	0	11784
10/1/2014	43862	0	14200
10/2/2014	39197	114210	22334
10/3/2014	28447	0	19684
10/4/2014	22659	0	13627
10/5/2014	23740	0	7192
10/6/2014	24874	0	11210
10/7/2014	22464	0	21330
10/8/2014	20105	0	25362
10/9/2014	21613	0	15899
10/10/2014	40125	0	5181
10/11/2014	41955	804379	13509
10/12/2014	34736	0	0
10/13/2014	81566	0	14763
10/14/2014	151550	655784	17034
10/15/2014	82680	982448	0
10/16/2014	50527	0	0
10/17/2014	40633	0	0
10/18/2014	33806	0	16787
10/19/2014	32280	0	5971
10/20/2014	29311	0	9085
10/21/2014	27813	0	19306
10/22/2014	26552	0	18549
10/23/2014	23381	0	11534
10/24/2014	22588	0	10430
10/25/2014	21095	0	12324
10/26/2014	19573	0	15142
10/27/2014	21020	0	23848
10/28/2014	24193	0	15520
10/29/2014	23168	98245	5283
10/30/2014	25178	0	14049
10/31/2014	24965	0	20820
11/1/2014	23350	185437	17413

11/2/2014	21790	0	12870
11/3/2014	21237	0	7192
11/4/2014	21214	0	5489
11/5/2014	22747	0	12066
11/6/2014	23784	0	20441
11/7/2014	24537	0	17791
11/8/2014	22779	0	12492
11/9/2014	26560	0	6814
11/10/2014	28263	0	11947
11/11/2014	31331	98245	0
11/12/2014	29849	0	18766
11/13/2014	25359	109297	8706
11/14/2014	27594	0	11356
11/15/2014	38968	0	17926
11/16/2014	37585	561224	12760
11/17/2014	30311	31930	0
11/18/2014	29341	0	14204
11/19/2014	30903	0	17791
11/20/2014	28331	0	9842
11/21/2014	35889	0	11356
11/22/2014	95210	1694723	11484
11/23/2014	131900	159648	11325
11/24/2014	202124	0	0

Appendix B: Water quality data.

Date	Sample Site:	Wastewater Effluent		
	Sp. C. us/cm	[Cl-]mg/L	$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	685	51	-2.90	-14.70
4/11/2014	686	43	-2.75	-12.53
4/25/2014	626	49	-2.35	-13.56
5/13/2014	724	49	-2.95	-13.97
5/28/2014	829	56	-2.99	-13.88
6/11/2014	814	56	-2.74	-12.88
6/25/2014	705	56	-2.62	-12.04
7/9/2014	697	56	-2.95	-13.52
7/22/2014	651	55	-3.06	-14.10
8/6/2014	658	53	-3.06	-14.71
8/22/2014	659	43	-3.19	-15.54
9/5/2014	624	48	-2.16	-10.67
9/19/2014	578	55	-2.85	-14.03
10/10/2014	581	48	-2.86	-14.04
10/27/2014	600	54	-2.52	-11.39
11/10/2014	739	55	-2.53	-12.20
11/24/2014	598	55	-3.17	-15.29

Date	Sample Site:	[Cl-]mg/L	Precipitation	
	Sp. C. us/cm		$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	10	<10	-7.36	-41.85
4/11/2014	28	<10	-3.29	-6.99
4/25/2014	15	<10	-4.45	-20.46
5/13/2014	22	<10	-1.95	-5.68
5/28/2014	59	<10	-4.31	-25.68
6/11/2014	15	<10	-3.00	-20.01
6/25/2014	27	<10	-2.68	-10.22
7/9/2014	15	<10	-6.62	-43.67
7/22/2014	23	<10	-4.24	-20.59
8/6/2014	32	<10	-4.02	-18.79
8/22/2014	38	<10	-3.63	-16.16
9/5/2014	17	<10	-2.53	-7.65
9/19/2014	12	<10	-5.31	-29.00
10/10/2014	36	<10	-6.14	-31.41
10/27/2014	23	<10	-4.39	-19.73
11/10/2014	35	<10	-6.50	-39.17

11/24/2014 18 <10 -3.73 -13.41

Date	Sample Site:	[Cl ⁻]mg/L	TA1	
	Sp. C. us/cm		$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	305	13	-4.62	-25.00
4/11/2014	313	13	-5.08	-26.60
4/25/2014	298	11	-5.27	-27.08
5/13/2014	320	13	-4.91	-25.85
5/28/2014	308	13	-4.94	-25.89
6/11/2014	131	13	-5.03	-26.04
6/25/2014	152	19	-4.95	-25.15
7/9/2014	198	23	-4.83	-23.97
7/22/2014	268	20	-4.88	-25.73
8/6/2014	290	13	-5.17	-26.64
8/22/2014	296	14	-5.12	-26.44
9/5/2014	290	15	-5.18	-27.13
9/19/2014	270	13	-5.12	-27.67
10/10/2014	248	15	-5.14	-26.58
10/27/2014	300	11	-5.13	-27.45
11/10/2014	295	13	-5.17	-27.78
11/24/2014	296	11	-5.18	-27.34

Date	Sample Site:	[Cl ⁻]mg/L	TA2	
	Sp. C. us/cm		$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	495	70	-3.97	-19.21
4/11/2014	460	37	-3.92	-18.90
4/25/2014	453	63	-4.12	-19.65
5/13/2014	478	63	-3.91	-19.14
5/28/2014	475	63	-3.97	-18.98
6/11/2014	460	63	-4.01	-19.08
6/25/2014	228	70	-3.07	-14.33
7/9/2014	465	56	-4.04	-20.03
7/22/2014	418	55	-2.66	-14.13
8/6/2014	429	49	-3.71	-18.76
8/22/2014	477	56	-3.68	-16.45
9/5/2014	510	55	-3.59	-17.11
9/19/2014	417	56	-3.99	-19.31
10/10/2014	389	56	-3.99	-18.76
10/27/2014	400	55	-3.90	-19.55
11/10/2014	461	88	-4.40	-21.87

11/24/2014 376 55 -3.59 -17.11

Date	Sample Site:	[Cl ⁻]mg/L	TA3	
	Sp. C. us/cm		$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	375	49	-4.98	-25.43
4/11/2014	368	48	-4.11	-18.61
4/25/2014	365	43	-3.88	-17.43
5/13/2014	415	49	-3.57	-16.33
5/28/2014	420	55	-3.56	-16.68
6/11/2014	412	70	-3.35	-15.70
6/25/2014	226	78	-3.61	-16.41
7/9/2014	420	70	-3.58	-17.50
7/22/2014	396	49	-3.80	-18.32
8/6/2014	319	43	-3.93	-18.75
8/22/2014	443	86	-3.60	-16.43
9/5/2014	469	97	-3.37	-15.87
9/19/2014	388	56	-3.86	-19.64
10/10/2014	380	49	-4.15	-20.99
10/27/2014	420	79	-3.69	-17.66
11/10/2014	490	64	-3.97	-18.75
11/24/2014	462	56	-3.93	-17.13

Date	Sample Site:	[Cl ⁻]mg/L	TASW	
	Sp. C. us/cm		$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	330	50	-4.15	-20.77849466
4/11/2014				
4/25/2014				
5/13/2014	398	63	-3.31	-14.54
5/28/2014	382	56	-3.49	-15.93
6/11/2014	357	63	-3.19	-15.14
6/25/2014	281	74	-2.91	-12.56
7/9/2014	456	70	-3.26	-15.32
7/22/2014	345	70	-3.77	-18.91
8/6/2014	229	43	-4.29	-21.54
8/22/2014				
9/5/2014	416	45	-3.53	-16.76
9/19/2014	270	48	-4.39	-22.73
10/10/2014	337	55	-3.74	-18.64
10/27/2014	420	56	-3.40	-15.67
11/10/2014	560	74	-3.51	-16.66

11/24/2014 441 55 -3.78 -17.28

Date	Sample Site:		TB1	
	Sp. C. us/cm	[Cl-]mg/L	$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	600	48	-3.37	-15.80
4/11/2014	691	32	-3.22	-14.37
4/25/2014	323	70	-3.12	-14.33
5/13/2014	574	94	-3.31	-14.46
5/28/2014	589	94	-3.34	-15.46
6/11/2014	498	94	-3.22	-15.00
6/25/2014	503	49	-3.04	-14.32
7/9/2014	487	94	-3.33	-15.65
7/22/2014	506	79	-3.01	-14.54
8/6/2014	511	86	-3.47	-15.43
8/22/2014	552	78	-3.70	-17.17
9/5/2014	500	78	-3.60	-17.92
9/19/2014	450	88	-3.48	-17.54
10/10/2014	445	78	-3.63	-17.27
10/27/2014	490	78	-3.83	-17.66
11/10/2014	498	78	-3.82	-18.01
11/24/2014	532	88	-3.57	-18.00

Date	Sample Site:		TB2	
	Sp. C. us/cm	[Cl-]mg/L	$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	650	70	-3.87	-18.20
4/11/2014	691	37	-4.31	-23.82
4/25/2014	302	63	-4.89	-26.79
5/13/2014	633	63	-4.50	-22.25
5/28/2014	662	63	-4.16	-21.31
6/11/2014	670	63	-3.88	-19.31
6/25/2014	670	70	-3.92	-19.74
7/9/2014	507	56	-4.07	-19.14
7/22/2014	495	55	-4.02	-20.11
8/6/2014	796	49	-4.45	-18.68
8/22/2014	550	56	-4.42	-20.79
9/5/2014	530	55	-4.28	-20.36
9/19/2014	431	56	-4.40	-19.00
10/10/2014	419	56	-4.26	-21.30
10/27/2014	420	55	-4.40	-21.95
11/10/2014	497	88	-4.30	-21.60

11/24/2014 430 64 -3.57 -20.05

Date	Sample Site:	[Cl ⁻]mg/L	TB3	
	Sp. C. us/cm		$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	158	14	-5.23	-18.20
4/11/2014	169	16	-5.31	-23.82
4/25/2014	68	14	-5.62	-26.79
5/13/2014	182	14	-5.22	-22.25
5/28/2014	172	13	-5.25	-21.31
6/11/2014				
6/25/2014				
7/9/2014				
7/22/2014				
8/6/2014	129	17	-3.15	-18.68
8/22/2014	172	20	-4.81	-20.79
9/5/2014	130	<10	-4.21	-20.36
9/19/2014	121	14	-4.23	-19.00
10/10/2014	127	13	-4.67	-21.30
10/27/2014	120	<10	-5.04	-21.95
11/10/2014	142	14	-4.99	-21.60
11/24/2014	138	<10	-4.88	-20.00

Date	Sample Site:	[Cl ⁻]mg/L	Watershed Outlet	
	Sp. C. us/cm		$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	194	14	-4.37	-23.13
4/11/2014	179	16	-4.42	-22.28
4/25/2014	150	14	-4.12	-21.58
5/13/2014	249	14	-3.78	-19.40
5/28/2014	383	13	-3.49	-18.60
6/11/2014	165		-2.62	-14.29
6/25/2014	119		-3.00	-14.23
7/9/2014	179		-3.99	-23.99
7/22/2014	174		-3.75	-18.72
8/6/2014	165	17	-3.80	-19.39
8/22/2014	179	20	-3.99	-20.13
9/5/2014	214	<10	-3.47	-16.85
9/19/2014	117	14	-4.70	-25.40
10/10/2014	183	13	-4.08	-21.13
10/27/2014	185	<10	-3.77	-20.10
11/10/2014	228	14	-3.71	-18.62

11/24/2014	214	<10	-3.38	-16.15
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Date	Sample Site: Sp. C. us/cm	[Cl ⁻]-mg/L	Control Well $\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014				
4/11/2014				
4/25/2014				
5/13/2014				
5/28/2014				
6/11/2014	10	<10	-4.46	-22.87
6/25/2014	17	<10	-4.42	-22.76
7/9/2014	53	<10	-4.35	-22.45
7/22/2014	53	<10	-4.01	-19.59
8/6/2014	48	<10	-4.03	-20.88
8/22/2014	45	<10	-4.32	-21.94
9/5/2014	47	<10	-4.46	-22.99
9/19/2014	51	<10	-4.31	-22.78
10/10/2014	53	<10	-4.29	-21.06
10/27/2014	49	<10	-4.38	-21.42
11/10/2014	51	<10	-4.69	-23.40
11/24/2014	55	<10	-4.30	-22.81

Date	Sample Site: Sp. C. us/cm	[Cl ⁻]-mg/L	JTRIB $\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	269	14	-4.65	-24.23
4/11/2014	277	14	-4.22	-21.62
4/25/2014	240	13	-4.19	-19.58
5/13/2014	265	16	-4.27	-21.47
5/28/2014	348	17	-3.93	-20.48
6/11/2014	150	15	-3.00	-15.52
6/25/2014	200	15	-3.14	-16.04
7/9/2014				
7/22/2014	274	17	-3.87	-19.58
8/6/2014				
8/22/2014	278	17	-4.01	-21.34
9/5/2014	256	18	-2.18	-10.54
9/19/2014	202	25	-4.71	-25.29
10/10/2014	233	17	-4.34	-22.29
10/27/2014	195	17	-4.03	-20.53
11/10/2014	163	19	-4.06	-21.19

11/24/2014	212	20	-3.59	-15.80
	Sample Site:		MW3	
Date	Sp. C. us/cm	[Cl-]mg/L	$\delta^{18}\text{O}$	$\delta^2\text{H}$
3/28/2014	52	10	-4.69	-24.82
4/11/2014	61	11	-4.90	-27.12
4/25/2014	64	10	-4.75	-23.82
5/13/2014	74	11	-4.55	-22.55
5/28/2014	88	11	-4.60	-22.68
6/11/2014	90	9	-4.43	-22.90
6/25/2014	55	13	-4.73	-23.22
7/9/2014	120	14	-4.59	-22.63
7/22/2014	126	14	-4.43	-21.76
8/6/2014	90	14	-4.50	-23.00
8/22/2014	71	15	-4.63	-24.06
9/5/2014	83	17	-4.52	-22.30
9/19/2014	52	10	-4.74	-25.09
10/10/2014	57	16	-4.69	-24.77
10/27/2014	70	13	-4.70	-24.27
11/10/2014	116	15	-4.60	-23.36
11/24/2014	107	13	-4.61	-23.17