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CHARACTERIZATION OF RUNOFF IN TWO URBAN WATERSHEDS IN LINCOLN, NEBRASKA

by

Michael James Florek III

A THESIS

Presented to the Faculty of The Graduate College at the University of Nebraska In Partial Fulfillment of Requirements For the Degree of Master of Science

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Under the Supervision of Professor Bruce I. Dvorak

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CHARACTERIZATION OF RUNOFF IN TWO URBAN WATERSHEDS IN LINCOLN, NEBRASKA

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University of Nebraska-Lincoln, 2012

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Characterization of runoff water quality and conditions for two urban watersheds in Lincoln, NE, was performed using data collected from 2008-2012. Water quality data from in-stream probes and storm sampling was combined with soil sample data, geographic information system (GIS) modeling, and nutrient isotope composition analysis to provide a more detailed picture of runoff mechanisms in the Taylor Park and Colonial Hills watersheds.

Soil sample data and GIS modeling were used to compare physical characteristics of the urban watersheds. Taylor Park and Colonial Hills are relatively similar, save for Colonial Hills being six times as large. Its time of concentration, 140 minutes, was found to be much longer than at Taylor Hills, 60 minutes. Water quality data collected for a previous study by Fisher (2011) was used to compare seasonal mass loadings of turbidity and total suspended solids (TSS). The ratio of turbidity to TSS was found to be higher at Colonial Hills for small storms and higher at Taylor Park for large storms, suggesting that large particles in runoff at Colonial Hills reach the watershed outlet in large storms, but are captured in small storms. Isotope analysis was conducted on soil samples collected in 2011 and 2012 and water quality samples collected in 2011 in order to identify possible sources of nutrients in storm water runoff. Samples were tested for ¹⁸O-NO₃, ¹⁵N-NO-₃, and ¹⁸O-PO₄ composition. Analysis showed that atmospheric deposition of nitrogen, in the form of precipitation on impervious surfaces, is likely to be a meaningful source of nitrate in the two watersheds.

Soluble reactive phosphorus (SRP) concentration and ¹⁸O-PO₄ composition were compared over the course of several storms. SRP showed a trend of increasing as a storm continued, while ¹⁸O-PO₄ appeared to change over time in larger storms. Estimated mass loadings of SRP and Total Phosphorus when SRP is high suggest meaningful phosphorus contribution during the later part of storms. These results may suggest that erosion of soil, such as stream bank soil, may be a source of phosphorus in storm water runoff.

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This thesis was a team effort from start to finish. The whole project, done for the City of Lincoln, has passed hands several times – from Patrick Hartman to Jake Fisher and to me – and has been aided by a number of smart, trustworthy undergraduates and graduates with a few free hours. I started on the project as an undergraduate assistant to Jake. It's a little funny that this thesis ends with Jake assisting me. I could not have done this alone.

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Chapter 1

Introduction

1.1 Background

Urban storm water runoff is a major contributor of nutrients, solids and other contaminants into the environment. Due to large areas of impervious surfaces, urban runoff flows faster and carries more pollutants than runoff from undeveloped areas. Storm water flow and water quality vary from storm to storm, depending on storm size, intensity and previous conditions. For these reasons, it is increasingly important to study how physical characteristics of urban watersheds can affect storm water runoff.

Patrick Hartman (2010) and Jake Fisher (2011) compiled water quality data for two watersheds in southeast Lincoln, NE. The Taylor Park and Colonial Hills watersheds were chosen for study due to their proximity to Holmes Lake, which had undergone treatment by the City of Lincoln to reduce the frequency of algal blooms. Currently, Holmes Lake is listed as impaired for total nitrogen, total phosphorus, pH and chlorophyll by the Environmental Protection Agency (EPA) (Rock Krzycki, personal communication, September 28, 2012). Despite appearing to share similar characteristics, the watersheds behaved differently for storms of varying size. In particular, runoff in Taylor Park tended to have a higher mass loading of solids during very small storms, while Colonial Hills showed higher solids loading for larger storms. Runoff in Taylor Park also had slightly higher event mean concentrations (EMC) of nitrate-nitrogen, total nitrogen and total phosphorus. Fisher produced a series of model equations to help estimate contaminant concentrations in runoff, which fit the data best for Colonial Hills, the larger of the two watersheds.

Hartman and Fisher were able to provide a broad picture of what was occurring during runoff periods in southeast Lincoln. However, some key information was unavailable. Detailed physical watershed characteristics had not been completely analyzed. Also, general hydrologic information had not been fully investigated and soil composition, including nutrient isotope ratios, had not been studied.

1.2 New Research

In order to put the research by Hartman (2010) and Fisher (2011) into perspective, the following objectives had to be addressed:

- Utilize high-resolution maps of elevation to evaluate runoff flow paths, time of concentration for runoff, the proportion of impervious and pervious cover, and areas of intermittent pervious flow. Then, use the watershed characteristics, along with soil sample data, to provide a better comparison of the two watersheds.
- 2) Discuss and interpret nutrient isotope samples from several sources within the watersheds and storm water samples, focusing on suggesting possible nutrient sources. Use watershed characteristics to evaluate the plausibility of sources.

1.3 Thesis Overview

The thesis is structured to follow the research process step-by-step. Chapter 2 is a literature review containing relevant background information on topics of interest and previous studies in Taylor Park and Colonial Hills. Chapter 3 describes how the sites were selected and how data was collected. Chapter 4 walks through sampling and testing

procedures, Geographic Information System (GIS) software modeling, and hydrologic calculations. Chapter 5 presents the results from calculations and isotope samples, including statistical analysis. Chapter 6 synthesizes the results into major conclusions.

Chapter 2

Literature Review

2.1 Introduction

Storm runoff from urban watersheds is a significant source of pollution. Research has been conducted on contaminants in storm runoff, as well as the hydrology of storms. In order to better understand a watershed, both physical and chemical components must be studied. The purpose of this literature review is to define the contaminants of interest, describe methods of identifying contaminant sources, and explain some aspects of watershed mechanics. For this review, the nutrients of interest are nitrogen and phosphorus.

In many settings, sources of nutrients in surface or ground water may be characterized by way of isotope analysis. This is especially true in cases where sources are isotopically distinct and little modification has occurred during transport. Physical characteristics of a watershed, including impervious surfaces, other land use and erosion potential, may be used to describe runoff. Geographic Information Systems (GIS) may be used to compile and incorporate watershed data into hydrologic models. The review will also introduce a previous study in the Taylor Park and Colonial Hills watersheds, which attempted to combine water quality and runoff data into pollutant estimation models.

2.2 Nutrients

Nitrogen and phosphorus are both naturally-occurring and human-applied nutrients important for the growth of vegetation. They are commonly used in fertilizers, especially in agricultural applications. However, when allowed to accumulate in a body of water, or leach into drinking water systems, nitrogen (typically in the form of nitrate, NO₃) and phosphorus can be considered contaminants of concern (Novotny, 2003). In order to identify sources of nutrients, researchers have adapted methods of isotope analysis, comparing typical isotopic ratios in fertilizer, manure, precipitation and soil to those found in watersheds of interest. Examples of some types of studies of nutrients in watersheds include Silva et al. (2002) and Kaushal et al. (2011) who investigated nitrogen and oxygen isotopes to identify sources of nitrate, McLaughlin et al. (2006) who studied oxygen isotopes in phosphate. Isotopes of water can be used for hydrologic studies such as that of Harvey (2001) who compiled data to research possible seasonal trends in atmospheric oxygen isotopes of water.

2.2.1 Nitrate Isotopes

Nitrate (NO₃) is a common soluble form of nitrogen and a contaminant of concern for nearly every surface- and groundwater system. Nitrogen is an important nutrient found in most commercial inorganic fertilizers, as well as organic sources such as animal waste. Nitrogen can also be deposited in precipitation, as shown in **Figure 2.1** (USGS, 2008). Lincoln, NE, is in an area with very high atmospheric deposition, with an average of over 1.8 tons of nitrogen per square mile per year.

Nitrate build-up in ground water can impair the quality of drinking water, causing "blue baby syndrome" in infants, and may contribute to eutrophication of bodies of surface water. Eutrophication occurs when organism growth exceeds the rate of food production, often resulting in an algal bloom (Novotny, 2003).

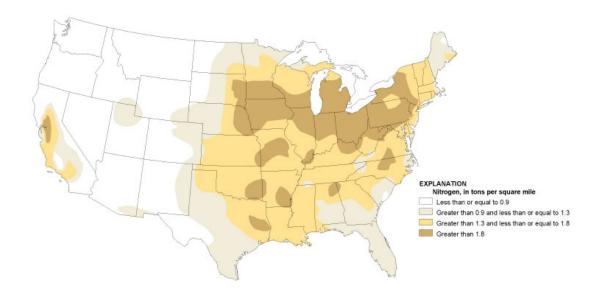


Figure 2.1 Estimated atmospheric deposition of nitrogen (from USGS, 2008).

Nitrate in surface and ground water can come from four general sources: atmospheric deposition, ammonium fertilizers, soil, and sewage (Silva et al., 2002). Coaland gas-burning utilities and industries are estimated to account for over half of atmospheric nitrogen in the form of NO_x (USGS, 2008). Automobile exhaust may also contribute a significant proportion of atmospheric nitrogen. Ammonium (NH₄) from fertilizers and organic nitrogen from soil can be oxidized to nitrate by nitrification, a natural bacterial process.

Due to the variety and quantity of nonpoint sources, researchers have made efforts to create methods designed to help identify these sources. One such method involves the measurement of nitrogen and oxygen isotopes in nitrate, with the hypothesis that different sources will have different isotopic composition. In these studies, the isotopes of interest are ¹⁵N and ¹⁸O, both stable minor isotopes of their respective elements. Atmospheric conditions affect the composition of ¹⁸O in NO₃. Volatilization of NH₃ leads to

enrichment of 15 N in ammonia and nitrification of the enriched NH₃ results in enriched NO₃. Denitrification of NO₃ also can cause enrichment and affect the composition of 15 N in NO₃.

To compare isotopic composition, researchers convert each element into a purified gas for measurement on a special instrument called a stable isotope mass spectrometer. For calibration, each element has an internationally recognized standard (atmospheric N₂ for nitrogen, seawater for oxygen) and also international standards IAEA-N3, USGS34 and USGS35 (Kaushal et al., 2011) to evaluate the conversion process. Isotope composition is expressed relative to the international standard using the equation:

$$\delta(\%_0) = \frac{(R)_{\text{sample}} - (R)_{\text{standard}}}{(R)_{\text{standard}}} \times 1000$$
(2.1)

where:

R = ratio of heavy to light isotope (such as ${}^{18}\text{O}/{}^{16}\text{O}$ or ${}^{15}\text{N}/{}^{14}\text{N}$).

The isotope composition is reported in parts per thousand (‰) relative to the standard. The standard chemicals for comparison are atmospheric N_2 and Vienna Standard Mean Ocean Water. Using this notation, very small differences in isotope abundance are easily distinguished.

Silva et al. (2002) used isotope analysis to identify sources of nitrate in urban environments in Austin, Texas, and Tacoma, Washington. The researchers collected samples during base flow and storm flow conditions. On a plot of δ^{18} O versus δ^{15} N, the base flow samples were grouped together with lower δ^{18} O and higher δ^{15} N, suggesting a single source of nitrate (Silva et al., 2002). In this case, the researchers suggested that, considering past studies and typical isotope concentrations, nitrogen may have been coming from a sewage source. The storm flow data was more scattered and tended to have higher δ^{18} O and lower δ^{15} N. The data indicated to the researchers that more nitrate sources were contributing during storm flow conditions, likely including atmospheric nitrate as an important source.

In a similar study, Kaushal et al. (2011) examined water quality data from agricultural, suburban and forest watersheds in Baltimore, Maryland. All samples collected for their research were taken on the falling limbs of storm hydrographs. On a plot of δ^{18} O versus δ^{15} N, the suburban watersheds showed concentrations in the ranges typical of soil nitrogen and sewage, possibly from leaking sewer lines. Values for δ^{18} O were typically higher than in the rural watersheds, leading the researchers to believe atmospheric deposition may have been a significant source. When including base flow and storm flow in the analysis, Kaushal et al. (2011) noticed that low flow tended to have isotope compositions similar to typical sewage, while high flow tended to have compositions closer to atmospheric sources.

2.2.2 Phosphate Isotopes

Phosphorus is a naturally-occurring element used by all living organisms. In the environment, phosphorus is a common fuel for cell metabolism. If an over-abundance of dissolved phosphorus is present in a body of water, microorganisms can grow and reproduce at accelerated rates (McLaughlin et al., 2006). To address phosphorus over-abundance during best management practices, it is important to know sources of phosphorus for a body of water.

Phosphorus can enter a water environment in several ways. It occurs naturally in soil in both soluble and attached forms (Novotny, 2003). Sorbed phosphorus is available for plant uptake and can be dissolved and washed away by runoff. Attached phosphorus is bound to soil particles and can only enter a water system if the soil particle is washed into the stream. Phosphorus is also introduced into the environment from plant and animal waste.

Two measures of phosphorus are commonly used. Soluble reactive phosphorus (SRP) tends to consist mostly of inorganic orthophosphate (PO₄) (McLaughlin et al., 2006). This form of phosphorus is used directly by plants. The concentration of SRP in a body of water can be used to indicate the risk of an algal bloom. Total Phosphorus (Total P) includes SRP, soluble unreactive phosphorus, and particulate phosphorus. Total P is also used as a measure of potential risk for increased algae activity in bodies of water (Novotny, 2003).

Most phosphorus found in aquatic systems is strongly bonded to oxygen (McLaughlin et al., 2006). For this reason, the researchers studied inorganic phosphorus in the form of phosphate (PO_4^{3-}). Phosphate is part of DNA, RNA, ATP and phospholipids in cell membranes. Phosphate can be formed naturally in a living organism then released into the environment as a waste product. Phosphate can also be manufactured and applied to land in a fertilizer.

McLaughlin et al. (2006) attempted to identify sources of phosphorus by studying differences in phosphate oxygen isotope composition present in water and soil samples. The researchers used ¹⁸O as the isotope of interest. ¹⁸O is a stable, naturally occurring oxygen isotope. Natural precipitation contains primarily ¹⁶O, but is also a source of ¹⁸O. The ratio of ¹⁸O to ¹⁶O, reported as δ^{18} O, can be used to measure the temperature of precipitation and interactions between nutrients in soil. δ^{18} O varies in precipitation in predictable ways for specific locations.

Harvey (2001) created a three-year trend graph of δ^{18} O in water for Mead, NE, as shown in **Figure 2.2**. δ^{18} O is lowest during cooler seasons, and peak δ^{18} O occurs during warmer seasons. The trend was consistent through all three years of the study.

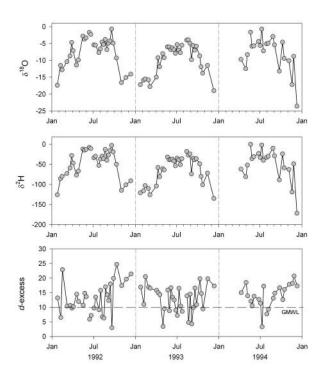


Figure 2.2 Seasonal isotope concentration trends (from Harvey, 2001).

 δ^{18} O can vary depending on certain conditions including water temperature, water salt content and living versus manufactured source. By comparing δ^{18} O_P, the ratio of ¹⁸O to ¹⁶O in PO₄³⁻, from different samples within an estuary in California, McLaughlin et al. (2006), were able to identify with relative certainty several sources of inorganic phosphorus, including fertilizer applied to nearby farms, phosphate dissolved in groundwater and ocean water from the mouth of the estuary. The researchers took samples from multiple locations at different times of the year. In that particular estuary, seasonal effects on phosphorus were not discovered, but may be important in other watersheds (McLaughlin et al., 2006). The researchers also noted that low $\delta^{18}O_P$ phosphate was removed preferentially by plant uptake and as phosphorus moved downstream.

2.3 Watershed Characteristics

The physical characteristics of a watershed greatly affect runoff behavior. As little as 10% impervious cover can lead to stream degradation in a watershed (Novotny, 1994). For example, faster flow velocities and higher stream stages can increase the chances of stream bank erosion (Schueler, 1994). In addition, computer software can be used to model how land use affects water quality and flow, such as that performed by Rust (2007).

2.3.1 Connected Impervious Drainage

Impervious surfaces are portions of a watershed where the ground cannot be penetrated by water. These surfaces include roads, parking lots, roofs and similar features. In an urban watershed, impervious surfaces can account for a large proportion of the total area.

Impervious surfaces can be divided into two hydrologic categories: connected and unconnected. Connected impervious surfaces contribute to overland flow and can be considered part of the storm water drainage system (Schueler, 1994). Unconnected impervious surfaces are not considered a direct part of the drainage system (May and Sivakumar, 2009). Runoff from unconnected surfaces is assumed to infiltrate into the soil. Unconnected surfaces are most commonly house roofs, patios and sheds.

An increase in impervious cover can have significant physical effects on a watershed. In general, runoff from points higher in the watershed reaches the outlet much sooner over impervious surface than over natural terrain. Stream stages during storm events also rise. The increased velocity and tendency towards bank-full flow increase contributions of sediment from stream bank erosion and scouring of stream beds.

Water quality is also affected by the fraction of impervious cover in a watershed. Impervious surfaces, particularly roads, can accumulate pollutants from the atmosphere or urban environment (Schueler, 1994). These pollutants can be quickly washed away in a storm event, rapidly entering and contaminating outlet streams.

2.3.2 Land Use Modeling

A Geographic Information System (GIS) is a digital method of storing, manipulating and displaying geographically-referenced information. Spatial analysis tools built into GIS software can be used to change or organize raw data into a more meaningful format. Interactive, informative maps can be built with GIS to describe water quality across an individual watershed, or an entire city. Rust (2007) used ArcDesktop to describe the city of Lincoln, Nebraska, in such a way. GIS can also take this data and use it as inputs in simulations, as Bhaduri et al. (2000) did using a combined Long-Term Hydrologic Impact Assessment (L-THIA) and Nonpoint Source (NPS) GIS model. Rust (2007) used GIS as one component in a storm water quality modeling project. Investigators visited 264 storm water outlets or manholes in Lincoln, NE, over a period of several years. Sites were recorded as having no flow, trickling flow, stagnant flow, or significant flow. Stagnant and significant flow sites were sampled for standard water quality parameters including nitrate, chlorine, chloride and fluoride. Rust (2007) took the collected data points and input them into GIS software.

To help model possible sources of contamination, Rust (2007) added land use information. Areas of Lincoln, NE, were marked as residential, commercial or industrial to differentiate human sources of contamination. Another layer showing the boundaries of the saline aquifer beneath Lincoln, NE, helped show groundwater influences on water quality. These, combined with the sampled data points, helped Rust (2007) develop a method of identifying high-risk storm water outlets.

Bhaduri et al. (2000) used GIS for long-term modeling. Their goal was to simulate the Little Eagle Creek watershed in Indianapolis, IN, over a period of several decades, taking into account changes in land use. They used GIS and historical records to model the watershed and simulate hydrologic functions at different points in time, creating a working historic model.

Bhaduri et al. (2000) included an L-THIA model to simulate nonpoint pollution. In an urban setting, point sources of pollution include storm water outlets, water collection tanks and other direct connections to the drainage system. However, much of the urban landscape can be considered as a nonpoint source, such as parking lots, road surfaces and construction sites.

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The researchers simulated the changes over time in the Little Eagle Creek watershed. They found that in areas where urbanization took place, projected flow volumes increased with impervious cover. Bhaduri et al. (2000) also observed that changes in zoning over time were reflected in runoff data. When commercial areas with high impervious cover were re-zoned to low-density residential areas with less impervious cover, projected runoff volumes decreased.

2.4 Past Colonial Hills and Taylor Park Watershed Studies

During the non-winter months of 2008 through 2011, the University of Nebraska-Lincoln (UNL) and the United States Geological Survey (USGS) monitored stream flow, precipitation, and water quality in two urban watersheds in Lincoln, NE. Fisher (2011) collected this data with three specific goals in mind. First, using in-line probe observations and climatic data, Fisher developed regression models for the Taylor Park and Colonial Hills watersheds. Second, using water quality data, Fisher calculated event mean concentrations (EMCs) and developed two regression models. One model included EMC and climatic data, the other included only climatic data. Finally, Fisher used these regression models to estimate seasonal mass loadings then compared the three variations to see which was most suited to the two watersheds.

In order to gather real-time information, the USGS, UNL and the City of Lincoln installed in-stream monitoring stations at the outlets of the Taylor Park and Colonial Hills watersheds. Each station was equipped with a YSI 6600 water quality sonde to measure conductivity, dissolved oxygen, turbidity, and temperature; an ISCO 4230 bubbler flow meter to measure flow depth; and an ISCO 2150 area velocity meter to measure flow velocity. The devices took measurements at 15-minute intervals throughout the

monitoring season, May through September. Fisher developed stage-discharge curves and

calibrated the devices as necessary.

Fisher (2011) collected water quality samples after precipitation events where greater than 0.25 inches of rain had fallen. The procedure is explained in detail in Fisher (2011). Water samples were tested for the parameters listed in **Table 2.1**.

Water Quality Parameter	Abbreviation			
Ammonia	NH ₃			
Chemical Oxygen Demand	COD			
Chloride	Cl			
Chlorine	Cl_2			
Conductivity	CDY			
Dissolved Oxygen	DO			
Escherichia coli	EC			
Fluoride	F			
Nitrate plus Nitrite Nitrogen	N+N			
Oil & Grease	OG			
pH	pН			
Soluble Reactive Phosphorus	SRP			
Surfactants	SF			
Suspended Sediment	SSC			
Concentration	330			
Total Kjeldahl Nitrogen	TKN			
Total Copper	Cu			
Total Phosphorous	TP			
Total Suspended Solids	TSS			
Turbidity	TBY			
Water Temperature	WT			

 Table 2.1 Water Quality Parameters from Fisher (2011).

All samples were tested according to Standard Methods (APHA, 1998), Hach spectrometer methods (Hach, 2008), or US EPA methods (US EPA, 2011).

Fisher (2011) compiled the in-stream and water quality data and calculated EMCs. An EMC is defined as the total constituent mass discharge (M) divided by the total runoff volume (V) (US EPA, 1983). An EMC can be calculated with the equation:

$$EMC = \frac{M}{V} = \frac{\int C(t)Q(t)dt}{\int Q(t)dt}$$
(2.2)

where:

C(t) = constituent concentration at time t, and

Q(t) = storm water discharge at time t.

A paired t-test was conducted to compare EMCs between the Taylor Park and Colonial

Hills watersheds, listed in Table 2.2 (from Fisher, 2011).

Table 2.2 EMC Statistics for Side by Side Comparison Between the Two Sites.

Monitoring Site	EMC Statistic	NH3 mg/L	COD mg/L	EC cfu/ 100 mL	N+N mg/L	SRP mg/L	TP mg/L	TSS mg/L	TKN mg/L
Colonial	Mean	0.06	58	31,780	0.46	0.23	0.41	180	1.6
Hills	Std Dev	0.05	27	41,767	0.15	0.09	0.06	211	0.5
Taylor	Mean	0.09	72	62,430	0.71	0.23	0.57	220	1.8
Park	Std Dev	0.05	50	33,487	0.27	0.08	0.42	340	0.8
Number of Events:		10	13	12	13	12	9	14	10
t-test (Pr > t):		0.24	< 0.01	0.17	0.01	0.09	< 0.01	< 0.01	< 0.01

EMCs were compared between the Taylor Park and Colonial Hills watersheds and found statistically significant differences for COD, N+N, TP, TSS, and TKN at the 95% confidence interval level. All of those constituents appeared to be higher at the Taylor Park watershed.

Fisher (2011) found that the regression models developed from continuous in-line probe measurements and EMCs generally performed better than those developed with climatic data and EMCs. Continuous measurements could take into account rapid changes in individual storm events, giving a more accurate picture of runoff. The regression models for the Colonial Hills watershed also appeared to perform better than Taylor Park, perhaps due to the difference in size.

Fisher (2011) also observed that storm size affected mass loadings. Data from the collected storms indicated that most of the total seasonal mass loading occurred during the largest runoff events. Also, comparing mass loadings from storms of different sizes revealed that the watersheds behaved differently. Fisher (2011) reported that the Colonial Hills watershed experienced much higher TSS mass loadings during the large storms than Taylor Park. This provided evidence of stream bank erosion, which could more readily occur with heavier precipitation and higher stream levels associated with the larger storms. Also, the trends of other water quality parameters, including nutrients, suggested that, for smaller storms, infiltration and natural attenuation were occurring at Colonial Hills.

Chapter 3

Site Description

3.1 Site Selection

The watersheds characterized in this thesis were studied previously by Fisher (2011), as discussed in **Section 2.4.1**, that describes past studies. The 239-hectare Colonial Hills watershed was chosen originally because it flows north into Holmes Lake, as shown in **Figure 3.1**. The intent was to observe the effects of best management practices (BMPs), specifically low-phosphorus fertilizer incentives, in the Colonial Hills neighborhood.

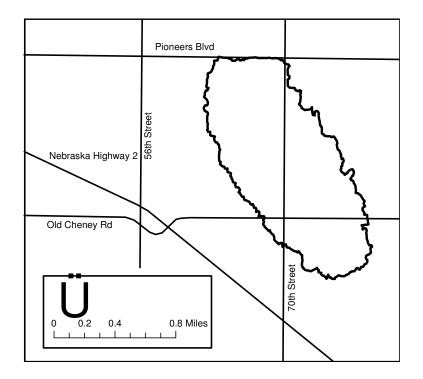


Figure 3.1 Colonial Hills watershed in southeast Lincoln.

The 39-hectare Taylor Park watershed was selected as a type of control site. It sits just north of Holmes Lake and drains north into Dead Man's Run, a tributary of Salt

Creek, as seen in **Figure 3.2**. Taylor Park was used for a control because of its relative similarity to Colonial Hills.

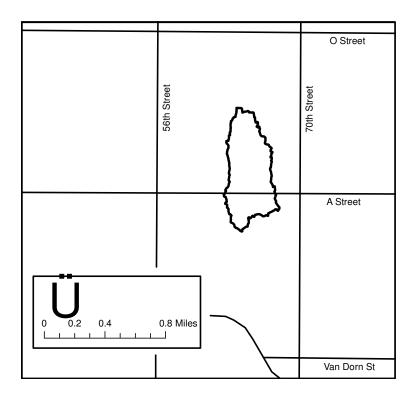


Figure 3.2 Taylor Park watershed in southeast Lincoln.

Both the Colonial Hills and Taylor Park watersheds are primarily residential areas. They share similar proportions of impervious land cover. Both watersheds had safely accessible water quality sampling locations. Both were situated in southeast Lincoln, in close proximity to Holmes Lake. At the time of selection, a detailed comparison of watershed characteristics had not been performed.

3.2 Water Quality Monitoring

Each site was equipped with a gauging station at the outlet, operated by the USGS, the City of Lincoln and the University of Nebraska-Lincoln. The stations were equipped with rain gauges, velocity flow meters, auto-sampling devices, and in-line

probes. Specific details about the monitoring stations are described in **Section 2.4** and in more detail in Fisher (2011).

3.3 Soil Characteristics

Existing soil maps available from the Natural Resource Conservation Service (NRCS) Web Soil Survey indicate that much of the top soil in the Taylor Park and Colonial Hills watersheds consists of silty clay loam (NRCS, 2012). Specifically, the survey of Taylor Park shows Colo-Nodaway silty clay loam around the watershed outlet, and Wymore silty clay loam throughout the rest of the watershed. Similarly, the survey for Colonial Hills shows Colo-Nodaway along the length of the stream, and a mixture of Aksarben and Wymore making up most of the rest of the watershed.

However, these maps show only the top soil and do not take into account urbanization that has occurred since being surveyed. Some subsoil may have been exposed or moved during excavation and construction. Hilltops may have been leveled and low areas filled. Also, many residential lots may have brought in commerciallymixed soil for their lawns.

Chapter 4

Materials and Methods

4.1 Introduction

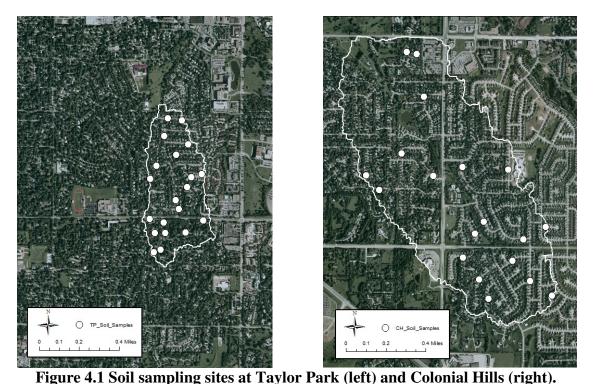
This chapter describes the materials and methods used to characterize the Taylor Park and Colonial Hills Watersheds. Included in this chapter are detailed sections describing soil sampling techniques, GIS methodology for delineating and analyzing watersheds, procedures for calculating time of concentration, and methods for analyzing samples for isotopes.

4.2 Soil Sampling

Twenty soil samples were collected from the Taylor Park and Colonial Hills watersheds in May, 2011. Samples were analyzed for basic soil parameters, including nutrient concentrations, in order to compare characteristics between the two watersheds.

4.2.1 Site Selection

Grids were laid over satellite imagery maps of both watersheds in ArcMap 10 to develop a grid coordinate system. Microsoft Excel's random number function was used to generate coordinates for each sample to be collected. Each square was enlarged and a sample site was chosen at random. The chosen soil sampling locations are shown in **Figure 4.1**. An effort was made to alternate north/south and east/west sides of streets with each subsequent sample. All samples were collected from the grass strip between the street and sidewalk.



Sampling tubes with one-inch diameters were used to extract the top three inches of soil, including biomass. Approximately eight ounces of soil were taken per sampling site. Grass blades and roots were removed as necessary and discarded. The eight-ounce soil samples were placed in sealable plastic bags and labeled to identify the site and date collected.

4.2.2 Tests Conducted

When all lawn soil samples were collected, the samples were shipped to Ward Laboratories, Inc. of Kearney, Nebraska, for testing. Ward Laboratories, Inc. specializes in testing agricultural soils to recommend fertilizer application and predict yield.

Each soil sample was tested by Ward Laboratories for:

- Soil pH according to methods described by McLean (1982), Nathan et al. (2006), and Watson and Brown (1998). Soil pH is a measure of the acidity or alkalinity of a soil.
- Soluble soil salts according to methods described by Rhoades (1982) and Whitney (1998). The concentration of soluble salts in soil varies seasonally. Soluble salts can affect soil pH measurement, raising pH during wet, cool periods, and lowering pH during hot, dry seasons.
- Nitrate-nitrogen according to methods described by Combs et al. (1998), Lachat Instruments (1995), and Geldeman and Beegle (1998). Nitrate-nitrogen is readily available for plant uptake and is not bound to soil particles.
- Total nitrogen according to methods described by Miller et al. (1997).
- Plant-available phosphorus using the Mehlich P-3 (Phosphorus) Method described by Mehlich (1984) and Frank et al. (1998). Mehlich phosphorus is readily available for plant uptake and is not bound to soil particles.
- Total phosphorus according to methods described by Helrich (1990) and Tisdale et al. (1985).
- Potassium according to methods described by Warncke and Brown (1998) and Haby et al. (1990).

4.3 GIS Characterization

The physical characteristics of the Taylor Park and Colonial Hills watersheds were evaluated using GIS. GIS is a rapidly developing method of visually representing data. GIS software takes recorded, geographically-referenced data as an input and uses specialized data analysis tools to sort, manipulate, or add to the data. Elevation information and global positioning system (GPS) coordinates of watershed outlets were used to delineate watershed boundaries. New layers were created over an imagery map to identify total and unconnected impervious cover. Smaller watersheds within Taylor Park and Colonial Hills were also found to show possible intermittent pervious areas. Finally, GIS was used to find the longest flow paths in the Taylor Park and Colonial Hills watersheds.

ArcGIS Desktop version 10, developed by ESRI in 2010, was used to project, store and analyze data. The ArcCatalog component was used to define coordinate systems and create a geodatabase for data storage. The ArcMap component was used for data manipulation and analysis. Several specific ArcToolbox functions were used within ArcMap and are described in detail in the following sections.

4.3.1 Drainage Area

Elevation data for the city of Lincoln, NE, was retrieved from the United States Geological Survey (USGS) website (seamless.usgs.gov). The digital elevation model (DEM) used had a resolution of 3 meters per pixel, as seen in **Figure 4.2**. The high resolution was chosen to best represent the small watersheds.

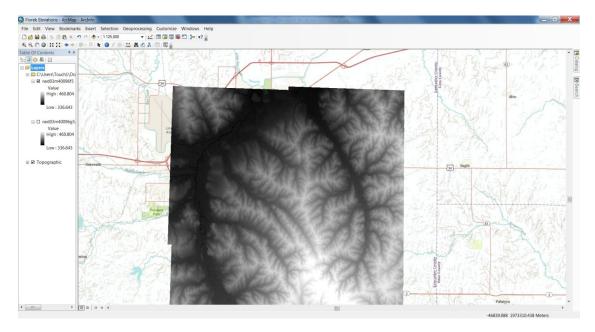


Figure 4.2 Digital Elevation Model of Lincoln, NE.

The shades of gray in the DEM in **Figure 4.2** represent the relative elevation. The highest elevations are light gray or white. The low points in the DEM are dark gray or black. To use the DEM, it was projected onto the USA Contiguous Albers Equal Area Conic spacial reference frame. This reference frame was used for all ArcGIS analysis. Sinks or low points in the DEM that would be interpreted as ponds, were eliminated by using the *Fill* function. By doing this, ArcGIS assumes all water will flow into some receiving stream and will not form pools.

The ArcGIS *Flow Direction* tool was used to apply the D8 (eight-direction) Method and create a map of predicted flow directions. The D8 method assumes that each pixel in the DEM is surrounded by eight other pixels, as shown by the example in **Figure 4.3**, and that water will flow in the direction of steepest slope. For this example, arbitrary elevations have been input into the boxes. The highest elevation is in the top-left corner and the lowest elevation is in the bottom-center pixel.

13	11	12
9	10	11
7	6	8

Figure 4.3 Example of D8 Method grid. Example elevations are in meters.

The *Flow Direction* tool computes the predicted flow direction and assigns that information to each pixel. In **Figure 4.3**, water from the center pixel would be computed as flowing to the bottom-center pixel. The *Flow Accumulation* tool takes this information as an input and outputs the potential runoff collection for each pixel.

The *Snap Pour Point* can be used to identify the lowest point in the watershed. For this project, the global positioning system (GPS) locations of USGS in-stream gauging stations were chosen as pour points. Flow direction, flow accumulation, and the pour point coordinates were input into the *Watershed* tool, resulting in delineated watersheds. The finished delineation of the Colonial Hills watershed can be seen in **Figure 4.4**.

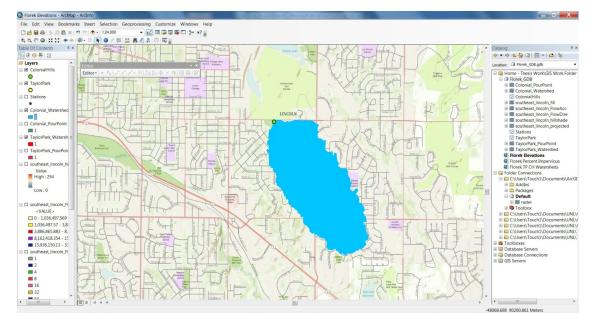


Figure 4.4 Colonial Hills watershed after delineation.

4.3.2 Streamline Determination

Streamlines were computed using the ArcGIS *Raster Calculator* and *Stream Link* functions with flow accumulation and flow direction as the inputs, respectively. *Raster Calculator*, as seen in **Figure 4.5**, calculates which 3-meter pixels fit chosen criteria. For the scope of this project, it was assumed that flow accumulations greater than or equal to 1000 pixels were significant. This means that 3-meter pixels that would receive flow from 1000 other pixels and that were inside the boundaries of a watershed would be considered as part of a stream. The result of using *Raster Calculator* in this way is a batch of unconnected stream segments.

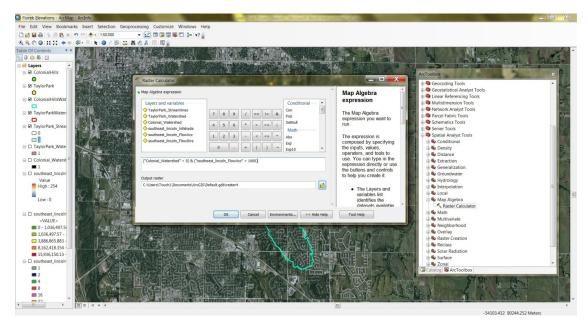


Figure 4.5 ArcGIS raster calculator computing streamlines for Colonial Hills.

The *Stream Link* function uses flow direction data and the output from the *Raster Calculator* to combine the streams into one network, as seen in **Figure 4.6**. The *Stream Link* results can be used not only to show overland flow paths, but also to delineate subwatersheds. It should be noted that ArcGIS assumes only overland flow occurring. Also, most streamlines appear to run along streets, which tended to have low elevation and therefore were interpreted by ArcGIS as having high flow accumulation.

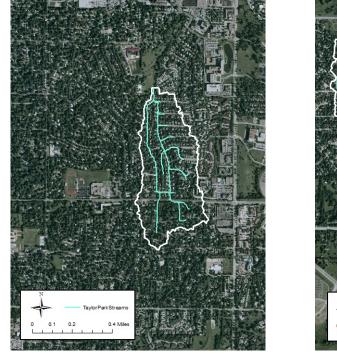




Figure 4.6 Streamlines at Taylor Park (left) and Colonial Hills (right).

4.3.3 Land Cover

All impervious surfaces in the Taylor Park and Colonial Hills watersheds were identified and marked, as shown in **Figure 4.7**. Impervious surfaces are defined as surfaces that do not allow for infiltration of precipitation. These surfaces include roads, roofs, and other man-made structures. In order to pick out impervious surfaces, the delineated watershed boundaries were placed over a satellite imagery basemap provided by ESRI. All roads and structures, representing total impervious area, were outlined and combined into one large object.



Figure 4.7 Impervious surfaces at Taylor Park (left) and Colonial Hills (right). A fraction of the total impervious surface was assumed to be unconnected. Unconnected impervious surfaces are defined as impervious surfaces which may direct flow onto pervious surfaces, rather than into a stormwater collection system or other impervious channel. Such surfaces could be rear-facing roofs, as seen in Figure 4.8, tennis courts surrounded by grass, personal swimming pools, and backyard sheds.

The total impervious area and unconnected impervious area were computed in ArcGIS and extracted from attribute tables. These areas were compared to the total watershed area and converted into a percentage. Once the watersheds had been characterized by land cover, it was possible to estimate time of concentration.

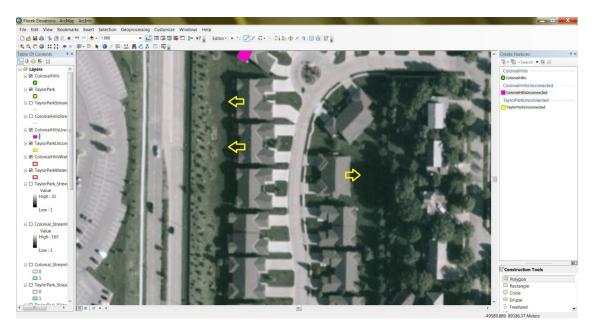


Figure 4.8 Unconnected impervious surface identification in Colonial Hills. 4.3.4 Time of Concentration

Time of concentration is the length of time it takes for water to flow from the furthest point of a watershed to the outlet. Time of concentration is useful to characterize watershed hydrology, typically by constructing unit hydrographs. The time of concentration and time to peak were calculated using the Natural Resource Conservation Service method (Novotny, 2003). This method assumes only overland flow is occurring and does not take into account the storm sewer system. Calculations involving storm sewers may result in a different time of concentration.

The ArcGIS *Flow Length* tool was used to find the longest flow length for each watershed. The longest flow path as found by GIS may be different from the actual longest flow path due to pixilation of the watershed. The slope of the flow path was calculated by subtracting the downstream elevation from the upstream elevation and dividing by the length of the flow path.

A Soil Conservation Service curve number (CN) of 83 was chosen to represent the Taylor Park and Colonial Hills watersheds. This curve number is assigned to ¹/₄ acre residential lots with an average imperviousness of 38%, Hydrologic Soil Group C, and antecedent soil moisture condition (AMC) II. AMC II is the average soil condition.

According to the NRCS method, lag time is computed first. Lag time is the average of the flow times from all points in the watershed and is found by:

$$t_{l} = \frac{1}{7053} \frac{L^{0.8}(S+25.4)^{0.7}}{(SI)^{0.5}}$$
(4.1)

where:

 $t_1 = lag time (hours),$

L = length of longest overland flow path (meters),

S = watershed storage (mm), and

SI = percent slope of watershed along longest flow path,

and:

$$S = \frac{25,400}{CN} - 254 \tag{4.2}$$

where:

S = watershed storage (mm), and

CN = Soil Conservation Service curve number.

For an urban watershed, a lag factor is used to correct for the imperviousness of the watershed. This lag factor is estimated by:

 $LF = 1 - PRCT(-0.006789 + 0.000335CN - 0.0000004298CN^{2} - 0.00000002185CN^{3})$

(4.3)

where:

LF = lag factor for urban watersheds,

PRCT = percent of impervious surface in watershed, and

CN = Soil Conservation Service curve number.

Time of concentration can then be found by:

$$t_c = \frac{t_l * LF}{0.6} \tag{4.4}$$

where:

 t_c = time of concentration (hours),

 $t_l = lag time (hours), and$

LF = lag factor for urban watersheds.

4.3.5 Intermittent Pervious Flow

After comparing flow paths and impervious surfaces, some intermittent runoff flows appeared to be going over pervious ground. Because flow over pervious surfaces could infiltrate and may affect runoff conditions, it was important to characterize the watersheds by intermittent flow area. For the purpose of this project, it was assumed that intermittent flow paths had to run at least 100 feet. The same procedure for delineated watersheds was used to mark boundaries of intermittent flow areas, represented in **Figure 4.9** by shaded areas. One intermittent flow area was found at Taylor Park, and a total of six were found at Colonial Hills.



Figure 4.9 Intermittent flow areas at Taylor Park (left) and Colonial Hills (right).

The percentage of impervious surface was found for each intermittent flow area using the ArcGIS *Clip* tool and attribute tables. The NRCS TR-55 procedure was followed to determine the impact of intermittent flow areas.

First, only intermittent areas with less than 30% impervious area and some unconnected impervious area were selected. Under these circumstances, the area is described by a composite curve number (NRCS, 1986). Rating charts from the TR-55

manual were used to determine a composite curve number for each intermittent flow area. To describe the pervious surface, primarily lawns with greater than 75% grass cover and in good condition, a curve number of 74 was chosen as an input for the rating charts.

Runoff for the intermittent flow areas was calculated by:

$$Q = \frac{(P - 0.2S)^2}{(P + 0.8S)}$$
(4.5)

where:

Q = runoff (mm),

P = precipitation (mm), and

S = watershed storage (mm),

and:

$$S = \frac{25,400}{CN} - 254 \tag{4.6}$$

where:

S = watershed storage (mm), and

CN = Soil Conservation Service curve number.

4.4 Water Quality Mass Loading

Turbidity and TSS mass loadings were calculated using **Equations 4.7** through **4.12** and compared for the Colonial Hills and Taylor Park watersheds. Mass loadings were then compared for the five largest and five smallest storms in each watershed. It

should be noted that precipitation varied slightly between the watersheds (Fisher, 2011), and that the selected storms were not identical. Storms were selected based on total precipitation, provided by the National Oceanic and Atmospheric Administration (NOAA) and the High Plains Regional Climate Center (HPRCC).

Storm flow and turbidity were measured every 15 minutes by USGS in-stream probes continuously during the sampling season, and every few seconds during a precipitation event. TSS mass loads were calculated water quality samples and storm flow. Data was stored by sampling year. In order to find mass loadings the interpolated flow rate was multiplied by the time interval between readings to estimate an incremental flow volume:

Incremental flow
$$(ft^3)$$
 = Interpolated flow $\left(\frac{ft^3}{sec}\right) \times$ Time interval (sec) (4.7)

Next, incremental mass loadings were calculated by multiplying incremental flow by the TSS concentration and turbidity recordings:

$$TSS_i = KQ_i \times TSS\left(\frac{mg}{L}\right)$$
(4.8)

where:

TSS = Total Suspended Solids (kg),

 TSS_i = Incremental TSS (kg),

 Q_i = Incremental Flow (ft³), and

 $K = Conversion factor (28.3 L/ft^3)$, and

$$TBY_i = KQ_i \times TBY\left(\frac{FNU}{100 \, mL}\right) \tag{4.9}$$

where:

TBY = Turbidity (FNU),

 TBY_i = Incremental turbidity (FNU),

 $K = Conversion factor (28.3 L/ft^3)$

These calculations were performed for all three years of interest. Conversion factors were used to correct units into the English system.

Start and end points of each selected storm were identified by comparing interpolated flow to base flow. Typically, a sharp rise in flow marked the start of a storm. The end of a storm was considered to be the point where flow began to level off. In some cases, the stream did not return to typical base flow for several days, but the storm was deemed over when flow stopped fluctuating rapidly.

Total storm loads were estimated as the sum of incremental loads between the start and end of selected storms, calculated by:

Total TSS mass loading
$$(kg) = \sum \int Incremental TSS(t) dt$$
 (4.10)

Total turbidity loading (FNU) =
$$\sum \int Incremental turbidity (t)dt$$
 (4.11)

To compare the watersheds, a ratio of average turbidity loading over average TSS mass loading was calculated for each storm:

$$\frac{Turbidity}{TSS} = \frac{Total turbidity loading (FNU)}{Total TSS mass loading (kg)}$$
(4.12)

Finally, the ratios of turbidity / TSS for the five largest storms were averaged and compared to the average of the ratios for the five smallest storms.

4.5 Isotope Analysis

Fifteen soil samples were collected and tested for δ^{18} O in PO₄ and NO₃ and δ^{15} N in NO₃. Seven sites across the watershed were sampled by Jesse Coffey in May 2011. Four sites had samples taken by Monica Gomes in June and July 2012.

Water samples were also taken for isotope testing by Coffey in the spring and summer of 2011. Grab samples from the stream were collected for the dry weather sample in April and during the storm in May. Samples were collected by an auto-sampler during the June and August storms. All isotope preparation and testing was done by the UNL Water Sciences Laboratory except for phosphate preparation.

4.5.1 Isotope Soil Sample Site Selection

Steam banks and residential lawns were chosen as primary sample locations. In the Taylor Park watershed, one site was near to the USGS station where water quality samples had been collected. The second Taylor Park site was a drainage ditch running behind houses. Three of the Colonial Hills sample locations were points on the main stream running through the watershed. One site was located on an intermittent flow path. The last three sample locations were in residential lawns. Isotope sample sites are shown in **Figure 4.10** and **Figure 4.11**.

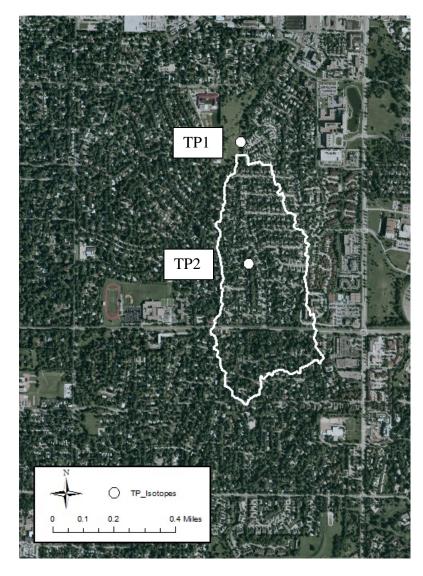


Figure 4.10 Isotope sample sites at Taylor Park.

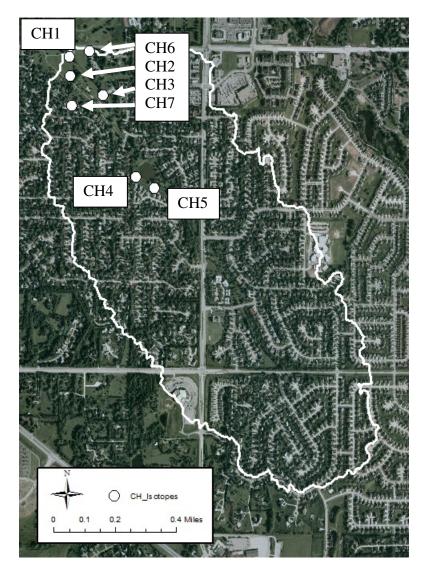


Figure 4.11 Isotope sample sites at Colonial Hills.

Sampling tubes with one-inch diameters were used to extract soil cores. Coffey collected the top six inches of soil, discarding the first inch if it included biomass. Gomes collected the top three inches of soil, discarding the top one and a half inches. The samples were deep enough that some root material was still collected from sites with vegetative growth. Approximately eight ounces of soil were taken per sampling site. Eight-ounce soil samples were placed in sealable plastic bags and labeled to identify the site and date collected. Soil was frozen before testing. Grass clippings were collected

close to soil sampling sites. Grass clippings were combined in one or two Ziploc bags. Grass was frozen before testing.

4.5.2 Nitrate and Phosphate Isotope Tests

Samples for nitrogen analysis of nitrate and ammonia were prepared following the procedure described by Gormly and Spalding (1979). Briefly, an aliquot of a water sample is placed in a 500 mL distillation flask and placed on a steam distillation line. The pH of the solution is raised to about 10 by adding magnesium oxide (MgO). The MgO reacts with ammonium and volatile organic compounds to produce ammonia which is then distilled off and collected in an Erlenmeyer flask containing 5 mL of boric acid indicator solution. The mass of ammonia-N recovered is determined by titrating distillate with a standardized sulfuric acid titrating solution. After the ammonia-N is removed, nitrate-nitrogen (NO₃-N) in the sample is quantitatively reduced to ammonia by adding finely ground Devarda's Alloy to the distillation flask. The ammonia produced is then distilled off separately, collected in the boric acid indicator, and titrated separately. After titration, each distillate is acidified to pH < 1 with sulfuric acid and slowly evaporated to near dryness before conversion of ammonia to nitrogen gas on a high vacuum preparation system. After quantitative conversion and collection of the nitrogen gas produced during the preparation step, the product gas is introduced into either a VG Optima or GVI Isoprime dual inlet stable isotope mass spectrometer.

Samples for oxygen isotope (¹⁸O) analysis of nitrate were prepared according to the procedure described by Silva et al. (2000). After determination of nitrate concentrations using a separate method, appropriate volumes of water samples are passed through both cation and anion exchange columns (BioRad AG1X 100-200 mesh anion exchange resin and AG50-WX8 100-200 mesh). Nitrate is then eluted from anion exchange resin with 3M HCl, neutralized with Ag₂O and oven dried yielding AgNO₃. The AgNO₃ is then transferred to silver sample cups and analyzed for oxygen isotope ratios (i.e. δ^{18} O). Dried and purified silver nitrate is then quantitatively converted to carbon monoxide (CO) gas by high temperature pyrolysis (1230oC) on a Eurovector elemental analyzer (EA) and the gas is immediately analyzed on a GV Isoprime continuous flow isotope ratio mass spectrometer. Helium carries the resultant CO gases through a packed gas chromatography column to separate the CO peak from the N₂ peak, and oxygen isotope ratios are determined at masses 29 and 30.

Samples for oxygen isotope analysis of dissolved phosphate use a similar preparation as nitrate and described in detail by McLaughlin et al. (2004). Phosphate is extracted by co-precipitation with magnesium hydroxide, and purified through a series of precipitations and ion exchange resin separations. Purified orthophosphate is then converted to silver phosphate (AgPO₄) prior to high temperature pyrolysis on graphitized carbon for isotope analysis of CO for δ^{18} O.

Chapter 5

Results and Discussion

5.1 Introduction

This chapter presents the results of soil chemistry tests, GIS characterization, TSS/turbidity mass load comparisons, and nutrient isotope data. The results are analyzed in detail to get a better picture of the different runoff mechanisms at work in the Taylor Park and Colonial Hills watersheds. The findings are also compared to previous research by Fisher (2011).

5.2 Soil Sampling

Twenty soil samples were collected from the Taylor Park and Colonial Hills watersheds in May, 2011, to compare soil quality in the two watersheds. Samples were randomly selected and collected on the same day. Sample selection and testing methods are explained in **Section 4.2**.

Soil Quality Parameter	Abbreviation	Expressed As:
Mehlich-3 Phosphorus	Mehlich P-3	(mg P)/L
Nitrate-Nitrogen	NO ₃ -N	(mg N)/L
Potassium	К	(mg K)/L
Soil pH	pН	pH units
Soluble Salts	S Salts	mmho/cm
Total Nitrogen	Total N	(mg N)/L
Total Phosphorus	Total P	(mg P)/L

 Table 5.1 Basic Soil Quality Parameters, Abbreviations, and Expressions Used.

All soil samples from the two watersheds were submitted to Ward Laboratories in Kearney, NE, for analysis, as discussed in **Section 4.2**. **Table 5.1** lists the parameters tested, abbreviations used, and units of expression for the parameters. Results from the soil tests were compiled and compared with basic statistical methods.

5.2.1 Average (Standard Deviation) Concentrations

Arithmetic means and standard deviations were calculated for all soil parameters and are presented in **Table 5.2**. Based on the arithmetic means, it appears that, on average, Taylor Park and Colonial Hills differ in basic soil chemistry. The soil at Taylor Park appears to have higher average concentrations of readily available nutrients (NO₃-N and Mehlich P-3). In contrast, the soil at Colonial Hills appears to have a higher average concentration of Total N. The average concentration of Total P was similar for both sites.

	pН	S Salts (mmho/cm)	K (ppm)	NO3-N (ppm)	Total N (ppm)	Mehlich P-3 (ppm)	Total P (ppm)
TP	7.17	0.525	416.4	7.7	1977.6	59.8	631.3
	(0.57)	(0.12)	(69.2)	(6.0)	(563.3)	(55.1)	(178.5)
СН	7.47	0.581	434.1	5.9	2299.6	41.3	637.9
	(0.24)	(0.07)	(86.2)	(6.8)	(482.7)	(39.8)	(179.6)

Table 5.2 Average (Standard Deviation) Parameter Concentrations in Soil Samples.

*Sample size n = 20.

Confidence levels were calculated using a t-test (Walpole, 2007) to determine if differences in the average soil concentrations for specific parameters at the two sites are significant. The t-test results are presented in **Table 5.3**. Differences in pH and S Salts were found to be statistically significant at the 95% confidence level. Soil nutrients, however, showed great variability. The difference in Total N was statistically significant ranges.

	pН	S Salts (mmho/cm)	K (ppm)	NO ₃ -N (ppm)	Total N (ppm)	Mehlich P-3 (ppm)	Total P (ppm)
CH vs. TP	0.0467	0.0463	0.520	0.333	0.0828	0.277	0.913

Table 5.3 T-Test Comparison of Averages of Colonial Hills Against Taylor Park.

*Bolded values indicate that the difference is statistically significant at the 95% confidence level calculated with a t-test.

The 90% statistically significant difference reported in **Table 5.3** provides evidence that soil may be a source of Total N in runoff. Statistically, a higher average concentration of Total N is available in soil in the Colonial Hills watershed to be washed into the stream. However, Fisher (2011) suggests a higher EMC for Total N at Taylor Park than at Colonial Hills, which is contrary to the soil results.

5.2.2 Ranked-Order Comparison

In addition to a statistical analysis, concentrations of NO_3 -N, Total N, Mehlich P-3 and Total P were sorted by magnitude for each watershed to observe any other trends in the results, given the high degree of variability within each watershed. The ordered samples are shown in **Figure 5.1** through **Figure 5.3**.

The variability of Mehlich P-3, shown in **Figure 5.1**, is readily apparent. Nine of the samples from Taylor Park had a concentration of 50 ppm or higher, as compared to just six from Colonial Hills. Mehlich P-3 concentrations in Taylor Park tended to be higher in general, as indicated by the average in **Table 5.2**. This may be due to the soil types in Taylor Park or may be a result of a history of more aggressive lawn fertilization in the Taylor Park watershed.

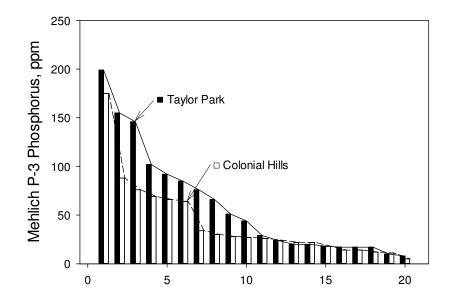


Figure 5.1 Soil samples ordered by average Mehlich P-3 concentration.

The soil concentration of Total P and NO_3 -N were fairly uniform at both Taylor Park and Colonial Hills, as shown in **Figure 5.2**. Clear differences were not observed for either parameter. This is consistent with the statistical results in **Table 5.2**.

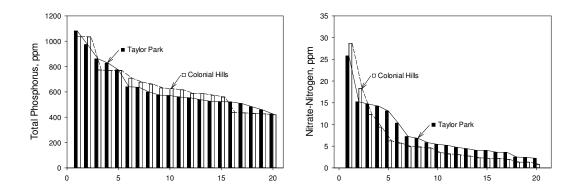


Figure 5.2 Soil samples ordered by Total P (left) and NO₃-N (right) concentration.Soil concentrations of Total N also differed between Taylor Park and ColonialHills. Total N tended to be relatively consistently higher in soil at Colonial Hills, as

shown in **Figure 5.3**. This consistent variation is statistically significant at the 90% confidence interval, as seen in **Table 5.3**.

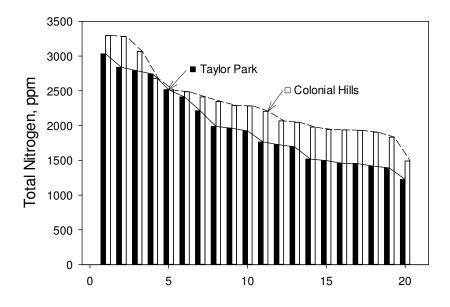


Figure 5.3 Soil samples ordered by Total N concentration.

5.3 GIS Characterization

Physical characteristics of the Taylor Park and Colonial Hills watersheds were compared using the methods described in **Section 4.3**. These characteristics include connected and unconnected impervious cover, intermittent flow area, and time of concentration. The purpose of the analysis was to identify any significant differences between the watersheds. The results of the comparison may provide evidence of certain runoff mechanisms, including stream bank erosion, which could affect water quality.

Results from GIS analysis and the NRCS method for time of concentration were compiled into **Table 5.4** for comparison. The primary difference between the watersheds was size. Colonial Hills was found to be nearly five times as large as Taylor Park in total area. The longest flow path and time of concentration in Colonial Hills were twice as long as in Taylor Park. Colonial Hills also had a greater proportion of intermittent flow area, where runoff may be flowing over and infiltrating into pervious surface.

 Table 5.4 Physical Characteristics of Taylor Park and Colonial Hills Watersheds.

Characteristic	Taylor Park	Colonial Hills
Drainage Area	39 ha	239 ha
Longest Flow Path	1600 m	3330 m
Time of Concentration (based on)	60 min	140 min
Intermittent Flow Area (%) of Watershed	2 ha (5%)	23 ha (10%)
Impervious Area (%) of Watershed	17 ha (35%)	91 ha (38%)
Unconnected Impervious Area (%) of	3 ha (7%)	15 ha (6%)
Watershed		

Each physical characteristic is discussed subsequently.

5.3.1 Land Cover

GIS analysis shows that 17 hectares (35%) of Taylor Park and 91 hectares (38%) of Colonial Hills could be considered impervious surface. Both watersheds are primarily small- to medium-lot residential, for which the percent impervious surface is reasonable. The proportion of total impervious surface was a factor in site selection (Fisher, 2011).

GIS analysis also showed that three hectares (7%) of Taylor Park and fifteen hectares (6%) of Colonial Hills may be unconnected impervious surface. An early hypothesis stated that a difference in the proportion of unconnected impervious surface could help explain differences in runoff. However, the watersheds have nearly identical proportions of unconnected impervious surface.

5.3.2 Intermittent Pervious Flow

Areas of intermittent pervious flow can influence the amount of runoff that reaches a watershed outlet. In a precipitation event, pervious surfaces will absorb water up to a point, determined by the soil type, preceding soil moisture content, and soil compaction. Infiltration over these areas could result in smaller runoff volume as compared to areas with impervious surface. If infiltration is occurring, that may suggest some entrapment of nutrients before they reach the watershed outlets.

One intermittent sub-watershed was identified at Taylor Park, compared with six intermittent watersheds at Colonial Hills. Intermittent watersheds in Colonial Hills are listed in **Table 5.5** and are identified by a unique number, as shown in **Figure 5.4**. The white sections in the figure represent areas where runoff may be crossing pervious area for at least 100 feet before joining another stream. The pervious channels have been drawn in black in **Figure 5.4**.

The potential impact on runoff volume was estimated following the TR-55 method (NRCS, 1986). The TR-55 method is described in detail in **Section 4.3.4**. Three intermittent flow areas in the Colonial Hills watershed qualified for composite curve numbers, identified as CH Int. 1, CH Int. 4, and CH Int. 6 in **Table 5.5**. The intermittent flow area in Taylor Park did not fit the TR-55 method for composite curve numbers and would not show a meaningful difference in estimated flow volume.

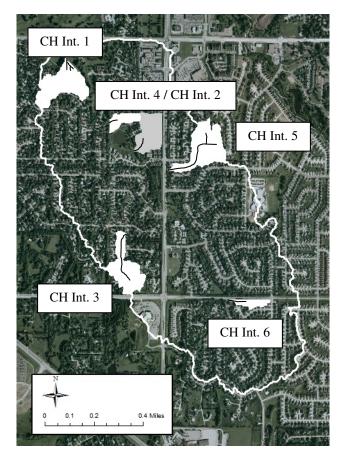


Figure 5.4 Intermittent flow areas in the Colonial Hills watershed.

Runoff was estimated based on three different storm sizes: 0.5 inches, 1 inch and 1.5 inches. The resulting runoff predications are listed for comparison in **Table 5.5**. The size of each intermittent flow area is given to show the contribution to the watershed.

From **Table 5.5**, 23 hectares (10%) of the Colonial Hills watershed may be considered as intermittent flow area. Two hectares (5%) of the Taylor Park watershed may also qualify. This suggests that the potential for runoff over pervious surface and infiltration is twice as high at Colonial Hills than at Taylor Park.

Area ID	Curve	Area	Runoff, Q (in)			
	Number	(ha)	P = 0.5 in	P = 1.0 in	P = 1.5 in	
CH, Total	83	239	0.004	0.13	0.38	
CH Int. 1	80	6	0.000	0.08	0.29	
CH Int. 2	83	4	0.004	0.13	0.38	
CH Int. 3	83	5	0.004	0.13	0.38	
CH Int. 4	81	2	0.000	0.10	0.31	
CH Int. 5	83	4	0.004	0.13	0.38	
CH Int. 6	78	1	0.000	0.06	0.23	

Table 5.5 Runoff from Intermittent Flow Areas at Colonial Hills (CH).

According to the TR-55 method, CH Int. 1, CH Int. 4, and CH Int. 6 may be affecting runoff in the Colonial Hills watershed. These three areas combine to make up 4% of the watershed. The areas also have lower curve numbers. In a storm with precipitation less than 0.5 inches, CH Int. 1, CH Int. 4 and CH Int. 6 may not experience runoff at all.

This suggests that for smaller storms, in which precipitation may not be enough to pond over pervious surfaces, about 96% of Colonial Hills may experience runoff. Because a portion of the precipitation does not reach the watershed outlet, nutrients and suspended solids from the intermittent areas would not reach the outlet, either. Though the difference appears small, it may help to explain why Taylor Park experienced higher average EMC for TSS in storms with less than 0.7 inches precipitation (Fisher, 2011).

5.3.3 Time of Concentration

Due to the difference in watershed size, a sizeable difference in time of concentration was expected. At Taylor Park, GIS analysis indicated the longest flow path was 1600 meters. Following the NRCS method, as discussed in **Section 4.3.4**, the time of concentration was estimated to be 60 minutes. In contrast, the longest flow path at

Colonial Hills was found to be 3330 meters, with a time of concentration of 140 minutes. The result makes sense, since Colonial Hills is six times larger in area than Taylor Park.

It should be noted that this method assumes only overland flow would occur and does not take into account the storm sewer system. Given that the longest flow path in Colonial Hills follows a lined channel, the time of concentration for that watershed may not differ greatly when accounting for storm sewers. At Taylor Park, however, there is no lined channel, so time of concentration may be shorter than that found with the NRCS method.

5.4 Water Quality Mass Loading

Fisher (2011) noted that TSS mass loadings tended to be higher at Taylor Park in storms of less than 0.7 inches precipitation, but higher at Colonial Hills for storms of greater than 1.2 inches. Stream bank erosion was proposed as a possible explanation. In order to better understand the effects of storm size and watershed characteristics, turbidity mass loadings were compared with TSS mass loadings for selected storms.

Ten storms from those sampled by Fisher (2011) were selected for each site, five with the most precipitation and five with the least precipitation, as shown in **Table 5.6** and **Table 5.7**, and evaluated for mass loads following the procedure in **Section 4.4**. Total precipitation was obtained from NOAA. Turbidity was measured by USGS in-line probes. TSS EMCs were calculated by Fisher (2011), as described in **Section 2.4**. Average turbidity / TSS ratios were calculated for the five largest and five smallest storms of each watershed.

The ratio of average turbidity / TSS was higher for larger storms at the Taylor Park watershed, as listed in **Table 5.6**. Also, four of the top five turbidity / TSS ratios for the largest storms occurred at Taylor Park. This means that, as storm size increases, turbidity and TSS mass loadings also increase at a fairly regular rate. Larger storms may be picking up more small particles which would affect turbidity.

	Date	Precipitation	Turbidity	TSS	Turb/TSS	
		(mm)	(FNU)	(kg)		
II	4/29/2010	28.98	2.28E+09	444	5.13E+06	
iinfa	5/20/2010	24.07	9.18E+08	136	6.75E+06	Avg.
it Ra	7/11/2010	48.82	3.97E+09	575	6.90E+06	5.82E+06
Largest Rainfall	11/12/2010	32.26	6.59E+08	181	3.64E+06	
La	8/12/2011	34.37	8.78E+08	131	6.70E+06	
Ila	7/14/2009	7.31	1.02E+08	69	1.49E+06	
Rainfall	5/12/2011	8.45	1.91E+09	335	5.69E+06	Avg.
st R.	5/24/2011	9.57	3.23E+07	41	7.87E+05	2.59E+06
Smallest	6/9/2011	11.59	2.17E+09	1209	1.79E+06	
Sm	10/10/2011	13.46	2.28E+08	72	3.17E+06	

Table 5.6 Ratios of Turbidity / TSS Mass Loadings at Taylor Park.

Conversely, the ratio of average turbidity / TSS was larger for smaller storms in the Colonial Hills watershed, as listed in **Table 5.7**. Four of the top five turbidity / TSS ratios for the smallest storms occurred at Colonial Hills. The inverse relationship suggests that the watersheds have different mechanisms at play. The TSS mass loading during large storms is much higher than during small storms. However, there is not a great difference in turbidity mass loadings.

This suggests that small storms at Colonial Hills may not be transporting as much TSS relative to turbidity, due to the larger percent of intermittent flow area to trap soil particles with vegetation or infiltration. It may also be that large storms are eroding stream banks and pulling much larger particles. Larger particles may not register as higher turbidity as compared to smaller, more dissolved particles. Turbidity readings are based on how well light passes through a well-mixed sample. Larger particles of a particular mass may not disperse into the sample as well and would not refract as much light as small particles with the same total mass would.

	Date	Precipitation	Turbidity	TSS	Turb/TSS	
		(mm)	(FNU)	(kg)		
	9/3/2009	41.22	2.54E+10	8964	2.83E+06	
Rainfall	4/29/2010	35.11	7.76E+10	23992	3.23E+06	Avg.
	7/11/2010	46.41	3.85E+10	3065	1.26E+07	5.27E+06
Largest	11/12/2010	32.51	7.84E+09	2017	3.89E+06	
La	8/12/2011	40.23	5.26E+09	1367	3.85E+06	
Ile	6/8/2010	16.71	5.15E+09	970	5.31E+06	
ainfa	5/12/2011	6.55	1.77E+09	273	6.49E+06	Avg.
st R:	5/24/2011	9.42	1.98E+09	386	5.14E+06	1.19E+07
Smallest Rainfall	6/9/2011	16.76	3.24E+09	83	3.90E+07	
Sm	10/10/2011	16.00	1.02E+09	273	3.72E+06	

 Table 5.7 Ratios of Turbidity / TSS Mass Loadings at Colonial Hills.

The comparison shows there is a difference between the two watersheds. This is consistent with modeling conducted by Fisher (2011) and with the expectation of stream bank erosion with higher flows. However, the relationship between turbidity and TSS does not entirely explain the difference. In order to provide evidence towards stream bank erosion in the Colonial Hills watershed, an analysis of nutrient isotopes in soil and water was conducted.

5.5 Isotope Analysis

Stable isotope characterization of nutrients in water and soil can be used to help identify nonpoint sources of nutrients (e.g. Silva et al., 2002; Kaushal et al., 2011; McLaughlin et al., 2006). Specifically, δ^{18} O as part of PO₄ and NO₃, and δ^{15} N as part of NO₃ can point towards possible contributors. Different sources of nutrients, including precipitation, soil, fertilizer, sewage, and vegetation can have distinct isotope signatures.

Atmospheric conditions can affect δ^{18} O in precipitation. Runoff directly from impervious surface could carry a strong influence from atmospheric δ^{18} O, whether in the form of NO₃ or PO₄. In the case of NO₃, the value of δ^{18} O would be higher than if another source were significant (Silva et al., 2002). For PO₄, atmospheric δ^{18} O can influence oxidation of organic P from lawns to PO₄. Inorganic PO₄ trapped in soil, especially in stream banks with less vegetation, might be identified with a different δ^{18} O signature (McLaughlin et al., 2006). Nitrification of NH₄ fertilizer and organic N, as well as oxidation of NO₂ can lead to δ^{15} N enrichment in NO₃. Runoff picking up soil particles from fertilized lawns or dense vegetation could have an isotopic signature with a smaller atmospheric δ^{18} O influence and a more significant contribution of δ^{15} N from soil.

5.5.1 Source Data

Isotope sampling and testing was conducted in 2011 by Jesse Coffey and in 2012 by Monica Gomes. Laboratory methods and the reasoning for site selections are described in detail in **Section 4.5**. The locations varied from stream banks to residential lawns, as summarized in **Table 5.8**. Samples are labeled "S" for soil, "G" for grass and "DG" for decayed grass, and "TP" and "CH" for Taylor Park and Colonial Hills. The last column represents the SRP concentration extracted from soil. SRP was not available for some of the samples, as indicated by "-".

 δ^{18} O-PO₄ samples collected from stream bank soil sites, which will be referred to as soil leachate, had an average composition of 18.51‰ and a standard deviation of 1.53‰. Soil leachate was relatively constant from site to site, with some variability at S-CH1 during different times of the year. Residential lawn soil leachate had an average δ^{18} O-PO₄ of 20.1‰ and a standard deviation of 4.39‰. It should be noted that the soil leachate samples were not taken from the obvious root zone, while lawn soil leachate samples did include grass roots in the samples. The physical make-up of the samples may have contributed to the differences.

Site ID	Date	Source	¹⁸ O-PO ₄ (‰)	SRP (mg/L PO ₄)
S-TP1	5/3/11	Stream bank next to sampling site	18.46	0.59
S-TP2	5/3/11 6/5/12 7/6/12	Residential lawn surrounding drainage area	27.82 21.00 20.36	1.00 0.67 1.51
S-CH1	5/3/11 6/5/12 7/6/12	Stream bank next to sampling site	18.97 17.23 21.62	0.96 0.66 1.34
S-CH2	5/3/11	Stream bank 50 yards upstream of sampling site on a low-flow fork	18.45	1.18
S-CH3	5/3/11	Stream bank far upstream in a wooded area next to a park	17.61	0.65
S-CH4	5/3/11	Stream bank near a pond surrounded by residential houses, groomed lawn	17.22	0.72
S-CH5	5/3/11	Soil overrunning a concrete drainage ditch in an urban development	15.04	0.66
S-CH6	6/5/12 7/6/12	Residential lawn on 63 rd Street	14.32 21.62	1.02 0.83
S-CH7	6/5/12 7/6/12	Residential lawn on Starling Circle	22.91 17.76	0.42 0.35

Table 5.8 δ^{18} O-PO₄ in Soil.

Lawn soil leachate was more variable than soil leachate. Some of this variability may be temporal, possibly as a result of the conversion of organic P in lawns and grass to inorganic P in the form of PO₄. The oxidation reaction allows for influences from δ^{18} O in the atmosphere and in precipitation, both of which have been shown to have seasonal trends (Harvey, 2001). Different lawn conditions, such as watering practices, trees and other vegetation, and fertilizer application may also have contributed to the variability.

Grass samples were also collected from the Taylor Park and Colonial Hills watersheds and were considered to be part of lawn soil leachate. Grass from Taylor Park was taken from the stream bank near the sampling site. Samples of grass from Colonial Hills were collected from each of the soil sampling sites and mixed together, as summarized in **Table 5.9**. δ^{18} O-PO₄ in grass samples taken in November 2011 is much lower than in the summer of 2012. This appears to be consistent with the seasonal trends in atmospheric δ^{18} O described by Harvey (2001) from **Section 2.2.2**, where δ^{18} O peaks in the warm summer months and is lowest in the cold winter months.

Site ID	Date	Source	¹⁸ O-PO ₄ (‰)	SRP (mg/L PO ₄)
G-TP1	11/17/11	Stream bank next to sampling site and drainage gate	17.1	11.9
G-CH1	11/17/11	Collected from each of the soil sampling sites and mixed together	15.48	13.3
G-CH2	6/5/12	Collected from each of the soil	22.41	21.3
	7/6/12	sampling sites and mixed together	23.30	23.1
G-CH3	6/5/12	Collected from each of the soil	18.60	22.2
	7/6/12	sampling sites and mixed together	23.76	24.5

Table 5.9 δ^{18} O-PO₄ in Grass.

A portion of the mixed grass samples from Colonial Hills was allowed to decay in the laboratory before isotope analysis, as listed in **Table 5.10**. Decayed grass is intended to represent vegetative matter washed into the storm drain and allowed to decompose. While the decayed grass did show a difference in SRP concentrations, δ^{18} O-PO₄ in decayed grass was relatively similar to that of regular grass clippings.

Site ID	Date	Source	¹⁸ O-PO ₄ (%)	SRP (mg/L PO ₄)
DG-CH1	6/5/12	Collected from each of the soil	21.87	6.27
	7/6/12	sampling sites and mixed together	23.66	15.5
DG-CH2	6/5/12	Collected from each of the soil	21.98	4.97
	7/6/12	sampling sites and mixed together	20.43	7.11

Table 5.10 δ^{18} O-PO₄ in Decayed Grass.

In addition to field samples, two types of fertilizer were analyzed for δ^{18} O-PO₄ as listed in **Table 5.11**. Both fertilizers are commercially available in Lincoln, NE. Both fertilizer samples had low compositions of δ^{18} O-PO₄, with the store brand as the lowest.

Table 5.11 δ^{18} O-PO₄ in Fertilizer.

ID	Date	Description	¹⁸ O-PO ₄ (%)	SRP (mg/L PO ₄)
FERT. 1	-	NHPO4	7.178	-
FERT. 2	-	Menard's store brand	1.806	-

Of the laboratory samples, stream bank soil showed the most consistency between the two sites and over the sampling period in terms of δ^{18} O-PO₄ composition. Lawn and grass samples showed variability from month to month and for different sample locations, as may be expected from seasonal changes in δ^{18} O-PO₄ in the atmosphere and precipitation.

5.5.2 Water Quality and Flow Data

In addition to soil isotope analysis, water samples were collected by Jesse Coffey for one dry day and three storms in 2011. Water was tested for nitrate, SRP and each of the nutrient isotopes. The samples were organized by the volume of flow that had passed at the time of collection (Vc) as compared to the total volume of flow from the storm (Vt).

The water quality and isotope data for Taylor Park are summarized in

Table 5.12. No clear trends were observed in the water quality data. However, the concentrations of nitrate and δ^{18} O-NO₃ were lowest in the August storm. This suggests that the constituents may have come from different sources than in earlier storms. It should be noted that for the August storm, all samples at Taylor Park were taken before half of the flow volume had passed the watershed outlet.

Date	Time	Vc/Vt	Nitrate NO ₃ +NO ₂ -N (mg/L)	SRP (mg PO ₄ /L)	¹⁸ O- PO ₄ (%)	¹⁵ N- NO ₃ (%0)	¹⁸ O- NO ₃ (%)
4/29/11	12:00	-	1.87	0.257	6.85	-	18.5
5/24/11	11:30	0.00	2.38	0.314	11.67	7.665	30
5/24/11	11:45	0.04	1.52	0.961	14.83	-1.768	30
5/24/11	12:45	0.56	0.344	0.396	18.28	0.137	35.3
5/24/11	13:00	0.71	0.48	0.466	14.63	1.63	33.5
6/25/11	4:55	0.1	0.412	0.256	6.08	-6.377	35.5
6/25/11	5:08	0.242	0.415	0.359	6.03	-2.164	23.2
6/25/11	5:33	0.55	0.568	0.654	8.58	-3.395	17.1
6/25/11	6:53	0.81	0.684	0.654	14.79	-2.598	37.1
8/12/11	0:48	0.05	0.188	0.398	24.87	-5.23	-3.2
8/12/11	1:00	0.16	0.705	0.652	22.76	-7.61	0.7
8/12/11	1:17	0.31	0.157	0.857	19.4	-3.17	-3
8/12/11	2:14	0.49	0.349	0.937	19.52	-3.56	12

Table 5.12 Water Quality and Isotope Composition at Taylor Park.

The results of the water quality and isotope analysis at Colonial Hills, as listed in **Table 5.13**, showed some differences with Taylor Park. In particular, δ^{18} O-PO₄ for the June storm increased over time at Taylor Park and decreases at Colonial Hills. It should be noted that Taylor Park was sampled throughout the whole June storm, while all samples at Colonial Hills were taken before peak flow, as seen in **Figure 5.5**. SRP

showed an increasing trend at both watersheds for the June and August storms, but this is not consistent with all storms sampled by Fisher (2011). SRP tended to increase over the duration of storms at Taylor Park, but was generally stable or decreasing at Colonial Hills.

Also, at Taylor Park, samples were taken throughout and after one time of concentration (60 minutes). At Colonial Hills, the time of concentration (140 minutes) was approached only once during sampling, for the August storm.

¹⁸O-¹⁵N-¹⁸O-Nitrate SRP Vc/Vt NO₃+NO₂-N Date Time PO_4 NO₃ NO₃ $(mg PO_4/L)$ (mg/L)(‰) (‰) (‰) 4/29/11 11:10 0.257 0.384 7.1 19.6 _ 4 5/24/11 0.937 20.3 11:48 0.00 0.486 9.04 5/24/11 12:33 0.20 0.814 0.583 14.51 2.141 39.3 5/24/11 13:03 0.281 0.42 12.94 29 0.61 6/25/11 5:05 0.03 0.418 0.273 6.04 -5.074 24.8 6/25/11 5:18 0.15 0.336 0.26 5.68 -5.847 17.3 6/25/11 5:24 0.24 0.371 0.334 2.27 20.7 6/25/11 5:29 0.32 0.348 0.427 -0.9 -4.369 10.9 8/12/11 1:28 0.09 0.04 0.304 30.49 8 8/12/11 12.2 1:45 0.18 0.083 0.382 24.65 -5.63 8/12/11 2:07 0.29 0.118 0.529 22.99 10.1 _ -2.97 6.7 8/12/11 2:53 0.40 0.117 0.721 26.46

 Table 5.13 Water Quality and Isotope Composition at Colonial Hills.

Of the three storms sampled in 2011, the August 12 storm was the longest at over

11 hours, as summarized in Table 5.14 and

Table 5.15. The August 12 storm was also the least intense, averaging between 0.12 and 0.13 inches per hour. The May storm produced less than half an inch of rain, making it the smallest of the three storms.

Date	Antecedent Dry Days	Precipitation (in)	Duration (hr)	Average Intensity (in/hr)	Peak Intensity (in/hr)
4/29/11	-	Dry Weather	-	-	-
5/24/11	4	0.38	2.0	0.19	0.20
6/25/11	1	0.71	4.0	0.18	0.44
8/12/11	4	1.35	11.3	0.12	0.61

Table 5.14 Storm Characteristics at Taylor Park.

Table 5.15 Storm Characteristics at Colonial Hills.

Date	Antecedent Dry Days	Precipitation (in)	Duration (hr)	Average Intensity (in/hr)	Peak Intensity (in/hr)
4/29/11	-	Dry Weather	-	-	-
5/24/11	4	0.37	2.0	0.19	0.20
6/25/11	1	0.87	4.0	0.22	0.55
8/12/11	4	1.58	12.0	0.13	0.49

The difference in storm flow between the May storm and the other two can clearly be seen in **Figure 5.5**. Sample collection times were generally spread throughout storms, taken before peak flow, at peak flow, and on the trailing edge of the hydrograph. However, at Colonial Hills, the June storm was sampled only on the leading edge of the hydrograph. As a result, the water quality data for that storm may not accurately depict trends.

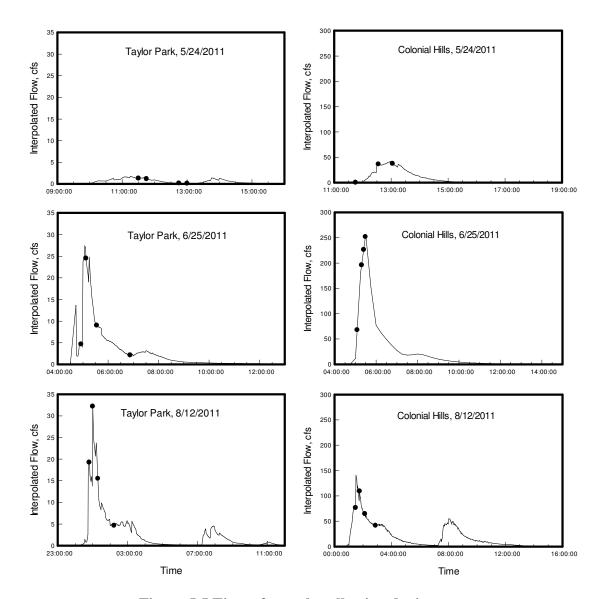
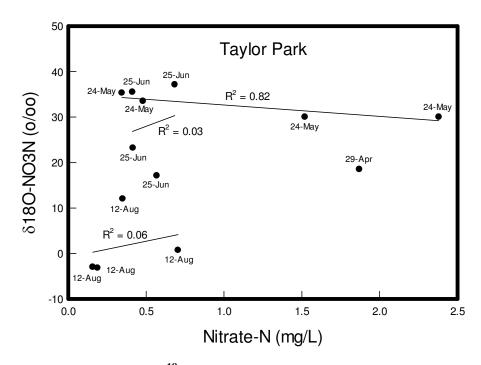


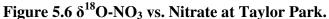
Figure 5.5 Time of sample collection during storms.

5.5.3 Nitrate Isotope Analysis

Water quality samples were tested for δ^{15} N-NO₃ and δ^{18} O-NO₃ using the procedures described in **Section 4.5.2**. Samples were also tested for the NO₃+NO₂ concentration in water. δ^{18} O-NO₃ was plotted against N+N at Taylor Park and Colonial Hills to show the relationship between sources of δ^{18} O-NO₃ and nitrate.

Three trends were observed in the Taylor Park watershed, as shown in **Figure 5.6**. For the May storm, δ^{18} O-NO₃ was relatively consistent for different concentrations of nitrate, falling in the range of 30-36‰. In the June and August storms, δ^{18} O-NO₃ tended to increase with nitrate concentration and also with time. This suggests that the same source of nitrate provided much of the δ^{18} O-NO₃ throughout the May storm, especially given the relatively low overall flow volumes, and that the primary source of δ^{18} O-NO₃ changed during the other two storms.





A different trend was observed for the Colonial Hills watershed, as shown in **Figure 5.7**. δ^{18} O-NO₃ seems to follow the nitrate concentration linearly. The size of the Colonial Hills watershed may have contributed to the averaging out of composition leading to a greater relationship between δ^{18} O-NO₃ and nitrate concentration. Because Colonial Hills is larger than Taylor Park, and the time of concentration is longer, some mixing of nitrate sources does occur; however, there are clear differences in primary sources of nitrate over the course of a storm.

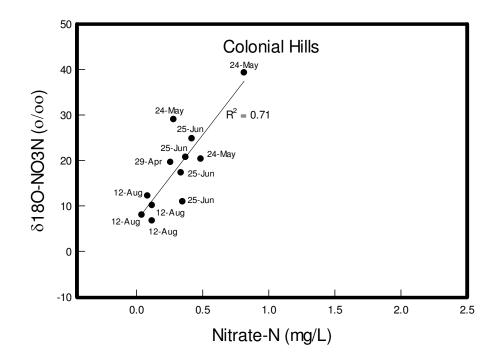


Figure 5.7 δ^{18} O-NO₃ vs. Nitrate at Colonial Hills.

 δ^{18} O-NO₃ and δ^{15} N-NO₃ were plotted against each other. Ranges for compositions associated with nitrification, fertilizer, and soil nitrogen were drawn as described by Kaushal et al. (2011). Several differences were found between the Taylor Park and Colonial Hills watershed. Several data points were not available for the Colonial Hills watershed due to insufficient sample volume to test for both ¹⁵N and ¹⁸O.

At Taylor Park, samples from the May and June storms almost all had higher δ^{18} O-NO₃ values than the suggested ranges, as shown in **Figure 5.8**. This may be due to a higher contribution from atmospheric sources of ¹⁸O. The first sample in May, also the

point of peak flow, has the largest δ^{15} N-NO₃. It may have significant organic nitrogen as a result of denitrification leading to ¹⁵N enrichment.

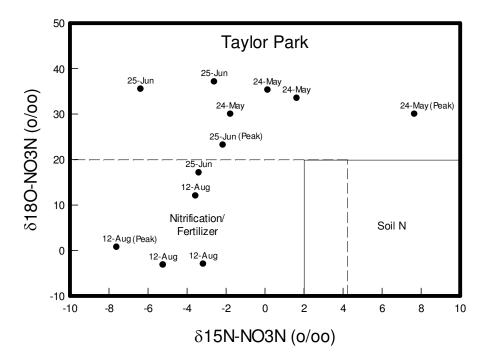


Figure 5.8 δ^{18} O-NO₃ vs. δ^{15} N-NO₃ at Taylor Park.

Water quality samples taken from the Colonial Hills watershed behaved similarly, as shown in **Figure 5.9**. Several data points were unavailable due to insufficient sample volume, so some trends may not be readily observable. As with Taylor Park, early-season samples tended to have higher δ^{18} O-NO₃. All late-season samples taken in August had δ^{18} O-NO₃ and δ^{15} N-NO₃ within the range suggested for nitrification and fertilizer. Neither watershed showed a δ^{15} N-NO₃ composition representative of waste water, which tends to have a δ^{15} N-NO₃ composition greater than 10% (Kaushal et al., 2011).

Using the hydrologic modeling described in Section 5.3.2, it appears that runoff from the May storm, which had less than half an inch of precipitation, would have come from primarily impervious surfaces. It makes sense, then, that δ^{18} O-NO₃ and δ^{15} N-NO₃

for the small storm would result in much of the nitrate coming from atmospheric sources and not sources such as runoff from residential lawns. The first samples in June, taken when flow was still small and likely from impervious cover, also suggest atmospheric sources. The larger flows in June and August would have crossed both impervious and pervious surfaces, allowing runoff to pick up nitrogen from soil and fertilizer.

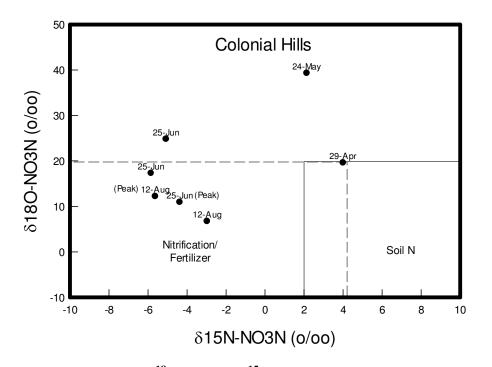


Figure 5.9 δ^{18} O-NO₃ vs. δ^{15} N-NO₃ at Colonial Hills.

In order to provide evidence of major contributions from atmospheric deposition, the models created by Fisher (2011) were used to create estimated N+N loads for the total drainage area (DA) of Taylor Park and Colonial Hills. It was assumed that all atmospheric nitrogen on impervious cover would be carried into the streams where samples were collected, while all atmospheric nitrogen that landed on pervious cover would be utilized for plant growth. The estimations were then compared to deposition data collected at Mead, NE, by the National Atmospheric Deposition Program (NADP, 2012), as summarized in **Table 5.16**. The NADP total was normalized for the total impervious area and connected impervious area then divided by the estimated load from Fisher (2011). It should be noted that the sample season for the NADP data (March through November) was slightly longer than the season for the estimated data (April through October). A major source of variability year to year in the results was change in atmospheric deposition in the NADP data.

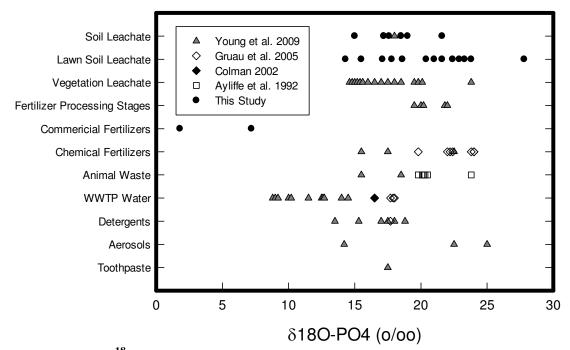
Year	Site	Estimated Load for Total DA (kg N+N)	NADP Load for Total DA (kg NO ₃ -N)	IA Deposition Contribution (%)	Connected IA Deposition Contribution (%)
2009	СН	198	348	67	56
2009	TP	43	70	57	45
2010	СН	411	392	36	30
2010	TP	128	79	22	17
2011	СН	308	616	76	64
2011	TP	116	124	37	30

 Table 5.16 Nitrate-Nitrogen Contribution from Impervious Area.

The estimated nitrate-nitrogen deposition contributions were high for Taylor Park and particularly Colonial Hills. This provides evidence that atmospheric deposition is an important source of nitrate-nitrogen in the watersheds. For all three sample years, the estimated contribution is higher for Colonial Hills, suggesting that less nitrogen mass loading may be attributed to sources other than atmospheric deposition in that watershed. The high potential contribution also indicates that reducing nitrogen loading at Holmes Lake may require activities beyond applying best management practices to residential lawns. It may require adding treatment systems for runoff.

5.5.4 Phosphate Isotope Analysis

Water quality samples were also tested for δ^{18} O-PO₄ and soluble reactive phosphorus (SRP). Various sources of δ^{18} O-PO₄ were compared to identify likely sources and corresponding composition ranges, as shown in **Figure 5.10**. Then, a comparison was made of the accumulated flow at various points in each storm, as shown in **Figure 5.11** and **Figure 5.12**. Finally, δ^{18} O-PO₄ and SRP were directly compared to investigate the possible sources of phosphorus, as shown in **Figure 5.13** and **Figure 5.14**. Ranges of expected δ^{18} O-PO₄ for specific sources were drawn using source samples collected by Coffey and Gomes.





First, it is useful to compare isotope source data to samples collected in previous studies to identify likely sources and ranges of δ^{18} O-PO₄. Data from Young et al. (2009), Gruau et al. (2005), Colman (2002), Ayliffe et al. (1992) and this study was sorted by

sample source and plotted against δ^{18} O-PO₄ composition, as shown in **Figure 5.10**. Soil leachate refers to samples collected from stream banks and below obvious root zones. Lawn soil leachate refers to samples collected from residential lawns and grass clippings.

Soil samples in this study and one taken from Young et al. (2009) fall in a similar δ^{18} O-PO₄ range. Lawn soil leachate samples from this study also share a δ^{18} O-PO₄ range with vegetation leachate samples from Young et al. (2009), although some had a higher composition. The composition range for the commercial fertilizers in this study was much lower than the ranges reported for fertilizer processing by Young et al. (2009) and chemical fertilizers by Young et al. (2009) and Gruau et al. (2005).

Animal waste samples tested by Ayliffe et al. (1992) and others were in a similar δ^{18} O-PO₄ composition range as the soil leachate and lawn soil leachate. However, visual inspection of the watersheds and *E. coli* data from Fisher (2011) did not indicate animal waste as a plausible primary phosphorus source. Wastewater and sewage has a mid-range composition, but since little surfactants and *E. coli* were observed in the watersheds, and δ^{15} N, as discussed earlier, was not consistent with wastewater, these are also not plausible primary sources of phosphorus. In addition, detergents, aerosols, and toothpaste are not believed to be major contributors to the watersheds.

 δ^{18} O is also affected by atmospheric influences. If precipitation is the dominant source, an equilibrium value close to 0‰ may be expected (Harvey, 2001). Based on the samples compared from this study and others, soil leachate, lawn soil leachate, and vegetation leachate are the most plausible sources of phosphorus in the watersheds.

 δ^{18} O-PO₄ compositions were compared over the duration of three storms. At Taylor Park, δ^{18} O-PO₄ from water samples appears to converge on the range of soil over time, as shown in **Figure 5.11**. This suggests soil erosion may be a meaningful contributor to the total phosphorus load. Samples from the June and August storms show a clear change in composition over time, tending to move towards the δ^{18} O-PO₄ signal. All water samples were well above the expected equilibrium value, suggesting that equilibrium conditions were not driving forces for the δ^{18} O-PO₄ compositions.

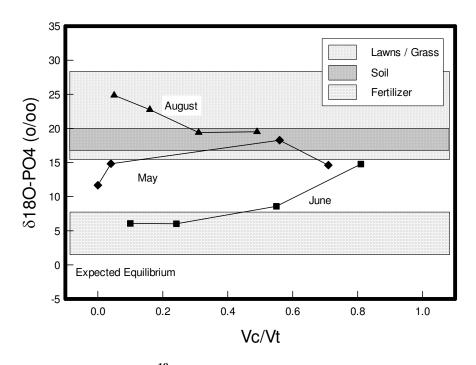


Figure 5.11 δ^{18} O-PO₄ during storms at Taylor Park.

For water quality samples at Colonial Hills, from **Figure 5.12**, the August storm showed a similar trend as in **Figure 5.11**, converging towards soil δ^{18} O-PO₄ values. The June storm seems to merge with the equilibrium isotope composition. However, samples were only tested from the leading edge of this storm.

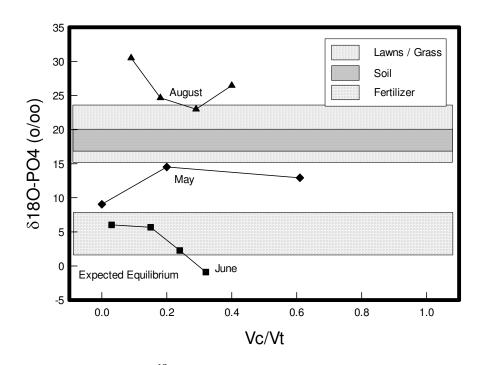


Figure 5.12 δ^{18} O-PO₄ during storms at Colonial Hills.

 δ^{18} O-PO₄ was also plotted against SRP. δ^{18} O-PO₄ for the May storm at Taylor Park appears to remain stable, as shown in **Figure 5.13**. Because the May storm was small, and storm water runoff can be assumed to come almost entirely from impervious surfaces, this suggests contributions from the same phosphate sources throughout the storm. Conversely, the June and August storms showed changes in δ^{18} O-PO₄ composition as storms went on. The sources of phosphate may be changing over time for larger storm events.

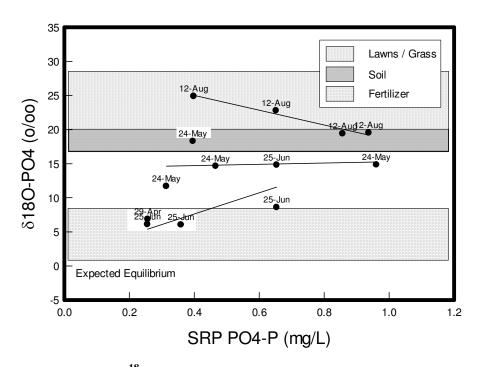


Figure 5.13 δ^{18} O-PO₄ vs. SRP during storms at Taylor Park.

The May storm behaved similarly at Colonial Hills as it did at Taylor Park. Once again, the δ^{18} O-PO₄ composition remained relatively similar throughout the storm, as shown in **Figure 5.14**. The August storm also showed a trend of changing δ^{18} O-PO₄ values as the storm went on, and appeared to converge on the δ^{18} O-PO₄ signals from lawns or (erodible) soil. The data from the June storm shows that sources seem to change during the first half of that storm, but data from the later parts of the storm was unavailable and δ^{18} O-PO₄ composition is unknown.

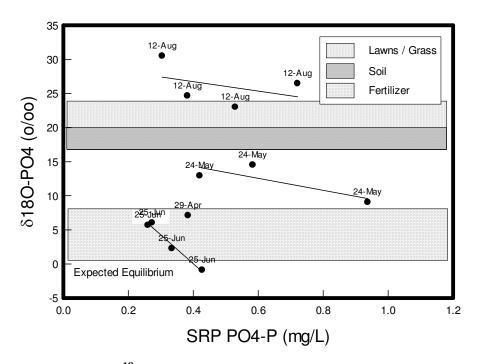


Figure 5.14 δ^{18} O-PO₄ vs. SRP during storms at Colonial Hills.

Because phosphorus data was generally missing for the later parts of the isotopemeasured storm events, the continuous mass load modals developed by Fisher (2011) were relied upon to fill the void. The total SRP and Total P loads occurring over the trailing edge of the hydrograph (when Vc/Vt > 0.5) were calculated for the 2010 sampling season. The percent contributions to the total 2010 loads were reported in **Table 5.17**. The results reveal that, in general, the majority of Total P is transported during the second half of the storm event at Colonial Hills. This finding suggests soil erosion that can occur following peak flows, especially from stream banks, may be an important source of Total P mass transport in the Colonial Hills watershed.

Site	SRP	Total P
Taylor Park	39%	42%
Colonial Hills	48%	73%

Table 5.17 Percent Contribution for 2010 when Vc/Vt > 0.5.

The high percent contribution estimates suggest that the processes occurring at high SRP concentrations are important contributors of PO₄. During this time, the δ^{18} O-PO₄ signal is consistent and tends to point to the 15% composition range. So, while sources of PO₄ appear to vary during the early stages of storms, it seems that composition evens out towards the end of storm events. The 15% composition range is close to average soil composition, and the turbidity analysis revealed the possibility of stream bank erosion, but the composition also overlaps with lawn soil leachate and some fertilizers, so the result in inconclusive.

Chapter 6

Conclusions

6.1 Thesis Summary

Characterization of two urban watersheds in Lincoln, NE, through soil analysis, GIS modeling, basic hydrology, water quality analysis, and nutrient isotope testing was conducted on data collected from 2008 to 2012. The water quality results from Hartman (2010) and Fisher (2011) were combined with soil data from 2011 and soil and water isotope composition data from 2012.

GIS was used to develop maps of connected and unconnected impervious area, as well as determine any areas of possible intermittent pervious flow. Time of concentration was calculated for both watersheds to show a fundamental hydrological difference. Soil and water samples were tested for nutrient isotope composition in an effort to identify possible sources of nutrients in runoff. Altogether, the analyzed data shows that different runoff mechanisms are at work in the two watersheds, and that while no single source of nitrogen or phosphorus could be pin-pointed with the data available, possible meaningful sources could be identified through isotope analysis.

Soil Characteristics

Soil sample characteristics for parameters such as Mehlich P-3, Total P, and NO_3 -N from the Taylor Park and Colonial Hills watersheds were not statistically different, in general. The exception was a tendency towards higher Total N concentrations in soil at Colonial Hills, which was statistically significant within a 90% confidence interval. Soil characteristics may have been affected by urban development, during which topsoil was shifted and subsoil exposed.

GIS Characterization

The Taylor Park and Colonial Hills watersheds share similar percent compositions of total and unconnected impervious area. Land use for both watersheds is typically ¹/₄-acre lot residential, so the watersheds share similar runoff coefficients. The most significant physical difference between the Taylor Park and Colonial Hills watersheds is size. Colonial Hills (239 ha) is six times as large as Taylor Park (39 ha). Size directly affected the time of concentration in the watersheds, with Colonial Hills (140 minutes) taking twice as long as Taylor Park (60 minutes).

Turbidity and Solids Mass Loading

The ratio of average turbidity versus TSS mass loading was higher at Colonial Hills for small storms, and higher at Taylor Park for larger storms. This suggests that during small storms, more large particles are being trapped by vegetation or infiltration before reaching the Colonial Hills outlet. During larger storms, with much higher runoff volumes, larger particles that would not affect turbidity as greatly may be eroded from stream banks and other sources.

Nitrate Isotope Analysis

Analysis of nitrogen and phosphorus isotopes in soil and water samples showed that different sources of nutrients are contributing at different points in storms. Atmospheric nitrogen appears to be a meaningful source of nitrogen in storm water, especially for small storms when nearly all runoff flows over impervious cover. If it is assumed that all atmospheric nitrate deposition washes from impervious cover into storm water and all atmospheric nitrate that lands on pervious cover is used by plants, 22 to 77% of the nitrogen mass load during non-winter months can be attributed to atmospheric deposition.

Phosphate Isotope Analysis

 δ^{18} O-PO₄ composition at both Taylor Park and Colonial Hills appeared to change over time during large storm events and stay relatively similar during small storms. δ^{18} O-PO₄ also appeared to converge on a 15% composition, similar to soil and lawn soil, when SRP was large. Estimated mass loads for SRP and Total P show a meaningful contribution from the later part of storms, when Vc/Vt is greater than 0.5. Combined with the turbidity analysis, soil seems to be a plausible meaningful source. Vegetation and chemical fertilizers may be affecting δ^{18} O-PO₄ composition in storm water, too.

6.2 Future Work

Nutrient isotope analysis suggested interesting results, but the small number of data points was insufficient for a firm result. Also, water quality data for isotope analysis was not collected uniformly for every storm. If isotope analysis were to be included in a future project in the Taylor Park and Colonial Hills watersheds, some changes may include:

• Sample collection throughout an entire storm. Data from the leading edge, peak flow, and the trailing edge of a hydrograph would show a more complete picture of runoff activity during a storm.

- Collection of sufficient samples to run multiple isotope tests. Some data points were not available because researchers did not have enough sample volume to conduct all isotope tests. Some trends may not have been observed accurately, or at all.
- The models developed by Fisher (2011), in particular for nitrate, did not include natural atmospheric deposition as a parameter. Given the results from this thesis, it may be worthwhile to revisit those models and include data from NADP.

Chapter 7

References

APHA, AWWA, and WEF. (1998). *Standard Methods for the Examination of Water and Wastewater, 20th Edition*, American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C.

Ayliffe, L. K., Veeh, H. H., Chivas, A. R. (1992). "Oxygen Isotopes of Phosphate and the Origin of Island Apatite Deposits." *Earth Plant. Sci. Lett.*, 108, 119-129.

Bhaduri, B., Harbor, J., Engel, B., and Grove, M. (2000). "Assessing Watershed-Scale, Long-Term Hydrologic Impacts of Land-Use Change Using a GIS-NPS Model." *Environmental Management*, 26(6), 643-658.

Colman, A. A., Blake, R. E., Karl, D. M., Fogel, M. L, Turekian, K. K. (2005). "Marine Phosphate Oxygen Isotopes and Organic Matter Remineralization in the Oceans." *Proc. Natl. Acad. Sci. U.S.A.*, 102, 13023-13028.

Combs, S. M., Denning, J. L., and Frank, K. D. (1998). "Sulfate-Sulfur." *Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Publiction No. 221 (revised)*, J. R. Brown, ed., University of Missouri Ag. Exp. Station, Columbia, MO, 35-40.

ESRI. (2010). ArcDesktop 10 (computer software), <http://www.esri.com>.

Fisher, J. (2011). "Water Quality Models for Stormwater Runoff in Two Lincoln, Nebraska Urban Watersheds," thesis, presented to the University of Nebraska-Lincoln in partial fulfillment of the requirements for the degree of Master of Science.

Frank, K., Beegle, D., and Denning, J. (1998). "Phosphorus." *Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Publiction No. 221 (revised)*, J. R. Brown, ed., University of Missouri Ag. Exp. Station, Columbia, MO, 21-29.

Geldeman, R. H., and Beegle, D. (1998). "Nitrate-Nitrogen." *Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Publiction No. 221 (revised)*, J. R. Brown, ed., University of Missouri Ag. Exp. Station, Columbia, MO, 17-20.

Gormly, J. R., and Spalding, R. F. (1979). "Sources and Concentrations of Nitrate-Nitrogen in Ground Water of the Central Platte Region, Nebraska." *Ground Water*, 17(3), 291-301.

Gruau, G., Legeas, M., Riou, C., Gallacier, E., Martineau, F., Henin, O. (2005). "The Oxygen Isotope Composition of Dissolved Anthropogenic Phosphates: A New Tool for Eutrophication Research." *Water Res.*, 39, 232-238.

Haby, V. A., Russelle, M. P., and Skoley, E. O. (1990). "Testing Soils for Potassium, Calcium and Magnesium." *Soil Testing and Plant Analysis, 3rd Edition*, R. L. Westerman, ed., Soil Sci. Soc. of Am., Madison, WI, 181-227.

Hartman, P. (2010). "Quantitative Comparison and Modeling of Urban Storm Water Mass Loadings in the City of Lincoln, Nebraska," thesis, presented to the University of Nebraska-Lincoln in partial fulfillment of the requirements for the degree of Master of Science.

Harvey, E. F. (2001). "Use of NADP Archive Samples to Determine the Isotope Composition of Precipitation: Characterizing the Meteoric Input Function for Use in Ground Water Studies." *Ground Water*, 39(3), 380-390.

Harvey, E. F. (2011). "Mead, Nebraska." *F. Edwin Harvey*, http://snr.unl.edu/harvey/mead.htm>.

Harvey, E. F. (2011). "Stable Isotope Basics." *F. Edwin Harvey*, <http://snr.unl.edu/harvey/isoprimer.htm>.

Helrich, K., ed. (1990). "Method No. 965.17." *Official Methods of Analysis of the Association of Official Analytical Chemists, 15th Edition,* AOAC, Inc., Arlington, VA.

Kaushal, S., Groffman, P., Band, L., Elliott, E., Shields, C., and Kendall, C. (2011). "Tracking Nonpoint Source Nitrogen Pollution in Human-Impacted Watersheds." *Environmental Science & Technology*, 45, 8225-8232.

Lachat Instruments. (1995). QuikChem. Method 10-107-04-1-A Nitrate/Nitrite. Nitrate in Surface Water, Wastewater. Milwaukee, WI.

May, D. and Sivakumar, M. (2009). "Prediction of Nutrient Concentrations in Urban Storm Water." *Journal of Environmental Engineering*, ASCE, 135(8).

McLaughlin, K., Cade-Menun, B., and Paytan, A. (2006). "The Oxygen Isotopic Composition of Phosphate in Elkhorn Slough, California: A Tracer for Phosphate Sources." *Estuarine, Coastal and Shelf Science*, 70, 499-506.

McLaughlin, K., et al. (2004). "A Precise Method for the Analysis of δ^{18} O of Dissolved Inorganic Phosphate in Seawater." *Limnology and Oceanography: Methods*, 2, 202-212.

McLean, E. O. (1982). "Soil pH and Lime Requirement." *Methods of Soil Analysis, Part* 2. *Chemical and Microbiological Properties-Agronomy Monograph no. 9 (2nd Edition)*, A. L. Page, ed., Soil Sci. Soc. of Am., Madison, WI, 199-209.

Mehlich, A. (1984). "Mehlich-3 Soil Test Extractant: A Modification of Mehlich 2 Extractant." *Commun. Soil Sci. Plant Anal.*, 15-16.

Miller, R. O., Kotuby-Amacher, J., Rodriguez, J. B. (1997). "Total Nitrogen in Botanical Materials – Automated Combustion Method." *Soil and Plant Analytical Methods*, Western States Laboratory Proficiency Testing Program, 106-107.

Nathan, M., Stecker, J., and Sun, Y. (2006). A Guide for Conducting Soil Tests in *Missouri*. Missouri Coop. Ext. Service, University of Missouri-Lincoln Univ.

NOAA. (2011). *National Oceanic and Atmospheric Administration's National Weather Service*, http://www.weather.gov>.

NRCS. (1986). *TR-55: Urban Hydrology for Small Watersheds*, Natural Resources Conservation Service, United States Department of Agriculture, Washington, D.C.

NRCS. (2012). Web Soil Survey. <websoilsurvey.nrcs.usda.gov> (Feb. 17, 2012).

Novotny, V. (2003). "Overland Routing by the NRCS Method." *Water Quality: Diffuse Pollution and Watershed Management, 2nd Edition*, John Wiley & Sons, Inc., Hoboken, NJ, 180-185.

Rhoades, J. D. (1982). "Soluble Salts." *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties-Agronomy Monograph no. 9 (2nd Edition)*, A. L. Page, ed., Soil Sci. Soc. of Am., Madison, WI, 167-179.

Rust, G. (2007). "Spatial and Statistical Analyses of Dry Weather Flow Data from Storm Drains," thesis, presented to the University of Nebraska-Lincoln in partial fulfillment of the requirements for the degree of Master of Science.

Schueler, T. R. (1994). "The Importance of Imperviousness." *Watershed Protection Techniques*, 1(3), 100-111.

Silva, S., et al. (2000). "A New Method for Collection of Nitrate from Fresh Water and the Analysis Nitrogen and Oxygen Isotope Ratios." *Journal of Hydrology*, 228, 22-36.

Silva, S., Ging, P., Lee, R., Ebbert, J., Tesoriero, A., and Inkpen, E. (2002). "Forensic Applications of Nitrogen and Oxygen Isotopes in Tracing Nitrate Sources in Urban Environments." *Environmental Forensics*, 3, 125-130.

Tisdale, S. L., Nelson, W. L., and Beaton, J. D. (1985). *Soil Fertility and Fertilizers, 4th Edition*, Macmillan Publishing Co., New York.

USGS, Pucket, L. J. (2008). *Nonpoint and Point Sources of Nitrogen in Major Watersheds of the United States*, United States Geological Survey, Washington, D.C. http://pubs.usgs.gov/wri/wri944001/wri944001.html

USGS. (2012). *Seamless Data Warehouse*, United States Geological Survey, Washington, D.C. http://seamless.usgs.gov (Dec. 28, 2010).

Walpole, R., Myers, R., Myers, S., and Ye, K. (2007). *Probability and Statistics for Engineers and Scientists, 8th Edition*, Pearson Prentice Hall, Upper Saddle Creek, NJ.

Warncke, D., and Brown, J. R. (1998). "Potassium and Other Basic Cations." *Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Publiction No. 221 (revised)*, J. R. Brown, ed., University of Missouri Ag. Exp. Station, Columbia, MO, 31-33. Watson, M. E., and Brown, J. R. (1998). "pH and Lime Requirement." *Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Publiction No. 221 (revised)*, J. R. Brown, ed., University of Missouri Ag. Exp. Station, Columbia, MO, 13-16.

Whitney, D. A. (1998). "Soil Salinity." *Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Publiction No. 221 (revised)*, J. R. Brown, ed., University of Missouri Ag. Exp. Station, Columbia, MO, 59-60.

Young, M. B., McLaughlin, K., Kendall, C., Stringfellow, W., Rollog, M., Elsbury, K., Donald, E., and Paytan, A. (2009). "Characterizing the Oxygen Isotopic Composition of Phosphate Sources to Aquatic Ecosystems." *Environmental Science & Technology*, 43(14), 5190-5196.

Appendix A

Raw Soil Sample Data and Statistics

All raw soil samples were tested by Ward Laboratories, Inc., of Kearney, NE.

Site ID	1:1 Soil pH	WDRF Buffer pH	1:1 S Salts mmho/cm	Nitrate- N ppm N	lbs N/A	Potassium ppm K	Mehlich P-III ppm P	Total N ppm	Total P ppm
CH1	7.2	7.2	0.63	28.7	26	362	26	2067	560
CH2	7.4	7.2	0.47	4.6	4	353	175	2413	1039
CH3	7.7	7.2	0.53	1.3	1	450	24	1491	426
CH4	7.6	7.2	0.61	2.7	2	416	34	3280	631
CH5	7.3	7.2	0.5	3.2	3	426	28	2347	677
CH6	7.1	7.2	0.52	3.5	3	439	88	2679	769
CH7	7.8	7.2	0.54	4.9	4	382	69	2487	1035
CH8	7.7	7.2	0.58	0.8	1	426	12	1939	419
CH9	7.7	7.2	0.61	5.7	5	309	11	2285	429
CH10	7.7	7.2	0.62	2.2	2	340	5	1904	434
CH11	7.7	7.2	0.73	4.8	4	452	22	1834	573
CH12	7.3	7.2	0.68	2.2	2	561	22	1932	587
CH13	7.3	7.2	0.48	1.9	2	411	14	2289	709
CH14	7.4	7.2	0.56	6.2	6	326	18	2206	438
CH15	7.8	7.2	0.55	1.3	1	611	64	2047	616
CH16	7.3	7.2	0.69	9.4	8	473	76	2509	662
CH17	7.6	7.2	0.6	12.3	11	339	27	3297	773
CH18	7.5	7.2	0.62	3	3	539	30	1977	586
CH19	7.3	7.2	0.55	2.3	2	541	66	1946	770
CH20	7	7.2	0.55	18.3	16	527	14	3064	625

Table A.1 Raw Soil Sample Data for Colonial Hills.

Site ID	1:1 Soil pH	WDRF Buffer pH	1:1 S Salts mmho/cm	Nitrate- N ppm N	lbs N/A	Potassium ppm K	Mehlich P-III ppm P	Total N ppm	Total P ppm
TP1	7.1	7.2	0.63	14.7	13	488	146	2213	974
TP2	7.8	7.2	0.57	6.8	6	385	24	1922	458
TP3	7.3	7.2	0.65	15.2	14	389	102	2789	774
TP4	7	7.2	0.7	13.1	12	507	85	3031	827
TP5	5.5	6	0.28	3.6	3	385	199	1988	1081
TP6	7.4	7.2	0.54	4.4	4	443	10	2839	553
TP7	7.3	7.2	0.46	2.5	2	398	17	1457	523
TP8	6.9	7.2	0.42	4.7	4	461	18	2516	571
TP9	7.4	7.2	0.59	7.2	6	503	20	1962	525
TP10	6.6	7.2	0.51	14.2	13	492	66	2739	598
TP11	6.5	6.9	0.45	4	4	359	20	1764	507
TP12	7.3	7.2	0.73	10.3	9	532	44	2412	559
TP13	6.4	6.8	0.36	2.4	2	342	76	1519	482
TP14	7.6	7.2	0.57	2.2	2	388	8	1497	538
TP15	7.4	7.2	0.37	5.8	5	459	29	1416	640
TP16	7.4	7.2	0.67	25.8	23	388	51	1392	574
TP17	7.4	7.2	0.42	3.6	3	413	155	1225	861
TP18	7.7	7.2	0.46	4	4	243	17	1453	425
TP19	7.9	7.2	0.64	5.4	5	376	92	1724	637
TP20	7.5	7.2	0.48	5.2	5	378	17	1695	520

 Table A.2 Raw Soil Sample Data for Taylor Park.

Table A.3 Averages of Soil Sample Results.

Site ID	1:1 Soil pH	WDRF Buffer pH	1:1 S Salts mmho/cm	Nitrate- N ppm N	lbs N/A	Potassium ppm K	Mehlich P-III ppm P	Total N ppm	Total P ppm
СН	7.47	7.2	0.581	5.965	5.3	434.15	41.25	2299.65	637.9
ТР	7.17	7.105	0.525	7.755	6.95	416.45	59.8	1977.65	631.35

Table A.4 Standard Deviations of Soil Sample Results.

Site ID	1:1 Soil pH	WDRF Buffer pH	1:1 S Salts mmho/cm	Nitrate- N ppm N	lbs N/A	Potassium ppm K	Mehlich P-III ppm P	Total N ppm	Total P ppm
СН	0.240	0	0.069	6.8	6.1	86.2	39.8	482.7	179.6
ТР	0.565	0.281	0.123	6.0	5.4	69.2	55.1	563.3	178.5

Appendix B

Watershed Area Characteristics

Total Watershed Area	239.3 ha	Time of Concentration	140 min.
Total Impervious Area	91.1 ha	% Impervious Area	38
Total Unconnected Area	15.2 ha	% Unconnected Area	6
Longest Flow Path	3330 m	% Slope of Flow Path	1.3
Intermittent Flow Area	23.2 ha	% Intermittent Area	9.7
Imperv. Intermittent	7.4 ha	% Imperv. Intermittent	3.1

 Table B.! Area Characteristics for the Colonial Hills Watershed.

Table B.2 Area Characteristics for the Taylor Park Watershed.

Total Watershed Area	48.8 ha	Time of Concentration	60 min.
Total Impervious Area	17.1 ha	% Impervious Area	35
Total Unconnected Area	3.2 ha	% Unconnected Area	7
Longest Flow Path	1600 m	% Slope of Flow Path	1.9
Intermittent Flow Area	2.3 ha	% Intermittent Area	4.7
Imperv. Intermittent	0.6 ha	% Imperv. Intermittent	1.3

 Table B.3 Area Characteristics for Colonial Hills Intermittent Watershed 1.

Subwatershed Area	5.8 ha	% of Total Area	2.4
Impossions Area	1 / bo	% Impervious Area	24
Impervious Area	1.4 ha	% of Total Impervious	1.5
Unconnected Ance	0.41.	% Unconnected Area	7
Unconnected Area	0.4 ha	% of Total Unconnected	2.6

Table B.4 Area Characteristics for Colonial Hills Intermittent Watershed 2.

Subwatershed Area	4.0 ha	% of Total Area	1.7
Impossions Anos	10 ho	% Impervious Area	46
Impervious Area	1.8 ha	% of Total Impervious	2.0
Uncomposed Area		% Unconnected Area	-
Unconnected Area	-	% of Total Unconnected	-

Subwatershed Area	4.9 ha	% of Total Area	2.0
Impossions Anos	1.6 ha	% Impervious Area	32
Impervious Area	1.0 11a	% of Total Impervious	1.7
Uncomposed Area		% Unconnected Area	-
Unconnected Area	-	% of Total Unconnected	-

Table B.5 Area Characteristics for Colonial Hills Intermittent Watershed 3.

 Table B.6 Area Characteristics for Colonial Hills Intermittent Watershed 4.

Subwatershed Area	1.5 ha	% of Total Area	0.6
Impossions Area	0.4 ha	% Impervious Area	27
Impervious Area	0.4 11a	% of Total Impervious	0.4
Unconnected Anos	0.1 ha	% Unconnected Area	5
Unconnected Area	0.1 na	% of Total Unconnected	0.4

Table B.7 Area Characteristics for Colonial Hills Intermittent Watershed 5.

Subwatershed Area	6.0 ha	% of Total Area	2.5
Impossions A see	2.1 ha	% Impervious Area	34
Impervious Area	2.1 Ila	% of Total Impervious	2.3
Unconnected Auco		% Unconnected Area	-
Unconnected Area	-	% of Total Unconnected	-

Table B.8 Area Characteristics for Colonial Hills Intermittent Watershed 6.

Subwatershed Area	1.0 ha	% of Total Area	0.4
Impossions Anos	0.2 ha	% Impervious Area	19
Impervious Area	0.2 na	% of Total Impervious	0.2
Uncomposed Anos	0.1 ha	% Unconnected Area	10
Unconnected Area	0.1 ha	% of Total Unconnected	0.7

Subwatershed Area	2.3 ha	% of Total Area	4.7
Imponsions Anos	0.6 ha	% Impervious Area	27
Impervious Area	0.0 11a	% of Total Impervious	3.6
Unconnected Area		% Unconnected Area	-
Unconnected Area	-	% of Total Unconnected	-

 Table B.9 Area Characteristics for Taylor Park Intermittent Watershed 1.

Appendix C

Hydrologic Characteristics

Hydrology Variable	Abbreviation
Curve Number	CN
Elevation at Start of Flow Path	Elev ₁
Elevation at Watershed Outlet	Elev ₂
Initial Abstraction	Ia
Lag Factor	LF
Lag Time	tı
Length of Flow Path	L
Peak Flow	q _p
Percent Impervious Surface	PRCT
Percent Slop of Flow Path	SI
Precipitation	Р
Runoff Volume	Q
Time of Concentration	t _c
Time to Peak	t _p
Watershed Area	А
Watershed Storage	S

Table C.1 Variables and Abbreviations Used in Hydrologic Calculations.

Watershed	L (m)	Elev ₁ (m)	Elev ₂ (m)	SI (%)	CN	S (mm)	t _l (hr)	PRCT (%)	LF	Adj. t _l (hr)	t _c (min)
Colonial Hills	3330	424	382	1.3	83	52	1.7	38	0.788	1.4	137
Taylor Park	1600	403	372	1.9	83	52	0.8	35	0.805	0.6	63

Drainage Area	CN	А	S	Ia	Runoff, Q (in)				
		(ha)	(in)	(in)	P = 0.5 in	P = 1 in	P = 1.5 in		
Colonial Hills	83	591.1	2.05	0.41	0.004	0.13	0.38		
CH-Int1	80	14.3	2.50	0.50	0.000	0.08	0.29		
CH-Int2	83	9.9	2.05	0.41	0.004	0.13	0.38		
CH-Int3	83	12.1	2.05	0.41	0.004	0.13	0.38		
CH-Int4	81	3.7	2.35	0.47	0.000	0.10	0.31		
CH-Int5	83	8.8	2.05	0.41	0.004	0.13	0.38		
CH-Int6	78	2.5	2.82	0.56	0.000	0.06	0.23		
Taylor Park	83	120.5	2.05	0.41	0.004	0.13	0.38		
TP-Int1	83	5.7	2.05	0.41	0.004	0.13	0.38		

Table C.3 Runoff from Intermittent Flow Areas in Three Storm Conditions.

Appendix D

Raw Isotope Analysis Data

Table D.1 Parameters and Abbreviations Used for Isotope Analysis.

Water Quality Parameter	Abbreviation
Ammonia	NH ₄ N
Cumulative Flow Volume	V _c
Nitrate	NO ₃
Nitrate plus Nitrite Nitrogen	NO ₃ +NO ₂ -N
Phosphate	PO_4
Soluble Reactive Phosphorus	SRP
Total Flow Volume	V _t
Total Kjeldahl Nitrogen	TKN
Total Phosphorous	TP

Sample Label	Sample Type	Date	Time	% Time Passed (T/T _t)	V _c /V _t	TKN (mg N/L)	Ammonia NH ₄ N (mg N/L)	Nitrate NO ₃ +NO ₂ - N (mg/L)	SRP (mg PO ₄ /L)	Total P as P (mg PO ₄ /L)	Total P as PO ₄ (mg PO ₄ /L)	¹⁸ O- PO ₄ (‰)	¹⁵ N- NO ₃ (‰)	¹⁸ O- NO ₃ (‰)
СН	DW	4/29/11	11:10	-	-	0.99	0.003	0.257	0.384	0.413	1.266	7.1	4	19.6
СН	WW	5/24/11	11:48	0	0.00	1.02	0.907	0.486	0.937	0.308	0.944	9.04	-	20.3
CH	WW	5/24/11	12:33	60	0.20	1.68	1.26	0.814	0.583	0.313	0.960	14.51	2.141	39.3
CH	WW	5/24/11	13:03	100	0.61	0.955	0.287	0.281	0.42	0.188	0.577	12.94	-	29
CH	WW	6/25/11	5:05	0	0.03	2.32	0.005	0.418	0.273	0.684	2.097	6.04	-5.074	24.8
CH	WW	6/25/11	5:18	54	0.15	3.54	0.002	0.336	0.26	2.65	8.126	5.68	-5.847	17.3
CH	WW	6/25/11	5:24	79	0.24	5.84	0.005	0.371	0.334	0.49	1.503	2.27	-	20.7
CH	WW	6/25/11	5:29	100	0.32	1.81	-	0.348	0.427	0.351	1.076	-0.9	-4.369	10.9
CH	WW	8/12/11	1:28	0	0.09	0.599	0.243	0.04	0.304	0.3	0.920	30.49	-	8
CH	WW	8/12/11	1:45	20	0.18	0.378	0.234	0.083	0.382	0.38	1.165	24.65	-5.63	12.2
CH	WW	8/12/11	2:07	46	0.29	0.344	0.254	0.118	0.529	0.53	1.625	22.99	-	10.1
CH	WW	8/12/11	2:53	100	0.40	0.402	0.194	0.117	0.721	0.72	2.208	26.46	-2.97	6.7
S-CH1	SOIL	5/3/11	-	-	-	-	-	-	0.96	-	-	18.97	-	-
S-CH2	SOIL	5/3/11	-	-	-	-	-	-	1.18	-	-	18.45	-	-
S-CH3	SOIL	5/3/11	-	-	-	-	-	-	0.65	-	-	17.61	-	-
S-CH4	SOIL	5/3/11	-	-	-	-	-	-	0.72	-	-	17.22	-	-
S-CH5	SOIL	5/3/11	-	-	-	-	-	-	0.66	-	-	15.04	-	-
G-CH1	GRASS	11/17/11	-	-	-	-	-	-	13.3	-	-	15.48	-	-

 Table D.2 Raw Isotope Analysis Data for Colonial Hills (from Jesse Coffey).

Sample Label	Sample Type	Date	Time	% Time Passed (T/T _t)	V _c /V _t	TKN (mg N/L)	Ammonia NH4N (mg N/L)	Nitrate NO ₃ +NO ₂ - N (mg/L)	SRP (mg PO ₄ /L)	Total P as P (mg PO ₄ /L)	Total P as PO ₄ (mg PO ₄ /L)	¹⁸ O- PO ₄ (%0)	¹⁵ N- NO ₃ (‰)	¹⁸ O- NO ₃ (‰)
TP	DW	4/29/11	12:00	-	-	1.23	0	1.87	0.257	0.257	0.788	6.85	-	18.5
TP	WW	5/24/11	11:30	0	0.00	0.417	1.53	2.38	0.314	0.125	0.383	11.67	7.665	30
TP	WW	5/24/11	11:45	17	0.04	0.415	1.73	1.52	0.961	0.61	1.871	14.83	-1.768	30
TP	WW	5/24/11	12:45	83	0.56	1.61	1.37	0.344	0.396	0.192	0.589	18.28	0.137	35.3
TP	WW	5/24/11	13:00	100	0.71	2.15	1.06	0.48	0.466	0.251	0.770	14.63	1.63	33.5
TP	WW	6/25/11	4:55	0	0.1	1.87	0.061	0.412	0.256	1.07	3.281	6.08	-6.377	35.5
TP	WW	6/25/11	5:08	11	0.242	1.55	-	0.415	0.359	0.382	1.171	6.03	-2.164	32.2
TP	WW	6/25/11	5:33	32	0.55	1.07	-	0.568	0.654	0.37	1.135	8.58	-3.395	17.1
TP	WW	6/25/11	6:53	100	0.81	1.21	-	0.684	0.654	0.326	1.000	14.79	-2.598	37.1
TP	WW	8/12/11	0:48	0	0.05	0.498	0.455	0.188	0.398	0.4	1.227	24.87	-5.23	-3.2
TP	WW	8/12/11	1:00	14	0.16	0.475	0.304	0.705	0.652	0.65	1.993	22.76	-7.61	0.7
TP	WW	8/12/11	1:17	34	0.31	0.271	0.306	0.157	0.857	0.86	2.637	19.4	-3.17	-3
TP	WW	8/12/11	2:14	100	0.49	0.345	0.225	0.349	0.937	0.94	2.883	19.52	-3.56	12
S-TP1	SOIL	5/3/11	-	-	-	-	-	-	0.59	-	-	18.46	-	-
S-TP2	SOIL	5/3/11	-	-	-	-	-	-	1.00	-	-	27.82	-	-
G-TP1	GRASS	11/17/11	-	-	-	-	-	-	11.	-	-	17.1	-	-
FERT. 1	FERT.	-	-	-	-	-	-	-	-	-	-	7.178	3.135	-
FERT. 2	FERT.	-	-	-	-	-	-	-	-	-	-	1.806	3.294	-

 Table D.3 Raw Isotope Analysis Data for Taylor Park (from Jesse Coffey).

Sample	Sample	Date	SRP	¹⁸ O-PO ₄
Label	Туре	Date	$(mg PO_4/L)$	(%0)
S-CH1	SOIL	6/5/12	0.66	17.23
		7/6/12	1.34	21.62
S-CH6	SOIL	6/5/12	1.02	14.32
		7/6/12	0.83	21.62
S-CH7	SOIL	6/5/12	0.42	22.91
		7/6/12	0.35	17.76
S-TP2	SOIL	6/5/12	0.67	21.00
		7/6/12	1.51	20.36
G-CH2	GRASS	6/5/12	21.3	22.41
		7/6/12	23.1	23.30
G-CH3	GRASS	6/5/12	22.2	18.60
		7/6/12	24.5	23.76
DG-CH1	DECAYED	6/5/12	6.27	21.87
	GRASS	7/6/12	15.5	23.66
DG-CH2	DECAYED	6/5/12	4.97	21.98
	GRASS	7/6/12	7.11	20.43

Table D.4 Raw Soil and Grass Isotope Analysis Data (from Monica Gomes).