INFLUENCE OF SOIL PHYSICAL AND CHEMICAL PROPERTIES ON SOIL CO₂ FLUX
IN SEMI-ARID GREEN STORMWATER INFRASTRUCTURE

by

Tyler K. Rockhill

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This thesis has been approved on the date shown below:

[Signature]

November 17th, 2017

Date

Thomas Meixner
Professor and Associate Department Head
Department of Hydrology and Atmospheric Sciences
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<tr>
<td>CH₄</td>
<td>Methane</td>
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<tr>
<td>NO₃⁻</td>
<td>Nitrate</td>
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<td>NO₂⁻</td>
<td>Nitrite</td>
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<td>TON</td>
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<tr>
<td>TIN</td>
<td>Total Inorganic Nitrogen</td>
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<tr>
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<td>Soil Organic Matter</td>
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<tr>
<td>NPOC</td>
<td>Non-Purgeable Organic Carbon</td>
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<tr>
<td>TC</td>
<td>Total Carbon</td>
</tr>
<tr>
<td>TN</td>
<td>Total Nitrogen</td>
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<tr>
<td>GI</td>
<td>Green Infrastructure</td>
</tr>
<tr>
<td>TR</td>
<td>Terminal</td>
</tr>
<tr>
<td>FT</td>
<td>Flow-Through</td>
</tr>
<tr>
<td>BX</td>
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ABSTRACT


Rapid population growth and urbanization in semi-arid and arid regions has led to alterations in the water, carbon (C), and nitrogen (N) cycles (Gallo et al. 2014), prompting demands for mitigation strategies. Green Infrastructure (GI) is one of the methods used in urban storm water mitigation that delays and attenuates stormwater runoff by storing water in vegetated depressions. In the Southwest these depressions, also called bioswales, have the potential to act as biogeochemical hot spots, encouraging nutrient cycling, infiltration, plant growth, and microbial activity (McClain et al. 2003). An influx of water to GI initiates a combination of physical and microbial processes that result in increased CO₂ efflux and N mineralization known as the Birch Effect (Birch, 1958). This study examines GI in Tucson, AZ through inducing an artificial precipitation regime and determining how soil properties, GI design, and biogeochemical characteristics influence the response. In natural systems it has been shown that soil moisture, soil properties, organic matter, length of dry period, nutrients such as carbon and nitrogen, and microbial biomass influence soil respiration and nitrogen mineralization (Borken and Matzner 2009). The purpose of this study is to determine the role that the Birch Effect plays in urban stormwater GI. Additionally we seek to determine how soil and nutrient properties and precipitation regime affect the amplitude of the response. It was found that soils from GI features tend to have higher concentrations of organic matter, total carbon, and total nitrogen, as well as higher water holding capacity and lower bulk density. It was also shown that soils originating from GI features tend to illicit a greater CO₂ flux upon rewetting than soils from adjacent areas. The linear relationships found between % clay, pH, bulk density, WHC, SOM, TC, and TN suggest that the reason for the greater response to wetting is due to the altered physiochemical composition. The results of this study can be utilized to increase microbial activity and remediation in urban GI features. This fits into the larger goal of GI to help mitigate many of the issues associated with Urban Stream Syndrome (USS) such as flashier hydrography response, increased nutrient and contaminant concentrations, increased erosion, altered channel morphology and reduced biodiversity (Meyers et al. 2005).
Chapter 1: INTRODUCTION

Rapid population growth and subsequent increase in urbanization in the Southwestern US has altered hydrologic and biogeochemical cycles (Lohse et al. 2008; Walsh et al. 2005). Urbanization of watersheds and corresponding downstream impacts to streams and rivers are considered to be one of the most significant impairments of waterways (USEPA, 2009). Urban stormwater management has typically focused on flood and pollution mitigation, without emphasis on hydrologic and biotic factors (Walsh et al. 2016). Recently there has been recognition for increased investigation of the multiple benefits of an ecohydrologic approach to urban stormwater management, particularly in the Southwest (Jennifer G Lee, Fisher, and Schumacher 2016; Walsh et al. 2016).

Urban Stream Syndrome (USS) is a term that has been developed to encompass the set of impairments emblematic of a degraded urban waterway. The symptoms of urban stream syndrome include flashier hydrograph response (Figure 1.1), elevated nutrient and contaminant levels, altered channel morphology, and alteration in sediment loads (Walsh et al. 2005). The majority of the symptoms associated with USS are typically correlated with increases in the amount of impervious contributing surfaces, which limit infiltration and concentrate runoff event flows (Lee and Heaney 2003; Walsh, Fletcher, and Ladson 2009). The higher input of atmospheric deposition in SW urban zones (Lohse et al. 2008) coupled with typical sources of urban pollution lead to increased levels of nutrients and contaminants in urban waterways (Walsh et al. 2005). One of the methodologies for mitigating the impacts of USS in semi-arid regions is by using Green Infrastructure (GI).
Green infrastructure includes a multitude of different low impact approaches to urban stormwater management and ecosystem rehabilitation including green roofs, permeable pavement, buffer strips, rain tanks and bioswales (Ahiablame, Engel, and Chaubey 2012). A bioswale, for the purpose of this study will be defined as a vegetated and/or mulched depression built adjacent to a sidewalk or section of pavement that is can receive water from the contributing street or pavement. Bioswales are typically designed to improve infiltration, filtration, onsite storage, evapotranspiration, biodegradation, and percolation (Ahiablame, Engel, and Chaubey 2012). Beyond the improvements to the urban stormwater hydrograph, GI shows promise in mitigating urban water quality issues as well. Previous studies have shown that bioswales have the ability to sequester both dissolved and suspended constituents such as nitrogen, phosphorus, carbon, arsenic, cadmium, chloride, chromium, copper, *E. coli*, fecal coliform, lead, mercury, oil and grease, total suspended solids, and total zinc (Li and Davis 2009; Bernhardt et al. 2012; Henderson, Greenway, and Phillips 2007). Constituents are removed through a combination of adsorption, precipitation, ion exchange, and biological processes (Li
and Davis 2009). This study will focus on examining the factors influencing microbial activity related to the cycling of nutrients in semi-arid environments.

One of the phenomena hypothesized to have an impact on the ability of GI to reduce the impacts of urban stream syndrome by improving nutrient cycling and microbial activity is known as the Birch Effect. The Birch Effect is a dynamic response of dry, inactive soil microbes to an increase in soil moisture, resulting in higher levels of CO$_2$ respiration and nitrogen mineralization (Birch, 1958) (Figure 1.2). The Birch Effect is known as a major driver of C and N cycles especially in Mediterranean, semi-arid, arid regions (Wang et al. 2015; Gallo et al. 2014; Sponseller 2007; Lado-Monserrat et al. 2014; Jarvis et al. 2007; Unger et al. 2012; Borken and Matzner 2009). There are four main hypotheses for the pulse of CO$_2$ respiration and nitrogen mineralization associated with the rewetting of dry soils. The first is that the wetting pulse induces the release of intracellular solutes used to maintain turgor that are rapidly consumed by the microorganisms that survived the drought and wetting event (Wang et al. 2015). It was later hypothesized that the mineralization of the carbon present in dead microbes was the substrate utilized for respiration (Fierer and Schimel 2002). The third is that the respiration pulse is triggered by the connection of microbes and substrate by the precipitation that has infiltrated into the soil matrix (Wang et al. 2015). The final hypothesis is that gasses trapped in the soil matrix that are physically displaced by the infiltration of water, therefore escaping to the atmosphere and adding to the pulse of CO$_2$ seen in the rewetting of dry soils (Wang et al. 2015). It is generally thought that the Birch Effect is a combination of all of these hypotheses, though the primary driver/s have not been fully determined. The progression of the C and N cycle and enhanced levels of microbial activity may play a role in the ability of GI to mitigate USS symptoms.
The purpose of this study is to examine the soil physiochemical properties (SOM, TC, TN, TC:TN, pH, WHC, soil texture, and bulk density) in GI basins and the soil response to a controlled precipitation regime, observing the soil CO$_2$ efflux as a proxy for the Birch Effect response. The results were used to test the following hypotheses: (i) soil physiochemical properties will differ in GI installations compared with soil samples taken outside of the GI features (ii) soils sampled from GI features will exhibit higher CO$_2$ respiration rates upon rewetting when compared to control soils and (iii) the difference in soil physiochemical properties will play a significant role in augmenting the CO$_2$ efflux of GI soils and/or control soils.
Chapter 2 Methods

2.1.1 Site Description

The GI in this study is located in both Bronx and High School (aka West University) Washes in the Lower Santa Cruz River Watershed, Tucson, AZ, United States (Figure 2.1, Figure 2.2, *WSGM*). The average elevation of Bronx Wash (NAD 83: 32.2436, -110.9692) and High School Wash (NAD 83: 32.224357, -110.951477) are 2411 ft. and 2414 ft., respectively. The average slope of Bronx and High School Wash is 2.21% and 0.66%, respectively. The drainage area to the most downstream point affected by GI in Bronx and High School Wash is 0.31 mi² and 1.38 mi², respectively. Located in the semi-arid Arizona Upland ecoregion, this region is dominated by paloverde-cactus shrub (Griffith et al. 2014). Other vegetation includes ocotillo, brittlebush, creosote, catclaw acacia, cholla, desert saltbrush, pricklypear, ironwood and mesquite (Griffith et al. 2014). The topography is consistent with typical Basin and Range characteristics, with the Tucson Metropolitan area in the alluvium basin between the Santa Catalina, Rincon and Tucson Mountains (Gallo et al. 2013). The soils in this region are dominantly Aridisols and Entisols, with hyperthermic soil temperatures and aridic soil moisture regimes (Griffith et al. 2014).

2.1.2 Site Hydrology

Bronx Wash is the northern of the two selected basins; it runs east to west from 1st Avenue and Linden St. to 6th Avenue and Linden St., Tucson, AZ (Figure 2.1). At 6th and Linden it is piped underneath Stone Ave and then continues in a concrete channel until it intersects with the Santa Cruz River. The channel is a concrete trapezoid that rises to meet the street elevation at intersections. Therefore stormwater runoff can have significant impacts on running or ponded water along the adjacent streets. GI installed on the adjacent streets is
designed to alleviate the flooding that occurs. Since the channel generally runs east to west the majority of the GI was installed on north/south streets, to mitigate the flow entering the wash. There are a total of 59 GI installations that contribute to the wash (Appendix A), consisting of 8 FT systems and 51 TR systems. The majority of these were installed by Conserve 2 Enhance / Watershed Management Group (WMG) in 2015.

High School Wash runs northeast to southwest from El Calle Corta and N Camino Esanola to its intersection with Arroyo Chico at E 8th St. Tucson, AZ at which point it also intersects with the Santa Cruz River (Figure 2.2). The wash is mostly a natural channel with manmade structures typically occurring when the stream intersects with streets. The GI in this wash is primarily located between Cherry St. and Tyndall St. There are a total of 86 GI installations that contribute to this wash, 53 of them are FT systems and 33 are TR systems (Appendix A). Watershed Management Group installed the majority of these GI systems in 2009. This system is slightly different than Bronx in that the majority of the GI systems were installed parallel to the wash, as opposed to perpendicular. FT systems in this wash tend to be chicanes that protrude into the street and run along the length of the street. TR systems were mostly installed on north/south streets and occur in clumped locations.

It should also be noted that the groundwater table in Tucson varies in depth from 50 to 700 ft. (Gelt et al. 1999). A water table at this depth means that the washes in this study tend to be losing reaches, where the water table is below the channel and therefore does not create perennial streamflow. Due to the high degree of urbanization in these catchments, combined with the high intensity of summer monsoonal precipitation means the majority of stormwater runoff occurs because infiltration is exceeded, as opposed to saturation excess runoff.
Figure 2.1 Details the sites selected in High School Wash, as well as the watershed outlines for the upper and lower reaches of the wash. Map created by Yoganand Korgaonkar

Figure 2.2 Details the sites selected in Bronx Wash, as well as the watershed outlines for the upper and lower reaches of the wash. Map created by Yoganand Korgaonkar
2.1.3 Site Hydrometeorology

Since Tucson lies in a semi-arid/arid region, where the annual potential evaporation is greater than the annual precipitation. The average annual precipitation in Tucson is 305mm whereas the average annual potential evapotranspiration is 1960 mm (Gallo et al. 2013; Gelt et al 1999). The average temperature in Tucson can range from 11° C in December to 36° C in July (Gelt et al. 1999). Combined with an average relative humidity of 48.5% in December and 42.5% in July creates a high vapor pressure deficit (Gelt et al. 1999). These conditions result in 250 mm of actual evaporation annually (Gallo et al. 2013). Approximately 52% of the annual precipitation occurs in the summer in the form of low duration, high intensity convective storms (Gelt et al. 1999). These storms are the product of warm, moist air from the Gulf of California and the Gulf of Mexico rising due to thermally induced lows (Gelt et al. 1999). These storms tend to create highly heterogeneous precipitation patterns. During December to March another 28% of the annual precipitation tends to fall as the remnants of fronts that develop over the Pacific Ocean (Gelt et al. 1999). These storms tend to be of longer duration and lower intensity compared to summer “monsoon” storms.

2.2 Soil Collection Methodology

Soils were collected on October 11 2016, which is in between the rainy seasons in Tucson. Taking the samples during October, when antecedent conditions are dry, allowed for the soils in each site to be as similar of a state as possible. Since the rainfall is so heterogeneous in this region if the soils were collected after a storm, the soils would likely have different conditions depending on the degree to which the storm impacted the soil. Therefore all soils samples were collected on the same day during the middle of the dry fall season.
In order to achieve a random subsampling of the GI in the basins considered in this study the entirety of the GI in each basin was surveyed. The survey included geometric and ecological characteristics of each GI site, which allowed for the random selection of five of each type of GI from each of the two catchments (Figures 2.1 and 2.2, Appendix D). After all of the GI were selected the lengths of each GI feature, measured parallel to the street, were input into a random number generator, to produce five subsampling sites along the thalweg of the GI. These sites would be the location of the soils to be collected for this study (Appendix A).

On the day of soil collection a tubular soil sampler was used to take 10 cm deep cores at each of the five specified locations in each GI feature. This design assured that equal proportions of each sampling location were represented in the final soil aggregate. The soil sampler was driven into the soil with a hammer in an enclosed pipe, which maintained a
perpendicular angle of penetration as much as possible. At the time of collection the soil
temperature, vegetation, and canopy cover were all recorded. The soils were then stored in
Ziploc bags and transported to the fridge.

After bringing soils to the lab the soils were stored in the fridge at 4°C. Then the mass
and volume of each sample were determined in order to double check that ample sample had
been collected and to determine the bulk density. It is important to note that this methodology of
collecting bulk density determines only the disturbed bulk density, which was assumed to
provide enough information as to be able to compare soil samples. After weighing the samples
were sieved to 2 mm in order to remove large particles that tend to be less readily reactive (Soil
Survey Staff, 2017). Furthermore particles below 2 mm tend to be considered “soil” while
particles larger than 2 mm are considered “rock” and most soil analysis methodologies advise for
sieving to 2 mm. Therefore 2 mm sieving was chosen so that results from this study were
comparable to similar studies.

The next step in preparing the soils for analysis was creating subsamples of the correct
weight and with the same distribution of soil particles as the original sample. This was
accomplished by using a riffled soil splitter. The entire sample was deposited into the splitter,
which divides each sample in equal parts with equal distributions of particle size. Then the
subsamples were split repeatedly until the desired soil sample size for each test was achieved
(Soil Science Division Staff, 2017). The subsamples were then stored in the freezer for C and N
analysis, pH analysis, and soil organic matter analysis. Subsamples for water holding capacity,
particle size distribution and respiration experiment were stored at room temperature and allowed
to dry evenly. The excess samples were stored in airtight containers in case additional samples
were needed.
The storage procedure for the samples used to determine respiration rates were stored in quart sized mason jars, open to the air. The jars were fitted with rubber septa by drilling a hole in the top and gluing the septa in the hole. The SCIGRIP Type 16 Fast set Clear, medium bodied solvent cement, acrylic (Stock #10315) glue was added to the top and bottom and the hole drilled was slightly smaller than the circumference of the septa (Figure 2.4). The jars were preliminarily checked for air tightness by submerging them under water, to assure that there were no major leaks. Further testing for proper seal occurred later. The samples used for all of the soil properties analysis were left in sealed containers at room temperature until needed.

Figure 2.4 Example photograph of jars used in the respiration experiment fitted with septa to allow for removal of air.
2.3 Soil Property Analysis

2.3.1 Soil Particle Size Distribution

Particle size distribution was determined by the modified pipette method (Gee and Bauder 1986, Kettler et al. 2001). This method was used to define the soil textural composition (% sand, silt, and clay) in order to classify soils based on the USDA classification scheme. Soil composition has been shown to play a role in soil-water retention, leaching, erosion potential, nutrient storage, organic matter dynamics, and carbon sequestration ability (Kettler, Doran, and Gilbert 2001). This particular method relies on a combination of sieving and sedimentation methods, using sodium hexametaphosphate (HMP) as a dispersant. The HMP replaces Ca⁺ with Na⁺ on the ion-exchange complex of soil particles, which breaks down soil aggregates. This method allows for the classification of soil types, but does not break down the texture components into farther classifications.

To determine the sand component, 15-30 g of dry soil were mixed with sodium hexametaphosphate at a concentration of 3% by weight and then shaken on a shaker table for 2 hrs. at 120 rpm. Soils that appeared to have a large sand component started out with a larger sample mass. Then the sample was mixed through a wet 0.053 mm sieve, using a brush to collect particles that did not pass through, the sample portion that did not pass through was set aside to dry at 55°C. Then this portion was heated to 450°C for 4 hours and then weighed. The portion of the sample that passed through the sieve was transferred to a beaker (400 mL – 1L size) and stirred thoroughly. Then the sample was transferred to a 50mL centrifuge tube and shaken again. Then the sample was allowed to sit at room temperature for between 90 minutes and 6 hours, but typically 4-5 hours. Then the suspended particles were decanted into a pre-weighed drying container. Finally the decanted portion was dried at 105°C until constant weight was
achieved. The soil texture composition was then calculated based on the following equations (Kettler, Doran, and Gilbert 2001):

\[
\begin{align*}
\text{Sand}\% &= \left( \frac{\text{oven dry sand mass}}{\text{original sample mass}} \right) \times 100\% \\
\text{Silt}\% &= \left( \frac{\text{oven dry silt mass}}{\text{original sample mass}} \right) \times 100\% \\
\text{Clay}\% &= 100 - (\text{Sand}\% + \text{Silt}\%)
\end{align*}
\]

After attaining the % compositions for sand, silt, and clay (results can be seen in Appendix A), the USDA soil texture classification scheme was used to determine soil type. This involved using the Excel version of the Soil Texture Calculator from the USDA (National Resource Conservation Service).

2.3.2 Soil pH

Soil pH was determined by using a 1:1 mix with DI water by weight (Soil Science Division Staff, 2017). A 10 g soil subsample was mixed with DI water in a volumetric beaker and stirred. Then the pH was measured with the Thermo Fisher Orion 5 Star Series and recorded.

2.3.3 Gravimetric Water Content

Soil gravimetric water content was determined by drying soils in a furnace. Approximately 10 g of soil was weighed out and placed in a numbered, tared weighing tin. The soil and tin were then dried at 105°C for 24 hours and cooled in a desiccator before being weighed and recorded. The gravimetric soil moisture was then calculated by the following equation (Carter and Gregorich 2006).

\[
\text{Soil Moisture (\%)} = \left( \frac{(\text{wet soil wt}) - (\text{dry soil wt} - \text{tin wt.})}{(\text{dry soil wt} - \text{tin wt.})} \right) \times 100
\]
2.3.4 Water Holding Capacity

The subsample for determining the Water Holding Capacity (WHC, $\theta_g$) was weighed out to 15 g, then placed into a funnel lined with a Whatman No. 42 (Fisher No. 09-856A) filter. The funnel was then placed in a 200 mL beaker and filled with distilled deionized water (DDI) until the filter paper in the funnel was submerged. At this point the soil was glistening, indicating that the water had wicked up, saturating the soil sample. Then the water from the beaker was removed and the sample was allowed to drip overnight into the 200 mL beaker. A piece of parafilm was then placed over the funnel and the soil was stored in a cabinet to prevent evaporation. The next day a subsample was collected from the soil and weighed in a tared, labeled beaker. The subsample was then dried overnight at 105°C. After that the gravimetric water content ($\theta_g$) was calculated by subtracting the dry mass from the wet mass and diving by the dry mass.

2.3.4 Soil Organic Matter Analysis

The Soil Organic Matter (SOM) was determined for each study site and corresponding control using Loss on Ignition (LOI) method. Each sample was weighed out to 5-10 g on tared crucibles, then loaded into a lab furnace set to 105°C for two hours. Then samples were removed and weighed to the nearest 0.001, then samples were placed back into the furnace for 16 hours at 400°C (Soil Science Division Staff, 2017). Samples were removed and cooled in a desiccator. When cool samples were weighed again. Then the LOI was calculated based on the following equation:

$$LOI\ (\%) = \frac{Weight\ at\ 105^\circ C - \ Weight\ at\ 400^\circ C}{Weight\ at\ 105^\circ C} \times 100$$

The LOI is used as a semi-quantitative measure of SOM. LOI is typically used in a linear regression with results from another SOM determination method in order to rapidly classify the SOM of multiple soils. In this case since this is a comparative study the LOI was assumed to be
approximately equal to SOM.

2.3.5 Total Organic Carbon Analysis

The “Fizz Test” is a simple method used to determine presence of absence of carbonates in a soil. Carbonates have the ability to disrupt both TOC and particle size distribution tests, and therefore need to be removed if the samples test positive for significant carbonates. Since carbonates typically accumulate in desert soils (Gile and Hawley 1966) the results of this test were used to confirm the conceptual understanding of this system. Especially since these soils had not had as long to develop as the soils surrounding them, because of the disturbance by GI implementation. Carbonates in soil can consist of various components, the most common being calcite (Soil Science Staff, Technical Note 5, 2017). Besides the potential for carbonates to disrupt TOC and PSD measurement they also play a role in soil fertility, erodability and available water capacity (Soil Science Staff, Technical Note 5, 2017).

The effervescence was then qualitatively assessed based on the Table 1 in the USDA NCRS Soil Survey Technical Note 5 to determine the relative abundance of carbonates in each soil. The 1M solution of HCL was prepared by adding 27 mL of 30% HCl to 106 mL of DDI water, then adding DDI water to bring the solution to 250 (Soil Science Staff, Technical Note 5, 2017).

2.3.6 Total Organic Carbon and Total Nitrogen in Solid Samples

Soil subsamples for Total Organic Carbon (TOC) were stored at 4°C to minimize the losses by microbial degradation, and were kept in sealed containers to minimize volatilization. Before analysis soils were ground with a mortar and pestle to maximize the surface area before ignition. To analyze for TOC both the Total Carbon (TC) were measured on a Shimadzu TOC with a Solid Sample Combustion Unit (SSM-5000a) in conjunction with a Total Nitrogen Unit. In this methodology three replicates of a sample are loaded into ceramic boats, which are
thermally oxidized at 900°C and subsequently the carbon dioxide is measured by nondisruptive infrared sensor (Shimadzu Corporation). The samples were then calibrated using a linear relationship of the measured CO₂ to samples of known CO₂ concentration. During the thermal oxidation process all of the Total Nitrogen (TN) bound in the soils is also converted to NO gas, the TNM-L analyzer was used to pass the gas through a chemiluminescence detector, which measured the TN (Shimadzu Corporation)

### 2.4 Wetting Experiment Methodology

To test the effects of soil wetting soil samples from each location were subjected to two wetting regimes and a control. The wetting experiments consisted of a relatively large event of 12 ml and a smaller event of 3 ml. The large event was applied once every four weeks, whereas the small event was applied every week. This resulted in the same amount of water being applied to each soil subsample. The control jar was kept open to the atmosphere for the duration of the experiment, and all jars were kept at room temperature of 24 °C. The size of the events was determined by using an average porosity of a typical semi-arid soil and determining an approximate volume of water required to reach saturation, assuming 50 g of soil in each experiment. This value corresponds with the volume of the large event, and the small event was determined by dividing by the frequency of wetting, so that the total amount of water applied over the duration of the experiment stayed the same.
Table 2.1 Details the date and amount at which small and large events were added during the respiration experiment.

<table>
<thead>
<tr>
<th>Date (2016-2017)</th>
<th>Small Event Application</th>
<th>Large Event Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/11</td>
<td>3 mL</td>
<td>12 mL</td>
</tr>
<tr>
<td>11/18</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>11/25</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>12/02</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>12/09</td>
<td>3 mL</td>
<td>12 mL</td>
</tr>
<tr>
<td>12/16</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>12/23</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>12/30</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>01/06</td>
<td>3 mL</td>
<td>12 mL</td>
</tr>
<tr>
<td>01/13</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>01/20</td>
<td>3 mL</td>
<td></td>
</tr>
<tr>
<td>01/27</td>
<td>3 mL</td>
<td></td>
</tr>
</tbody>
</table>

The chemical composition of the water applied in each experiment was determined by bringing concentrations of cations and anions, as well as pH, to levels annual average concentrations found in the Chirichaua National Atmospheric Deposition Program (National Atmospheric Deposition Program, 2016). The major cations and anions, as well as pH were averaged over the available time period to approximate the chemical composition of rainwater in the region. The compounds found in the atmospheric deposition database were then added to DDI water in the following mounts; 0.76 mg CaSO₄, 0.146 mg (NH₄)₂SO₄, 0.807 mg NH₄Cl, 0.073 mg MgCl₂, 0.063 mg KCl, 0.184 mg NaCl, and 1.02 HNO₃ per 1 L.

2.5 Carbon Dioxide Respiration

CO₂ efflux from the mason jars was measured using a Qubit S151 Infra-Red Gas Analyzer (IRGA) in the Soil Pedology Lab, University of Arizona, Tucson, Arizona, as shown in picture below.
Figure 2.5 Details the CO$_2$ analyzer set up used to measure, record, and calibrate CO$_2$ respiration data (S151 CO$_2$ Analyzer Manual, Loligo Systems).

The S151 was also connected to a LabPro, which was used with Logger Pro software to record the CO$_2$ level on a computer. The following set up and methodologies were motivated by Sherrod et al. 2012 (Figure 2.5). Along with this system, NO gas was used as a carrier gas, which draws the input gas through a drying column, filled with a desiccant. In order to calibrate the S151 different volumes of pure CO$_2$ gas were introduced to the system in order to create a linear relationship between the measured CO$_2$ and the mg of CO$_2$ added to the system. Then three samples of ambient are were taken close to the ground, to minimize the impacts of human respiration elevating CO$_2$ levels.
After the IRGA was calibrated, the jars were all capped (after being uncapped to allow for drying). After an hour a background sample was drawn from all control soils, and small and large soils, depending on which were being sampled that day. The sample was drawn by inserting a syringe (Syringe TB 26Gx58 1CC [Fisher 1482910F]) into the mason jar, plunging the syringe between 5 and 10 times, in order to mix the air thoroughly, and then quickly withdrawing 1 mL of air from the mason jar and injecting the 1mL of air into the rubber septa leading to the IRGA (unless levels were below or above the calibration curve, then injection amount was varied in order to fall in curve). The peak of the CO$_2$ efflux pulse was recorded in order to measure the integral of the CO$_2$ curve. For the first time step of each week (T=0), all control soils were measured, along with any jars that were going to be subjected to wetting that week. Samples of the ambient atmosphere to be used as blanks were taken during calibration, after sample 15 and 30, as well as after all soils were measured. After each injection the jars were uncapped in order to let the jar equilibrate with the atmosphere for about 5 minutes. Then the designated amount of artificial rainwater was added to the corresponding Mason jar and the jars were capped. Then subsequent CO$_2$ measurements were taken at 1, 3, 6, 12, 24, and 48 hours after the artificial rainwater was added. These measurements were taken with the same
procedure as T=0 measurements, allowing for equilibration with the atmosphere, and then capping for the duration of the time in between measurements. In between measurements the soils were stored in a dark room at constant temperature. First the raw CO$_2$ rate was converted to valid CO$_2$ concentrations using the linear calibration curve. After recording all of the corresponding areas under the CO$_2$ curve for each peak (of a soil) the moles of CO$_2$ gas respired could be calculated by rearranging the ideal gas law:

$$PV = nRT$$

where P is pressure in bars, V is volume of gas injected in liters, R is gas constant (R = 0.0820457), T is temperature in Kelvin, and n is moles of gas injected. The pressure was assumed constant at 0.996 atm, to compensate for elevation. The temperature of the room was constant at 297.15 °K, and the volume of the jars were calculated to be 0.48 L on average for all jars (after being filled with soil). This amount was then converted into the g of C respired by the soil. Then the g of C in the ambient atmosphere was calculated based on a moving average of the atmospheric blank samples. The difference between the composition in the jar and the atmospheric composition was taken as the mass of C respired in the given time period for that particular soil. The rate and respiration per gram of soil were also calculated. The sum of all of the g of C respired by a given soil during the 48 hour period was assumed to be the cumulative C respiration. This assumption was made in order to compare soil responses, even though it was evident that the reaction had not gone to completion in some cases.
Figure 2.7 Shows an example of the CO$_2$ respiration data collected using the IRGA and LoggerPro. Each peak is a different soil sample, the area under the curve minus the ambient CO$_2$ concentration is equal to the respiration produced by the microbial/physical response to rewetting.

2.6 Statistical Methodology

Results gathered in this experiment were compiled in MATLAB for statistical analysis and plotting. The Wilcoxon Ranked Sum test for statistical significance between two populations was used with 95% confidence bounds. The Wilcoxon test was used because the populations tended to non-normal distributions (Wilcoxon, 1945) (Appendix B). Soil samples were also often grouped into the similar geographic and basin design types to increase the statistical power of examining differences as shown below (Table 2.2).
Table 2.2 Details the grouping of composite soils samples into basin type and locations, in order to compare using Wilcoxon tests.

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Grouping</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>HSFT</td>
</tr>
<tr>
<td>6-10</td>
<td>HSTR</td>
</tr>
<tr>
<td>11-15</td>
<td>BXFT</td>
</tr>
<tr>
<td>16-20</td>
<td>BXTR</td>
</tr>
<tr>
<td>21-25</td>
<td>HSFT Ctrl</td>
</tr>
<tr>
<td>26-30</td>
<td>HSTR Ctrl</td>
</tr>
<tr>
<td>31-35</td>
<td>BXFT Ctrl</td>
</tr>
<tr>
<td>36-40</td>
<td>BXTR Ctrl</td>
</tr>
</tbody>
</table>

HS = High School Wash, BX = Bronx Wash, FT = Flow-Through Basin, TR = Terminal Basin, Ctrl = adjacent to GI basin.

Chapter 3: RESULTS

3.0 Overview

Water Holding Capacity, Soil Organic Matter, Soil Texture, Bulk Density, soil pH, Total Carbon, Total Nitrogen, and Carbon to Nitrogen Ratio were successfully analyzed for the 40 soil samples collected. The CO₂ efflux as a response to the addition of water was recorded for nine out of the possible twelve weeks of the small event, and for three out of three weeks for the large event application. Cumulative CO₂ effluxes as well as CO2 efflux rate were calculated for each time step. Results are separated into three distinct categories; soil characteristics, which details the analysis done on the physical and chemical properties of the soil, Birch Effect response, which focuses on the response of each soil to rewetting using CO₂ efflux, and interaction between soil characteristics and response, which details the relationship between the Birch Effect response and soil physiochemical characteristic. In all relevant plots the thick red boxplot lines indicate means, the thin blue lines indicate medians. Box plots not sharing the same letter are significantly different (p<0.05).
3.1 Soil Characteristics

3.1.a Particle Size Distribution

Results from the particle size distribution show proportions of sand to be between 40 and 80% (Figure 3.1), with no statistical significance between the different basins and control soils. Proportions of silt range from 6 to 40% (Figure 3.1) and also show no statistical significance between groups. However proportions of clay range from 10 to 25% (Figure 3.1). FT basins and Ctrl basins tended to have statistically higher proportions of clay when compared to TR basins (Appendix B). The weight of the particles over 2 mm was recorded during the sieving process, the results indicate that between 16 and 80% of the soil collected was above 2 mm. The relatively high values of large particles (mostly large organic matter and mulch) necessitated recollection of additional soil in order to perform the required analysis, which was carried out
two days after initial collection. However there was no statically significant relationship between the location or type of basin and the proportion of large particles (Figure 3.1d).

![Diagram of soil particle size analysis transposed onto the USDA soil classification chart.](image)

**Figure 3.2** Distribution of soil particle size analysis transposed onto the USDA soil classification chart. Deviations in the marker style indicate different basin category.

Based on USDA soil classifications, 36 of the soils were considered sandy loam soils, two were considered to be loam soils, one loam was recorded and one sandy clay loam (Figure 3.2).
3.1.b Bulk Density and Water Holding Capacity

Figure 3.3 Plot A shows the results of the Bulk Density analysis, grouped by basin and GI type, Plot B shows the results from the Water Holding Capacity analysis, also grouped by basin and GI type.

Results from the bulk density measurement indicate that the bulk density of the disturbed soil samples was higher (about 1.2 g/cm³) in control soils as compared to the soils collected in GI basins (about 0.8 g/cm³) (Figure 3.3). This resulted in statistical significance between control soils and both FT and TR basins. Visual inspection of the soils yielded significant portions of mulch and leaf litter in the majority of GI soils. The WHC of GI soils was typically between 40 and 110%, whereas the WHC of control soils tended to be between 30 and 40% (Figure 3.3). Therefore for both TR and FT basins, the WHC was higher at a statistically significant level, but there difference between HS and BX and TR and FT basins was not significant. The variation in WHC for controls soils was also much lower than in GI soils.
3.1.3 Soil Organic Matter and pH

Figure 3.4 Plot A shows Soil Organic Matter as a % of soil weight as determined by Loss on Ignition, plot B shows pH for each composite soil extracted with DI water, both grouped by basin and type of GI

Results from SOM analysis behaved very similarly to WHC, likely because the WHC is partially dependent on SOM. Both types of GI basins had higher proportions of SOM at statistically significant levels. The % SOM varied in GI basins from 3 to 15%, whereas in control soils it varied from 3-5% (Figure 3.4). Similarly to as in WHC, the variation in SOM levels was much greater in GI basins than in control soils. The pH did not vary with statistical significance between basin types, with the exception of all TR basins having less alkaline soils than the TR control soils.
3.1.d Total Carbon, Total Nitrogen and Total Carbon to Total Nitrogen Ratio

Figure 3.5. Plot A shows the Total Carbon as analyzed by combustion in the Shimadzu, Plot B shows the Total Nitrogen as analyzed by combustion in the Shimadzu, Plot C shows the ratio between Total Carbon and Total Nitrogen, all plots are grouped by basin and GI type.

Total Carbon from GI soils ranged from 3 to 28 mg C / g soil, and below 5 mg C / g soil for control soils (Figure 3.5). Similarly to WHC and SOM, statistically significant higher concentration existed between both TR and FT basins as compared to control soils, but not between FT and TR or between wash locations. Furthermore the variation in TC levels varied more in GI soils as compared to in control soils.

Total Nitrogen ranged from 0.2 to 1.5 mg N / g soil in GI basins and between 0.1 and 0.5 mg N / g soil in control soils (Figure 3.5). Statistically different populations were found between wash locations as well as between TR basins and control soils. Similarly to TC, WHC, and SOM variation in TN were higher in GI basins than in control soils. It is interesting to note that the
difference in populations between FT and control soils was almost found to be statistically significant as well.

The results from the Total Carbon: Total Nitrogen analysis deviate from the trends seen in previous results. In this case values for GI soils ranged from 10 to 40, whereas control soils ranged from 10 to 60 (Figure 3.5) with typically higher variation in the control soils. Similarly to the TN results there were statistically significant differences between the TR basins and the control soils, but in this case there was also statistically significant differences between all soils from BX and HS wash.

3.1.e Change in Soil Water Content

Figure 3.6 Shows the average change in soil water content for each soil in the study. The left figure details the application of small events, whereas the right figures details the change in soil water content found after applying large events.

The average change in soil water content for each soil was also monitored for both the small and large event applications, to assure that each pulse was approximately the same size and to check for variation within soils due to starting masses. Results from the change in soil water content analysis show that small event applications created a change in SWC between 5 and 9 % for small events and between 18 and 35 for large events (Figure 3.6). Though for both small and large events there were no populations that showed statistically significant differences.
3.2 Birch Effect Response

3.2.1 Small Event

Figure 3.7 Details the average cumulative CO$_2$ efflux from each soil for each small event measured, grouped into the respective category. The lower image further categorizes the small event fluxes.

The mean cumulative CO$_2$ efflux from soil given the small precipitation regime is 1.757 mg C g$^{-1}$ soil, with an upper bound of 6.48 mg C g$^{-1}$ soil and a lower bound 0.4688 mg C g$^{-1}$ soil. There was no statistically significant difference between HS and BX washes, but there is a significant difference in the response from FT and TR basins as well as between FT, TR and control soils (Appendix B, Figure 3.7).
3.2.b Large Event

Figure 3.8 Details the average cumulative CO₂ efflux from each soil for each large event measured, grouped into the respective category. The lower image further categorizes the large event fluxes.

The mean cumulative CO₂ efflux over the duration of the large event applications was 7.67 mg C g⁻¹ soil with an upper bound of 35.84 mg C g⁻¹ soil and a minimum of 0.955 mg C g⁻¹ soil. Similarly to the small event application, there was no statistical significance between BX and HS basins, but there was between both FT and TR basins and FT, TR, and the control soils. It is interesting to note that the means for each type of basin, the mean of the large event is greater than 4 times the mean of the small event, meaning that the increase in efflux may be nonlinear and that change in SWC is likely a controlling factor in cumulative CO₂ efflux.
3.2.c GI and Control

Figure 3.9 Compares the average cumulative CO\textsubscript{2} efflux for GI and control basins for both large and small events.

Comparing large and small events, it is shown that all of the sample populations are significantly different with the exception of the small event applied to GI and the large event applied to control soils. The mean of the large events is seen to be greater than that of the small events for both GI and control soils. Furthermore the variability of large events also tended to be higher.

3.2.d Respiration over Time

Comparing the cumulative CO\textsubscript{2} respiration rates over the duration of the 12-week experiment was not analyzed statistically, but from the least square regression line for each basin type, the majority of the basins display a decrease in respiration over time, for both small and large events. Furthermore it is shown that the basins that had higher rates of CO\textsubscript{2} respiration during the beginning weeks of the experiment tended to have a steeper least square line.
Meaning that they tended to decrease the cumulative respiration efflux faster than soils that started with lower cumulative respiration rates. The gap in data from small event application experiments reduces the confidence in this finding, but the same trend appears in the large event application as well. Graphical results from this analysis can be found in Appendix C.

The rate of CO₂ production by the soils after rewetting was also consistent with previous studies. Results showed that CO₂ respiration rates for both small and large event application peaked in the first time step after rewetting then decreased in each subsequent time step. This pattern is consistent with results from multiple studies (Miller et al. 2005; Sun et al. 2015; W Borken et al. 2006; Rey et al. 2005; Jarvis et al. 2007; Sponseller 2007) (Appendix C).

3.3 Relationships Between Soil Physiochemical Properties and CO₂ Respiration

The presence of a linear relationship between soil physiochemical properties and cumulative CO₂ efflux were analyzed using the fit linear model feature in MATLAB, which returns RMSE, R² and p–values (Table 4.2).

3.3.a Soil Texture

![Figure 3.0 MATLAB results from the linear regression between soil CO₂ efflux (small on top, large on bottom) and the soil texture categories; sand, silt, and clay, from left to right.](image)
Examining the linear relationship between the % sand, silt, and clay and small and large cumulative CO$_2$ efflux showed that variations in soil composition didn’t tend to have strong linear relationships with CO$_2$ efflux. For both large and small events, % clay was the only relationship which showed a negative linear relationship with statistical significance, with $p = 0.0233$ for small and $p = 0.0326$ for large, and $R^2$ of 0.128 for small and 0.115 for large. Other linear relationships were non-significant.

**3.3.b Bulk Density and Water Holding Capacity**

![Graph A](image1.png)  
**Bulk Density and Cumulative CO$_2$ Efflux for Large and Small Events**

![Graph B](image2.png)  
**Comparison of CO$_2$ Efflux and Water Holding Capacity**

Figure 3.11 Plot A linear relationship between bulk density and cumulative CO$_2$ efflux for large and small precipitation events. Plot B linear relationship between water holding capacity and cumulative CO$_2$ efflux for large and small precipitation events.

The linear relationship between bulk density and CO$_2$ efflux turned out to be significant with $R^2 = 0.465(p < 0.001)$ and $0.539 (p < 0.001)$, for small and large, respectively. The linear trend for this relationship is also negative, meaning that soils with higher bulk densities tended to have lower cumulative CO$_2$ efflux rates. Water Holding Capacity also showed a positive linear relationship with cumulative CO$_2$ efflux, for both large and small events. The $R^2$ values for this relationship were $0.474 (p < 0.001)$ for small, and $0.438 (p < 0.001)$ for large events. Again the $R^2$ value was slightly better for small events compared to large events due to more outliers in the large events.
3.3.c SOM and pH

Figure 3.2 Plot A linear relationship between soil organic matter and cumulative CO₂ efflux for large and small precipitation events. Plot B linear relationship pH and cumulative CO₂ efflux for large and small precipitation events.

Soil organic matter showed a positive linear relationship with cumulative CO₂ efflux for both large and small events. The R² value for small and large events was 0.492 (p < 0.001) and 0.408 (p < 0.001), respectively. The outliers in this relationship tended to appear in the large event analysis. This likely contributed to the improved R² value in small events compared to large. The linear relationship between pH and cumulative CO₂ efflux for large and small events is statistically significant to have an impact on cumulative CO₂ but was not as strong as the majority of the other chemical variables. The relationship is also slightly negative, with decreasing CO₂ efflux with increasing pH. The R² values for small and large events were 0.195 (p = 0.0043) and 0.151 (p = 0.0131), respectively.
### 3.3.d Total Carbon, Total Nitrogen, and Total Carbon to Total Nitrogen Ratio

A

**Comparison of CO2 Efflux and Total Carbon for Small and Large Event**

B

**Comparison of CO2 Efflux and Total Nitrogen for Small and Large Event**

C

**Comparison of CO2 Efflux and Total Carbon to Total Nitrogen Ratio for Small Events**

**Comparison of CO2 Efflux and Total Carbon to Total Nitrogen Ratio for Large Events**

![Data fitted curve](image)

**Figure 3.13** Plot A linear relationship between total carbon, Plot B total nitrogen and cumulative CO₂ efflux for large and small precipitation events. Plot C linear relationship TC:TN and cumulative CO₂ efflux for large and small precipitation events.

Analysis determined a significant positive linear relationship between total carbon and cumulative CO₂ efflux for both large and small event application. The R² values for these relationships were 0.559 (p < 0.001) for small events and 0.603 (p < 0.001) for large events. This case being the exception to the trend of better R² values for the small event respiration rates. It is important to note that there is a clump of low total carbon and low respiration points that
represent control soils, which could impact the $R^2$ values, because the distribution of data points is not normal.

There also exists a positive linear relationship between total nitrogen and cumulative CO$_2$ efflux for both large and small events, with $R^2 = 0.483$ ($p < 0.001$) for small events and $R^2 = 0.434$ ($p < 0.001$) for large events. In this case the $R^2$ value for small events was better than for large events, which is similar to the majority of parameters. This parameter also exhibits the clumping of control soil data points that was found in total carbon as well.

The linear relationship between the total carbon and total nitrogen ratio to the cumulative CO$_2$ efflux was insignificant, so a polynomial fit was analyzed with MATLAB curve fitting application. The optimal relationship was a second-degree polynomial with $R^2 = 0.1533$ for small event cumulative CO$_2$ and $R^2 = 0.1261$ for large event cumulative CO$_2$. These relationships also did not have a normal distribution, but showed a similar clumping of values towards the low end of C:N.

**Chapter 4 : DISCUSSION**

**4.1 Soil Physical and Chemical Properties**

Grouping soil samples into the type and location of GI that they were collected in allowed for improved statistical power as well as an analysis of the variability created by or inherent within GI types and locations. Overall, soils from GI features showed higher values of SOM, WHC, TC, and TN and a lower value for bulk density as compared to control soils. No significant differences were found in soil texture, pH, and % fines. This result is similar, but showed more variation than in some previous studies (Pouyat et al. 2007).
Table 4.1 Soil Physical and Chemical properties separated by basin and location. Each is averaged from the 5 soil samples taken to represent each category. Numbers in parenthesis indicate the standard deviation.

<table>
<thead>
<tr>
<th>Basin</th>
<th>Soil Organic Matter</th>
<th>%</th>
<th>Total Carbon</th>
<th>mg C g⁻¹ soil</th>
<th>Total Nitrogen</th>
<th>mg N g⁻¹ soil</th>
<th>Soil pH</th>
<th>C:N Ratio</th>
<th>Bulk Density</th>
<th>Fraction of fine earth</th>
<th>Maximum Water Holding Capacity</th>
<th>Sand</th>
<th>Clay</th>
<th>Silt</th>
</tr>
</thead>
<tbody>
<tr>
<td>BXFT</td>
<td>4.949 (±3.21)</td>
<td></td>
<td>9.726 (±0.05)</td>
<td>0.441 (±0.31)</td>
<td>8.478 (±0.50)</td>
<td>26.851 (±10.29)</td>
<td>0.873 (±0.15)</td>
<td>60.449 (±11.63)</td>
<td>54.300 (±13.68)</td>
<td>61.358 (±8.65)</td>
<td>18.424 (±1.91)</td>
<td>20.216</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BXTR</td>
<td>6.538 (±2.99)</td>
<td></td>
<td>14.568 (±3.83)</td>
<td>0.580 (±0.24)</td>
<td>8.500 (±0.15)</td>
<td>26.710 (±5.88)</td>
<td>0.697 (±0.15)</td>
<td>56.668 (±16.73)</td>
<td>68.153 (±7.64)</td>
<td>12.453 (±2.26)</td>
<td>19.392 (±6.01)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSFT</td>
<td>8.657 (±4.76)</td>
<td></td>
<td>12.518 (±6.82)</td>
<td>0.846 (±0.37)</td>
<td>14.937 (±1.88)</td>
<td>0.792 (±0.80)</td>
<td>67.663 (±12.69)</td>
<td>59.565 (±7.46)</td>
<td>17.689 (±3.72)</td>
<td>22.745 (±12.59)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSTR</td>
<td>10.276 (±3.41)</td>
<td></td>
<td>15.313 (±3.07)</td>
<td>0.838 (±0.15)</td>
<td>3.610 (±0.16)</td>
<td>18.294 (±1.88)</td>
<td>0.802 (±0.24)</td>
<td>64.936 (±17.95)</td>
<td>63.341 (±4.51)</td>
<td>14.047 (±2.13)</td>
<td>22.610 (±3.40)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BXFT Ctrl</td>
<td>1.624 (±0.54)</td>
<td></td>
<td>3.657 (±0.15)</td>
<td>0.175 (±0.04)</td>
<td>8.516 (±0.12)</td>
<td>21.513 (±7.29)</td>
<td>1.228 (±0.02)</td>
<td>61.358 (±25.78)</td>
<td>71.134 (±17.95)</td>
<td>13.988 (±4.51)</td>
<td>14.877 (±4.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BXTR Ctrl</td>
<td>1.526 (±0.14)</td>
<td></td>
<td>3.016 (±0.10)</td>
<td>0.070 (±0.02)</td>
<td>8.656 (±0.30)</td>
<td>44.251 (±14.54)</td>
<td>1.916 (±0.11)</td>
<td>53.265 (±5.45)</td>
<td>68.008 (±3.34)</td>
<td>17.773 (±1.03)</td>
<td>21.832 (±6.65)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSFT Ctrl</td>
<td>2.389 (±0.17)</td>
<td></td>
<td>3.798 (±0.06)</td>
<td>0.229 (±0.06)</td>
<td>8.612 (±0.18)</td>
<td>17.085 (±4.83)</td>
<td>1.146 (±0.10)</td>
<td>63.03 (±4.97)</td>
<td>62.026 (±6.33)</td>
<td>16.141 (±1.71)</td>
<td>21.832 (±6.65)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSTR Ctrl</td>
<td>1.800 (±0.28)</td>
<td></td>
<td>3.190 (±0.54)</td>
<td>0.126 (±0.06)</td>
<td>8.858 (±0.15)</td>
<td>32.268 (±18.53)</td>
<td>1.218 (±0.22)</td>
<td>61.863 (±12.09)</td>
<td>64.818 (±9.77)</td>
<td>16.786 (±2.79)</td>
<td>18.394 (±7.86)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bulk density of soil particles can reflect the relative proportions of organic or mineral matter in a soil (Curtin and Cambell 2006). The reduction in the bulk density of GI soils is most likely due to the increased organic matter through mulch and leaf litter, because the bulk density of leaf litter and organic matter is lower than that of soil (USDA, 1998). But also could have been impacted by the typically higher clay proportions in GI basins, since the bulk density of clay is typically lower than that of sand (USDA, 1998).

Alterations in the pH of soils were not statistically significant with the exception of TR basins and the control soil surrounding TR basins, the small range of value likely plays a role in this. Nevertheless, it can be seen that the pH of HS GI basins have decreased from the control soil more so than in BX, where the decrease is negligible. This could be due to the age of the soils, or time since disturbance, or the physical/chemical processes that occur in GI.

The WHC and SOM in soils showed very similar trends, having statistically higher values in GI basins as opposed to control soils. Some degree of this similarity is likely due to the codependence of SOM and WHC (Bot and Benites, 2005), by which SOM creates porosity and voids in which water can occupy. In both cases there was no statistical distinction between BX
and HS locations or between FT and TR basins. The variability in the SOM content in each soil could be due to heterogeneity within the GI basins, or the type/amount of vegetation present in each basin. Water holding capacity could also be impacted by inter-basin variability, but could also be impacted by vegetation creating macropores, bioturbation, or directly from creating SOM and therefore increasing WHC (Garcia, Roldan, and Hernandez 2005).

The total carbon analysis results also followed the same trend as the SOM and WHC results, with statistically lower values in control soils, higher values for GI basins of each type. It is known that soil organic carbon and soil organic matter are highly correlated (Hoogsteen et al. 2015; X. Wang, Wang, and Zhang 2012). However it has also been shown that semi arid and arid soils tend to be high in inorganic carbon (Gile, Peterson, and Grossman 1966)), which was not differentiated in this study, though would be important for future work. This is because total organic carbon is a parameter that is consistently associated with CO$_2$ respiration (Sun et al. 2015; Harms and Grimm 2008; Miller et al. 2005; Gallo et al. 2014; Song et al. 2003; Borken and Matzner 2009). But since total carbon could not be analyzed for this study SOM and TC must be used as proxies. The carbon present in the GI and control soils could have different sources, and are likely composed of different portions of organic and inorganic. The decomposing organic material in GI basins likely contributes more organic carbon, whereas inorganic carbon likely originates from biogenic secondary carbonates (Lal 2008) in control areas. All soils from both control and GI basins are known to have inorganic carbon as a result of the Fizz test.

The analysis of the total nitrogen did not follow the same trend as SOM, TOC, and WHC exactly. Though the TR soils showed statistically higher TN concentrations over control soils, the FT soils did not. Furthermore BX soils were statistically lower in TN concentration when compared with HS. The source of this total nitrogen could be from increased biological N fixation (Curtin and Cambell 2006), but this does not explain the difference between BX and HS
concentrations, since the locations are spatially very close. It could also be due to increased mineralization of N from SOM (Curtin and Campbell 2006), but this would not explain the difference in one type of GI basin over the other, because both are experiencing higher rates of mineralization over control soils. The third option is that there is different N loading occurring in each basin from stormwater runoff, which could explain the difference between HS and BX but not between TR and FT. Therefore it could potentially be a combination of possible explanations. Increased loading in the HS basin causes higher TN concentrations in control soils and in GI basins, and this provides more mineralizable N, which TR basins are able to use more effectively than FT basins.

The carbon to nitrogen ratio in the soils follows a similar trend as TN (Figure 3.5). The optimal range for microbial activity typically occurs when C:N ratios are near 24:1 (NRCS 2011) the soils in this study do fall around this range, but most of the soils fall above to 24:1 line, with the exception of HS soils, which also happen to have the highest concentrations of TN. Furthermore this relatively high ratio of C:N could be the result of woody branches or desert shrubs, which have C:N ratios of 70:1 and 100:1 respectively, where as roots range from 30:1 (Austin et al. 2004). Therefore woody matter is artificially raising the C:N of the soil, reflecting the C:N of the composite.

The change in soil water content was monitored throughout the study in order to determine if small differences in soil weight in each jar were contributing to the CO₂ respiration pulse. Many studies have shown the relationship between increased wetting and increase in CO₂ respiration (Lebron et al. 2007; Rey et al. 2005; Sponseller 2007; Harms and Grimm 2008; McIntyre et al. 2009) due to the increased connectivity of substrate, lysing of cells, or displacement of soil gasses. Therefore it was necessary to exclude any variations in the change in SWC caused by variations in the mass of soil in each jar. However, the results from the SWC
analysis showed no statistically significant difference in the populations response to the same size wetting event, therefore suggesting that CO₂ respiration variation was not significantly altered by soil mass variations (Figure 3.6).

The soil physiochemical properties analyzed in this study are known to have an impact on the magnitude of the Birch Effect C and N mineralization response. The differences in composition between GI and control soils are hypothesized to impact the CO₂ respiration experiment in this study.

4.2 Birch Effect Response

The Birch Effect response measured in this study (efflux of CO₂) was shown to be significantly higher in soils originating from GI features, when the large wetting event as applied, and in terminal basins (compared to flow-through basins). The CO₂ pulse associated with the addition of water to dry soils experienced in this experiment acted similarly to some previous studies (Gallo et al. 2013; Lado-Monserrat et al. 2014; Jarvis et al. 2007; Gómez-Gener et al. 2016; Sponseller 2007; Song et al. 2003; McIntyre et al. 2009). After the water was added there was an immediate (or as short as sampling interval allowed) increase in the CO₂ production, then the pulse of CO₂ quickly reached peak production rate, and then tapered off to near background CO₂ concentrations. The Birch Effect response also was higher in soils which received more water, in all cases except for when the small event in GI was compared to the large event control soils (Figure 3.9), which is consistent with previous findings (Lado-Monserrat et al. 2014).

One of the primary parameters found to increase the Birch Effect is also the time between wetting events, which is theorized to allow for the accumulation of lysed microbial cells, utilizable substrate, or deposition of inorganic N (Song et al. 2003; Austin et al. 2004). In this study it was not possible to show whether the increase in CO₂ pulse from large events was caused by the increased time between wetting events, or by the increased amount of water added.
However other studies have pointed out that the amount of water added is a controlling parameter on the soil response, whereas the results regarding the time in between events are less conclusive (Fierer and Schimel 2002; L. Wang et al. 2015). Further supporting the input of water as the main driver is the lack of environmental inputs into the system, because the soils were not exposed to nutrient deposition, with the exception of atmospheric. Although it is not possible to parse out in this study, it is well known that both size of wetting event and time between wetting play a role in CO₂ respiration pulse size (Borken and Matzner 2009).

Another primary factor in the response of the Birch Effect is that the amplitude of the pulse tends to decrease over the duration of the wetting experiment or wet season. (Lado-Monserrat et al. 2014; Jarvis et al. 2007; Borken and Matzner 2009; Miller et al. 2005). This is typically posited to the utilization of available nutrients either from SOM or from osmolytes released by microorganism cell lysis. This phenomenon was observed in this experiment for the majority of the soils. Though this is difficult to prove statistically because of the gap in the respiration data, most soils tend to decrease in CO₂ efflux over the duration of the experiment. This is likely due to the lack of input of nutrients; therefore microorganisms are utilizing the available substrate, decreasing the available nutrients pool or the next wetting event.

The CO₂ efflux rate of soils following the application of water tends to decrease exponentially over time until it reaches a background rate, which typically occurs less than 48 hours after rewetting (Sponseller 2007; Gallo et al. 2014). For most weeks in the small rewetting events the peak respiration is at one hour after rewetting, however in some weeks the third hour after rewetting is the peak respiration rate, which could be due to osmotic shock or a time lag to allow for infiltration. Furthermore for some weeks there is a secondary peak at six hours post rewetting, which is not observed in other experiments. This phenomenon can most readily be observed in week 5 for small events and week 4 in large events. This could be a mathematical
error, in that the rates are averages over the previous time period. An issue in the methodology could also possibly explain this, in that the time between measurements is smaller immediately post rewetting than at the end of the experiment. It could be that there was not enough time to accumulate CO$_2$ in between uncapping the jars.

When comparing the average cumulative CO$_2$ efflux between groups of soils there are statistically significant differences in the responses of GI soils compared to control soils, terminal basins compared to flow-through basins for both large and small events (Figure 3.9). However there was not a statistically significant difference in control or GI soils in the HS or BX washes (Figure 3.7 and 3.8). This means that the different locations did not have a significant impact on the Birch Effect response, but basin design and basin vs. control soils. This is likely due to the different soil physical and chemical compositions in GI soils compared with control soils. Most of the differences in soil composition are also typically associated with increased amplitude of Birch Effect response, such as higher SOM, WHC, TC, TN, and lower bulk density, this relationship will be further investigated in the next section. However the CO$_2$ efflux results indicate that some process or characteristic of terminal GI basins provide a soil composition that tends to increase the amplitude of the Birch Effect biogeochemical cycling than either control soils or flow-through basins, but either GI type is more effective than control soils.

4.3 Relationship Between Birch Effect and Soil Physiochemical Properties

Analyzing the linear relationship between cumulative CO$_2$ respiration and soil physiochemical properties yielded positive relationships with SOM, TC, TN, and WHC and negative relationships with pH, %Clay, and bulk density. Results were inconclusive when comparing % sand, and % clay. In previous studies SOM, WHC, TC, TN, TOC, TIC, and TIN have been associated with higher amplitude of Birch Effect (Gallo et al. 2014; Lado-Monserrat et al. 2014; Jarvis et al. 2007; Miller et al. 2005; Unger et al. 2012). Other soil characteristics have
been shown as inversely associated with Birch Effect response, such as bulk density, % clay, TON, and C:N (Gallo et al. 2014; Lado-Monserrat et al. 2014; Unger et al. 2012). These properties tend to have a high degree of interdependence as well, such as the relationship between SOM and WHC (Bot and Benites 2005). However for this study only the individual parameters are analyzed for their relationship with cumulative CO$_2$ efflux, which serves as a proxy for the amplitude of the Birch Effect response. Furthermore each soil characteristic was compared to both the cumulative CO$_2$ efflux from both the average of the large and the average of the small event application. But there appeared to be no deviation in the behavior between large and small, so they will generally be grouped together in this section.

There are two general classes of relationships between the physiochemical properties and the cumulative CO$_2$ flux; negative or positive. The parameters that show significant positive linear correlation with cumulative CO$_2$ efflux are; SOM, WHC, TC, and TN. The parameters that show significant negative linear relationships with cumulative CO$_2$ efflux are % Clay and bulk density. The % Silt, % Sand, C:N, and ΔSWC did not show significant relationships with CO$_2$ efflux, and pH showed a weak, but still significant positive relationship (Table 4.2).

Table 4.2 Details the linear relationships found between soil physiochemical parameters and the small and large event cumulative CO$_2$ respiration during the 48-hour period. $R^2$, p-value, and equation of the linear trend line included.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Small Event</th>
<th>Small Event</th>
<th>Small Event</th>
<th>Large Event</th>
<th>Large Event</th>
<th>Large Event</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>p - value</td>
<td>Equation</td>
<td>$R^2$</td>
<td>p - value</td>
<td>Equation</td>
</tr>
<tr>
<td>% Sand</td>
<td>0.00707</td>
<td>0.606</td>
<td>$y = -0.0124x + 2.5624$</td>
<td>1.55e-07</td>
<td>0.998</td>
<td>$y = -0.00035x + 7.702$</td>
</tr>
<tr>
<td>% Silt</td>
<td>0.0615</td>
<td>0.123</td>
<td>$y = 0.03925x + 1.001$</td>
<td>0.0224</td>
<td>0.357</td>
<td>$y = 0.1429x + 4.9234$</td>
</tr>
<tr>
<td>% Clay</td>
<td>0.128</td>
<td>0.0233</td>
<td>$y = -0.1286x + 3.805$</td>
<td>0.115</td>
<td>0.0326</td>
<td>$y = -0.7335x + 19.351$</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>0.465</td>
<td>&lt;0.001</td>
<td>$y = -3.1086x + 4.850$</td>
<td>0.539</td>
<td>&lt;0.001</td>
<td>$y = -20.182x + 27.753$</td>
</tr>
<tr>
<td>ΔSWC</td>
<td>0.0258</td>
<td>&lt;0.001</td>
<td>$y = 0.2095x + 0.511$</td>
<td>0.013</td>
<td>0.489</td>
<td>$y = -0.2849x + 14.556$</td>
</tr>
<tr>
<td>SOM</td>
<td>0.492</td>
<td>&lt;0.001</td>
<td>$y = 0.2043x + 0.792$</td>
<td>0.408</td>
<td>&lt;0.001</td>
<td>$y = 1.1231x + 2.3776$</td>
</tr>
<tr>
<td>WHC</td>
<td>0.474</td>
<td>&lt;0.001</td>
<td>$y = -0.0416x - 0.1937$</td>
<td>0.438</td>
<td>&lt;0.001</td>
<td>$y = 0.24109x - 3.628$</td>
</tr>
<tr>
<td>pH</td>
<td>0.195</td>
<td>0.0043</td>
<td>$y = 1.7356x + 16.54$</td>
<td>0.151</td>
<td>0.0131</td>
<td>$y = 9.2107x - 86.11$</td>
</tr>
<tr>
<td>TC</td>
<td>0.559</td>
<td>&lt;0.001</td>
<td>$y = 0.146x + 0.5596$</td>
<td>0.603</td>
<td>&lt;0.001</td>
<td>$y = 0.9127x + 0.1735$</td>
</tr>
<tr>
<td>TN</td>
<td>0.483</td>
<td>&lt;0.001</td>
<td>$y = 2.345x + 0.7781$</td>
<td>0.434</td>
<td>&lt;0.001</td>
<td>$y = 13.415x + 2.131$</td>
</tr>
</tbody>
</table>

Early studies of the Birch Effect noted the association of increased mineralization with SOM, which was posited to an increase in microbial populations in the soil organic matter layers,
combined with structural alterations upon rewetting (Griffiths and Birch 1961). The new microbial community is then able to utilize labile carbon and nitrogen pools in soil organic matter layer (Austin et al. 2004). The structural reorganization and creation and destruction of soil aggregates during rewetting were realized in this study in the large wetting events, but not as much in the small events. However more recent studies have indicated that microbial populations accumulate solutes rich in carbon and nitrogen during drought times to resist desiccation, then upon rewetting, release these solutes. After a new water potential equilibrium is reached, then microorganisms are able to utilize the released solutes which produce the notable releases in CO$_2$, NO, N$_2$O, and CH$_4$ (Lado-Monserrat et al. 2014; Fierer and Schimel 2002). The results from this study suggest that SOM has the highest degree of linear correlation with cumulative CO$_2$ efflux; SOM also shows a 0.863 $R^2$ value with TC and 0.919 $R^2$ with TN. This high correlation suggests that the source of C and N originates from the organic matter, as opposed to the release of solutes from microorganisms, because C and N analysis was done before the wetting experiment, when soils were dry. It is possible that microorganisms tend to release more labile C and N, which causes the pulse in mineralization. However the relatively strong correlation with soil C and N concentrations before wetting to the respiration pulse suggest that the C and N found in the initial composition play a role in the Birch Effect.

The correlation with WHC and Birch Effect response is likely interdependent with other attributes, but also appears to play its own role. It is know that WHC is typically a function of SOM and soil texture (Viji and Rajesh 2012), however in this study no significant relationships were found between any soil class and the WHC. Conversely there was a very strong relationship between SOM and WHC ($R^2 = 0.902$). This shows that the WHC of the soil is conveying the pores created by SOM, which could help microorganisms utilize the SOM that was unavailable
under dry conditions. WHC may also alter the infiltration through the creation of soil aggregates, which has been hypothesized to impact biogeochemical cycling (Unger et al. 2012).

Both bulk density and the % clay were shown to have negative correlations with the average cumulative CO$_2$ efflux from the wetting of the dry soils. These two properties were not significantly interrelated, meaning that their impact is likely interdependent. It has been shown that sand soils typically produce less CO$_2$ than loam soils (Gallo et al. 2014), therefore the when % clay decreases and % sand decreases then possibly more loamy soils are created, which could increase microbial response. Some of the impact of bulk density is likely derived from the negative correlation with SOM ($R^2 = 0.654$). But it is also likely that the degree of compaction of the soil or the cumulative indication of soil texture could also impact the microbial response.

Typically high C:N results in the immobilization of N as opposed to mineralization, however it has been shown that microbial cytoplasm has a low C:N ratio, which is one of the possible substrates of the Birch Effect response (Austin et al. 2004). This could explain the decrease in associated CO$_2$ respiration at the higher end of C:N. Furthermore this points to the theory that the C:N of the utilized substrate is more critical to the Birch Effect than that of the soil matrix. Another implication of this finding is that bacteria are usually associate with lower C:N than fungi, and fungi are typically more drought tolerant than bacteria, which could point to a fungi-dominated microbiome in these basins (Austin et al. 2004).

The high degree of interdependence of the analyzed parameters suggests that certain types of soils, which share comparative values, are associated with increased microbial or physical response due to the rewetting of dry soils through the release of CO$_2$. It was also shown that these particular soils also tended to occur in GI basins of either type. Since these soils have the signature characteristics of the Birch Effect, for the reasons typically cited, it can be theorized that GI soils also experience the nitrogen mineralization also associated with the Birch
Effect, however this still needs to be proved, but is likely based on the nitrogen mineralization found in ephemeral waterways in Southern Arizona (Gallo et al. 2014).

In conclusion the soil physiochemical properties SOM, WHC, TC, TN, bulk density, and % Clay were statistically different GI soils than in control soils. The soil samples from both types of GI features exhibited higher CO₂ respiration rate than in control soils upon rewetting. Additionally terminal basins tended have higher cumulative CO₂ efflux than flow through basins. The large size of the precipitation pulse in this study created a CO₂ efflux of equal to the magnitude of the cumulative impact of soil physiochemical properties in the small GI event. The soil physiochemical properties SOM, WHC, TN, TC, and bulk density showed strong linear relationships with soil CO₂ efflux, where as the relationship was weak with pH, % clay and TC:TN.

Before application to real world systems it is necessary to examine some inherent differences between this study and GI in the real world. First implementing a precipitation regime was designed for the small event to mimic a direct rainfall event, where little to no runoff is generated. The large event is designed to represent a runoff event, where the GI basin is inundated. The stochastic nature of the natural precipitation regime was not intended to be replicated. Secondly the lab soils used for the respiration experiments were cut off from natural inputs and outputs, that is interaction with atmosphere, inputs from runoff events, and interactions with vegetation. This limits the influx of new nutrients and substrate that could potentially be utilized. Furthermore maintaining the soil samples in a lab setting limits the temperature fluctuation that is observed in a natural setting, which could alter the magnitude of the Birch Effect. Finally it is known that severe drought conditions can cause microbial death (especially with below water potential of -15 MPa) (Manzoni and Katul 2014), these levels were
not reached in this study, whereas this water potential is feasible in the Southwestern US, thus altering the microbial biomass and microbial response to wetting.

The results from this paper are significant in that they provide evidence that the soil property differences that are created by the implementation of GI increase the function of the microbial community. The increased cycling of nutrients supplements plant growth, providing temperature mitigation and ecohydrological benefits. The creation of a hot spot of high microbial activity also may provide the backdrop for microbial mediation of urban stormwater runoff, of nitrogen or other contaminants (Jiang, Yuan, and Piza 2015). Potentially mitigating the effects of rapid urbanization currently happening in the southwestern US. Green infrastructure could play a unique role in urban stormwater management in the future, in that it provides a multitude of benefits, from runoff mitigation, pollution reduction, shade and habitat creation, and reconnection to the ecology of the surrounding ecosystem (Walsh et al. 2016). Improving microbial habitat and production through soil physiochemical properties is crucial to capitalizing on the potential benefits of urban stormwater green infrastructure.
References


