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The Seasonality of Oxygen and Hydrogen Isotopes of Rain, Stream and Groundwater in Fredericksburg, VA

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Recommended Citation

Elliott, Kathleen C.; Grothe, Pamela R.; and Konecky, Bronwen, "The Seasonality of Oxygen and Hydrogen Isotopes of Rain, Stream and Groundwater in Fredericksburg, VA" (2019). *Student Research Submissions*. 273.
https://scholar.umw.edu/student_research/273

The Seasonality of Oxygen and Hydrogen Isotopes of Rain, Stream and Groundwater in Fredericksburg, VA

By
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Thesis submitted to the faculty of the University of Mary Washington in partial fulfillment of the requirements for graduation with Honors in Earth and Environmental Science
2019

ABSTRACT

Stable isotopes of oxygen and hydrogen, $\delta^{18}O$ and δD, are tracers of climatic changes within the hydrologic cycle, and thus are a potential link in the relationship between climate-influenced changes to the hydrologic cycle and modern and paleoenvironments. The Chesapeake Bay region, located on the boundary between subtropical and subpolar precipitation, is projected to see increased precipitation rates specifically during winter and spring under enhanced levels of greenhouse gases (Najjar et al., 2010). Additionally, paleoclimate archives from the Bay, which are sensitive to freshwater input from rivers, provide a baseline of past natural climate variability, recorded through changes in their $\delta^{18}O$ composition that reflects the $\delta^{18}O$ of the water from which it precipitated (e.g. LeGrande and Schmidt, 2009). Studies have shown that the isotopic content of surface water and groundwater parallel meteoric water (e.g. Dutton et al., 2005); however, there is no previous work connecting $\delta^{18}O$ and δD isotopes from meteoric water with nearby river and groundwater in the vicinity of the Fredericksburg, Virginia, region.

In this study, the $\delta^{18}O$ and δD content of meteoric and surface water in the Fredericksburg region was analyzed over the course of a year to understand the seasonality of the $\delta^{18}O$ and δD of precipitation, and its relationship between the isotopic values of river water and groundwater. Surface water samples were collected from the Rappahannock River and Hazel Run tributary in Fredericksburg, VA, and precipitation and groundwater samples were collected on the University of Mary Washington campus. We have found precipitation in winter months to be more depleted in heavy isotopes than in warmer months. There is a muted correlation between the $\delta^{18}O$ and δD values of precipitation and stream water; however, periods of prolonged dryness resulted in deviations of this trend due to high rates of evaporation and the inflow groundwater into the stream. This work will provide the foundation of using $\delta^{18}O$ and δD of meteoric water to study changing precipitation patterns as climate changes in the local Fredericksburg, VA, region, as well as understanding the controls of the $\delta^{18}O$ and δD of surface water for more robust interpretations from proxy records in regional paleoclimate studies.

ACKNOWLEDGEMENTS

To begin, I would like to thank the University of Mary Washington, the College of Arts and Sciences Undergraduate Research Fund, as well as Dr. Charles Whipkey and Dr. Melanie Szulczewski for the continued support during this research. I would also like to thank Dr. Bronwen Konecky and Dr. Jack Hutchings of Washington University in St. Louis for the analysis of our water isotope content and other contributions to this project. Finally, I would like to thank Dr. Pamela Grothe for her guidance and support in all things throughout the duration of this project.

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CHAPTER 1 - INTRODUCTION

Overview

The hydrologic cycle is an earth process that is susceptible to changes in climate. As climate continues to warm, forecasts predict an intensification of the global hydrologic cycle, most specifically related to extreme weather events (Huntington, 2005). However, the resulting effects are latitudinally dependent, where an increased frequency of stronger rainfall events is expected in tropical regions, and decreased rainfall is expected in the mid-latitudes, thus driving the mid-latitudes to become drier on a global scale (Sherwood and Fu, 2014). On average, annual precipitation across the United States has increased 4% between the years 1901 to 2015 and precipitation events have become more intense and frequent (USGCRP, 2017). Annual increases in precipitation are observed throughout most of the United States, however, seasonal increases in rainfall are significantly greater in the autumn in the Southeast and Midwest as opposed to the other three seasons, where increase rates of drying are prevalent (Figure 1.1) (Hoffman et al., 2019).

Virginia is located on the boundary between subtropical and subpolar precipitation and is expected to see an increase in average annual precipitation as projected by climate models with enhanced levels of greenhouse gases (Najjar et al., 2010). Notably, increased precipitation rates will occur specifically during winter and spring as seasonal air temperatures are expected to warm (Najjar et al., 2010). An increase in autumnal precipitation has already been observed in Virginia over the past three decades (Figure 1.2), which is not consistent with model projections of rainfall with enhanced levels of greenhouse gases. Air surface temperatures in Virginia have also increased over the past three decades (Figure 1.3), alongside changes in seasonal precipitation, with greater warming rates occurring in the winter season (Hoffman et al., 2019).

The combination of changes in precipitation patterns and increasing temperature poses a significant issue because this apparent intensification the hydrologic cycle will result in changes to regional water balances. Periods of dryness from increasing surface air temperatures and a lack of precipitation will result in more frequent droughts and associated issues such as wildfires and a decline in available water resources due to increased background dryness of the environment. In between those periods of dryness, more intense rainfall events are expected, which may result in significant flooding and higher runoff rates (Sherwood and Fu, 2014). Understanding how changes to the hydrologic system affect regional watersheds is significant for many reasons, including better managing water resources, mitigating for floods, and planning for crop resiliency, just to name a few. It is imperative that we understand the controls and influences over the hydrologic cycle that will drive it to change as the climate continues to warm (e.g. IPCC, 2014), to better prepare for those changes in regional water balances and the future at large.

To study these changes in climate and precipitation, we can use stable oxygen and hydrogen isotopes of water as they are tracers of water origin and movement throughout the hydrologic cycle (e.g. Gat, 2010). The isotopic composition of water is controlled by a series of climatic processes (e.g. Faure and Mensing, 2005), which results in each body of water having a unique isotopic “fingerprint,” (Liu, Bowen and Welker, 2010). By measuring this fingerprint and changes of the fingerprint, we can determine environmental conditions such as temperature, precipitation patterns as well as any associated changes to hydrologic cycle. Global maps of both oxygen and hydrogen have been developed (Figure 1.4), however, the resolution of these maps is coarse (Bowen and Wilkinson, 2002). Regional and local studies are necessary in order to develop higher-resolution datasets, especially in the Virginia and Chesapeake Bay region, in order to more closely observe changes in the hydrologic cycle through isotope values.

Beyond solely studying the changing patterns of modern waters, we also have the ability to measure the isotopic composition of paleoclimate natural archives, which serves as proxies to paleoclimatic conditions. Proxies are natural materials whose geochemistry is an imprint of past climate due to their isotopic composition being governed by environmental conditions (Grothe, pers. comm.). Paleoclimate studies help us understand the past by putting modern and future climate change into perspective of natural climate variability. Many natural archives record climate variability through changes in their $\delta^{18}O$ composition (e.g. LeGrande and Schmidt, 2009). The $\delta^{18}O$ values recorded by natural archives reflect both the temperature and the $\delta^{18}O$ of the water from which it precipitated (e.g. Cronin et al., 2005; Sanford et al., 2013). Studies have identified a link between the $\delta^{18}O$ isotopic value of both river water and groundwater with meteoric water (e.g. Dutton et al., 2005; Pape et al., 2010). Specifically, in the Chesapeake Bay region, the $\delta^{18}O$ of the water is heavily dependent on freshwater input from the major tributaries (Palmo and Grothe, 2018). Climate proxies such as oyster shells and foraminifera, found in the Chesapeake Bay, record climate conditions through the isotope values of their calcium carbonate shells which are derived from the water in which they formed. As they reflect not only temperature but also the oxygen isotope of the water (Grothe, pers. comm.), developing an understanding of the controls over the isotopic values of modern waters is important when interpreting paleoclimate records.

Objectives and Approach

Through this study, we analyzed the stable isotopic content of meteoric and surface water in the Fredericksburg, Virginia, region (Figure 1.5). The first objective of this research was to record the seasonal variability in $\delta^{18}O$ and δD of precipitation in Fredericksburg, VA, over the course of one year (May 2018- May 2019). This was done by analyzing the $\delta^{18}O$ and δD content of meteoric water, or water derived from precipitation, collected from a rain gauge in front of the Jepson Science Center on the campus of the University of Mary Washington (Figure 1.5). By recording the isotopic values of precipitation over four seasons in Fredericksburg, we hoped to observe seasonal variability in $\delta^{18}O$ and δD, and how those values trace the seasonal changes associated with storm trajectories. The study will provide one year of baseline data that will ultimately be used in a long-term monitoring project to track future changes in extreme weather events in Virginia related to seasonal shifts in storm trajectories.

The second objective of this research is to understand how or if the $\delta^{18}O$ and δD values of meteoric water influence the isotopic composition of the local watershed, including nearby streams and groundwater. To date, there is no previous work connecting $\delta^{18}O$ and δD from meteoric water with nearby river and groundwater in the vicinity of the Fredericksburg region. To study this relationship, I collected river water from the Rappahannock River and the Hazel Run tributary, and groundwater samples from a groundwater monitoring well on the UMW campus (Figure 1.5). Through examining the relationship between the isotopic values of each local water reservoir with meteoric water, we hoped to improve our understanding of the controls that affect the $\delta^{18}O$ of the local watershed. This will ultimately aid in interpreting the geochemistry from regional paleoclimate archives as they record the $\delta^{18}O$ of the water from which they precipitate (e.g. LeGrande and Schmidt, 2009). This research will be particularly important in ongoing research in Dr. Grothe's lab interpreting δ^{18}O in oyster shells from the Rappahannock River to infer paleoclimate variability in this region of Virginia.

Research Significance

The overarching goal of this study is to further our understanding of the physical processes that control isotopic content of meteoric water and how they are translated into bodies of surface water and groundwater in the Fredericksburg region. By developing a better understanding on the controls that affect the δ^{18}O of the water from which natural archives (e.g. calcite of foraminifera, ostracods, bivalves, coral skeletons, and cave deposits) precipitate, we will be able to more to accurately interpret the climate signal recorded in these natural archives (e.g. Tibert et al., 2012) from the region. Current global distribution patterns of δ^{18}O and δD in meteoric waters show that there is a relationship between weather events and the isotopic composition of precipitation (Rozanski, Araguás-Araguás and Gonfiantini, 1993). This distribution is inferred from isotope resolution maps and models, which report high-resolution global records of δ^{18}O values. These records are useful when comparing paleo precipitation and temperature across the globe; however, they cannot be used for regional comparisons due to limited spatial and temporal coverage (Bowen and Wilkinson, 2002). This study will work towards developing an understanding of the regional controls on the isotopic values within the hydrologic cycle that cannot be inferred from global records. Results from this study will be archived at the WaterIsotope database, located at the University of Utah. Additionally, this data has broad application for use in isotope-enabled climate models to further our understanding of how climate change is affecting the hydrologic cycle.

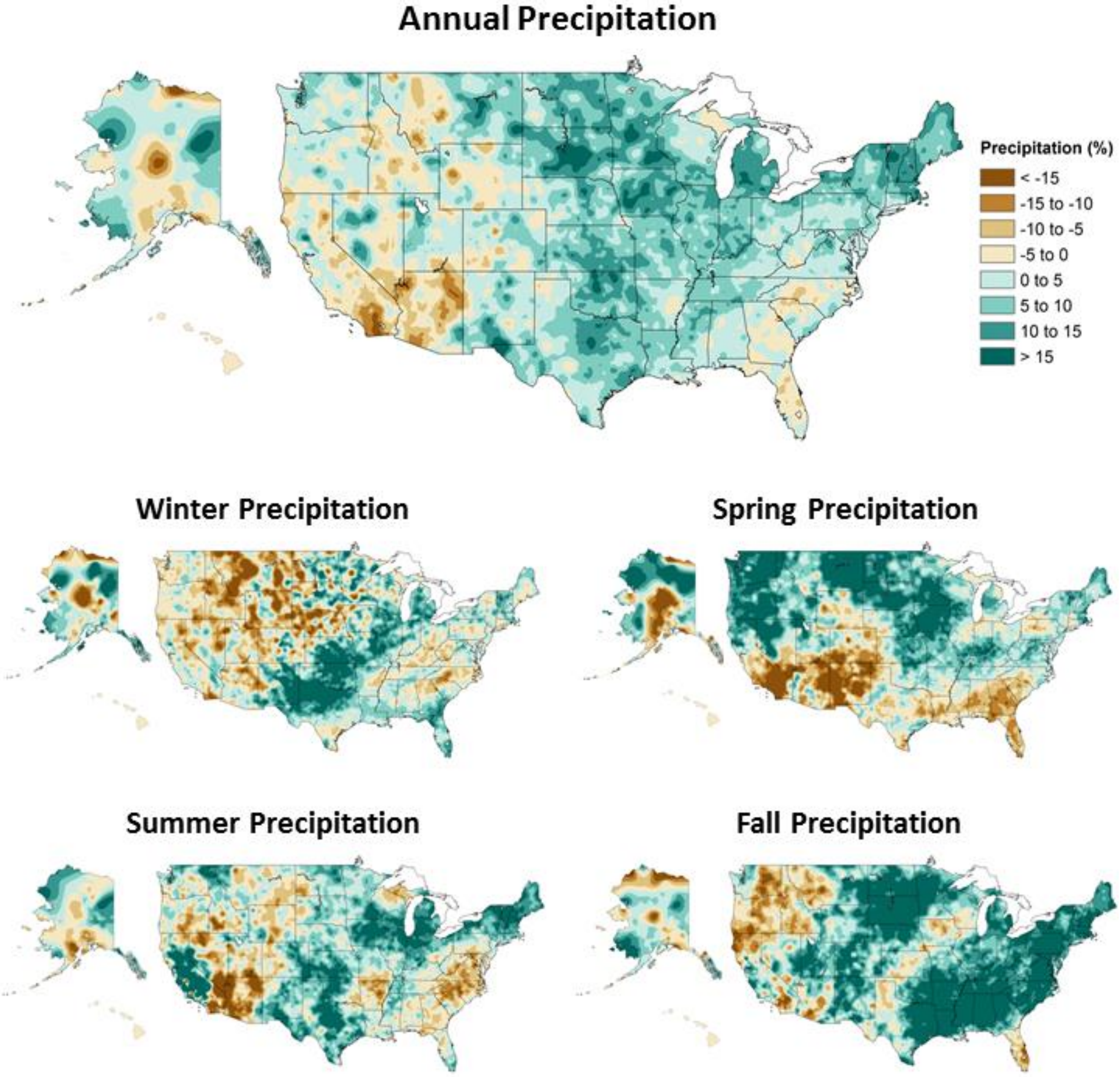
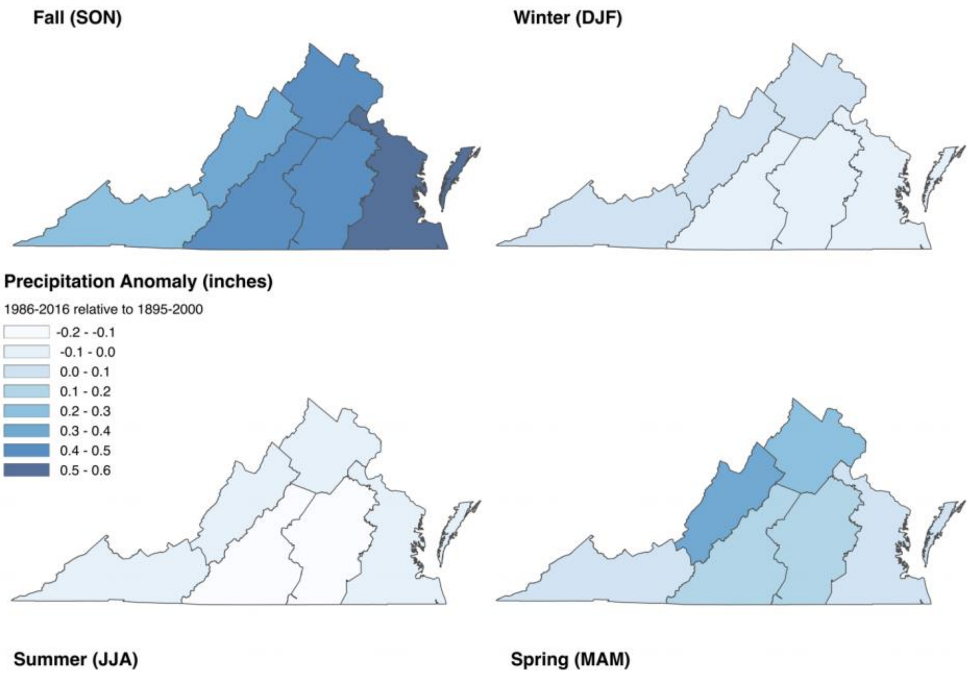


Figure 1.1. Annual and seasonal changes in precipitation across the conterminous United States in the years between 1986-2015, relative to the first half of the century (1901-1960) (USGCRP, 2017).



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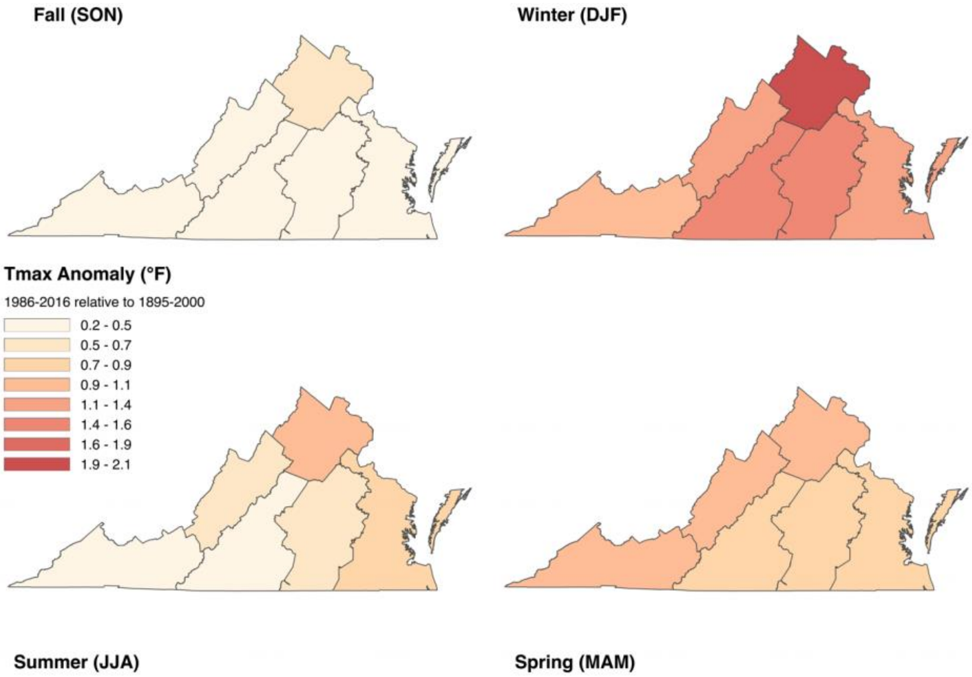

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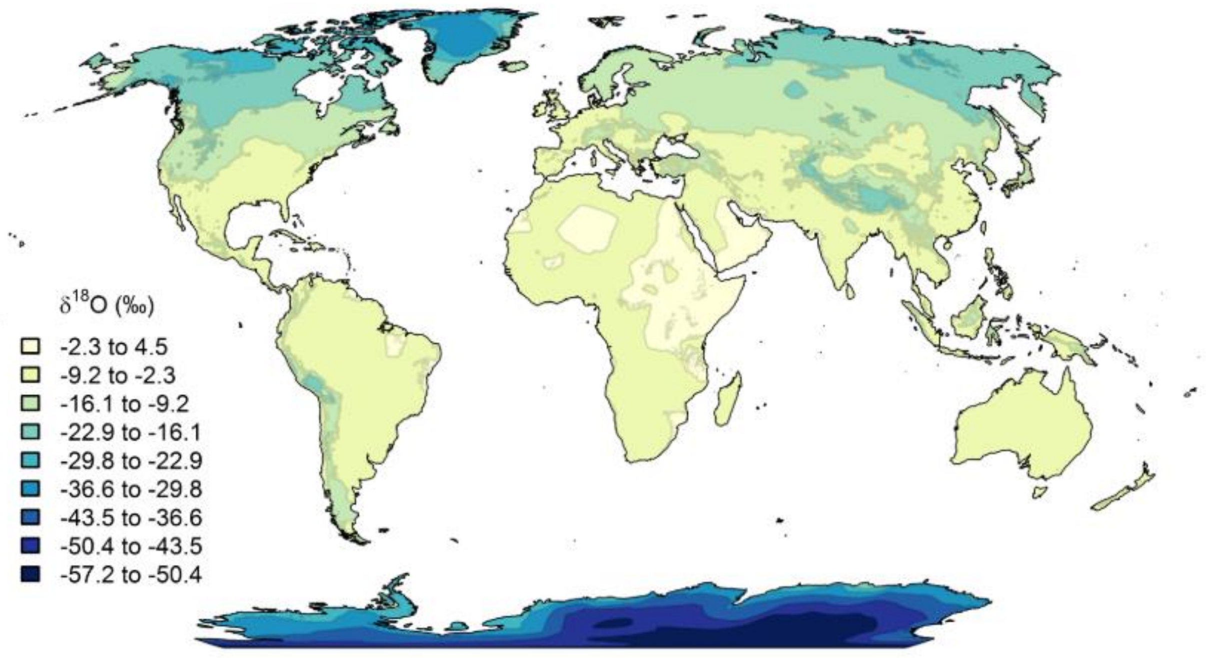

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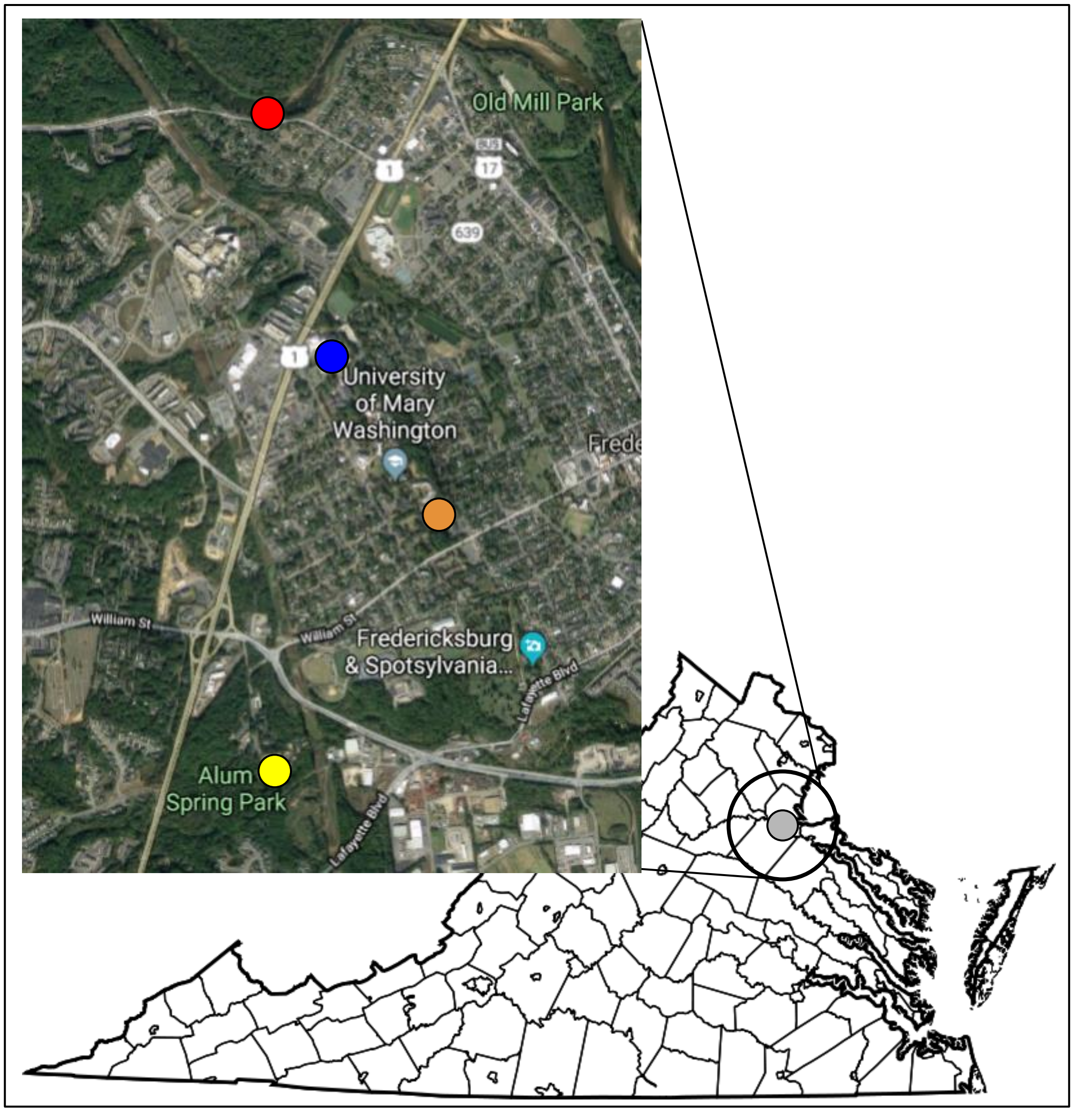

Figure 1.5. Location map of Fredericksburg, VA, and sample collection sites. The red marker indicates the collection site of the Rappahannock River sample and the yellow marker is the Hazel Run sample location. The blue marker indicates the location of the rain gauge and the orange marker the location of groundwater sampling, both of which are on the University of Mary Washington campus.

CHAPTER 2 - BACKGROUND

Stable Oxygen and Hydrogen Isotopes

Stable isotopes are atoms of an element that have the same number of protons in the nucleus as the standard atom, but have a different number of neutrons, with stable denoting that these isotopes do not decay (West *et. al,* 2010). There may be multiple isotopes for elements that each have a unique number of neutrons. Of the two elements analyzed in this study, there are two stable isotopes of hydrogen (^{1}H and ^{2}H) and three stable isotopes of oxygen (^{16}O,^{17}O, and ^{18}O). These isotopes are naturally occurring in nature, in bodies of water and geologic material. Not all isotopes are abundant and measurable, but of the isotopes of hydrogen and oxygen, ^{1}H, ^{2}H, ^{16}O, and ^{18}O exist in abundant amounts and can be measured through mass spectrometry (e.g. West *et. al,* 2010 and Gibson, Fekete and Bowen, 2010). Each isotope has a different mass due to their different number of neutrons; this difference in mass is a significant factor when it comes to which isotopes are present in a material due to fractionation (Gat, 2010). Fractionation, or the separation of isotopes of different masses, occurs when molecules undergo a phase change between liquid, solid, and vapor, with heavier isotopes favoring the liquid and solid phase, and lighter isotopes favoring the vapor phase (Ichiyanagi, 2007). Isotopic values of water molecules vary between the different precipitatory and evaporative phases of the hydrologic cycle and their ratios of heavy to light isotopes are representative of those phases.

Each isotope of oxygen and hydrogen exist in nature in different abundances. ^{18}O, the heaviest of the oxygen isotopes, has a natural abundance of 0.200% in the hydrologic cycle whereas the most abundant isotope of oxygen is ^{16}O and has a natural abundance of 99.762% (Gat, 2010). The hydrogen isotopes, Deuterium (denoted as D or ^{2}H), is considered a heavy isotope because it has two neutrons, rather than one. It has a natural abundance of 0.015% in the hydrologic cycle whereas the major hydrogen isotope, ^{1}H, exists in hydrologic cycle in abundance of 99.985% (Gat, 2010).

The abundance of an isotope is expressed as the ratio of the abundance of heavy isotopes to that of the light isotopes. This ratio value of isotopes, denoted by *R*, represents the number of atoms of the isotopes rather than their masses. The ratios of oxygen and hydrogen isotopes are measured using mass spectrometry, and are expressed in terms of the heaviest isotope, $\delta^{18}O$ and δD, respectively. Rather than using the *R* value to represent the isotope abundance, the value is reported as the deviation (δ) from a common standard isotope reference value (Gourcy, Groening and Aggarwal, 2005). $\delta^{18}O$ is defined by the relationship

$$\delta^{18}O = \frac{(R_{spl} - R_{std})}{R_{std}} \times 10^3 ‰$$

where $R_{spl} = {}^{18}O/{}^{16}O$ is the ratio of the sample and $R_{std} = {}^{18}O/{}^{16}O$ is the ratio of the standard abundances; δD is defined by

$$\delta D = \frac{(R_{spl} - R_{std})}{R_{std}} \times 10^3 ‰$$

The values of $\delta^{18}O$ and δD can be positive, negative or zero, where a positive value indicates a larger abundance of the heavy isotope, or a higher ratio of ^{18}O to ^{16}O, and a negative value indicates a lower abundance of the heavy isotope (Faure and Mensing, 2005).

The ratios of the abundance of stable isotope within water are compared to a "standard mean ocean water" (SMOW) ratio, which is a standard value originally determined relative to the NBS—1 standard, which was an arbitrarily chosen water sample from Potomac River, by Craig in 1961 (Gat, 2010). The SMOW values were determined from the equations

$$R(^{18}O/^{16}O)_{SMOW} = 1.008.R(^{18}O/^{16}O)_{NBS\text{-}1};$$

$$R(^{18}O/^{16}O)_{SMOW} = 1.050.R(^{18}O/^{16}O)_{NBS\text{-}1}$$

where R is the ratio value and NBS-1 is the sample collected from the Potomac River (Craig, 1961). Today, these ratio values are compiled in a database of the International Atomic Energy Agency (IAEA) in Vienna, Austria, and are classified at VSMOW reference standards (Gat, 2010).

Controls over Isotopic Values of Meteoric Water

Phase Changes

As water undergoes phase changes between solid, liquid, and gas, the isotopic content of the water molecules changes. This is due to the process of fractionation where the molecules are separated based on mass. As water undergoes evaporation, the molecules with the lighter isotopes change from a solid or liquid to a gas before the heavier isotopes (e.g. Gat, 2010 and Faure and Mensing, 2005). Likewise, water molecules with heavier isotopes condense into liquid before molecules with lighter isotopes (e.g. Gat, 2010 and Faure and Mensing, 2005). This relationship between isotopic values and phase changes has an effect on the overall water isotope content within an air mass, which is reflected in the isotopic values of precipitation (Gedzelman and Lawrence, 1990).

Temperature Effect

The isotopic process of fractionation is dependent on a number of climate factors, including temperature. Surface air temperatures during rainfall events play a role in the fractionation process and the determining of isotopic values (e.g. Tappa et al., 2016). Figure 2.1

illustrates the correlation between average $\delta^{18}O$ and the local surface air temperature of precipitation collection from 325 stations within the global network of isotopes in precipitation (GNIP) (Gourcy, Groening and Aggarwal, 2005). The figure compares the correlation between surface air temperature and $\delta^{18}O$ of precipitation between the latitudes of 60S and 60N and precipitation that falls outside of those latitudes. Within both ranges of latitudes, as surface air temperatures increase, the abundance of ^{18}O does as well. The relationship between surface air temperature and average $\delta^{18}O$ values of meteoric water is represented by the equation:

$$\delta^{18}O_a = 0.698T_a - 13.6$$

where $\delta^{18}O_a$ = the annual mean of meteoric water $\delta^{18}O$ values and T_a = the average annual surface air temperature, measured in ^{o}C (Dansgaard, 1964). Studies have found that the isotopic composition of precipitation in regions where mean annual surface air temperature is greater than $18^{o}C$ shows little dependence on the temperature effect due to the influence of more dominant effects, such as the location where the precipitation falls (Gourcy, Groening and Aggarwal, 2005).

Seasonal variations in temperature are a source of isotope variability within meteoric water. Measures of monthly minimum and maximum isotope values have indicated that winter precipitation tends to be more depleted in heavy isotopes, ^{18}O and D, than summer precipitation (Gibson, Fekete and Bowen, 2010). The seasonality of the temperature effect on $\delta^{18}O$ within precipitation is shown in Figure 2.2, which compares the globally-averaged temperature effect on meteoric water to that of the Northern and Southern Hemispheres (Ichiyanagi, 2007).

Amount Effect

Studies of isotope composition of meteoric water collected throughout a rainfall event have found that precipitation becomes more depleted with time due to the heavy isotopes preferentially raining out before light isotopes (e.g. Gedzelman and Lawrence, 1990). As precipitation rains out of an air mass, the more depleted values correspond to the middle and end of the storm event (Gat, 2010). As air masses move and precipitation falls, water molecules enriched with the heaviest isotopes, ^{18}O and ^{2}H (or D), rain out at the front of the air mass, meaning the water that falls later in a storm event is depleted in those values (Liu, Bowen and Welker, 2010). This effect explains discrepancies in isotope composition in meteoric water over the period of a long storm events and for storm events that travel a large distance.

Physical Location

Another influence on the isotopic content of meteoric water is where it exists relative to altitude, latitude and distance inland from the ocean. These three factors have an effect on isotopic distribution within precipitation because as air masses and the water vapor they contain are transported away from the water vapor source, the precipitation goes through multiple cycles of condensing and evaporating, resulting in a depletion of heavy H and O isotopes (Gibson, Fekete and Bowen, 2010). This is the case for water that originates from oceans and is precipitated over continents. Precipitation at high latitudes is often so depleted in heavy isotopes that it resembles the VSMOW reference values of water close to the Equator, which generally has high ^{16}O values due to fractionation caused by evaporation (Gibson, Fekete and Bowen, 2010). The effect of distance from the equator in both the Northern and Southern Hemispheres at which water precipitates can be compounded with the temperature effect. The $\delta^{18}O$ and δD

values become more negative as distance from the water vapor source increases due to the combined effects of temperature and rainout on the isotope content of the water vapor in the air masses as they move (Faure and Mensing, 2005). The latitude effect is approximately $\Delta\delta(^{18}O) = -0.6‰$ per degree of latitude in North America (Gat, 2010).

The altitude at which water condenses within an air mass has an effect on the isotopic values of meteoric water as well. A higher abundance of lighter isotopes exists at higher altitudes within an air mass because the gaseous water molecules have undergone fractionation from the base to the top. As the water molecules fall through the air mass, the isotopes equilibrate with the heavy isotopes that exist at lower altitudes within the air mass due to the fact that the water at the base of the air mass has not undergone the same amount of fractionation (Gedzelman and Lawrence, 1990). Figure 2.3 (Gedzelman and Lawrence, 1990) is a schematic that represents the δD within convective and stratiform air masses that illustrates the combined effects of fractionation and altitude on isotopic values within water molecules. The lightest isotopes exist at the top of each of the two air masses, represented by a greater depletion of heavy isotopes within the water. As the water molecules precipitate and fall, the isotopic values become heavier, represented by a less negative value.

The Meteoric-Water Line

The combination of the oxygen and hydrogen isotopes within water molecules means that they both undergo the same hydrologic processes of evaporation and condensation, and as such, there is a linear correlation between the two values which is represented by a water line plot (Faure and Mensing, 2005). The Meteoric Water Line (MWL) is a water line plot of precipitation isotope values generated using a least squares regression equation that gives equal weight to all data points, regardless of the precipitation amount; however, a few studies have developed alternative equations that do take precipitation amount into account to correct potential biases caused by rainfall amount on water line plots (e.g. Hughes and Crawford, 2012). The Global Meteoric Water Line (GMWL) was first derived by Craig (1961) and expressed by the equation,

$$\delta H^2 = 8.13\ \delta^{18}O + 10.8$$

using $\delta^{18}O$ and $\delta^{2}H$ values from the International Atomic Energy Agency (IAEA) (Tappa et al. 2016). Figure 2.4 is plot of the GMWL published by Faure and Mensing (2005) and is based on data from Rozanski et al. (1993).

As $\delta^{18}O$ and δD values of meteoric water is dependent on factors that vary with increased distance from the equator, such as temperature and rainout, the values of the isotopes on the MWL plot reflect the latitude at which the water precipitated (Faure and Mensing, 2005). Deviations of isotope values from the MWL are attributed to variations in regional weather and precipitation events (Gourcy, Groening and Aggarwal, 2005) as well as the meteoric oceanic and terrestrial sources of the water (Tappa et al. 2016). For example, water vapor sourced from arid regions will result in a LMWL with a smaller slope than that of the GWML and a higher y-intercept, due to the effects of greater rates of evaporation on the water vapor (Figure 2.5) (e.g. Wang, Chen and Li, 2014 and Araguás-Araguás, Froehlich and Rozanski, 2000). Another factor involved is rainfall event size. Smaller precipitation events have heavier isotope values, whereas larger precipitation events generally become more depleted in heavy isotopes overtime (Hughes and Crawford, 2012). This difference between different sized rainfall events, which is determined by regional factors, can result in variations from the GMWL. Discrepancies from the GMWL can be explained through the development of local MWL. Global and local MWLs can be compared in order to infer systemic changes in isotope values as differences between the two types of MWLs may be indicative of large-scale climate changes.

Applications of Meteoric Water Stable Isotopes for Climate Studies

Due to the compounded effects of temperature, rainfall amount and physical characteristic of rainwater, the isotopic composition of precipitation is an indicator of water vapor origins and other aspects of the hydrologic cycle, including storm events, moisture levels in the atmosphere, and rates of evaporation within a region (Kendall and McDonnell, 1998). Isotopes can be used to trace precipitation of different origins, as air masses that originate from different regions have specific isotopic "fingerprints" in their moisture content (Liu, Bowen and Welker, 2010). Cole et al. (1999), found that shifts among water vapor sources have an effect on isotopic variability observed in precipitation records. For example, a study by Scholl and Murphy (2014) established isotopic signatures from major weather patterns in Puerto Rico in an effort to monitor changing atmospheric dynamics as a result of climate change. Additionally, Ichiyanagi (2007) found that the isotopic content of monsoons in Southeast Asia was mostly controlled by moisture source and transport patterns. However, the significance of water vapor origins on isotopic content of precipitation may vary by region, as studies have found local climate, temperature and rainfall amount played more of a role in the Andes Mountains, for example, than water vapor origin (Ichiyanagi, 2007).

Stable Isotopes as Tracers of the Interaction of Water Within the Hydrologic Cycle

Water from different sources can affect the composition of water in another reservoir as it moves throughout the hydrologic cycle, such as atmospheric water affecting a surface water reservoir. Studies have been conducted on the influence of meteoric water on the isotopic values of surface water. Local and regional studies have found that the stable isotopic composition of rivers can be vastly different from the values of local precipitation (Dutton et al., 2005), a difference that has been attributed to environmental and climate factors such as snowmelt, especially in high elevations (Friedman et al., 1992). The difference between the isotopic values in rivers and precipitation has also been attributed to the origin of the river water itself. As river water is derived from precipitation upstream of where samples are collected, otherwise known as the 'catchment effect,' the primary isotopic values will reflect the upstream precipitation rather than the local precipitation (Dutton et al., 2005). This conclusion was derived from a study of the 48 conterminous United States, which implies that, on average, the isotopic values of river water reflect the climatic events and characteristics of meteoric water upstream of sampling locations.

To understand the isotopic characteristics and controls of groundwater and their relationship with precipitation, cave drip waters have been studied as well. A study in Austin, Texas found that, on average, the $\delta^{18}O$ values within cave drip water were lower than the weighted average of the values in precipitation, indicating that there may be a threshold precipitation amount needed to infiltrate into the groundwater system for precipitation to have an effect on groundwater stable isotopes (Pape et al., 2010). Drip waters from multiple caves within the Central Texas region did display a spatial gradient inland that suggests the isotopic values of groundwater are affected by a combination of continental (or location) and temperature effects, with deviations from the gradient brought about by changes in storm paths or moisture sources (Pape et al., 2010). A study conducted in China found that, when taking percolating rates of the water into consideration, the isotopic composition of cave drip water generally parallels the seasonality of precipitation, with higher $\delta^{18}O$ and δD values occurring April through June and in

January, and lower values occurring from September to December (Wu et al., 2014). The results of these studies suggest there is a correlation between the isotopic values of surface and groundwater and the climate-influence values of precipitation. Precipitation runs off as surface water or infiltrates into groundwater, which in turn flows into stream systems, thus linking the three water types and their isotope content together. When correlating the isotopic values of the three bodies of water, the movement of water within the hydrologic cycle must be taken into consideration when interpreting the trends between values.

The Values of Stable Isotopes Within Climate Proxies as Paleoenvironmental Indicators

Many natural archives (e.g. calcite of foraminifera, ostracods, bivalves, coral skeletons, and cave deposits) record climate variability through changes in their δ^{18}O composition, which reflects not only temperature, but also the δ^{18}O of the water from which their calcium carbonate shells are precipitated (e.g. LeGrande and Schmidt, 2009). The values of the stable isotopes within a body of water or ice, or within the shells of organisms, such as oysters, are representative of the fractionation process which is influenced by environmental factors such as temperature. It is for this reason that the ratio between light and heavy isotopes (^{18}O/^{16}O) is indicative of paleoenvironments (Robertson, 2017). Paleoclimate archives are important in understanding past natural variations in climate change which is useful for contextualizing our present and future climate change.

Local studies use foraminifera and oyster shells to infer how climate changes impact modern and paleo fluvial environments (e.g. Cronin et al., 2005 and Sanford et al., 2013). These studies used foraminifera from sediment cores in their analyses and found that river discharge had a significant effect on temperature and salinity within the Chesapeake Bay (Cronin et al., 2005). Precipitation and groundwater can also have an effect on the stable isotope composition of archives due to their influence on river water (e.g. Dutton et al., 2005 and Pape et al., 2010). Other studies of the Chesapeake Bay have used oyster shells to analyze the salinity and temperature of water, and to track the changes in these values as climate temperatures increase (Najjar et al. 2010). Others have attributed the decrease of salinity, as inferred from foraminifera, to the combined effects of climate trends and aggressive land use in the Chesapeake Bay watershed (Tibert et al., 2012) rather than from the influence of river or groundwater.

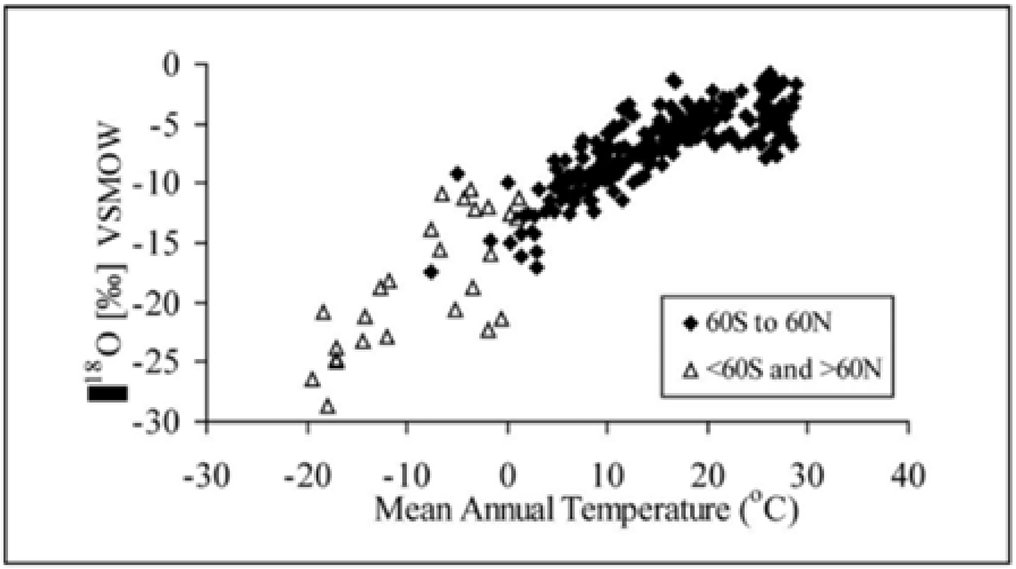

Figure 2.1. The correlation between average δ^{18}O and the local air temperature of precipitation collection from 325 stations within the global network of isotopes in precipitation (GNIP) (Gourcy, Groening and Aggarwal, 2005).

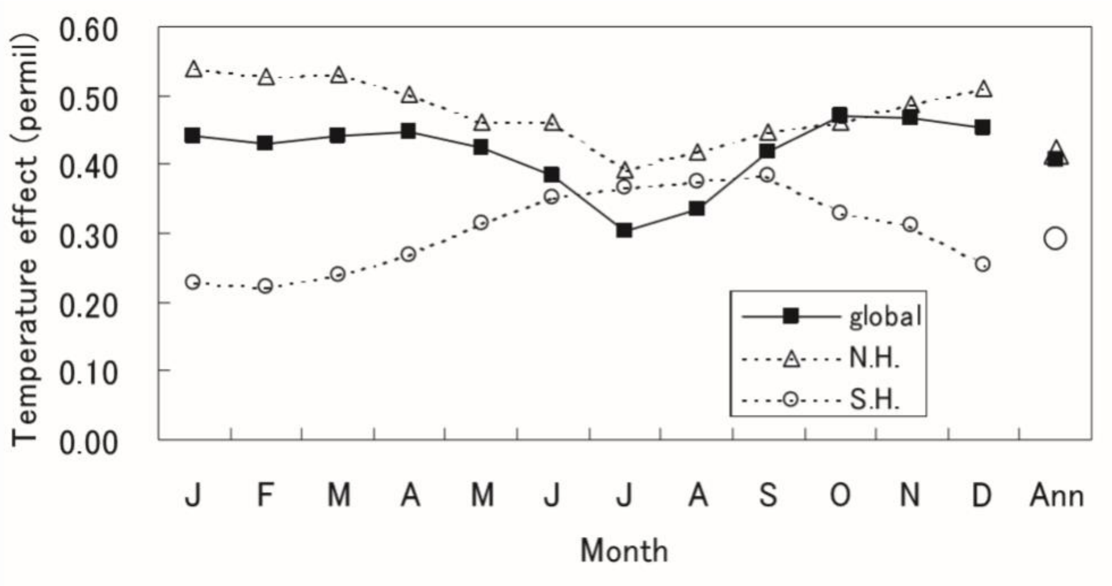

Figure 2.2. The seasonality of the influence of temperature effect on δ^{18}O in precipitation globally, and in the Northern and Southern Hemispheres (Ichiyanagi, 2007). Monthly averages are plotted and paired with annual averages.

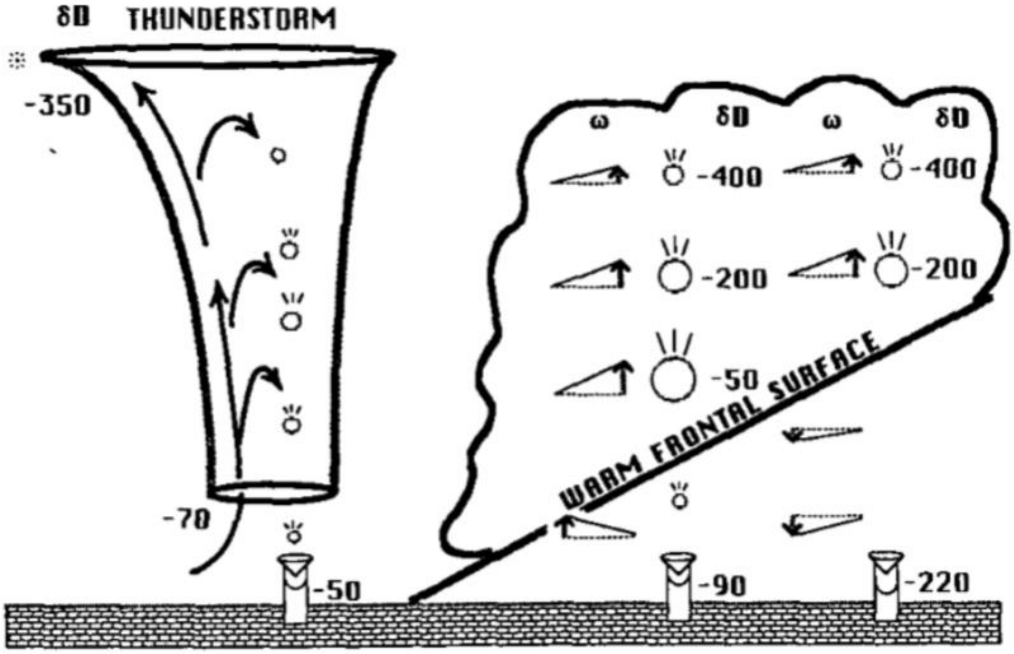

Figure 2.3. A schematic of δD values of water molecules within convective and stratiform air masses (Gedzelman and Lawrence, 1990). Divide the values by 8 to get $\delta^{18}O$ values.

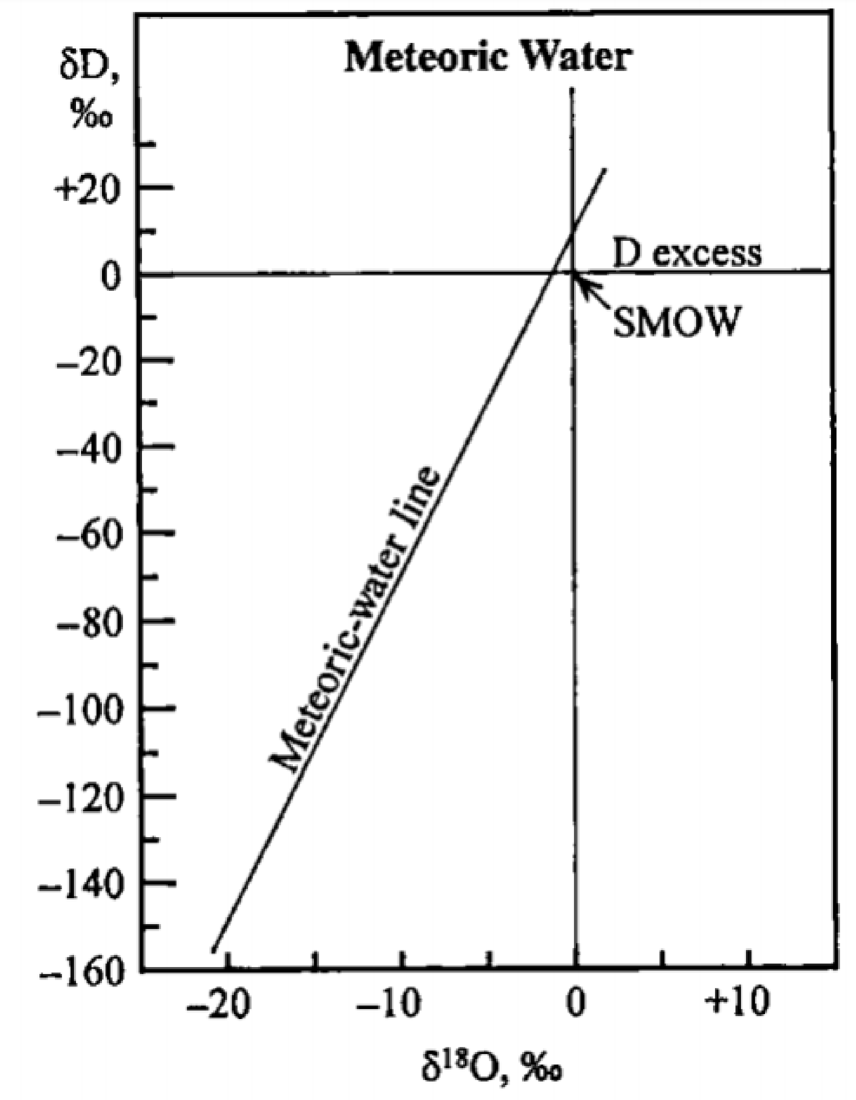

Figure 2.4. The meteoric-water line of $\delta^{18}O$ and δD values of precipitation based on monthly-average global data from the International Atomic Energy Agency (Faure and Mensing, 2005).

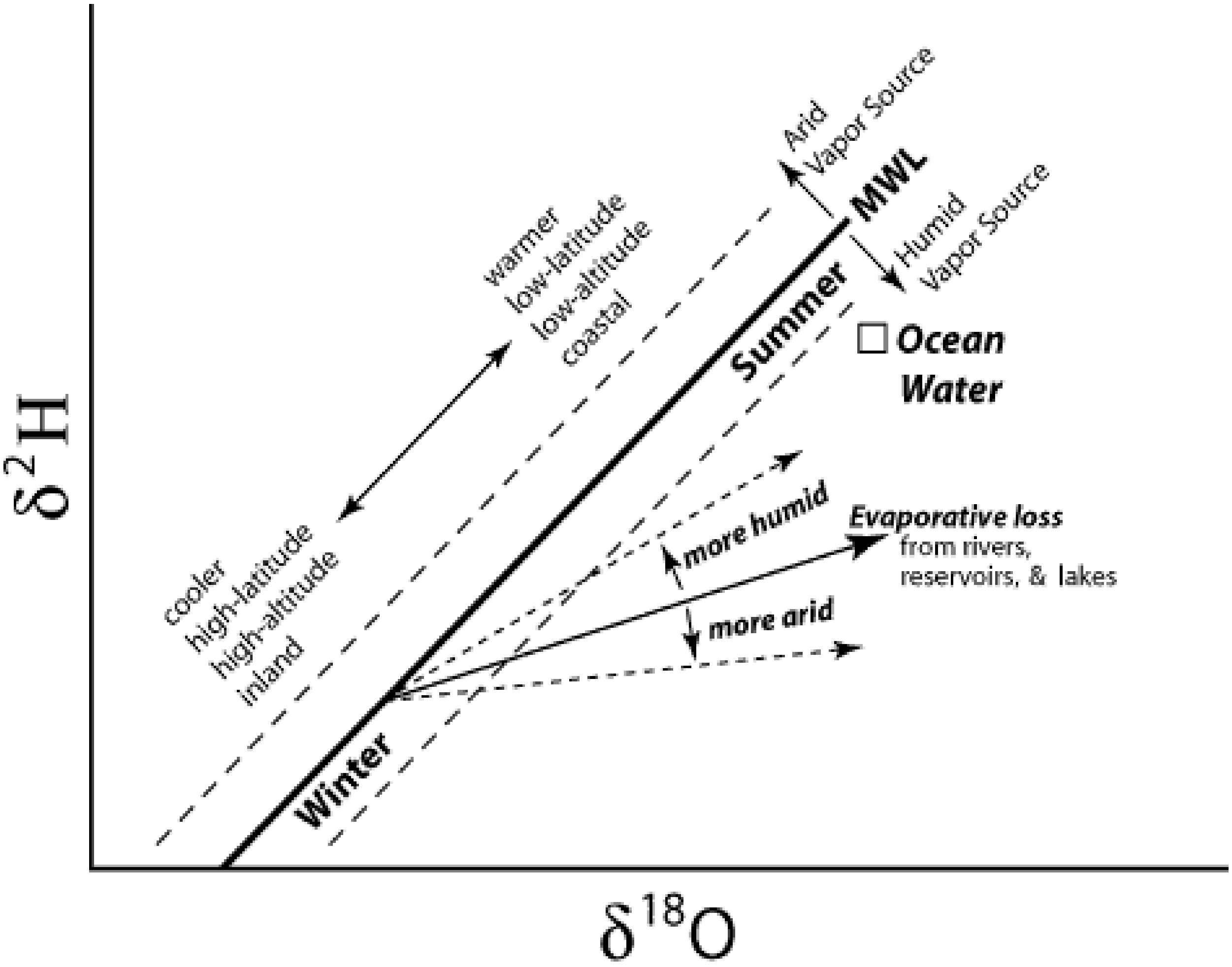

Figure 2.5. Schematic of the reasons behind deviations of a LMWL from the GMWL (web.sahra.arizona.edu).

CHAPTER 3 - METHODS

Sample Collection

Between May 28, 2018, and April 20, 2019, duplicate rainwater samples were collected on a per-event basis from a rain gauge located in front of the Jepson Science Center on the University of Mary Washington campus, Fredericksburg, VA (Figure 1.5). Rainwater samples were collected no more than three hours after the conclusion of each rainfall event to minimize the effect of evaporation on isotope composition. Samples were stored at ~4°C in 15 x 45 mm clear Borosilicate screw top glass vials with the tops wrapped in parafilm. Seven events where rainfall lasted over the course of at least one day were sampled two to three times throughout the duration of the event. When sampling these events, the rain water collector was emptied each time to prevent the influence of earlier water on the samples. The weather station, located directly next to the rain gauge, provided an independent measurement of rainfall amount, to compare with the recorded amount from the rain collector itself. Air temperature at the time of rainwater sample collection was another variable recorded and was supplemented by data from the Thunder Eagle Daily Weather Archive for Fredericksburg, VA, database.

Water samples were collected from the Rappahannock River and Hazel Run on a weekly basis between June 13, 2018, and April 24, 2019, for the Rappahannock River and September 28, 2018, and April 24, 2019, for Hazel Run (Figure 1.5). Although water samples from the main current would have been ideal, for safety reasons the samples were sourced from eddies along the river edge and stream bank. The locations of the sample sites were chosen based on ease of access as both sample collection locations are accessible by roads. At the time of each water sample collection, the water temperature was recorded using a YSI Data Logger. Discharge values of the Rappahannock River was recorded at the time of sample collection from a database maintained by the U.S. Geological Survey (https://waterdata.usgs.gov/nwis/uv?01668000).

Groundwater samples were collected from a 29.6-foot deep groundwater monitoring well on the southwest corner of the University of Mary Washington campus, where the water table elevation is approximately 68 feet (Whipkey, pers comm.), on a weekly basis between September 12, 2018, and April 24, 2019. Water sourced from this well, which has a well screen height of 10 feet, is from an unconfined aquifer, with water coming from below the water table (Whipekey, pers. comm.). To ensure the groundwater sample was free from surface drainage into the well, the well was emptied two times before collecting the sample using a groundwater bailer by removing approximately 6.4 gallons of water, a value determined from the depth and diameter (2 inches) of the well. To confirm that the well water was being replaced by flowing groundwater as the well emptied, the pH was recorded after approximately every two gallons were removed from the well.

Sample Analysis

In the lab, river and groundwater samples were filtered using a syringe and a 0.20 µm nylon filter in order to remove all sediment from the water before sample analysis. Filtered samples were transferred into Picarro vials and then were wrapped in parafilm and stored at ~4°C to reduce the effects of evaporation on the samples. Each water sample type was numbered in sequential order based on the order of sample collection and had a unique sample ID that indicated the type of water. Rainwater was labeled RW, Rappahannock River water was labeled VOC (after the sample collection site the Virginia Outdoor Center), HR stood for Hazel Run and groundwater was labeled GW. The rain, river and groundwater samples were analyzed in the lab of Dr. Bronwen Konecky of Washington University in St. Louis in a Picarro water isotope analyzer, which recorded the of $\delta^{18}O$ (‰), $\delta^{17}O$ (‰), and δD (‰) content of the water. The Picarro analyzer had yet to be calibrated for $\delta^{17}O$ (‰) at the time of analysis so the quality assurance nor control could be provided for the results, therefore the values are not included in this study. I sent water samples collected over the summer and during the Fall semester to Dr. Konecky in December 2018. In March 2019, I traveled to Washington University to learn the process of sample analysis and personally ran water samples collected through the first half of the Spring semester. I worked alongside Dr. Konecky's lab manager, Dr. Jack Hutchings, who taught me the analysis process.

The Picarro analyzer uses Cavity Ring-down Spectroscopy to determine the isotopic content of a water sample. A sample is injected into the instrument by a syringe and is then vaporized. The water vapor enters a cavity within the machine and a laser is reflected in a triangular fashion in the cavity by mirrors. Isotopes absorb photons of different wavelengths so isotopes are identified by absorbance of the laser. As the laser circulates around the cavity, some of the beam immediately exits the cavity; the remaining energy of the laser slowly is emitted as the beam is reflected. Absorbance of the laser is measured after some energy is emitted because the initial energy of the laser, before reflection, is too high for the instrument to analyze. Isotopic abundance is determined from the absorbance data and is then corrected for drift and machine memory, or the effect of residual vapor from the previous sample affect the sample being tested. The water samples were analyzed six times, with the final data value being the average of the last three values. Samples were analyzed in a series with control samples of USGS45 and water from Kona, Hawaii, and VSMOW (Vienna Standard Mean Ocean Water) standards to minimize machine drift and maintain calibration (Hutchings, pers. comm.). Data from the Picarro was analyzed and plotted using the statistical analysis function of Microsoft Excel.

CHAPTER 4 – RESULTS

Presented here are the results from the water samples collected from May 28, 2018, to February 28, 2019. Samples collected since March 1, 2019, will be analyzed at a future date. The isotopic data of the four water types were analyzed for seasonal trends. Seasonal divisions of the data were determined based on the winter and summer solstices, and the spring and autumnal equinoxes (Table 4.1). These results do not contain a years' worth of data as spring data has yet to be analyzed. It is important to note that reported winter seasonal averages do not include data from March 1 – March 20.

Seasonal Climate Conditions

Daily high temperature was recorded for each day a rainfall event occurred. During the summer, daily high temperatures ranged between 19.4 ^{o}C and 35 ^{o}C, with an average value of 26.26 ^{o}C. Daily high temperatures had a greater range in the fall with temperature ranging between 3.9 ^{o}C and 28.3 ^{o}C. The average daily high temperature for this season was less than that of the summer, with a value of 16.31 ^{o}C. The winter had the lowest daily high temperature average of the three seasons sampled. The average value was 11.92 ^{o}C for this season, but temperatures ranged between 3.8 ^{o}C and 17.2 ^{o}C.

Water temperatures of the Rappahannock River and Hazel Run fluctuated with less variability than daily high temperatures, however, both bodies of water followed a seasonal trend of becoming cooler over the course of the year. In the summer season, Rappahannock River water temperature ranged between 21.9 ^{o}C and 27.8 ^{o}C, and had an average water temperature of 23.8 ^{o}C. The average water temperature of the Rappahannock River dropped to 14.9 ^{o}C in the fall. During this season, water temperatures ranged between 6 ^{o}C and 21.3 ^{o}C. Hazel Run water temperatures ranged between 7.8 ^{o}C and 20.8 ^{o}C during the fall, and had an average temperature of 14.6 ^{o}C, similar to the Rappahannock River water temperatures during this season. Stream water temperatures were the coldest during the winter, compared to the two previous seasons, with the Rappahannock River temperature averaging 4.8 ^{o}C and Hazel Run averaging 6.6 ^{o}C. Rappahannock River water temperature ranged between 3 ^{o}C and 6.7 ^{o}C during this season, and Hazel Run water temperatures ranged between 5.2 ^{o}C and 8.6 ^{o}C. Hazel Run was not sampled during the summer of 2018. Likewise, groundwater temperature was not recorded.

Rainfall amounts were totaled based on the rainfall of sampled events. Rainfall in the summer seasons totaled an amount of 17.32 inches. Rainfall increased in the fall months, with a total amount of 29.51 inches of sampled rainfall. During the winter season, sampled rainfall was less than the two previous seasons, with a total of only 8.40 inches. Seasonal rainfall totals were not consistent with past trends as there is usually more rain in the summer seasons than in the fall season in Fredericksburg. Total rainfall in July through September averages approximately 11.5 inches, whereas rainfall total averages approximately 10.3 inches in the months October through December (U.S. Climate Data, 2019).

The discharge of the Rappahannock River was recorded at the time of sample collection from a database maintained by the USGS. Discharge in the summer months ranged from 841 ft^3/sec to 27,800 ft^3/sec, and averaged 7,798 ft^3/sec. During the fall, average discharge was 9,302 ft^3/sec, with discharge values falling in the range between 1,340 ft^3/sec and 24,200 ft^3/sec. Average river discharge was the lowest in the winter than the two previous seasons, with a value of 7,510 ft^3/sec. The range of river discharge during this season was 2,480 ft^3/sec to 15,200.

Precipitation

A total of 56 samples of rainwater were collected between May 28, 2018, and February 24, 2019 (Table 4.2). The $\delta^{18}O$ values ranged from -1.14 ‰ to -14.08 ‰, with the average value being -6.44 ‰, which is within an expected range of $\delta^{18}O$ values based on the latitude of Fredericksburg, VA (Figure 4.1a) (Bowen and Wilkinson, 2002). The maximum $\delta^{18}O$ value of -1.14 ‰ occurred on the warmest day of sampled rainfall events, recorded on July 16, 2018 at 35°C, which is expected as temperature has a strong influence on the $\delta^{18}O$ of the water. There is a general seasonal trend observed in the $\delta^{18}O$ values, where summer values average -5.01 ‰, fall values -7.81 ‰, and winter values -6.21 ‰. The standard deviations of these averages were 2.16, 2.79 and 2.26, respectively. Temperature is most likely the strongest control, especially on the more enriched summer values. However, other factors, such as rainfall amount and moisture source, which are also seasonal dependent, mostly likely affect the values, especially during the fall season which recorded 29.51 inches of rainfall, a factor of 1.7 times more than summer and 3.5 times more than winter. The δD values ranged from 3.24 ‰ and -92.96 ‰, and the average value was -36.25 ‰ (Figure 4.2a). The seasonal trends are similar as the $\delta^{18}O$ values, where the summer values are most enriched, averaging -26.04 ‰, with a standard deviation of 16.8, and the fall values are most depleted, averaging -45.48 ‰, with a standard deviation of 22.5, again most likely related to a combination changes in temperature and rainfall amount.

For rainfall events sampled throughout their duration, five out of seven events became more enriched in heavy isotopes over time (Table 4.6; Figure 4.3). This is inconsistent with the amount effect as heavier isotopes rain out of an air mass at the beginning of a rainfall event, leaving the remaining water to get progressively more depleted in heavy isotopes (e.g. Faure and Mensing, 2005 and Gedzelman and Lawrence, 1990). Event one, sampled midway through the storm, became more depleted in the hour between sample 1 and 2, but then proceeded to become more enriched between sample 2 and sample 3. Event three was the only event to become more depleted from midway through the storm until the end of the rainfall event (Tale 4.6). All other events became more enriched as the rainfall event progressed, with not obvious correlation between rainfall amount and isotope enrichment. For example, event 6, which became more enriched, only saw .06 inches of rainfall between sample collection, whereas event 1, which become more depleted between the first two samples collected, saw an increase of .30 inches of rainfall.

Surface Water

From June 13, 2018, to February 24, 2019, a total of 25 samples were collected from the Rappahannock River (Table 4.3). The Rappahannock River $\delta^{18}O$ values range between -8.91 ‰ and -5.89 ‰, and average -6.85 ‰ (Figure 4.1b). The δD values range between -54.58 ‰ and -32.31 ‰, and average -40.65 ‰ (Figure 4.2b). Like precipitation, the Rappahannock River surface water follows a seasonal trend with more depleted values in the cooler fall and winter months than summer months. During the warmer summer months, values for $\delta^{18}O$ and δD averaged -6.42 ‰ and -38.48 ‰, respectively, whereas the fall months averaged -7.05 ‰ and -42.03 ‰ and winter -7.29 ‰ and -42.13 ‰. The standard deviations of the $\delta^{18}O$ averages was 0.33 in the summer, 0.95 in the fall and 0.07 in the winter. The standard deviations of the δD values was 3.2, 7.09 and 0.48 for the summer, fall and winter. Colder temperatures are associated with more depleted values due to the lack of evaporation of ^{18}O (e.g. Faure and Mensing, 2005).

As expected, the isotopic values of Hazel Run followed trends similar to those of the Rappahannock River. A total of 15 water samples were collected from Hazel Run between September 28, 2018, and February 24, 2019 (Table 4.4). The minimum $\delta^{18}O$ value of the Hazel Run samples is -8.79 ‰, whereas the maximum is -5.54 ‰, with an average of -7.34 ‰ (Figure

4.1c). The minimum δD value is -55.34 ‰ compared to a maximum of -29.6 ‰; the average value is -44.07 ‰ (Figure 4.2c). The average δ^{18}O value of the water in the fall was -7.30 ‰, with a standard deviation of 1.09, and an average δD of -44.32 ‰, with a standard deviation of 8.14. The average abundance of δ^{18}O of the Hazel Run water was more depleted in the winter than in the fall with average value of -7.42 ‰, which had a standard deviation of 0.41. Conversely, the δD value of the water was more enriched in the winter than in the fall with an average of -43.57 ‰ and a standard deviation of 3.08.

Groundwater

Between the dates of September 12, 2018, to February 28, 2019, 15 groundwater samples were collected (Table 4.5). Of all types of water samples analyzed in this study, groundwater isotope values fluctuate the least, with the range of 0.33 ‰ for the δ^{18}O values and 1.44 ‰ for the δD values. The minimum δ^{18}O value is -7.19 ‰ and the maximum -6.86 ‰, and the average value is -7.06 ‰ (Figure 4.1d). The minimum δD value is -42.98 ‰ and the maximum is -41.54 ‰, and the average is -42.55 ‰ (Figure 4.2d). Groundwater values were slightly more enriched δ^{18}O values in the winter months (average of -7.04 ‰, standard deviation of 0.03) compared to the fall (average of -7.06 ‰, standard deviation is 0.11).

Table 4.1 Summary of seasonal climate and isotope data

	Summer 6/21/18 -- 9/21/18	**Fall 9/22/18 -- 12/21/18**	**Winter 12/22/18 -- 2/28/19**
Surface Air Temp (avg.)	26.26 °C	16.31 °C	11.92 °C
Rainfall Amount (total)	17.32 in	29.51 in	8.40 in
Rapp. Water Temp (avg.)	23.8 °C	14.9 °C	4.8 °C
HR Water Temp (avg.)	-----------	14.7 °C	6.6 °C
Precip. δ^{18}O (avg.)	-5.01 ‰	-7.81 ‰	-6.21 ‰
Std. Deviation	2.16	2.79	2.26
Precip. δD (avg.)	-26.04 ‰	-45.48 ‰	-33.64 ‰
Std. Deviation	16.83	22.51	17.77
Rapp. δ^{18}O (avg.)	-6.42 ‰	-7.05 ‰	-7.29 ‰
Std. Deviation	0.33	0.95	0.07
Rapp. δD (avg.)	-38.48 ‰	-42.03 ‰	-42.13 ‰
Std. Deviation	3.21	7.09	0.48
HR δ^{18}O (avg.)	-----------	-7.30 ‰	-7.42 ‰
Std. Deviation		1.09	0.41
HR δD (avg.)	-----------	-44.32 ‰	-43.57 ‰
Std. Deviation	-----------	8.14	3.08
GW δ^{18}O (avg.)	-----------	-7.06 ‰	-7.04 ‰
Std. Deviation		0.11	0.03
GW δD (avg.)	-----------	-42.51 ‰	-42.54‰
Std. Deviation	-----------	0.50	0.17

Table 4.2 Rainwater isotopic composition results

Sample ID	**Event Date**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Weather Station Amount (in)**	**Daily High Temp. (ºC)**
RW 1	5/28/2018	-4.73	-30.06	--	22.77778
RW 3	5/31/2018	-5.58	-40.96	0.03	30
RW 4	6/11/2018	-3.48	-12.63	1.02	21.11111
RW 6	6/20/2018	-3.78	-22.19	0.38	31.66667
RW 8	6/22/2018	-6.87	-42.21	2.21	23.88889
RW 10	6/22/2018	-8.51	-55.30	2.51	23.88889
RW 12	6/22/2018	-7.30	-44.66	2.76	23.88889
RW 14	6/25/2018	-6.11	-38.22	0.24	28.33333
RW 16	7/16/2018	-1.14	-3.38	0.05	35
RW 17	7/23/2018	-8.68	-57.34	4.28	27.77778
RW 19	7/24/2018	-3.58	-15.89	4.48	27.77778
RW 21	8/20/2018	-5.83	-32.17	0.05	26.66667
RW 22	9/8/2018	-4.26	-17.19	0.26	24.44444
RW 24	9/9/2018	-5.91	-25.51	2.26	19.44444
RW 26	9/14/2018	-2.75	-10.03	--	25
RW 28	9/14/2018	-2.68	-9.45	--	25
RW 30	9/15/2018	-3.66	-14.42	--	26.66667
RW 32	9/15/2018	-4.12	-14.79	--	26.66667
RW 34	9/18/2018	-3.77	-16.18	2.67	26.66667
RW 36	9/21/2018	-4.39	-20.48	0.27	26.66667
RW 38	9/23/2018	-6.14	-29.27	1.35	17.77778
RW 40	9/23/2018	-5.64	-24.28	1.52	17.77778
RW 42	9/24/2018	-5.77	-24.83	1.67	19.44444
RW 44	9/25/2018	-3.66	-8.67	2.12	28.33333
RW 46	9/27/2018	-4.74	-21.09	0.24	22.22222

RW 48	9/28/2018	-6.25	-30.02	1.05	25
RW 50	10/11/2018	-10.22	-69.85	3.21	28.33333
RW 52	10/17/2018	-7.08	-40.54	0.04	20
RW 54	10/20/2018	-3.50	-23.49	0.14	20
RW 56	10/21/2018	-5.77	-41.42	0.19	11.66667
RW 57	10/28/2018	-14.08	-91.87	1.79	16.11111
RW 59	11/3/2018	-8.48	-52.97	0.53	16.11111
RW 61	11/5/2018	-9.23	-56.14	1.85	12.22222
RW 63	11/6/2018	-7.72	-46.26	2.53	17.22222
RW 65	11/6/2018	-7.60	-46.43	2.87	17.22222
RW 67	11/6/2018	-5.36	-28.11	2.96	17.22222
RW 69	11/9/2018	-7.72	-43.93	0.30	9.444444
RW 71	11/9/2018	-7.56	-42.38	0.36	9.444444
RW 72	11/12/2018	-12.75	-92.96	0.30	9.444444
RW 74	11/13/2018	-12.80	-87.47	0.70	10
RW 76	11/15/2018	-9.44	-52.56	0.43	3.888889
RW 78	11/16/2018	-9.81	-57.65	1.49	11.66667
RW 80	11/25/2018	-10.97	-65.04	1.52	17.22222
RW 82	11/26/2018	-6.44	-30.60	0.15	12.22222
RW 84	12/3/2018	-6.53	-29.26	0.20	17.77778
RW 86	12/28/2018	-4.91	-15.61	0.32	13.88889
RW 88	12/28/2018	-2.87	-3.24	1.28	13.88889
RW 90	1/20/2019	-7.57	-41.91	0.56	12.22222
RW 92	1/24/2019	-7.35	-43.58	0.80	16.66667
RW 94	2/7/2019	-1.98	-11.07	0.05	11.66667
RW 95	2/12/2019	-8.60	-50.87	1.06	3.888889
RW 97	2/13/2019	-6.78	-37.08	1.18	10.55556

RW 98	2/18/2019	-8.47	-58.16	0.64	11.66667
RW 100	2/21/2019	-7.55	-40.12	1.21	13.33333
RW 102	2/23/2019	-7.54	-46.01	0.30	6.111111
RW 104	2/24/2019	-4.70	-22.39	1.00	17.22222

Table 4.3 Rappahannock River isotopic composition results

Sample ID	**Collection Date**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**Water Temp. (°C)**	**Discharge (ft^3/sec)**
VOC 1	6/13/2018	-6.23	-36.66	20.8	2590
VOC 2	6/20/2018	-6.28	-37.35	28	1340
VOC 3	6/22/2018	-6.88	-42.76	22.4	27800
VOC 4	6/26/2018	-6.87	-42.69	21.9	6280
VOC 5	7/12/2018	-6.41	-39.53	27.8	884
VOC 6	9/8/2018	-6.14	-36.85	26.6	841
VOC 7	9/9/2018	-6.12	-35.54	--	1040
VOC 8	9/18/2018	-6.15	-35.25	22.4	14100
VOC 9	9/21/2018	-6.34	-36.77	21.9	3640
VOC 10	9/25/2018	-5.89	-32.31	19.7	12000
VOC 11	9/28/2018	-6.09	-33.66	18.8	22000
VOC 12	10/7/2018	-6.39	-37.28	21.3	2000
VOC 13	10/12/2018	-7.23	-46.14	20.8	9310
VOC 14	10/19/2018	-6.42	-38.12	14.7	1380
VOC 15	10/20/2018	-6.38	-38.03	14.7	1340
VOC 16	10/28/2018	-8.16	-50.86	11.9	3660
VOC 17	11/3/2018	-6.74	-40.1	15.2	9510
VOC 18	11/6/2018	-7.78	-46.73	12.9	11300
VOC 19	11/16/2018	-8.91	-54.58	6	24200
VOC 20	11/27/2018	-7.51	-44.47	7.7	5620
VOC 21	1/25/2019	-7.37	-41.68	4.8	10400
VOC 22	2/4/2019	-7.18	-41.56	3	2480
VOC 23	2/16/2019	-7.27	-42.37	--	3150
VOC 24	2/21/2019	-7.33	-42.59	4.6	6320
VOC 25	2/24/2019	-7.29	-42.46	6.7	15200

Table 4.4 Hazel Run isotopic composition results

Sample ID	Collection Date	$\delta^{18}O$ (‰)	δD (‰)	Water Temp. (°C)
HR 1	9/28/2018	-5.54	-29.6	19.8
HR 2	10/7/2018	-6.01	-34.91	20.8
HR 3	10/12/2018	-8.05	-52.64	18.9
HR 4	10/19/2018	-6.62	-40.74	13.2
HR 5	10/20/2018	-6.28	-38.76	15.2
HR 6	10/28/2018	-8.79	-55.34	13.2
HR 7	11/3/2018	-7.95	-49.18	14.7
HR 8	11/6/2018	-7.81	-47.04	13.8
HR 9	11/16/2018	-8.19	-49.13	9.2
HR 10	11/27/2018	-7.77	-45.9	7.8
HR 11	1/25/2019	-8	-47.84	5.7
HR 12	2/4/2019	-7.46	-44.09	5.2
HR 13	2/16/2019	-7.42	-44.08	7.7
HR 14	2/21/2019	-7.4	-42.53	5.7
HR 15	2/24/2019	-6.84	-39.31	8.6

Table 4.5 Groundwater isotopic composition results

Sample ID	Collection Date	$\delta^{18}O$ (‰)	δD (‰)
GW 1	9/12/2018	-7.18	-42.88
GW 3	9/28/2018	-7.19	-42.98
GW 4	10/7/2018	-7.15	-42.89
GW 5	10/12/2018	-7.12	-42.8
GW 6	10/19/2018	-7.05	-42.43
GW 7	10/28/2018	-7.11	-42.78
GW 8	11/3/2018	-7.07	-42.66
GW 9	11/6/2018	-7.08	-42.69
GW 10	11/16/2018	-6.92	-41.81
GW 11	11/30/2018	-6.86	-41.54
GW 12	1/25/2019	-7.05	-42.37
GW 13	2/4/2019	-7.06	-42.51
GW 14	2/16/2019	-7.06	-42.77
GW 15	2/22/2019	-7.04	-42.65
GW 16	2/28/2019	-6.99	-42.42

Table 4.6. Date, $\delta^{18}O$ (‰) abundance and rainfall amount information for event-based trend sampling

Event Number	**Date**	**Time of Sample Collection**	**$\delta^{18}O$ (‰)**	**WS Amount (in) at Time of Collection**	**Cumulative Rainfall Amount (in)**
1	6/22/2018	8:50 am	-6.87	2.21	
		9:50 am	-8.51	0.30	
		10:50 am	-7.30	0.25	2.76
2	9/14/2018	8:00 am	-2.75	No Data	No Data
		12:50 pm	-2.68		
3	9/16/2018	2:15 pm	-3.66	No Data	No Data
		4:45 pm	-4.12		
4	9/23/2018	12:50 pm	-6.14	1.35	
		9:04 pm	-5.64	0.17	1.52
5	11/6/2018	8:30 am	-7.72	2.53	
		9:00 am	-7.60	0.34	
		11:40 am	-5.36	0.09	2.96
6	11/9/2018	2:40 pm	-7.72	0.30	
		5:36 pm	-7.56	0.06	0.36
7	12/28/2018	9:00 am	-4.91	0.32	
		3:00 pm	-2.87	0.96	1.28

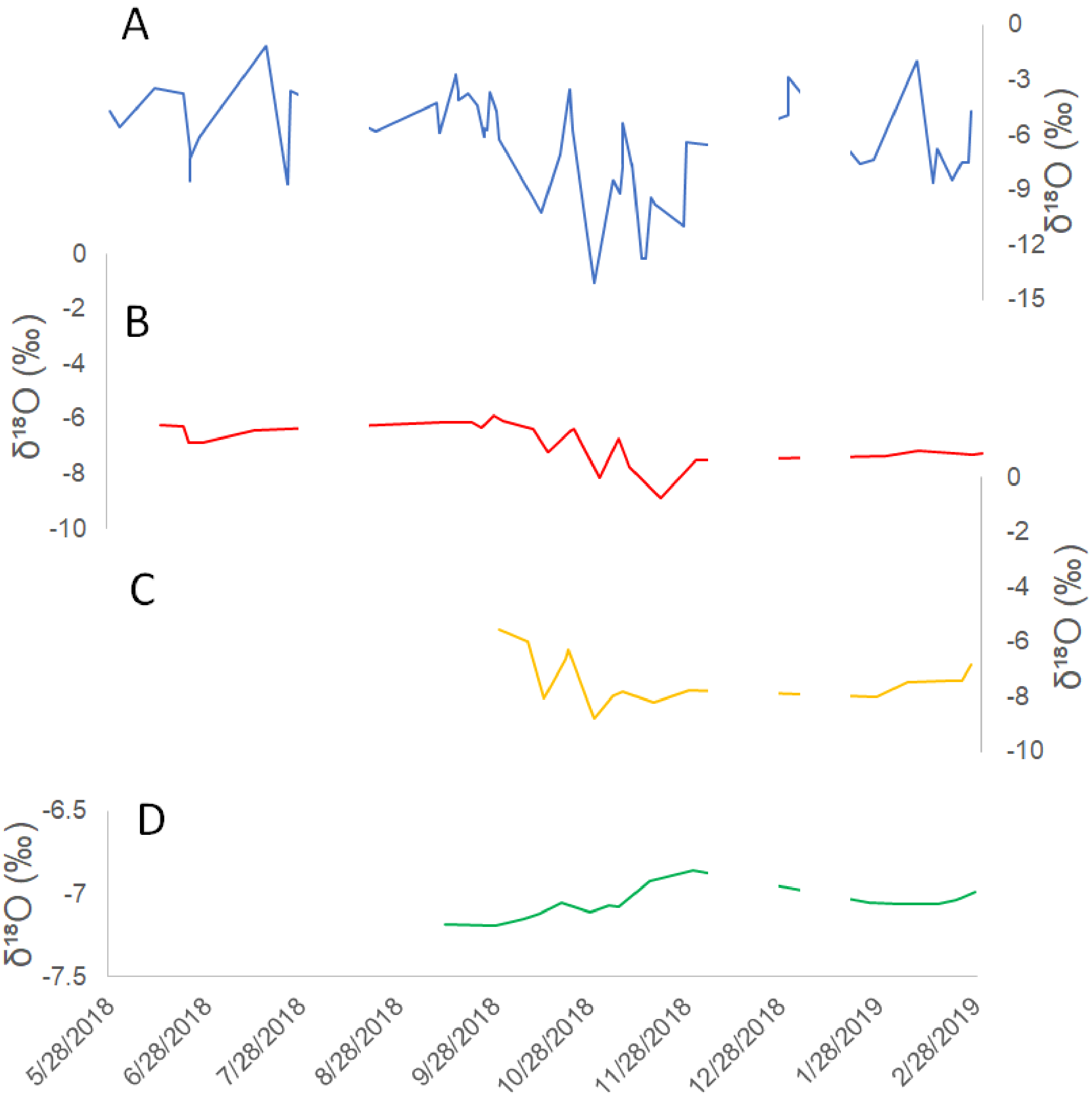

Figure 4.1. Plots of δ^{18}O (‰) values of (A) Precipitation, the (B) Rappahannock River, (C) Hazel Run, and (D) Groundwater.

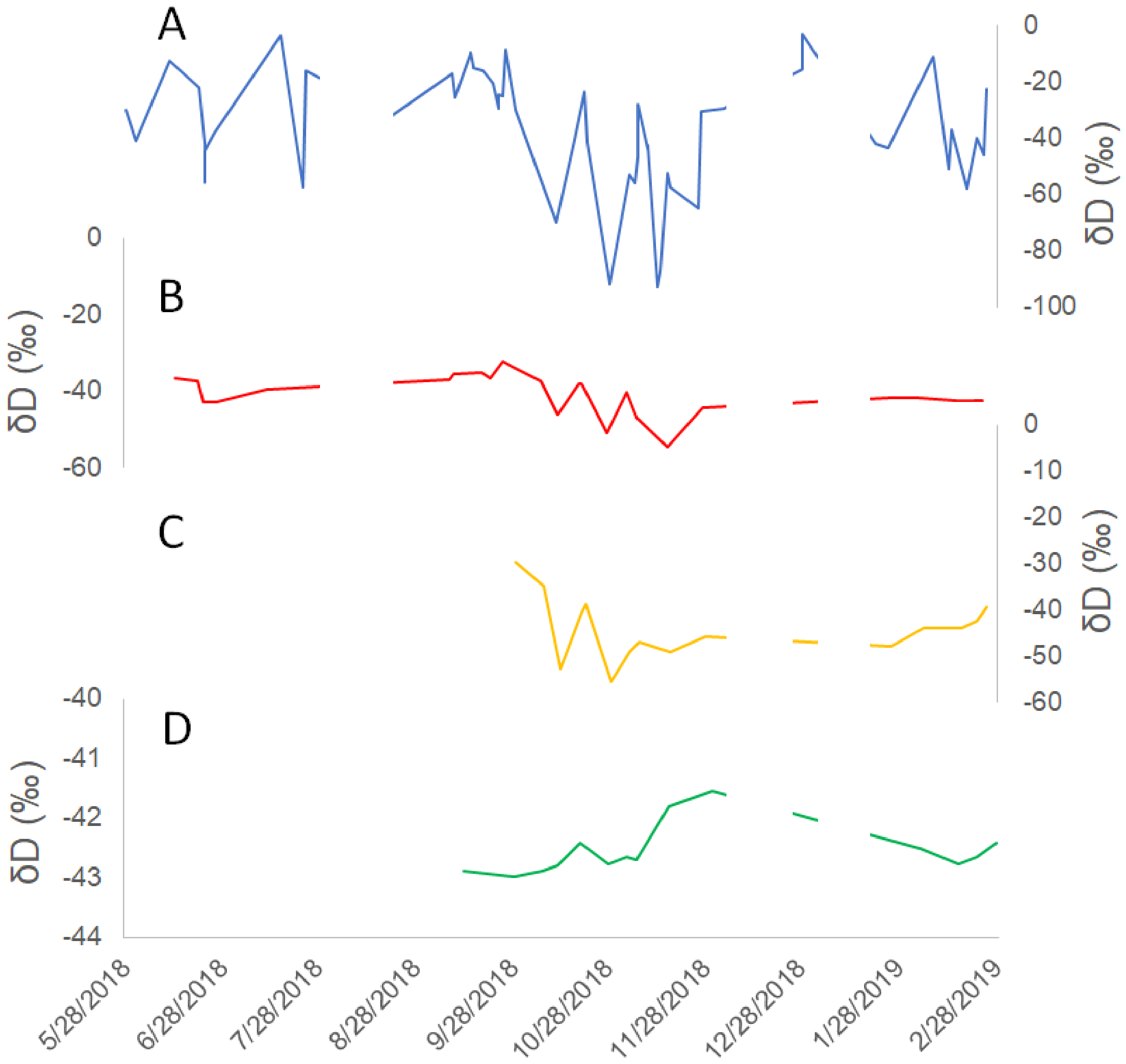

Figure 4.2. Plots of δD (‰) values of (A) Precipitation, the (B) Rappahannock River, (C) Hazel Run, and (D) Groundwater.

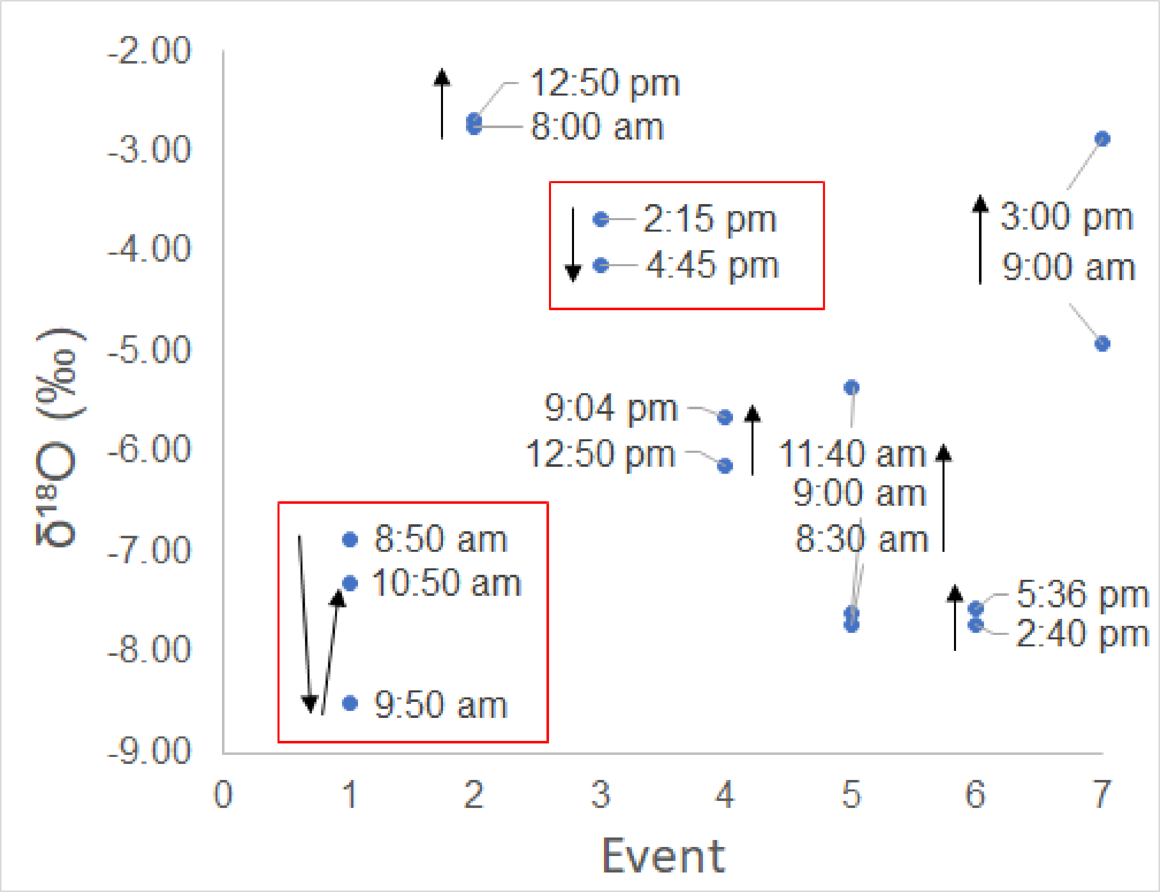

Figure 4.3. Rainwater δ¹⁸O (‰) of samples collected throughout a rainfall event. Black arrows pointing up indicate heavy isotope enrichment and arrows pointing down indicate heavy isotope depletion. Events bounded by a red box indicate isotopic depletion occurred during the event.

CHAPTER 5 – DISCUSSION

Trends in Isotopic Composition

Seasonal Variability

The $\delta^{18}O$ and δD compositions of precipitation follow a general seasonal trend of becoming more depleted in heavy isotopes in late fall and early winter months. Though the $\delta^{18}O$ and δD values of the Rappahannock River and Hazel Run reflect a similar trend (Figure 5.1a), the overall variability is muted. The range in precipitation $\delta^{18}O$ values is about four times the range observed in the stream water, which is not unexpected (e.g. Dutton et al., 2005). The seasonal trend of isotopic content seems to be strongly connected to changes in daily temperature and is most likely a strong control over the isotopic composition of both precipitation and stream water (e.g. Gedzelman and Lawrence, 1990). As daily high temperatures and river temperatures decrease over the course of the year (Figure 5.1d), precipitation and stream water become more depleted of heavy isotopes (Figure 5.1a and b). The warmer summer months, both precipitation and stream water values are more enriched. In fact, the rainfall event most enriched in ^{18}O occurred in the summer with the highest daily temperature of 35°C. The rainfall event most depleted in $\delta^{18}O$ occurred on a cooler day in the fall where the daily high was 16.1°C. However, this was not the coldest recorded day, indicating there are other factors than temperature alone influencing the values of precipitation. Yet, a positive correlation between water temperature and isotopic composition is evident for both precipitation and stream water, as seen in Figures 5.2a and 5.3a, with warmer temperatures correlating with more enriched water (e.g. Scholl and Murphy, 2014; Dutton et al., 2005). This result is expected as the temperature effect results in warmer water, or summer precipitation, being more enriched with heavy isotopes such as ^{18}O and D, and for cooler waters, or winter precipitation, to be more depleted in heavy isotopes (e.g.

Ichiyanagi, 2007; Gibson et al., 2010) due to seasonal changes in condensation rates of water (Araguás-Araguás et al., 2000). Additionally, the isotopic composition of precipitation is expected to show dependence on the temperature if the mean annual temperature is lower than 18°C (Gourcy et al., 2005), which it is for Fredericksburg, VA, region, where the mean annual temperature is 13°C (U.S. Climate Data, 2019).

Though temperature has a control over the δ^{18}O and δD values of the rainwater and stream water, it is not the single factor influencing the values. The data also suggest an observable trend in the isotopic values stream water with rainfall frequency. Surprisingly, there is a slight negative correlation with δ^{18}O of the rainwater and rainfall amount (Figure 5.2b). This is probably related to the fact that the large swings in seasonal temperature in the Fredericksburg region have a stronger control on the isotopic values (e.g. Gourcy et al., 2005). However, there does seem to be a correlation between frequency of rainfall events and the isotopic values of the steam water (Figure 5.1e). During periods of little to no rainfall events, primarily during summer and winter, stream isotope values are relatively constant, even after a single rainfall event. However, during periods of frequent rainfall events, the stream water isotopic values show more variability that follow the same trend as the precipitation values, though more muted in range (Figure 5.1a, b, c, and e). The stream water values do not vary as much because a river is the average of the entire watershed. The muted trend is the result of the averaging of the isotopic values of multiple sources of inflow into the stream system (Dutton et al., 2005; Bronwen Konecky, personal communication, 2019), and not the values of precipitation which are more directly affected by atmospheric changes and influences (e.g. Gedzelman and Lawrence, 1990, Rozanski, Araguás-Araguás, and Gonfiantini, 1993). During periods of few rainfall events, stream isotope values appear to follow the relatively constant trend, similar to that of groundwater, indicating that during drier times, groundwater is the primary source of inflow to the river and possibly the major influence on the isotopic content (e.g. Dutton et al., 2005). During periods of frequent rainfall, such as observed in the fall months (Figure 5.2e), precipitation and surface runoff is the main source of inflow into a river, and thus most likely is a strong influence on the isotopic values. This is apparent in Figure 5.3b, which shows a slight negative correlation with river discharge and $\delta^{18}O$ of the Rappahannock River water. Note, it may also be possible that a single large rainfall event could also influence the stream water isotope values; however, we cannot conclude this based on this dataset. The single large rainfall event that occurred July 28, 2018, does not have a subsequent river water sample. It must be noted that there exists significant breaks in sample collection during summer (July 17 and August 18, 2018) and winter break (December 4, 2018 – January 19, 2019), though those short periods of no data most likely would not affect the overall observed trends. Additionally, sampling did not begin from Hazel Run and the groundwater well until September 2018, limiting robust comparison across the summer to fall seasons among all the different datasets.

There are many controls and influences over the isotopic composition of water including, but not limited to, both the temperature effect and the amount effect. Only 25% of the variance of the precipitation $\delta^{18}O$ data is explained by temperature and only 2% is explained by rainfall amount (Figure 5.3). Likewise, only 50% of the Rappahannock River $\delta^{18}O$ variance and 19% of variance of $\delta^{18}O$ data of Hazel Run is explained by temperature and, for the Rappahannock River, only 10% of the data variance is explained by river discharge. This indicates that other factors may be playing a role in determining isotopic abundance of the water in Fredericksburg along with the influence of temperature. An alternative control that may explain more of the data variance could be water vapor source origin, as the source of water vapor and the distance an air mass travels from source location is another determining effect of isotopic composition. Future work of this project includes determining water vapor source of a rainfall event through tracking the storm’s trajectory and comparing the known isotopic values of the source water to those of Fredericksburg water to identify a correlation or lack thereof.

Event-Based Trends

Per the amount effect, precipitation is expected to become more depleted of heavy isotopes over the duration of the event as heavy isotopes, such as $\delta^{18}O$ and δD, rain out at the front of the air mass, leaving the lighter isotopes to rain out during the middle and conclusion of the rainfall event (e.g. Dansgaard, 1964; Gedzelman and Lawrence; 1990, Gat, 2010; Liu et al., 2010). There is a weak correlation between rainfall amount and isotopic composition, with greater precipitation amount correlating with more depleted isotopes (Figure 5.2b). This is expected as the amount effect is seen to have more of an influence over isotopic composition in the tropics rather than mid- and high-latitudes, where precipitation amounts are higher and temperature fluctuations are less (e.g. Dansgaard, 1964; Araguás-Araguás et al., 2000).

The amount effect, however, is more commonly observed when examining single rainfall events. Seven rainfall events were sampled two to three times throughout the duration of the event. Out of those events, 5 are seen to become more enriched in heavy isotopes over the course of the rainfall event (Figure 4.3). This trend was unexpected as it does not follow with the amount effect (e.g. Dansgaard, 1964; Ichiyanagi, 2007). The cause of this trend could be evaporation of the rainwater in the rain gauge (Scholl and Murphy, 2014). However, this is probably not likely as events that were sampled every hour with continued rainfall show enrichment (e.g. event 1), along with events that were sampled much farther apart where the last sample was not collected for a couple hours after the rainfall stopped (event 3) (Table 4.6). The more likely explanation is the progressive mixing in marine-sourced moisture as the events progress (Bronwen, pers. comm.). If more depleted air masses from the south or west mix with more enriched air masses from the coast mid-rainfall event, as suggested occurs by Figure 5.4, this could explain why isotopic values become more enriched. Future work needs to be done to help further explain this rainfall event data. This include running back-trajectories on the movement of air masses during a rainfall event to determine if air mass mixing occurred, using the Hybrid Single Particle Lagrangian Integrated Trajectory model, or HYSPLIT (Grothe, pers. comm.), for example. Future work also includes running a test to determine whether or not evaporation occurs within the rain gauge, and thus driving values to become more enriched as time continues after the rainfall event concludes, we can sample the rainwater at different time intervals at the conclusion of a rainfall event. Additionally, future work should include developing a rain gauge that seals post-rainfall to limit evaporation, especially when the sample cannot be collected immediately at the termination of the event.

Regional Waters Compared to Global Averages

The average isotopic values of water from the Fredericksburg region are an indication of where the water was sourced from and how it has behaved as it was transported to the local area. The average $\delta^{18}O$ value from this study is -6.44 ‰. Compared to global values, this value is expected as it is similar to averages from other mid-latitude sites sampled in previous studies (e.g. Bowen and Wilkinson, 2002). More-enriched values indicate a tropical water source, as precipitation from oceanic and tropical sources have an enriched isotopic value of $\delta = -2$ to -3‰ (Araguás-Araguás et al., 2000). In Fredericksburg, VA, isotopic composition reflects a tropical source, but is more depleted due to gradual depletion that occurs as the water vapor is transported to towards the poles (e.g. Dutton et al., 2005; Araguás-Araguás et al., 2000), but does not reflect a polar source as polar is significantly more depleted in heavy isotopes than what is observed at the sample site (Bowen and Wilkinson, 2002).

There is a very predictable relationship between global precipitation $\delta^{18}O$ and δD values that form the Global Meteoric Water Line (GMWL). When plotting the Fredericksburg rainwater isotopic values against the GMWL (i.e. the Local Meteoric Water Line (LMWL)), the LMWL is slightly shallower, with a slope of 7.48 compared to the GMWL slope of 8.13 (Figure 5.5). The two trend lines are similar, with the LMWL only slightly deviating from the GMWL slope and y-intercept. This indicates that similar processes affect local waters as those that affect the average isotopic content of global waters (Bronwen, pers. comm.). The lower slope value of the LMWL, however, is an indication of the influence of evaporative loss on the isotopic content of the precipitation source water (e.g. Rozanski et al, 1993), and the higher y-intercept of the LMWL versus the GMWL is indicative of an arid vapor source region of the precipitation (Araguás-Araguás et al., 2000). Evaporation is a contributing factor to the temperature effect, one of the primary controls over isotopic content (e.g. Faure and Mensing, 2005; Ichiyanagi, 2007). Evidence of the greater role of evaporation as a control over the isotopic content of precipitation based on the LMWL suggests that the temperature effect is one of the leading controls over isotopic composition of rainwater in the study region.

Stream water lines plot closely with that of the LMWL. The water lines of the Rappahannock River and Hazel Run have slopes of 6.81 and 7.24, respectively. Like the LMWL of rainwater, both stream water slopes are smaller than the GMWL, yet the y-intercepts of each are lower than that of the GMWL (Figure 5.5). This is an indication of the influence of evaporation on the stream isotopic values (e.g. Kendall and Coplen, 2001) rather than water vapor source, which is seen to have a greater influence on precipitation. The closeness of the stream water line with the LMWL may reflect the influence precipitation has on stream isotope values (e.g. Dutton et al., 2005; Kendall and Coplen, 2001).

Of each of the water types sampled, groundwater deviates the most from the GMWL. The slope of the groundwater line is the smallest, with a value of 4.25. The greater difference between the slope groundwater and the slopes of the GMWL, LMWL, and stream water lines indicate greater exposure of surface water to evaporation before infiltrating into the groundwater system (e.g. Wassenaar, Athanasopoulos and Hendry, 2011). It could also be explained by the time delay effect of groundwater (Wang et al., 2014), in which case slower flow rates and infill rates of groundwater versus precipitation, stream and surface water results in a lag in the timing of when recent rainfall events infiltrate into the groundwater and when it is sampled (e.g. Wu et al. 2014). If this were to be the case, the groundwater sampled would not match recent rainfall, isotopically, and therefore their water lines would differ. Even so, the shallow slopes of the stream and groundwater water lines indicates the control of evaporation on the isotopic composition of the water sampled.

Influence of Meteoric Water on Paleo and Modern Environments

The isotopic values observed in this study reflect the influence of temperature on the seasonality of the isotopic composition of both meteoric and stream water in the Fredericksburg, VA, region. These results support the notion that isotopic values of climate proxies derived from surface water are primarily governed by temperature in the region (e.g. Harding et al., 2010). However, meteoric water does influence the isotopic composition of surface water during periods of frequent rainfall events, mainly driving the $\delta^{18}O$ values more negative, which may cause an artifact in temperature reconstructions from proxies. A multiproxy approach, such as paired δ^{18}O and Mg/Ca ratios in carbonate shells, would provide a more robust temperature reconstruction as well as a method to calculate the δ^{18}O of the water.

As modern climate warms, precipitation patterns are expected to change. Studies predict to see an increase in winter and spring precipitation as well as shift in the vapor source of rainfall events, with models predicting an increase in subpolar precipitation depleted in heavy isotopes in the winter months (Najjar et al., 2010). Should this trend continue, we would expect to see it be reflected in the isotopic composition of meteoric and surface water in the region. However, other regional studies have found that over the past three decades, relative to the last century, there has been a significant increase in precipitation in Autumn (September, October and November), in Virginia (Hoffman et al., 2019). Autumnal precipitation, tropical in source (e.g. Hendon, Lim and Nguyen, 2014), is enriched in heavy isotopes (Araguás-Araguás et al., 2000). Should this increase continue, it is expected that baseline isotopic composition in the region will become more enriched in heavy isotopes, a change that will be observed through the continuation of this monitoring project. However, to help improve our understanding of these results as it relates to future climate change, additional atmospheric data should be collected with each rainwater sample, such as wind direction, humidity, and moisture source.

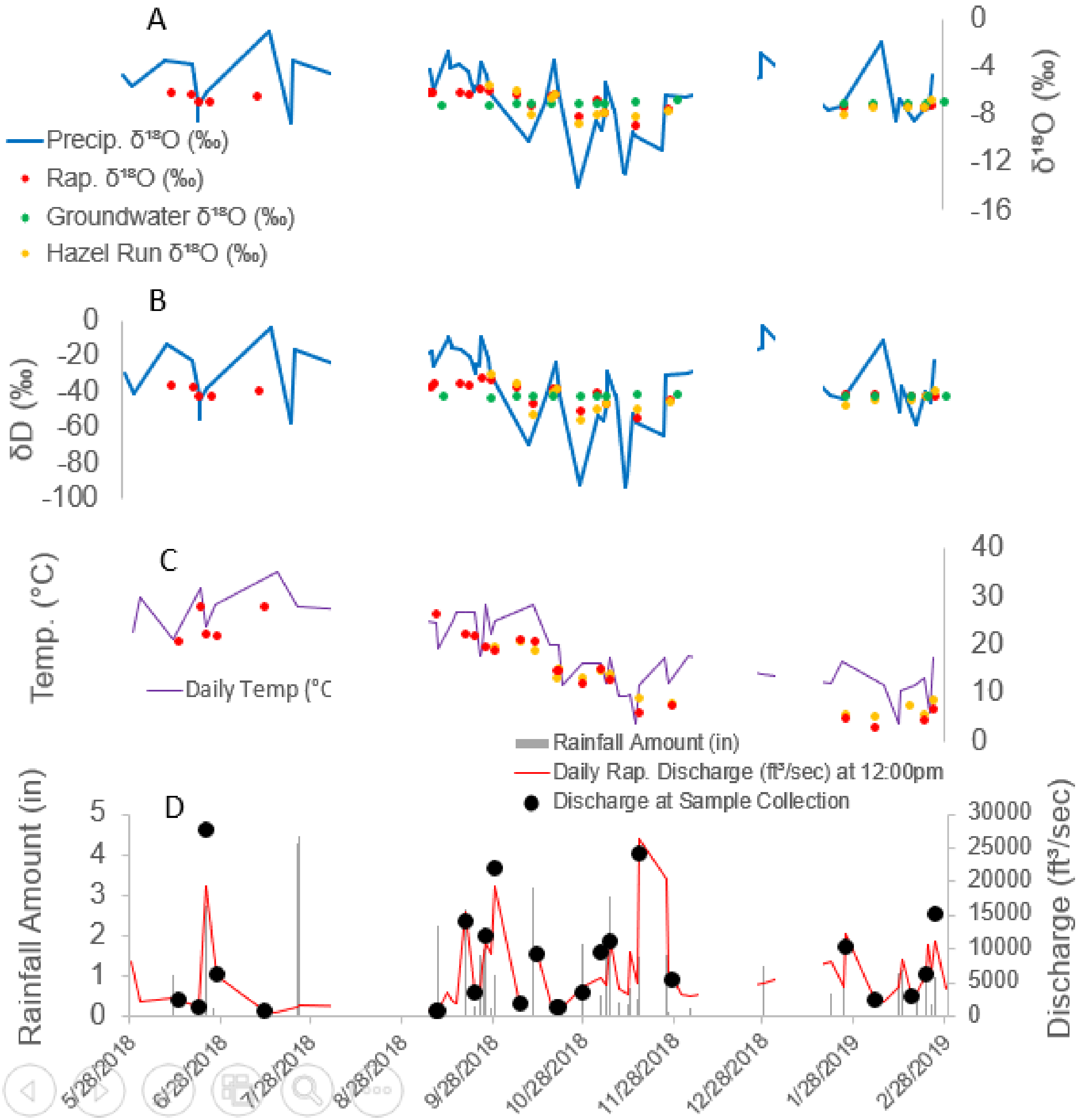

Figure 5.1. Plots of (A) δ^{18}O (‰) and (B) δD (‰) of precipitation, Rappahannock River, Hazel Run and groundwater sample, (C) daily high temperature (°C) and temperature (°C) of the Rappahannock River and Hazel Run paired, and (D) precipitation amount of each rainfall event and discharge (ft³/sec) of the Rappahannock River.

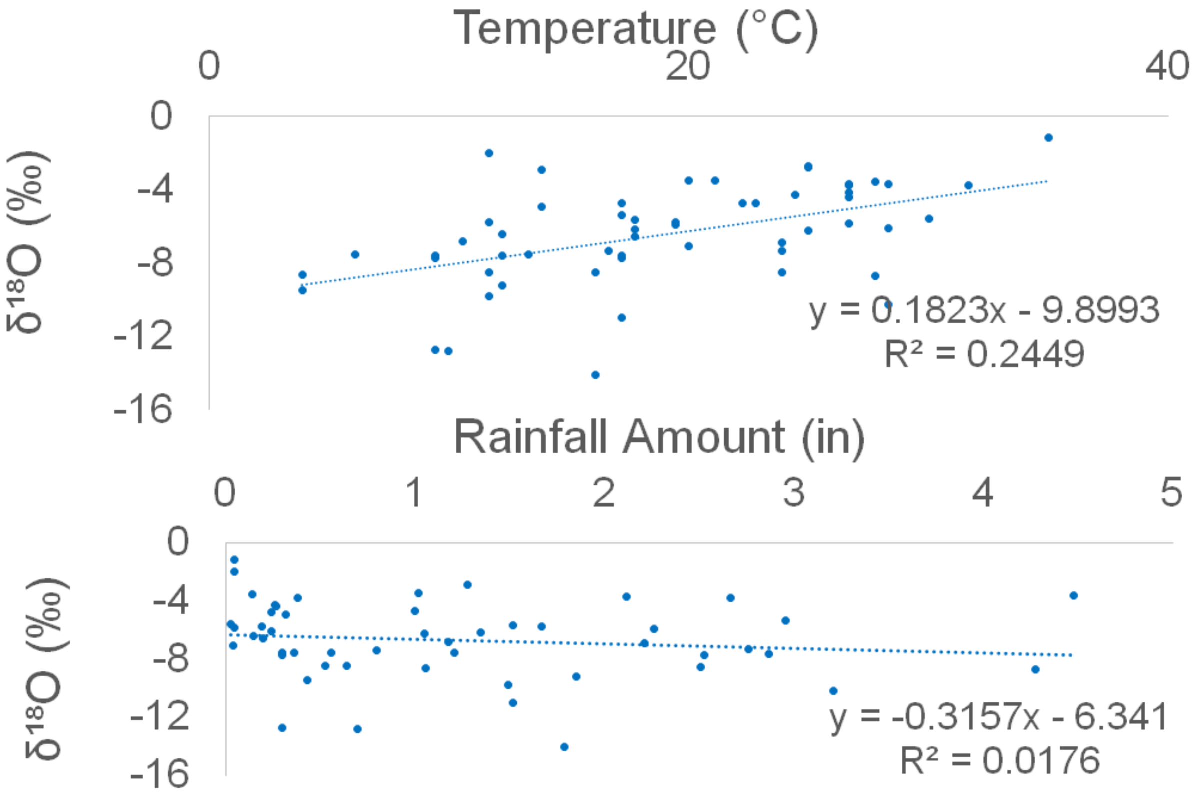

Figure 5.2. Precipitation δ^{18}O (‰) paired with (A) daily high temperature and (B) rainfall amount.

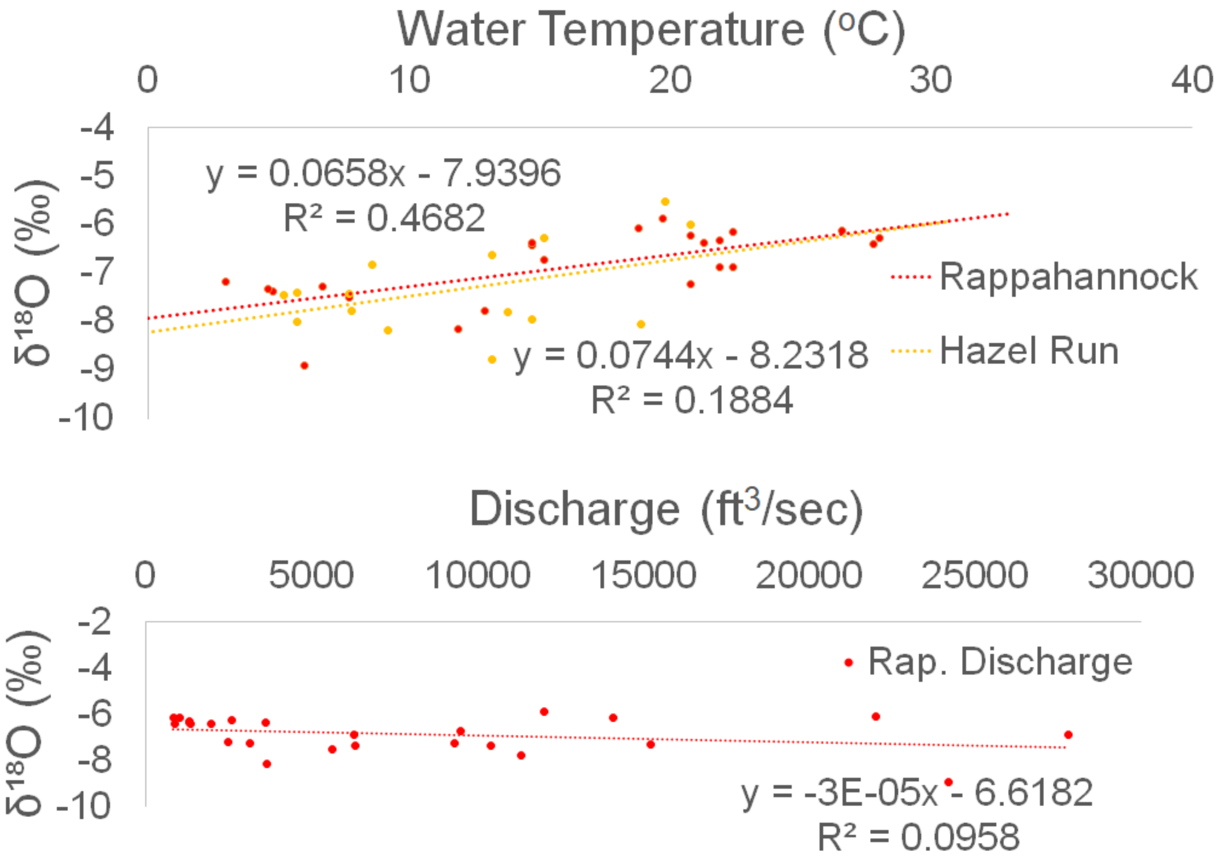

Figure 5.3. (A) Rappahannock and Hazel Run δ^{18}O (‰) paired with water temperature (°C); (B) Rappahannock δ^{18}O (‰) paired with river discharge (ft^3/sec). The R^2 of the Rappahannock River paired δ^{18}O—Temperature data is 0.47 and 0.10 for δ^{18}O—Discharge. The R^2 for Hazel Run paired δ^{18}O—Temperature data is 0.19.

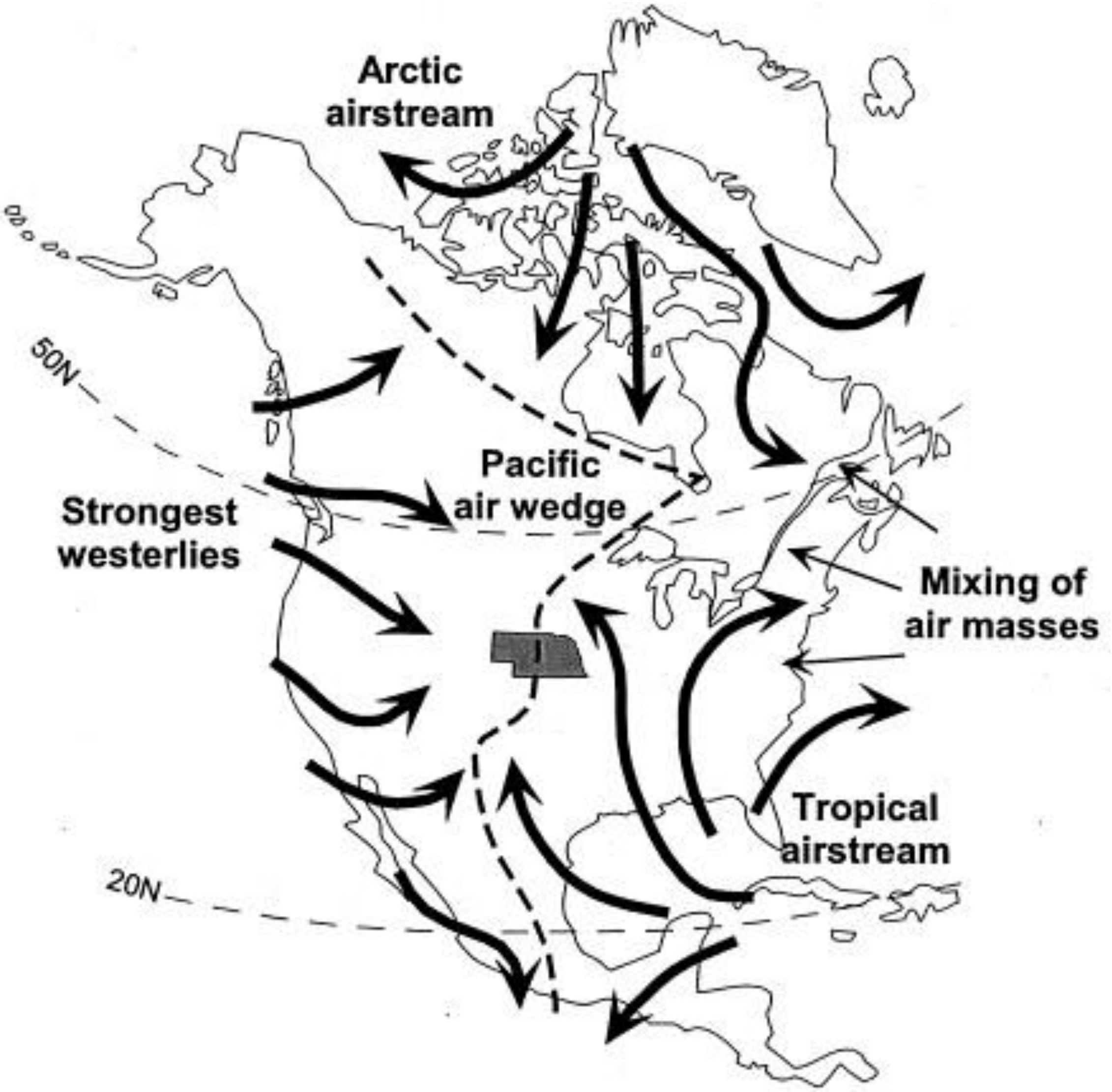

Figure 5.4. A map of air mass movement and interaction in North America (Harvey and Welker, 2000).

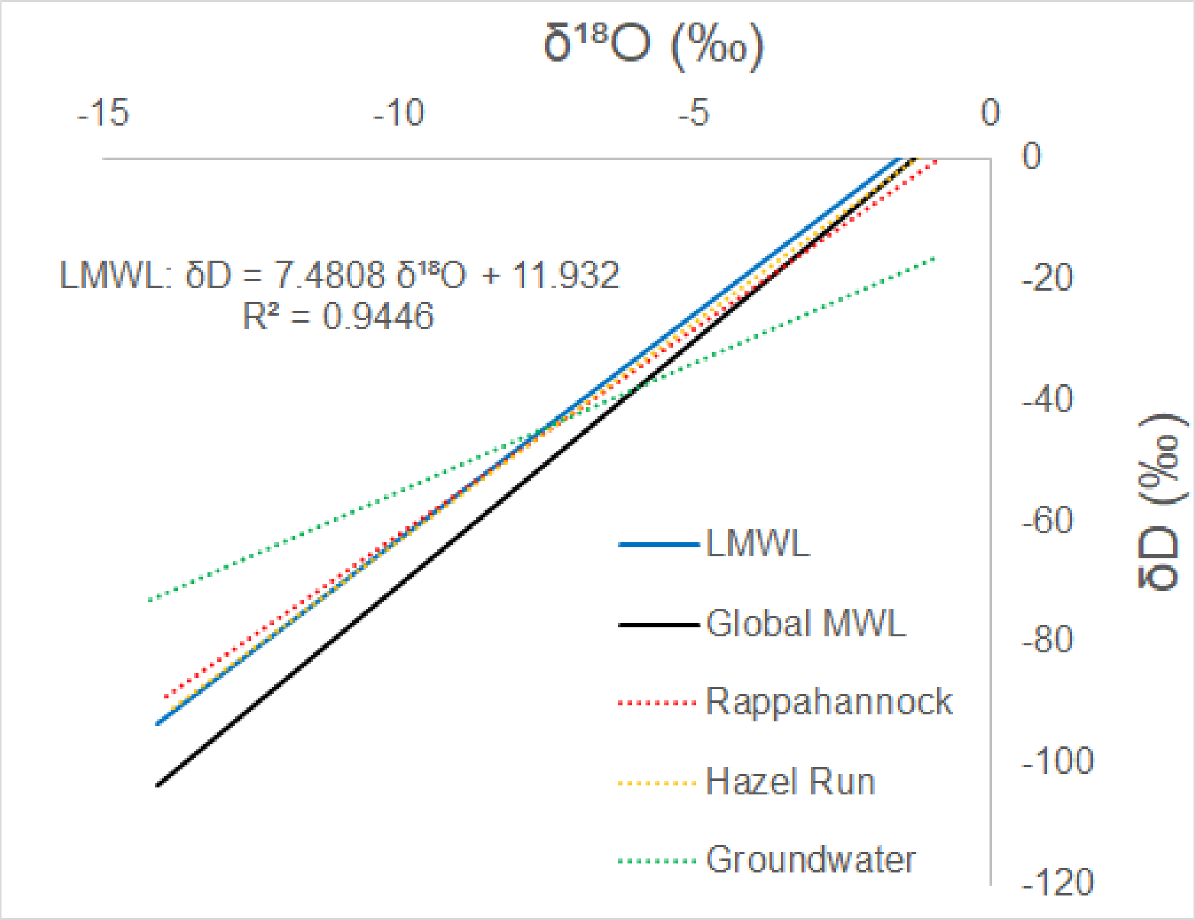

Figure 5.5. Global Meteoric Water Line (GMWL) of Fredericksburg, VA, paired with the Local Meteoric Water Line (LMWL), and the $\delta^{18}O$ (‰) and δD (‰) values of Rappahannock River, Hazel Run and groundwater samples. The R^2 value of the Rappahannock water line is 0.9343, 0.9457 for the Hazel Run water line, and 0.894 for the groundwater water line.

CHAPTER 6 – CONCLUSION

The objectives of this study were two-fold. The first was to develop a baseline understanding of the seasonality of the isotopic composition of water in the Fredericksburg, VA, region and the second was to understand how the $\delta^{18}O$ and δD values within meteoric water influences the stable isotopic composition of stream and groundwater in the region. Through the analysis of rain, stream and groundwater samples over the course of a year, we sought to provide information on the behavior of isotopic composition in the region, as no previous work on the topic had been conducted to date. The purpose of these objectives was to develop a more thorough understanding of the controls over isotopic composition in the region, and in surface water, in particular, to aid paleoclimate reconstruction from climate proxies within the Rappahannock River and greater Chesapeake Bay.

To answer these questions, the isotopic composition of precipitation, Rappahannock River water, Hazel Run water and groundwater were analyzed for seasonal trends and relationships. Over the course of the year, isotopic values became more depleted as daily high temperatures and water temperatures became colder, a trend consistent with the temperature effect. The correlation between isotopic composition and temperature was observed to be more prominent than the correlation with rainfall amount or river discharge. Stream values remain relatively constant throughout the year, which could be a reflection of groundwater isotopic values; however, during periods of frequent rainfall events, stream values are observed to trend more closely with precipitation values, although the trend is muted. Based on these relationships, we hypothesize that temperature is a leading control over the isotopic values of water in the Fredericksburg region, and that groundwater has greater influence over the variability in stream values except for during periods of frequent rainfall, at which point precipitation becomes a leading control over the isotopic composition of the stream because it is the main source of inflow into the stream system.

These findings and hypotheses have significant implications for paleoclimate reconstructions and understanding how the isotopic composition of water in the area will change with expected changes in precipitation patterns associated with continuous climate warming. Based on the influence of temperature and rainfall frequency on the isotopic composition of stream water, we can expect proxy records from the Rappahannock River to be governed primarily by temperature and the precipitation effect of paleoclimates. As modern precipitation patterns continue to change in the region, in the form of changes in seasonal rainfall frequency and water vapor source, we expect the isotopic composition of regional waters to reflect this change.

This study was only the initial steps in what will be a long-term monitoring project of the isotopic composition of regional waters. There are limitations in the data, such as significant breaks in sample collection, that necessitate a longer dataset to determine more conclusive isotopic trends. By continuing this project, we hope to gain a better understanding of how seasonal trends in isotopic composition of meteoric and stream water, as well as climate archives like oyster shells in the Rappahannock River, will change as climate continues to warm. This will help us to make more robust interpretations and reconstructions of the paleoclimate of the region, which, in turn, will allow us to better predict and prepare for future climatic changes.

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