ISOTOPIC ANALYSIS OF A CATCHMENT IN MĀNOA, HAWAIʻI

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We certify that we have read this thesis and that, in our opinion, it is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

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ABSTRACT

Exploring the isotopic weather dynamics within the Mānoa catchment of Hawaiʻi reveals insights into the region's hydrological processes and atmospheric-water interactions through isotopic analysis of rainwater and streamwater. This study uses δ^2H and $\delta^{18}O$ isotopes as natural tracers, showing the seasonal fluctuations and underlying mechanisms governing precipitation and steam flow from February to December 2023. Seasonal isotopic patterns are clearly defined, reflecting the direct influence of local climatic conditions on water sources. This research emphasizes the variable isotopic signatures of precipitation, which underscore the impact of shifting weather patterns. Anomalies were detected, specially marked isotopic enrichment in June's stream water, and signal deviations possibly tied to altered hydrological pathways, such as increased evaporation or modified groundwater influxes. Here, one can see the interplay between rainwater characteristics and streamflow dynamics, but it also furnishes critical insights into the nuanced interplay of tropical island hydrology.

Keywords: Catchment; Isotopic Analysis; Precipitation; Streamwater; Mānoa, Oʻahu

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1.0 INTRODUCTION

1.1 Catchment in Mānoa, Hawaiʻi

Hawaiʻi has a unique geography and climate that has shaped its water catchments, which plays a crucial role in the hydrology of the islands. These water catchment systems are intricately tied to the island's biophysical processes, climate, and geography (Giambelluca et al., 2013). Hawaii's islands have a diverse topography that ranges from coastal plains to high mountain tops. The variation in elevation helps create distinct climate zones ranging from arid regions to tropical rainforests, significantly affecting local hydrological cycles. The trade winds, blowing from the northeast, bring moisture that gets lifted up the steep mountains, resulting in high precipitation on the windward sides of the islands, called orographic rainfall (Giambelluca et al., 2014).

Water catchments in Hawaiʻi are areas of land where rainfall is collected and stored through primarily natural processes. The Hawaiian Islands depend on these catchment systems for various uses such as agriculture, groundwater recharge, domestic water supply, and maintaining natural habitats. A significant portion of Hawaii's freshwater supply is stored underground in aquifers. Rainwater that falls on the islands percolates through the soil and volcanic rock, replenishing the underground aquifers (Oki et al., 2015).

Streams and rivers in Hawaiʻi are primarily fed by rainfall. Due to the island's steep terrain and high rainfall, certain areas will experience rapid changes in flow, affecting water availability and quality. More than 99% of the freshwater in Hawaiʻi comes from rainfall (Gingerich & Oki, 2000). The project aims better to understand the hydrology of water catchments in Hawaiʻi. By collecting samples of rainwater and stream water and conducting isotopic analyses, these comparisons will allow us to constrain how much water from rain contributes to the water that flows in streams. Previous studies have shown that most stream runoff after a rain event comes from "older" groundwater rather than "new" rainwater.

1.2 Isotopic Analysis

Water isotope ratios are sensitive to the physical processes that a sample undergoes; therefore, they are well suited to provide insights into the history of the sample itself. Isotopic ratios are essential to diagnose how much water in the stream comes directly from rain. Isotopic analysis of water is a scientific technique that investigates the composition of water samples by analyzing the different isotopes of hydrogen and oxygen they contain. Isotopes are atoms of the same element with equal numbers of protons but differing numbers of neutrons, resulting in varied atomic masses. The most prevalent isotopes of hydrogen are protium ^{1}H and deuterium ^{2}H; for oxygen, it is ^{16}O and ^{18}O. The ratios of these isotopes in water molecules can provide invaluable insights into the water's origins, the pathways it has traversed, and the processes it has undergone (Clark & Fritz, 1997).

The principle behind the isotopic analysis is that water isotopic ratios, specifically those of ^{2}H and ^{18}O, undergo slight variations due to evaporation, condensation, and precipitation. These changes are affected by factors like temperature, humidity, and the geographic origin of water. Researchers can trace the water's movement through the hydrological cycle by measuring these isotopic ratios in a water sample, providing clues about climate conditions, water cycle dynamics, and various geological and ecological processes (Dansgaard, 1964). Isotopic analysis is instrumental in exploring groundwater recharge, flow paths, and interactions between surface water and groundwaters. It can pinpoint the age of groundwater, sources of aquifer recharge, and the origins of water pollutants (Clark & Fritz, 1997). The isotopic composition of water is often used in the study of island water resources, but more high-frequency datasets are needed. This study aims to investigate the isotopic composition of rainfall and streamwater.

1.3 Deuterium and Oxygen-18

Deuterium is a stable isotope of hydrogen with a natural abundance in water. It is denoted by the symbol D or ^{2}H. Unlike the most common hydrogen isotope, which consists of just one proton, deuterium contains one proton and one neutron, double the mass of the typical hydrogen atom. The difference in mass leads to slight differences in the chemical and physical properties of water molecules that contain deuterium, often called "heavy water." Water molecules that contain more common hydrogen isotopes are called "light water." There are important reasons why deuterium is analyzed in water.

Deuterium is used to trace water movement within the Earth's hydrological cycle. The ratio of deuterium to hydrogen (D/H) in water changes in a predictable way with processes like evaporation and condensation, making it a valuable tracer for studying the origins and movement of water in the environment (Clark & Fritz, 1997). Higher concentrations of deuterium in precipitation can indicate that the water vapor originated from evaporation under high temperatures. Since lighter water molecules evaporate more readily than heavier ones, a higher temperature leads to a slightly higher proportion of deuterium in the vapor phase compared to the liquid phase. During condensation, heavier water molecules condense out preferentially, but if condensation occurs quickly or the vapor does not cool much before condensing, the resulting precipitation can be enriched in deuterium (Dansgaard, 1964).

Precipitation with high deuterium content often suggests that the moisture source was a warm ocean or sea with high evaporation rates. Evaporation processes enrich the vapor phase in the heavier isotopes (Clark & Fritz, 1997). As moisture-laden air masses move and cool, raindrops form, and deuterium gets depleted with each successive rainout event. Early precipitation is richer in deuterium, while later precipitation, having undergone more rainout stages, is depleted in deuterium. Therefore, rain with high deuterium levels may indicate that it has yet to travel far from its source or has experienced fewer condensation events (Gat, 1996). High deuterium levels also serve as climate indicators, indicating warmer periods when evaporation rates are higher (Jouzel et al., 2003).

Oxygen-18, denoted as ^{18}O, is a stable isotope of oxygen with 8 protons and ten neutrons, making it heavier than the most abundant isotope of oxygen, oxygen-16. The presence and variation of ^{18}O in water molecules provide valuable insights into numerous environmental and scientific studies (Clark & Fritz, 1997). The variation in the ratio of ^{18}O to ^{16}O, denoted as $\delta^{18}O$, in precipitation, is influenced by several factors, which can be used to interpret atmospheric circulation patterns, climate conditions, and evaporation processes. Generally, air masses lose moisture as they cool, with water molecules containing ^{16}O preferentially condensing out first, leading to precipitation that is progressively enriched in ^{18}O as temperature decreases. Higher $\delta^{18}O$ values in precipitation can indicate warmer conditions at the condensation point and vice versa (Dansgaard, 1964).

As moist air masses travel and cool, the first raindrops to form and fall will be richer in ^{18}O. At the same time, successive precipitation becomes increasingly depleted in ^{18}O due to the preferential removal of ^{16}O water molecules. This "rainout" process results in a geographical and altitudinal gradient, where precipitation becomes progressively lighter (^{16}O enriched) with distance from the moisture source and elevation (Rozanski et al., 1993). Water evaporating from warm tropical oceans tends to be richer in ^{18}O than from cooler, higher latitude oceans. By analyzing $\delta^{18}O$ values in precipitation, researchers can infer the origins and trajectories of storm systems and atmospheric circulation patterns (Gat, 1996).

1.4 Previous Research

The research conducted in this project continues to build on the research by Giuseppe Torri and Alison Nugent found in the article "The Isotopic Composition of Rainfall on a Subtropical Mountainous Island," and it examines the isotopic composition of rainfall on Oʻahu, Hawaiʻi. Torri's and Nugent's research investigates the stable isotopes of hydrogen and oxygen in rainfall to help better understand the processes influencing the isotopic composition of precipitation in the complex terrain of subtropical mountainous islands. This study helps us understand hydrological processes, including atmospheric circulation, condensation, and evaporation.

The study observes variations in the isotopic composition ($\delta^{18}O$ and δD) of rainfall across different elevations and geographical locations on the island. This is due to the orographic effect, where moist air ascends the mountain, cools, and then precipitates, leading to rain with different isotopic signatures at different altitudes. The study also shows seasonal variations in the isotopic composition of rainfall, with differences between wet and dry seasons. The data shows significant differences in isotopic ratios produced by different weather systems. By analyzing the isotopic composition of rainfall, this research sheds light on the sources of moisture and the mechanisms driving rainfall variability (Torri et al., 2023).

This research also focuses on streamwater due to research findings in the article "A Rationale for Old Water Discharge Through Macropores in a Steep, Humid Catchment" by McDonnell that shows research findings on the phenomenon of old water discharge in a steep, humid catchment area. A study like this has yet to be done on Oʻahu, Hawaiʻi. McDonnell's study provides evidence that in these environments, similar to the environments of the Hawaiian Islands, the rapid discharge of water during storm events is predominantly composed of "old water," which means water that was groundwater or stored in the soil prior to the rainfall event, rather than newly fallen rain.

The research challenges the traditional view of runoff generation, emphasizing the newly fallen precipitation's role in streamflow. Most water contributing to streamflow during and immediately after rainfall is not the recent rain, but the water stored in the catchment for some time. This suggests that the catchment response to rainfall is more complex than a simple direct input-output relationship. The origin of the water in the stream can be analyzed by looking at the isotopic composition of the streamwater.

1.5 Significance

Water represents the fundamental component of the hydrologic cycle, and studying how rainwater and streamwater interact will lead to a better understanding of the dynamics of catchments in Hawaiʻi. This can help predict and project future changes in water resources so that actions can be taken by various stakeholders and policymakers thanks to a robust understanding of how these components integrate. To our knowledge, a study like this has yet to be done in Hawaiʻi or a similar tropical climate location. This could improve the understanding of water quality by determining the rate at which rainwater accumulates in groundwater before it enters streams. Alongside the isotopic analysis of this research, a chemical analysis of the rainwater and streamwater will also be conducted to identify potential sources of contamination. This research aims to study the isotopic composition of rainfall and streamwater to better understand island water resources.

2.0 METHODS

2.1 Equipment and Sampling Locations

The project's goal was achieved by using rain sample buckets to catch rainwater and directly sampling streamwater by dipping a 20 mL glass vial into the streamwater and sealing it immediately. Rain sample buckets had been previously purchased for other projects. The rain sample buckets were placed in open areas, with minimal disruption from surrounding factors such as humans and wildlife. The rain buckets are enclosed in a metallic casing with a small tube that allows rainwater to enter to ensure that evaporation does not occur.

Figure 1. Rain Sample Bucket

The rain sample bucket at the University of Hawaiʻi at Mānoa is installed on the roof of the Hawaiʻi Institute of Geophysics, and the other is installed at Lyon Arboretum. Data collection began from February 2023 to December 2023, a total of 45 weeks. Rainwater samples of 20 mL were collected weekly from each site and streamwater was collected weekly in 20 mL vials from each site. The isotopic analysis was then performed at the Biogeochemical Stable Isotope Facility at the University of Hawaiʻi at Mānoa.

2.2 Sampling Methods of Rainwater

As 20 mL of rainwater was sampled each week at the University of Hawaiʻi at Mānoa and Lyon Arboretum, data was recorded in a Google Spreadsheet consisting of the date and time of collection of the rain sample bucket, the time of sampling as when the rainwater from the rain sample bucket was transferred to the 20 mL glass vials, the volume sampled, any special weather events, and the total weight of the rain sample bucket before the sample was taken to record how much rain was collected that week. If there was not enough rain in the rain sample buckets during a week, it would be left, and no sample would be collected.

2.3 Sampling Method of Streamwater

The sampling method of streamwater at the two locations of Mānoa Stream, the University of Hawaiʻi at Mānoa and at Lyon Arboretum, was done by directly dipping the 20 mL glass vial into the stream, preferably in an area with running water instead of stagnant water. It was sealed directly after collection to preserve the isotopic composition and not allow the sample to interact with air. The data was also recorded in a Google Spreadsheet with the date and time of sampling. Volume sampled and unique weather events, such as thunderstorms or brown stream water from heavy rain, were also recorded.

2.4 Laboratory Analysis

The isotopic analysis of the water sample was performed at the Biogeochemical Stable Isotope Facility for isotope analysis. The average of ^{18}O and ^{2}H was taken for each sample, and the standard deviation for ^{18}O and ^{2}H was calculated for each sample. The instrumentation used was the Picarro L2130-i High Precision ^{18}O and D Isotopic Water Analyzer via A0211 High Precision Vaporizer and Picarro A0325 Autosampler. Isotopic corrections are calculated using standards prepared by the laboratory and run along with the samples. All samples were analyzed at least triplicate, and isotopic values are reported in delta-notation relative to V-SMOW. The software Chemcorrect was used to flag for organic contamination. All samples are clear of contamination unless otherwise noted.

3.0 RESULTS

3.1 Results for Precipitation in Lyon Arboretum

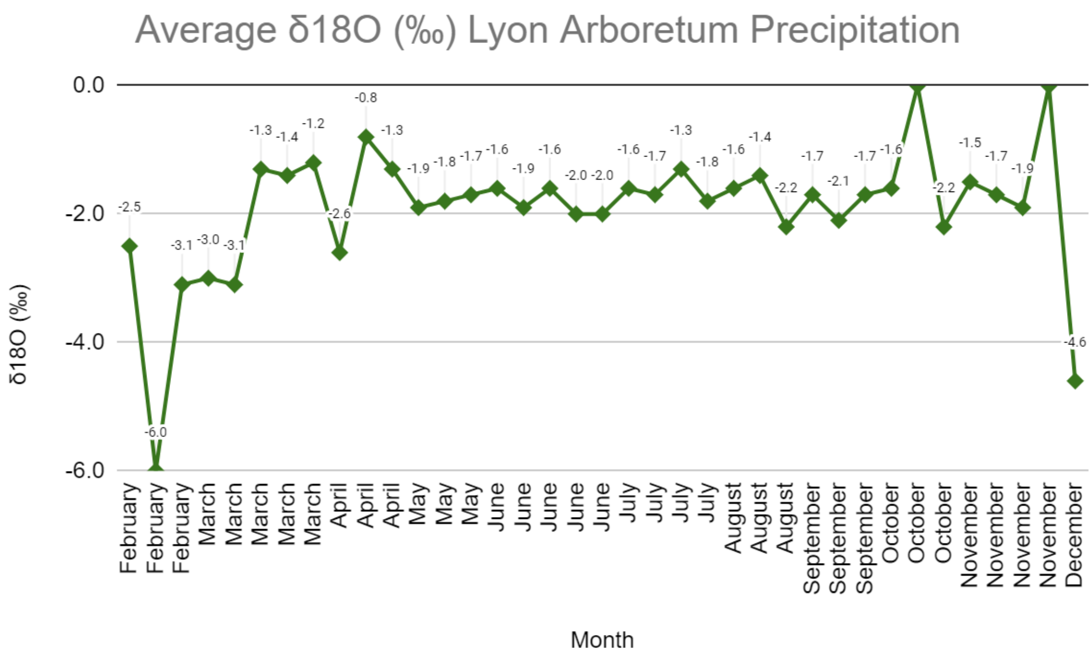

Figure 2. Average δ^{18}O of Precipitation at Lyon Arboretum

Figure 2. represents the average values of δ^{18}O in precipitation between February 2023 and December 2023 at Lyon Arboretum, located at the upper end of Mānoa Valley in Hawaiʻi. The y-axis of the graph shows the average δ^{18}O values per mil (‰). The x-axis represents the months from February to December 2023. February shows significant variability in δ^{18}O with a notable low at -6.0‰, which could indicate a period of colder temperatures or intense rainout effects typical of winter conditions. In March, the δ^{18}O values increase slightly but remain on the lower side, suggesting a continuation of cooler,

wet conditions typical of early spring. In April, there is an increase in variability with a mix of lower and higher values, suggesting transitional weather as spring progresses.

The $\delta^{18}O$ values in May are consistently negative but less so than in February, indicating warming temperatures but still relatively cool and moist conditions. The values are consistently around -1.6 to -2.0‰ in June, indicating stable weather conditions, possibly the onset of summer with slightly warmer temperatures. July's values reflect typical summer conditions with slightly higher values than in June, with possible variations in rainfall sources or temperatures. August's values show some variability but remain consistent with July's, suggesting that stable summer conditions continue.

The slight decrease in $\delta^{18}O$ values in September potentially shows the beginning of the transition to autumn. October shows unusual variability with a value reaching 0.0‰, which is significantly higher than other months. November returns to more typical autumn values but includes a 0.0‰ reading. A significant drop occurs in December with a value of -4.6‰, suggesting a return to colder weather.

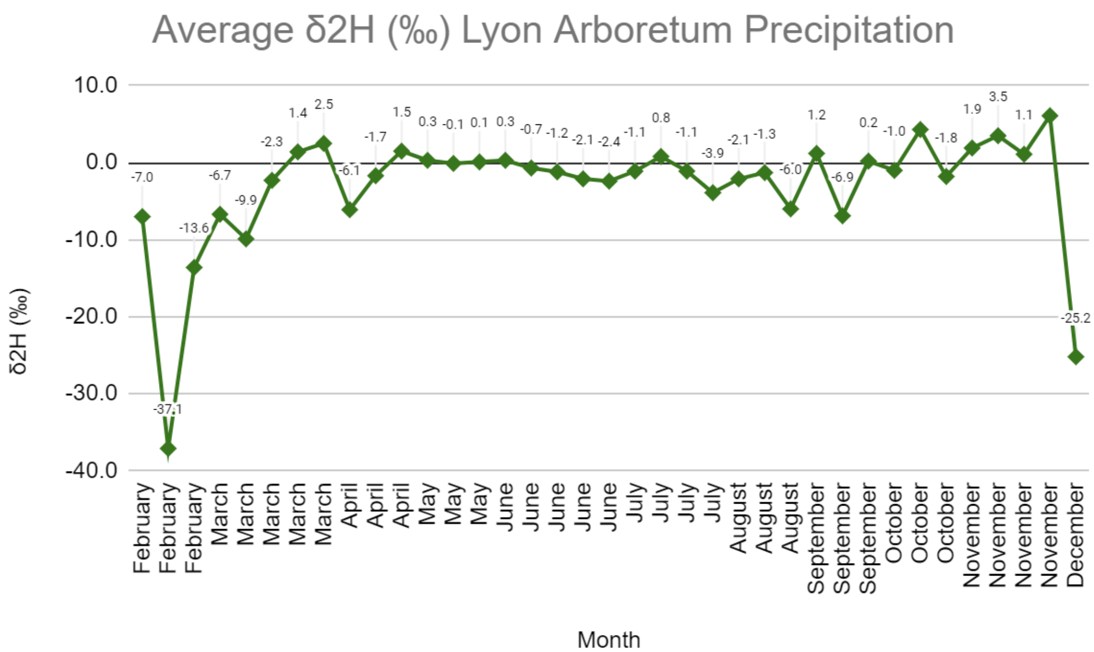

Figure 3. Average δ^2H of Precipitation at Lyon Arboretum

Figure 3. represents the average values of δ^2H (deuterium to hydrogen ratio) in precipitation between February 2023 and December 2023 at Lyon Arboretum, located at the upper end of Mānoa Valley in Hawaiʻi. The y-axis of the graph shows the δ^2H values per mil (‰). The x-axis represents the months from February to December 2023. The graph indicates fluctuations in δ^2H values throughout these months, typically due to seasonal changes affecting precipitation and its isotopic composition. February has a significant spread in δ^2H values with an extreme low at -37.1‰. The average is lower than in other months, suggesting colder conditions or different atmospheric patterns. March sees an increase in δ^2H values with high reaching up to 2.5‰, reflecting a possible warming trend or changes in the moisture source.

In April, values begin to stabilize, showing a slight upward trend towards more positive δ^2H values, which may indicate the start of warmer or more stable weather conditions. May shows consistent values around zero, suggesting stable conditions without significant changes in temperature or moisture sources. June's values are close to zero but slightly negative on average, indicating minor variations in weather conditions. July's values show a mix but are generally lower, suggesting a slight cooling or changes in precipitation sources. August shows a decrease in δ^2H values, possibly due to a shift towards cooler temperatures or different atmospheric conditions.

September has a wide range again, with an extreme low at -6.9‰ indicating variable conditions within the month. October shows a significant increase, especially with a value of 4.3‰, possibly indicating a warm spell or change in the source of precipitation. November average increases, highlighted by the high value of 6.1‰, suggesting possibly warmer temperatures or a change in moisture sources. December shows a dramatic decrease with a value of -25.2‰, indicating a significant change in weather, likely due to colder temperatures.

3.2 Results for Streamwater in Lyon Arboretum

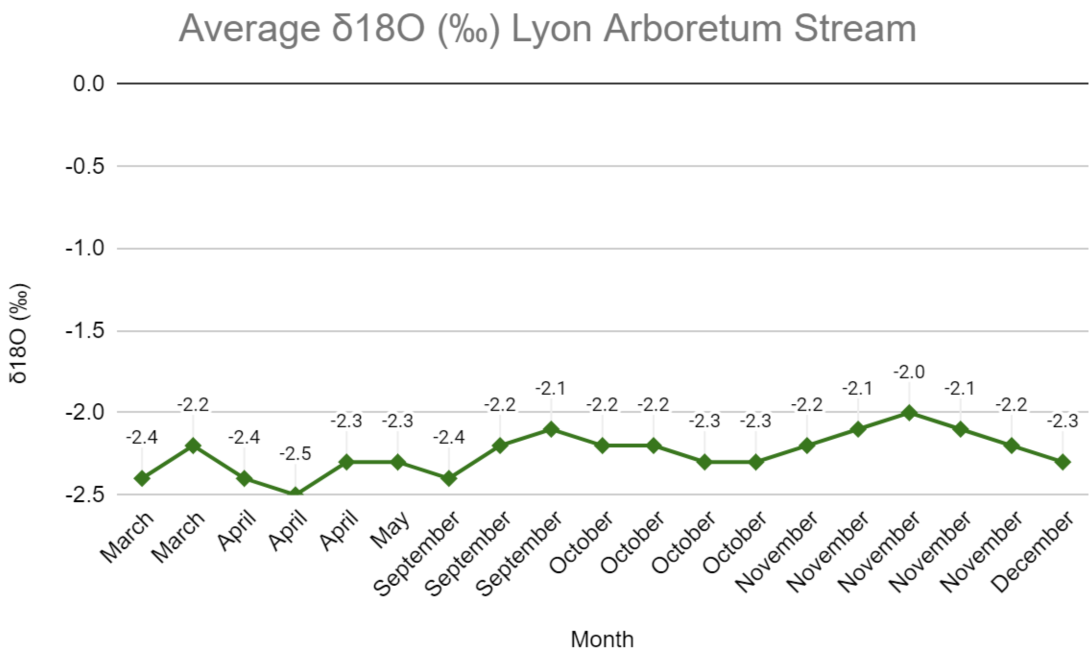

Figure 4. Average $\delta^{18}O$ of Lyon Arboretum Stream

The graph seen in Figure 4. represents the average values of $\delta^{18}O$ at the stream in Lyon Arboretum between March 2023 and December 2023, located at the upper end of Mānoa Valley in Hawaiʻi. The y-axis shows the $\delta^{18}O$ values per mil (‰). The x-axis represents the months from March to December 2023. Generally, $\delta^{18}O$ values in stream water can tell us about sources of water, evaporation effects, and seasonal variations in a watershed. Lower $\delta^{18}O$ values can indicate upstream sources with colder temperatures or higher precipitation inputs, while higher values can suggest evaporation effects or contributions from lower altitude or warmer sources. The $\delta^{18}O$ values start in March at around -2.3 ‰ and show slight variation throughout May. These consistently low values indicate a stable source of water, likely reflecting consistent rainfall or recharge from groundwater.

Between September and October, there is a slight increase in $\delta^{18}O$ values, though they remain relatively low (-2.1‰ to -2.4‰). This slight increase could be due to reduced rainfall, increased evaporation, or a change in the water source. The values in November slightly increase to around -2.1‰ but then decrease again in December to -2.3‰. The initial increase could be associated with the beginning of the winter season.

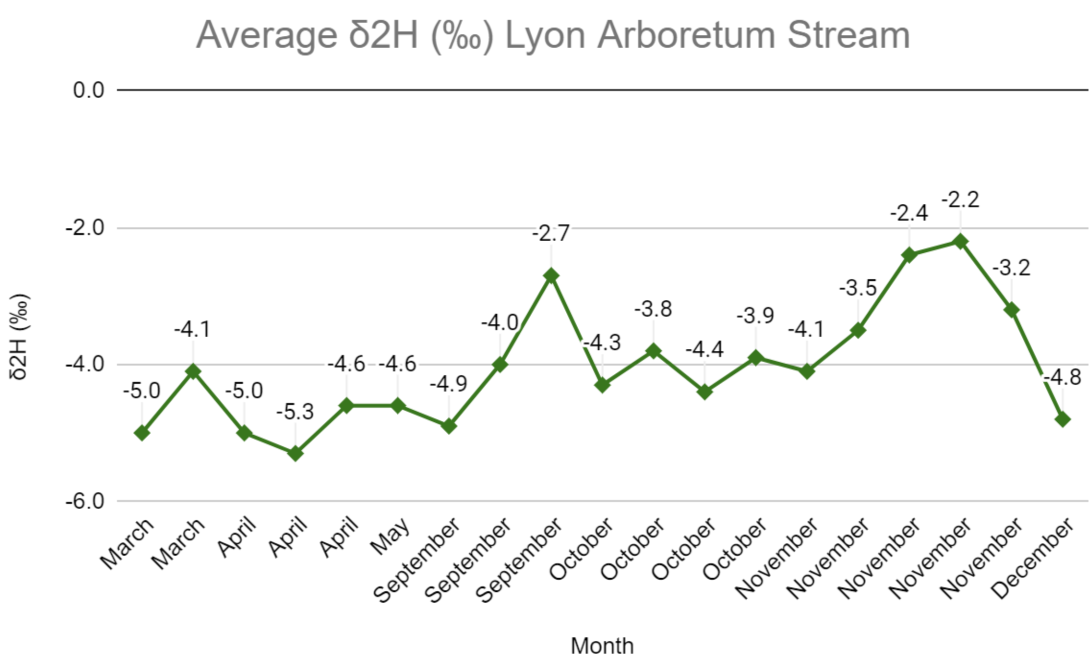

Figure 5. Average δ^2H of Lyon Arboretum Stream

Figure 5. shows the average values of δ^2H at the stream in Lyon Arboretum between March 2023 and December 2023, located at the upper end of Mānoa Valley in Hawaiʻi. The y-axis of the graph shows the δ^2H values per mil (‰). The x-axis represents

the months from March to December 2023. Typically, δ^2H (or deuterium) values in stream water can provide information similar to δ^{18}O values. High δ^2H values generally indicate less fractionation, which could be associated with warmer temperatures or less evaporation. In comparison, lower values indicate more fractionation, often associated with colder temperatures or higher evaporation rates.

From March to May, the δ^2H values are relatively consistent, ranging from -4.6‰ to -5.3‰, indicating a stable isotopic composition. In September, a noticeable range in δ^2H values from -2.7‰ to -4.9‰ indicates more variability. The values in October and November show some variation but generally indicate a trend towards less negative values, especially in November, where they reach up to -2.2‰. This trend could be associated with autumnal changes. In early December, the δ^2H values decrease again to -4.8‰, suggesting a return to conditions that favor more negative δ^2H values, likely due to colder temperatures, increased precipitation, or a combination of both.

3.3 Results for Precipitation at the University of Hawaiʻi at Mānoa

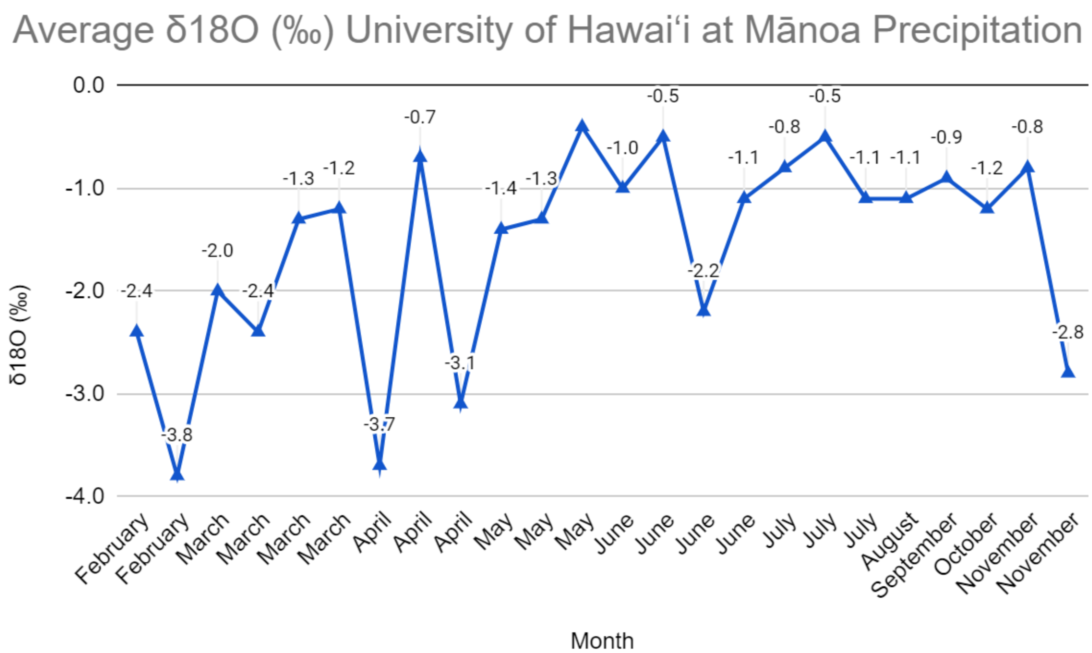

Figure 6. Average $\delta^{18}O$ of Precipitation at the University of Hawaiʻi at Mānoa

The graph in Figure 6. represents the average values of $\delta^{18}O$ in precipitation between February 2023 and November 2023 at the University of Hawaiʻi at Mānoa, located at the lower end of Mānoa Valley in Hawaiʻi. The y-axis shows the $\delta^{18}O$ values per mil (‰). The x-axis represents the months from February to November 2023. In February, there is a notable variation in $\delta^{18}O$ values, with an average that falls below zero, indicating a period of cooler temperatures or precipitation that has traveled far distances, typically associated with more intense weather systems. The values in March show less variability than in February but still range from -2.4‰ to -1.2‰. This could reflect transitional weather conditions as the region moves from winter to spring.

There is significant variation in April from -3.7‰ to -0.7‰, indicating a possible mix of weather patterns or changing sources of moisture, perhaps due to seasonal shifts impacting where precipitation originates. As we move to May, values become less negative, moving closer to zero, ranging from -1.4‰ to -0.4‰, suggesting warmer temperatures or less intense rainout processes as the season transitions towards summer. In June, a mix in values, from -2.2‰ to -0.5‰, indicates variable weather patterns, including possible passing storms or fluctuating temperatures. The $\delta^{18}O$ values are consistently less negative in July, indicating warmer temperatures and possibly more local or less fractionated sources of Precipitation.

August and September maintain values around -1.1‰ to -0.9‰, suggesting stable but slightly warmer climatic conditions typical of late summer. October shows a slight decrease in $\delta^{18}O$ values to -1.2‰, perhaps signaling the beginning of the transition to cooler weather. November exhibits a significant spread from -0.8‰ to -2.8‰, indicating potential variability in weather conditions.

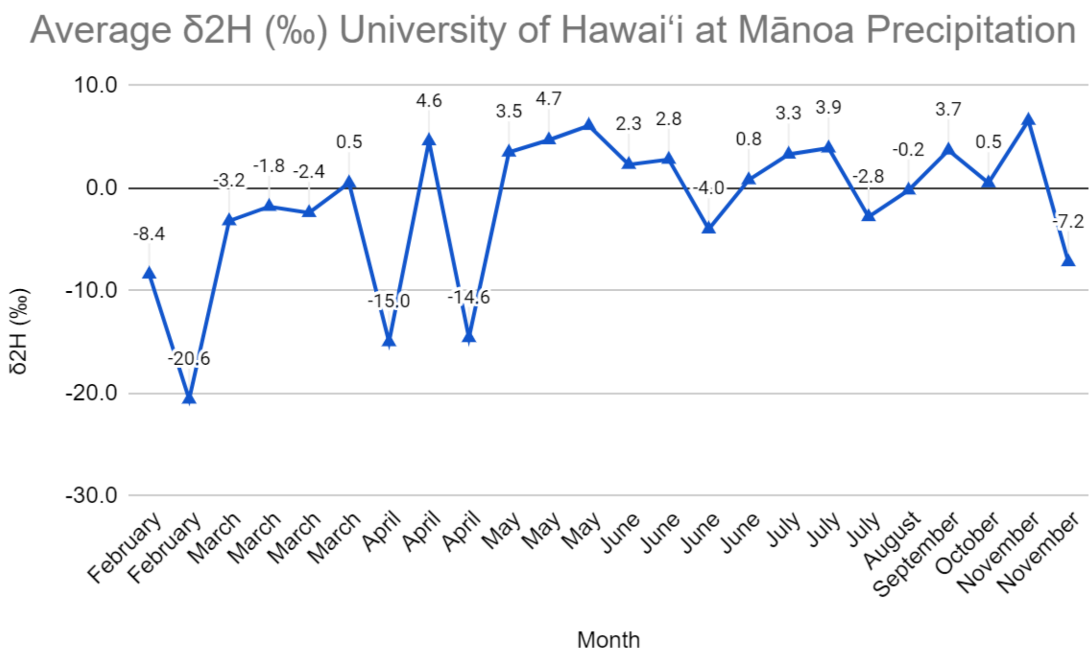

Figure 7. Average δ^2H of Precipitation at the University of Hawaiʻi at Mānoa

Figure 7. represents the average values of δ^2H in Precipitation between February 2023 and November 2023 at the University of Hawaiʻi at Mānoa, located at the lower end of Mānoa Valley in Hawaiʻi . The y-axis of the graph shows the δ^2H values in per mil (‰). The x-axis represents the months from February to November in 2023. February shows significant variability with δ^2H values ranging from -8.4‰ to -20.6‰. This could indicate a transition from colder, possibly more dynamic weather patterns. In March, a wide range of δ^2H values from 0.5‰ to -3.2‰ suggests variability in precipitation sources or weather conditions within the month. April also displays a considerable range with values from -15.0‰ to 4.6‰, highlighting significant fluctuations in weather conditions or isotopic composition of incoming moisture. The high variability could reflect changing atmospheric conditions as the season transitions from spring to summer.

May trends towards higher δ^2H values (3.5‰ to 6.1‰), suggesting warmer temperatures and potentially less rainout during precipitation formation. This indicates a likely shift to typical warmer, late spring to early summer conditions. June contains positive and negative values (-4.0‰ to 2.8‰), indicating varied weather conditions. Positive and negative values could reflect transitional weather patterns or intermittent rain events. July generally shows higher δ^2H values from 3.3‰ to 3.9‰, with one notable drop to -2.8‰, suggesting warm conditions with a possible brief return to cooler or more intense precipitation events. August presents a slightly negative value (-0.2‰), indicating stable conditions as summer progresses. September returns to higher δ^2H values (3.7‰), consistent with late summer weather patterns that might be warmer and drier. October shows a value of 0.5‰, suggesting continued warm conditions with potentially decreased precipitation intensity or frequency. November exhibits a significant range from 6.6‰ to -7.2‰, a dramatic shift in conditions, possibly from an extended period of warmer weather to a sudden onset of cooler weather.

3.4 Results for Streamwater at the University of Hawaiʻi at Mānoa

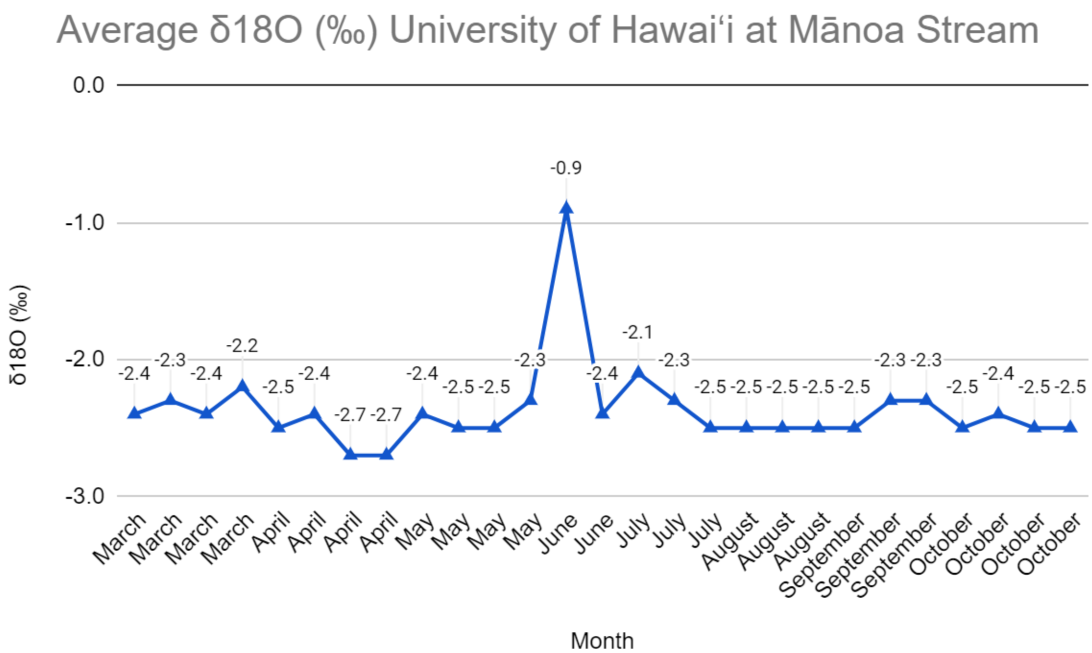

Figure 8. Average δ^{18}O at the University of Hawaiʻi at Mānoa Stream

Figure 8. shows the average values of δ^{18}O at the University of Hawaiʻi at Mānoa Stream between March 2023 and October 2023. The stream is located at the lower end of Mānoa Valley in Hawaiʻi and is part of the same river as the Lyon Arboretum stream. The y-axis of the graph shows the δ^{18}O values per mil (‰). The x-axis represents the months from March to October in 2023. From March to May, the δ^{18}O values are consistently negative, fluctuating between -2.5‰ and -2.2‰. This suggests a stable isotopic composition likely influenced by regular precipitation patterns typical of the spring season in Hawaiʻi. The consistency could indicate a continuous supply from similar sources.

A noticeable anomaly occurs in June, where $\delta^{18}O$ values show a significant split (-0.9‰ and -2.4‰). This divergence could indicate a sudden change in water source or atmospheric conditions. From July to October, the $\delta^{18}O$ values return to a more stable and consistently negative range between -2.1‰ and -2.5‰. This period likely represents the influence of consistent weather patterns, such as the typical summer to early autumn conditions in Hawaiʻi, characterized by steady rainfall contributing to the stream or consistent recharge from groundwater.

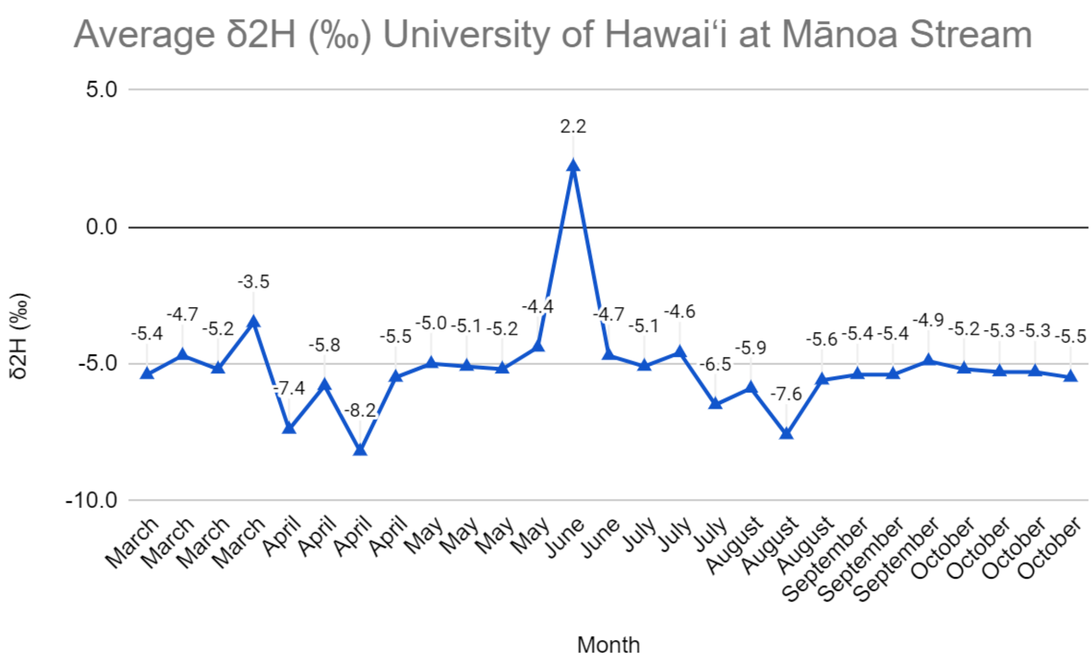

Figure 9. Average $\delta^{2}H$ at the University of Hawaiʻi at Mānoa Stream

Figure 9. shows the average values of $\delta^{2}H$ at the University of Hawaiʻi at Mānoa Stream between March 2023 and October 2023. In March, the $\delta^{2}H$ values range from -5.4‰ to -3.5‰, indicating relatively consistent and slightly negative values typical for stream water influenced by local rainfall in cooler conditions. The spread suggests slight

variability in weather conditions or water sources during this time. There is a notable dip in δ^2H values in April, ranging from -8.2‰ to -5.5‰, which could indicate a change in weather conditions and potentially cooler temperatures. May's values slightly increase compared to April but remain consistently negative (-5.2‰ to -4.4‰), suggesting stabilization of the water source with conditions similar to March.

A significant anomaly appears in June with one value at 2.2‰, markedly different from all other negative monthly averages. This anomaly could indicate a drastic change in the stream's water source or conditions, such as reduced rainfall leading to increased evaporation and enrichment of heavy isotopes or mixing with another water source with high δ^2H values, possibly groundwater. The June anomaly could also possibly be due to an analysis error. From July to October, the δ^2H values return to a more stable, negative range from -6.5‰ to -4.6‰, which suggests the re-establishment of more typical hydrological conditions after the anomaly in June.

4.0 DISCUSSION

4.1 Precipitation at Lyon Arboretum

December and February, considered winter season in Hawaiʻi, have notable low δ^{18}O values, especially the -6.0‰ in February, aligning with typical winter conditions. The wide range in February indicates variability, possibly due to fluctuating temperatures or different storm tracks affecting the region. From March to May, the δ^{18}O values gradually increase from winter into spring, which is expected as temperatures rise. They remain relatively low, reflecting the continuing influence of cooler temperatures and spring rains, typical as the season transitions from the colder winter months. Between June and August, there are fewer negative δ^{18}O values, likely representing more local evaporation contributing to precipitation. The slight decrease in δ^{18}O values from September to November indicates cooler temperatures and the possible transition into the wetter, cooler season.

Nevertheless, a 0.0‰ value in October and November suggests significantly different weather conditions, possibly warmer spells due to late-season heatwaves or atypical moisture sources, like evaporated water from a warm local source. The sharp decrease to -4.6‰ in December is notable because it suggests a significant change back to colder conditions, more intense than the usual seasonal shift might indicate. This could be due to a sudden cold spell or a shift in weather patterns bringing colder, more isotopically depleted air masses to the region.

The data illustrates a clear seasonal cycle, with colder, possibly drier months showing more negative δ^{2}H values and warmer, potentially wetter months showing higher values. This cyclical nature is typical due to the seasonal changes in temperature, atmospheric circulation, and precipitation sources. The extreme values in February and December stand out and could be attributed to specific weather events or shifts in the typical patterns, such as cold fronts or oceanic moisture sources. These anomalies could be further investigated to understand their causes and implications for local weather and climate patterns.

While δ^2H values provide valuable insights into precipitation and climate, interpreting these values requires context, such as local temperature records, atmospheric circulation patterns, and changes in sea surface temperatures, which can all influence isotopic composition. Also, factors like evaporation, condensation, and transportation of water vapor can significantly affect δ^2H values, leading to month-to-month variability.

4.2 Streamwater at Lyon Arboretum

The stream's isotopic composition remains relatively stable across the months, with only slight variations. This stability suggests a consistent hydrological regime, possibly dominated by groundwater inflows. There is a minor seasonal effect on δ^{18}O values, with slightly higher values during the warmer months and lower values during the cooler months. This aligns with general patterns of isotopic fractionation due to temperature. Unlike precipitation, which can show significant variability in δ^{18}O values due to rapid changes in weather conditions, the stream values are more stable. This suggests that the stream integrates water over a larger area or time. The absence of significantly higher δ^{18}O values throughout the year could indicate that the stream does not experience significant evaporation, which would enrich δ^{18}O in the remaining water.

The data lacks significant spikes or drops that would indicate dramatic shifts in the water source, such as a sudden switch to a significantly different groundwater source, a large-scale change in land use, or a significant climatic event. This consistency suggests that the stream's catchment area is relatively stable and not subject to rapid changes in land cover or hydrology. There is an apparent seasonal influence on the δ^2H values, with more negative values in the colder months (March, April, May, and December) and less negative values during the warmer months or transition periods (September, October, and November). The wide range of values in September stands out, possibly indicating a transition period where varying weather conditions and water sources impact the stream's isotopic composition.

The wide range of values could reflect unusual weather events, such as a dry spell followed by heavy rain. While a trend towards less negative values in autumn could be expected due to natural seasonal changes, the extent of this change, particularly the values as high as -2.2‰ in November, could be considered anomalous. This suggests that additional factors may be at play, such as unusually warm weather, increased contribution from a different water source, or significant changes in the surrounding environment.

4.3 Precipitation at the University of Hawaiʻi at Mānoa

There is an evident seasonal influence on the δ^{18}O values, with more negative values typically observed in the cooler months and less negative values during the warmer summer months. The transitional months (March, April, and November) exhibit considerable variability in δ^{18}O values. The significant variation in April, from -3.7‰ to -0.7‰, stands out as a potential anomaly. This range suggests a sudden change in weather conditions within the month, such as an abrupt transition from a late cold front to typical tropical conditions or varying sources of moisture affecting the region. Similarly, November shows a wide range from -2.8‰ to -0.8‰. This could indicate an unusual weather event, such as an early cold snap or late-season tropical influence, leading to a significant shift in the isotopic signature of Precipitation within the month.

While not an anomaly per se, the relatively stable $\delta^{18}O$ values from May to September could reflect a particularly uniform climate during this period, which is somewhat unusual given the typical variability associated with island weather patterns. This steadiness might be worth exploring in the context of more significant climatic trends or anomalies affecting the region. The substantial spread of $\delta^{2}H$ values from -8.4‰ to -20.6‰ in February stands out.

While February is typically cooler, such a wide range suggests that there might have been a mix of local and distant precipitation sources or an unusual climatic event affecting the area's weather patterns. April's $\delta^{2}H$ values range from -15.0‰ to 4.6‰, which signifies significant weather variability. This could be due to an unusual sequence of weather events, such as an atypical cold front. The range from 6.6‰ to -7.2‰ in November is particularly noteworthy. Such a range suggests a drastic shift in weather conditions during the month, which could be associated with late-season tropical activity or sudden changes in temperature and moisture sources.

4.4 Streamwater at the University of Hawaiʻi at Mānoa

The less negative values in June could suggest a period where groundwater, with a different isotopic composition than typical rainwater, could potentially contribute more significantly to the stream. If the local groundwater has been subject to fewer fractionation processes than rainwater, it would have a higher δ^{18}O value, which, when mixed with stream water, could raise the stream's overall δ^{18}O average for that time. The consistent isotopic values outside of June suggest that direct precipitation dominates the stream's input during those months. However, the role of groundwater might still be overshadowed by the more significant volume of rainwater. Groundwater typically exhibits less seasonal variation than surface water which can moderate temperature fluctuations and isotopic composition changes.

Groundwater can contribute to streams in various ways, particularly in volcanic regions like Hawaiʻi, where geological formations can significantly influence water movement. During periods of less rainfall, such as the anomaly seen in June, the proportion of groundwater flow into the stream may increase, altering the stream's isotopic signature. Both stream locations, Lyon Arboretum and the University of Hawaiʻi at Mānoa, should exhibit similar seasonal consistencies in isotopic values if they are primarily influenced by local precipitation. The differences between the two locations may indicate varying microclimatic conditions, different catchment areas, or varying degrees of groundwater influence. The June anomaly in the University of Hawaiʻi at Mānoa stream location δ^{2}H values can be contrasted with Lyon Arboretum's stream data for the same period.

If no similar anomaly is observed in the Lyon Arboretum data, it could suggest that localized factors affecting the Mānoa stream, such as urban runoff, irrigation, or specific watershed characteristics, are not impacting the Lyon Arboretum stream that is located higher up in the valley. Suppose the Lyon Arboretum stream location lacks similar anomalies and maintains a stable isotopic composition. In that case, it might suggest less evaporation influence or a more negligible groundwater contribution than the University of Hawaiʻi at Mānoa stream. This makes sense because Lyon Arboretum receives more precipitation. An absence of the June spike in δ^2H values at Lyon Arboretum highlights different environmental impacts or evaporation rates. This could be due to differences in vegetation cover, stream flow rates, or anthropogenic influences.

5.0 CONCLUSION

This thesis explores the isotopic composition of rainwater and streamwater in the distinct catchment area of Mānoa, Hawaiʻi, aiming to understand the dynamics of local water cycles and the influence of various hydrological processes. Through weekly sampling and analysis from February to December 2023, this study provides insights into the interplay between precipitation and streamflow within this unique hydrological setting. The results indicate clear seasonal patterns in the isotopic composition of rainwater and streamwater, aligning with expected changes due to local climatic conditions. Notably, the isotopic signatures of rainwater and streamwater varied consistently with seasonal shifts, reflecting the typical meteorological patterns of Mānoa, Hawaiʻi.

The isotopic analysis of rainwater revealed distinct seasonal patterns, with δ^{18}O and δ^{2}H values fluctuating by temperature variations and precipitation intensity. Notably, the rainwater isotopic signatures also highlighted possible influences of trade winds and storm events, which are crucial in shaping the local climate and, consequently, the isotopic composition of precipitation. Anomalies are observed from the data, such as the unusual δ^{2}H values observed in June for the stream at the University of Hawaiʻi at Mānoa, suggesting potential shifts in water sources or processes during this period. When compared to the data from the Lyon Arboretum Stream, differences and similarities in isotopic signatures highlight the complex nature of hydrological responses within the same geographic region. These comparisons have shed light on the factors influencing isotopic variations, such as elevation, and rainfall patterns.

The findings from this research contribute to a deeper understanding of the hydrological cycle in Hawaiʻi, emphasizing the importance of isotopic studies in unraveling the nuances of water movement and distribution. The anomalies detected underscore the need for ongoing monitoring and investigation to discern the underlying causes and their implications for water resource management. Collecting and analyzing rainwater at Lyon Arboretum and the University of Hawaiʻi at Mānoa will continue to look at long-term averages every week.

LITERATURE CITED

Clark, I.D., and Fritz, P. (1997). Environmental Isotopes in Hydrogeology. CRC Press.

Dansgaard, W. (1964). "Stable isotopes in precipitation." Tellus, 16(4), 436-468.

Gat, J.R. (1996). "Oxygen and hydrogen isotopes in the hydrologic cycle." Annual Review of Earth and Planetary Sciences, 24, 225-262.

Giambelluca, T. W., et al. (2013). "Online Rainfall Atlas of Hawai‘i." Bulletin of the American Meteorological Society, 94(3), 313-316. doi:10.1175/BAMS-D-11-00228.1.

Giambelluca, T. W., et al. (2014). "Evapotranspiration of Hawai‘i." Final Report prepared for the Commission on Water Resource Management, Department of Land and Natural Resources, State of Hawai‘i. Retrieved from https://evapotranspiration.geography.hawaii.edu/.

Jouzel, J., Alley, R.B., Cuffey, K.M., Dansgaard, W., Grootes, P., Hoffmann, G., Johnsen, S.J., Koster, R.D., Peel, D., Shuman, C.A., Stievenard, M., Stuiver, M., and White, J. (2003). "Millennial-scale climate instability during the last glaciation." Science, 299(5615), 2001-2004.

McDonnell, J. J. (1990). A rationale for old water discharge through macropores in a steep, humid catchment, Water Resources Research, 26(11), 2821–2832, doi:10.1029/wr026i011p02821.

Oki, D. S., et al. (2015). "Long-term Groundwater Resource Management Plan for the Honolulu Volcanic-Rock Aquifer, Island of O‘ahu, Hawai‘i." U.S. Geological Survey Scientific Investigations Report 2014–5156. doi:10.3133/sir20145156.

Rozanski, K., Araguás-Araguás, L., & Gonfiantini, R. (1993). "Isotopic patterns in modern global precipitation." In Climate Change in Continental Isotopic Records (pp. 1-36). American Geophysical Union.

Torri, G., Nugent, A. D., & Popp, B. N. (2023). The isotopic composition of rainfall on a subtropical mountainous island. Journal of Hydrometeorology, 24(4), 761–781. https://doi.org/10.1175/jhm-d-21-0204.1.