Chemical Analysis of Rain and Stream Water 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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To my dad, Tracey Tamura, my mom, Jacqueline Tamura, my siblings, and the rest of my family.

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ABSTRACT

Understanding the relationship between precipitation and stream water is essential for identifying if the freshwater bodies meet water quality standards. Identifying the source is important to understand water pathways, for example whether rainwater travels over the surface to the stream, or by leaching into groundwater first. Precipitation and stream water chemistry has been widely studied across the continental United States but little or no research exists regarding a tropical catchment system and the complex relationship that this system might have. Therefore, rainwater and stream water samples were collected weekly and analyzed using Ion Chromatography to find the concentration (mg/L) of each major ion in the sample. The analysis of precipitation and stream water in a tropical climate can add to the understanding of water quality including which processes contribute to water quality standards. The abundant ions identified were chloride, sodium, magnesium, sulfate, and calcium. Chloride and sodium were dominant in both rain and stream water samples, leading to the assumption that the rainwater was mostly sourced from marine aerosol. Scatter plots and the Pearson Correlation Coefficient were used to compare ions against each other to understand how rainwater contributes to streams chemically and where potential sources are located. Determining the relationship between the major ions can identify what activities lead to higher concentrations of the ions which can impact long-term water quality. This study has analyzed the chemical interactions in a tropical catchment system and underscores the critical role of rainfall and stream water interactions and their influence on water quality.

Keywords: Major ions, rainwater, stream water, Mānoa, Hawaiʻi.

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1.0 INTRODUCTION

Understanding the interconnectedness of precipitation and stream water is critical for managing this essential natural resource of fresh water. In Hawaiʻi, the combination of its tropical climate, terrain, and volcanic geology creates a unique environment and hydrological network. Runoff and stream flow that begins at the peak of the mountain range travels through the catchment, eventually emptying into the ocean. As precipitation reaches the ground, it can enter the stream or leach into the groundwater. The chemical composition of both rainwater and stream water can determine changes in environmental conditions such as water quality.

The hydrological cycle in Hawaiʻi is unique because of the island's geography and tropical climatology. Due to its geographical location, the Hawaiian Islands experience a tropical lowland climate that is humid and have minimal snowfall that only occurs above an altitude of 2,000 m (Lau & Mink, 2006). In Hawaiʻi, freshwater is found as atmospheric water vapor, rainwater, surface water, and groundwater, where this freshwater will recharge the island's aquifers and drinking water supply for the island's population (Lau & Mink, 2006). This cycle is dynamic, with water transported across vast distances. It begins with ocean water which evaporates, rises to lower atmospheric pressures, cools, and condenses, forming clouds that release rain through various precipitation processes. Rainfall occurs as orographic precipitation, convective precipitation, or frontal precipitation which all contribute to rain rates and patterns across the island (Lau & Mink, 2003). Some rainfall infiltrates the ground, recharging aquifers, and streams, while the rest may evaporate or run off over the surface (Oki, 2003). Notably, all streams and groundwater eventually drain back into the ocean where the cycle will repeat (Lau & Mink, 2006). Since all water eventually reenters the ocean, protecting and maintaining water quality in streams and groundwater is vital for protecting coastal ocean health.

1.1 Major Ion Dynamics

Water quality can be affected by the concentration of major ions, which are the dissolved materials found in water. These solutes often originate from the atmosphere, soil, rock weathering, or different biological processes (Webster & Valett, 2006). The most abundant cations in fresh water include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}) and the most abundant anions include bicarbonate (HCO_3^{-}), chloride (Cl^{-}), and sulfate (SO_4^{2-}) (Bartos & Muller Ogle, 2002). The variability within the concentration of these combined cations and anions can influence the health of a water body. For example, sodium and chloride are two common ions found in water and can increase salinity making the water unpleasant to taste and can impact freshwater species' ability to live in a high salinity environment (Lau & Mink, 2006). Another example is calcium, whose source is usually traceable to degradation and weathering of rocks (Bird et. al., 2018). High concentrations of calcium can form calcium scale buildup in pipes and reduced water flow. These ions are crucial to track as they can indicate the potential sources of these ions that can impact human health and aquatic ecosystems.

Analyzing how solutes, like the ones mentioned above, move, and interact with an ecosystem can assist in determining their interaction with the environment and can identify where majority of these ions come from. Solute dynamics encompass the transport, transformation, and interactions between each solute and its environment. Water is a major contributor to the transport of solutes in a catchment where advection, dispersion, and diffusion can influence where solutes go (Lau & Mink, 2006). An efficient transport system of solutes can govern nutrient availability and ecosystem productivity. If this system is inefficient, the natural balance that exists within a water body is then disrupted, resulting in an unhealthy ecosystem. However, defining a "healthy" ecosystem is not straightforward and depends on each environment and the factors that are in play in that area such as the type of species, population size, and location (Bird et. al., 2018). This complex interplay determines how these solutes move through the environment, shaping the ecosystem's health.

1.2 Precipitation Traits on Oʻahu

While tracing solute dynamics unveils the sources of major ions, understanding Oʻahu's distinct precipitation patterns reveals much more about how these solutes enter and travel through the hydrologic system. Precipitation on Oʻahu can be characterized by its spatial variability, intensity, frequency, and chemical composition. On the windward side of the island, the areas to the east of the Ko'olau mountain range experiences a magnitude of rainfall greater than the leeward, or west side of the island, annually (Giambelluca, 1986; Lau & Mink, 2006; Hartley & Chen, 2010). This heavier rainfall is caused by orographic precipitation and leeward areas experience substantially less rainfall due to a rain shadow effect. Oʻahu usually experiences short, intense bursts of rainfall, especially during convective precipitation events, and can be seasonally dependent (Lau & Mink, 2006). Higher rainfall rates occur in the winter season due to increased Kona lows, tropical cyclones, upper-level troughs, and cold-fronts (Kodama and Barns, 1997; Longman et al., 2021).

The primary driver of O‘ahu’s precipitation is persistent northeasterly trade winds that propel orographic precipitation in windward areas (Brennis et. al., 2023). These trade winds act as efficient carriers of both marine and non-marine aerosols, contributing to the ion concentration found in the hydrologic cycle. Three dominant sources of the major ions in precipitation include terrestrial dust, marine sea salt aerosols, and anthropogenic activity. Rock weathering contributes to terrestrial dust that enters the atmosphere through aeolian transport (Brennis et. al., 2023). Marine sea salt aerosols are created by bubbles bursting at the ocean’s surface due to waves breaking (Ackerman et. al., 2023). Anthropogenic sources include the combustion of fossil fuels, industrial processes, and agriculture, which all can impact ion concentration in rain (Brennis, et. al., 2023). These different sources shape the solute composition of O‘ahu’s precipitation, and it is critical for effectively managing this vital resource.

Managing and tracking rainfall has become easier over time with the advancement of technology including satellite remote sensing, weather radars, and *in situ* measurements with rain gauges that can record rainfall rates (Lau & Mink, 2006). These advancements have helped in improving accuracy in predicting and monitoring rainfall and increasing real-time data of rainfall rates which is important for weather forecasting, flood prevention, and water-resource management. However, due to variability in rainfall, consistent water quality testing is not always possible. Majority of the State’s monitoring programs are focused on coastal and inland waterways rather than directly collecting rainfall samples.

1.3 Stream Water Traits on O‘ahu

As precipitation falls, it enters the complex network of streams contributing to the stream’s chemical makeup. The protection and management of stream water resources is an important issue due to the concern for accessibility to clean water resources. Streamflow accounts for all the water that accumulates and travels in a stream channel (Lau & Mink, 2006). Both direct surface runoff and groundwater discharge contribute to the volume of streamflow. The volume of direct surface runoff depends on the intensity and persistence of rain, and the size, geology, and morphology of the catchment (Lau & Mink, 2006). While precipitation contributes to streamflow, groundwater discharge is often the main source of baseflow of the stream and can contribute to the overall ion concentration (Lau & Mink, 2006).

Protecting and managing stream water on O‘ahu is essential for maintaining the hydrologic cycle, minimizing pollution, and ensuring the responsible use of water. Over time, erosion can alter stream paths, and human activities like irrigation diversions can impact flow and change the stream water’s chemical composition. Like precipitation, major ions that are found in stream water are sourced from the weathering of volcanic rocks, atmospheric deposition, and marine aerosols (Lau & Mink, 2006). Understanding the sources and dynamics of the abundant ions is critical for managing stream water resources. Monitoring these chemical constituents can provide insight into the health of the waterways and therefore the ability to implement effective strategies that will limit high fluxes of ions and keep the stream water within water quality standards.

1.4 Previous Work

Determining the relationship and interaction between precipitation and streamflow chemically can help in understanding pollutant transport and assessing water quality. Similar studies have focused on precipitation and stream water chemistry variability throughout the year mostly in the continental U.S. and some European countries (Feller, 2010; Stottlemyer & Toczydlowski, 1996; Sutcliffe & Carrick, 1983). However, there have not been similar studies conducted in Hawaiʻi that compare the ion concentrations in rain and streams using correlations. One similar study that compared both rain and stream water was done by Shanley et al., in 2011 and found that during rainfall events, as stream flow increases, stream chemistry shifts towards rainfall composition (Shanley et al., 2011). Another study focused on the source of precipitation for Oʻahu was conducted in 2023 and found that the major source of the precipitation originates as sea spray through sea salt aerosol correction, crustal and marine enrichment factors, regression analysis, and principal component analysis (Brennis, et. al., 2023). However, that study did not include stream water in its analysis and focused solely on precipitation. This study will focus on how precipitation contributes to streamflow chemically to identify potential sources of the major ions through graphical and mathematical analysis.

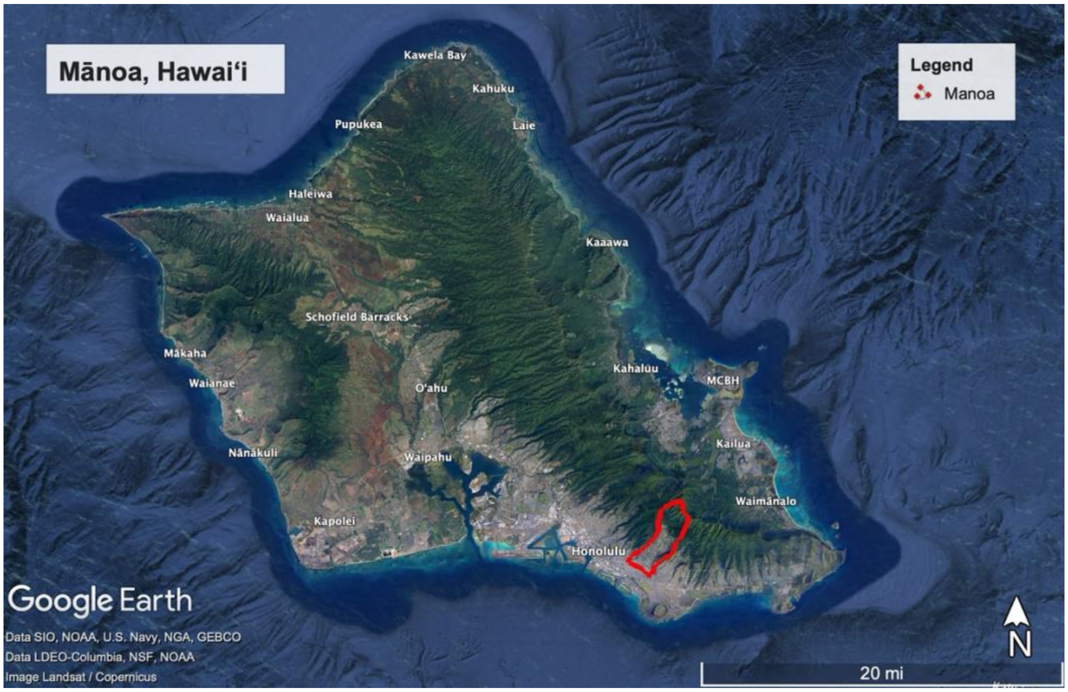
2.0 METHODS

2.1 Mānoa catchment

On the island of Oʻahu, the Mānoa catchment situated to the north of Waikīkī, has an area of 11 km^2 and receives an annual maximum rainfall of 3,900 mm and a minimum rainfall amount of 1,000 mm (Huang & Tsang, 2017). Mānoa is situated in the South of Oʻahu, on the leeward slope of the Koʻolau mountain range. Although Mānoa is on the leeward side of the Koʻolau Range, it experiences more annual rainfall compared to the catchments on the leeward side of the Waiʻanae mountain range because of its local wind patterns and location adjacent to the Koʻolau Mountains. The town comprises forest reserves, residential areas, educational institutions, and urban areas, which influence the input of pollutants into the atmosphere and stream flow. With more urban runoff, the potential of non-point source pollution increases because there are more impervious surfaces, buildings, and denser populations. These decrease the infiltration of rainwater into the ground and allow the rainwater to travel over impervious surfaces and collect pollutants on the way to the stream. Mānoa stream was studied because it is a major contributor to the Ala Wai Canal. Lyon and Campus are both situated adjacent to the Mānoa stream allowing for easy access for weekly sampling. The Mānoa catchment was chosen due to its abundant rainfall inside the valley, its complex network of streams, and its accessibility to areas where measurements could be made.

2.2 Sampling sites

Samples were obtained approximately weekly at two sites for both rain and stream water. The two sites included the Harold L. Lyon Arboretum (Lyon) and the University of Hawaiʻi at Mānoa's campus (Campus). At Lyon, the rain sampler was in a grass area and attached to a 4 ft metal pipe. The pipe was used to elevate the rain sampler off the ground to avoid any contamination when landscaping activities occurred in the area. The Lyon Stream site was in a forested area where the stream ponded before continuing to flow downstream. At Campus, the rain sampler was located on the roof of the Hawaiʻi Institute of Geophysics (HIG) building with no overhead obstructions. The Campus Stream site was adjacent to the Japanese Garden at the East-West Center. This stream site had a heavy coverage from trees and has a hiking trail that runs along the stream. Lyon is more secluded and located higher in the valley, experiencing more rainfall and fewer human interactions. Whereas Campus is in a highly trafficked area with commuters traveling throughout the area daily.



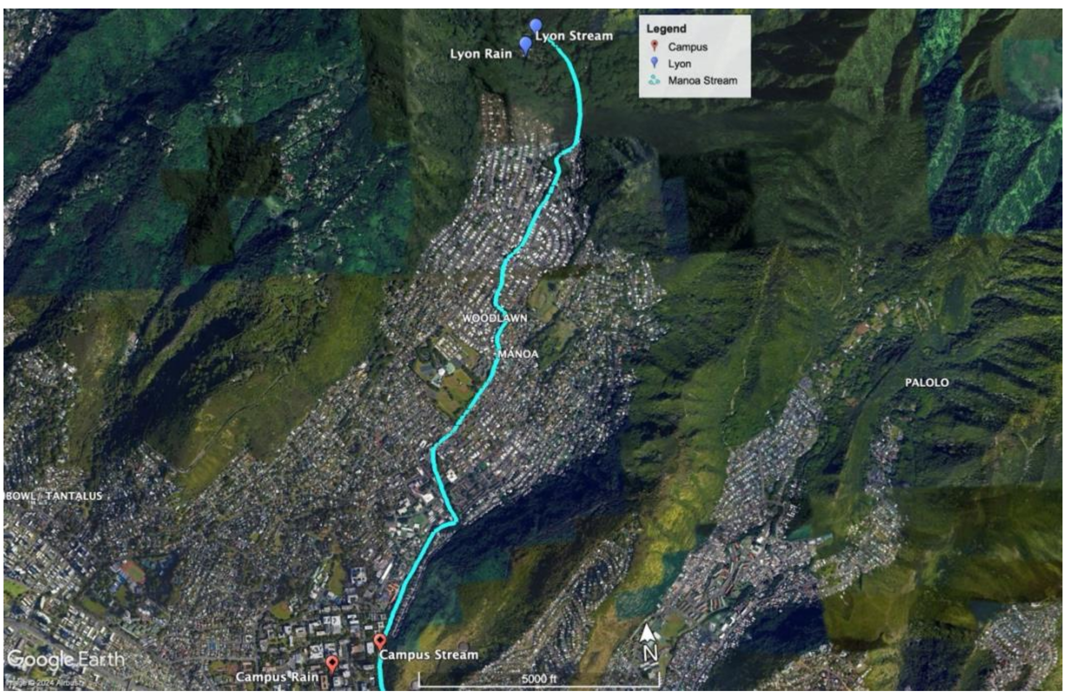


Figure 1: Map of Sampling Sites

Mānoa catchment outlined in red (top). Mānoa Stream outlined in light blue. Lyon sampling locations (blue pin) and Campus sampling locations (red pin).

2.3 Rain and Stream Water Sample Collection

The frequency of sampling was approximately weekly for both sites and sample types, which occurred from February 2023 to February 2024. This frequency was determined after doing three weeks of sampling twice a week, where it was found that sample concentrations were similar between sampling dates, and most of the time there wasn't enough rainwater collected for lab analysis to be conducted. The rainwater played a role in determining the frequency of sampling because of the infrequency of water volume collected. Whereas the stream would always have enough water to sample, it was difficult to know if there would be enough rainwater to sample twice or more times a week. It was assumed that weekly sampling was sufficient for capturing an average ion concentration for that week and allowed for enough rain to be collected for sampling to occur.

Rainwater samples were collected using two Palmex Ltd. Rain Samplers. The Rain Sampler is designed for collecting rainwater for laboratory analysis and avoids re-evaporation. Avoiding evaporation is critical for ensuring that the rain collected has an accurate representation of the ions present in the sample. If rainwater was allowed to evaporate, it could change the ion concentration and impact the results. Rain buckets were exchanged weekly and weighed before preparing a 15 mL test tube with the samples. A 10-cc syringe was rinsed three times with deionized (DI) water and a 0.2 µm hydrophilic polypropylene (GHP) Acrodisc 13 mm diameter filter was attached to the syringe. The rainwater was poured from the Rain Bucket into the syringe and then the sample was pushed through the filter into a rinsed 15 mL test tube. Test tubes were rinsed with DI water. Most times especially in the Campus Rain Bucket, rain rates were very low resulting in a low volume of rainwater collected. For rainwater samples, about 5 mL to 15 mL was collected, depending on accumulated rainfall during the previous week. The minimum sample volume for ion chromatography analysis is 5 mL.

Stream samples were collected from Mānoa Stream at Lyon and further downstream at Campus. The 15 mL test tube and 10 cc syringe were rinsed with DI water before sampling occurred. Stream water was collected using a rinsed 15 mL test tube and filled to the top. Samples were filtered about an hour after initial collection to let larger particles settle at the bottom of the test tube. The stream water was filtered the same as the rain samples. About 10 mL of filtered stream water was collected in another rinsed 15 mL test tube for both sites.

2.4 Lab Analysis

Rain and stream samples were analyzed at the Water Resources Research Center (WRRC) Environmental Chemistry Lab. The ions that were analyzed include fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), bromide (Br^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), lithium (Li^+), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}). Ion chromatography was used to determine the major inorganic ion concentration in all the rain and stream samples. A Dionex AS-DV autosampler was used to prepare 25 L of the sample to load into two Dionex Aquion ion chromatographs. Dionex IonPac AS22 column with 4.5 mM sodium carbonate and 1.4 mM sodium bicarbonate was used to separate anions. The cations were separated on a Dionex IonPac CS12A column with 20 mM methanesulfonic acid. The ambient temperature remained around 23°C and separation was conducted at flow rates of 1.2 and 1.0 mL per minute for both anions and cations. AERS 500 Carbonate suppressor was used for eluent suppression. It was operated at 41 mM for anions and cations, the CDRS 600 suppressor was used at 59 mM. The detection of anions and cations was done through conductivity and cell temperature, which was maintained at 35°C.

2.5 Pearson Correlation Coefficients and Scatter Plots

The Pearson correlation coefficient, *r*, was calculated for each of the four sampling sites to determine the linear relationship between each of the abundant major ions (1). First, the major ions in rain and stream were compared at the same location to determine how rainfall contributes to the stream chemically. Then, each abundant major ion was compared to each other in the following way: sodium and chloride, magnesium and chloride, sulfate and chloride, calcium and chloride, magnesium and sodium, calcium and sodium, sulfate and sodium, calcium and magnesium, and sulfate and magnesium. This calculation can quantitatively determine the co-variation of ion concentrations at each site. The *r*-value ranges from -1 to +1. Positive correlations indicate that as the concentration of one ion increases, the other ion tends to increase as well. A negative correlation suggests an inverse relationship where if one ion increases, the other ion tends to decrease. Values that are closer to 0 suggest a weak or no linear relationship between the two variables compared. Analyzing the correlation coefficient allows for a comparative assessment of the association between each abundant major ion. This can reveal variability or consistency of the concentrations of each ion across various environmental settings.

$$r = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 (y_i - \bar{y})^2}} \quad (1)$$

2.6 Daily Variations and Weather

Throughout the study, rainfall data was measured daily at Campus and published by the UH Mānoa Atmospheric Sciences Weather Data group (UH Mānoa Atmospheric Sciences Weather Data). Lyon rainfall data was published by Longman et. al., for the Hawaiʻi Climate Data Portal (Longman et al., 2024). Observations of the current weather and forecast discussions were noted when collecting samples. Cloud cover, current conditions, water depth (Lyon only), and water clarity were considered as well. Sample collection spanned one year, from February 2023 to February 2024, resulting in 30 samples analyzed for Lyon and Campus Stream, 20 samples for Lyon Rain, and 11 samples for Campus Rain. Sampling paused for the summer from May to August. All available samples were analyzed for Lyon and Campus Stream. However, 4 sampling days were missed for Lyon Rain and 14 sampling days were missed for Campus Rain because of little or no rainfall in the prior day.

3.0 RESULTS

The purpose of this study was to determine the relationship between stream water and rainwater in the Mānoa catchment. Complete results from the laboratory analysis, including sampling dates, are listed in the appendix. The ion concentrations were measured in milligrams per liter (mg/L).

3.1 Daily Rain Rate

At Campus, there were a total of 375 days recorded and 203 of those days resulted in 0” of rain (UH Mānoa Atmospheric Sciences Weather Data). The maximum daily rainfall recorded at Campus was 2.05” of rain over the study duration. At Lyon, out of the 375 days throughout this study, 116 days were recorded as “NA” and had no data, and 63 days recorded 0” of rain (Longman et al., 2024). The maximum daily rainfall recorded was 4.72”. Rainfall at Lyon was about 2 times greater than rainfall at Campus. The change in rainfall is displayed in Figure 2.

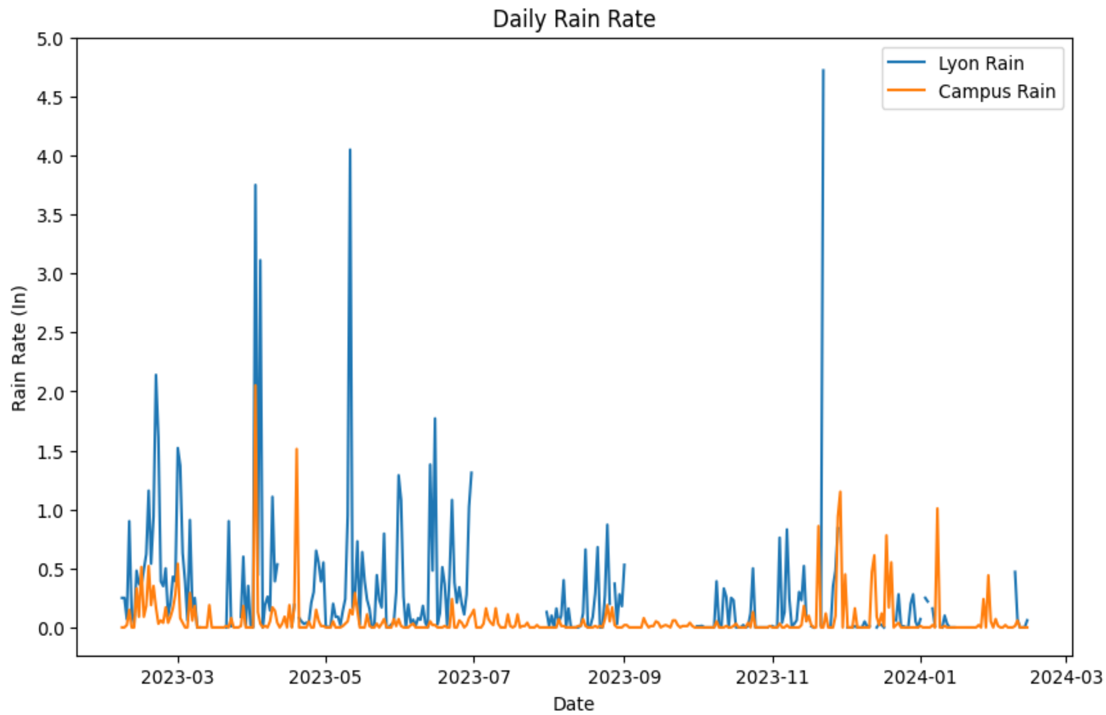


Figure 2: Daily Rain Rate

Time series of daily rain rate (inches) at Lyon (blue) and Campus (orange) over the sampling duration from February 2023 to February 2024.

3.2 Abundant Major Ion Concentrations

Chloride and sodium were found to be the most abundant ions in each sample compared to the other ions (Table 1). Chloride had the highest concentration among all the other major ions for each site. The next four abundant ions were sodium, magnesium, calcium, and sulfate. Since, fluoride, nitrite, bromide, nitrate, phosphate, lithium, ammonium, and potassium were measured at less than 0.1 mg/L for more than two sites, these ions were ignored in further analysis.

Table 1: Average Major Ion Concentration
from all four sampling sites, averaged over all available samples, with the number of available samples shown in the parenthesis.

	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na^+	NH_4^+	K^+	Mg^+	Ca^{2+}
Lyon Stream (30)	0.00	20.02	0.00	0.06	0.11	0.04	2.73	0.00	11.72	0.01	0.67	5.98	4.50
Campus Stream (30)	0.02	18.10	0.01	0.06	0.98	0.07	5.58	0.00	14.91	0.01	1.15	7.65	10.47
Lyon Rain (20)	0.01	8.95	0.01	0.03	0.09	0.07	1.33	0.00	4.81	0.05	0.48	0.64	0.39
Campus Rain (11)	0.01	20.65	0.00	0.05	0.55	0.03	3.38	0.00	11.90	0.01	0.74	1.37	2.12

The following figures compare the concentrations of chloride, sodium, magnesium, calcium, and sulfate at each sampling site over time (Figures 3-6). The stream ion concentrations were found to be consistent over time with low variation from week to week. Whereas the rain ion concentrations were found to vary greatly with sharp increases and decreases in concentration from week to week. All the data collected has been made available in Appendix A.

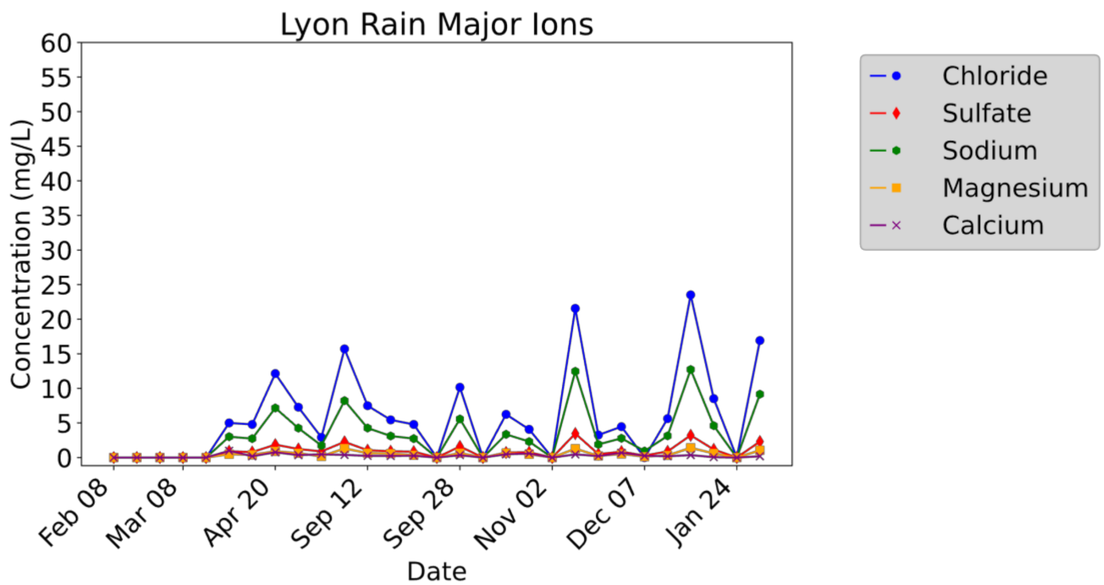


Figure 3: Lyon Rain Major Ions

Concentration of abundant major ions (mg/L) found in the Lyon Rain samples over time. Chloride and sodium seem to vary between samples while sulfate, magnesium, and calcium are more consistent over time. Chloride is the most abundant and calcium is the least abundant.

The ion concentrations in Lyon Rain resulted in variable concentrations in chloride and sodium levels, while the other ions stayed fairly consistent throughout the sample period (Figure 3). Chloride concentrations ranged from about 3 mg/L to 24 mg/L. Sodium concentrations ranged from 1 mg/L to 13 mg/L. Sulfate, magnesium, and calcium were measured at the lowest concentrations ranging from about 0.05 mg/L to 3.5 mg/L.

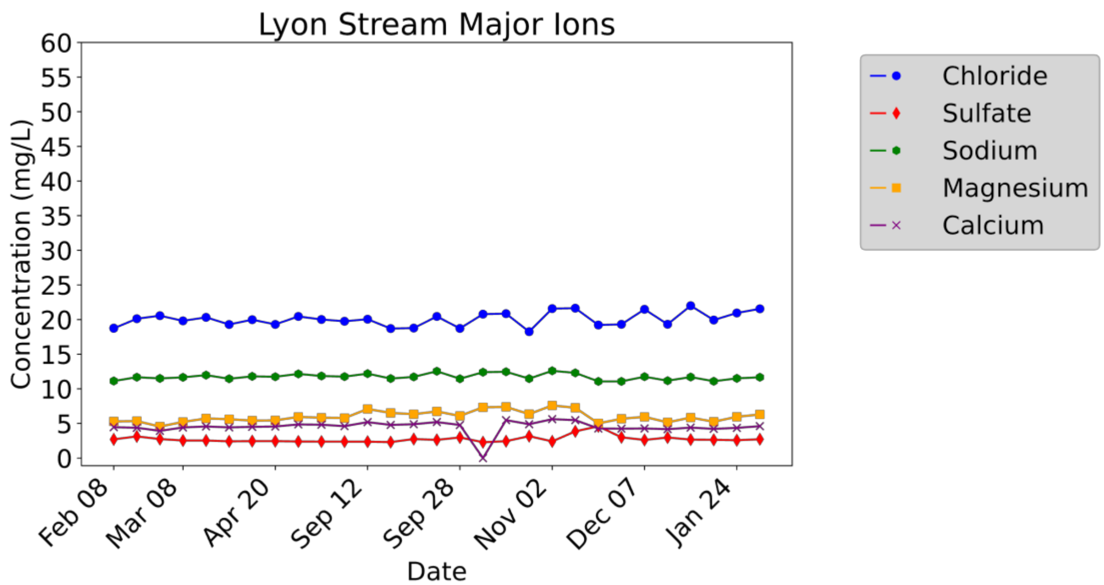


Figure 4: Lyon Stream Major Ions

Concentration of abundant major ions (mg/L) in Lyon Stream over time. Chloride concentration is the most abundant while sulfate is the least abundant. All ions follow a similar trend over time.

The ion concentrations found at Lyon Stream were consistent over the study period for all ions analyzed (Figure 4). Chloride was measured at a concentration range from about 18 mg/L to 22 mg/L, and sodium was measured at a range from about 11 mg/L to 13 mg/L. Sulfate, magnesium, and calcium varied like each other and had a concentration range of about 0.1 mg/L to 5 mg/L. On October 12, the calcium concentration dipped from its consistent range to a value of 0 mg/L. There is no clear evidence as to why this occurred, but observations taken on that day include a deposit of an oil-like film over the water, which may contribute to this result.

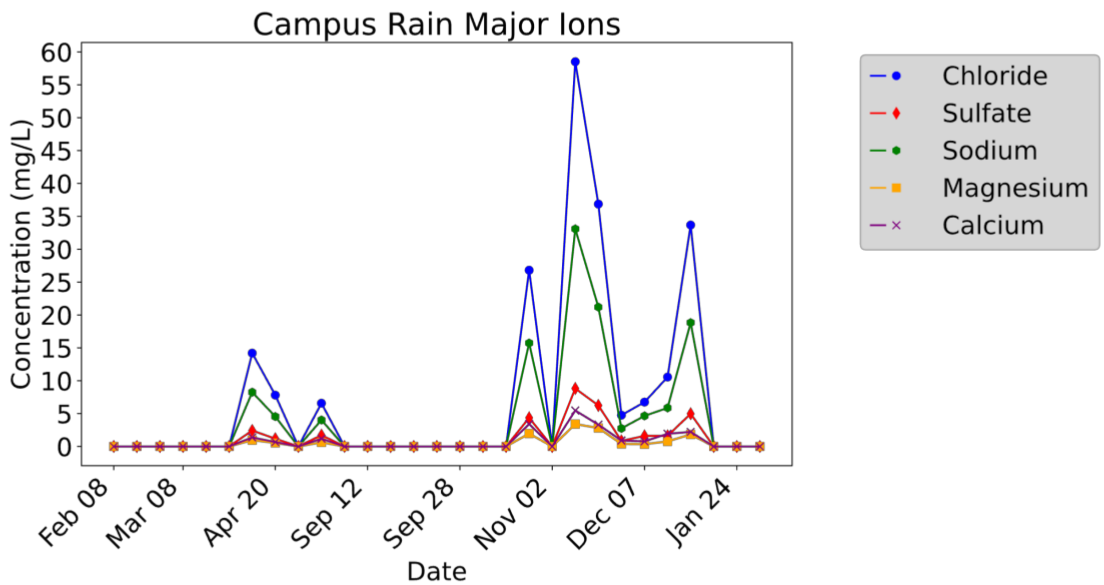


Figure 5: Campus Rain Major Ions

Concentration of abundant major ions (mg/L) found in the Campus Rain samples over time. Chloride and sodium dominate the sample being the two highest concentrations, while sulfate, magnesium, and calcium stay consistent with each other over time.

The ion concentrations measured at Campus Rain was highly variable throughout the study period (Figure 5). The range in concentrations for chloride was about 5 mg/L to 59 mg/L and for sodium it was about 3 mg/L to 33 mg/L. The Campus Rain site saw the highest measured value for the chloride concentrations. The concentration range for sulfate, magnesium and calcium was measured to be 0.35 mg/L to 8 mg/L. Most of the samples were collected following periods of heavy rain that came from the occasional passing cold fronts.

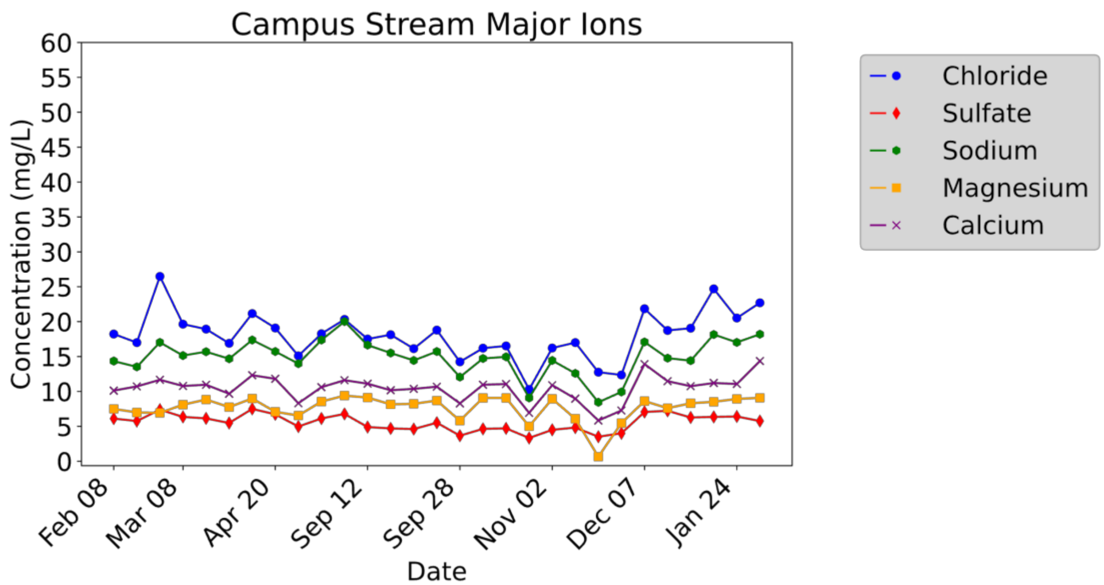


Figure 6: Campus Stream Major Ions

Concentration of abundant major ions (mg/L) in the Campus Stream over time. The ions in the Campus Stream are closer in concentration to each other compared to the Lyon Stream. All the ions follow a similar trend over time and vary similarly to each other.

The Campus Stream site resulted in a consistent trend of ion concentrations over time, where it was shown that the ions fluctuated according to one another. The chloride concentrations ranged from about 10 mg/L to 27 mg/L. The sodium concentrations ranged from 8 mg/L to 20 mg/L and the sulfate, magnesium, and calcium concentrations ranged from 0.65 mg/L to 15 mg/L. On November 21, the magnesium concentration dropped to a level close to 0. The observations noted on that day were that there was a fast streamflow, and the water had a brown color.

3.3 Major Ion Relationships

The potential relationships between the major ions found in stream and rainwater samples were examined using correlation calculations and scatter plots to visualize the data. The five abundant ions; chloride, sodium, magnesium, calcium, and sulfate were compared to each other using this technique. These ions are referred to as the "major ions" and each are paired with one another.

3.3.1 Correlation Between Rain and Stream Samples

The Pearson correlation coefficient formula (1) was used to mathematically analyze and compare the ion concentrations in the rainwater and the stream water. The results from conducting this correlation will identify how rainfall contributes to streamflow chemically. Lyon Rain ion concentrations were compared to Lyon Stream ion concentrations (Table 2) and Campus Rain ion concentrations were compared to Campus Stream ion concentrations (Table 3). The *r-values* are colored in a blue-red range. Values closer to +1 are in the blue range, values closer to -1 are in the red range, and values close to 0 are in the white range.

The comparison between the rain and stream ion concentrations at Lyon resulted in a mostly positive correlation between rain and stream ions. The highest *r-value* was found between chloride in the rain and stream (r = 0.72). The lowest *r-value* was measured between chloride in the rain by calcium in the stream (r = -0.20). Comparing calcium and sulfate between sample types resulted in a *r-value* close to 0 in most relationships. The rain and stream were positively correlated at Lyon.

Comparing the ions in the rain and stream at Campus resulted in a mostly negative correlations between the ions. The lowest *r-value* was measured between magnesium concentrations in both the rain and stream (r = -0.58). The highest *r-value* was measured between chloride in both the rain and stream (r = -0.26). The Campus sites resulted in a negative correlation between all ions measured.

Table 2: Lyon Rain VS. Lyon Stream Ion Concentrations

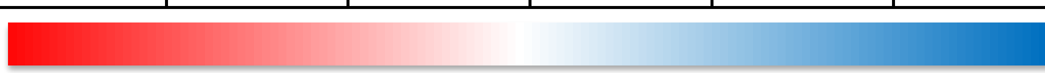
R-values comparing rain and stream ion concentrations. Values range from -1 (red) to +1 (blue).

	Cl^-	Na^+	Mg^+	Ca^{2+}	SO_4^{2-}
Cl^-	0.72	0.30	0.23	0.14	0.05
Na^+	0.56	0.29	0.24	0.21	0.09
Mg^+	0.46	0.32	0.30	0.26	-0.05
Ca^{2+}	-0.20	0.06	0.04	0.10	-0.10
SO_4^{2-}	0.52	0.29	0.23	0.23	0.09

Table 3: Campus Rain VS. Campus Stream Ion Concentrations

R-values comparing rain and stream ion concentrations. Values range from -1 (red) to +1 (blue).

	Cl^-	Na^+	Mg^+	Ca^{2+}	SO_4^{2-}
Cl^-	-0.26	-0.44	-0.43	-0.45	-0.45
Na^+	-0.27	-0.44	-0.43	-0.45	-0.45
Mg^+	-0.39	-0.55	-0.58	-0.57	-0.55
Ca^{2+}	-0.41	-0.52	-0.48	-0.53	-0.47
SO_4^{2+}	-0.28	-0.45	-0.46	-0.47	-0.47



3.3.2 Correlation Values Between Ion Pairs

The relationship between the various abundant ions in the stream and rainwater samples was determined using the Pearson correlation coefficient and correlation plots. The results from comparing these ions will assist in identifying potential sources of the ions and if the ion pairs have a related source. The ion pairs were correlated to each other at all four sites; Lyon Rain (Table 4), Lyon Stream (Table 5), Campus Rain (Table 6), and Campus Stream (Table 7). When an ion was paired with itself in the same location, the *r-value* resulted in a perfect correlation (r = 1.00) which is expected because there is no deviation from a perfect linear relationship when comparing an ion to itself.

Table 4: Lyon Rain Ion Pair Correlations
Each ion is paired and correlated to the other ions. Values range from -1 (red) to +1 (blue).

Cl^-	1.00				
Na^+	1.00	1.00			
Mg^+	0.95	0.94	1.00		
Ca^{2+}	-0.06	0.01	0.10	1.00	
SO_4^{2-}	0.98	0.99	0.92	0.05	1.00
	Cl^-	Na^+	Mg^+	Ca^{2+}	SO_4^{2-}

The correlations between ion pairs in Lyon Rain resulted in a mostly positive correlation between most ions. Correlating calcium with the other ions resulted in no correlation or a weak negative correlation. However, the other ion pairs resulted in strong positive correlations ranging in *r-value* from 0.92 to 1.00. The ion pairs found in Lyon Rain are highly positively correlated suggesting a strong relationship between the ions in this site.

Table 5: Lyon Stream Ion Pair Correlations

Each ion is paired and correlated to the other ions. Values range from -1 (red) to +1 (blue).

Cl^-	1.00				
Na^+	0.59	1.00			
Mg^+	0.38	0.77	1.00		
Ca^{2+}	-0.03	0.08	0.09	1.00	
SO_4^{2-}	-0.12	-0.33	-0.19	0.11	1.00
	Cl^-	Na^+	Mg^+	Ca^{2+}	SO_4^{2-}

The Lyon Stream ion pair correlations resulted in no correlation or negative correlation values when comparing calcium and sulfate to the other ions. The lowest *r-value* was measured between sulfate and sodium (r = -0.33) resulting in a weak negative correlation. The highest value was measured between magnesium and sodium (r = 0.77) resulting in a strong positive correlation. No correlations were measured between calcium and sodium, calcium and magnesium, and sulfate and calcium.

Table 6: Campus Rain Ion Pair Correlations

Each ion is paired and correlated to the other ions. Values range from -1 (red) to +1 (blue).

Cl^-	1.00				
Na^+	1.00	1.00			
Mg^+	0.98	0.98	1.00		
Ca^{2+}	0.94	0.95	0.95	1.00	
SO_4^{2-}	0.99	1.00	0.99	0.94	1.00
	Cl^-	Na^+	Mg^+	Ca^{2+}	SO_4^{2-}

Campus Rain found that all ion pairs resulted in a strong positive correlation. It was found that as one ion concentration increased, it is more than likely that any other ion in that site will also increase. The highest *r-value* was measured between sodium and chloride (r = 1.00) and the lowest *r-value* was measured between calcium and chloride and sulfate and calcium, both pairs measured at an *r-value* of 0.94.

Table 7: Campus Stream Ion Pair Correlations

Each ion is paired and correlated to the other ions. Values range from -1 (red) to +1 (blue).

Cl^-	1.00				
Na^+	0.84	1.00			
Mg^+	0.55	0.82	1.00		
Ca^{2+}	0.80	0.86	0.80	1.00	
SO_4^{2-}	0.84	0.74	0.51	0.74	1.00
	Cl^-	Na^+	Mg^+	Ca^{2+}	SO_4^{2-}

The Campus Stream also resulted in strong positive correlations between all ion pairs. The highest *r-value* was measured between calcium and sodium (r = 0.86). The lowest *r-value* was measured between sulfate and magnesium (r = 0.51). The Campus Stream results show that the ions in this site share a positive relationship where if one ion increases in concentration, it is more than likely that the other ions will also increase in concentration.

3.3.3 Scatter Plots of Ion Pair Correlations

The ion pairs were then compared graphically using scatter plots to display their linear relationship visually. Each ion pair for all four sites were graphed on the scatter plot. A linear relationship between each ion pair results in a strong relationship between the two ions and corresponds to a positive correlation.

Sodium and chloride concentrations showed a positive correlation across all sites (Figure 7), with the strongest correlations observed in the rain samples (Lyon Rain and

Campus Rain: $r = 1.00$). The stream samples showed weaker correlations (Lyon Stream: $r = 0.59$; Campus Stream: $r = 0.84$). Figure 7 shows the spread of the data. Lyon Stream data points are clustered and graphically does not show a linear relationship. Whereas Lyon Rain and Campus Rain have a more defined linear shape to their graphs. Campus Stream has a mix of clustering and linearity that was found.

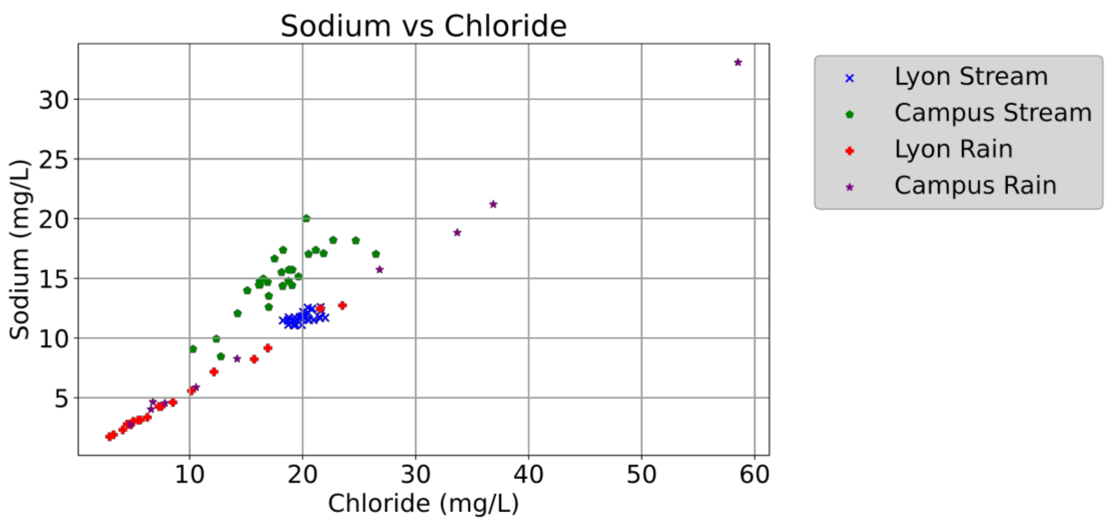


Figure 7: Sodium and Chloride Scatter Plot

Sodium and chloride concentrations are compared in all four sites: Lyon Stream (blue "x"), Campus Stream (green pentagon), Lyon Rain (red "+"), and Campus Rain (purple (*).

The magnesium and chloride concentrations resulted in a positive correlation in all four sampling sites (Figure 8). The strongest correlations were found in the rain samples (Lyon Rain: $r = 0.97$; Campus Rain: $r = 0.99$). The stream samples had a positive correlation but were weaker than the correlation in the rain (Lyon Stream: $r = 0.38$; Campus Stream: $r = 0.55$). From the scatter plot, it was found that Lyon Stream and

Campus Stream had a clustered spread of data and little to no linear relationship between magnesium and chloride. However, the opposite was shown in the rain samples for both sites where there is a visual linear relationship that exists.

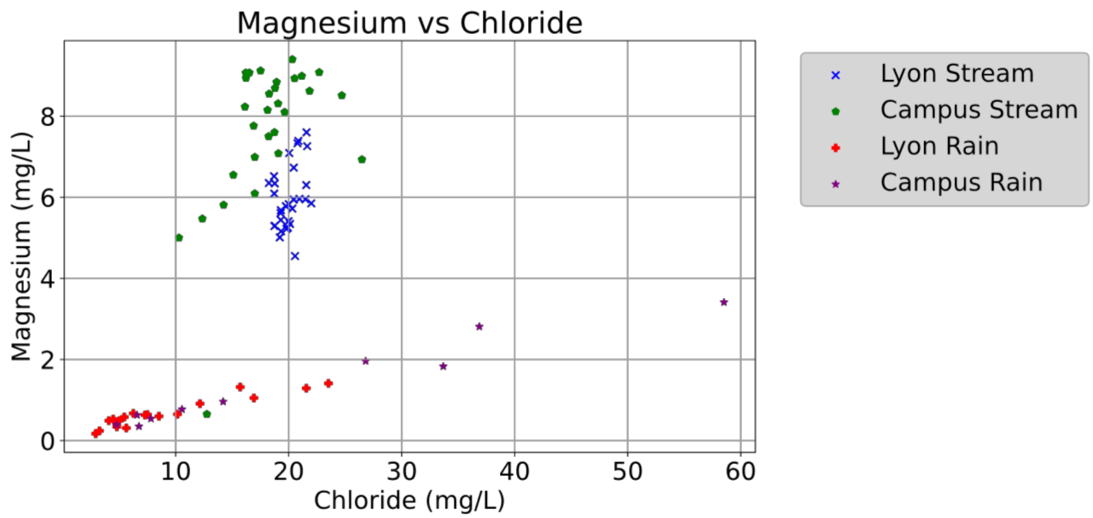


Figure 8: Magnesium and Chloride Scatter Plot

Magnesium compared to chloride concentrations at all four sites: Lyon Stream (blue "x"), Campus Stream (green pentagon), Lyon Rain (red "+"), and Campus Rain (purple (*).

The relationship of magnesium and sodium in the rain samples exhibited a linear relationship (Figure 9). The stream samples resulted in a clustered relationship in the top center of the plot (Figure 9). The sodium concentration values ranged from 0 - 35 mg/L and the magnesium concentration values ranged from 0 - 10 mg/L. The strongest correlations between magnesium and sodium were found in the rain samples (Lyon Rain: $r = 0.97$; Campus Rain: $r = 0.99$). The stream samples resulted in high correlation values as well (Lyon Stream: $r = 0.77$; Campus Stream: $r = 0.82$).

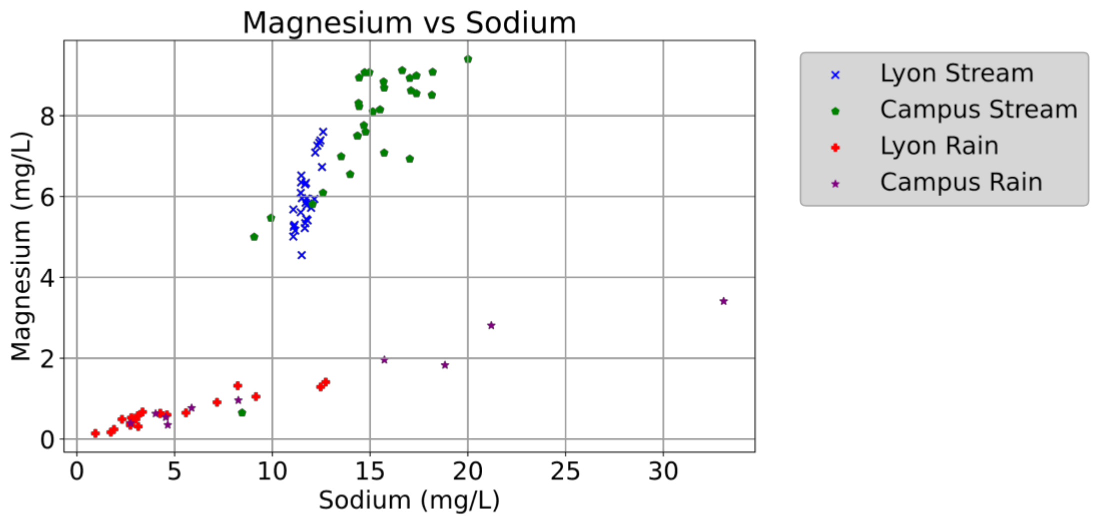


Figure 9: Magnesium and Sodium Scatter Plot

Magnesium is compared to sodium concentrations for all four sites: Lyon Stream (blue "x"), Campus Stream (green pentagon), Lyon Rain (red "+"), and Campus Rain (purple (*).

These ion pairs that resulted in a negative or no correlation in one or more sites include: sulfate and chloride, calcium and chloride, calcium and sodium, sulfate and sodium, calcium and magnesium, and sulfate and magnesium.

The relationship between sulfate and chloride in the rain samples were observed to have a positive correlation and wider spread over the plot (Figure 10). The sulfate and chloride concentrations were strongly correlated in the rain samples (Lyon Rain: $r = 0.99$; Campus Rain: $r = 1.00$). The correlation between sulfate and chloride was weaker in Campus Stream and had an *r-value* of 0.84. Lyon Stream had a negative correlation value ($r = -0.12$). Figure 10 displays a clustered data spread for the Lyon Stream correlation between sulfate and chloride and the other locations resulted in a fairly linear relationship.

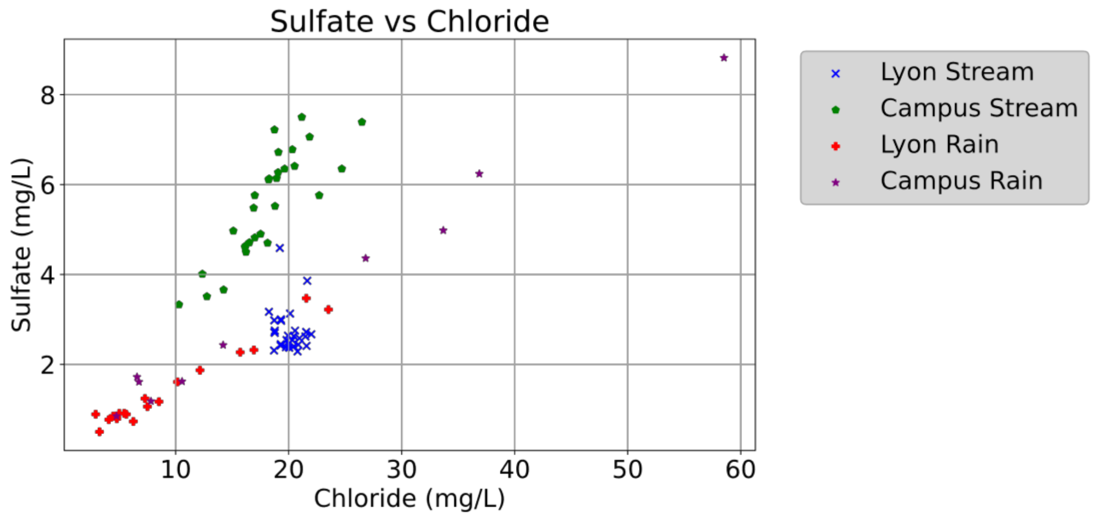


Figure 10: Sulfate and Chloride Scatter Plot

Sulfate concentrations are compared to chloride concentrations at all four sites: Lyon Stream (blue “x”), Campus Stream (green pentagon), Lyon Rain (red “+”), and Campus Rain (purple (*).

Calcium and chloride concentrations were compared in Figure 11. The chloride concentration values ranged between 0 - 60 mg/L and the calcium concentration values ranged between 0 - 15 mg/L. There was a higher amount of chloride compared to calcium in all four sites. At Lyon Stream, the correlation was very clustered, while the other three sites had a linear correlation. The strongest correlation value was observed in the Campus Rain (r = 0.97). The next strongest correlation was in Campus Stream, (r = 0.80) then in the Lyon Rain (r = 0.44). In the Lyon Stream, the r value was -0.02 which resulted in a weak negative correlation. The negative correlation at Lyon Stream is difficult to visualize on the scatter plot (Figure 11) due to the clustering of data in that site.

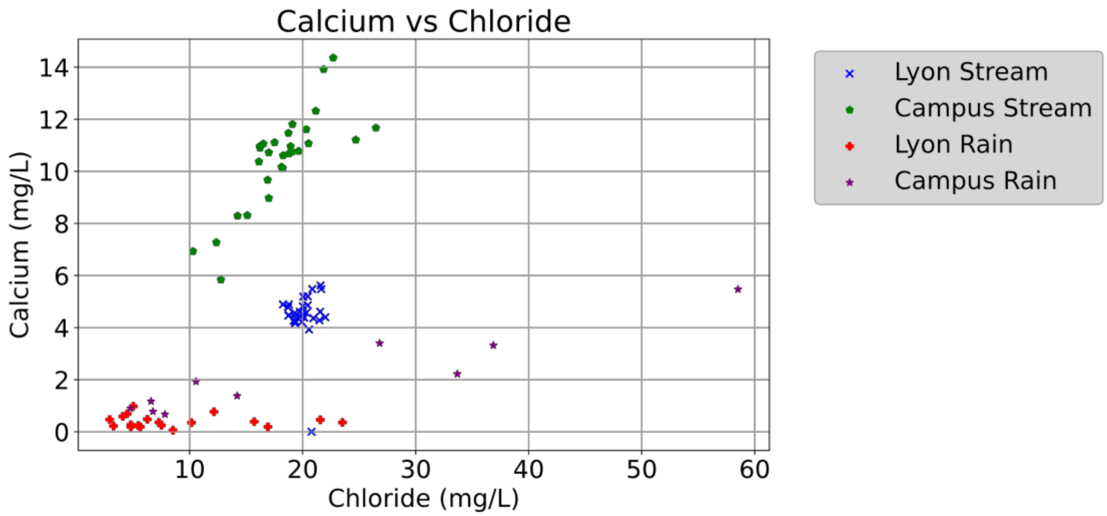


Figure 11: Calcium and Chloride Scatter Plot

Calcium is compared to chloride concentrations at all four sites: Lyon Stream (blue "x"), Campus Stream (green pentagon), Lyon Rain (red "+"), and Campus Rain (purple (*).

The relationship between calcium and sodium was like the relationship between calcium and chloride. The concentration values of sodium ranged from 0 - 30 mg/L and the concentration values of calcium ranged from 0 - 14 mg/L. Campus Rain had a wide spread of data points while Lyon Stream samples were clustered in the center of the plot (Figure 12). The strongest correlation value was found in the Campus Rain samples with an *r* value of 0.97. The next strongest correlation was found in the Campus Stream with an *r-value* of 0.86 and then in Lyon Rain with an *r-value* of 0.46. Lyon Stream had a very low and weak correlation with a *r* value of 0.07. There is a spread of data seen at three of the sites except for Lyon Stream, where the clustering of data points is continued in this comparison.

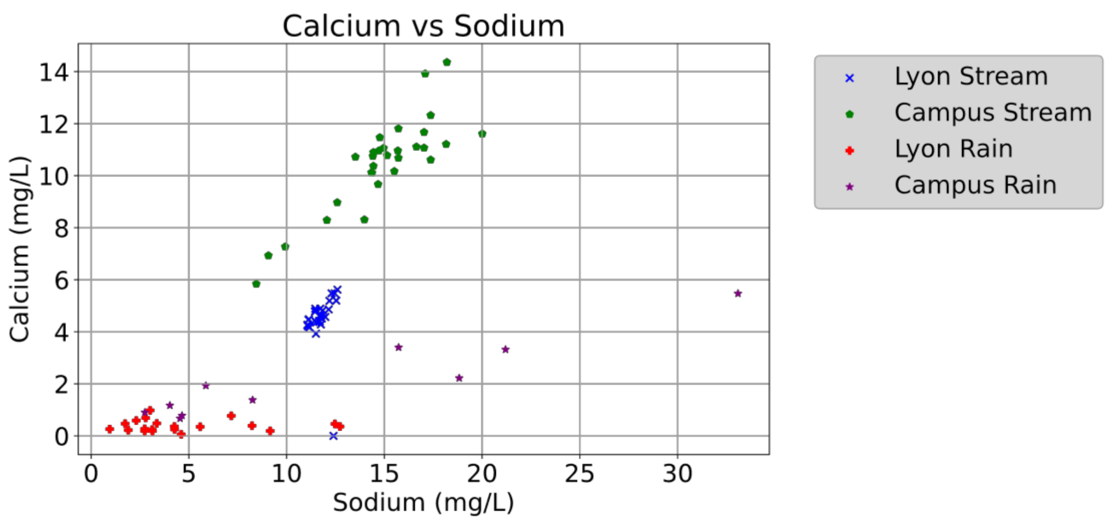


Figure 12: Calcium and Sodium Scatter Plot

Calcium concentrations are compared to sodium concentrations at all four sites: Lyon Stream (blue “x”), Campus Stream (green pentagon), Lyon Rain (red “+”), and Campus Rain (purple (*).

Sulfate and sodium were compared and observed to have a strong linear relationship in the Campus Stream, Lyon Rain, and Campus Rain (Figure 13). The Lyon Stream data points were highly clustered and were not observed to have a strong correlation. The strongest correlation was found to be in the rain samples (Lyon Rain: r = 0.99; Campus Rain: r = 1.00). The next strongest correlation was found to be in the Campus Stream, r = 0.74. The Lyon Stream samples had a very low negative correlation with a *r-value* of -0.33.

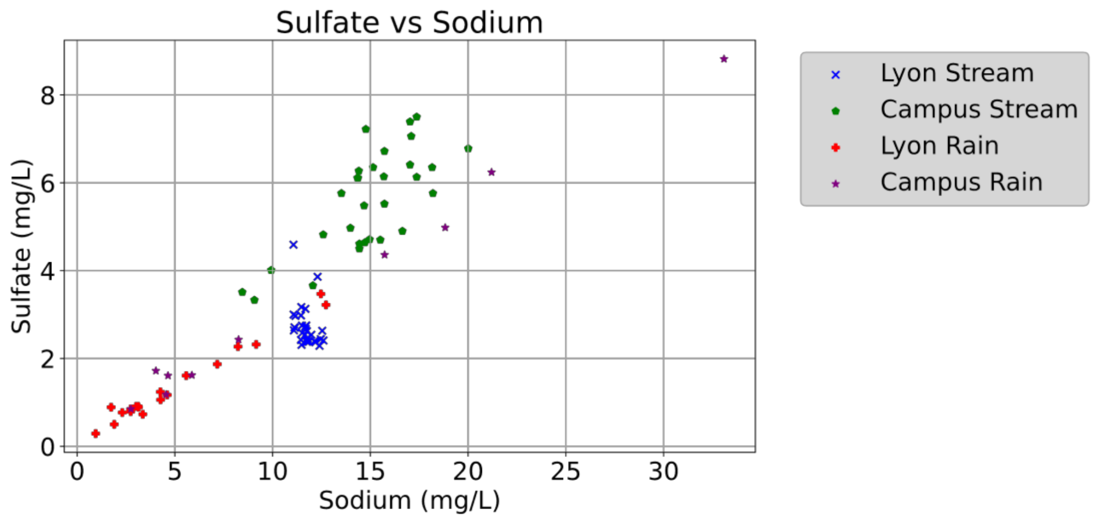


Figure 13: Sulfate and Sodium Scatter Plot

Sulfate concentrations are compared to sodium concentrations at all four sites: Lyon Stream (blue "x"), Campus Stream (green pentagon), Lyon Rain (red "+"), and Campus Rain (purple (*).

Figure 14 displays the relationship between calcium and magnesium. The comparison between these ions was found to have a somewhat linear relationship in the Lyon Stream, Campus Stream, and Campus Rain. Lyon Rain was found to be clustered towards the 0 - 2 mg/L range for both calcium and magnesium. The concentration of magnesium ranged from 0 - 10 mg/L and the concentration of calcium ranged from 0 - 15 mg/L (Figure 14). The strongest correlation was to be in the samples from Campus (Campus Stream: $r = 0.80$; Campus Rain: $r = 0.98$). Lyon Rain was found to have a *r-value* of 0.56. Lyon Stream was found to have a low *r-value* of 0.08. Lyon Rain's data spread was clustered at this site while the data spread for Lyon Stream was spread across the graph.

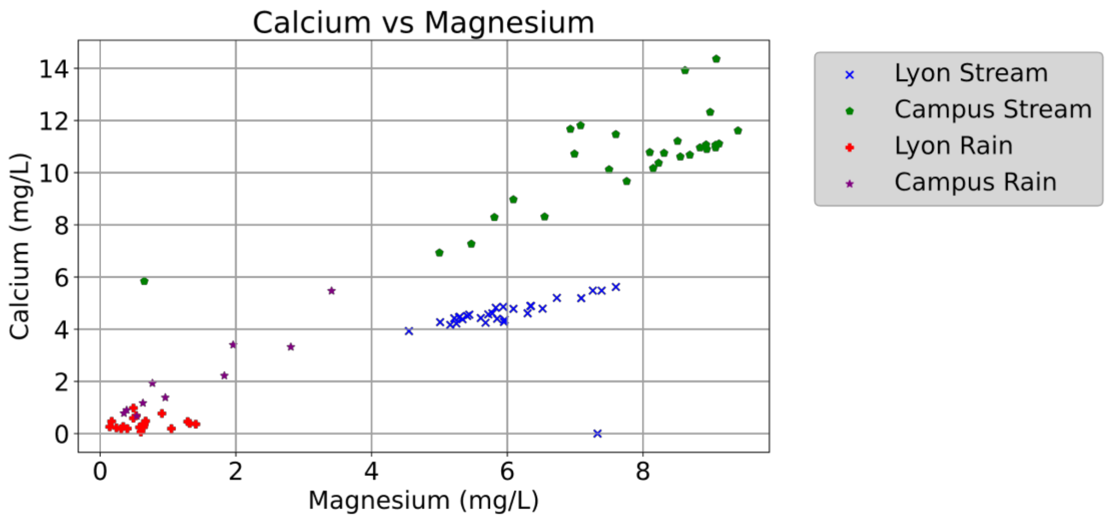


Figure 14: Calcium and Magnesium Scatter Plot

Calcium concentrations are compared to magnesium concentrations at all four sites: Lyon Stream (blue “x”), Campus Stream (green pentagon), Lyon Rain (red “+”), and Campus Rain (purple (*).

The relationship between sulfate and magnesium is depicted in Figure 15. The rain samples were observed to have a strong positive linear relationship while the stream samples were variable. The strongest correlation was found in the rain samples (Lyon Rain: $r = 0.96$; Campus Rain: $r = 0.99$). The stream samples had weaker correlations compared to the rain samples (Lyon Stream: $r = -0.19$; Campus Stream: $r = 0.51$). Lyon Stream was shown to have a negative correlation. The rain samples had a steep slope according to the graph while the stream samples had little to no linearity to the data.

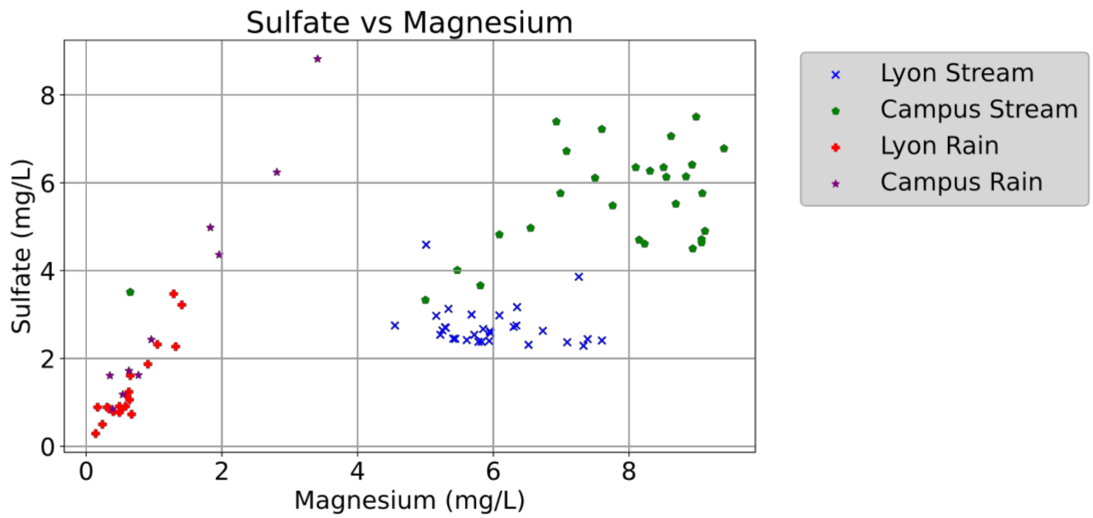


Figure 15: Sulfate and Magnesium Scatter Plot

Sulfate concentrations are compared to magnesium concentrations at all four sites: Lyon Stream (blue “x”), Campus Stream (green pentagon), Lyon Rain (red “+”), and Campus Rain (purple (*).

4.0 DISCUSSION

This study investigated the relationship between the abundant major ions (chloride, sodium, magnesium, sulfate, and calcium) in stream and rain samples collected at four different sites. The Pearson correlation coefficients (*r*) were used to quantify the strength and direction of these relationships. This analysis revealed distinct patterns in the correlations between the different ion pairs. These patterns can highlight the potential influence of various factors on their co-occurrence and ion chemistry. Notably, these relationship trends often differed between stream and rain samples and the sites where the samples were taken, suggesting the influence of specific processes that exist in those environments can impact the concentrations of these ions.

4.1 Comparison of Stream and Rain Samples

This study demonstrated that between the stream and rain samples, the major ions found in rain samples were more closely correlated than ions found in the stream samples. This finding suggests that there is a higher degree of association between the major ions in rainwater. Rain samples might experience stronger correlations between major ions because of the limited variation in the rain's source, the rain's similar transport mechanism, and the rain has less influence of local factors such as weathering, biological activity, and sediment interaction, impacting its composition. Rainwater typically originates from the evaporation of ocean water, during this process, ions dissolve into the water vapor and result in a relatively consistent ratio of those ions in the rainwater. The rainwater is also rarely in contact with external influences during transport since most of the rainwater collected falls directly from the sky into the collector. Unlike the stream samples, rain samples are less likely to be influenced by local factors.

While the rain samples experienced strong correlations between most of the major ions, the stream samples displayed a consistent weaker and more variable relationship. The variability in the correlation can be attributed to the many local factors that can influence the ion concentrations within the stream's environment compared to the more correlated composition of the rainwater samples. Unlike rainwater, streams are constantly interacting with their surroundings which can increase the input of ions from more sources and disrupt the initial correlations seen in the rain.

4.2 Comparing Samples from Lyon and Campus

Lyon's rain and stream had an overall positive correlation compared to Campus rain and stream. At Lyon, a discrepancy exists when comparing calcium and sulfate concentrations between the rain and stream samples, where those *r-values* were close to 0. This could be caused by the low inputs of calcium and sulfate in this location since both ions consistently were measured at the lowest abundancy level. The strong positive correlations between rain and stream at Lyon could be that the ions are coming from the same source. This main source is driving the ion concentrations and producing this strong relationship between the rain and stream's chemistry. At Campus all the ions in rain and stream resulted in a negative correlation. This could be due to the existence of multiple sources for the ions in this location. Having multiple sources for the ions can result in the negative correlation where there isn't a definitive relationship between the ions found in the rain and stream samples.

The study also revealed a pattern of higher variability of ion concentrations in both rain and stream samples collected at the Campus sites compared to the Lyon sites. Figures 3 to 6 and Tables 2 and 3 depict the variability seen in the Campus samples compared to the Lyon samples. The concentration levels of the five abundant ions were at their highest in the Campus Stream, except for chloride, where the highest concentration level was found in the Lyon Stream. Campus Rain also had higher levels of each ion compared to the Lyon Rain. While the specific reasons for this difference require further investigation, several potential contributing factors may be explored.

One factor could be the variations in the source of stream and rainwater at the Campus sites. It could be assumed that since the Campus sites were situated in a more urban area, contributions from industrial or agricultural sources nearby could lead to the variability seen in the Campus samples. In contrast, the Lyon sample sites are situated higher in the valley with more forested areas.

Another factor that could influence the variations seen in the Campus sites could be the geological properties in the surrounding areas. Rock weathering has been identified as a main source of ions in stream water. If the Campus sites are situated in areas that have rocks rich in specific minerals, the weathering of those rocks can contribute to the change in ion concentrations. Rock weathering can influence the composition of the stream and rain through dust or aerosol deposition.

A last factor that could be influencing the higher concentrations of ions found at the Campus sites could be anthropogenic activities. Again, where the sampling sites are located around the Campus area, can be subjected to more human activities. These human activities can introduce pollutants and dissolved ions into the environment through the air or as surface runoff from urbanized areas. Depending on what type of activities are done near the sampling sites, these activities can lead to elevated levels of specific ions.

4.3 Correlations Between Ion Pairs

4.3.1 Sodium and Chloride

The consistent positive correlation between sodium and chloride at all four sampling sites can imply that the higher concentrations of sodium are typically accompanied by higher concentrations of chloride and vice versa. Both sodium and chloride are major components of seawater and typically originate from this source when found in rainwater. The strong correlation between sodium and chloride in the rain samples suggests that the contribution of these ions is potentially sourced from seawater (Brennis et. al., 2023; Seto et. al., 1969). The *r-value* for the rain samples should be interpreted with caution due to the relatively low number of samples collected which could limit the generalizability of the observed correlation. However, even with the limitations of sample size, the observed positive correlation in the rain samples can provide valuable preliminary insights into the potential relationship between sodium and chloride in rain samples. For the stream samples, the Campus samples had a stronger correlation compared to the Lyon samples. The difference in correlation between the top of the stream at Lyon compared to the bottom of the stream at Campus could be attributed to different local sources and processes, such as proximity to the coastline and wind patterns. These factors could influence the concentration levels of sodium and chloride in these sites.

4.3.2 Magnesium and Chloride

Magnesium and chloride concentrations had a higher positive correlation in the rain samples compared to the stream samples. This relationship implies that the higher the level of magnesium in rain samples the higher the chloride level might be. The source of magnesium is most likely from marine aerosols, and as a result, due to the strong positive correlation between these two ions, it would be reasonable to assume both magnesium and chloride are coming from the same source (Feller, 2010).

4.3.3 Sulfate and Chloride

The relationship between sulfate and chloride resulted in a positive correlation for the Campus Stream, Lyon Rain, and Campus Rain. For Lyon Stream, there was a negative correlation that was close to the value of 0. Since the correlation for the Lyon Stream was close to 0, it suggests that there is little to no correlation between sulfate and chloride at the site. It could be assumed that at Lyon Stream, there may be low inputs of sulfate compared to chloride where the concentration values are not sufficient to formulate a correlation between the two ions. Sulfate levels could originate from natural sources such as volcanic eruption, or anthropogenic sources such as fertilizer use for landscaping. These sources can increase sulfate levels in rain and increase its concentration in both streams and rainwater. The strong positive correlation of sulfate with chloride can point toward atmospheric deposition or geological formations (Brennis et. al., 2023).

4.3.4 Calcium and Chloride

A positive correlation was observed between calcium and chloride in the Campus Stream, Lyon Rain, and Campus Rain. This correlation implies that higher levels of calcium can often coincide with higher levels of chloride. Calcium can originate from dust particles, rock weathering, or groundwater inflow for streams (Brahney, et. al., 2013). There was little to no correlation found between calcium and chloride in the Lyon Stream and the positive correlation in the Lyon Rain is lower compared to the Campus Rain correlation. This finding could be attributed to a deficit in calcium at Lyon but not at the Campus sites. The higher levels of calcium found at Campus is probably due to the urbanized area that comprises this region. Calcium concentrations have been found to be enriched in urban areas due to the use of calcium-rich materials such as cement structures and impervious surfaces (Wu et al., 2018). The urbanized area around the Campus sites is probably contributing to the higher calcium levels found.

4.3.5 Magnesium and Sodium

Magnesium and sodium have the positive correlations at all four sites. The rain samples were more strongly correlated than the stream samples. The source of magnesium and sodium in rainwater can be linked to marine aerosols. The marine aerosols can contain both magnesium and sodium, like the chloride relationships. These ions can be deposited into rainwater but can vary from site to site. In streams, the strong positive correlation between magnesium and sodium suggests that rock weathering or groundwater inflow plays a significant role in increasing these ion concentrations (Brennis et. al., 2023; Xiao, 2016).

4.3.6 Calcium and Sodium

The correlation between calcium and sodium was found to be positive in Campus Stream, Lyon Rain, and Campus Rain. Similar to other ion relationships, calcium and sodium had little to no correlation in the Lyon Stream. The source of the positive correlation likely stems from a combination of factors. In rain, the source of this correlation might be linked to dust particles containing calcium carbonate that are transported by wind which can deposit these ions into rainwater (Brahney et. al., 2013). In streams, the correlation is likely to come from rock weathering or agricultural practices. The weathering process can release calcium from rocks and soil into the streamflow. The use of calcium-rich fertilizers can also influence calcium levels in streams.

4.3.7 Sulfate and Sodium

Sulfate and sodium were found to have a positive correlation in the Campus Stream, Lyon Rain, and Campus Rain. The positive correlation between these two ions could point towards anthropogenic activities being a major contributor to these ions. If there was a weaker correlation, it could be assumed that specific local activities are influencing sulfate concentrations. In streams, the correlation is probably influenced by rock weathering, where those rocks can release sulfate and sodium into the streamflow and contribute to the correlation (Saltzman et. al., 1986). In rain, the correlation can be associated with anthropogenic activities that release pollutants containing sulfate and sodium ions into the atmosphere (Saltzman et. al., 1986).

4.3.8 Calcium and Magnesium

Like other ion relationships, calcium and magnesium have a positive correlation in the Campus Stream, Lyon Rain, and Campus Rain. Lyon Rain has a weaker correlation compared to the Campus Rain samples. The source of the correlation in the rainwater is most likely associated with dust particles and in streams the source is likely from rock weathering (Xiao, 2016). A strong positive correlation can suggest that rock weathering plays a significant role in increasing the ion concentrations. A weaker correlation could be attributed to other sources such as atmospheric deposition or specific human activities.

4.3.9 Sulfate and Magnesium

The sulfate and magnesium relationship found a positive correlation in the Campus Stream, Lyon Rain, and Campus Rain. The rain samples for this comparison were strongly correlated and the Campus Stream correlation was weaker but still a positive correlation. The Lyon Stream found no correlation between sulfate and magnesium in that site. The correlation in Lyon Rain was weaker than the correlation in Campus Rain. The source of this correlation likely arises from some contributing factors. In rainwater, this association might be linked to natural sources and wind transport. In streams, the correlation likely stems from rock weathering and potential human activities. Human activities like agricultural practices can introduce these ions, that are present in soils, into the stream potentially influencing the observed correlation (Sherman et. al., 1947). This correlation can provide indirect evidence about potential sources that contribute to the sulfate and magnesium concentrations. The combined effects of natural processes and human activities can influence the overall water quality of streams.

5.0 CONCLUSION

5.1 Trends in Major Ion Distributions

This study investigated the relationships between the major ions in streams and rain samples collected from four different sites. The analysis has revealed intricate and distinct patterns in the correlations between rain and stream water as well as the ion pairs studied. These relationships have highlighted the influence that environmental factors have on ion chemistry. It was determined that the most abundant ions found in rain and stream water were chloride, sodium, magnesium, sulfate, and calcium. The results have suggested that rain samples more often exhibit stronger correlations between ion pairs compared to stream samples. Rainwater may be more strongly correlated due to the limited exposure that traveling rainwater has with minimal influence from the environment. It is assumed that the rainwater collected was most likely deposited directly into the rain bucket, experiencing little to no additional ions as it was transported. It was found that rain and stream samples in the upstream site at Lyon contained less variation than in the downstream Campus location. The potential contributing factors could include increased exposure to anthropogenic activities in the more urbanized and trafficked region surrounding the Campus location. Most of the factors that contribute to ion presence can be attributed to rock weathering, wind transport, groundwater inflows, and anthropogenic activities.

Though the results indicated that the Campus rain and stream samples were less correlated compared to Lyon's rain and stream samples, further research is needed to explore the specific reasons behind the observed variations. This also would apply to the observation that rain ions were more correlated than stream ions. Strong correlations between certain ion pairs can point towards specific sources that those ions most likely came from. For example, a strong sodium and chloride correlation can suggest marine aerosol influence, and a correlation between calcium and magnesium might indicate a mostly rock weathering source. This information could inform future efforts in water resource management, environmental protection, and monitoring freshwater sources.

5.2 Future Work

As mentioned, similar studies were conducted in the continental U.S. and in Europe. The findings in this study were comparable to those in previous studies. Notably, the abundance of the ions and hierarchy was similar across all studies. Rock weathering is a common trend as a major source of calcium and magnesium, however, there is a lack of mention of marine sea salt aerosol contributions for chloride and sodium concentrations. It is notable that since this study focused on the Mānoa catchment, which is located on an island, the major source of chloride and sodium is mostly coming from marine sea salt aerosols.

Future work could involve investigating the underlying mechanisms in the hydrologic cycle that could also be influencing major ion dynamics. This could include measuring the ion concentrations in groundwater and in soil moisture. Measuring the ion concentration in these water sources could provide more insight into the transport of ions because it is known that rainwater infiltrates into groundwater as well. It would also be beneficial to conduct this sampling regime over a longer period. The lack of rainfall in the dry season had impacted the total amount of samples collected. A longer study period could also capture more variation and identify long-term trends that may not have appeared in the short-term collection period.

APPENDIX A

LIST OF TABLES

The following tables A1-A4 includes all the major ion concentrations collected in the Lyon and Campus stream, and the Lyon and Campus rain. All collection dates are shown, and the averages from these tables are shown in Table 1.

Table A1: Major Ion Concentration in Lyon Stream														
Date	Volume (ml)	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
2023-03-29	12.5	0.01	19.29	NA	0.06	0.12	NA	2.42	0	11.45	0.01	0.65	5.61	4.43
2023-04-12	13.5	0.01	19.98	NA	0.06	0.04	NA	2.45	0	11.8	0.006	0.7	5.41	4.51
2023-04-20	11	0.01	19.3	NA	0.07	0.04	NA	2.45	0	11.74	0.002	0.67	5.44	4.56
2023-04-26	10.5	0	20.45	NA	0.06	0.07	NA	2.4	0	12.15	0.006	0.68	5.94	4.86
2023-05-03	11	0.01	20.01	NA	0.06	0.07	0.03	2.38	0	11.85	0.009	0.74	5.83	4.82
2023-05-10	10	0.01	19.75	NA	0.07	0.05	NA	2.38	0	11.76	0.009	0.64	5.78	4.61
2023-09-12	10	NA	20.05	NA	0.07	0.11	NA	2.37	0	12.19	0.009	0.67	7.09	5.19
2023-09-14	10	NA	18.7	NA	0.05	0.13	NA	2.31	0	11.48	0.006	0.83	6.52	4.79
2023-09-19	10	0	18.77	NA	0.04	0.08	NA	2.75	0	11.72	0.006	0.69	6.34	4.89
2023-09-21	11	NA	20.45	NA	0.08	0.14	NA	2.63	0	12.54	0.008	0.68	6.73	5.2
2023-09-28	11	NA	18.72	NA	0.06	0.21	NA	2.98	0	11.45	0.008	0.78	6.09	4.78
2023-10-12	11	NA	20.78	NA	0.06	0.15	NA	2.29	0	12.4	0.011	0.65	7.33	0
2023-10-19	10.5	NA	20.85	NA	0.11	0.06	NA	2.44	0	12.46	0.01	0.9	7.39	5.48
2023-10-24	12	NA	18.25	NA	0.07	0.25	NA	3.17	0	11.47	0.017	0.91	6.35	4.89
2023-11-02	11	NA	21.58	NA	0.11	0.15	NA	2.41	0	12.6	0.016	0.66	7.6	5.62

2023-11-16	14	0	21.64	NA	0.07	0.08	NA	3.86	0	12.3	0.01	0.89	7.26	5.48
2023-11-21	11	0.01	19.21	NA	0.05	0.44	NA	4.59	0	11.07	0.004	0.9	5.01	4.27
2023-11-27	11	NA	19.31	NA	0.06	0.21	NA	3	0	11.07	0.017	0.6	5.68	4.25
2023-12-07	11	0	21.48	NA	0.06	0.08	NA	2.62	0	11.75	0.014	0.44	5.95	4.28
2023-12-14	15	0	19.32	NA	0.06	0.09	0.05	2.97	0	11.17	0.005	0.58	5.16	4.17

Table A2: Major Ion Concentrations in Campus Stream

Date	Volume (mL)	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
2023-03-29	13.5	0.02	16.9	0.01	0.06	1.26	0.08	5.48	NA	14.68	0.02	1.19	7.76	9.67
2023-04-12	12	0.03	21.16	0	0.08	1.26	0.06	7.5	0	17.37	0.01	1.27	8.99	12.32
2023-04-20	14	0.03	19.09	0.01	0.06	1.75	0.15	6.72	0	15.72	0.02	1.54	7.08	11.81
2023-04-26	11	0.02	15.1	NA	0.05	0.66	0.07	4.97	0	13.98	0.01	1.14	6.55	8.31
2023-05-03	11.5	0.02	18.27	NA	0.07	1.17	0.08	6.13	0	17.37	0.01	1.41	8.55	10.61
2023-05-10	11	0.03	20.32	NA	0.08	1.29	0.1	6.78	0	20.01	0.01	1.64	9.4	11.61
2023-09-12	11	0.02	17.51	NA	0.05	0.96	NA	4.9	0	16.64	0.01	1.28	9.12	11.11
2023-09-14	10	0.01	18.13	NA	0.08	0.81	0.11	4.7	0	15.51	0.01	1.16	8.15	10.17
2023-09-19	10	0.01	16.13	NA	0.06	0.84	NA	4.61	NA	14.44	0.01	1.11	8.23	10.37
2023-09-21	10	0.02	18.79	NA	NA	0.84	NA	5.52	0	15.72	0.01	1.12	8.69	10.68
2023-09-28	11	0.01	14.24	NA	NA	0.73	NA	3.66	0	12.06	0.01	1.04	5.81	8.29
2023-10-12	10	0.01	16.2	NA	0.05	0.74	NA	4.64	NA	14.72	0.01	1.03	9.07	10.96

2023-10-19	10.5	0.01	16.52	NA	0.07	0.84	NA	4.71	0	14.96	0.01	1.09	9.07	11.06
2023-10-24	11	0.01	10.29	NA	NA	0.95	NA	3.33	0	9.07	0.01	1.08	5	6.93
2023-11-02	11	0.01	16.22	NA	0.06	0.43	NA	4.5	0	14.44	0.01	1.04	8.94	10.9
2023-11-16	12	0.02	17	0.01	0.05	0.68	0.07	4.82	0	12.59	0.01	1.27	6.09	8.97
2023-11-21	11	0.01	12.76	NA	0.03	0.56	0.07	3.51	NA	8.45	0.01	0.93	0.65	5.84
2023-11-27	11	0.01	12.36	NA	0.04	0.64	NA	4.01	NA	9.93	0.02	0.93	5.47	7.27
2023-12-07	11	0.02	21.85	NA	0.09	1.31	0.08	7.06	0	17.09	0.01	1.12	8.62	13.92
2023-12-14	12	0.02	18.74	NA	0.07	1.49	NA	7.22	NA	14.77	0.01	1.06	7.6	11.47

Table A3: Major Ion Concentrations in Lyon Rain

Date	Total Mass (g)	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
2023-03-29	549.4	0	5.01	NA	0.01	0.01	NA	0.91	0	3.02	0	0.08	0.49	0.98
2023-04-12	3652.4	NA	4.79	NA	0.01	0.01	0.05	0.79	0	2.74	0.02	0.49	0.4	0.19
2023-04-20	711.4	NA	12.15	NA	0.03	0.02	0.03	1.87	0	7.17	0.01	0.45	0.91	0.77
2023-04-26	453.2	0	7.28	NA	0.02	0.02	0.13	1.24	0	4.26	0.01	0.58	0.63	0.36
2023-05-03	976.8	0	2.92	0.01	0.01	0.08	NA	0.89	NA	1.74	0.91	0.27	0.17	0.47
2023-05-10	1165.9	0.01	15.71	NA	0.03	0.05	0.1	2.27	0	8.23	0.01	3.57	1.32	0.39
2023-09-12	584.5	NA	7.5	NA	NA	NA	NA	1.06	0	4.27	0.01	0.38	0.64	0.25
2023-09-14	401.6	NA	5.45	NA	NA	NA	NA	0.91	0	3.12	0.01	0.19	0.58	0.24
2023-09-19	1136.5	NA	4.79	NA	NA	NA	NA	0.85	0	2.74	0.02	0.14	0.34	0.27

2023-09-21	0	-	-	-	-	-	-	-	-	-	-	-	-	-
2023-09-28	891.3	NA	10.16	NA	NA	NA	NA	1.61	0	5.58	0.01	0.39	0.65	0.35
2023-10-12	0	-	-	-	-	-	-	-	-	-	-	-	-	-
2023-10-19	512.3	NA	6.25	NA	NA	0.03	NA	0.73	0	3.36	0.01	0.37	0.67	0.48
2023-10-24	413.9	NA	4.08	NA	NA	NA	NA	0.77	0	2.31	0.01	0.23	0.49	0.59
2023-11-02	0	-	-	-	-	-	-	-	-	-	-	-	-	-
2023-11-16	1002.5	0.02	21.56	NA	0.07	0.51	NA	3.47	0	12.47	0.01	0.65	1.29	0.46
2023-11-21	2125.1	NA	3.26	NA	NA	0.03	NA	0.5	NA	1.9	0.01	0.06	0.24	0.22
2023-11-27	1261	NA	4.47	NA	NA	0.33	NA	0.85	0	2.79	0.02	0.48	0.53	0.69
2023-12-07	2063.2	NA	NA	0.01	0.01	NA	NA	0.29	NA	0.95	0.01	0.06	0.14	0.26
2023-12-14	1319.2	NA	5.63	NA	0.03	0.07	NA	0.89	0	3.14	0.01	0.15	0.31	0.19

Table A4: Major Ion Concentrations in Campus Rain

Date	Total Mass (g)	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
2023-03-29	0	-	-	-	-	-	-	-	-	-	-	-	-	-
2023-04-12	310.5	0	14.2	NA	0.04	0.19	NA	2.43	0	8.26	0.01	0.34	0.96	1.38
2023-04-20	698.4	NA	7.81	NA	0.03	0.21	0.02	1.18	0	4.55	0.01	0.24	0.54	0.67
2023-04-26	0	-	-	-	-	-	-	-	-	-	-	-	-	-
2023-05-03	278.2	0.01	6.58	NA	0.02	0.67	NA	1.72	0	4.03	0.02	0.33	0.63	1.17
2023-05-10	0	-	-	-	-	-	-	-	-	-	-	-	-	-

2023-09-12	0	-	-	-	-	-	-	-	-	-	-	-	-
2023-09-14	0	-	-	-	-	-	-	-	-	-	-	-	-
2023-09-19	0	-	-	-	-	-	-	-	-	-	-	-	-
2023-09-21	0	-	-	-	-	-	-	-	-	-	-	-	-
2023-10-12	0	-	-	-	-	-	-	-	-	-	-	-	-
2023-10-19	0	-	-	-	-	-	-	-	-	-	-	-	-
2023-10-24	401.6	0.02	26.81	NA	0.07	1.02	NA	4.36	0	15.73	0.03	1.34	1.96	3.4
2023-11-02	0	-	-	-	-	-	-	-	-	-	-	-	-
2023-11-16	306.3	0.01	58.52	NA	0.12	1.1	NA	8.82	0	33.09	0.01	1.8	3.41	5.47
2023-11-21	223.4	NA	36.87	NA	0.05	1.18	NA	6.24	0	21.2	0.02	1.77	2.81	3.32
2023-11-27	558.6	NA	4.76	NA	0.02	0.2	NA	0.85	0	2.75	0.05	0.27	0.39	0.9
2023-12-07	491.1	NA	6.75	NA	0.04	0.67	0.03	1.61	0	4.65	0.01	0.25	0.35	0.78
2023-12-14	238.9	NA	10.56	NA	0.03	0.2	NA	1.62	0	5.87	0.01	0.33	0.77	1.93

The following Table A5-A8 shows the minimum, maximum, average, and standard deviation of the major ions in Lyon and Campus rain, and Lyon and Campus stream.

Table A5: Minimum, Maximum, Average (Avg.), and Standard Deviation of Major Ions in Lyon Stream

	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
Min. Lyon Stream	0	18.25	0	0.04	0.04	0.03	2.29	0	11.07	0.00	0.44	5.01	0

Max. Lyon Stream	0.01	21.64	0	0.11	0.44	0.05	4.59	0	12.6	0.02	0.91	7.6	5.62
Avg. Lyon Stream	0.01	19.89	0	0.07	0.13	0.04	2.74	0	11.82	0.01	0.71	6.23	4.55
STDEV. Lyon Stream	0.01	1.01	0	0.02	0.10	0.01	0.58	0	0.48	0.00	0.12	0.79	1.15

Table A6: Minimum, Maximum, Average (Avg), and Standard Deviation of Major Ions in Campus Stream

	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
Min. Campus Stream	0.01	10.29	0	0.03	0.43	0.06	3.33	0	8.45	0.01	0.93	0.65	5.84
Max. Campus Stream	0.03	21.85	0.01	0.09	1.75	0.15	7.5	0	20.01	0.02	1.64	9.4	13.92
Avg. Campus Stream	0.02	16.88	0.01	0.06	0.96	0.09	5.24	0	14.48	0.01	1.17	7.44	10.11
STDEV Campus Stream	0.01	2.93	0.01	0.02	0.34	0.03	1.27	0	2.90	0.00	0.19	2.10	1.98

Table A7: Minimum, Maximum, Average (Avg), and Standard Deviation of Major Ions in Lyon Rain

	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
Min. Lyon Rain	0	2.92	0.01	0.01	0.01	0.03	0.29	0	0.95	0	0.06	0.14	0.19
Max. Lyon Rain	0.02	21.56	0.01	0.07	0.51	0.13	3.47	0	12.47	0.91	3.57	1.32	0.98
Avg. Lyon Rain	0.01	7.56	0.01	0.02	0.11	0.08	1.17	0	4.11	0.06	0.50	0.58	0.42
STDEV Lyon Rain	0.01	5.06	0	0.02	0.16	0.05	0.77	0	2.86	0.22	0.81	0.34	0.23

Table A8: Minimum, Maximum, Average (Avg), and Standard Deviation of Major Ions in Campus Rain													
	F^-	Cl-	NO_2^-	Br	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na+	NH_4	K^+	Mg^{2+}	Ca^{2+}
Min. Campus Rain	0	4.76	0	0.02	0.19	0.02	0.85	0	2.75	0.00	0.24	0.35	0.67
Max. Campus Rain	0.02	58.52	0	0.12	1.18	0.03	8.82	0.0	33.09	0.05	1.80	3.41	5.47
Avg. Campus Rain	0.01	19.21	0	0.05	0.60	0.03	3.20	0.0	11.13	0.01	0.74	1.31	2.11
STDEV Campus Rain	0.01	18.26	0	0.03	0.42	0.01	2.73	0.00	10.29	0.01	0.69	1.14	1.63

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