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Where does the water come from? A temporal geochemical characterization of water sources in the lives of storms

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Where does the water come from? A temporal geochemical characterization of water sources in the lives of storms

A Capstone Project Submitted in Partial Fulfillment of the
Requirements of the Renée Crown University Honors Program at
Syracuse University

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and Renée Crown University Honors
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Honors Capstone Project in Physics

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Date: May 7, 2013

Abstract

An analysis of the ion chemistry, $\delta^{18}O$, and $\delta^{2}H$ values of precipitation may allow for the characterization of their water sources. As water evaporates, it retains a signature of its source in the ions that it carries and in the amount of fractionation of the oxygen and hydrogen isotopes. Precipitation samples for coastal, lake effect, and continental sources were collected over the months of October- January in Syracuse, New York throughout the duration of each storm, including one hurricane, one thunderstorm, two lake effect snowstorms, and seven rain events. These samples were run through IC, ICP-OES, and cavity ring-down laser ablation spectrometry methods; the measured ion concentrations and isotope values were plotted in partial Piper plots and on the local meteoric water line for each storm, respectively. These results were found to be characteristic of the expected trends for each type of storm.

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Preface

If you had told me a year ago that my senior Capstone project would be about storm systems, I would have gotten a good laugh out of it. This is not a project that I would have considered back then, but it is one that I regard as among the most valuable of my college career.

This project was conducted outside of either of my major departments of physics and chemical engineering. During the summer before my senior year, I participated in an NSF-supported REU program in the Department of Applied Ocean Physics and Engineering at the Woods Hole Oceanographic Institute, where I worked on the development of a prototype water sampler for autonomous and continuous river chemistry observations. While searching for a Capstone project for the fall of my senior year, I found an opportunity to work on water chemistry in the Earth Sciences department. My river sampler project was designed to provide a means to conduct water chemistry studies, and would hook up to IC and ICP-MS equipment along the lines of what I used in this Capstone project. At the time, I thought that this would be a good fit with my coursework and would allow for something of a continuation of environmental study from my previous work. What I didn't realize was how important this project would become as I enrolled in at least three courses that involved ion chemistry and stable isotopes. For this reason, this project has been extremely useful in my academic success and in my research abilities. Most importantly, this project has allowed me to continue working under the philosophy of interdisciplinary research in which I have found that committing to a field of study is, thankfully, not always a necessity.

Acknowledgements

Dr. Don Siegel, my advisor for this project, has been fantastic in sharing his ideas and enthusiasm for this project. I am grateful for his guidance in both this Capstone and in my future academic career in choosing a graduate degree program. I would also like to acknowledge Dr. Laura Lautz and Maggie Zimmer for all of their time and advice in running samples through the Earth Sciences IC and Picarro, and Deb Driscoll for allowing me to stay to learn how to run samples through the ICP-OES in the Analytical Services Lab at SUNY ESF.

I would like to thank the Honors College for accommodating the schedule of this project. It is unusual to delay large portions of a scientific Capstone project to the spring semester of senior year, but under the sampling constraints of the project and my evolving career goals, certain delays in reaching Capstone deadlines became necessary. I sincerely appreciate the extensions in my schedule allowed and approved by Honors over the past few semesters, and I sincerely appreciate the advice and guidance of the many Honors advisors.

I would like to thank the Syracuse University librarians and reference staff for their 24 hour assistance throughout this project. They helped me to gain access to many important scientific articles both late at night and at the last minute, and I am very grateful for their patience.

Finally, I can't begin to thank my family enough for their love and support throughout many difficult semesters of my undergraduate career. I would especially like to thank my mom, Kathleen Ringham, for her help in collecting storm samples throughout this project while I was on campus. I could not have completed this study without her.

Advice to Future Honors Students

My best advice to future honors students would be to take advantage of the help and flexibility the Honors staff offers to students. There have been times when I knew that I could not complete certain Honors requirements as they were written in the curriculum, but I found that the advisors were always willing to work with me to adjust schedules and requirements to fit both my abilities and interests and the spirit of the Honors curriculum.

To a lighter note, on the advice of older Honors students, I have found great success in assuring that hot chocolate packets would always be available to me in the Honors lounge by strategically placing them in and behind books around the room. I believe it is only fair to pass this advice on to the next class.

Introduction

Rainwater chemistry is typically studied post-precipitation. Few studies, if any, have been undertaken to characterize precipitation chemistry over time during a storm. The purpose of this Capstone project is to use a series of rainwater samples collected during different storms in Syracuse, NY, to determine the geochemistry of the water sources over which these storms originated.

The chemistry of rainwater varies by time and by location. Because water is a polar molecule, it has a strong ability to dissolve and retain ionic substances. When the water evaporates, it brings with it some of the dissolved ions from its source. When this water condenses to form precipitation, we expect these ions to rain out in such a way that precipitation samples collected at the beginning of a storm will have a greater ionic concentration than precipitation samples collected at the end of a storm, under the influence of gravity on ions that are often heavier than the water molecules themselves, and the often lower affinity of water to these ions than water to itself. Chemical analyses of a precipitation sample can determine the concentration of anions and cations present at a given time in a storm event, and these ion concentrations may be used to determine the source at which the water was originally evaporated.

In addition to ion concentrations, rainwater is characterized by stable isotope values. Water molecules may be composed of oxygen with 8, 9, or 10 neutrons (^{16}O, ^{17}O, or ^{18}O, respectively), and hydrogen with 1 or 2 neutrons (^{1}H or ^{2}H (also referred to as D, for deuterium), respectively.) The relative abundances of these heavier isotopes are very small, <0.5%, but the mass differences are enough that oxygen and hydrogen reservoirs will fractionate under many conditions, including evaporation and condensation. When water evaporates, the lighter isotopes are preferentially evaporated so that the water vapor is depleted in heavy oxygen and hydrogen isotopes relative to the liquid water left behind. (If evaporation continues, eventually enough heavy isotopes remain in the liquid form that they will have to be picked up, but in an open system such as a lake or an ocean, there exists an isotopic equilibrium in evaporation processes.)

Concentrations of isotopes on their own are generally not useful. Instead, a relationship between the heavy to light ratios of samples to standards is calculated as follows:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{sam} - (^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}}\right] \times 10^3$$

These values are called "delta" values, and are expressed in parts per million (‰). A negative delta value indicates depletion in the heavier isotope, while a positive delta value indicated enrichment. In the case of oxygen and hydrogen, V-SMOW (Vienna-Standard Mean Ocean Water) is identified as the standard, with $\delta^{18}O$ and $\delta^{2}H$ values of 0‰. As $\delta^{18}O$ values vary between water sources, especially between fresh water and seawater (with the Great Lakes typically expressing $\delta^{18}O$ and $\delta^{2}H$ values of approximately -7‰ and -49‰, respectively), stable oxygen isotope values can be useful in characterizing storms by their water sources (Jascheko, 2011).

Together, ion concentrations and stable isotope values should be able to serve as tracers for storm systems both spatially and temporally. This study aims to determine the accuracy of these measurements in relation to actual storm tracks for weather systems approaching Syracuse, NY from varying directions over several winter months, and to characterize the sources from which precipitation originated. Other studies along these lines may prove useful in current and future meteorological modeling applications and in predictions of precipitation chemistry (Bowen and Revenaugh, 2003). In this kind of study, Syracuse presents an interesting selection of storm types in any given year. In a general classification scheme, storms approaching the Central New York region may come over the Great Lakes from the Northwest bringing water vapor evaporated from fresh water, from Northeasters bringing water from cold ocean water across several states, up the coast from the Southeast bringing water warm, salty water, or across the states from the South and Southwest. Since the composition of rainwater reflects that of its source, we can expect marine-originating precipitation to have a high concentration of sodium and chloride relative to storms passing over fresh water bodies, and storms passing over large tracts of land may exhibit high calcium, sulfate, or bicarbonate concentrations from the ground over which the storms pass (Root et al., 2004). Collecting and analyzing precipitation samples from a variety of storm types in this region allows for direct comparisons of the isotopic and ionic composition of storms.

Methods

To collect precipitation samples throughout winter storm systems, a simple funnel system was set up in North Syracuse, NY, located about 2.5km from the weather station for Syracuse at Hancock International Airport. A funnel (0.2m in diameter) was attached to a Nalgene water bottle and mounted high on

Figure 1: Water collection setup

the top of a fence so that precipitation was uninterrupted during collection (see Figure 1). During a weather event, precipitation samples were collected as often as possible, when convenient and when at least 20mL of sample were available in the collection system. This resulted in a range of sample sizes between ~20mL and 100mL collected at uneven time intervals throughout the duration of a storm. (Time intervals for collection during storms varied between 1 and 24 hours.) Rain samples were poured from the collection bottle into pre-rinsed sample bottles, and snow samples were first brought indoors to melt and then stored in sample bottles. The Nalgene collection bottle was not rinsed between samples or weather events. Forty-eight precipitation samples were collected in this way between October 29, 2012, and January 20, 2013. They were placed in a cool, dark area for storage, but they were not acidified or refrigerated, nor were they filtered. Collection date, time, approximate temperature, and wind strength/direction were logged for each sample.

The samples collected represented the range of weather events experienced by Central New York throughout the ~3month study. These included the long-arm effects of Hurricane Sandy in late October, seven separate rain events, one thunderstorm, and two lake-effect storms. These storms approached Syracuse from a range of directions, with the lake effect storms, the thunderstorm, and one rain event coming over the Great Lakes from the Northwest, the hurricane coming up the coast from the Southeast, and six rain events coming from varying southerly directions.

These samples were run through a Thermo Scientific Dionex Ion Chromatograph (IC) in the Earth Sciences Department at Syracuse University to measure the concentration of anions (fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-})) and cations (calcium (Ca^+), sodium (Na^+), potassium (K^+), Magnesium (Mg^{2+}), and ammonium (NH_4^+)) present in solution. The samples were also run through a Perkin Elmer Optima 3300 DV Inductively Coupled Plasma- Optical Omission Spectrometer (ICO-OES) in the Analytical and Technical Service Laboratory at SUNY ESF to measure calcium (Ca^+), potassium (K^+), magnesium (Mg^{2+}), and sodium (Na^+) in solution as a comparison to the IC values of the same cations. Finally, the samples were run through a Picarro Cavity Ringdown Spectrometer to determine the $\delta^{18}O$ and δ^2H values of each sample relative to the V-SMOW standard.

Results

Once ion concentrations were measured for all samples, errors were determined from the blank and standard comparisons used in each testing system. The concentration of each ion was converted from the reported ppb to meq/L, and these concentrations were plotted against time since the start of the study for each storm system. These plots may be found in the Appendix.

Partial Piper plots of Mg^{2+}, Ca^{2+}, and Na^+ were created using a USGS EXCEL for Hydrology spreadsheet. In the absence of alkalinity data at this time, the anion side could not be completed, and is left for future study. A partial Piper plot for the overall study may be found in Figure 2 below.

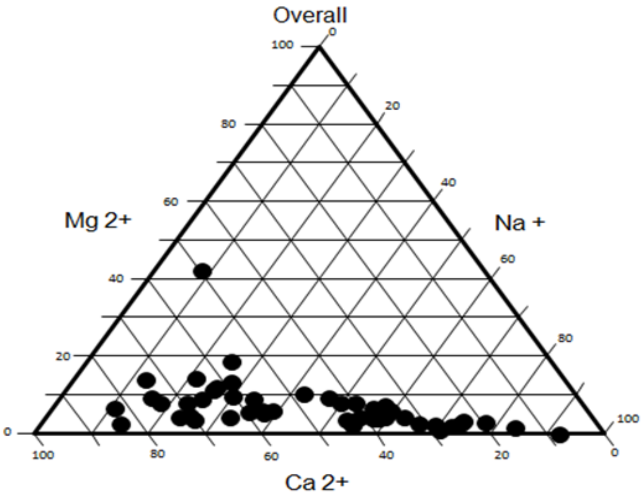

Figure 2: Overall Piper Plot

A plot of isotopic signatures for each sample was generated and was fit with a linear trendline representing the Local Meteoric Water Line; the Global Meteoric Water Line is also represented on this plot in Figure 3 (Burnett et al., 2004).

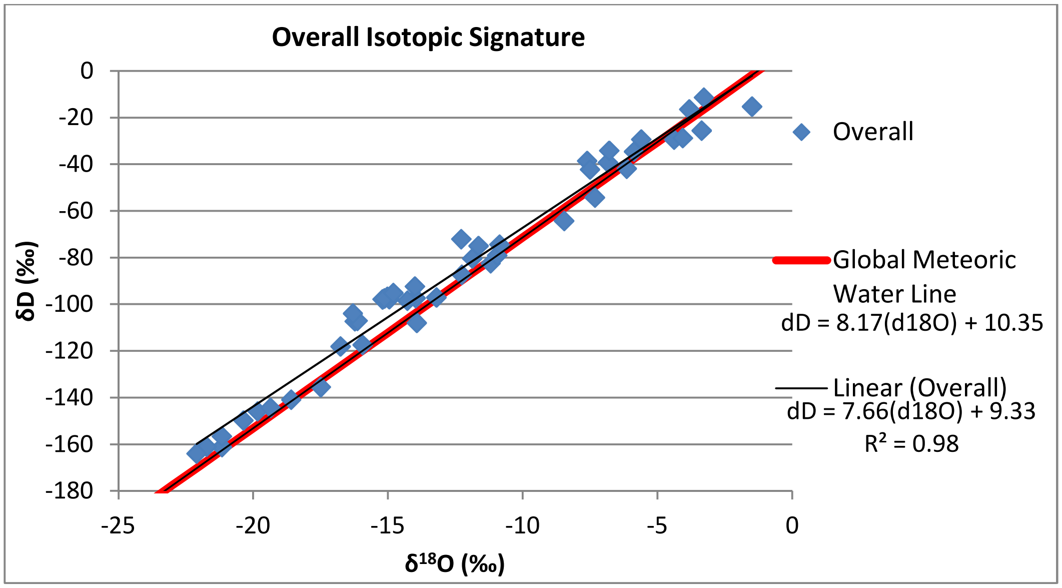

Figure 3: Overall Isotopic Data

This figure may be broken down into component storms as seen in Figure 4.

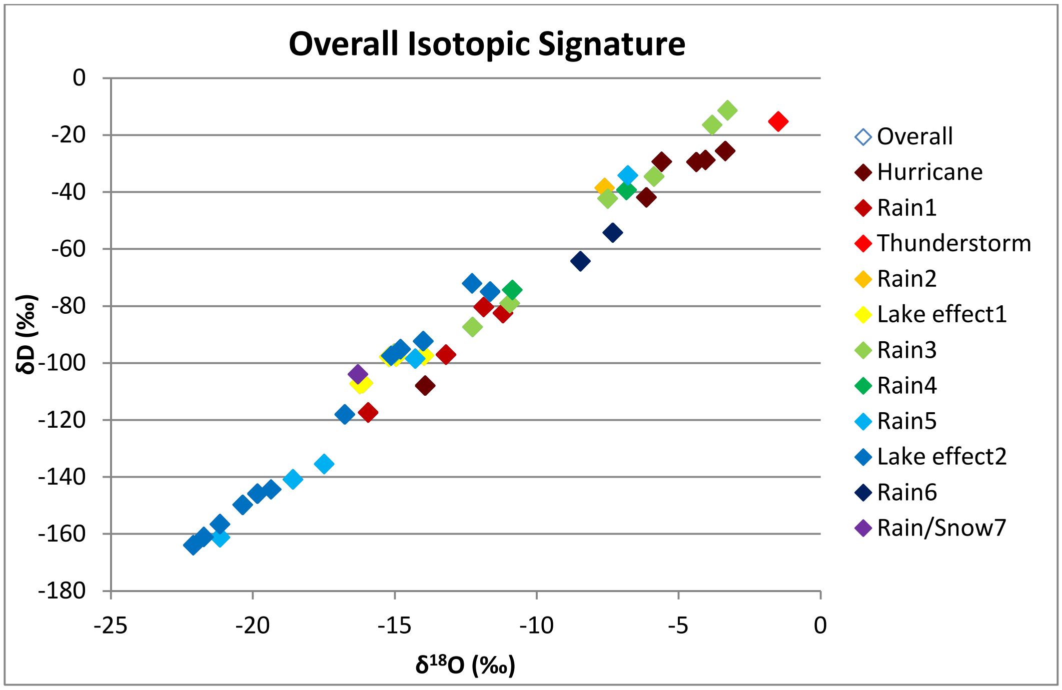

Figure 4: Overall Isotopic Data by Storm

A selection of the partial Piper plots and isotopic signatures for the 6 of the 11 sampled storms may be found below, where the remaining ion concentration plots, piper plots, and isotope plots may be found in the Appendix.

First, the long-arm effects of Hurricane Sandy were sampled between October 29, 2012 and October 31, 2012. This storm came up the coast from the Southeast, but like all hurricanes, swirled in towards the land and into Syracuse from the Northeast. A Piper Plot and isotope plot for this storm may be seen in Figures 5 and 6 below.

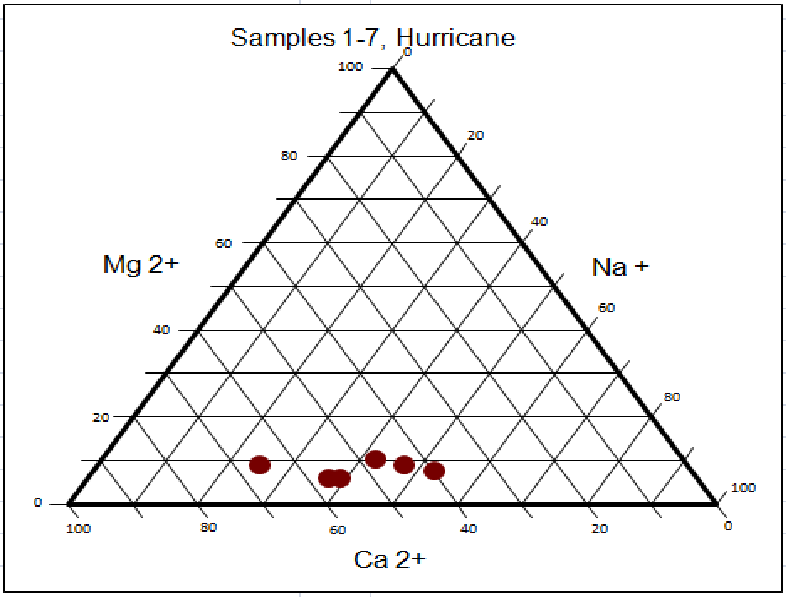

Figure 5: Hurricane Piper Plot

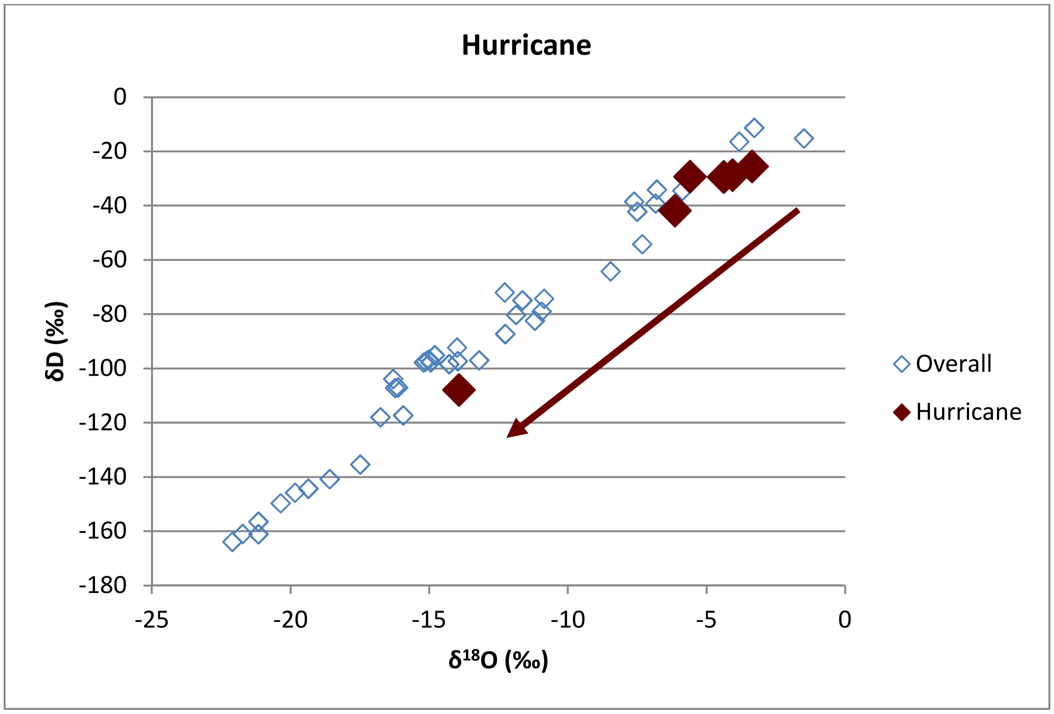

Figure 6: Hurricane Isotopic Composition

In this figure, the arrow indicates the sample composition changes over time, where the first sample taken appears in the top right corner and samples become more isotopically depleted over time down towards the bottom left corner.

Next, a Piper plot and isotope plot for the thunderstorm can be found in Figures 7 and 8 below. This storm occurred on November 11, 2012, and only one data point is shown because only one sample was collected during the very short duration of this storm.

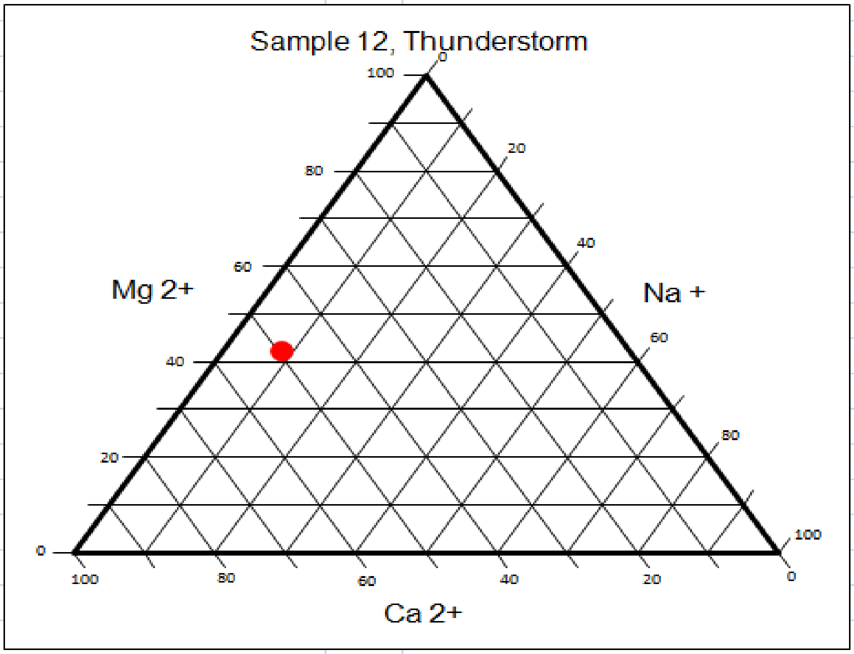

Figure 7: Thunderstorm Piper Plot

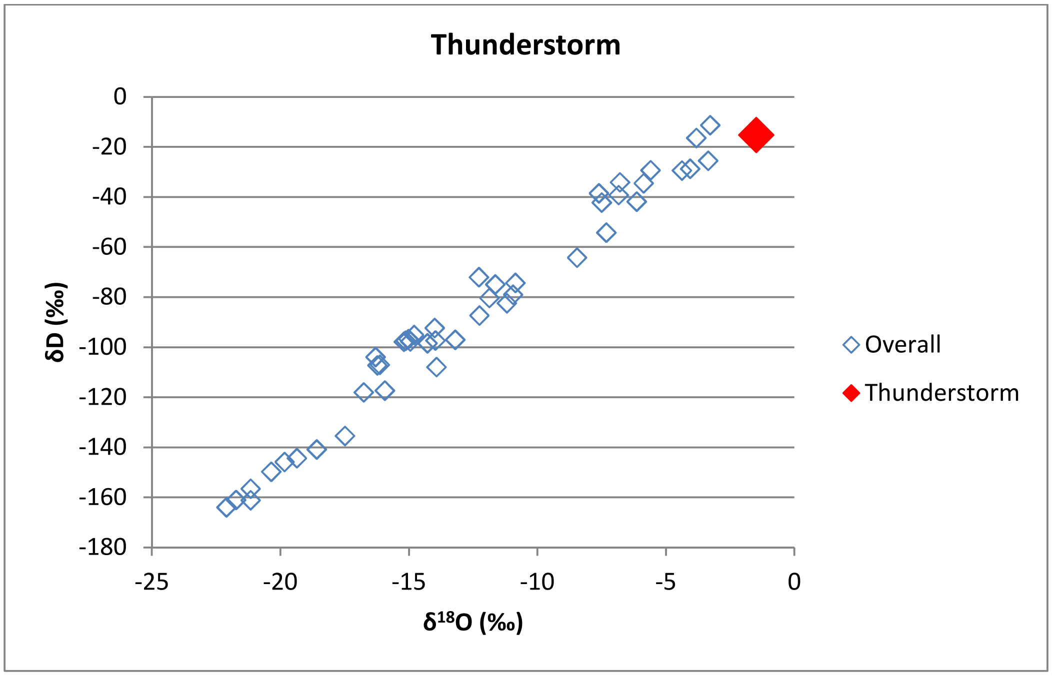

Figure 8: Thunderstorm Isotopic Composition

Six rain events were sampled throughout this study; to show the typical data patterns for rain storms, a rain storm on December 2 - 8, 2012 and another on December 17-19, 2012 are shown in Piper plots and isotope plots in Figures 9-12 below, where the first is Rain Event 3 that came from the South/Southeast, and the second is Rain Event 5, which came from the West/Southwest.

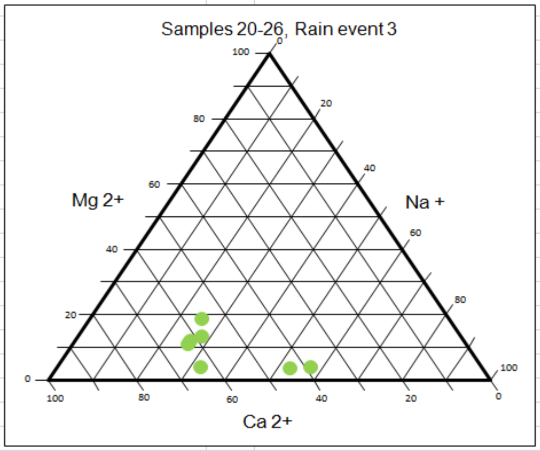

Figure 9: Rain Event 3 Piper Plot

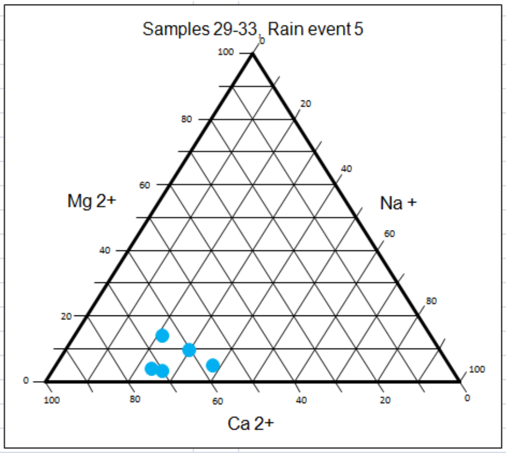

Figure 10: Rain Event 5 Piper Plot

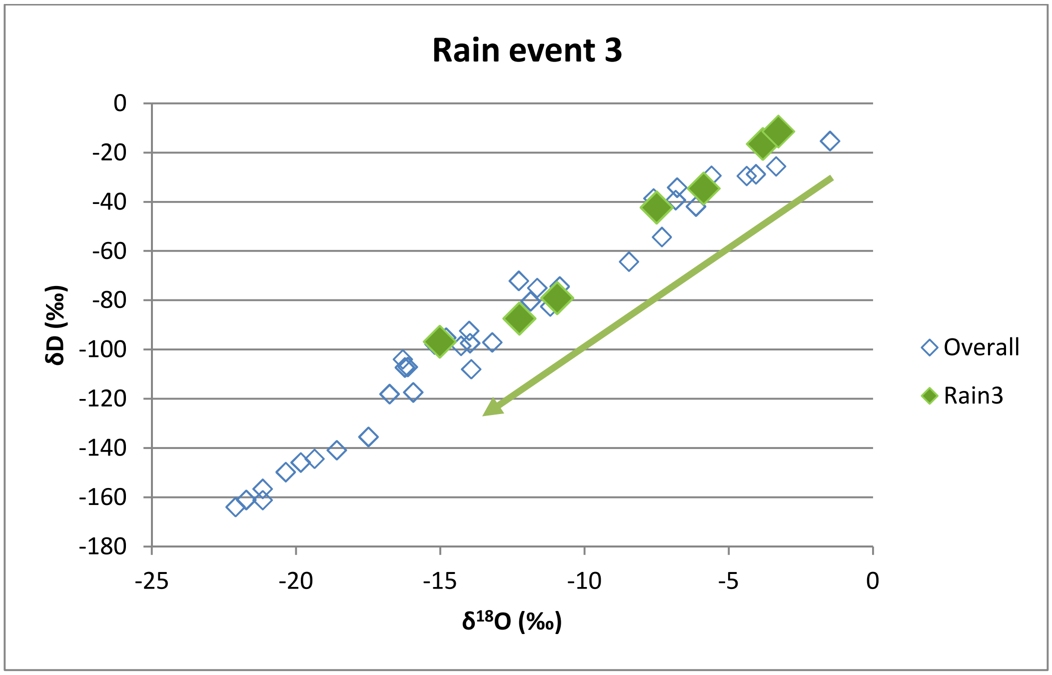

Figure 11: Rain Event 3 Isotopic Composition

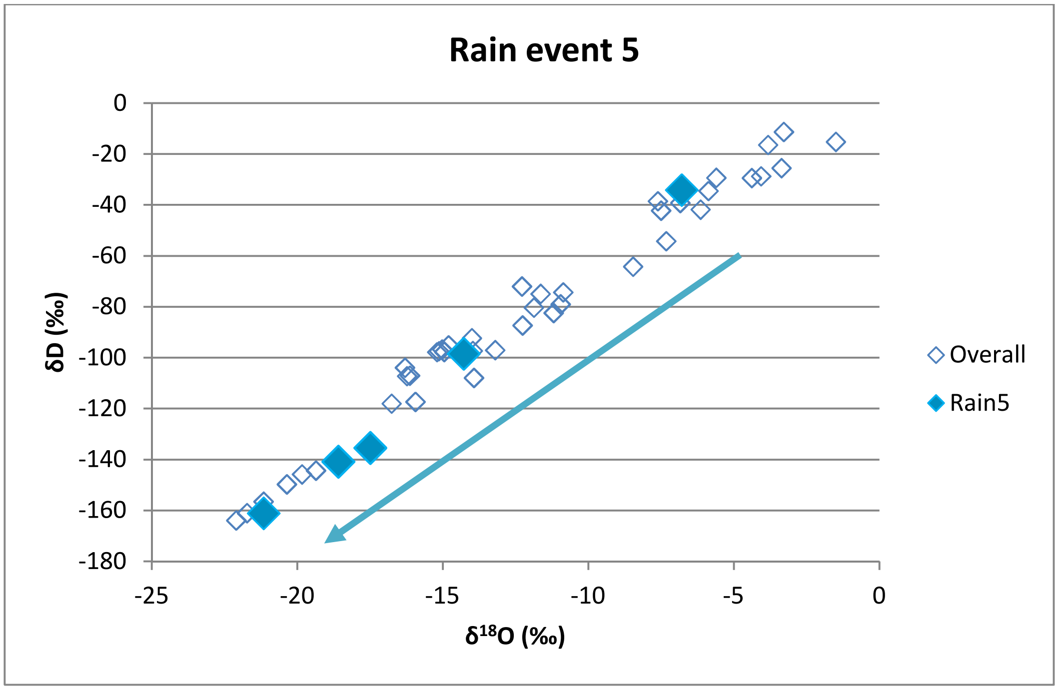

Figure 12: Rain Event 5 Isotopic Composition

Finally, two lake effect snowstorms were sampled From November 24-27, 2012 and from December 21, 2012 to January 2, 2012. Their Piper plots and isotope plots may be seen in Figures 13-16 below.

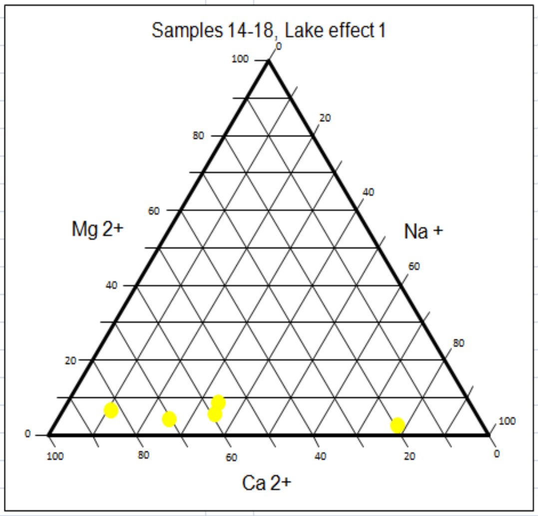

Figure 13: Lake Effect 1 Piper Plot

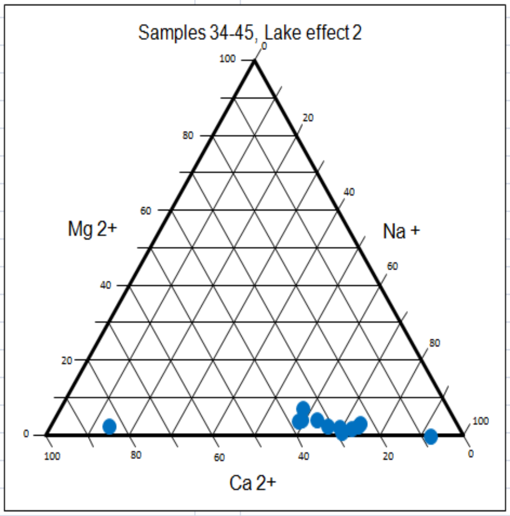

Figure 14: Lake Effect 2 Piper Plot

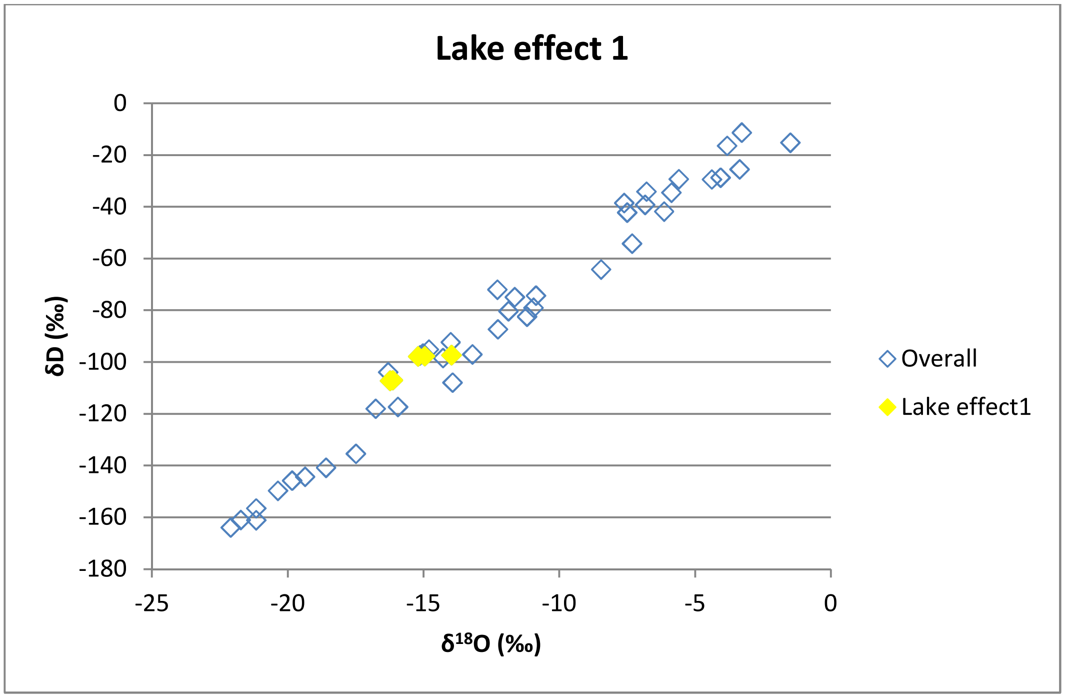

Figure 15: Lake Effect 1 Isotopic Composition

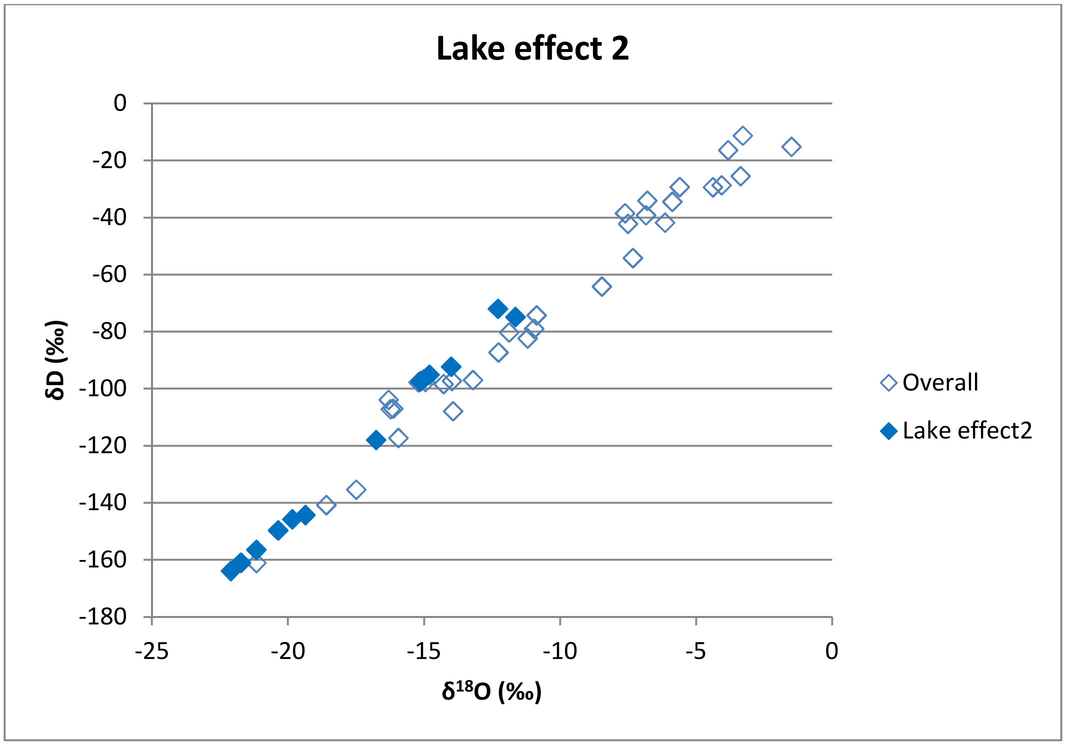

Figure 16: Lake Effect 2 Isotopic Composition

Discussion

The results for the highlighted storms above showed the characteristics of each storm. For the late October hurricane, a partial Piper plot showed that this precipitation had a high Na^+ and Ca^{2+} concentration, which was expected from water coming from the warm, salty ocean. Plots for the ion concentration for those not considered in the Piper plot generally showed the concentrations to be highest at the beginning of the storm, and relatively rained out by the end (see Appendix). An isotopic analysis of the $\delta^{18}O$ and $\delta^{2}H$ showed that the samples became relatively depleted in these heavy isotopes over time, as expected of this type of system.

The single data point for the thunderstorm made interpretations of its results uncertain, but that single sample showed characteristics expected of this type of storm. The ionic concentration of this sample showed a low $[Na^+]$, as expected of a storm with a fresh water Great Lakes source. This sample also showed the highest concentration of magnesium and a high calcium concentration, likely indicative of the ground over which the storm passed, since thunderstorms are very turbulent and can pick up ions easily over the ground. The isotopic signature of this storm was the highest (least depleted) of all of the storms sampled. This is because thunderstorms are characterized by very strong local downdrafts and because they rain out very quickly. This dumps all of the precipitation at once, so the concentrations of ^{18}O and ^{2}H in the sample are similar to the levels in the source. In this short period storm, raindrops do not have time to interact with ambient air as well, which reduces the isotopic fractionation during rainout.

In the two typical rain events shown, the ionic concentrations fall in the partial Piper plots as expected, with lower Na^+ concentrations than seen in the coastal hurricane, and higher Ca^{2+} concentrations than the hurricane, reflecting their longer path over land. The rainstorm coming from the West/Southwest (rain event 5) had a lower concentration of Na^+ than the rainstorm from the South/Southeast (rain event 3) because it moved from further away from the coast, while #3 may have picked up some salt from sources near the ocean. The isotopic compositions of these two storms over time decreased with the samples collected, showing the isotopic rainout and fractionation over time, as in the hurricane sample, and the variation between the range of delta values for the storms was likely due to both their sources and the total distances traveled before the storms reached Syracuse, because the path lengths may have differed, allowing one or the other to experience more isotopic depletion by the time it reached Central New York.

Finally, the two lake effect storms showed some interesting issues that are likely affected by ionic inputs other than the precipitation itself. In each of these cases, the concentration of Na^+ for at least one sample of the storm was much higher than expected for an event originating over the freshwater Great Lakes. At least one sample of each storm had a higher Ca^{2+} concentration than expected as well. This is very likely due to inputs from road salt during these heavy snowstorms. The collection bottle itself was located at a distance from the nearest road, however when snowplows come through and salt, they spray a great deal of NaCl into the air, and the strong turbulent winds associated with a lake effect storm may pick up and mix the Na^+ and Cl^-, eventually depositing them in increasing concentrations in the samples through the duration of the storm. The increased levels of Na^+ are seen in the Piper plot, and the Cl^- would be seen in the anion side of a Piper plot as well, were alkalinity data available to plot these points. Anion and cation data through time for these storms may be found in the Appendix. The increased Ca^{2+} concentrations are also likely due to artificial inputs during these winter storms as well; the sampling site is located nearby the Hancock airport, where both calcium and sodium are used as components in aircraft deicing fluid. As these aircraft land and take off, it is highly plausible that some of these chemicals are spread throughout the local storm system, and are eventually deposited with the samples collected.

The isotopic signatures are similarly difficult to read throughout these storms. Unlike the other types of precipitation events, no strong trend can be identified on the isotopic composition plots of the samples becoming more depleted or enriched throughout the lifetime of the storms; instead, relatively depleted and relatively enriched values may be found varying throughout time. This is likely caused by the formation of ice particles, where ^{18}O and ^{2}H concentrations cannot be easily predicted, and the precipitation of the snow, where highly turbulent conditions and varying winds allow precipitation to be mixed and swept throughout a storm system with little chronology in terms of which particles fall first from the clouds and which first hit the ground. Because the isotopic exchange between snow and ambient air is also limited by turbulent conditions, the precipitation is expected to be and seen to be more depleted than if it had simply rained (Gat, 1996). Over the lifetime of the storm, the isotopic fractionation is less effective and less easy to track than in other types of storms, which makes further study on this type of storm an interesting prospect.

Conclusion and Recommendations

The final results of this study show that a characterization of precipitation in Central New York through ion and isotope measurements may be carried out throughout the duration of storms, and will show the changing chemistry of precipitation. These studies will be continued to complete alkalinity measurements or estimations, allowing for the construction of complete Piper plots that will better display the geochemical differences between storm systems.

This type of project should expand into a larger study that encompasses full-year and multi-year measurements. To accurately depict the geochemical lives of storms, where possible, increased sampling frequency will allow for better understanding of ionic and isotopic signature changes, and the measurement of samples from more storms throughout one or more years will allow for much better characterization of short-lived storms, such as thunderstorms, that may only allow for one sample collection each before they are completely rained out.

It is recommended that a new sample site is chosen to better understand the lake effect storms; while samples from this location provided a characteristic picture of what we know of temporal lake effect chemistry, the extra inputs of salt and deicers interfere with our data. The addition of other sampling sites, as well, such as in Oswego, NY, or closer to New York City, would allow for a comparison of precipitation samples of a storm near its source to track the differences in, for example, rainstorms coming across the Great Lakes towards Syracuse, or coastal storms coming up the coast (i.e., the continental isotope gradient) (Araguas-Aragues et al., 2000). With additional sampling sites, larger studies could be taken of the progress of storms throughout the United States by successive collection stations (such as airports or universities) as the storm progressed.

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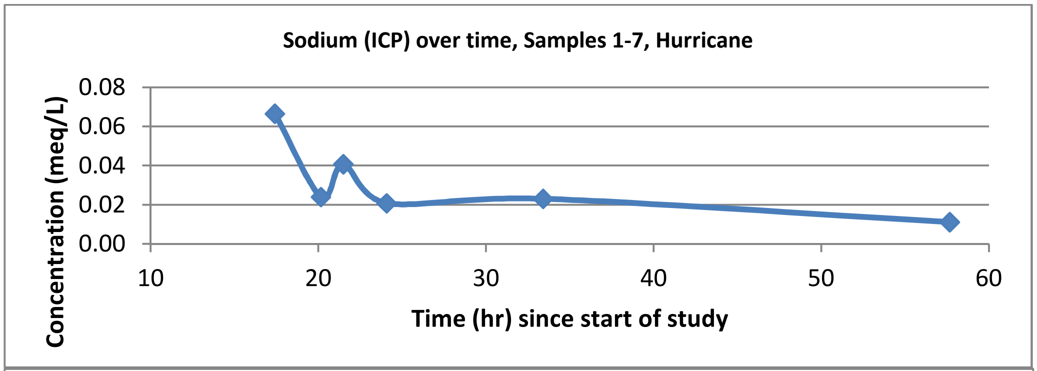
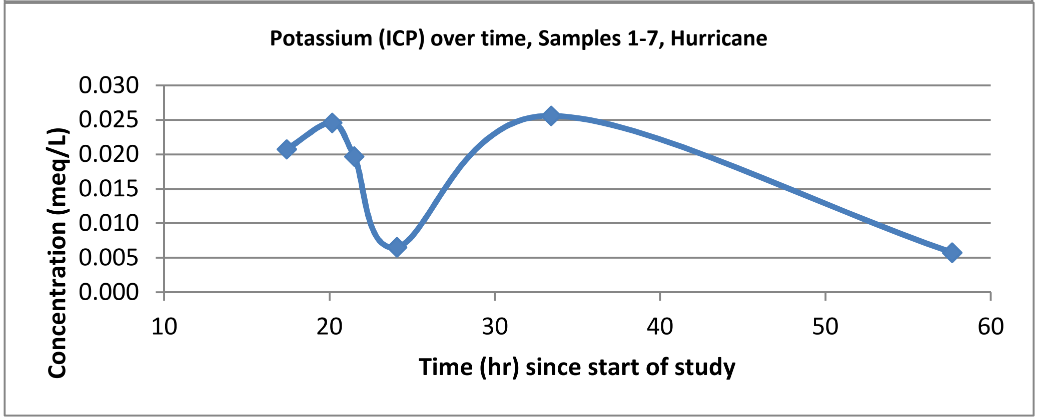
Appendices

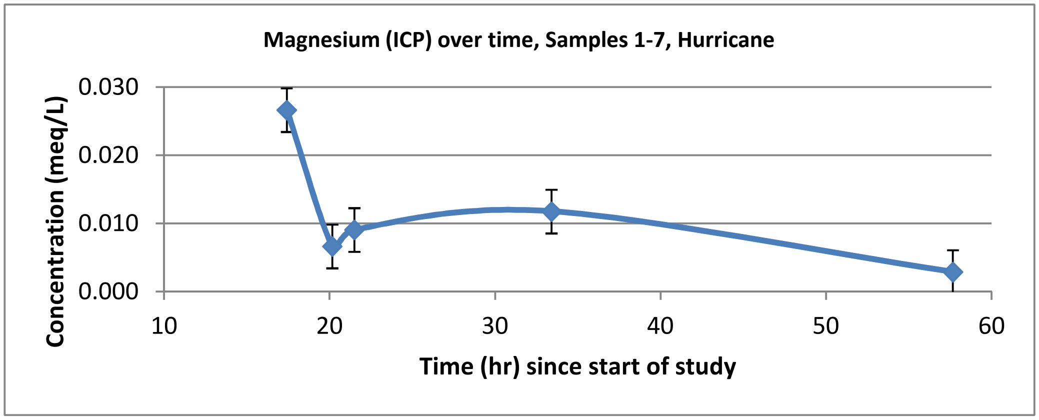
Appendix A: Storm Sample Types and Conditions

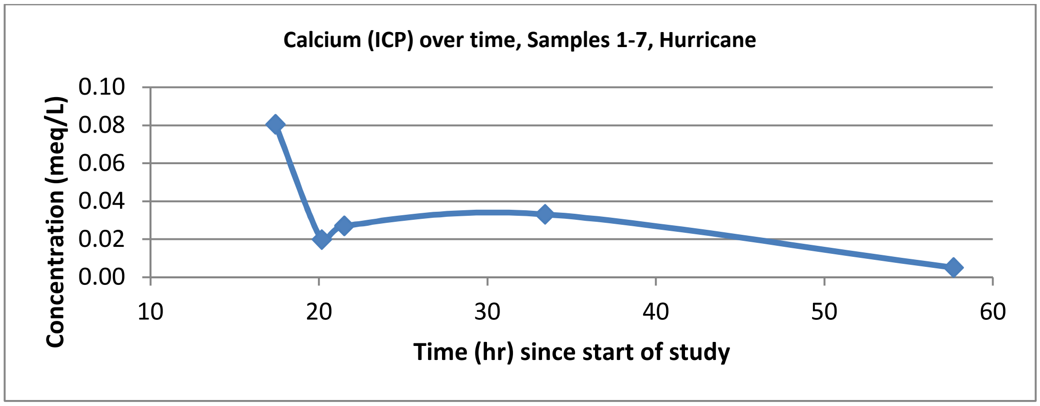
Sample	Type:	Wind (mph) and conditions	Cumulative rainfall"	Date	Time
1	Hurricane	N 27, rain, 55F	-	10/29/2012	5:25pm
2	Hurricane	N 14, rain, 55F	-	10/29/2012	8:10pm
3	Hurricane	N 16, rain, 57F	0.36	10/29/2012	9:30pm
4	Hurricane	NE 12.7, rain, 59F	-	10/30/2012	12:05am
5	Hurricane	E 13.8, rain, 56F	0.67	10/30/2012	9:25am
7	Hurricane	SE 4.6, rain, 45F	0.71	10/31/2012	9:40am
8	Rain event	NEW 10, rain, 46F	0.93	11/1/2012	3:50pm
9	Rain event	NW 15, rain, 41F	1.09	11/2/2012	9:50am
10	Rain event	W 14, rain, 39F	1.09	11/3/2012	9:25am
11	Rain event	NW 9, rain, 40F	1.09	11/4/2012	10:50am
12	Thunderstorm	NW 19.6, rain, 56F	1.12	11/11/2012	9:00am
13	Rain event	S 23, rain, 42 F	1.31	11/13/2012	11:20am
14	Lake effect snow	W 16, snow, 32F	1.37	11/24/2012	9:00am
15	Lake effect snow	W 6, snow, 30F	1.47	11/25/2012	9:30am
16	Lake effect snow	W 12, snow, 30F	-	11/26/2012	11:10am
17	Lake effect snow	WNW 15, snow, 35F	1.62	11/26/2012	3:00pm
18	Lake effect snow	WNW 3, snow, 37F	1.62	11/27/2012	10:40am
20	Rain event	SW 10, rain, 49F	1.89	12/2/2012	1:30pm
21	Rain event	W 10, rain, 45F	1.89	12/3/2012	8:50am
22	Rain event	SE 3, rain, 48F	2.3	12/4/2012	9:45am
23	Rain event	SE 17, rain, 39F	2.46	12/5/2012	8:50am
24	Rain event	SE 2, rain, 33F	2.46	12/6/2012	12:30pm
25	Rain event	ESE 4, rain, 39F	2.51	12/7/2012	6:00pm
26	Rain event	ESE 9, rain, 38F	2.6	12/8/2012	9:00am
27	Separate rain event	S 12, rain, 54F	3.68	12/10/2012	9:30am
28	Separate rain event	W 8, rain, 32F	3.69	12/11/2012	8:50am
29	Rain event	E 13, rain, 37F	4.23	12/17/2012	7:30am
30	Rain event	E 16, rain, 40F	-	12/18/2012	6:30am
31	Rain event	calm, heavy rain, 45F	-	12/18/2012	11:30am
32	Rain event	NW 25, rain, 40F	-	12/18/2012	6:00pm
33	Rain event	W 12, rain, 37F	4.23	12/19/2012	9:30am
34	Lake effect snow	ESE 24, rain-snow, 33F	5.06	12/21/2012	10:00am
35	Lake effect snow	W 20, snow, 27F	-	12/22/2012	9:00am
36	Lake effect snow	W 24, snow, 27F	5.39	12/22/2012	2:30pm
37	Lake effect snow	SW 13, snow, 32F	5.63	12/23/2012	9:20am
38	Lake effect snow	E 9, light snow, 29F	5.65	12/24/2012	7:00pm
39	Lake effect snow	NW 9, snow, 26F	5.82	12/25/2012	12:30pm
40	Lake effect snow	NE 11, heavy snow, 26F	6.34	12/26/2012	9:00pm
41	Lake effect snow	NW 6, heavy snow, 20F	-	12/27/2012	7:00am
42	Lake effect snow	NW 15, heavy snow, 25F	7.79	12/27/2012	2:00pm
43	Lake effect snow	NE 4.6, heavy snow, 29F	8.09	12/29/2012	1:00pm
44	Lake effect snow	W 16, snow, 25F	8.13	12/30/2012	10:00am
45	Lake effect snow	W 12, snow, 24F	8.15	1/2/2013	11:40am
46	Rain event	E 8.1, rain, 40F	-	1/11/2013	3:20pm
47	Rain event	ESE 16, rain, 40F	8.34	1/11/2013	6:00pm
48	Rain and snow event	SW 18, rain/snow, 44F	8.34	1/19/2013	12:30pm
49	Rain and snow event	W 27, rain, 33F	8.34	1/20/2013	12:30pm

Appendix B: Hurricane Data: Ion Concentrations
ICP-OES

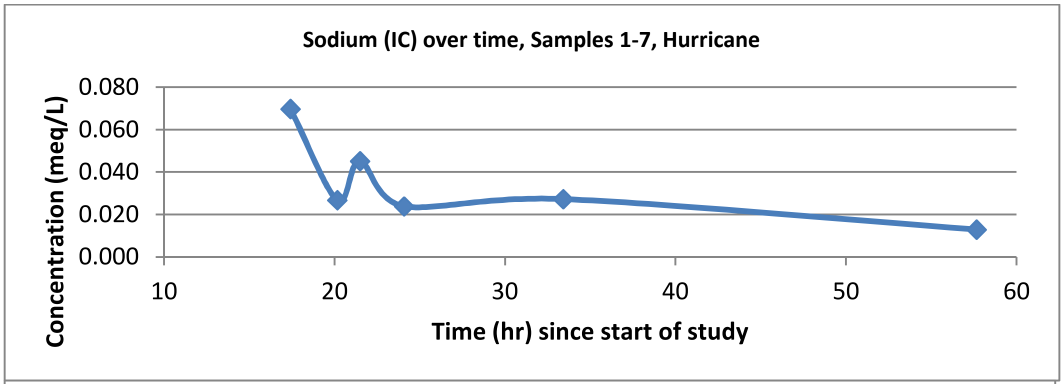


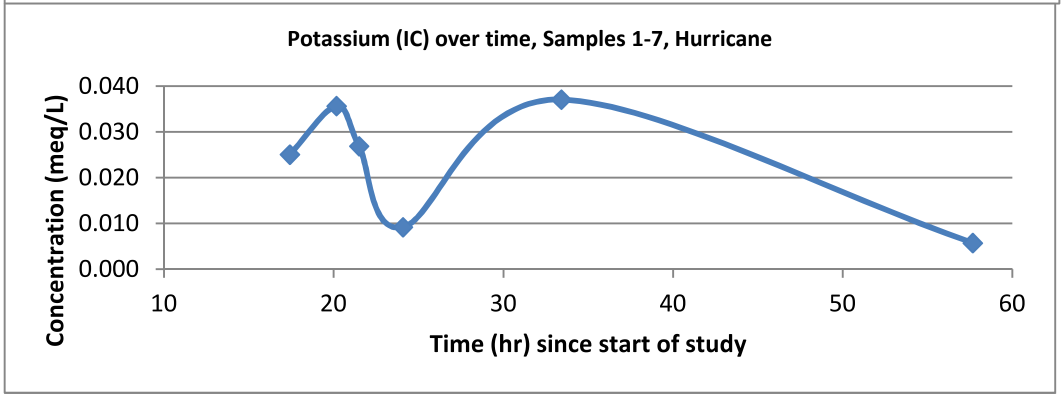


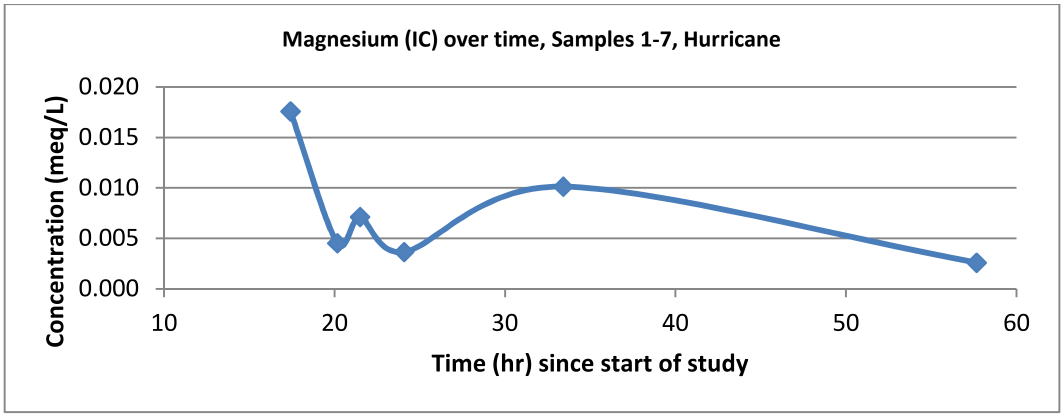


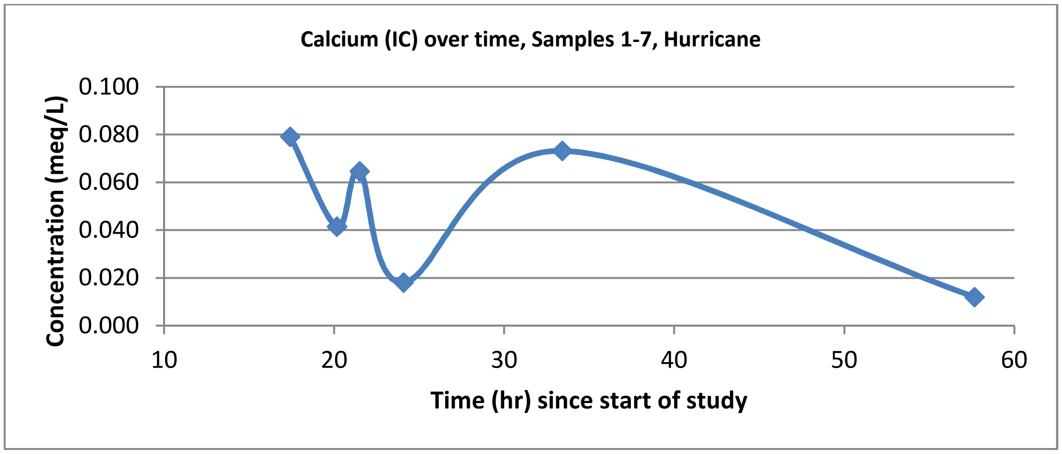


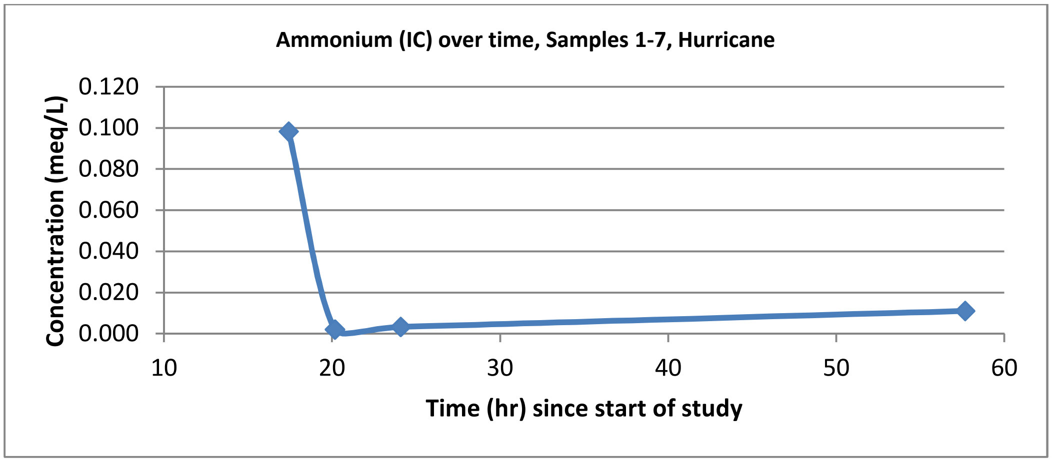
IC:

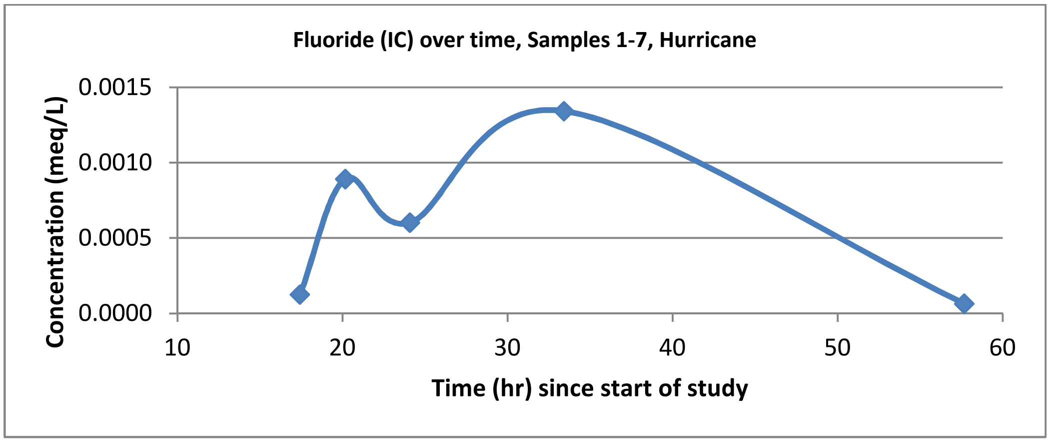

Sodium (IC) over time, Samples 1-7, Hurricane

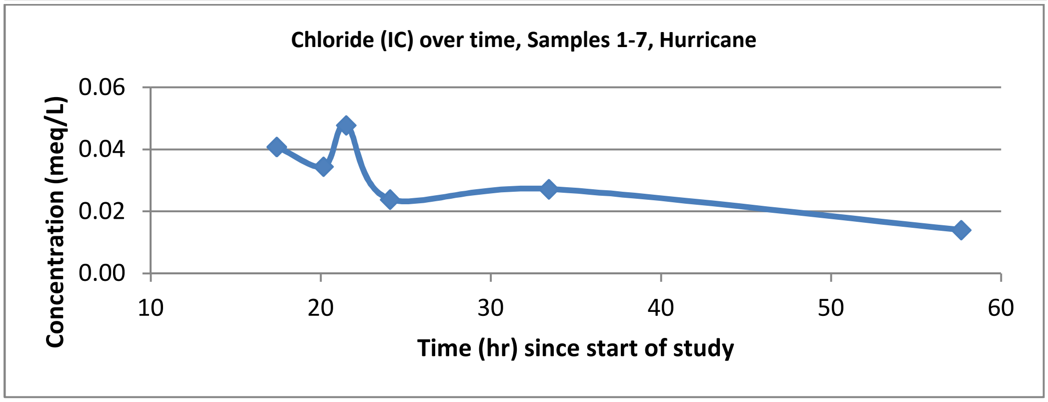

Potassium (IC) over time, Samples 1-7, Hurricane

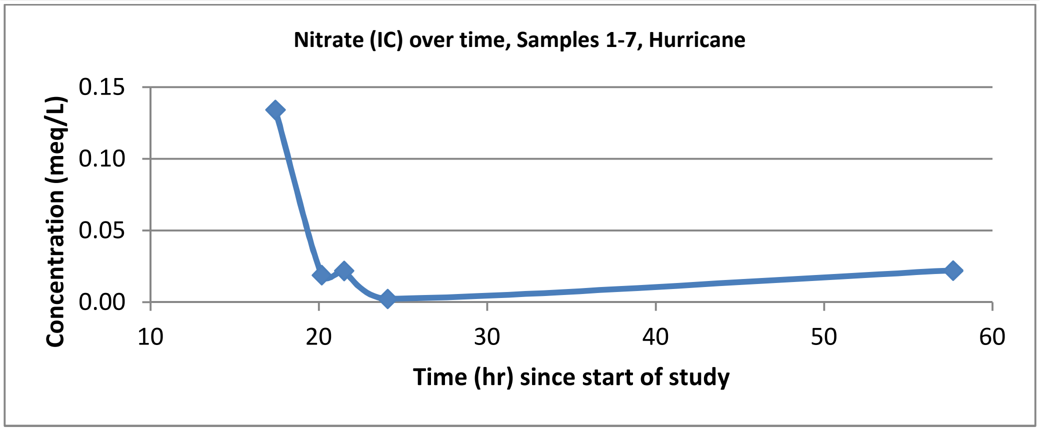

Magnesium (IC) over time, Samples 1-7, Hurricane

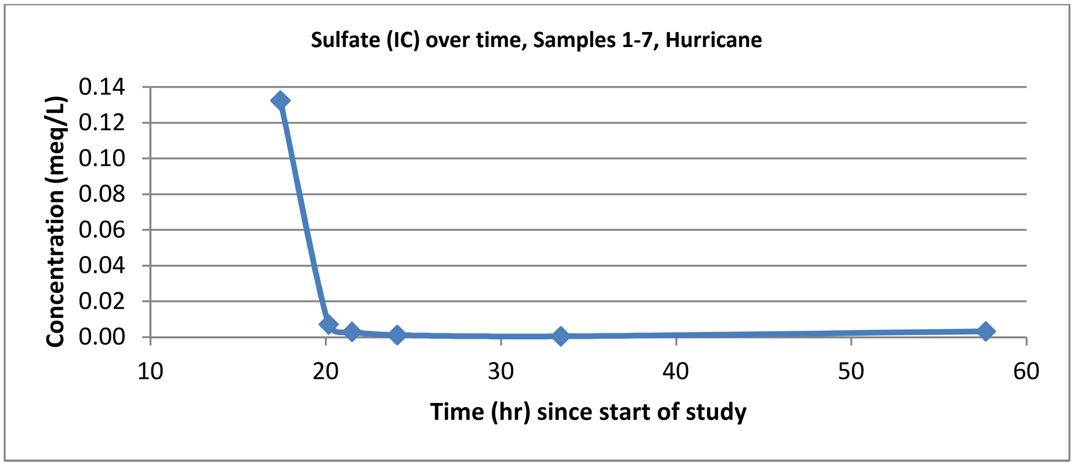

Calcium (IC) over time, Samples 1-7, Hurricane


Ammonium (IC) over time, Samples 1-7, Hurricane
Concentration (meq/L)
0.120
0.100
0.080
0.060
0.040
0.020
0.000
10
20
30
40
50
60
Time (hr) since start of study

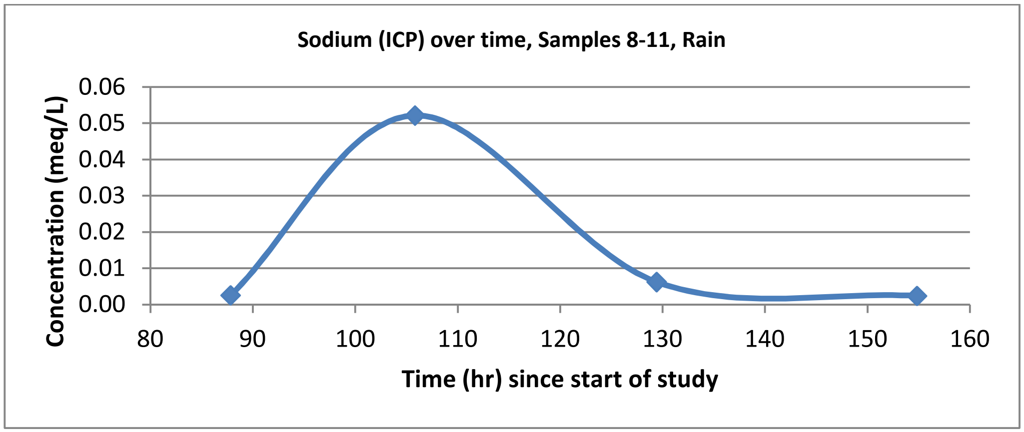

Fluoride (IC) over time, Samples 1-7, Hurricane
Concentration (meq/L)
0.0015
0.0010
0.0005
0.0000
10
20
30
40
50
60
Time (hr) since start of study

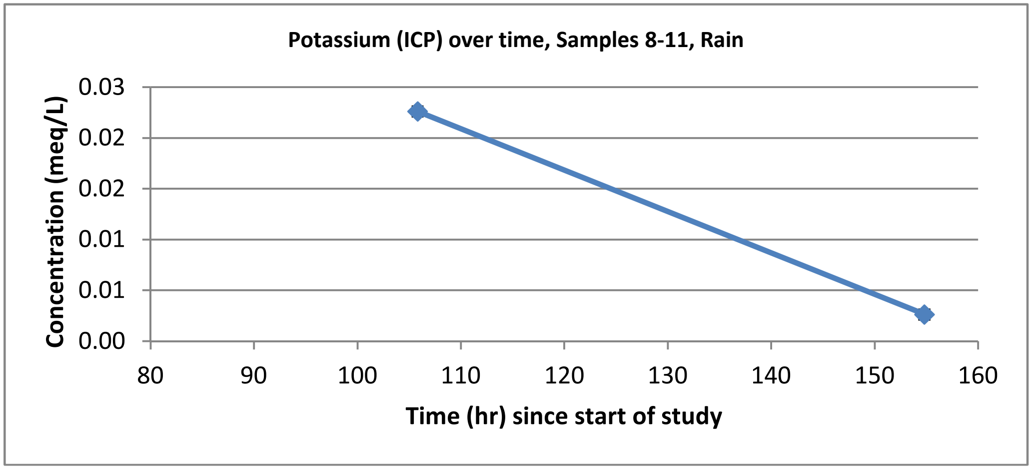

Chloride (IC) over time, Samples 1-7, Hurricane
Concentration (meq/L)
0.06
0.04
0.02
0.00
10
20
30
40
50
60
Time (hr) since start of study

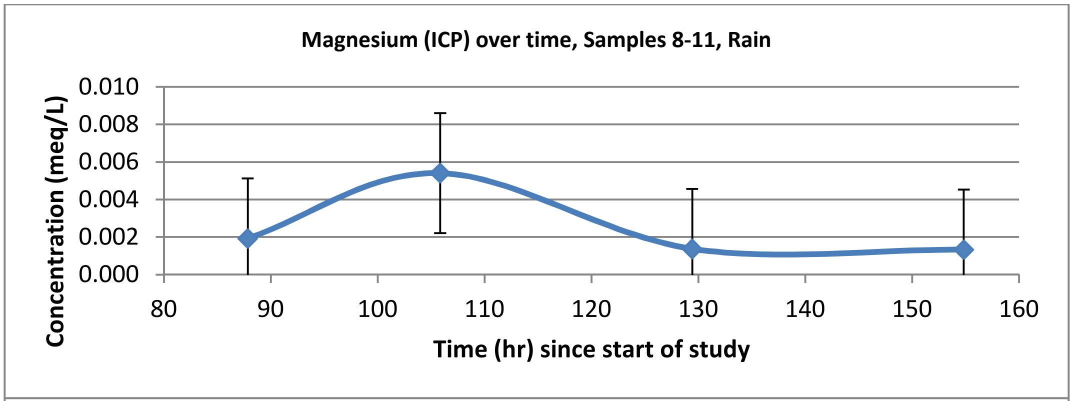

Nitrate (IC) over time, Samples 1-7, Hurricane
Concentration (meq/L)
0.15
0.10
0.05
0.00
10
20
30
40
50
60
Time (hr) since start of study



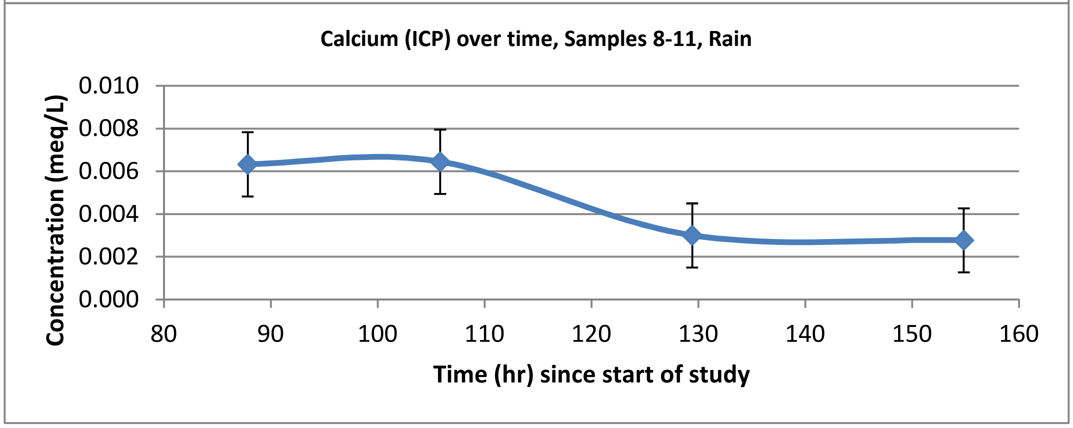
Appendix C: Rain Event 1: Ion Concentrations
ICP-OES





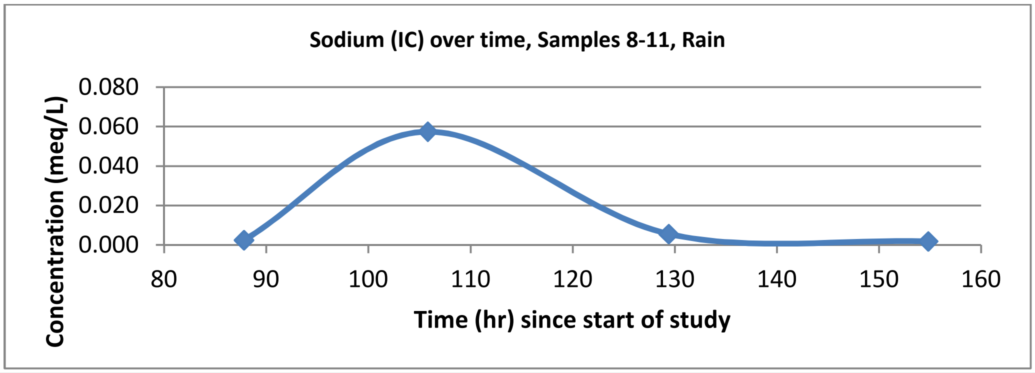


Magnesium (ICP) over time, Samples 8-11, Rain

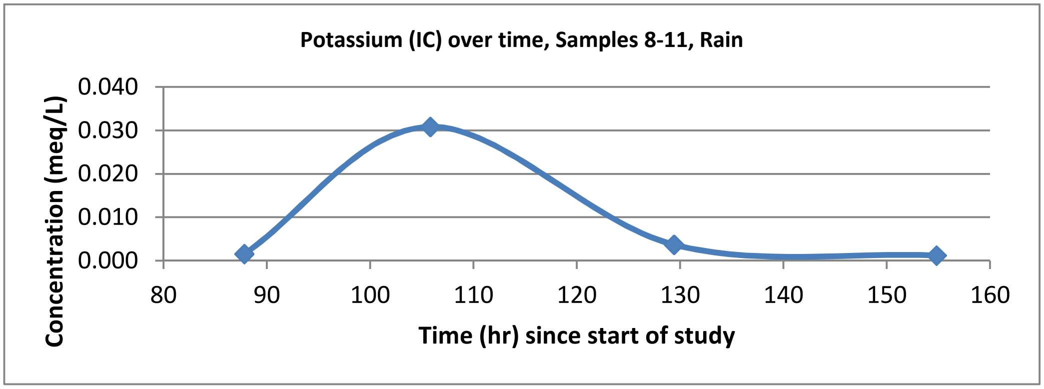


Calcium (ICP) over time, Samples 8-11, Rain

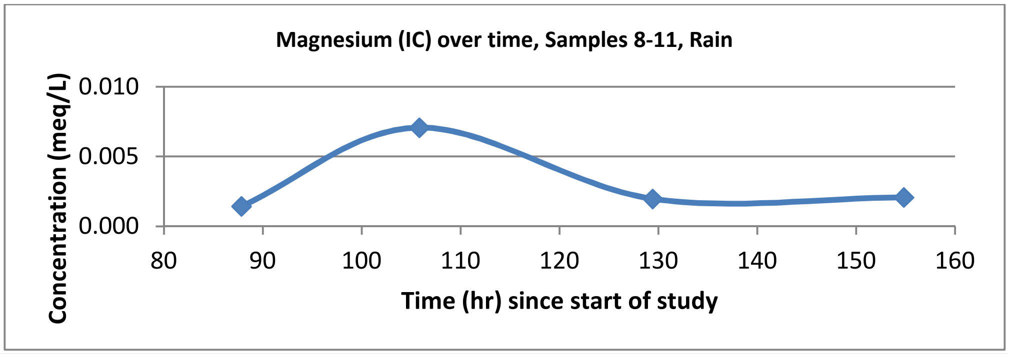
IC:

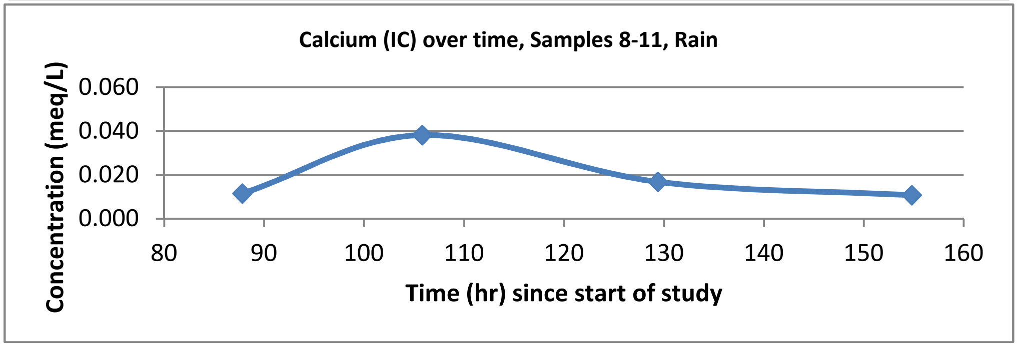


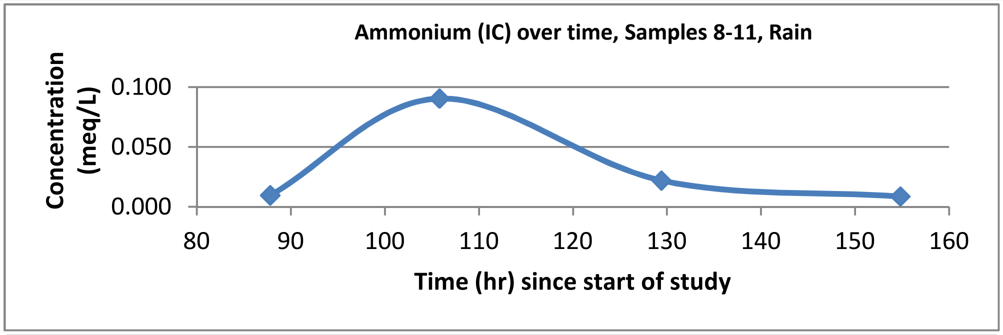
Sodium (IC) over time, Samples 8-11, Rain

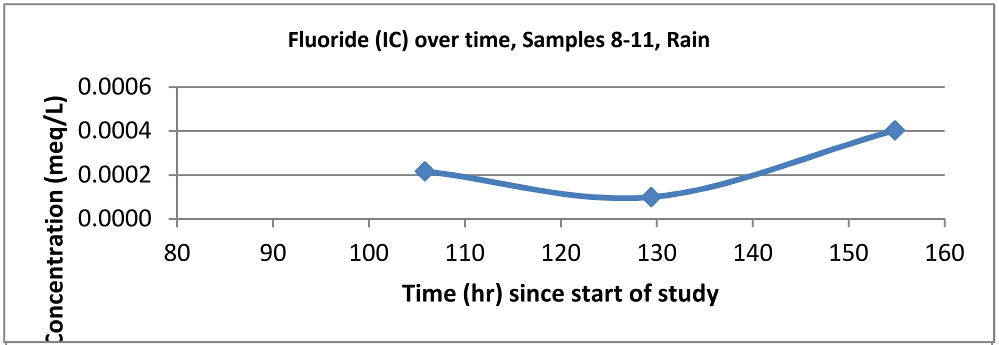


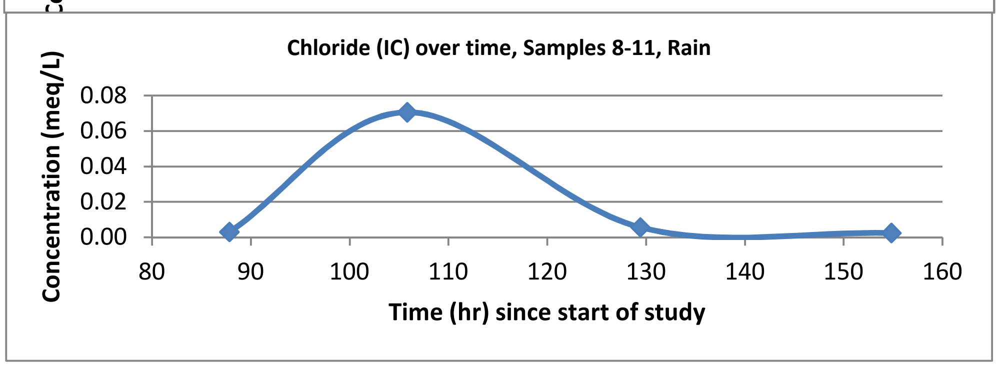
Potassium (IC) over time, Samples 8-11, Rain

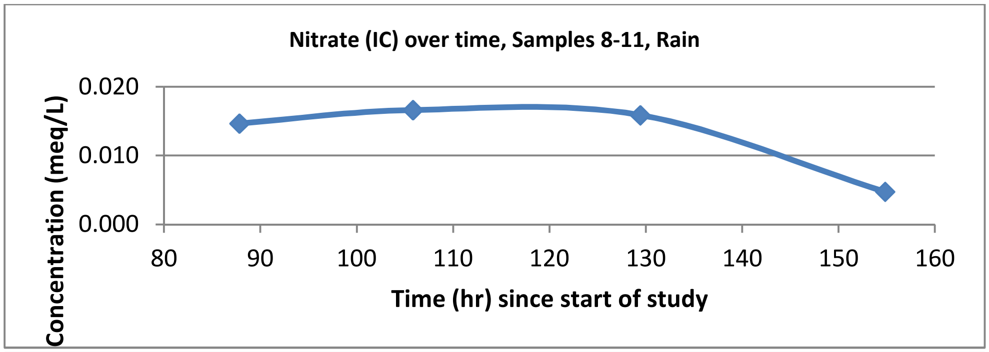

Magnesium (IC) over time, Samples 8-11, Rain
Concentration (meq/L)
0.010
0.005
0.000
80
90
100
110
120
130
140
150
160
Time (hr) since start of study

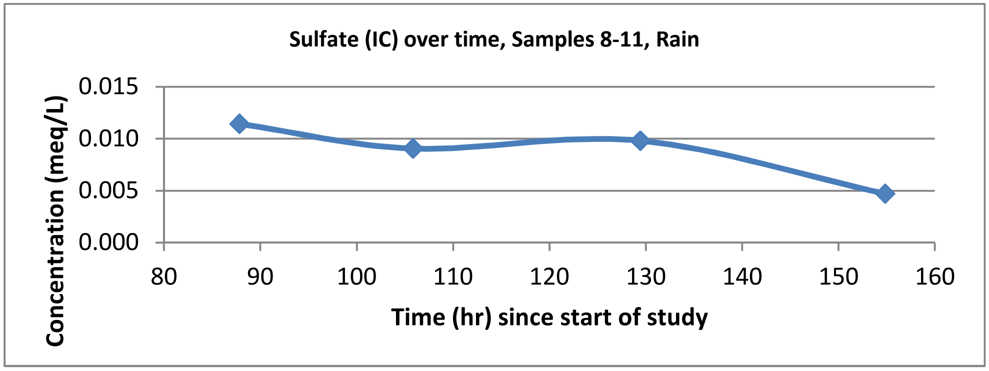

Calcium (IC) over time, Samples 8-11, Rain
Concentration (meq/L)
0.060
0.040
0.020
0.000
80
90
100
110
120
130
140
150
160
Time (hr) since start of study


Ammonium (IC) over time, Samples 8-11, Rain
Concentration (meq/L)
0.100
0.050
0.000
80
90
100
110
120
130
140
150
160
Time (hr) since start of study

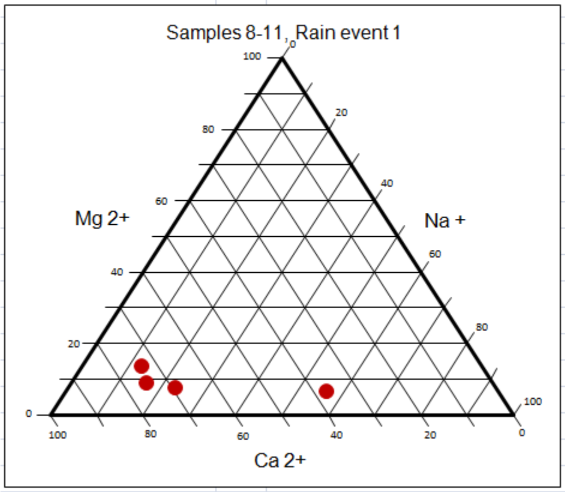

Fluoride (IC) over time, Samples 8-11, Rain
Concentration (meq/L)
0.0006
0.0004
0.0002
0.0000
80
90
100
110
120
130
140
150
160
Time (hr) since start of study


Chloride (IC) over time, Samples 8-11, Rain
Concentration (meq/L)
0.08
0.06
0.04
0.02
0.00
80
90
100
110
120
130
140
150
160
Time (hr) since start of study

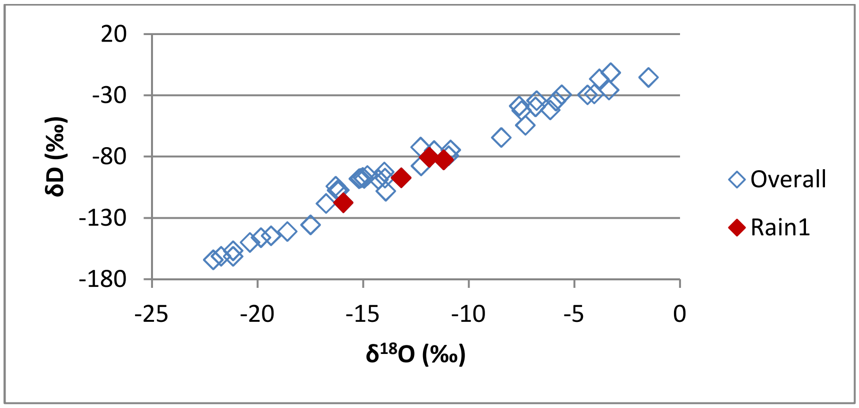




Piper Plot:

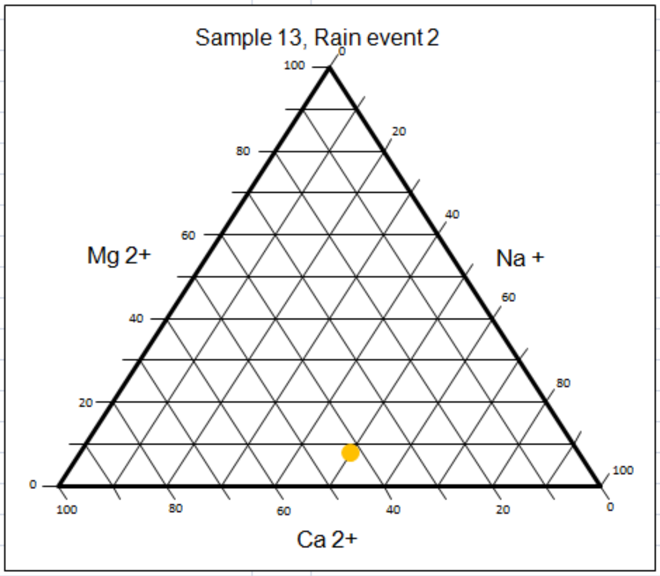


Isotopic Composition:

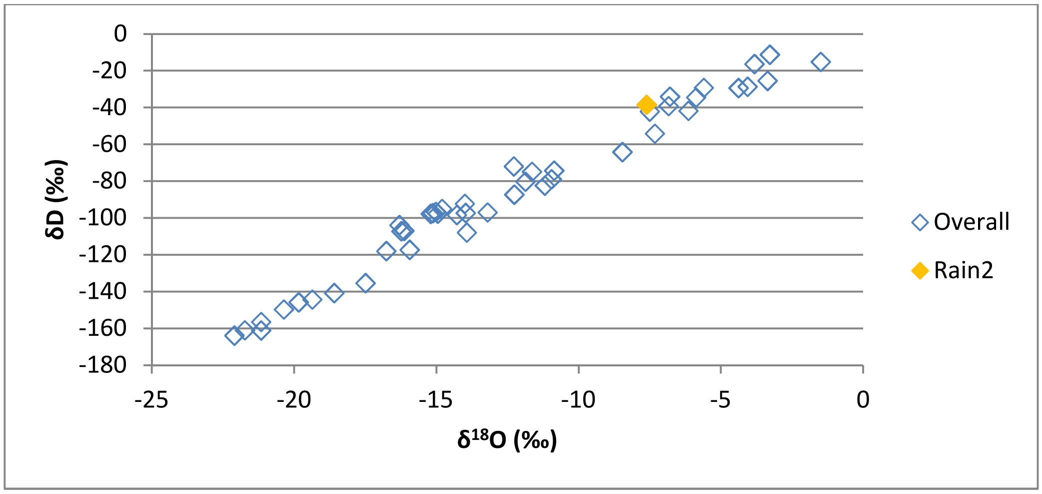


Appendix D: Rain Event 2

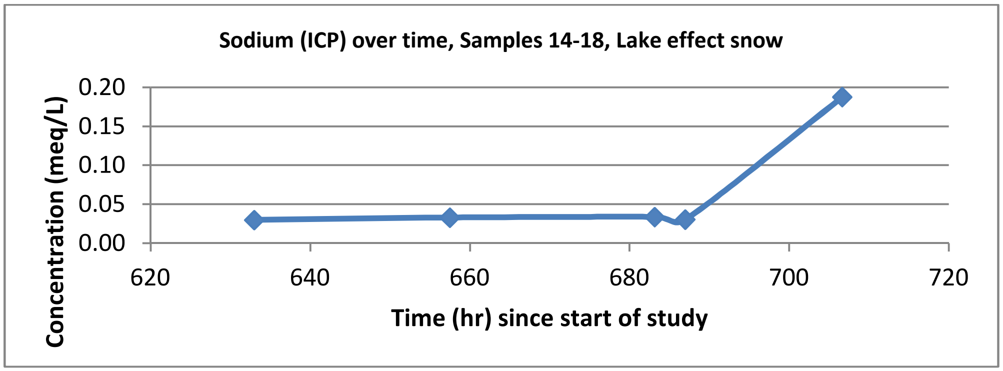
Piper Plot:

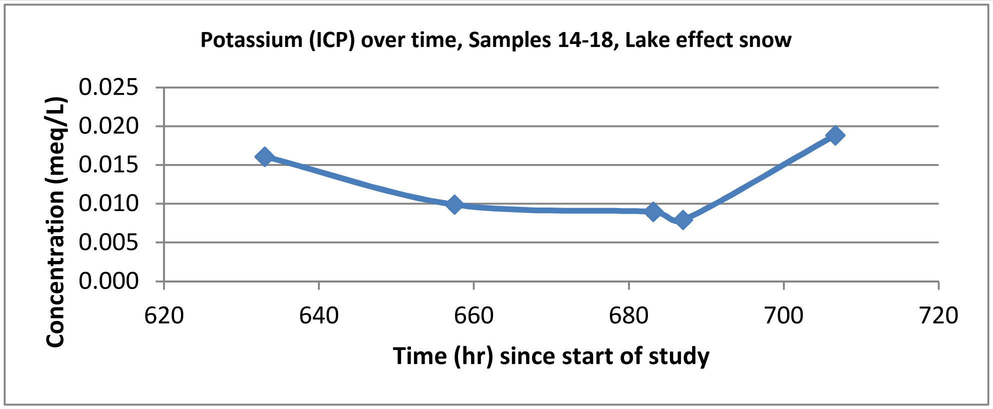


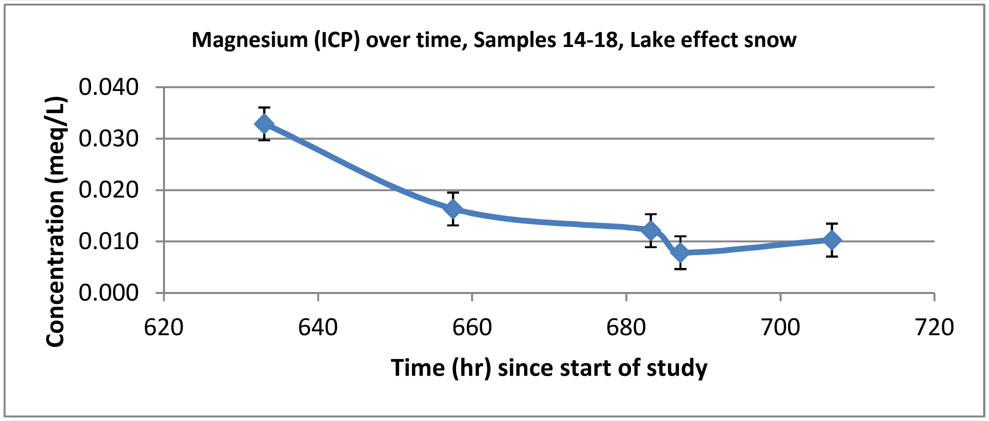
Isotopic Composition:

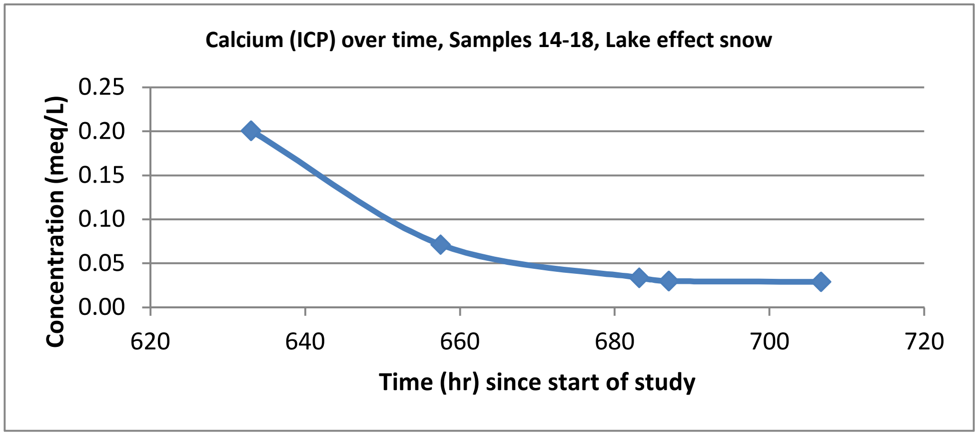


Appendix E: Lake effect 1: Ion Concentrations
ICP-OES

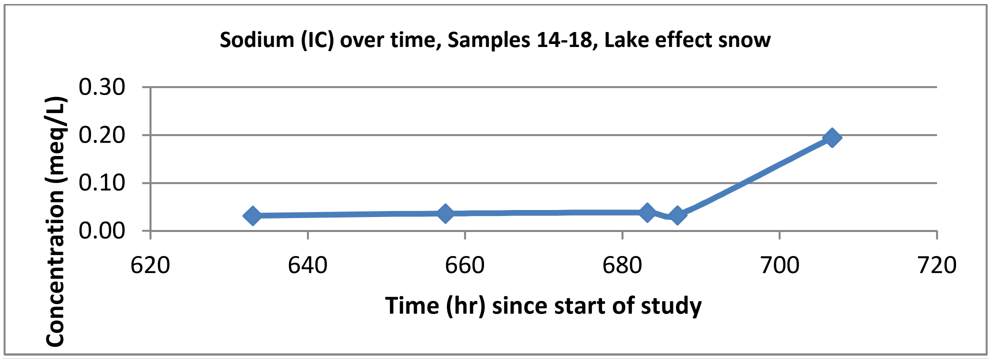


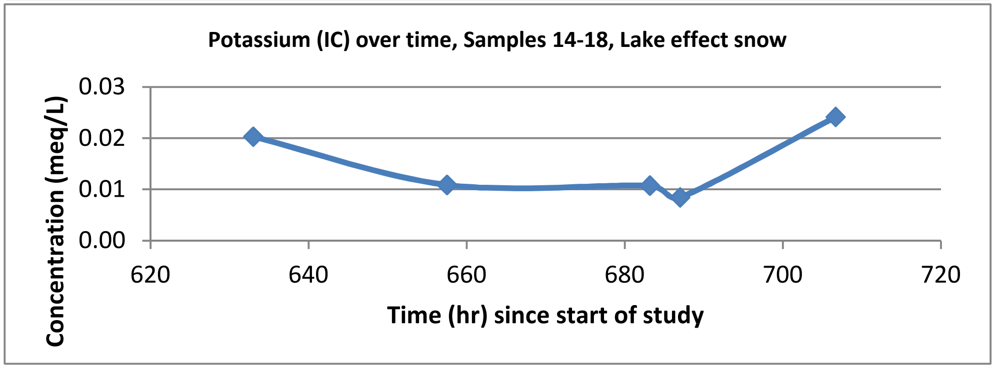


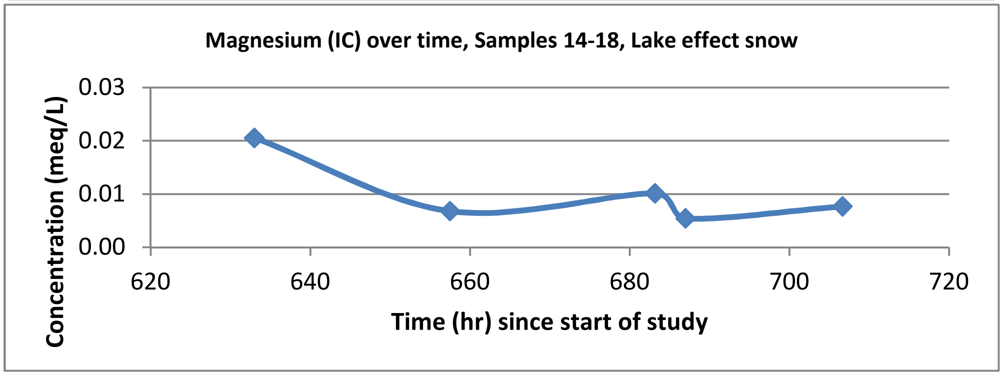


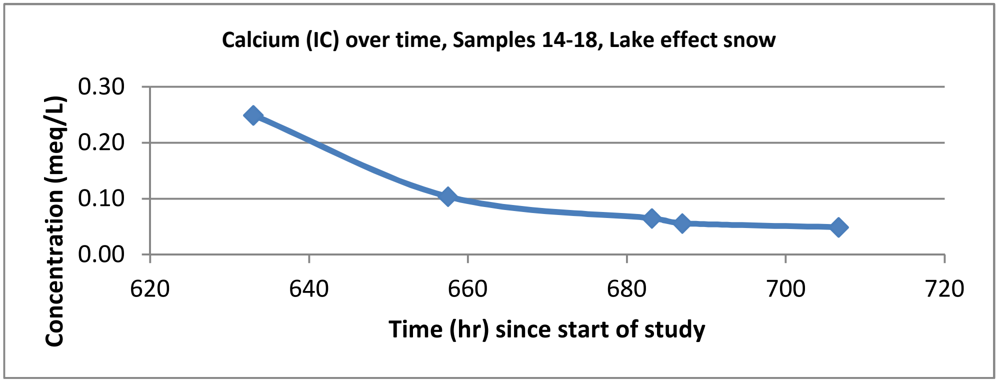


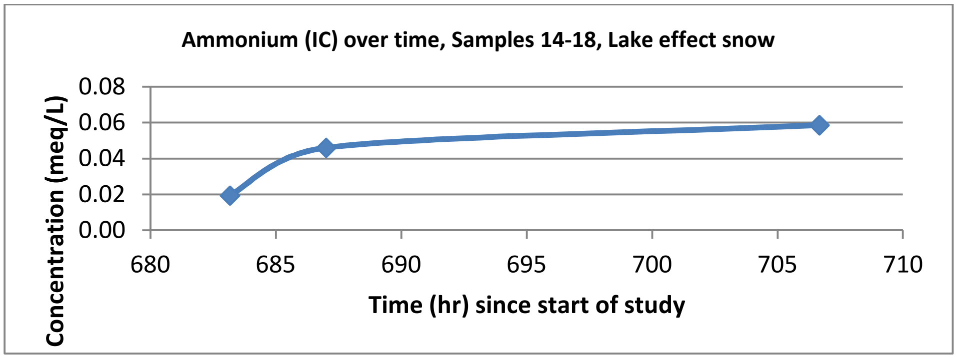
IC:

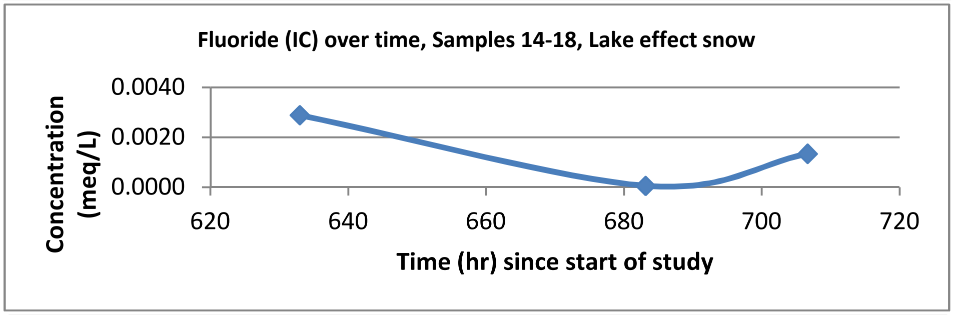

Sodium (IC) over time, Samples 14-18, Lake effect snow
Concentration (meq/L)
0.30
0.20
0.10
0.00
620
640
660
680
700
720
Time (hr) since start of study

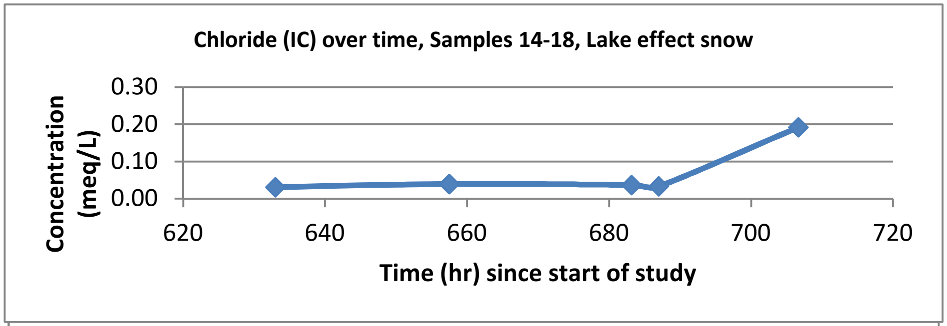

Potassium (IC) over time, Samples 14-18, Lake effect snow
Concentration (meq/L)
0.03
0.02
0.01
0.00
620
640
660
680
700
720
Time (hr) since start of study

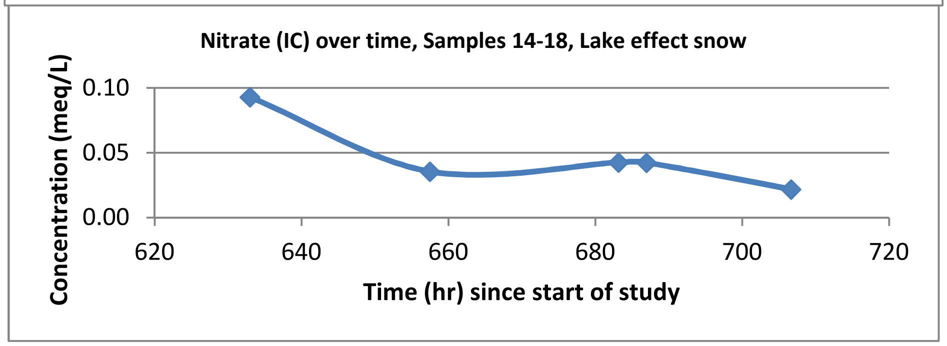

Magnesium (IC) over time, Samples 14-18, Lake effect snow
Concentration (meq/L)
0.03
0.02
0.01
0.00
620
640
660
680
700
720
Time (hr) since start of study

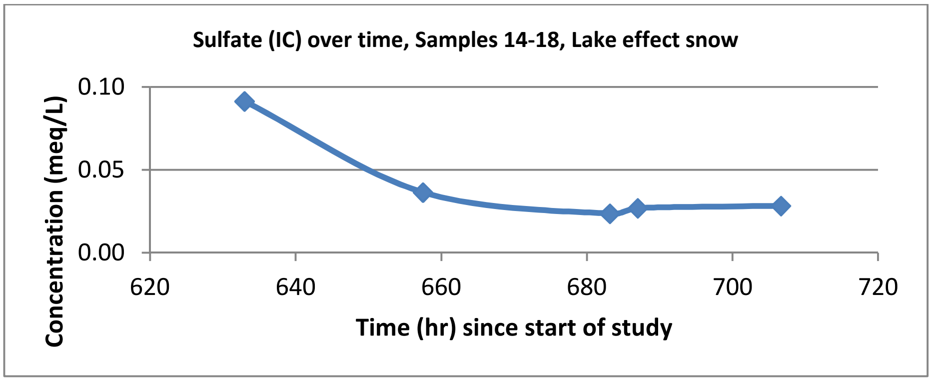

Calcium (IC) over time, Samples 14-18, Lake effect snow
Concentration (meq/L)
0.30
0.20
0.10
0.00
620
640
660
680
700
720
Time (hr) since start of study


Ammonium (IC) over time, Samples 14-18, Lake effect snow

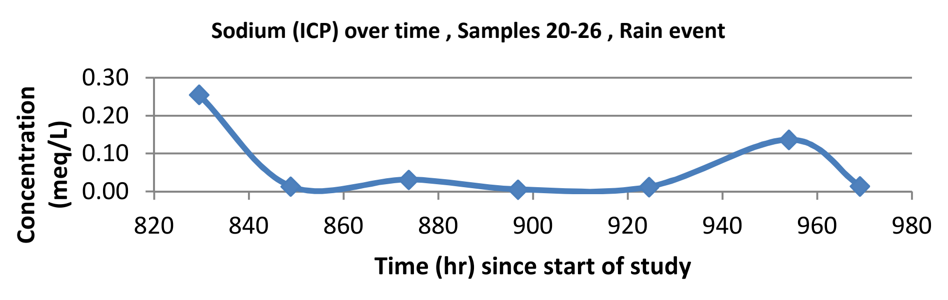

Fluoride (IC) over time, Samples 14-18, Lake effect snow


Chloride (IC) over time, Samples 14-18, Lake effect snow

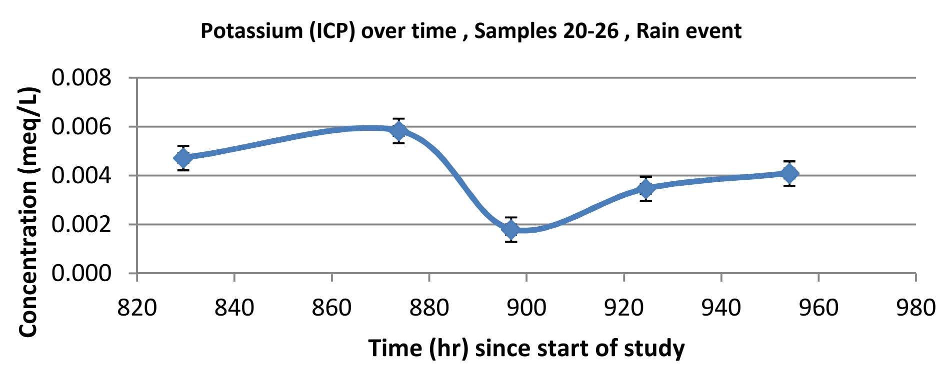

Nitrate (IC) over time, Samples 14-18, Lake effect snow


Sulfate (IC) over time, Samples 14-18, Lake effect snow

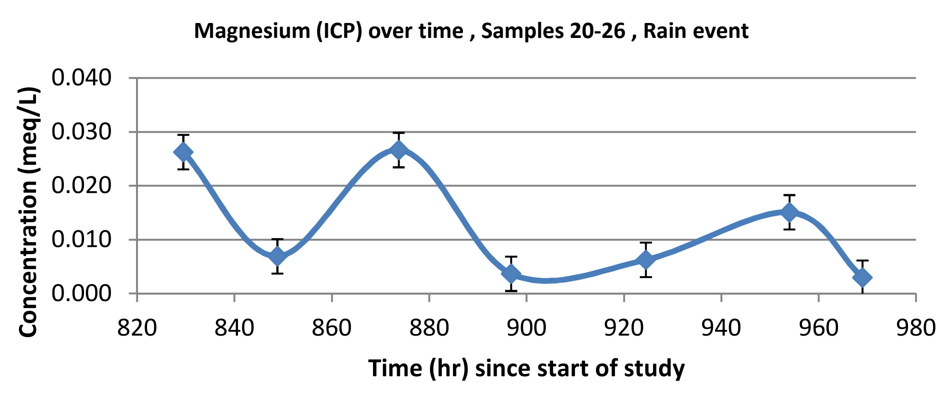
Appendix F: Rain Event 3: Ion Concentrations
ICP-OES



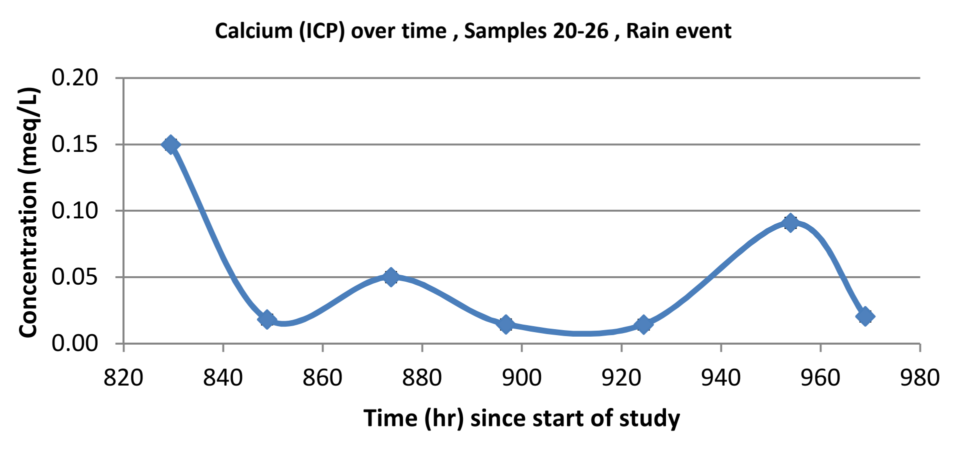
Sodium (ICP) over time , Samples 20-26 , Rain event



Potassium (ICP) over time , Samples 20-26 , Rain event

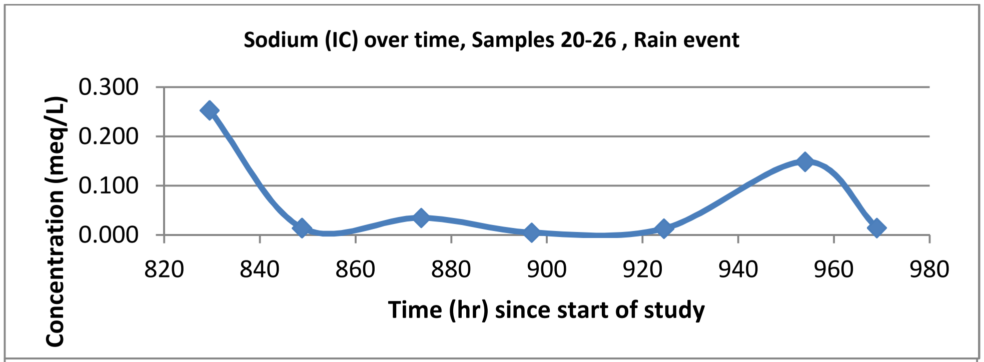


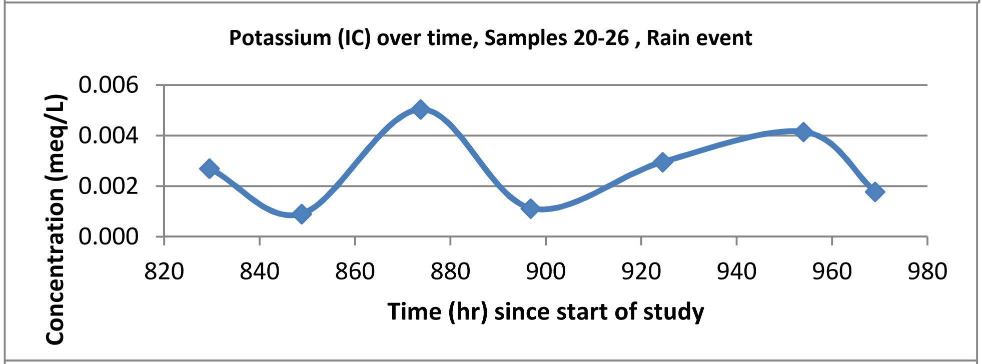
Magnesium (ICP) over time , Samples 20-26 , Rain event

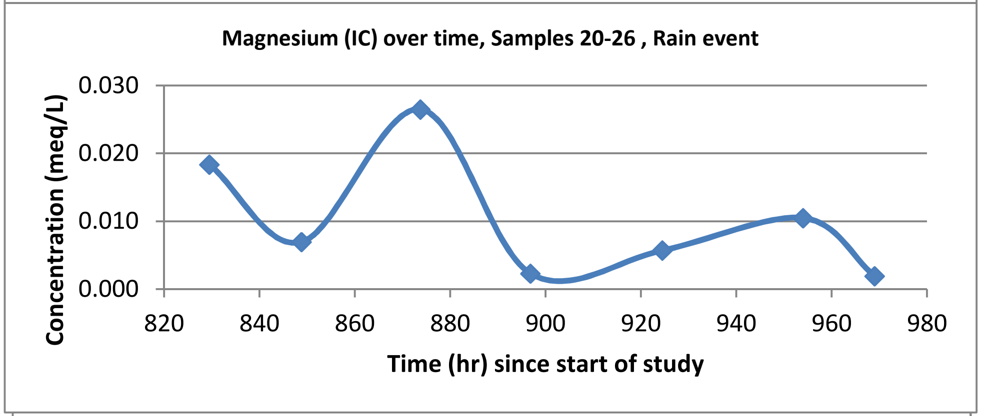


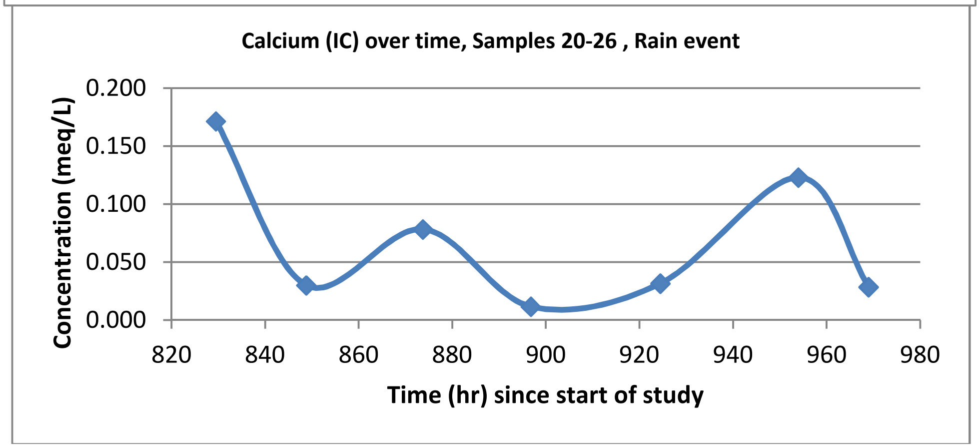
Calcium (ICP) over time , Samples 20-26 , Rain event

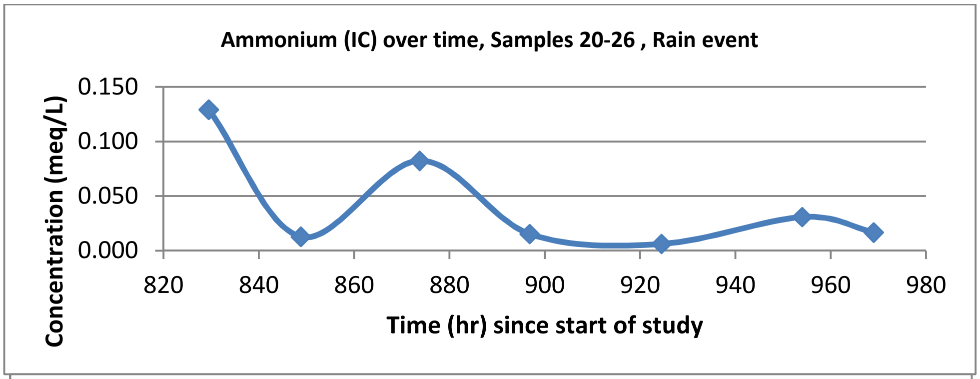
IC:

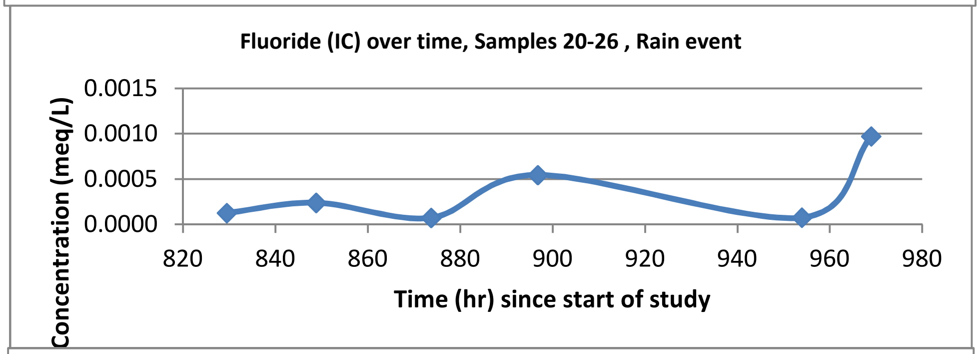

Sodium (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.300
0.200
0.100
0.000
820
840
860
880
900
920
940
960
980
Time (hr) since start of study

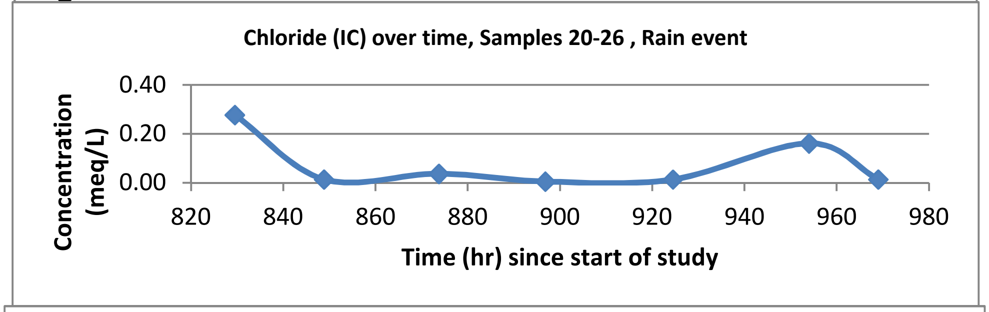

Potassium (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.006
0.004
0.002
0.000
820
840
860
880
900
920
940
960
980
Time (hr) since start of study

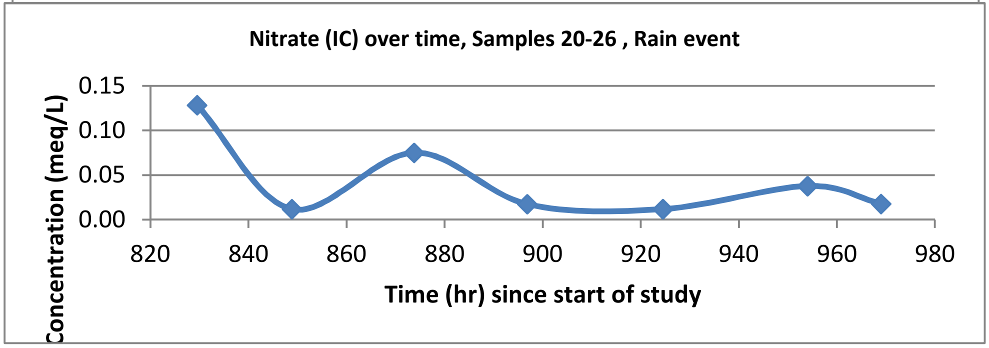

Magnesium (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.030
0.020
0.010
0.000
820
840
860
880
900
920
940
960
980
Time (hr) since start of study

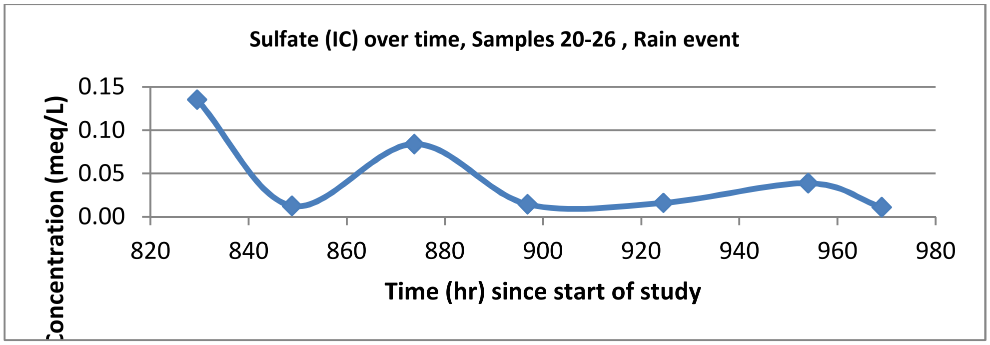

Calcium (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.200
0.150
0.100
0.050
0.000
820
840
860
880
900
920
940
960
980
Time (hr) since start of study


Ammonium (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.150
0.100
0.050
0.000
820
840
860
880
900
920
940
960
980
Time (hr) since start of study


Fluoride (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.0015
0.0010
0.0005
0.0000
820
840
860
880
900
920
940
960
980
Time (hr) since start of study

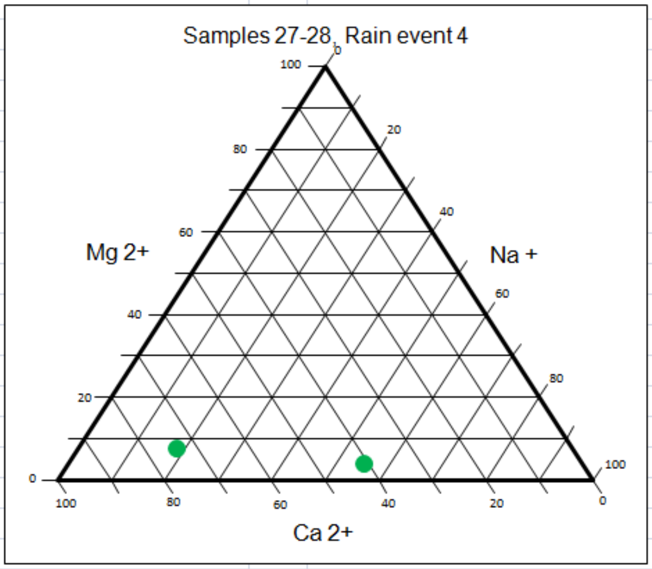

Chloride (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.40
0.20
0.00
820
840
860
880
900
920
940
960
980
Time (hr) since start of study


Nitrate (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.15
0.10
0.05
0.00
820
840
860
880
900
920
940
960
980
Time (hr) since start of study

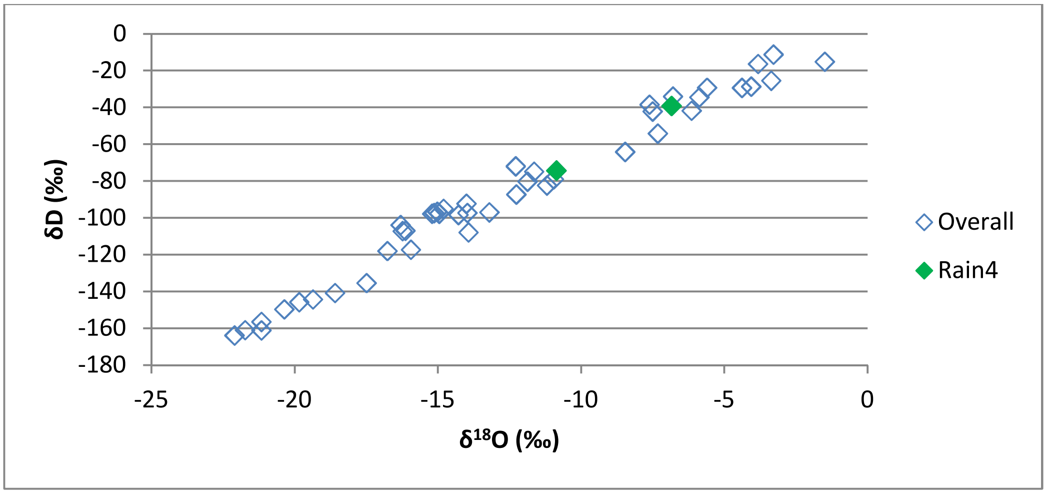

Sulfate (IC) over time, Samples 20-26 , Rain event
Concentration (meq/L)
0.15
0.10
0.05
0.00
820
840
860
880
900
920
940
960
980
Time (hr) since start of study

Appendix G: Rain Event 4

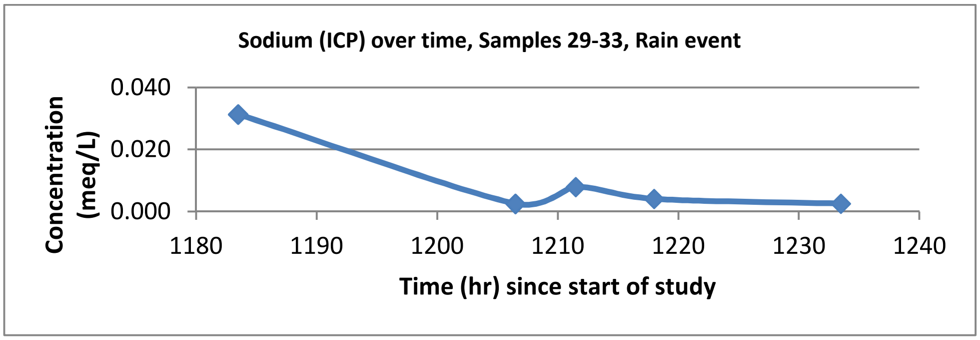
Piper Plot:

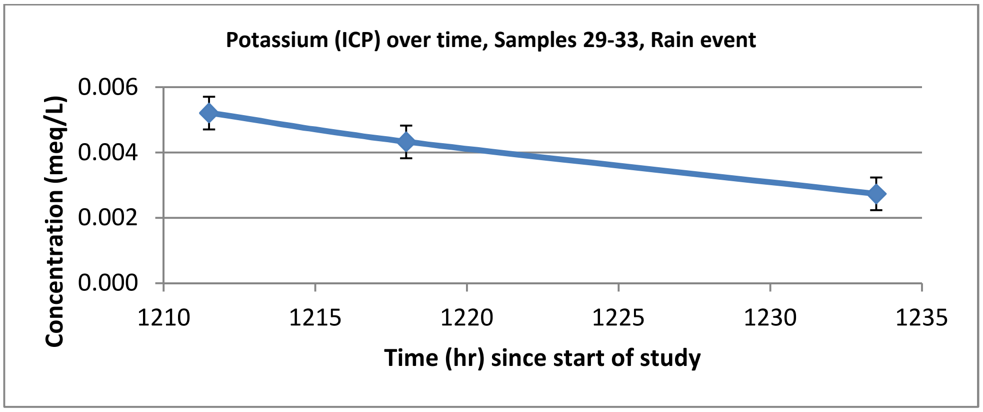


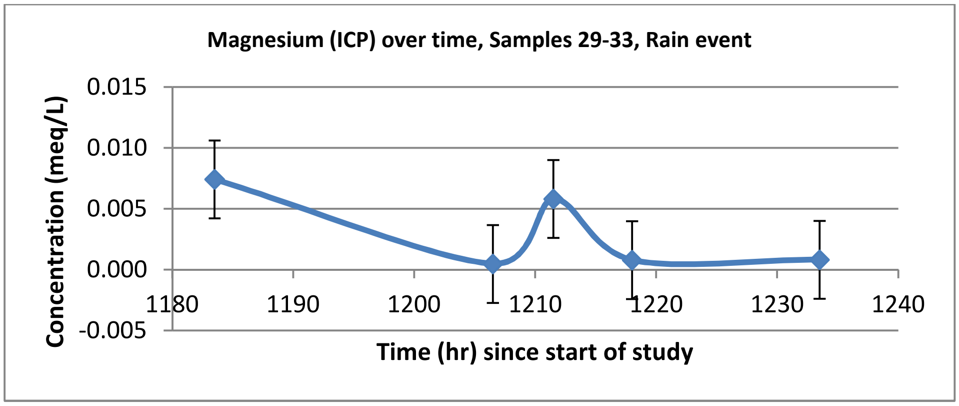
Isotopic Composition:

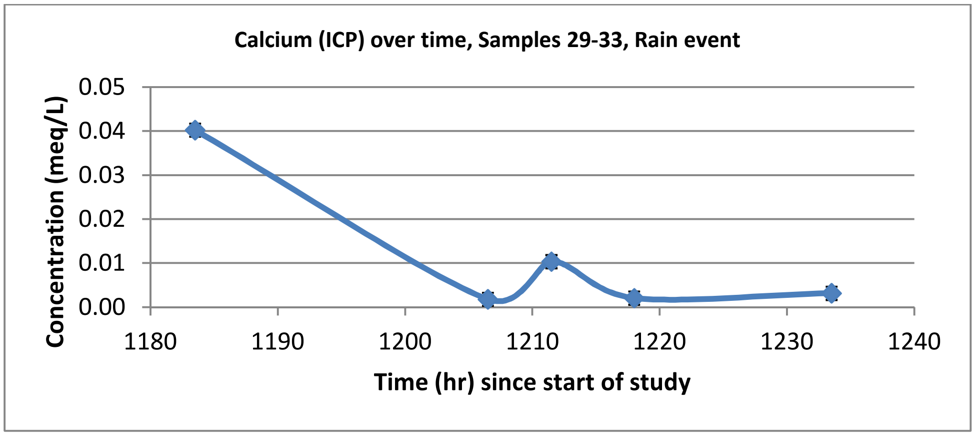


Appendix H: Rain Event 5: Ion Concentrations
ICP-OES

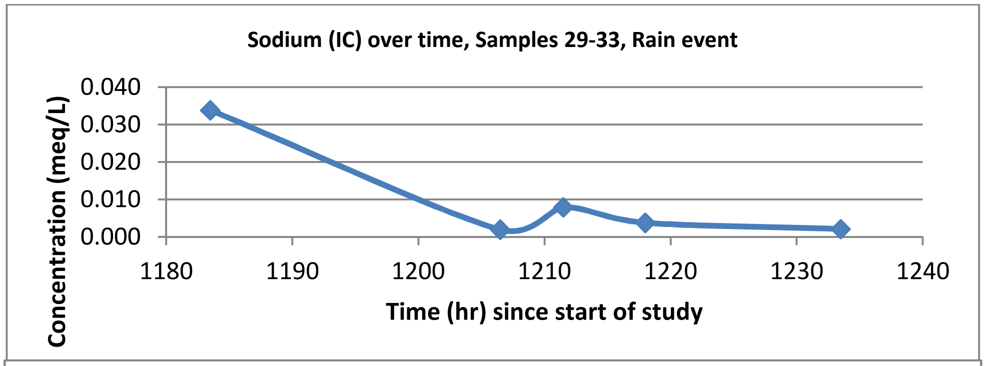


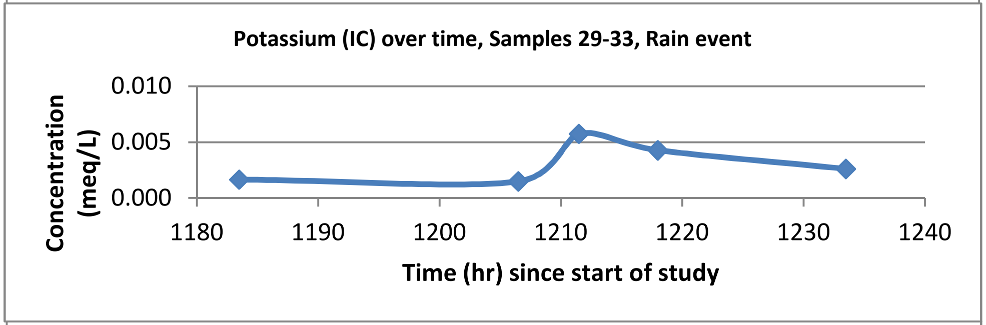


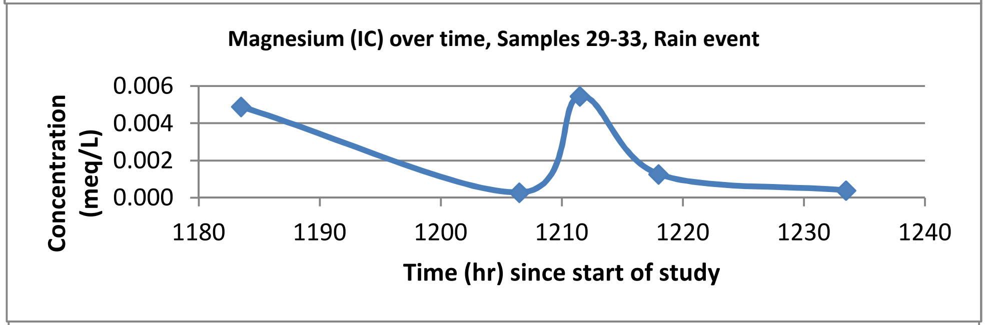


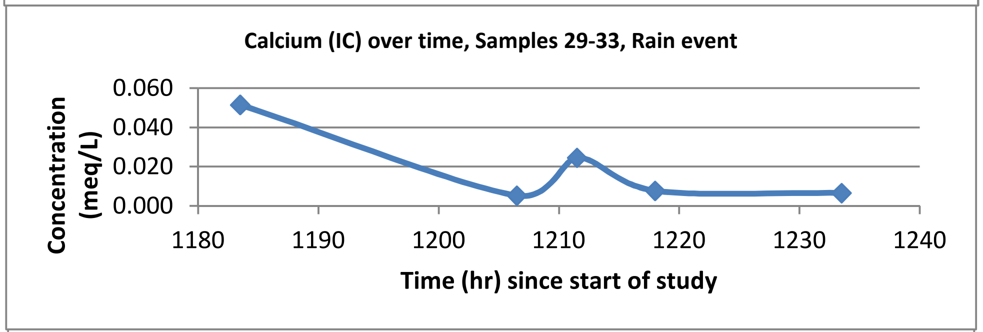


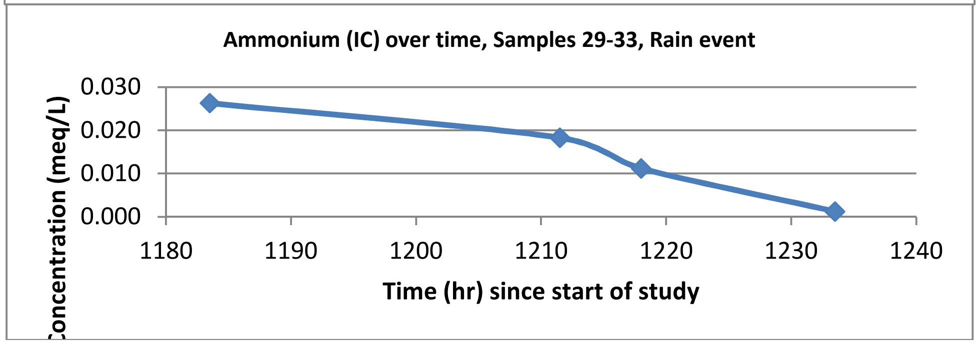
IC:

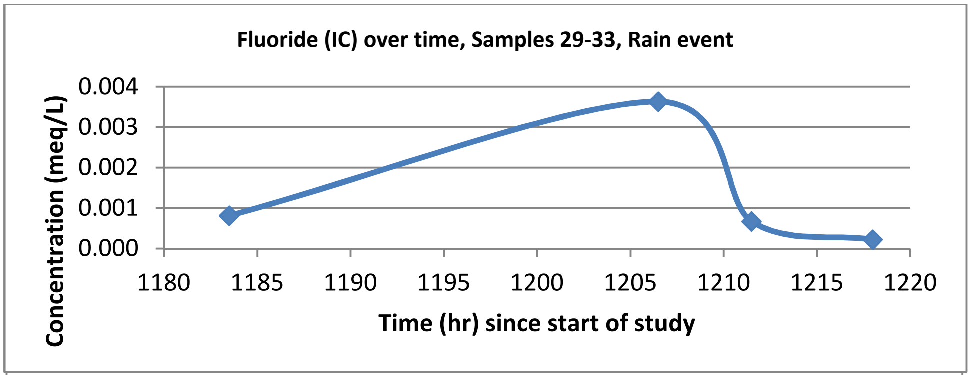

Sodium (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.040
0.030
0.020
0.010
0.000
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study

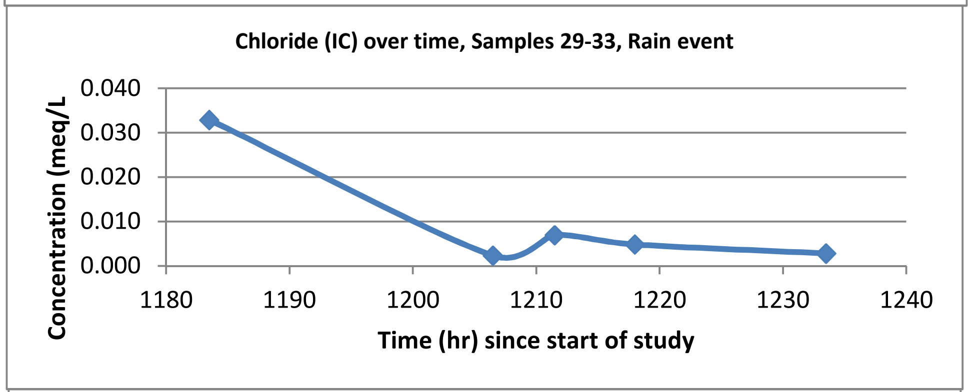

Potassium (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.010
0.005
0.000
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study

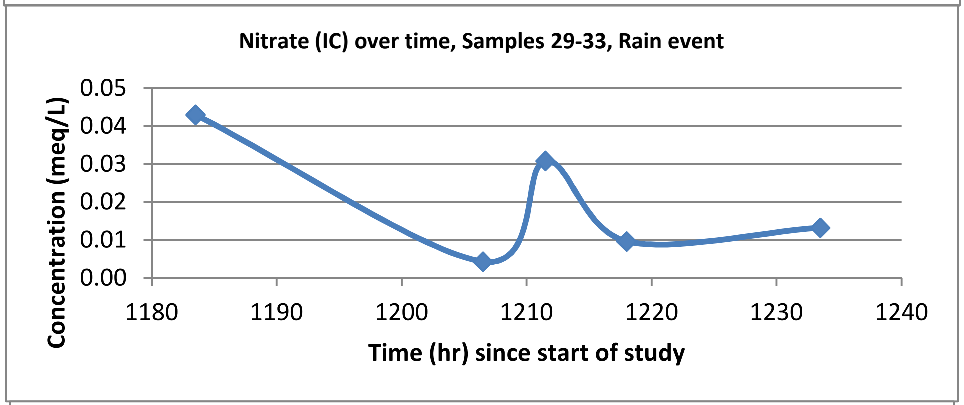

Magnesium (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.006
0.004
0.002
0.000
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study

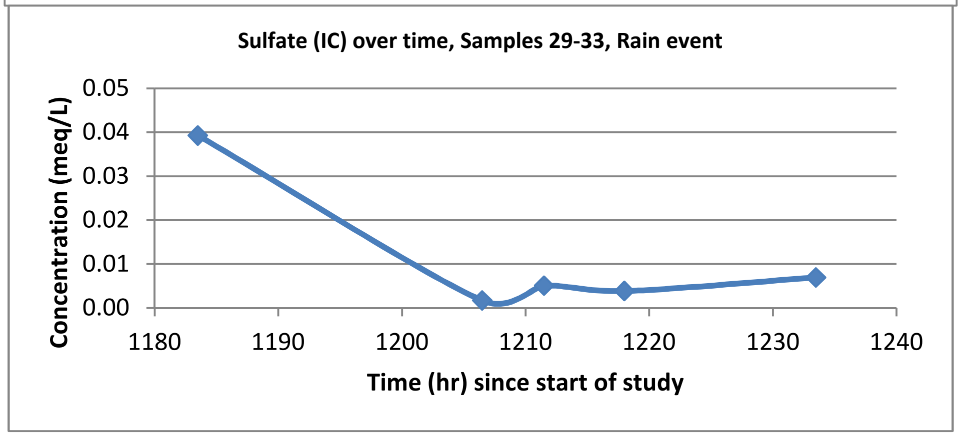

Calcium (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.060
0.040
0.020
0.000
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study


Ammonium (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.030
0.020
0.010
0.000
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study

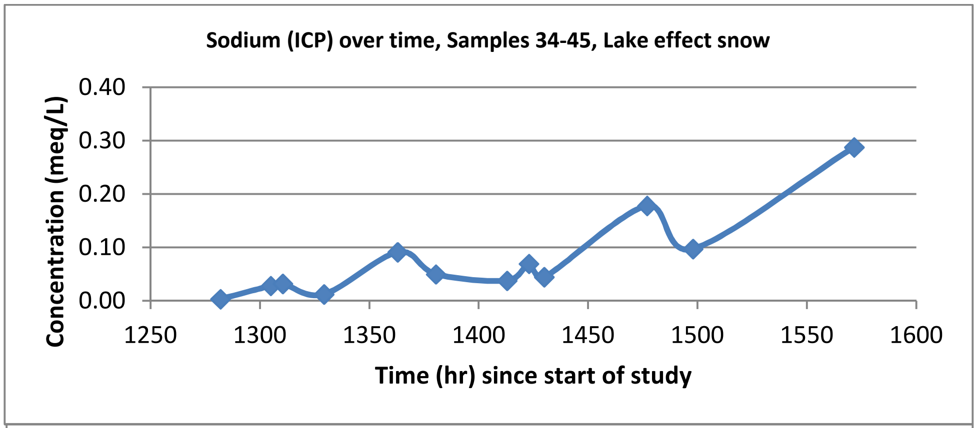

Fluoride (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.004
0.003
0.002
0.001
0.000
1180
1185
1190
1195
1200
1205
1210
1215
1220
Time (hr) since start of study

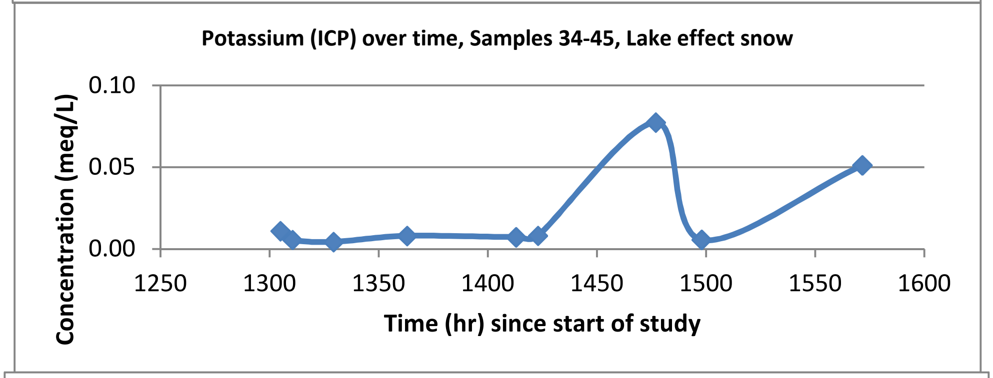

Chloride (IC) over time, Samples 29-33, Rain event
Concentration (meq/L
0.040
0.030
0.020
0.010
0.000
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study

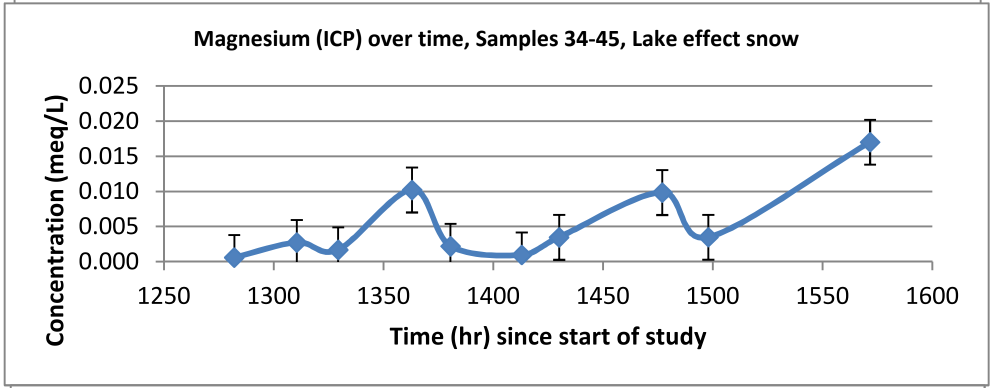

Nitrate (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.05
0.04
0.03
0.02
0.01
0.00
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study

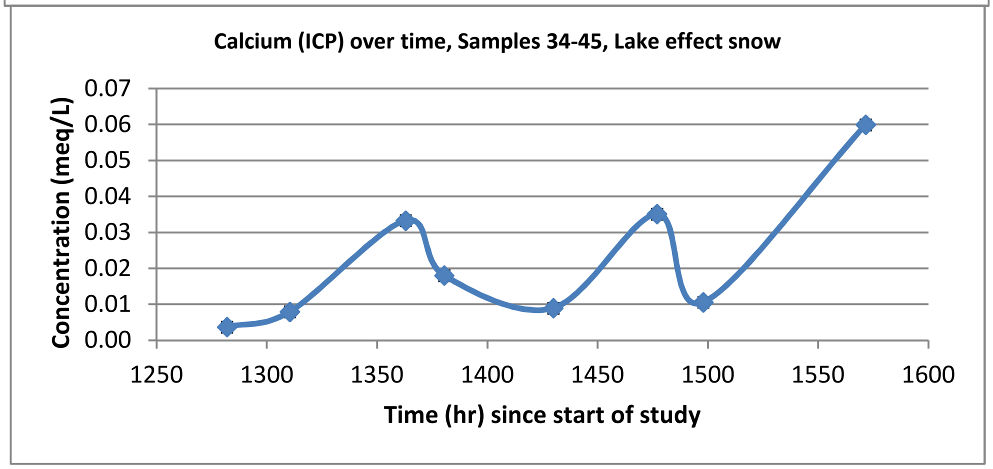

Sulfate (IC) over time, Samples 29-33, Rain event
Concentration (meq/L)
0.05
0.04
0.03
0.02
0.01
0.00
1180
1190
1200
1210
1220
1230
1240
Time (hr) since start of study

Appendix I: Lake Effect 2: Ion Concentrations
ICP-OES

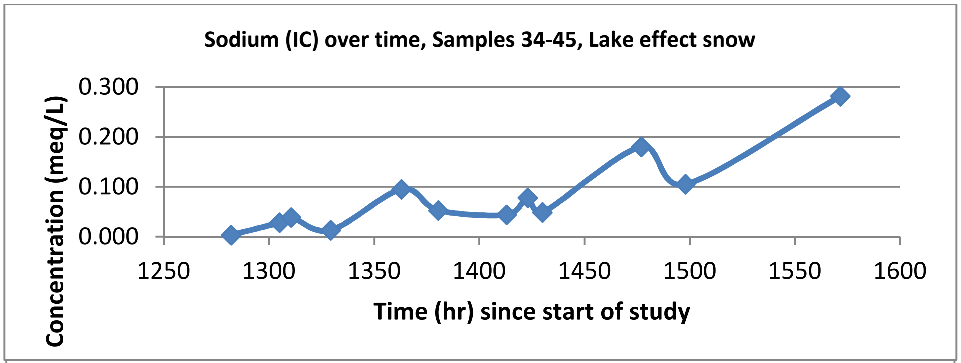


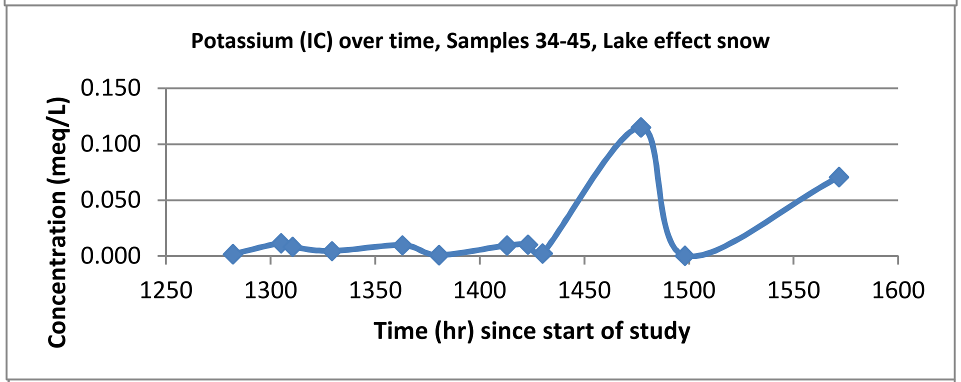


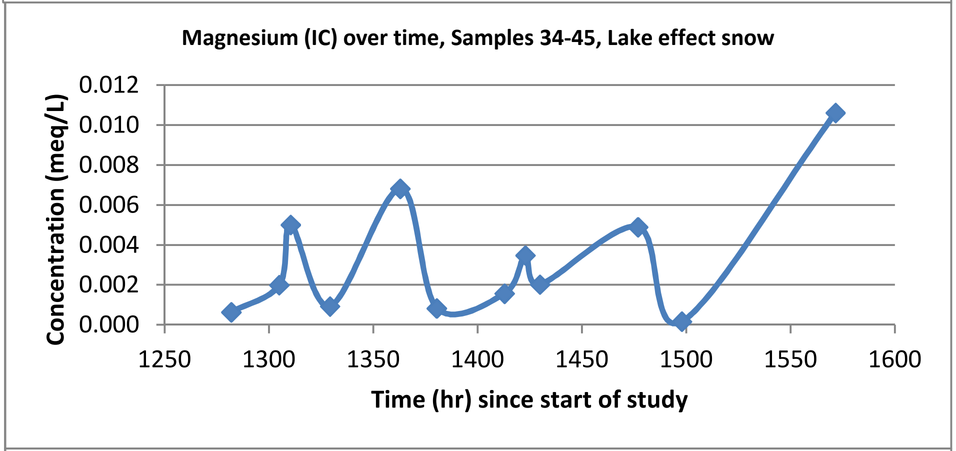


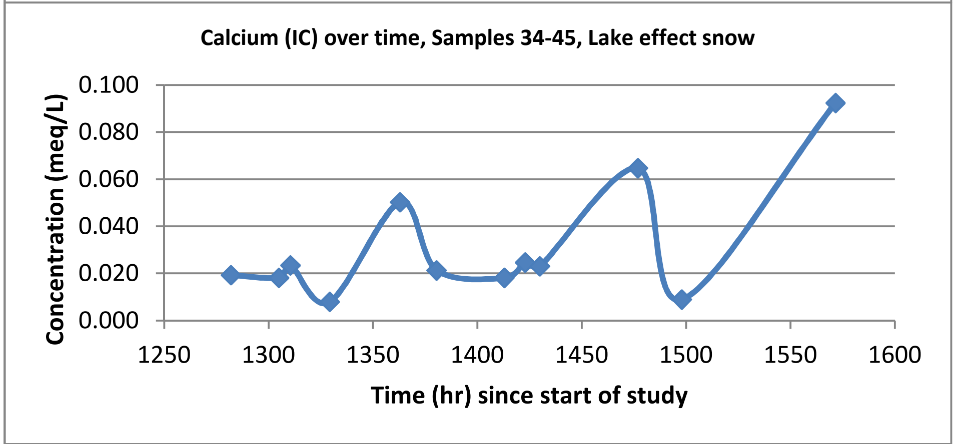


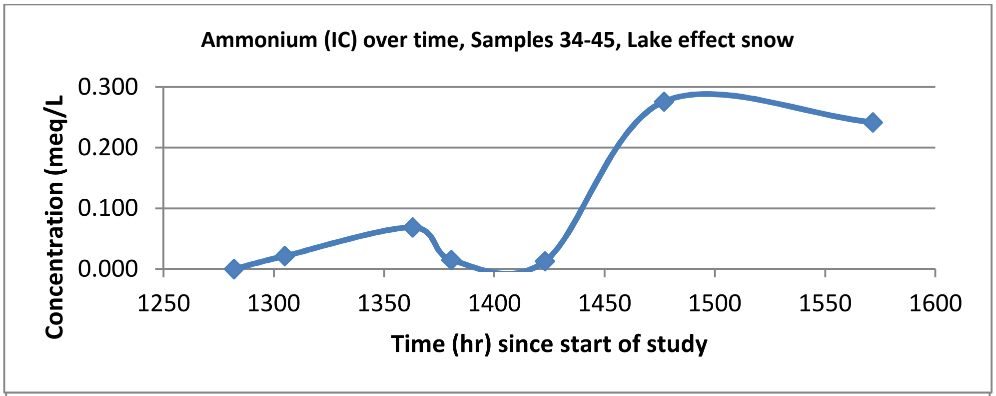
IC:

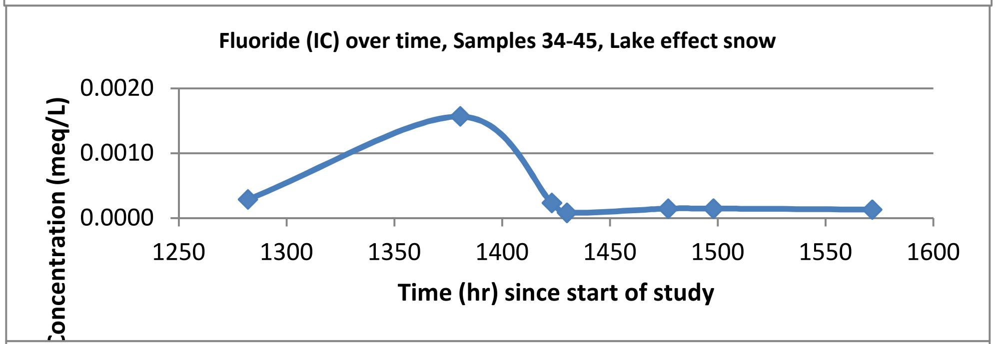

Sodium (IC) over time, Samples 34-45, Lake effect snow

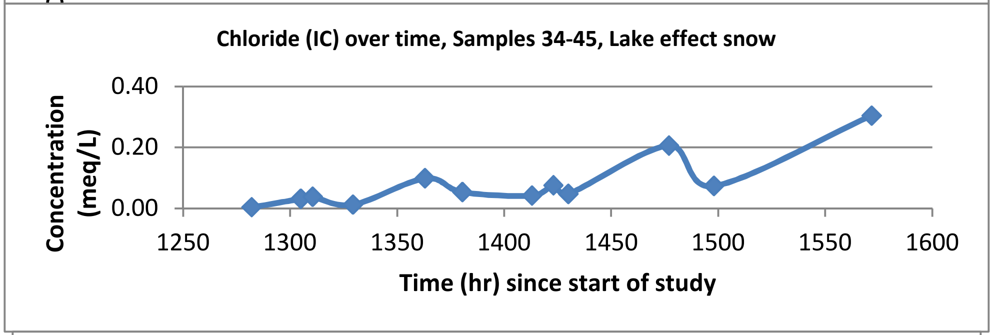

Potassium (IC) over time, Samples 34-45, Lake effect snow

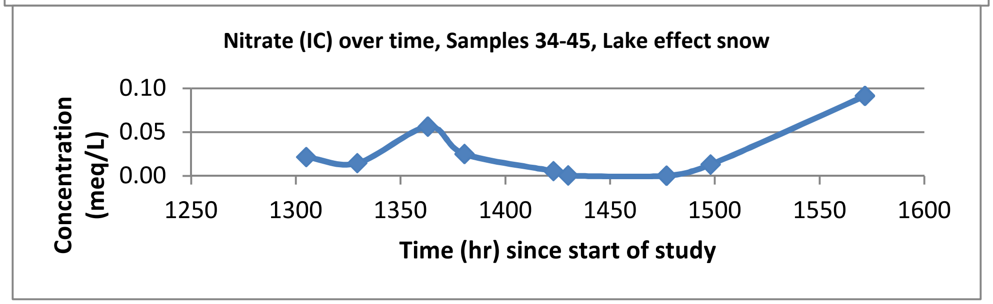

Magnesium (IC) over time, Samples 34-45, Lake effect snow

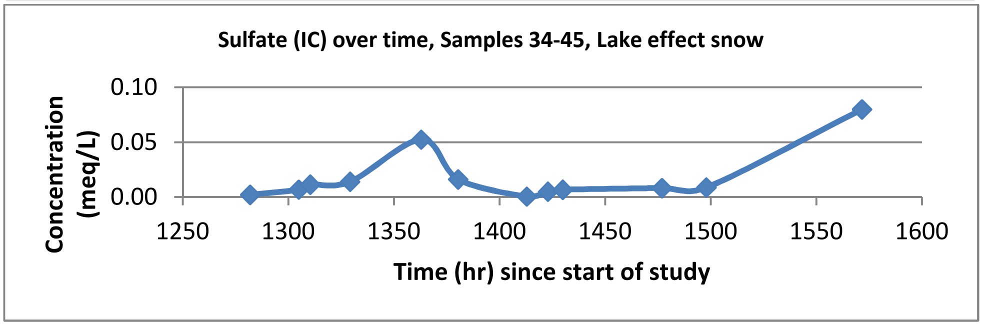

Calcium (IC) over time, Samples 34-45, Lake effect snow


Ammonium (IC) over time, Samples 34-45, Lake effect snow
Concentration (meq/L
0.300
0.200
0.100
0.000
1250
1300
1350
1400
1450
1500
1550
1600
Time (hr) since start of study


Fluoride (IC) over time, Samples 34-45, Lake effect snow
oncentration (meq/L)
0.0020
0.0010
0.0000
1250
1300
1350
1400
1450
1500
1550
1600
Time (hr) since start of study

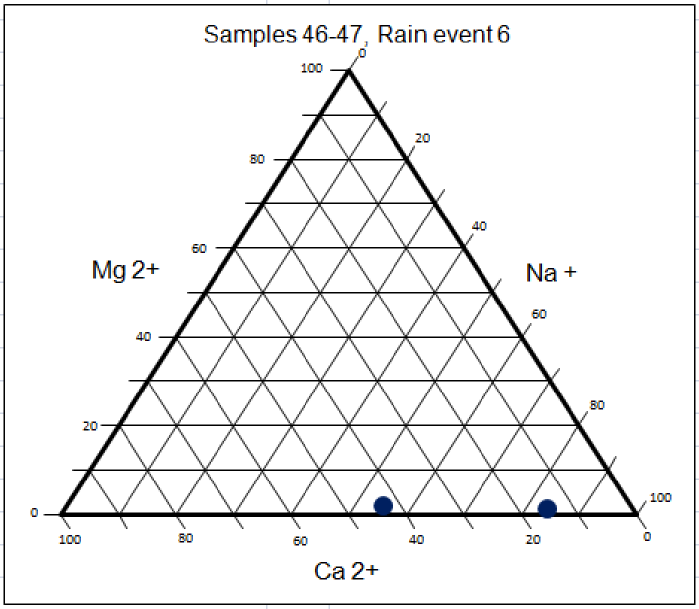

Chloride (IC) over time, Samples 34-45, Lake effect snow
Concentration (meq/L)
0.40
0.20
0.00
1250
1300
1350
1400
1450
1500
1550
1600
Time (hr) since start of study


Nitrate (IC) over time, Samples 34-45, Lake effect snow
Concentration (meq/L)
0.10
0.05
0.00
1250
1300
1350
1400
1450
1500
1550
1600
Time (hr) since start of study

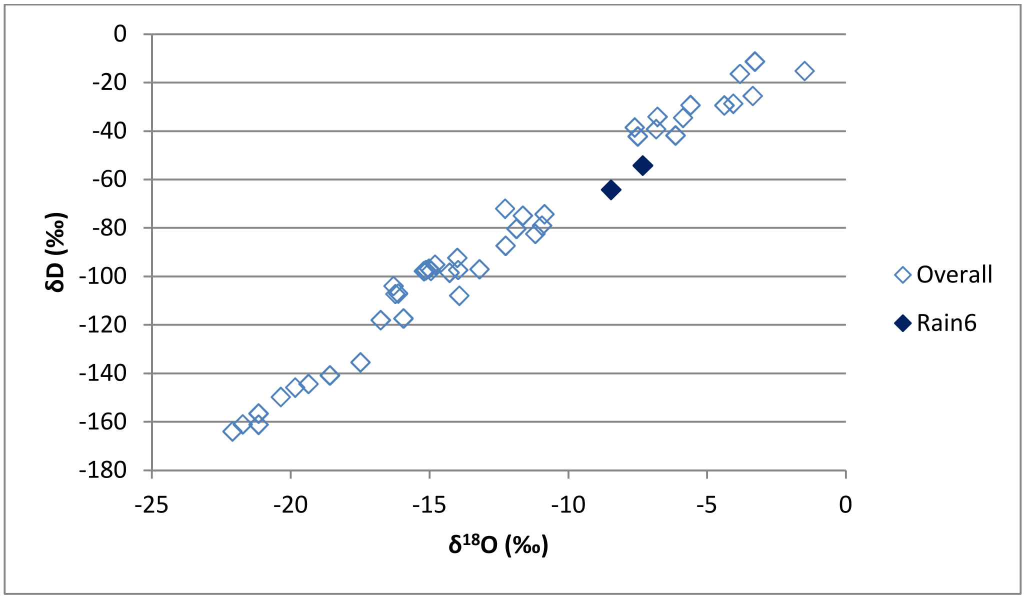

Sulfate (IC) over time, Samples 34-45, Lake effect snow
Concentration (meq/L)
0.10
0.05
0.00
1250
1300
1350
1400
1450
1500
1550
1600
Time (hr) since start of study

Appendix J: Rain Event 6

Piper Plot

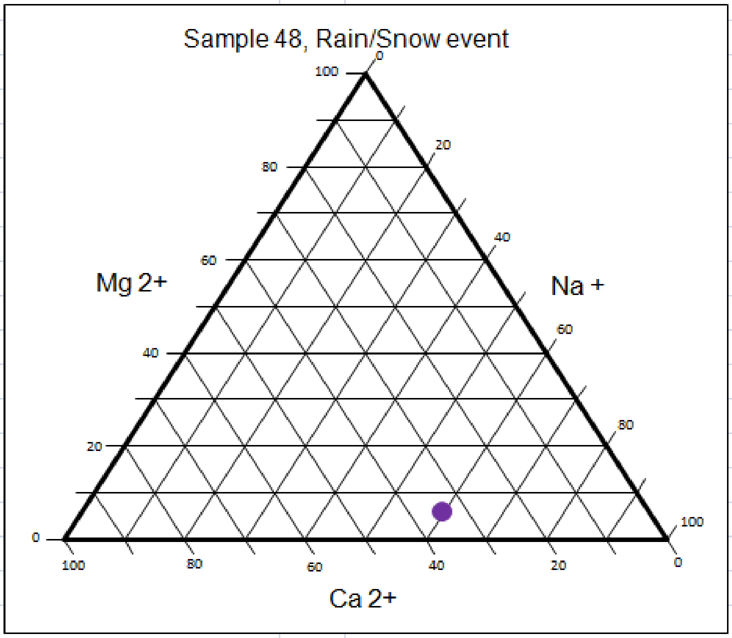


Isotopic Composition:

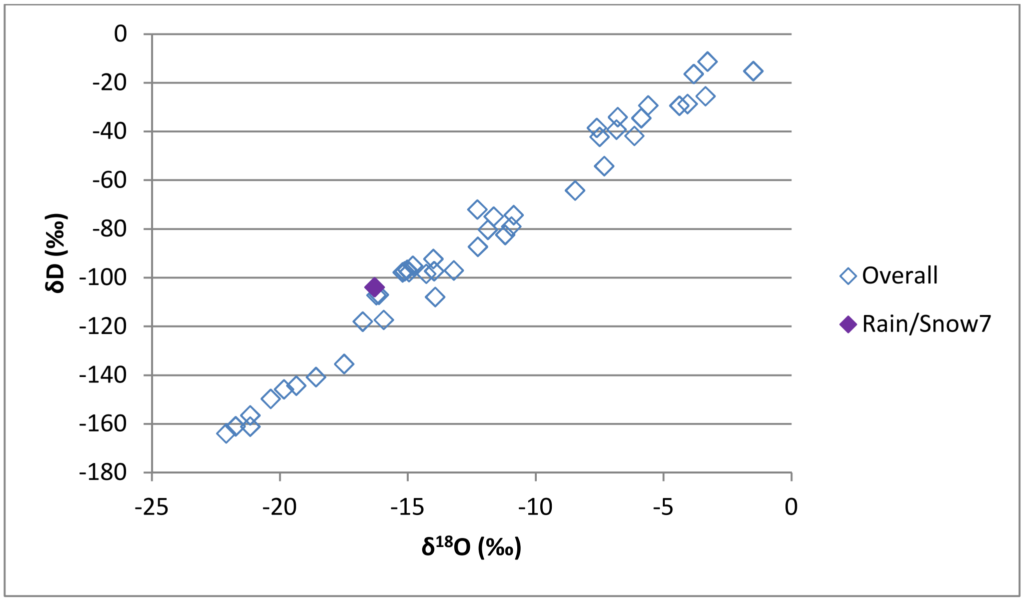


Appendix K: Rain Event 7

Piper Plot:



Ionic Composition:



Summary of Capstone Project

This project involved the measurement and characterization of precipitation chemistry during the lives of storms in Central New York. Because water retains a signature of its source when it evaporates, it is possible to identify where a rain or snowstorm came from by measuring the concentration of ions and isotopes in water samples. For example, when water evaporates from a fresh body of water, such as a lake, it carries less sodium and chlorine than water evaporated from an ocean; when a rainstorm passes over land, it can pick up calcium and magnesium from the soil. The concentration of these ions, which are chemical species that have uneven numbers of electrons and protons, causing them to have an electrical charge, will decrease over time as a storm system rains out because many of these ions are heavier than water, and we can track the changing concentrations during the lifetime of a storm. Similarly, isotopes may allow us to distinguish between changes in storm chemistry. An isotope is an element that has a different number of neutrons than the base element identified on the periodic table. These isotopes may be radioactive isotopes, which decay over time, or they may be stable, which do not decay. Oxygen atoms carry 8 protons and 8 neutrons in 99.9+% of all oxygen (^{16}O); however, stable isotopes of oxygen exist with 9 neutrons (<0.01% of cases, ^{17}O), and with 10 neutrons (<1% of cases, ^{18}O). Hydrogen atoms may have one proton (99.9+%, ^{1}H), or one proton and one neutron (^{2}H). Heavier isotopes are more difficult to evaporate and more easy to condense. This causes “fractionation” of the isotopes which may be measured in comparison to a standard of known concentration.

In this study, samples of different types of storms precipitating over Syracuse, NY were collected throughout the duration of each storm. The samples were run through an ion chromatograph (IC) and an inductively coupled plasma optical emission spectrometer (ICP-OES), which measure the concentrations of various ions in the samples. The samples were also run through a Picarro cavity ring-down laser ablation spectrometer, which measures the concentrations of oxygen and hydrogen isotopes in the water molecules themselves and compares them to a recognized standard of known composition. These ionic and isotopic compositions were then plotted in Piper diagrams, which allow for visual comparisons of the concentrations of given sets of ions, and on a plot of O/H isotope ratios. The results for each storm were analyzed and the results from similar storm types were grouped together and compared. This analysis allowed for a characterization of storm chemistry both for different types of storms and for each storm over time.

This type of project is mostly significant in confirming certain aspects of storm chemistry that are expected, but that have not been shown in many studies or in many types of storms to date. A greater understanding of storm chemistry will allow for better predictions of chemical changes in the formation and lifetimes of storms, which is important in atmospheric models, models of acid rain, and other projects. Further down the line, this type of project could also become important in studies dealing with the measurement and quantification of contaminants in water and air systems.

Reflective Essay

During my time at Syracuse University, I have participated in a range of different research projects. I have worked on structured assignments throughout my college courses, and I have participated on much more open-ended research projects in independent studies and in summer programs. These projects have been both individual and group-based, involving a mix of other undergraduates, professors, and graduate students as both colleagues and supervisors. I have had the opportunity to work in physics, chemistry, biomedical, and ocean engineering departments. But even though my research background has been extremely varied for an undergraduate curriculum, this Capstone project was highly unusual for me in many ways.

At first glance, the scientific method dictates the approach of any research project and the approach to research appears to be the same. But every lab group has its own unique culture based on the size of the group, the pace and type of work, and the personalities involved. In addition to lab group cultures, every department and every field of science and engineering may be characterized by cultural differences to some degree. This Capstone project was unusual for me in that it was conducted outside of either of my major degree programs of physics and chemical engineering; instead, I worked in the Earth Sciences Department, and I found that this is very different from either of my major areas. During my time in my major departments, I found that in many cases, physics can be characterized as a highly individual discipline, where each lab member completes a given set of research objectives with limited interaction with those that are not supervisors. In biomedical and chemical engineering, in the projects that I worked on, the pace is generally very quick in cases where experiments are iteratively adjusted and redone. In comparison, I found earth sciences to be a much more laid-back field, where collaboration and discussion between other fields and other professionals was the key of research. Earth and environmental sciences are highly interdisciplinary, and research may require an understanding of elements of biology, chemistry, and physics. The culture of collaboration creates networks of scientists across many universities and research institutions, and it greatly affects the way any one researcher works. For my project, I communicated with several different earth scientists and environmental scientists to run my samples and to assess the results of my chemical data, with meteorologists to obtain storm tracks, and with local airport support staff to determine standard sampling methods.

In prior research projects, my work has been mostly with other students in my position or with primary investigators (PI's, or supervisors) on the project, with little cross-collaboration between scientists and professors outside of my lab group or my field. The extensive collaborations that I found in the earth sciences department fostered an important open-door policy throughout the department. I greatly enjoyed this unique culture, and my experiences working in this department for my Capstone project have played a surprisingly large role in my decision to remain here at Syracuse University for a Masters program in Earth Sciences.

However, a healthy balance of the collaborative spirit and an independent aspect of my Capstone were extremely important to me. I knew from prior research projects that I work best with a hands-off approach from my advisors, and Don Siegel was very good about suggesting a few courses of action and allowing me to work through what I found to be the best avenues of approach for this Capstone. In this way, I was able to complete a variety of tasks, including sampling, working with ion and isotope machines, analyzing data, and hunting down appropriate literature, and I could check in with him when necessary. This was an approach that worked very well for me, and it was useful to have some time to get used to a more hands-off approach than can often be found in undergraduate courses as a method of graduate school preparation. If I ever end up in a teaching situation, this is the kind of approach I would choose to use. I believe independence in research allows for some creative approaches and an investment a specific project; this is especially important in something of an unfamiliar field, where it would become easy to follow instructions and not really learn anything.

I believe that my range of research projects has given me a little more confidence in my work than I have seen in other students in science and engineering programs. As students completing projects in classes, we expect everything we work on to have a beginning, middle, and end, with clear-cut answers or explanations for why things might not have worked. Because I have been involved in independent research since freshman year, I have had a great deal of experience in projects that do not work and become dead ends, that have unclear or evolving goals, or that prove inconclusive. In this Capstone, I had to be satisfied with inconclusive results and results that are not statistically significant without many more data points. As I will continue in the Earth Sciences Department, I intend to tie up some of these loose ends if possible, (especially involving alkalinity data and Piper plots, but possibly including sampling frequency as well), but it can still be frustrating to spend a semester on something that does not quite pan out. My Capstone was generally successful in fulfilling the goals my advisor and I set for this semester, but there is always room for improvement. The ability to accept that results are inconclusive is something that only time and experience can quite fix, and I am grateful to have had some of each beforehand.

The most unusual aspect of this Capstone for me is the philosophy of the research itself. In all of my past projects, and in my education in an engineering curriculum, I have viewed research as means to an end. Everything I have worked on, including a drug delivery project, a nanoparticle project, a water sampling prototype project, and a variety of class projects, has had a practical purpose, such as creating a product for use or for sale. Engineering has been a path to "adding value" to something, and until recently, I viewed projects that didn't have a practical end goal as ones that may be valuable to others, but not ones I wanted to do. This Capstone is truly the first project I have worked on that does not have some sort of direct application to it; yes, there are possibilities for use in contamination studies or in use by other researchers, but in truth, the motivation of this project has been to see if we could do it. This was something that I struggled with at the beginning of this project, and every time I delved into related literature to look something up, I kept an eye out for what could be done immediately with the results of this study. It has turned out that at this stage, there really is not much that can be done with it directly beyond to expand it into a greater study or to provide some ideas for other researchers. In the future, this study might feed into someone else's work on improving sampling systems or measurement schemes. It may inspire questions on how to sample within a storm system. But at the end, the value is to scientists in the field of precipitation and ground water alone, and will remain so for quite some time. But this is not something that should be discounted, and it has taken me some time to come to that realization.

In the past few semesters, I have had long discussions with my fellow students in both the Engineering and Arts & Sciences colleges concerning this debate. I have always leaned towards the typical engineering stance of needing to produce something tangible, something that could be sold or used in some way. I avoided projects that would only produce items of interest for certain academic sectors, and I investigated potential graduate school and career paths on the basis of where I thought I could make a difference in the world, which to me, could only be in something tangible.

This project was my first honest taste of research for research's sake. And to be honest, after I got used to the idea that it did not have to be tangible, I enjoyed this project. I had more freedom to explore possibilities for why my data looked the way it did than if I had to turn it into something directly valuable; I did not have to work to such a regimented schedule as I had in the past, where I had projects based around building and testing instruments. I found the challenge of explaining my project to anyone outside of a scientific field was actually pretty enjoyable; justifying hours of lab work on storm chemistry is vastly different from justifying hours of lab work on a physical product to someone outside of a scientific field. Because of this project and in explaining it to other people outside of my lab group, I have gained a new interest in transparency and outreach in scientific studies, especially for more esoteric subjects.

This is something that I hope to carry with me into my next project, and in fact I plan to; I will be continuing on in Earth Sciences, contrary to every plan I had in working in engineering immediately after graduation. When I applied to graduate schools between the fall and spring semesters of my senior year, I picked a variety of programs in environmental science and engineering programs. At that time, I expected to pick one of the specific engineering programs, full of tangible product-based goals. That was before the majority of this Capstone was completed. Throughout this semester, I have become much more comfortable with knowledge-based research, and because I want to hold onto the values of that side of science, together with an interest in filling in some gaps in my knowledge of geology and environmental sciences, I decided to pick the graduate program least likely to produce something directly valuable outside of academia. This is a great philosophical change for me and it is difficult to put into words why I find it so important, but this has been the most valuable aspect of my Capstone project. I knew that my Capstone would provide me with honors distinction, some interesting lab work, a chance to work with an IC and ICP-OES, and something of a change of pace for my senior year. I did not expect it to play so heavily into the plans for my future after graduation.

For that, I would like to take one last chance to acknowledge and thank my advisors, in my Capstone and in Honors, for providing me with an unexpected opportunity to learn more about my own goals throughout my senior year. It is easy to pick a major and go with it, but without experience in a field it can be difficult to get an idea of what it would really be like to work in science or engineering; similarly, with some experience, it can be easy to pick a few projects and go with them, but can really be necessary to try a variety of different types of projects to decide what works. Especially for those types of projects that we may become set against without ever actually experiencing them. I have had a truly interesting experience working through this Capstone and I am grateful to those who helped me to explore it.