

Characterizing the Waters of Six Rivers in Upstate New York With a Focus on Physical Hydrologic Controls on Water Quality

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Abstract.

Rivers are key passageways connecting inland waters to the world's oceans. They are responsible for the mobilization and transport of nutrients, sediments, and weathered materials. Rivers have been influential in the development of human civilization and are hubs for people and businesses to populate. As our population puts a heavier burden on these waterways, there is a need to better understand the controls on their water quality.

The overarching goal of this research is to improve our understanding of the hydrology and water resources of the Upper Hudson and Mohawk watersheds. This is critical to our understanding of the ecological and environmental roles these watersheds play while ensuring ample clean water. To address these issues, we studied six rivers in the Upper Hudson and Mohawk watersheds, looking at how lithology, land use, and physical hydrology impact the geochemistry and water quality of the rivers.

I performed an analysis of the physical hydrology of the rivers with a focus on streamflow patterns and long-term trends in flow characteristics. This includes looking at shifts in flow timing, duration and magnitude of low flows, and shifts in annual mean flows. Our results help to paint the picture of how climatic changes are linked with the streamflow values and how they are changing now. I also developed concentration discharge curves to couple with the hydrograph analysis to look at how elemental fluxes vary with changes in streamflow. In addition to the hydrograph analysis, we performed in depth characterizations of water quality and geochemical conditions in the rivers. We sampled under both low flow and high flow conditions on all of the streams. Our results revealed a strong geologic control on stream chemistry however, we observe that some chemical parameters are highly influenced by anthropogenic activities. Notably, we see that our measurements of Na and Cl are higher than historic measurements by the USGS taken on these same streams. Given that other constituents such as Ca, Mg, and K have remained at typical historic levels, we believe that the elevated levels of Na and Cl are due to anthropogenic impacts of road salting. Of particular concern, all of the streams have elevated levels of Na and Cl under baseflow conditions when the stream is fed by groundwater discharge. Thus, our results show that groundwater resources have been impacted by road salting which will continue to pollute the streams and will take decades to flush.

Acknowledgments

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Introduction

Rivers provide a key passageway between terrestrial water sources to the oceanic reservoirs. While on the scale of the whole water cycle, rivers do not contain a large amount of water, their importance stems from the major role that they play in transporting water, as well as suspended and dissolved solids (Berner and Berner 2012). They are a key habitat for a number of organisms and are a part of everyday life for humans. The water that comes to feed these rivers comes from a complex mixture of hydrologic processes which help to formulate the geochemical composition of these rivers. All rivers have a different geochemical signature as the hydrologic processes and geology that each river goes through exert different controls on them. In this paper we look to characterize the watersheds of six different rivers that are all located in Upstate New York. The rivers we are studying fall within the Hudson-Mohawk watersheds which are two of the largest rivers in New York state. These watersheds run from the very northern part of the state, flow over the Adirondacks, into the Mohawk Valley, and funnel out into New York Harbor. These rivers are essential in providing biodiversity, transportation, and a water resource for the people in the watersheds. The Hudson River watershed encompasses 5 million people and is a central part of their wellbeing (“The Hudson Estuary: A River That Flows Two Ways,” n.d.). While these two larger rivers have been studied, their tributaries have not been well studied and documented. The goal of this research is to examine the geochemical composition of each river and try to see if it can be explained by the physical hydrologic processes, geology, and land use of the watersheds, or if there was another input such as anthropogenic effects. To do this the rivers were sampled under low flow and high flow conditions to provide current data on the stream chemistry. This data was then paired with climatic data, historical observations and

modeled data to construct a characterization of the physical hydrology of the watersheds and controls on geochemistry. To do this we produced runoff ratios, hydrologic flux calculations, hydrograph analysis, concentration discharge curves and timeseries plot. All of this analysis was completed to understand what factors influence the geochemistry the most, so that the health of the waterways could be better understood. Rivers and surface water are essential to human health and have tremendous ecological controls, which is why any pollution to these resources can have far reaching consequences (Appelo and Postma 2010). With a large majority of people living near waterways like rivers, anthropogenic impacts on these delicate systems are becoming larger and larger. In order to be able to see if there are anthropogenic inputs on these rivers, a comprehensive look across the geology, land use, hydrology, and geochemistry in each watershed must be done to tease out trends in these critical water resources. By finding how and why any anthropogenic impacts are affecting the rivers, there can be discussions about how to fix the problems. Water is our most valuable resource and rivers are one of the most crucial, and least studied terrestrial reservoirs of this valuable resource. This paper hopes to provide a in depth characterization of each watershed and its geochemistry, and how these have been molded and changed over time.

Hydrology and Geology

The hydrology and geology of a river basin play immense roles in the formation and characteristics of a river. In Upstate New York where our rivers are located, there is seasonal variability in hydrologic fluxes, differences in land use and varying geology across each of the six watersheds. The six rivers of our study span wide ranges in length with our two largest rivers being 6922 km and 6387 km long for the Mohawk and Upper Hudson rivers respectively, down to our four smaller watersheds that range from 23.15 km long at Caroga Creek (CC) to 150.45 km at Otsquago Creek (OC). The six rivers of the study in located in Upstate New York and all

fall within the Mohawk and Upper Hudson watersheds (Figure 1). The Upper Hudson is that of the river where it starts in the Adirondacks and flows south to where it mixes with the Mohawk above the estuary and tidal influence (“The Hudson Estuary: A River That Flows Two Ways,” n.d.). The large variability in size and lengths of the rivers and watersheds allows for us to further investigate how factors such as hydrology, geology and land use of the watersheds affects the geochemistry in the rivers and reservoirs that feed them (Table 1). By better understanding the general trends of the region of our rivers and how they compare to the rest of New York, the rest of the country, and the rest of the world, we are able to frame our results and place their meaning into a better understood context. In conducting hydrograph analysis, hydrologic flux calculations, and geochemical analysis we are able to understand the controls on river water quality and highlight anthropogenic inputs. Comprehending the composition of a watershed and the chemistry of the water within its boundaries is crucial to ensuring the health of the watershed and all of the organisms that use and inhabit it. This project hopes to provide a model for the characterization of a watershed and stream chemistry that can be translated and expanded to larger regional hydrology.

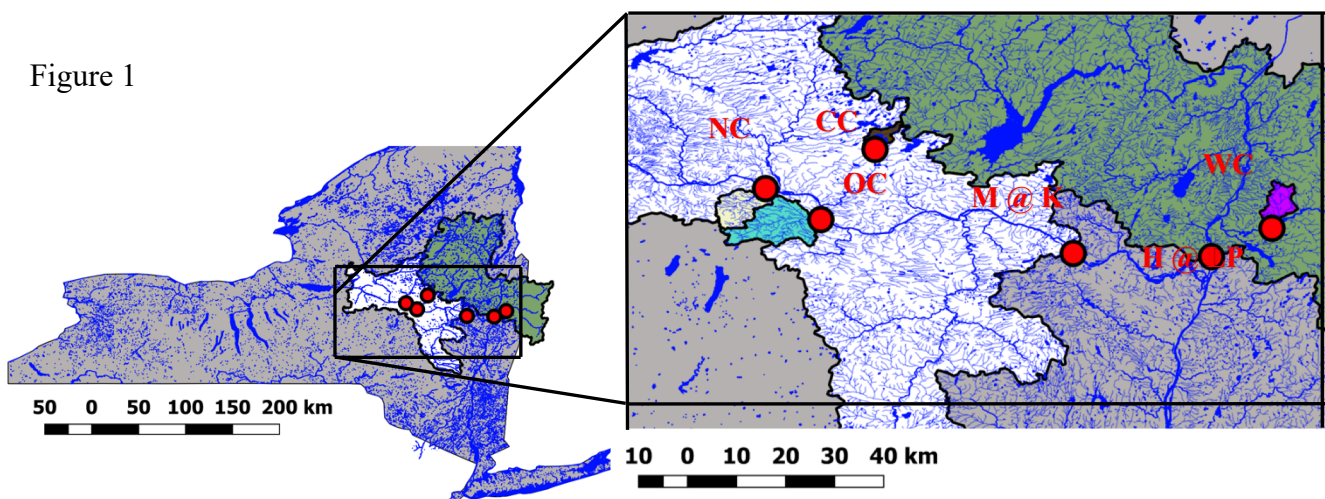


Figure 1: This displays a map of New York State with a zoomed in map showing our watersheds by color and labeled where sampling took place

Table 1

Rivers	Length of River(km)	Area of Watershed (km²)
Wampecack Creek (WC)	30.61	50
Otsquago Creek (OC)	150.45	159
Upper Hudson River	6387	11863
Mohawk River	6922	9015
Nowadaga Creek (NC)	85.3	82
Caroga Creek (CC)	23.15	29

Table 1: The lengths and area of the rivers and basins are listed in the table. It can be seen that there is a wide range in the size of the watersheds and lengths of rivers allowing

Geology

The watersheds were selected with the intentions of having different geologies to help tease out the impact of certain geologic formations on the geochemistry of the rivers. The lithologies in each watershed stem from the lithology of the Hudson and Mohawk, as all of the rivers fall within their watersheds. The lithology of the Hudson–Mohawk watershed may be divided into three distinct groups. These group are the metamorphic and igneous formation of the Adirondack Mountains to the north, metamorphosed foreland basin deposits and glacial till to the east of Albany, and sedimentary lithologies of the Mohawk Valley to the west comprised of shales and limestones.(Longworth et al. 2007). The Hudson River as a mixed geology over the course of its flow scheme. It starts in the southern Adirondacks which are comprised crystalline and metamorphose formations, then flows down through some metasedimentary and glacial till. Wampecack Creek that falls within the Hudson watershed is underlain by metasedimentary with pockets of glacial till. Caroga Creek which sits just within the Mohawk watershed has the lithology of crystalline rock found throughout the rest of the southern Adirondacks. This is also

where the headwater for the Mohawk originates, and then flows through number of shales and limestone formations. The watersheds of Otsquago and Nowadaga Creeks are located right next to each other on the boundary of the Mohawk basin. Both of these watersheds are similar in size and are underlain by the Ordovician Utica Shale from the Trenton Group as well as the Onondaga limestone (Longworth et al. 2007). By having these different lithologies that are comprise of distinct minerals and that weather and erode at different rates we can compare across watersheds and geochemistry to see how water quality is being affected by the geology of a basin. The geology of a watershed is also linked to the land use practices that go on within the basin. For instance across the studied rivers the majority of the agriculture practices are concentrated in regions of the watersheds that are underlain by sedimentary formations and OM rich shales like those of WC, OC, and NC. (Longworth et al. 2007). Land use practices are also a key factor in water quality and have distinct signature that will show up in the geochemistry such as nutrient loading, salination due to crops or urban runoff, and organic matter from forested and agricultural areas (Foley et al. 2005). By having different proportions of land use types there will be different geochemical impacts on each watershed related to the proportions of land use type in each watershed (Figure 2). The different geologies and land use practices will also be further investigated and coupled with the different hydrologic fluxes in each watershed as well as seasonal and regional differences to paint the whole picture of element and ion mobilization into the water geochemistry.

Figure 2

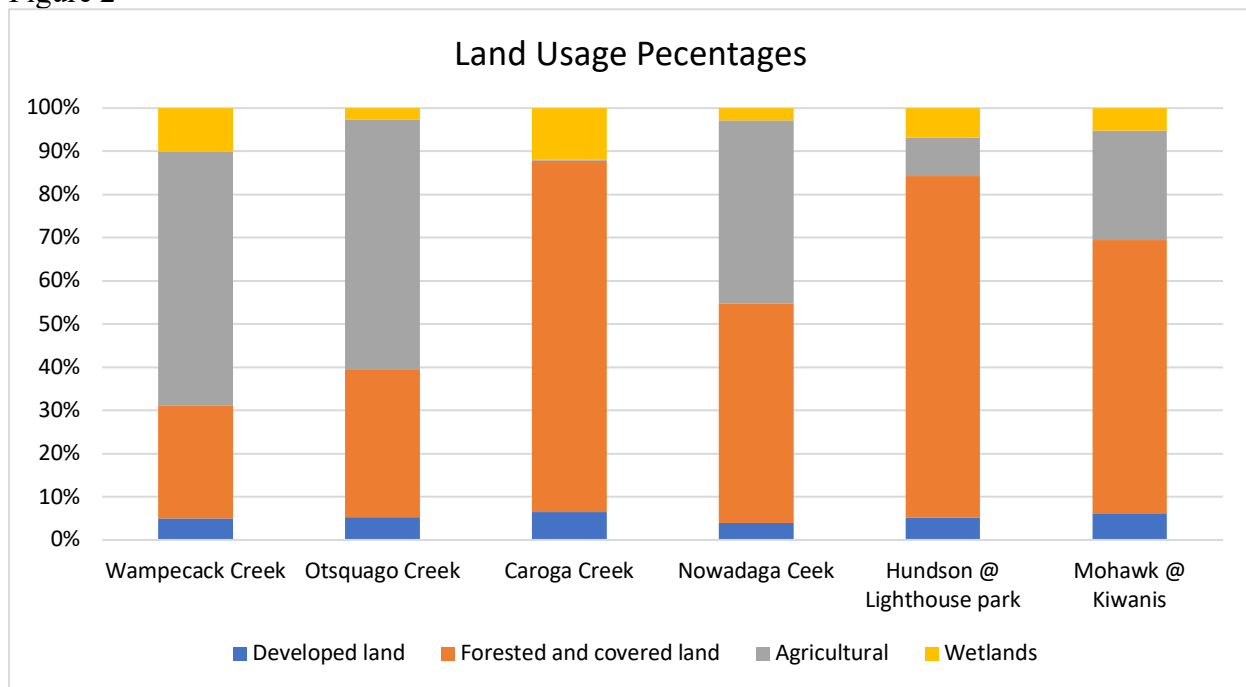


Figure 2: The percentage of land use coverage is shown in this figure. The major differences in land use practice tends to be between the percentage of agriculture and forested and covered land. This has a connection to the geology of the watershed as discussed above and will have an impact on the geochemistry of the water in the watershed.

Hydrology

Field Sampling

I collected field samples under both low flow and high flow conditions. Low flow samples were collected in the summer months of July and August, while the high flow samples were gathered right after storm events in October. When collecting samples in the field, we first established the general parameters of the location. We would take pictures, record the coordinates, date, time and then began to take general water property measurements such as the temperature, specific conductivity and pH using the YSI probe. When taking these measurements, we made sure to let the YSI equilibrate to get the most accurate readings. The YSI was cleaned rigorously, recalibrated after every use, and stored in buffer solution to ensure

that we were getting the most accurate and precise measurements. After recording these general parameters, we began to collect our samples. We used a large tarp as our working area to provide a clean working surface where we deployed our peristaltic pump and filters. The plasticizer free tubing from the pump was run out along a pole attached to a buoy to ensure samples were taken away from the shoreline and representative of the whole river. We collected 8 samples from each location in 15 ml and 50 ml falcon tubes. These samples include ICP-MS (2x), IC (2x), stable water isotope (1x), and ammonia (1x) in the 15 ml falcon tubes as well as alkalinity (2x) in the 50 ml falcon tube. The water for the samples was pumped to our working station by the peristaltic pump and then filtered through a 0.2 μm syringe filter. Once the samples were collected, they were labeled and placed in a cooler with ice-packs and brought back to the lab for analysis. Once the field data had been analyzed in the lab, the data was, cleaned and tidied.

Data collection and Analytical Methods

In order to construct hydrographs, study the different hydrologic fluxes, and characterize the watersheds, there needed to be a sufficient amount of data to ensure the best analysis. To do this I compiled large data sets from multiple organizations and agencies, to supplement our collected field samples to place current data into context. Some of the datasets include precipitation gathered from NOAA and the EPA, streamflow data from USGS stream gauges, runoff data collected from the Waterwatch by the USGS, and land usage data from National Land Cover Database 2011. These datasets were also cleaned and organized to be loaded into the programming language R. It is in R that the data analysis and data visualization was conducted. The data analysis included calculating runoff ratios, statistical analysis on monthly and annual streamflow, and calculations for the different fluxes, flow exceedance curves, and shifts in flow timing. In R this data is analyzed and then transformed into visual representations allowing for trends to be seen and then further investigated.

Regional Climate

The hydrology of an area is inextricably linked with the climatic patterns of that region. The flow of a river is the representation of the complex response of various climatic inputs such as precipitation and temperature playing major roles. The changes in hydrologic fluxes and flows in a river can be a good indicator and example of climatic changes (Hodgkins, Dudley, and Huntington 2003). It is necessary to understand the general climatic patterns of a region, to then be able to give reasoning to hydrologic fluxes of your area of focus. Precipitation varies greatly across the United States, but the national average is 76.5 cm annually. New York state ranks 25th out of the states in the U.S. in precipitation receiving an average of 103.8 cm of precipitation annually. This is consistent with the regional precipitation of the Northeast (“NOAA Precipitation Data,” n.d.). This could be shifting as the average precipitation has been increasing in both New York and Nationally (Figure 3). The fourth National Climate Assessment argues that the Northeast, Midwest, and the Great Plains will be experiencing increased levels of precipitation. The national precipitation has increased by 4% since 1901 and the increase is coming from sharp increases in specific areas one of them being the Northeast (Reidmiller, D.R., C.W. Avery, D.R. Easterling, K.E. Kunkel, K.L.M. Lewis, T.K. Maycock 2018). The increase in precipitation could have profound effects on the watersheds of the region and the balance of hydrologic fluxes.

Figure 3

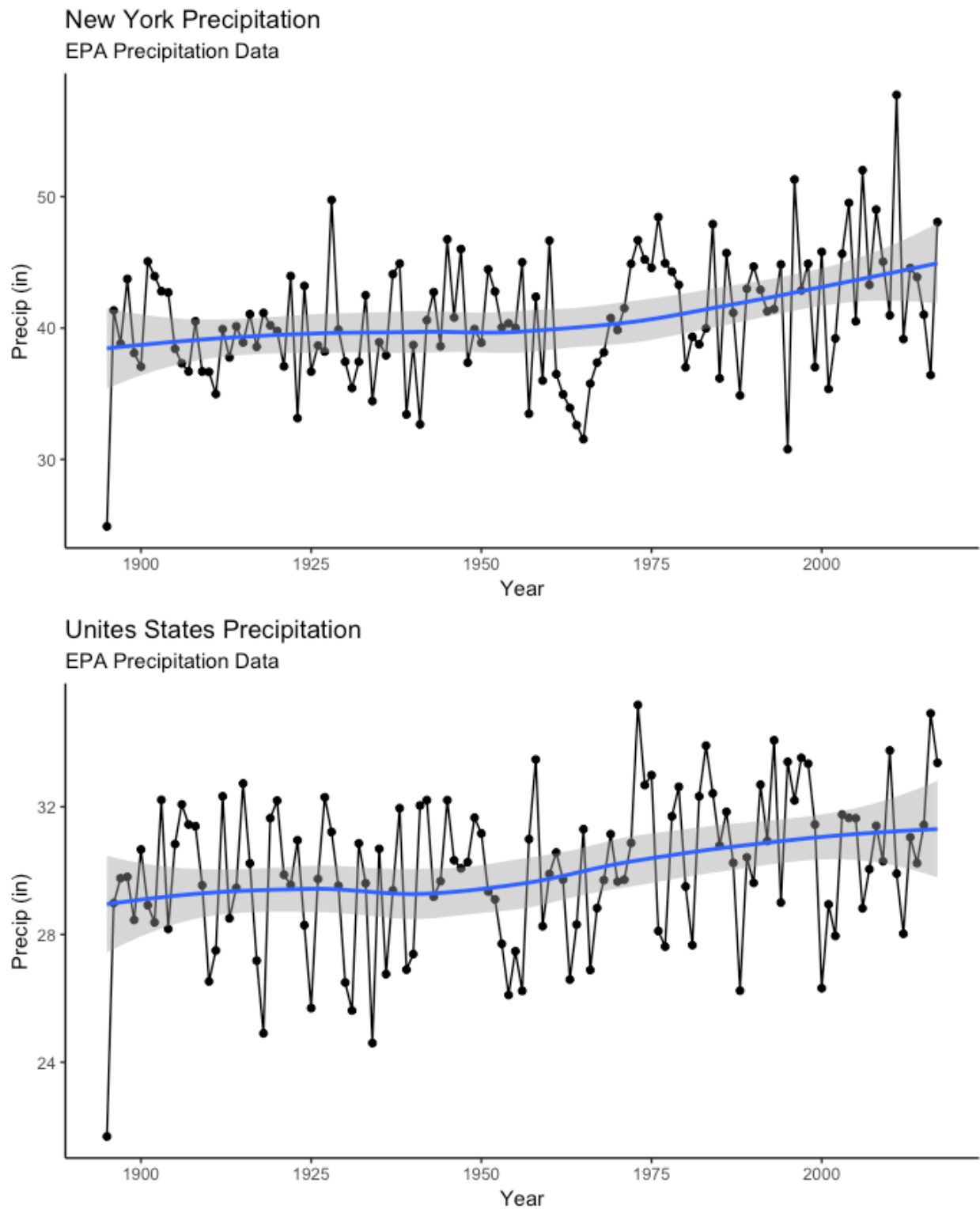


Figure 3: Data from NOAA shows how the precipitation in the United States and in New York State has been increasing since the 1960s onward.

Climatic Patterns

When narrowing the scope of focus to our watersheds of interest, the EPA values for annual precipitation reported for the watersheds of interest are slightly lower than the state average annual precipitation. This slight difference is because the spatial scale of the river basins is much smaller than that of the whole state of New York, with the local climate differing from the overall state averages. The values that were measured for the watersheds range from Wampecack Creek (WC) receiving the most precipitation at 102 cm and Mohawk River receiving the least amount of precipitation with 92.3 cm annually (“Meteorological Data” 2006). There are some seasonal patterns in the precipitation with lowest mean precipitation across all of the watersheds coming in the months of January, February and March the highest monthly averages typically coming in the months of May, June, July, and August (Table 3). In addition to being the months that receive the most precipitation these months also had the highest levels of E.T. . This makes conceptual sense as these months are typically the hottest and have the highest primary production by the plants. The three highest monthly E.T. values for sites occurred at OC, NC, and WC, with 12.14 cm, 12.09 cm, and 11.47 cm of evapotranspiration respectively. These three watersheds also correspond to the watersheds with the highest percentage of agriculture land cover with WC having 58.8 %, OC having 57.9% and NC having 42.2% agriculture land coverage. The data for land use type percentages was collected from the National Land Cover Database 2011 (Homer, C.G., Dewitz, J., Yang, L., Jin, S., Danielson, P., Xian, Coulston, J., Herold, N., Wickham, J. and K. Megown. 2015, Reidmiller, D.R., C.W. Avery, D.R. Easterling, K.E. Kunkel, K.L.M. Lewis, T.K. Maycock 2018). The increased level of E.T. in these months and across these agriculture intensive watersheds, we see in turn have an impact on the fluxes in and around the rivers. The climatic trends are linked to the amount of runoff that is observed in a river.

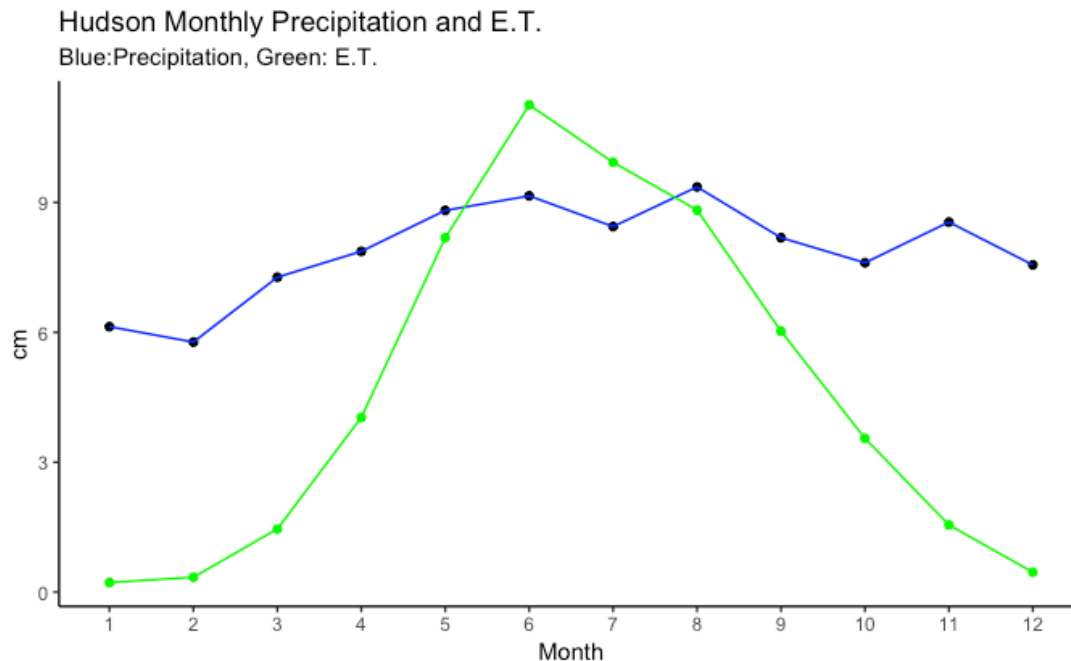
Table 2

	Monthly Precipitation (cm)											
Watersheds	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
WC	7.33	6.98	8.33	8.69	9.57	9.36	8.1	9.05	8.56	8.13	9.23	8.68
OC	5.97	5.61	7.23	8.03	8.5	9.42	8.89	8.87	8.56	7.7	8.82	7.78
CC	5.97	5.61	7.23	8.03	8.5	9.42	8.89	8.87	8.56	7.7	8.82	7.78
NC	5.97	5.61	7.23	8.03	8.5	9.42	8.89	8.87	8.56	7.7	8.82	7.78
H @ LP	6.13	5.78	7.27	7.87	8.82	9.15	8.44	9.36	8.19	7.61	8.55	7.56
M @ K	5.68	5.37	6.89	7.66	8.41	9.15	8.78	9.12	8.21	7.38	8.33	7.26
	Monthly E.T. (cm)											
WC	0.31	0.48	1.98	4.94	10.56	11.74	8.89	8.25	6.62	4.37	2.01	0.63
OC	0.24	0.36	1.42	3.86	7.35	12.09	12.14	8.96	5.75	3.36	1.54	0.49
CC	0.22	0.33	1.32	3.59	6.83	9.81	9.35	8.3	5.32	3.07	1.41	0.45
NC	0.25	0.36	1.45	3.96	7.53	12.09	11.76	8.87	5.78	3.4	1.57	0.5
H @ LP	0.22	0.34	1.46	4.03	8.18	11.26	9.93	8.82	6.03	3.55	1.55	0.46
M @ K	0.20	0.30	1.29	3.76	7.68	9.65	8.89	8.41	5.87	3.40	1.47	0.43

Table 2: The monthly precipitation and E.T. values for each watershed are listed. The precipitation data is gathered from the EPA and the E.T. is modeled data from the GWLF-E

Figure 4

A



B

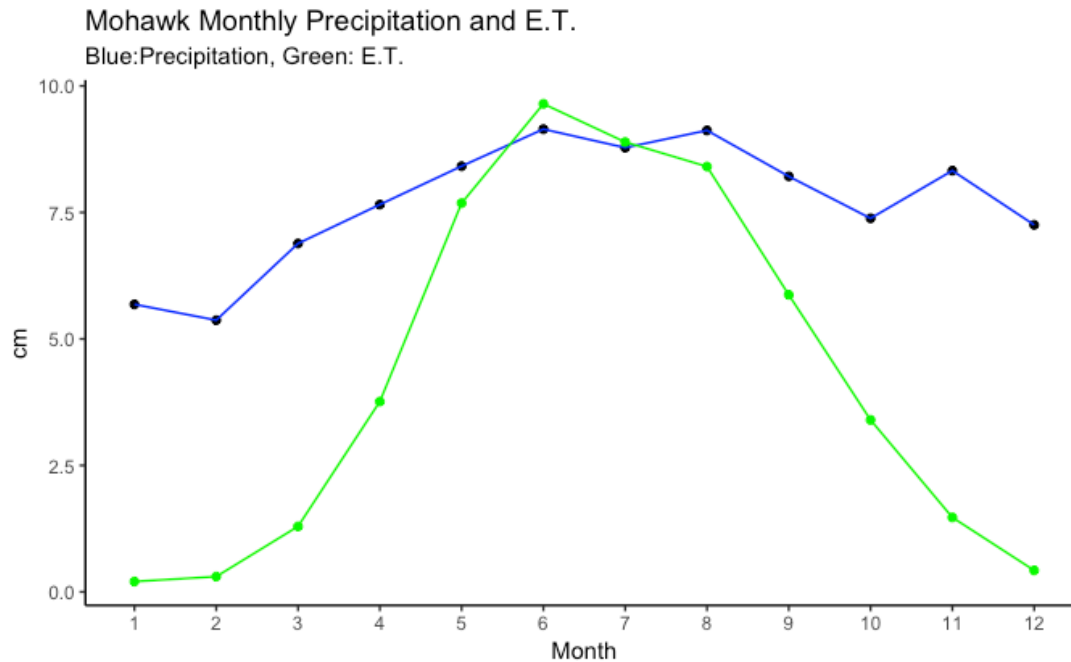


Figure 4: The monthly precipitation and E.T. are plotted against each other for Hudson (A) and Mohawk (B). This displays the increase in E.T. in the summer months while precipitation stays relatively constant increasing slightly in the spring and summer.

Runoff and Hydrograph Analysis

The runoff ratios have been calculated, in R, for both the United States and New York by taking USGS runoff data and pairing it with NOAA precipitation data (“The Hudson Estuary: A River That Flows Two Ways,” n.d.; “Meteorological Data” 2006). Run off ratios are calculated by a simple equation

$$\text{Runoff Ratio} = \frac{\text{Runoff}}{\text{Precipitation}}$$

The average annual runoff ratios came to be 0.542 for New York state and 0.307 for the Continental United State. In term of an even larger spatial reference, North America has a runoff ratio of 0.38 and the global ratio is 0.46 (Berner and Berner 2012). The annual runoff ratios were

then calculated for the rivers of interest, which all fall above the ratio for North America and slightly below the ratio for New York (Table 3). When looking at the monthly runoff ratios, there is much more variability which is tightly linked to the changes in climate over the course of a year (Table 3, Figure 5). All of the rivers generally follow a similar pattern of increasing ratio going into the winter months and reaching its peak through the spring and drops to very low values in the summer months. These changes show the complex relationship between the climate and runoff ratios, as the lowest runoff ratios come in the summer months when there is still substantial precipitation. The reason for this is an increased in temperature coupled with an increase in primary productivity driving up the levels of evapotranspiration. These factors strictly limit the amount of precipitating that actually is able to reach the rivers. The relationship between the levels of runoff as well as other hydrologic fluxes are tied to the climatic variation and the seasonal and temporal trends can be drawn between the changes in climate and the fluxes in the watersheds.

Table 3: Monthly and Annual Runoff Ratios

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
WC	0.68	0.88	0.95	0.75	0.39	0.25	0.11	0.07	0.06	0.14	0.21	0.50	0.42
CC	0.81	0.94	1.04	0.77	0.50	0.23	0.15	0.06	0.11	0.29	0.47	0.76	0.51
NC	0.69	0.89	1.01	0.75	0.48	0.20	0.12	0.04	0.08	0.12	0.22	0.53	0.45
OC	0.69	0.92	1.04	0.75	0.47	0.19	0.12	0.04	0.10	0.13	0.22	0.54	0.50
M@K	0.79	0.90	1.03	0.82	0.48	0.22	0.12	0.08	0.11	0.28	0.43	0.71	0.43
H@LP	0.72	0.86	0.98	0.82	0.46	0.25	0.12	0.06	0.05	0.16	0.28	0.59	0.42

Table 3: The runoff ratios in each month and the mean annual runoff ratio for each river. The seasonal variability can be seen as the wetter months like January through April have the highest ratios and the lowest ratios are in the summer months with the highest temperature and E.T.

Figure 5

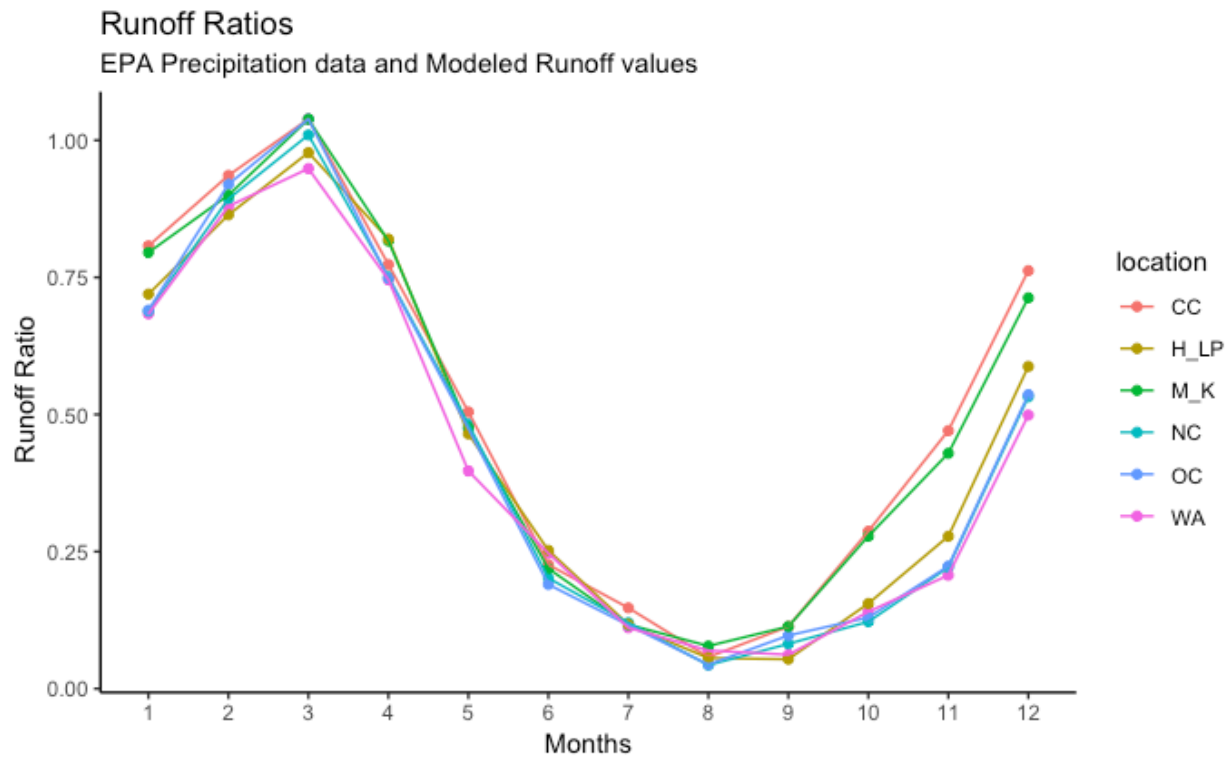


Figure 5: The monthly precipitation runoff ratios for each location showing the monthly shifts in response to changes in climatic patterns and seasonality.

On three of the rivers of interest there are stream gauges that have daily historic records taken by the USGS. These records allow for hydrograph analysis on each river looking at shifts in flow patterns over time using real observed data. Monthly flows and seasonal trends can be seen related to the climatic shifts in temperature and precipitation, as well as the levels of E.T. talked about above. It can be seen that the stream flow in the months of March, April, and May are when these rivers reach their highest average monthly flow which comes in the months where the watersheds receive the high levels of precipitation with little primary productivity. In contrast to this the rivers reach their lowest flow in the months of June July and August when there is roughly the precipitation, but increased temperatures and E.T. as crops and flora become more active (Figure 6). Teasing out these patterns help to validate the relationship with runoff

and climatic variations. To get a broader picture of how these rivers are changing over time, the flows can be analyzed on an annual scale to determine long term flow trends.

Figure 6

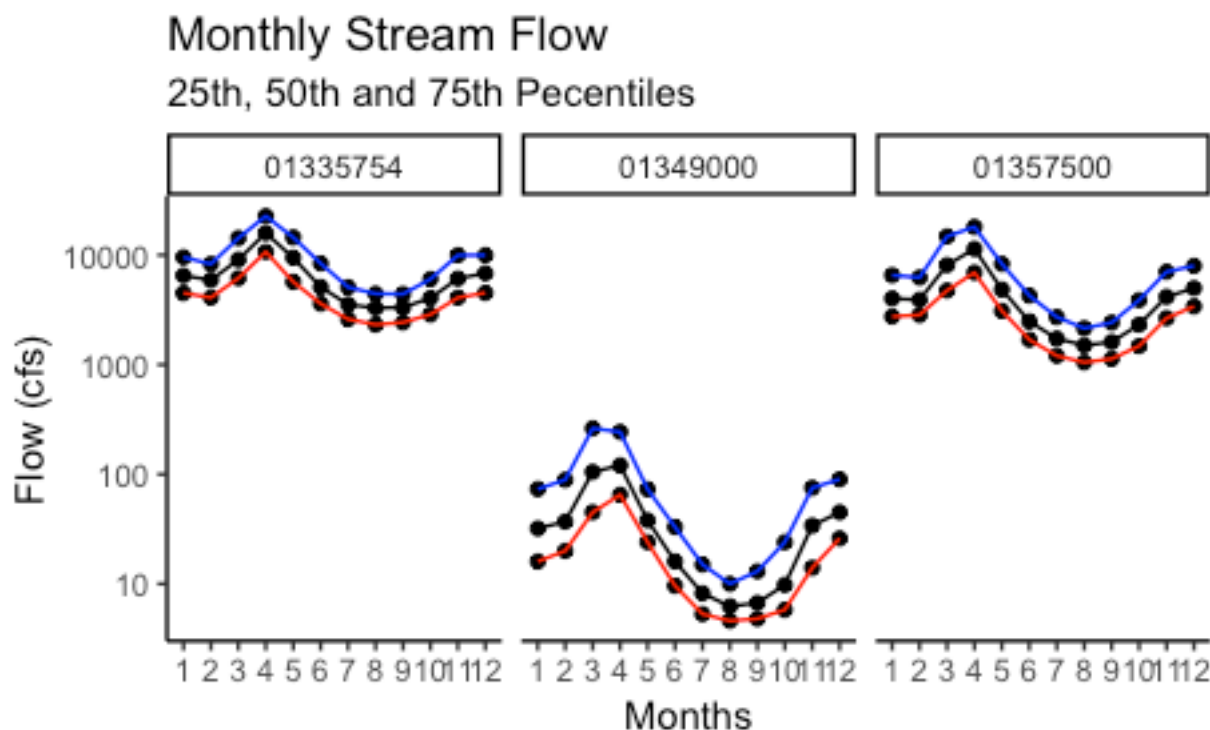


Figure 6: The average monthly 25th (red), 50th (black), and 75th (blue) percentile flows for Hudson (01335754), OC (01349000), and Mohawk rivers (01357500). The seasonal patterns in flow can be seen.

The stream gauges have an extensive amount of observations and provide a very detailed and consistent recording process. By having so many observations large general physical flow statistics can be constructed to give a good understanding of the river as a whole (Table 4). In looking at this data over such a vast temporal scale shift in flow patterns can be traced as well as identifying key historic hydrologic moments. For instance, the large drought of the late 1950s to early 1960s can be seen in the annual minimum flow figures for Mohawk and Otsquago (Figure 10 A, Figure 11 A). drought is backed by the precipitation record as well as historic records as they show a multi-year event that was estimated to be one of the most severe droughts have

occurred in the region (Hayhoe et al. 2007; Leathers, Grundstein, and Ellis 2000; Seager et al. 2012). Once events are identified, shifts in flow patterns and timing can be analyzed. For example, we see the annual mean flow for Hudson Mohawk and OC are increasing in recent years (Figure 9 B, Figure 10 B, Figure 11 B) can be explained by the shifts in the maximum and minimum flow for the rivers, as well as an increase in the amount of annual precipitation.

Table 4

River	Site No.	Start Year	End Year	Number of Observations	Min Flow	Max Flow	Mean Flow	25th	50th	75th
Hudson	01335754	1887	2018	40553	170	114000	78544.43	3520	5630	9950
Otsquago	01349000	1949	2018	16230	1.42	3500	85.10	9.2	26	72
Mohawk	01357500	1917	2018	36921	23	112000	5924.96	1910	3500	6980

Table 4: The general information on the stream gauges parameters and the broad flow characteristics of each river

The Upper Hudson is experiencing an increase in the amount of annual minimum flow it is receiving and a slight decrease in the maximum flow (Figure 9 A and C). However, the maximum flow is not decreasing by a significant amount, while the 7-day low flow is increasing which helps to explain the overall rise in average stream flow for the Hudson river (Figure 9 D). This shift becomes even more apparent when looking at the flow exceedance curve when it is partitioned into pre and post 1960 periods (Figure 7 A and B). It can be seen that in the Post 1960 period the low flow or the higher flow percentile has shifted up in its amount of flow, while the high flow or low flow percentile areas have not changed significantly. Furthermore, the ratio of Post to Pre 1960 reaches a magnitude of upwards of 6 at the high flow percentiles and stays at or around 1 for the first quartile of flow percentile (Figure 7 C). The Mohawk River has an

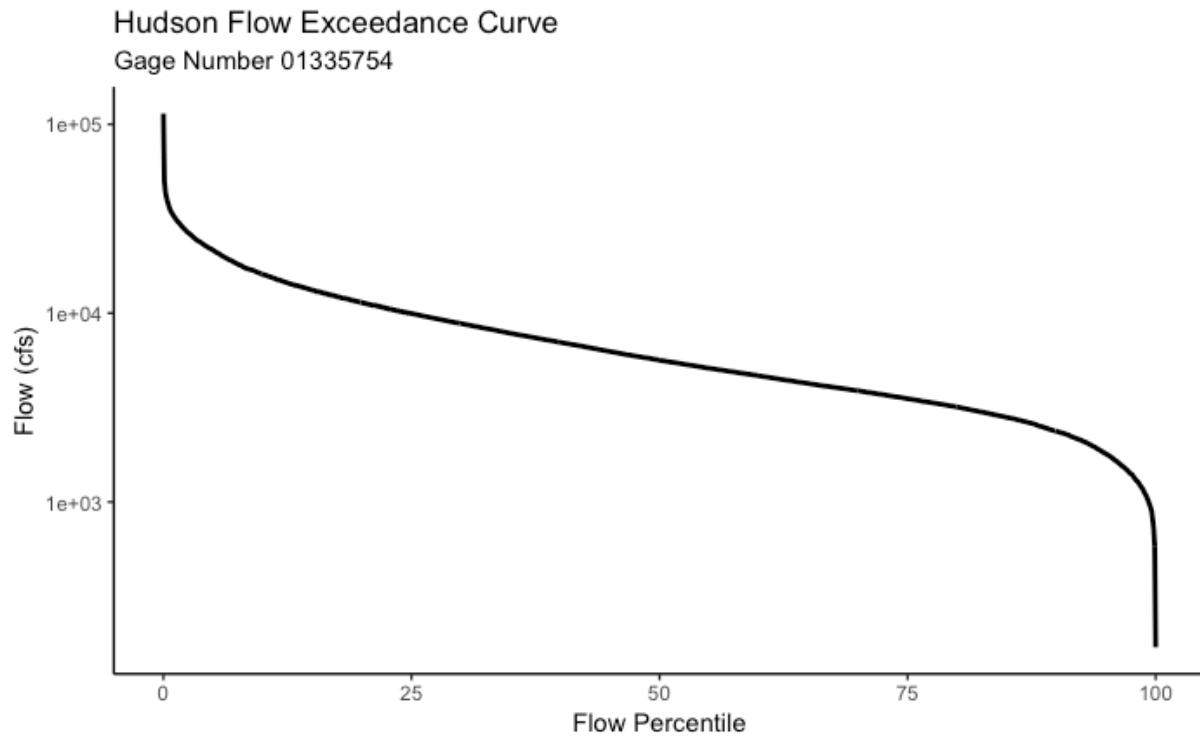
overall steady max flow hydrograph, but an increasing minimum flow from the mid 1960s onward (Figure 10 A). This is consistent with the observations of the extreme draught in the 1960, then followed by a wet decade in the 1970s and has continued to increase since (Darmer 1987). The 7-day low flow has also increased displaying that the low and extended low flow periods are happening at less intensity as extensive draughts like that of the 60s are not as prevalent (Figure 10 D). Looking at the flow exceedance curve and the partitioned time scale display the increase in the upper flow percentiles, and a shift in the mean flow (Figure 10 B). The shift in mean flow is most likely due to the increase annual precipitation. This shift has implications for the ecosystem and for the geochemistry which will be discussed later.

In Otsquago Creek there are less observations than the other two stream gauges, but none the less, trends can be drawn. The minimum flow appears to remain relatively consistent from wateryear to wateryear, the same with the 7-day low flow (Figure 11 A and D). The mean and maximum flows appear to be increasing which could be representative of the increased precipitation in the recent years causing large spike events for maximum flow in storm conditions (Figure 11 A, B, C). Otsquago is a much smaller stream than the Upper Hudson and Mohawk Rivers and therefore there is much more variability and response to changes in hydrologic inputs. There is less of a buffer and impacts can be seen almost immediately. By looking at the annual scales we can see the smoothened shifts over time not immediate jerk reactions by the watershed.

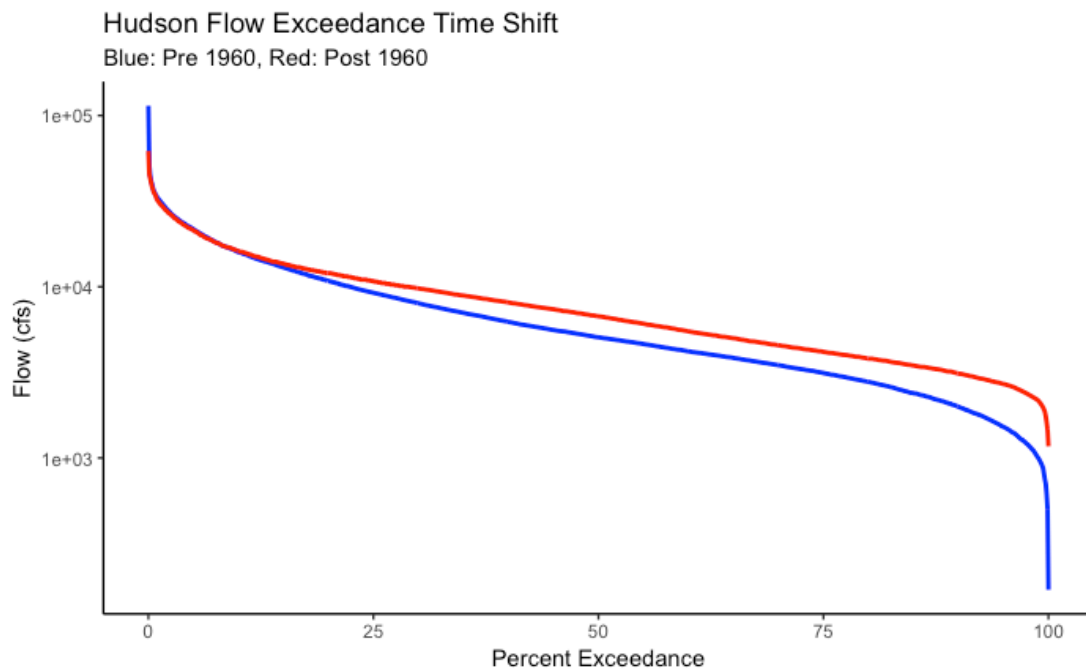
Having stream gauges are essential to be able to have real observations of stream flow and provide the historic record so shifts over time can be seen. The problem with stream gauges is that they only give us the variable of streamflow. We are unable to measure all of the different components that go into the discharge value that the stream gauge produces. Furthermore, if a stream does not have a gauge on it, like some of our studied rivers do, then there can be no

observed flow values. In order to establish an understanding of the fluxes that go into the formation of the stream discharge, there needs to be a model run to produce values for the missing fluxes.

Figure 7
A



B



C

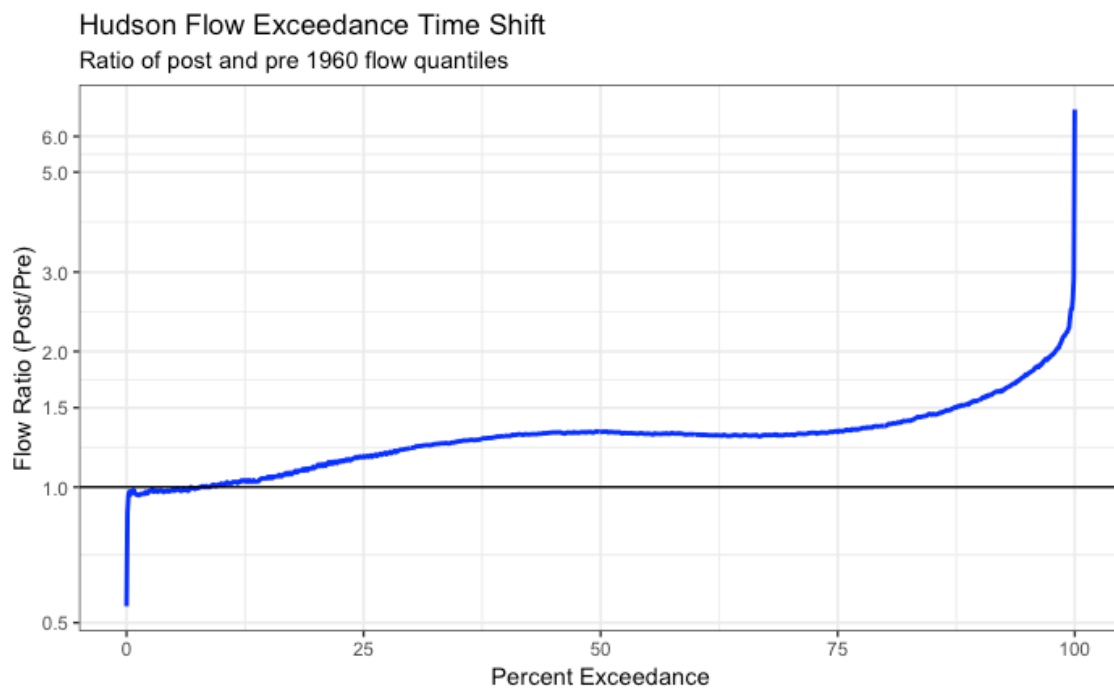
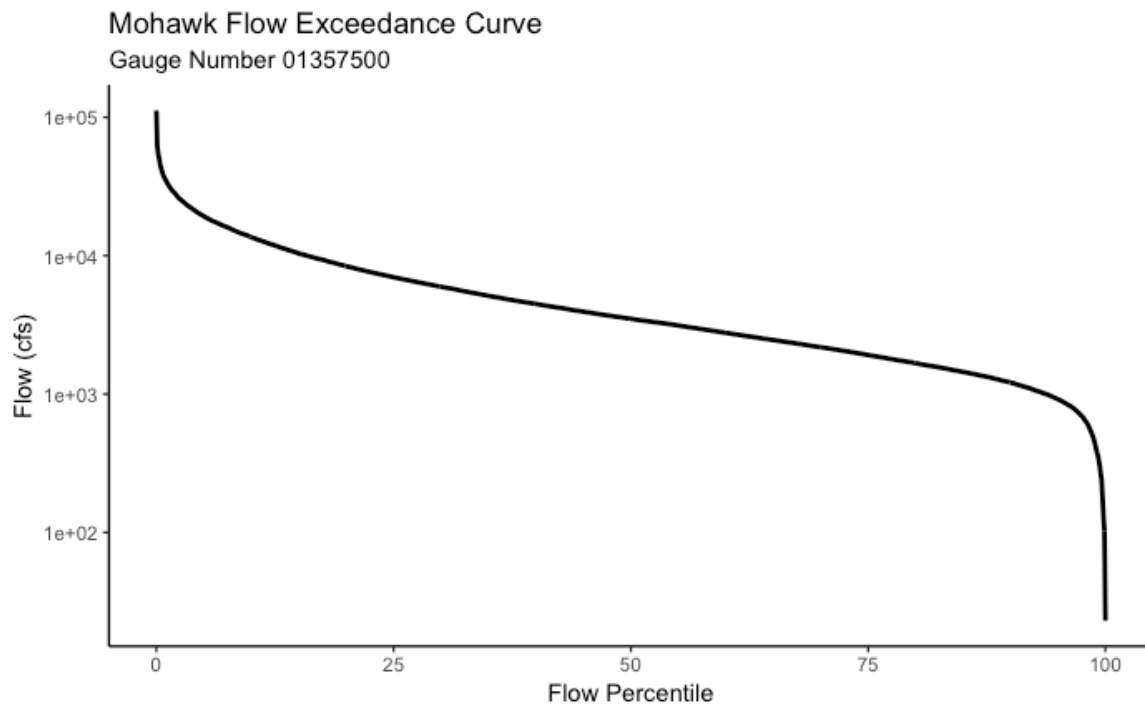


Figure 7: The flow exceedance curve tells us how much flow we can expect to get at a certain percentile (A). When partitioning the curve into pre and post 1960 we can see the sharp increase in the min and mean flow since the 1960s (B). Additionally, we can see to what extent this shift has happened by looking at the magnitude of the shift

Figure 8

A



B

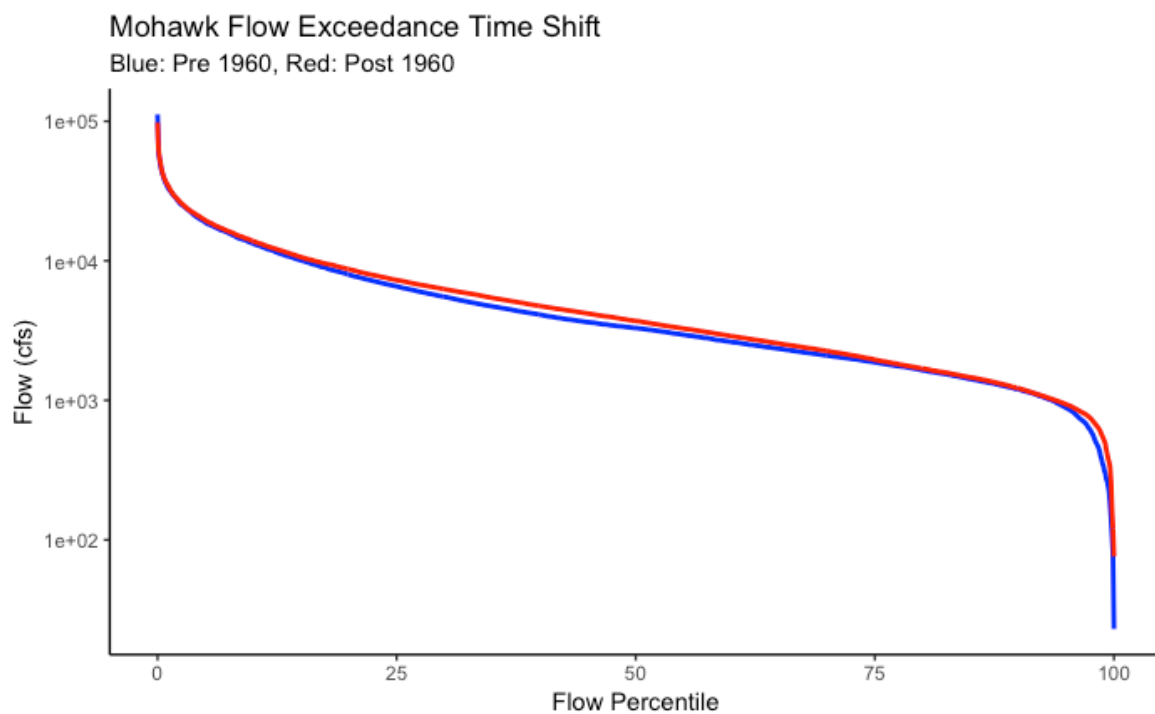
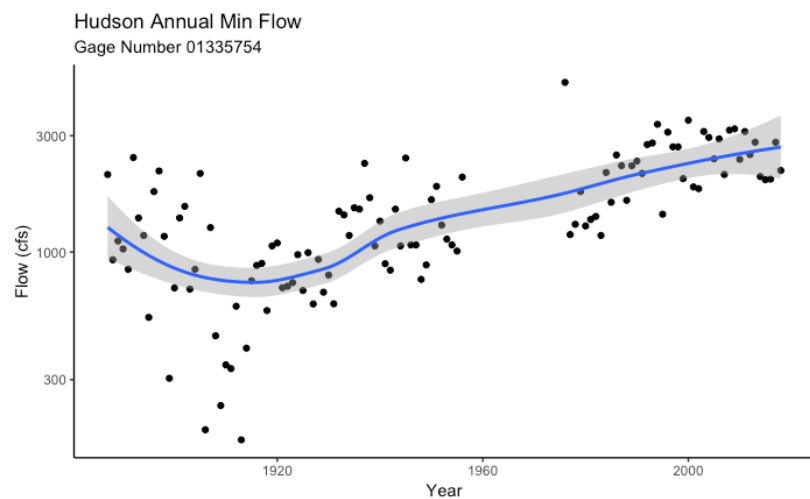


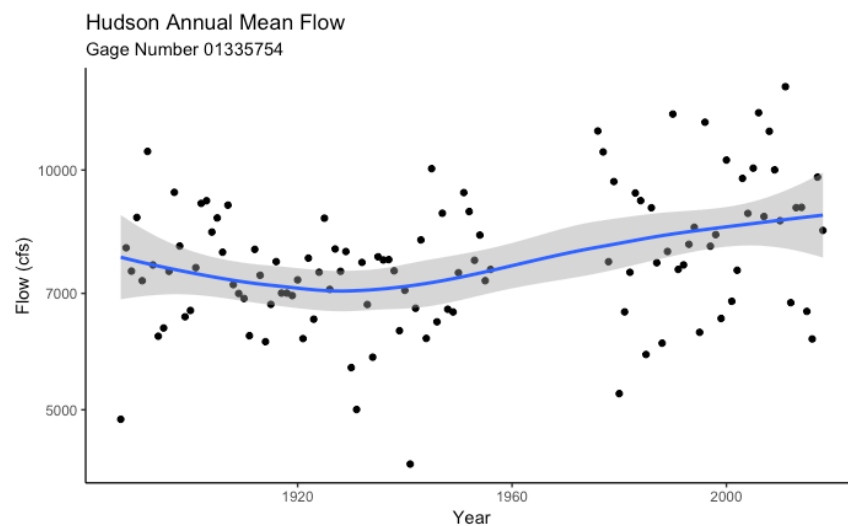
Figure 8: The flow exceedance curve tells us how much flow we can expect to get at a certain percentile (A). When partitioning the curve into pre and post 1960 we can see the slight increase in the min and mean flow since the 1960s, while the max flow has not changed.

Figure 9

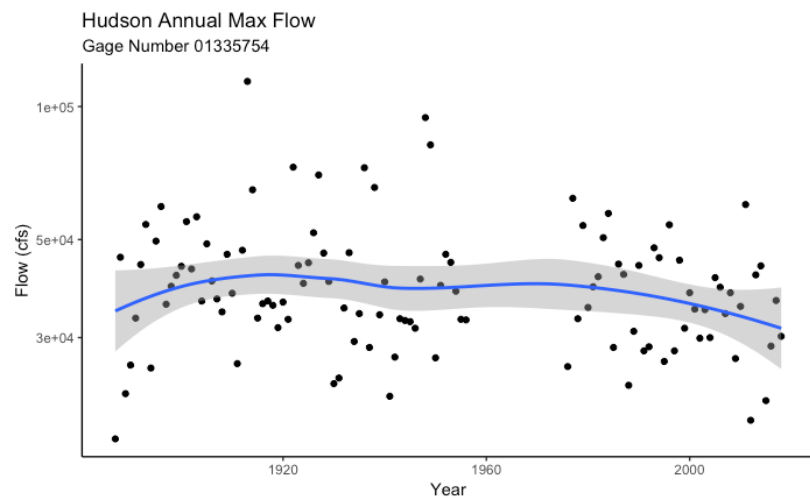
A



B



C



D

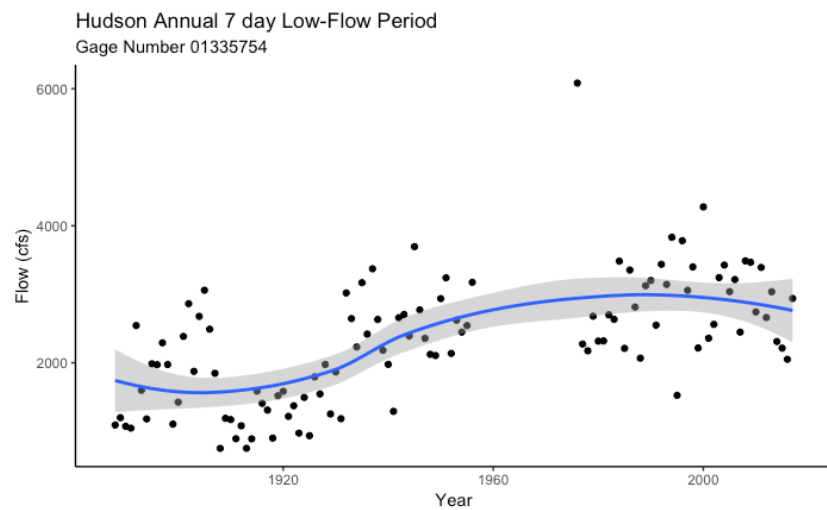
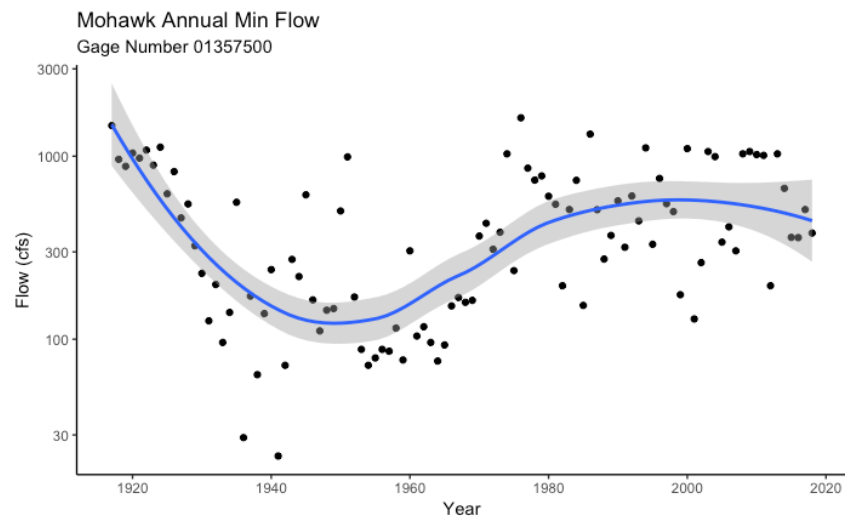


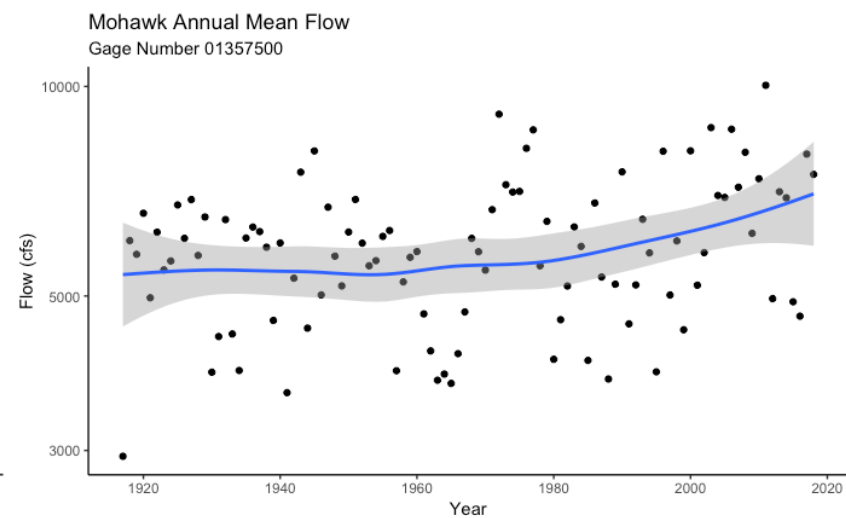
Figure 9: These figures show the annual minimum flow(A), mean flow(B), the max flow(C), and the 7-day low flow(D) for Hudson

Figure 10

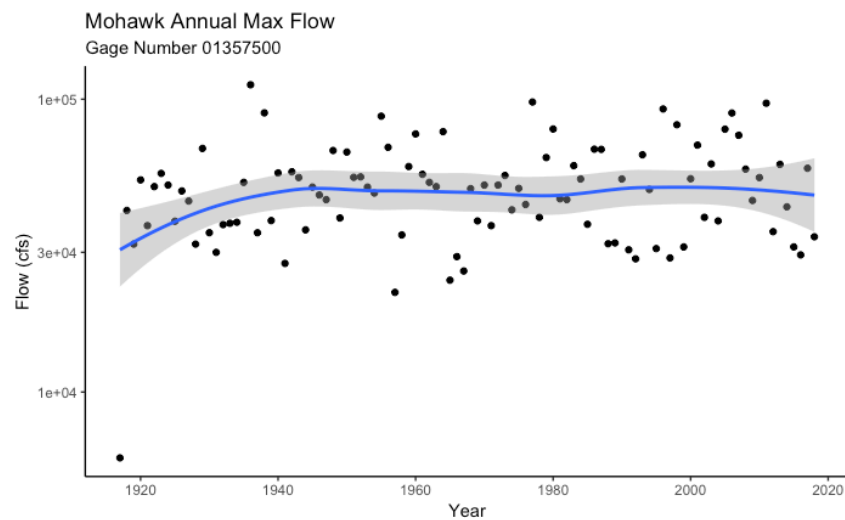
A



B



C



D

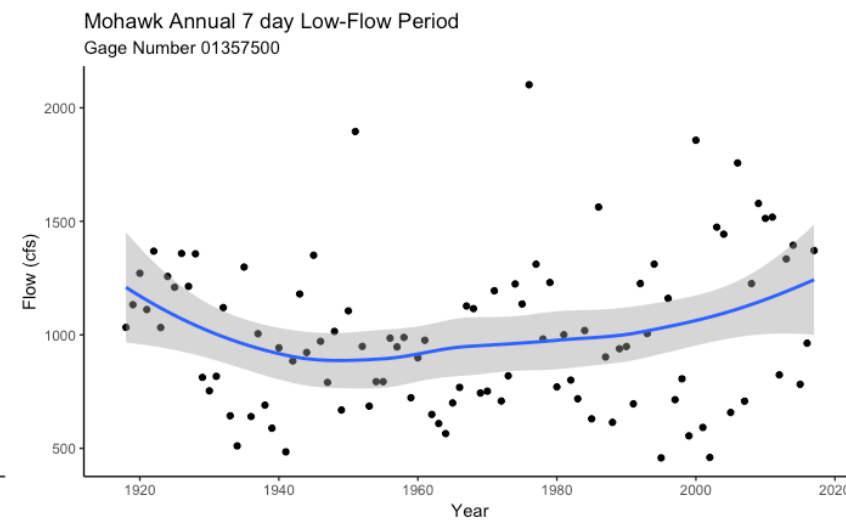
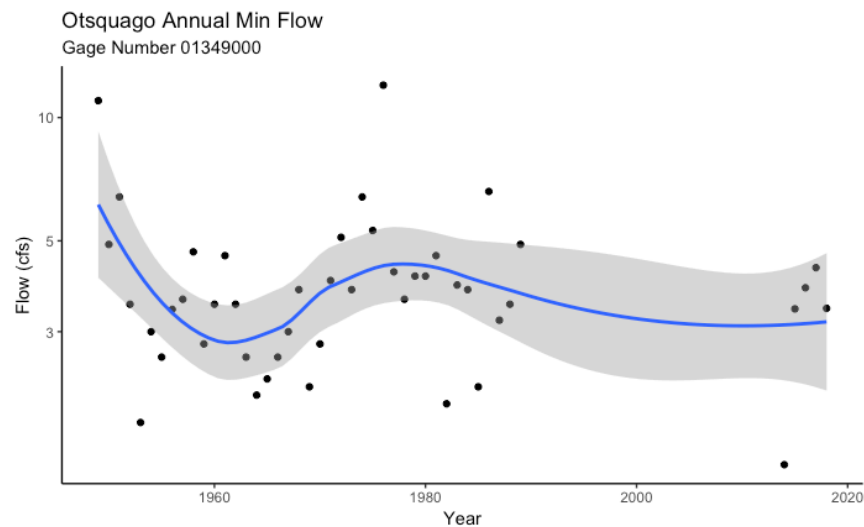


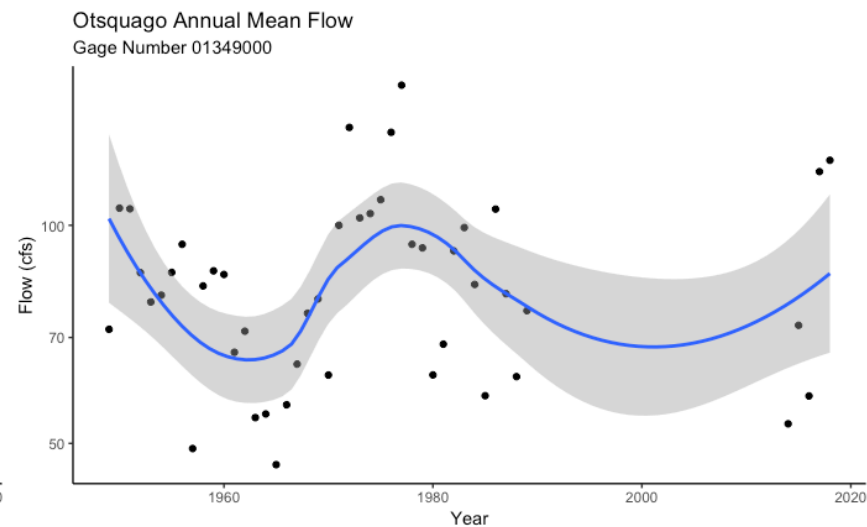
Figure 10: These figures show the annual minimum flow(A), mean flow(B), the max flow(C), and the 7-day low flow(D) for Mohawk

Figure 11

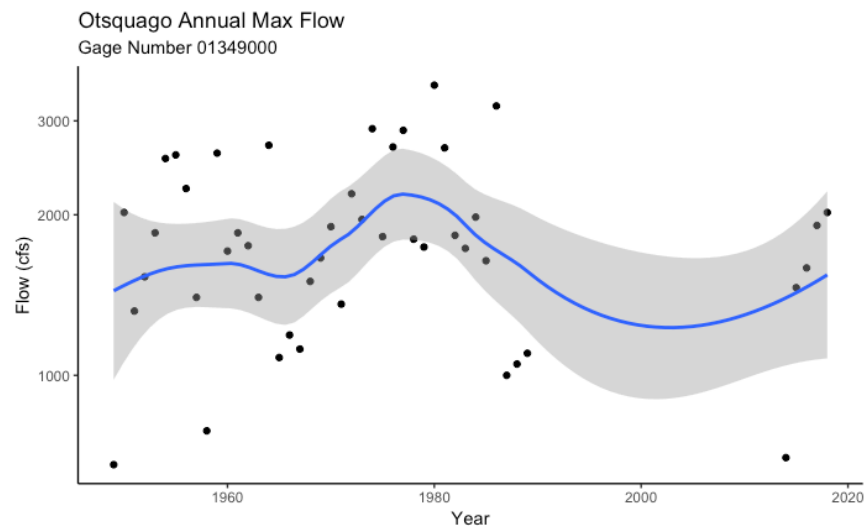
A



B



C



D

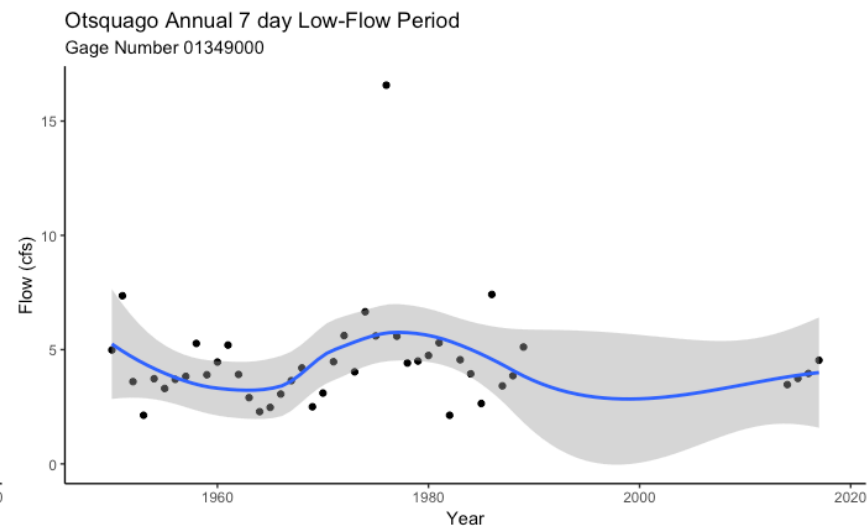


Figure 11: These figures show the annual minimum flow(A), mean flow(B), the max flow(C), and the 7-day low flow(D) for Otsquago

Modeling

Model Description

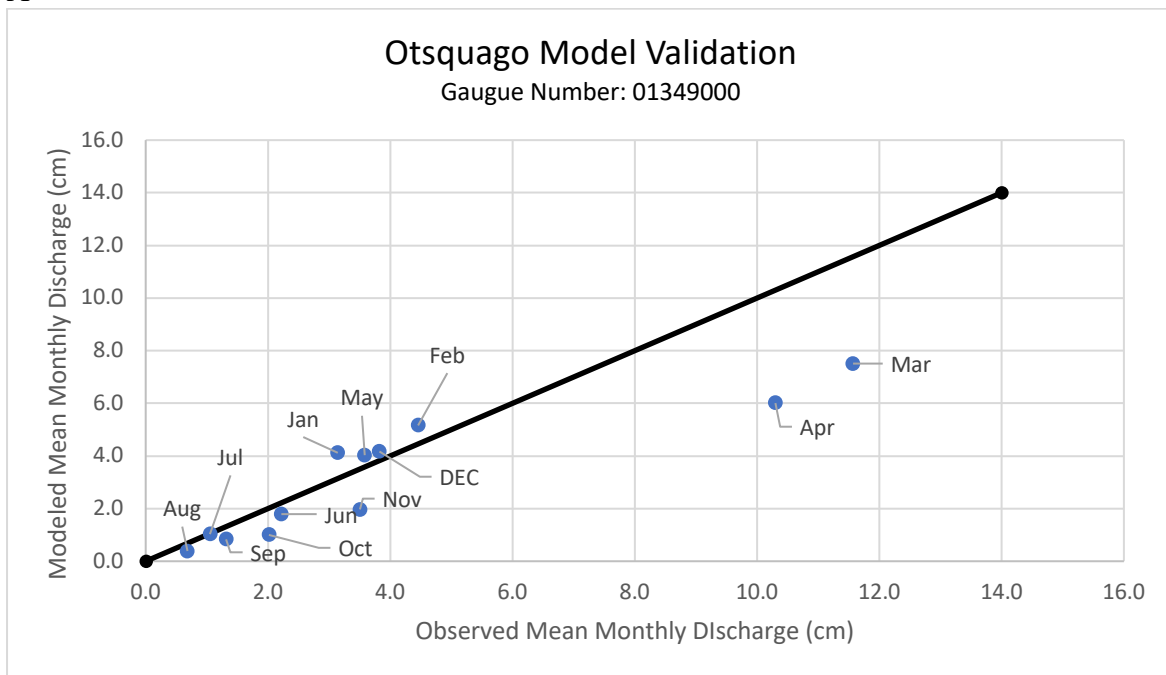
The model we run is the GWLF-E Model through the Wiki-Watershed interface. This model simulates 30 years of daily streamflow, sediment fluxes, nutrient loading levels, by combining various datasets. The model was created at Penn State and uses algorithms and combination with several reputable data sources. The model uses GIS-Based estimations to set the parameters of what data gets inputted to the GWLF-E. Some of the data sets from which the model draws its information are the 2011 National Land Cover Dataset, GSSURGO Soil Data, USEPA National Climate Data, Discharge Monitoring Report (DMR) Data, and 30-Meter Elevation Data. The GWLF-E takes the information contained in all of the data sets and uses algorithms and GIS processing to run the model and compute values that otherwise would be impossible to measure. An example of this modeling is the combination of streamflow data and a watershed given land use and soil data to model the sediment and nutrient loading in the streams. The model outputs the monthly mean hydrographs, the land use areas and percentages, sediment loads, and some of the hydrologic fluxes for the watersheds allowing for analysis and comparison across watersheds. Some rivers of our study do not have gauges to give us observed data such as WA, NC, and CC, so the model helps to provide modeled data so that hydrograph analysis can be conducted.

Model Validation

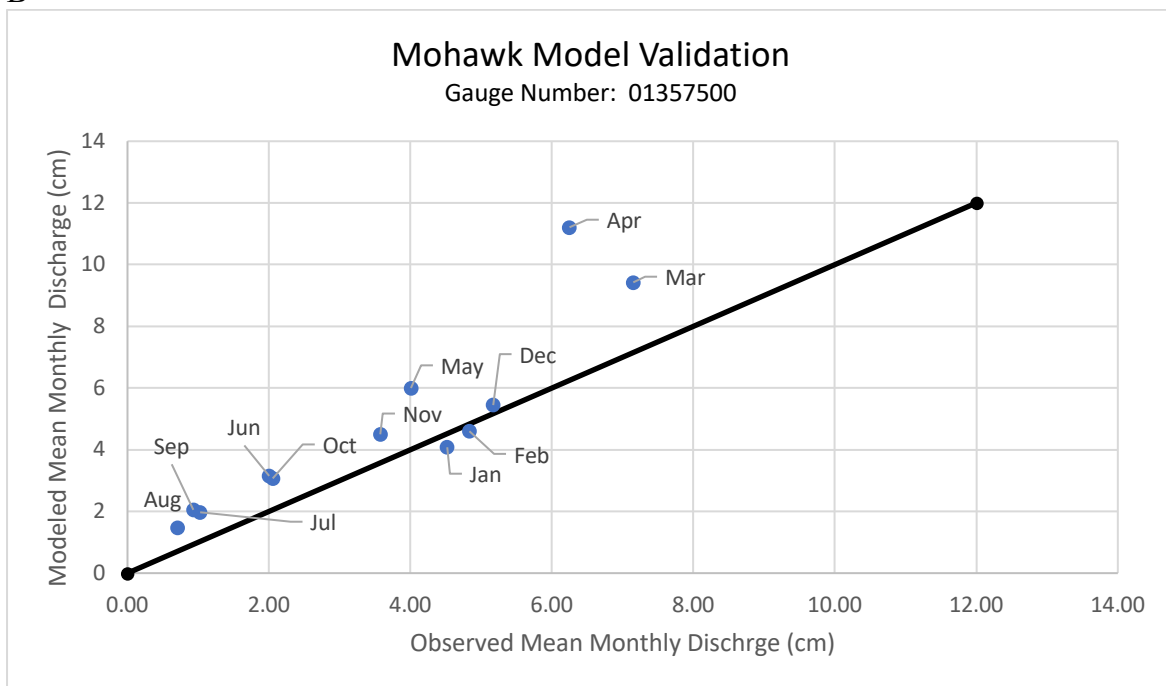
We are able to compare and validate the model to the observed data that we have for streams that have stream gauges, which are Hudson, Mohawk, and Otsquago. The model has

already been calibrated and tested on 39 test watersheds by looking at the stream flow and load calculations. They took the observed data from 1990 to 2015 and used this to test against what the multi-year model outputs were. The goal of this validation step is to see how close the estimates of the model were actually to the observed data, and to fine tune and fix the areas where the model was off. In general, the model is very good and generated good data for the multi-year model. The model did not have and calibration testing for New York. Because of this we decided to compare our model data to the observed stream flow data from USGS. The model uses data the years from 1960-1990 and so we took the streamflow data Hudson, Mohawk, Otsquago, which had stream gauges for those years, and compared the observed monthly streamflow averages to the model monthly streamflow averages. The validation showed that the model worked well and showed where values were overestimated and underestimated. The model for OC worked very well for the majority of the months, but slightly under valued the flow in the high flow months like March and April (Figure 12 A). The Mohawk model like the OC model worked very well for most months, however it over valued the flow for the river in the high flow month of March and April (Figure 12 B). The Hudson model was the least accurate out of the three and undervalued the flow in most months. These values do seem to be on par with the slope of the reference line, just shifted lower by a factor (Figure 12 C). Overall the model validation shows that the model works fairly well and helps to tease out where the biases may lie for a given watershed. In addition to using observed stream flow to help validate the model we also used stable water isotopes to help further hone in on the models deficits and strengths. The use of stable water isotopes will be discussed later on.

Figure 12
A



B



C

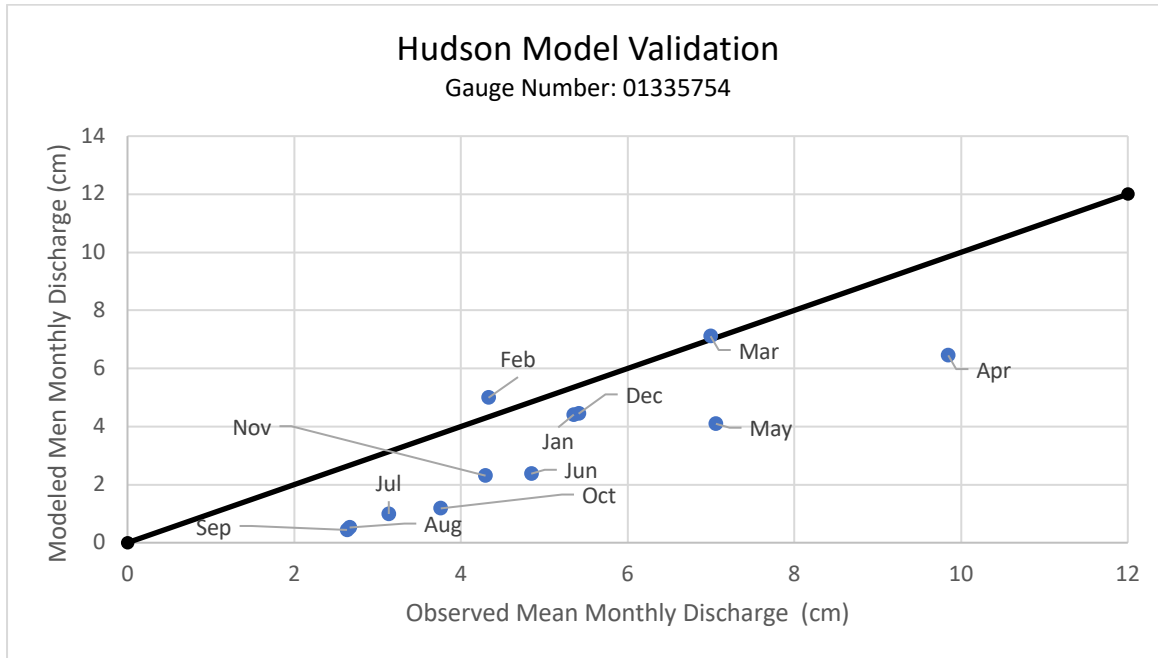


Figure 12: The model validation for Otsquago (A), Mohawk (B), and Hudson(C), are made by plotting the modeled mean monthly discharge against the observed mean monthly discharge from the stream gauges.

Modeling Analysis

By running the model, we are able to partition the overall flow of a river into its surface runoff, subsurface flow, stream flow and point source flow that we could not see before. We can then use these hydrologic fluxes to compute the baseflow index, recharge rates, and use stable water isotopes to help further validate the model and draw some broader hydrologic patterns. We first calculated what percentage of the precipitation are baseflow, surface runoff and E.T. comprised of. There is some variability across the sites most notably Caroga Creek's E.T. as a percent of precipitation was 8% lower than the other sites. This could be explained because there is almost no agriculture in CC which would reduce the levels of E.T (Figure 2, Table 5, Figure 14). From these percentages we then looked at the baseflow indexes for all of the location. The baseflow index is the amount of total stream flow that is comprised of baseflow which is

essentially flow coming from groundwater. The levels of these indexes are important because groundwater is where the majority of the geochemistry of a stream comes from. It contains high concentrations of ions as it moves through the lithology through recharge and other complex movements through aquifers. The quality of groundwater is imperative to the long-term health of a stream, as traditionally this makes up a large portion of the total discharge and is essential in times of little precipitation and low flow. To calculate the Baseflow Index (BFI) I used the following equation

$$BFI = \frac{\textit{The Subsurce Flow}}{\textit{Total Flow}}$$

The base flow indexes for our streams range from 76% of total stream flow at Wampecack Creek, to 85% at Caroga Creek. These values show that the BFIs for our streams are critical to the health of them. In addition to this groundwater is not quickly replaced so if there are contamination issues then it will take a long stretch of time before the groundwater is replenished. We then investigated the monthly changes in storage to see how much recharge was occurring and over what months it took place. The change in storage was calculated by taking the difference between precipitation, E.T., surface runoff, and subsurface flow.

$$\textit{Change in Storage} = \textit{Precipitation} - \textit{E.T.} - \textit{Surface Runoff} - \textit{Subsurface Flow}$$

The recharge is then calculated by taking the sum of the change in storage and subsurface flow.

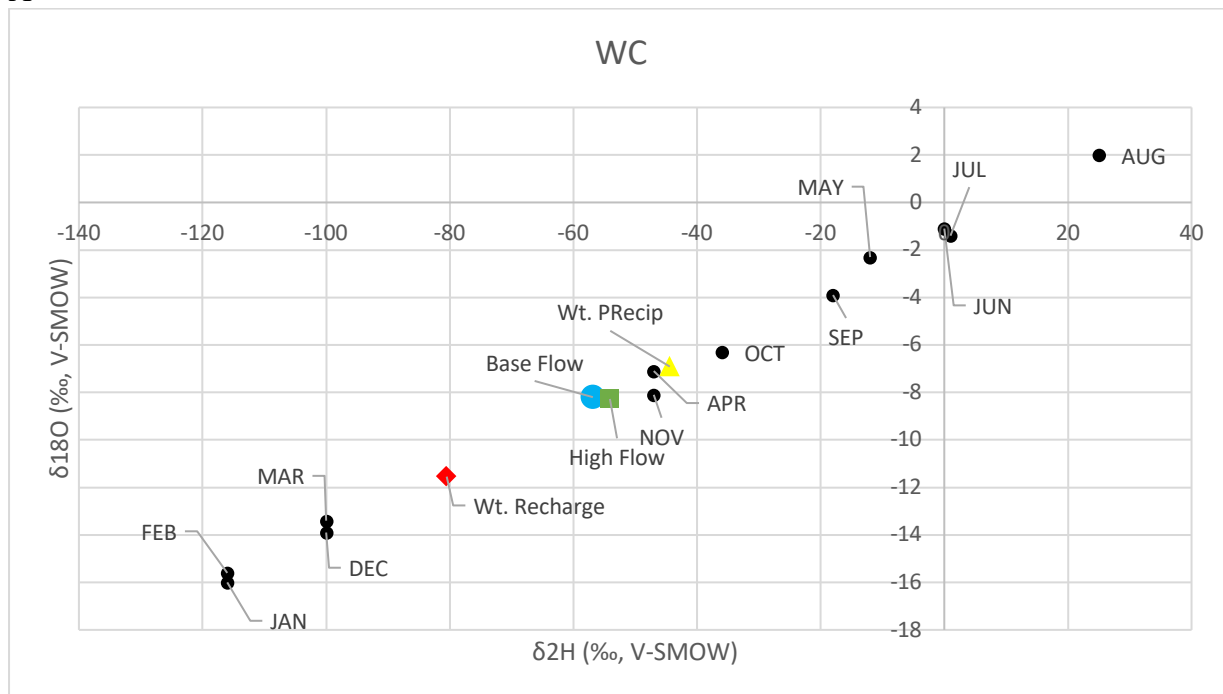
$$\textit{Recharge} = \textit{Chang in Storage} + \textit{Subsurface Flow}$$

The recharge values across the watersheds shows a loss of recharge in the months of June and July and in some watersheds a loss in recharge in May and August (Table 5). This is due to

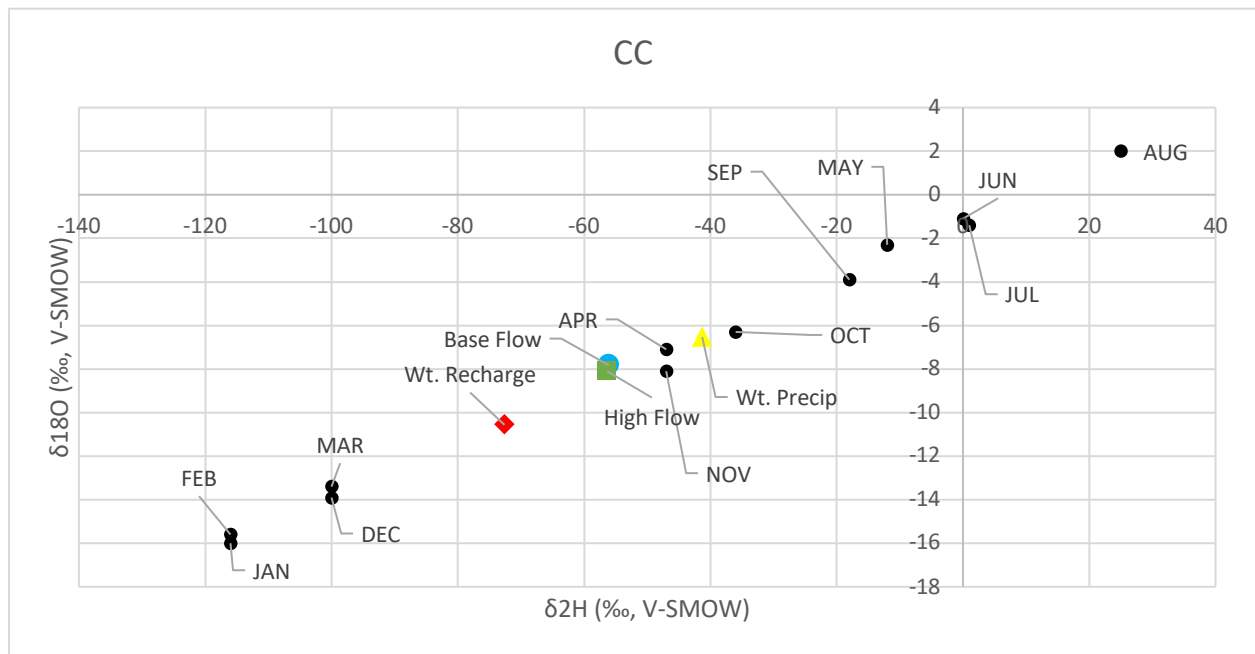
decreased precipitation and the increase in temperature, E.T. and flux baseflow to the stream. We then calculated the precipitation fractions and recharge fractions to couple with stable water isotopes data from OIPC: The Online Isotopes in Precipitation Calculator from the University of Utah, giving us our weighted precipitation and weighted recharge to help further validate the model (“Waterisotopes.Org,” n.d.). By taking the sum product of the monthly precipitation and recharge fraction with the corresponding stable water isotope we are able to plot the values and see how the model compares to the samples we took. We collected samples under low flow condition in the summer months and under storm flow condition in the fall which serve as references to compare the model’s values against. The stable water isotope analysis shows that there are complex hydrologic movements in the watersheds. We can see that the values for the collected samples do not fall directly on or around the weighted precipitation or recharge values (Figure 13) which indicated that the stream is not flow at either 100% baseflow or 100% surface runoff which is logical. The analysis shows that the samples do not correspond with isotopic signatures of the months of sampling but are located in the region of higher runoff ratio months with heavier isotopes. This is because the runoff ratios are telling us how much of the precipitation received is actually making it to the streams. In the summer month the runoff ratios are much smaller, and the majority of the precipitation does not even make it into the rivers. This explains why the values for our samples are shifted more towards the higher runoff ratio months of the fall and winter. There also appears to be little change in the isotopic signature between the majority baseflow fed samples in the summer and the majority surface runoff fed samples of the fall except for at Otsquago Creek (Figure 13). At OC the two samples partition in the direction of the majority flux during the time of sample collection. OC has large amounts of evapotranspiration and a substantial amount of agricultural land use. These combine to provide very low runoff ratios in the summer months (Table 3). This means that the precipitation in these

months barely reaches the river which results in the flow being generated by almost entirely baseflow which is recharged in the fall and winter months which is why the isotopic signature is closer to that of those months than the weighted precipitation value. All of these watersheds have complex hydrologic processes going on and the isotopic validation shows that it is not simply the weighted precipitation or recharge value, but a combination of understanding the fluxes and their timing. By analyzing the timing and extent of the fluxes, we are able to better characterize the watersheds of interest and begin to understand how the hydrology, lithology and land use are linked and exert controls over water quality and geochemistry in rivers.

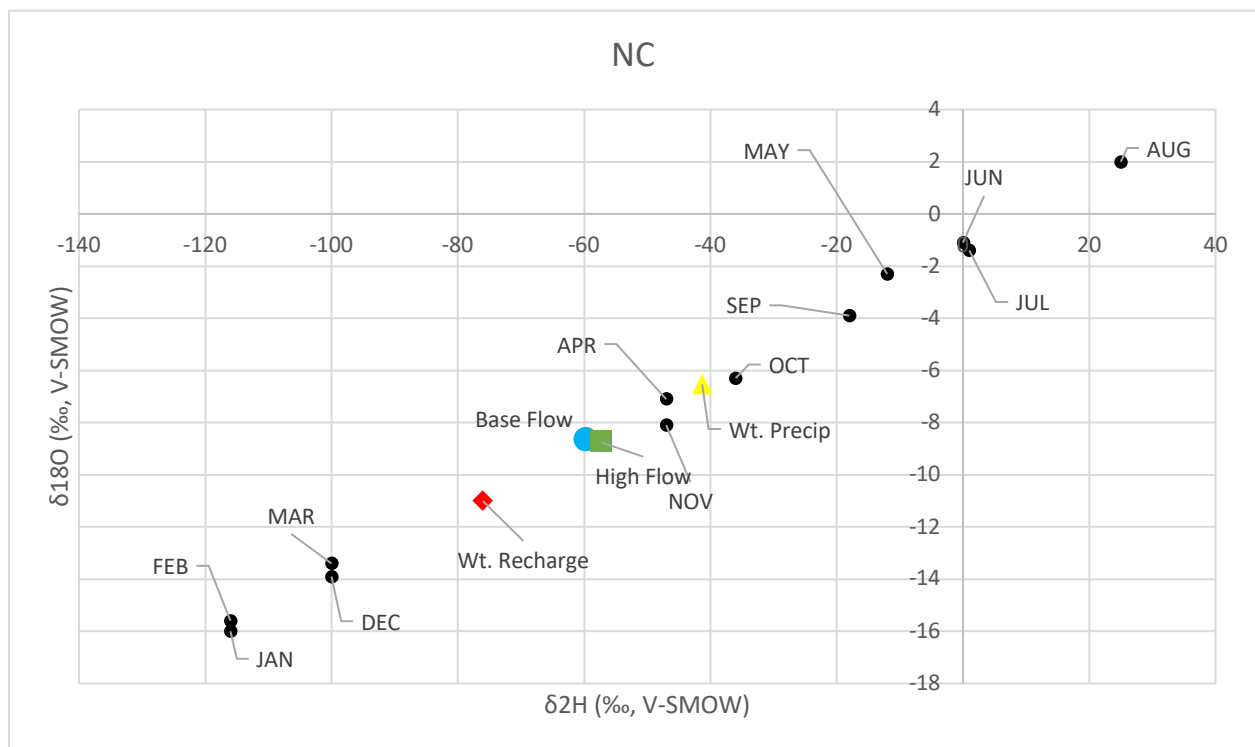
Figure 13
A



B



C



D

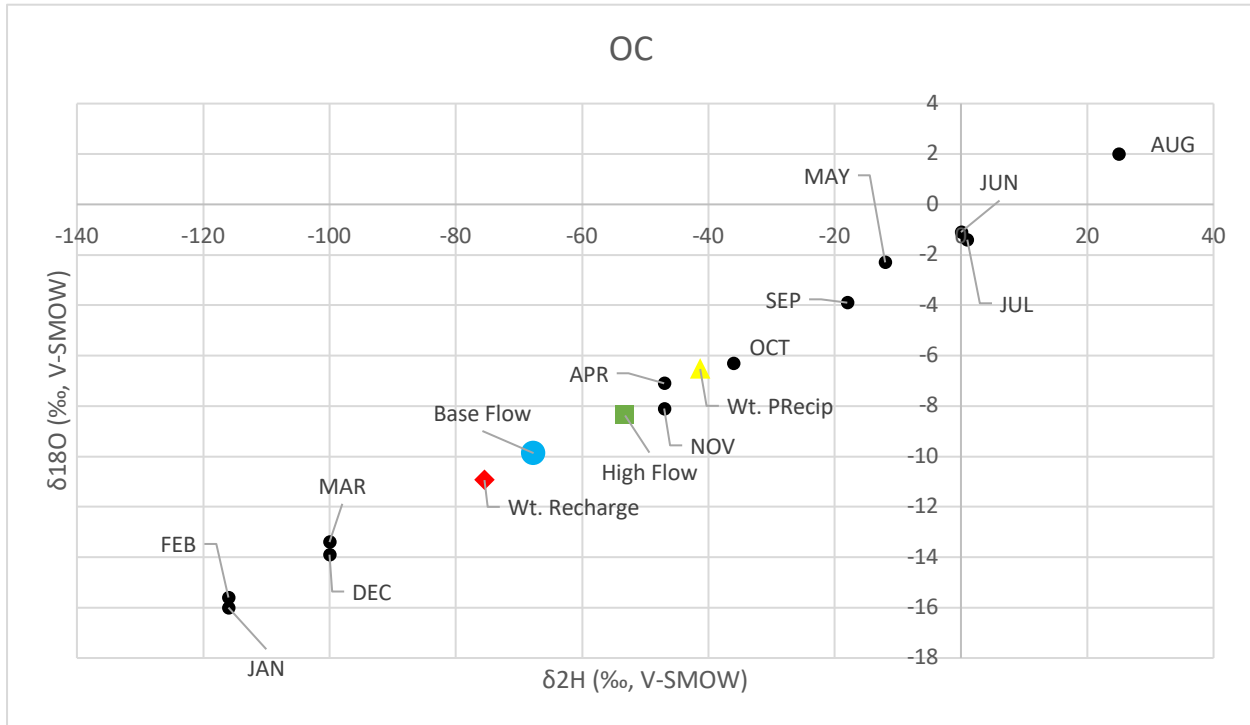


Figure 13: The stable water isotope validation for Wampecack Creek (A), Caroga Creek (B), Nowadaga Creek (C), and Otsquago Creek (OC) point to more complex hydrologi processes than simply precipitation and recharge.

Table 5

	Monthly Change in Storage (cm)											
Watersheds	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
WC	2.01	0.36	-1.55	-2.73	-4.79	-4.69	-1.69	0.17	1.41	2.62	5.31	3.72
OC	1.65	0.12	-1.67	-1.81	-2.84	-4.42	-4.24	-0.44	2.02	3.38	5.34	3.16
CC	0.93	0.03	-1.6	-1.77	-2.62	-2.52	-1.77	0.06	2.28	2.42	3.26	1.4
NC	1.61	0.24	-1.52	-1.96	-3.13	-4.57	-3.94	-0.38	2.08	3.36	5.3	3.13
H @ LP	1.55	0.48	-1.25	-2.57	-3.41	-4.37	-2.42	0.06	1.77	2.93	4.67	2.71
M @ K	1.07	0.34	-1.45	-2.24	-3.17	-2.39	-1.03	0.12	1.52	2.04	3.44	1.78
	Monthly Recharge (cm)											
WC	5.55	4.79	4.74	3.01	-1.25	-2.83	-0.93	0.43	1.5	2.98	6.5	6.71
OC	4.82	3.89	4.09	3.72	0.65	-2.84	-3.55	-0.29	2.06	3.75	6.79	6.24
CC	5	4.17	4.49	4.09	1.28	-0.52	-0.7	0.42	2.62	4.13	7.03	6.45
NC	4.97	4.15	4.37	3.73	0.58	-2.8	-3.11	-0.15	2.16	3.8	6.88	6.41
H @ LP	5.13	4.51	4.74	3.42	0.47	-2.30	-1.55	0.34	1.89	3.61	6.60	6.36
M @ K	4.71	4.00	4.09	3.41	0.56	-0.63	-0.20	0.51	1.97	3.47	6.41	5.99

Table 5: Table listing the monthly change in storage and monthly recharge for each watershed.

Figure 14

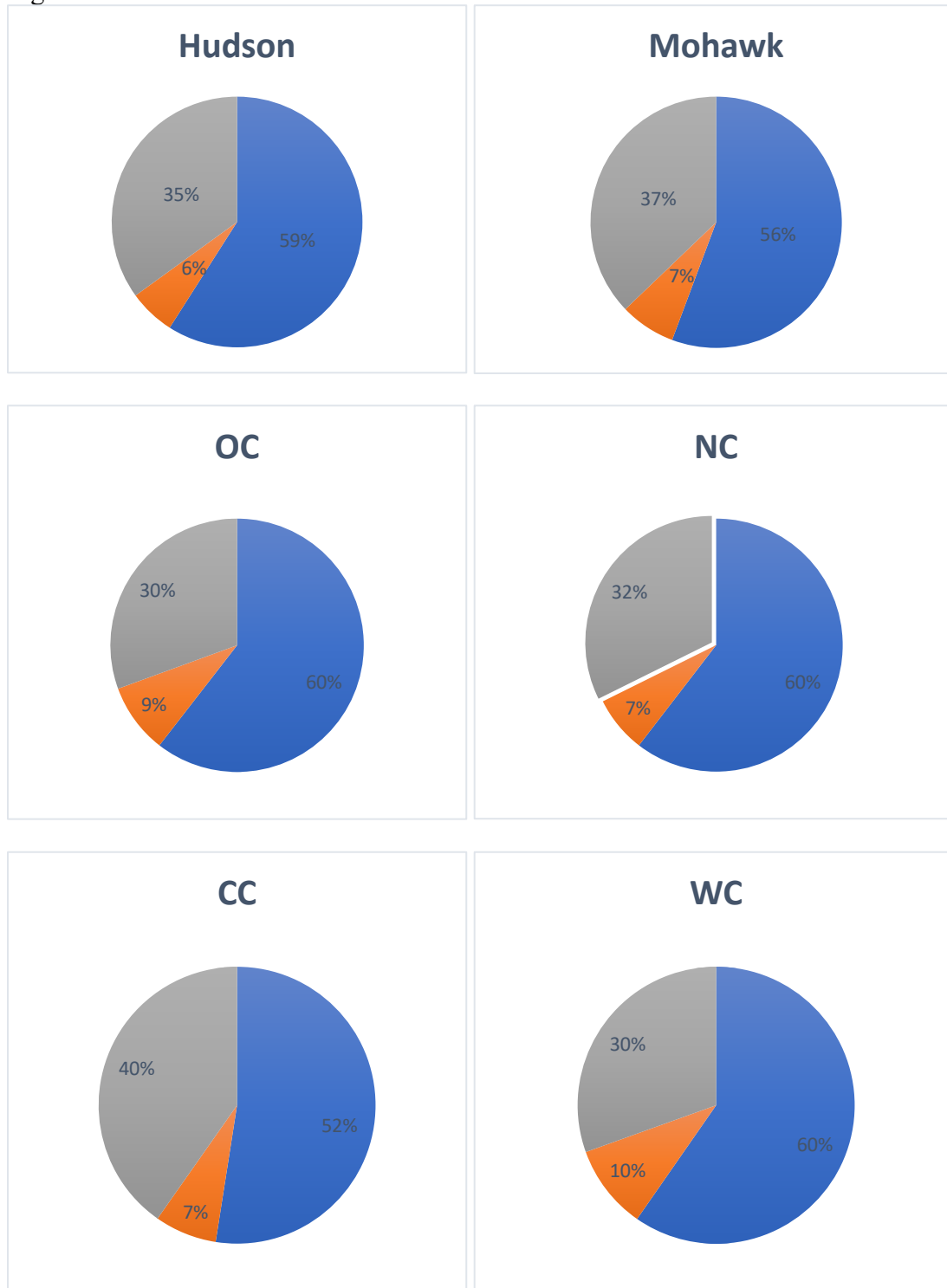


Figure 14: The percent of precipitation is broken up into the fluxes of E.T. (blue), surface runoff (orange), and baseflow (grey) for each watershed.

Chemical Hydrology

The purpose of conducting all of the research on the nexus formed by the geology, hydrology and land use of each watersheds, was to be able to look at the chemistry of the riverine water to see what impact these have on water quality. Furthermore, knowing the sourcing and timing of the water flowing in a river is critical to understanding the chemical characteristic of the stream water. These chemical signatures are greatly influenced by whether precipitation results in surface runoff flowing over soil and vegetation, or if it recharges and interacts with deeper soil and the underlaying geology (Patrick 1995). Thus, by characterizing the hydrology of the watersheds I established how the natural system worked and what could be expected in the geochemistry. Establishing the how the framework of natural hydrologic system works is essential to then see how anthropogenic activity is influencing the waterways (Drever 1997). Understanding the chemistry of water and why the levels of ions and nutrients are at the levels that they are, is essential to ensure that there are clean rivers and watersheds. This is imperative for human health, ecological health, and environmental health. To be able to do this there needs to be extensive laboratory analysis of the collected samples.

Laboratory Analysis Methods

After collecting the field samples, we conducted extensive laboratory analysis to investigate the geochemistry of the riverine samples. When in lab, precautions were taken to mitigate any possible issues with contamination and to get truly representative results. Samples were handled while always wearing gloves and stored in plastic zip-lock bags in the fridges. The samples were run on a number of instruments including the Ion Chromatograph (IC), the Ion Chromatograph Plasma Mass Spectrometer (ICP-MS), the auto-titrator, and stable water isotopes

for major elements and trace metals like Li, Na, Mg, K, Ca, Sr, Mn, Fe, Cl, Si, bicarbonate, sulfate, and nitrate.

To run samples on the Agilent 8900 ICP-MS samples were acidified with HNO_3 to a pH below 2. This was done using single use plastic pipet tips to ensure that there was no contamination. When running the samples in the instrument extensive calibration work was done to equilibrate the instrument and prepare it to run. These included 5 check standards, 2 blanks and SLR-6 reference water, to provide ample references and to ensure analytical accuracy. In addition to these standards and checks, all of the river samples were run in duplicate to give the most accurate results.

When running the IC there are two instruments used, one for the cations and one for the anions. These two instruments are the Dionex DX-500 (CS16 column) for the cations and the Dionex ICS-2100 (AS19 column) for the anions. Samples were transitioned into the containers needed for the instrument. Like the ICP-MS a set of 7 reference standards, blanks and reference waters were also all run to allow proper equilibration and analytical accuracy. All of these precautions were to make sure that the samples were properly analyzed and that the instrument was operating correctly.

When running the auto titrator we calibrated the instrument by putting it through pH 4 and 7 to equilibrate the probes. We then created fresh standards and ran 4 of them with our samples. The programming used by the machine for auto sampling was Teamo. The results were then taken and run through a USGS alkalinity calculator which uses the Gran titration method using the F1 function. This was used to calculate the alkalinity and bicarbonate.

The stable water isotopes were run by the Union College Geology Department's stable isotopes lab. Samples were measured via a Thermo Gas Bench II connected to a Thermo Delta Advantage mass spectrometer in continuous flow mode. Three standards were used to provide

correction factors and to assign the data to the correct isotopic scale using linear regression. All of the results from these machines were gathered and compiled to produce an extensive geochemical profile for each river (Table 6).

General Geochemistry

The geochemical signatures for each of the studied watershed are very different. The majority of the chemical constituents in the river water stems from the groundwater. Groundwater quality of a watershed can be quickly analyzed by looking at the relationship between the Total Dissolved Solids (TDS) and the ratios of few chemical constituents. The constituents are Na^+ , Ca^{2+} , Cl^- , and HCO_3^- and they are related based on their levels in the precipitation and the compounds that they form at certain saturations. The principle is that rain water contains the dominant ions of Na and Cl when it falls and so before any weathering takes place the $\text{Na} / (\text{Na} + \text{Ca})$ ratio and the $\text{Cl} / (\text{Cl} + \text{HCO}_3)$ ratio should both be close to 1 and the TDS should be very low as the only source of dissolved solids is from the low TDS in precipitation. As the precipitation starts to flow through the lithology and weather rocks mainly calcite and Ca-silicates the Ca and HCO_3 levels increase driving down that ratio, while the TDS continues to increase. This continues in some watersheds until the groundwater becomes to saturated with these ions that calcium-bicarbonate begins to precipitate out and the ratio moves back towards 1 while the TDS continue to rise (Appelo and Postma 2010). The harder to weather lithologies are found with low TDS and the ratio closer to 1 while the easily weatherable watersheds find themselves high in TDS and after the shift back towards the ratio of 1 (Figure 15). It can be seen that the $\text{Cl} / (\text{Cl} + \text{HCO}_3)$ reached saturation and began to precipitate out the bicarbonate. The $\text{Na} / (\text{Na} + \text{Ca})$ ratio displays broadly the same trend where the ratio decrease as more weathering takes place and TDS increases. We can see that the watersheds that are underlain by more easily weathers geology like those of OC and NC, which are comprised of

shales and limestones, have much higher ion concentrations and TDS than the rivers that have harder lithologies like CC and WC. We also see that the size of a watershed has an impact on the levels of ion concentrations as the two biggest rivers the Hudson and Mohawk have some of the lowest ion concentrations (Figure 16).

Figure 15

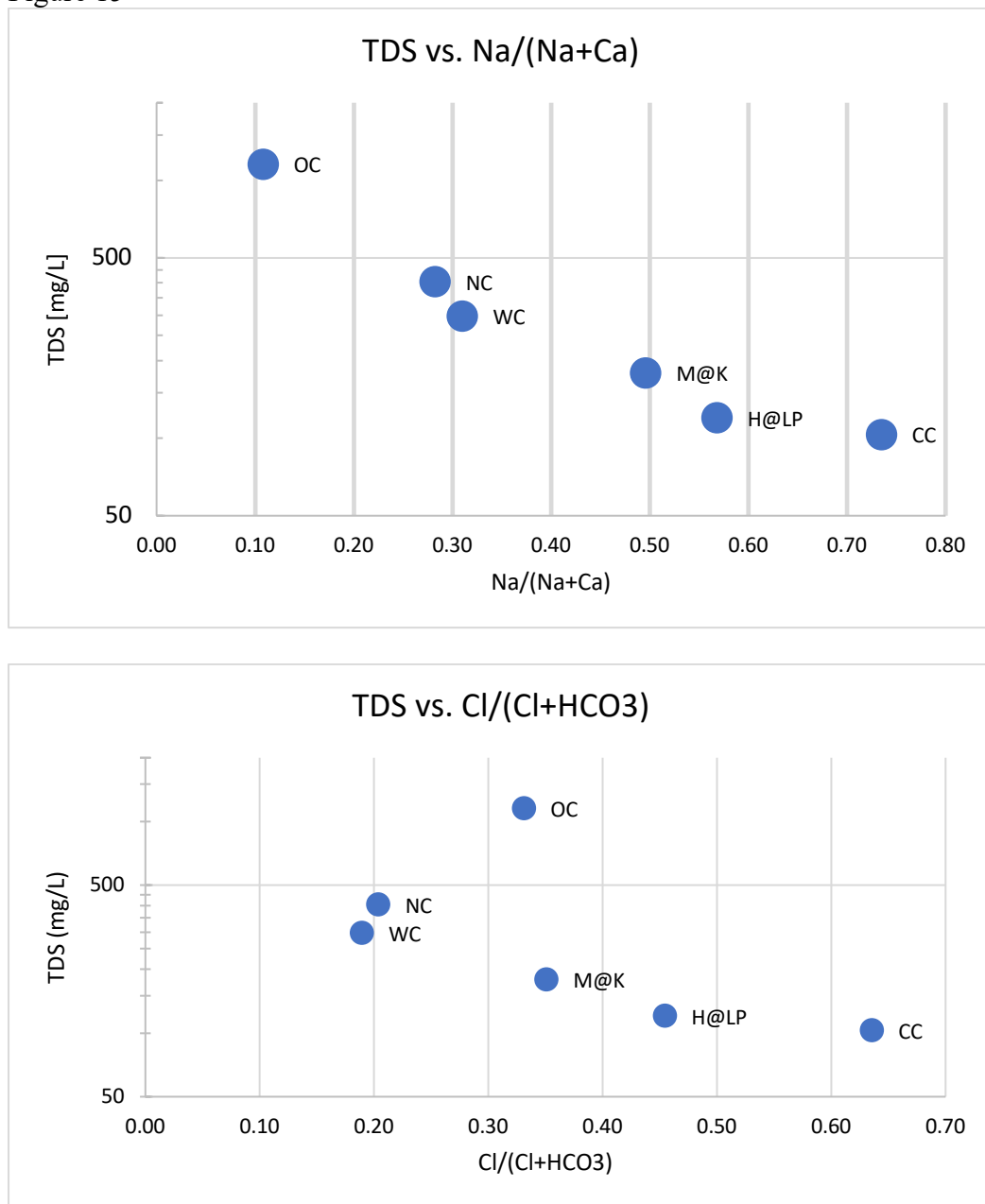


Figure 15: TDS plotted against the ratios of $\text{Na} / (\text{Na} + \text{Ca})$ and $\text{Cl} / (\text{Cl} + \text{HCO}_3)$ indicated levels of weathering.

Table 6
A

	Location	USGS Gauge	Area	Sampling Date	Latitude	Longitude	pH	Sp. Cond	Alkalinity
	-	-	<i>km^2</i>	-	-	-	-	<i>uS/cm</i>	<i>meq/L</i>
Baseflow	WC	N/A	50	12-Jul-18	42.908864	-73.5215306	8.17	380.4	3.175
	OC	1349000	157	16-Jul-18	42.930378	-74.6395028	8.09	1438	1.85
	H @ LP	1335770	11880	18-Jul-18	42.838475	-73.6714944	7.25	188.1	0.753
	M @ K	1357500	8506	30-Jul-18	42.846675	-74.0141222	7.67	259.2	1.413
	NC	1346865	82.04	31-Jul-18	43.007236	-74.7765417	8.25	549	2.971
	CC	1348580	28.99	6-Aug-18	43.10412	-74.505195	7.43	170	0.547
High Flow	WC	N/A	50	5-Oct-18	42.908864	-73.5215306	7.9	333	2.38
	OC	1349000	157	3-Oct-18	42.930378	-74.6395028	8.12	351	2.77
	H @ LP	1335770	11880	5-Oct-18	42.838475	-73.6714944	7.63	233	1.1
	M @ K	1357500	8506	29-Oct-18	42.846675	-74.0141222	8	257	1.78
	NC	1346865	82.04	3-Oct-18	43.007236	-74.7765417	7.79	309	2.55
	CC	1348580	28.99	21-Oct-18	43.10412	-74.505195	7.26	124.5	0.39

Figure 6 A: The sampling information and general chemistry can be seen for all of the sampling events. pH and specific conductivity were measured using field probes, while the alkalinity was measured using an auto titrator and alkalinity calculator

B

	Location	Li	Na	Mg	K	Ca	Sr	Ba	NH4	Mn	Fe	As
	-	mM	mM	mM	mM	mM	mM	mM	mM	mM	mM	mM
Baseflow	WC	1.10E-04	5.40E-01	4.80E-01	6.80E-02	1.20E+00	2.10E-03	4.60E-04	5.00E-05	4.30E-04	3.60E-04	6.90E-06
	OC	2.90E-03	7.90E-01	1.50E+00	7.10E-02	6.50E+00	1.10E-01	8.50E-04	3.00E-04	1.30E-04	4.40E-04	4.50E-06
	H @ LP	1.10E-04	5.40E-01	1.30E-01	2.00E-02	4.10E-01	6.80E-04	9.20E-05	2.20E-02	1.10E-04	1.10E-03	4.10E-06
	M @ K	2.20E-04	6.60E-01	2.00E-01	2.70E-02	6.70E-01	2.60E-03	1.60E-04	4.80E-03	2.00E-04	2.80E-04	1.10E-05
	NC	9.20E-04	7.10E-01	6.40E-01	6.70E-02	1.80E+00	1.70E-02	4.90E-04	2.70E-04	1.30E-04	2.00E-04	3.70E-06
	CC	3.50E-05	7.50E-01	8.30E-02	1.10E-02	2.70E-01	7.30E-04	9.40E-05	2.20E-04	2.10E-04	2.70E-03	2.90E-06
High Flow	WC	6.51E-05	4.84E-01	3.49E-01	9.76E-02	9.82E-01	1.92E-03	4.07E-04		2.07E-04	8.72E-04	5.47E-06
	OC	1.85E-04	3.52E-01	3.05E-01	9.08E-02	1.34E+00	8.75E-03	2.04E-04		6.42E-05	6.48E-04	6.37E-06
	H @ LP	9.95E-05	6.66E-01	1.73E-01	3.11E-02	4.63E-01	8.86E-04	9.98E-05		3.65E-04	1.06E-03	3.61E-06
	M @ K	1.22E-04	4.87E-01	1.94E-01	4.10E-02	7.69E-01	2.70E-03	1.46E-04		1.97E-04	1.37E-03	4.73E-06
	NC	2.57E-04	2.88E-01	2.33E-01	5.27E-02	9.44E-01	7.57E-03	2.11E-04		5.62E-05	3.98E-04	5.12E-06
	CC	2.31E-05	5.22E-01	5.22E-02	9.10E-03	1.73E-01	4.43E-04	6.25E-05		6.49E-05	1.19E-03	2.34E-06

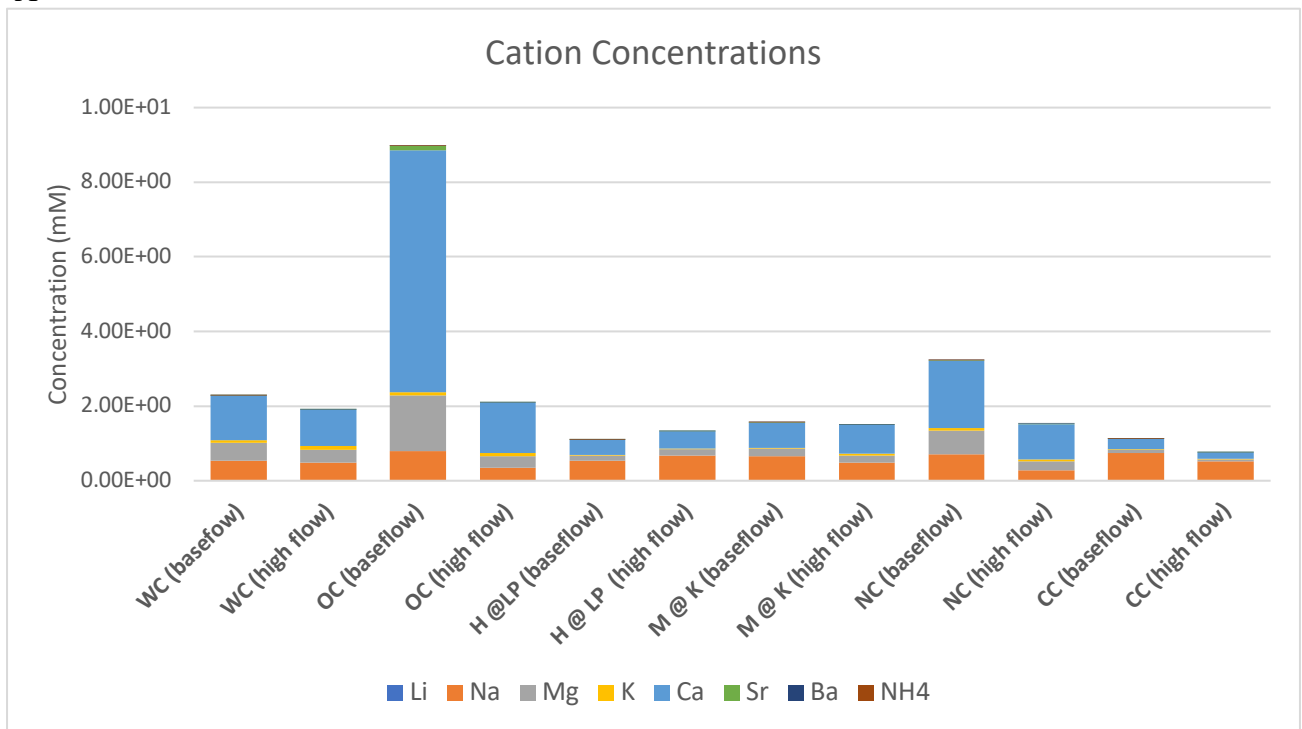
Table 6 B: The cation chemistry for each river for sampling under baseflow and high flow. Ions were measured on the IC and ICP-MS. Ammonia was not measured for the high flow samples.

C

	Location	NO3	F	PO4	SO4	Cl	Br	Al	Si	HCO3
	-	mM	mM	mM	mM	mM	mM	mM	mM	mM
Baseflow	WC	1.70E-02	3.50E-03	2.90E-04	9.30E-02	7.10E-01	0.00E+00	9.10E-05	6.20E-02	3.04E+00
	OC	9.20E-03	1.20E-02	5.30E-07	7.20E+00	8.20E-01	3.50E-04	4.20E-05	6.90E-02	1.65E+00
	H @ LP	4.00E-02	3.40E-03	3.60E-04	1.50E-01	6.20E-01	3.10E-04	3.50E-04	6.10E-02	7.44E-01
	M @ K	2.30E-02	3.30E-03	9.40E-04	1.70E-01	7.50E-01	1.60E-04	2.60E-04	5.60E-02	1.39E+00
	NC	8.30E-03	6.40E-03	3.20E-06	1.00E+00	7.10E-01	8.00E-05	3.50E-05	7.60E-02	2.77E+00
	CC	1.10E-02	1.90E-03	5.30E-07	3.90E-02	9.40E-01	1.10E-04	5.70E-04	4.40E-02	5.39E-01
High Flow	WC	8.55E-02	2.86E-03	4.15E-04	1.31E-01	6.86E-01	1.13E-04	1.11E-04	1.20E-01	1.95E+00
	OC	6.09E-02	4.94E-03	1.10E-03	3.35E-01	3.11E-01		3.20E-04	9.94E-02	2.27E+00
	H @ LP	5.62E-02	3.13E-03	5.93E-04	1.19E-01	7.25E-01	3.60E-04	4.53E-04	7.26E-02	1.12E+00
	M @ K	2.54E-02	2.65E-03	6.37E-04	1.38E-01	5.29E-01	9.01E-05	8.57E-04	6.08E-02	9.05E-01
	NC	2.57E-02	4.22E-03	4.65E-04	1.78E-01	2.96E-01		2.27E-04	6.96E-02	2.09E+00
	CC	6.39E-04	1.19E-03		2.83E-02	6.23E-01		8.77E-04	3.94E-02	3.92E-01

Table 6 C: The anion chemistry for each location for baseflow and high flow. Ions were measured on the IC and ICP-MS and using the alkalinity calculator for bicarbonate. Highlighted cells indicate samples below detection limits.

Figure 16
A



B

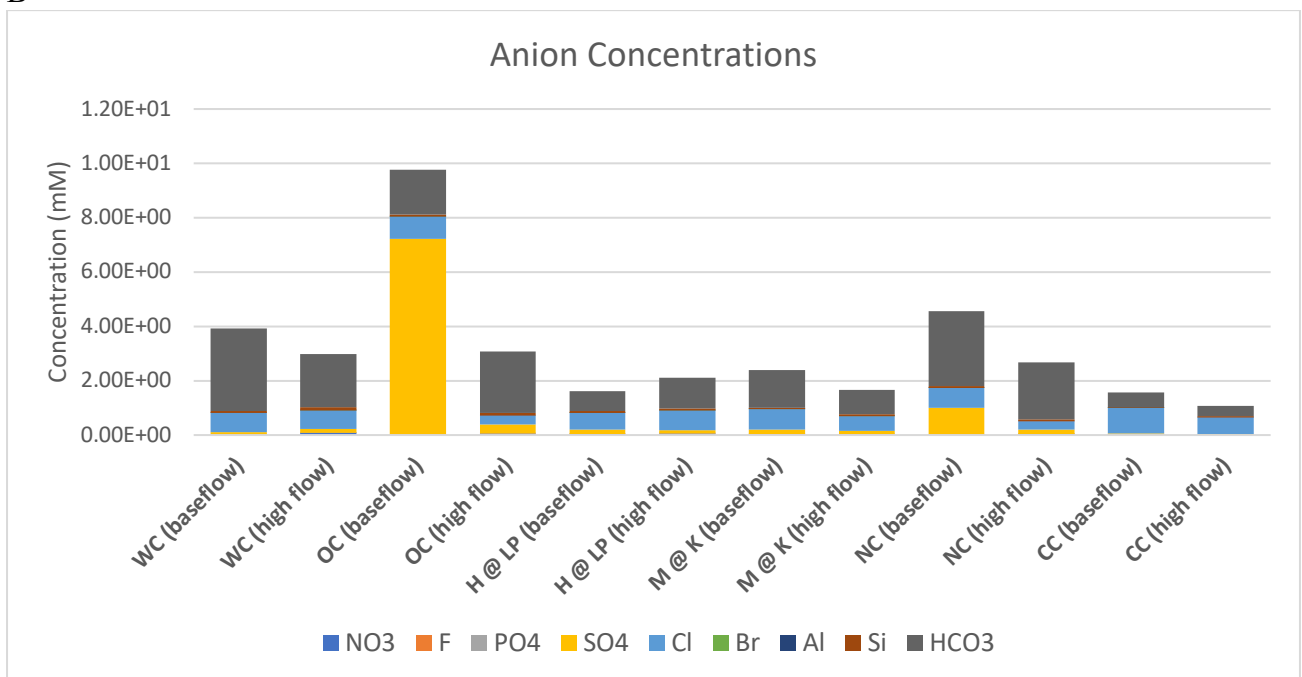


Figure 16: The total cation (A) and anion (B) for each river under baseflow and high flow sampling. We can see how the concentrations change as discharge increases.

When looking closer at the composition of the water chemistry we can see some of the geologic and land use controls on the concentrations and composition of ions in the rivers. (Figure 17).

In Wampecack Creek we have low concentrations of ions, consistent with its metamorphic and metasedimentary geology that is relatively resistant to weathering. The ions present are largely comprised of Na, Mg, Ca, HCO_3 , and Cl. This reflects a hard to weather lithology of the metamorphose and metasedimentary geology. WC does have some glacial till which could have easily erodible crushed material causing the ion concentrations to be about average across the watersheds. When comparing the chemistry of baseflow to high flow the total concentrations and TDS decreased as notably the levels of potassium increased. This could possibly be to surface runoff bringing K into the stream.

At Otsquago Creek there are extremely high ion concentrations, which reflects the watersheds very easily erodible geology composed of mostly shales and limestones (Figure 16). The major constituents of Otsquago are Ca, Mg, Na, SO_4 and HCO_3 . We believe that the highly elevated levels of SO_4 come from pockets of gypsum that protrude throughout the watershed. Gypsum is easily erodible and when it dissociates into water it gives off SO_4 and Ca which are found at similar concentrations. OC is comprised of mainly shales and limestones which gypsum can often be found in. While it is possible that some of this sulfate is coming from pollution, we believe that it is from gypsum due to the paring of Ca and SO_4 which is at a ratio of 0.903 in relation together. This gives value to the argument of the elevated sulfate levels stemming from gypsum weathering. Furthermore, 28% of the sulfate in rivers comes from pollution, while 68 % comes from the weathering of rocks and furthermore, 46% of natural rock weathering sulfate inputs come from gypsum and anhydrite (Berner and Berner 2012). When calculating the ration of Ca and Mg to SO_4 the ratio comes out to be 1.11 Which also gives weight to the sourcing of

anhydrite for some of the sulfate measured. Additionally, we see that the total concentration drops drastically when going from baseflow to high flow. The shift in concentration is because of the decrease in the level of sulfate and calcium, as they both drop about 6 millimoles. This again highlights the likelihood of gypsum being the source for the extreme sulfate levels we see. Due to the less input of gypsum we see the levels of bicarbonate increase in the high flow concentration reflective of the shales and limestones.

Nowadaga Creek has a similar chemical composition to OC, but in much lower concentrations. There are still the elevated levels of SO_4 and Ca, but NC has a lower concentration of sulfate and a higher concentration of bicarbonate which would indicate less gypsum pockets and more of the carbon rich shales and limestones. Nowadaga along with WC and OC have the three highest concentrations of potassium out of the watersheds and they also happen to be the three watersheds with the highest percentages of agricultural land out of the watersheds. This could be a connection between the use of fertilizers and the tilling of crop lands leading to an increased level of potassium in the streams. Additionally, OC and NC have the highest concentrations of Sr out of the watersheds and this is most likely to some small pockets of the mineral celestine (SrSO_4) which is a strontium sulfate mineral. This is the most likely source of the Sr and is consistent with the high sulfate levels across these two watersheds. Like OC, in NC we see the sulfate and calcium concentrations decrease under high flow conditions again giving further support to the sourcing of calcium. Likewise, we see the levels of Sr go down as flow increases also giving support to the possibility of celestine as a source of Sr and sulfate.

The Mohawk River was sampled at Kiwanis Park. Upstream of this sampling point drains a majority of shales and limestones like those of its tributaries OC and NC, but also includes some metamorphic and crystalline rocks. The watershed of the Mohawk is much bigger than the

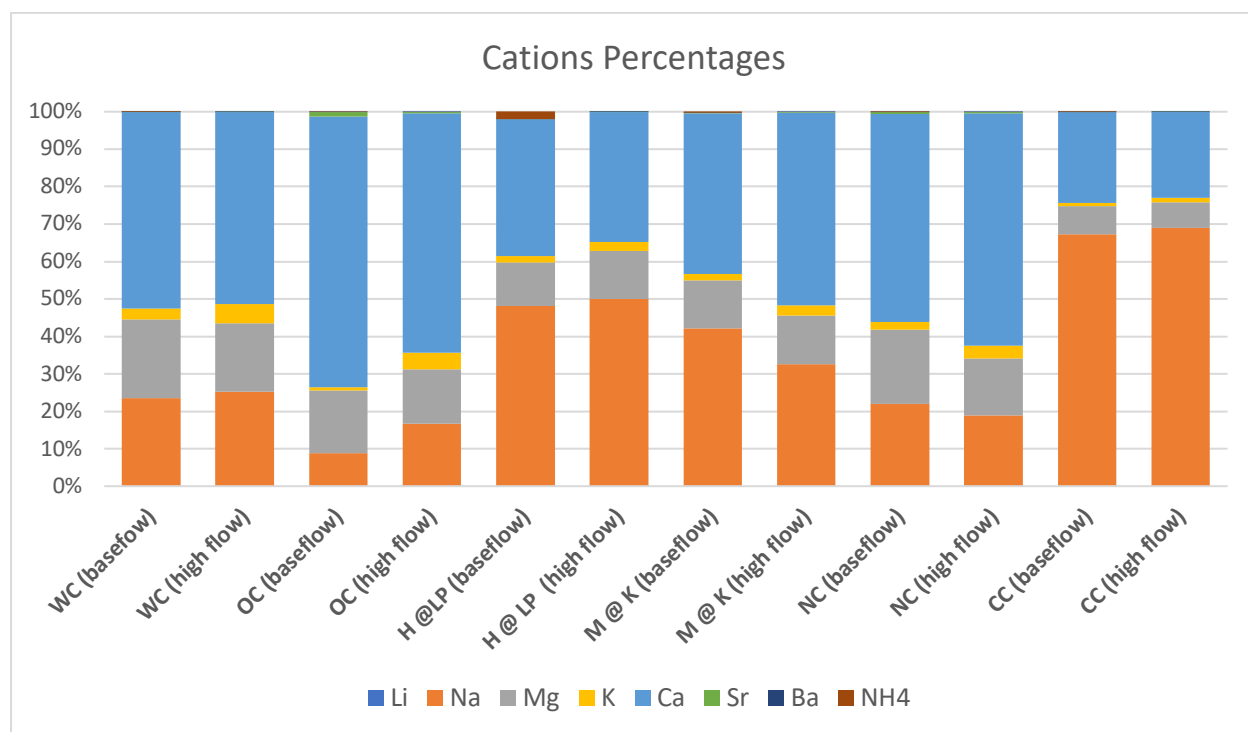
smaller watersheds which results in much lower TDS and ion concentrations than those smaller ones. The watershed pulls from so many tributaries and receives a much larger streamflow responsibility, so it mixes all of the other sub watersheds together giving it a middle of the road chemical signature comprised of mostly Ca, HCO_3 , Cl, and Na which is consistent with a mixing of lithologies. The Mohawk has 24.9% of its watershed dedicated to agriculture, with the other main land use type being forested land which makes up 62.4% (Figure 2). The agricultural land could be a possible reason for why the potassium levels increased under higher flow.

The Hudson River is the largest out of all of the watersheds with a drainage basin area of 11880 km². Like the Mohawk because the river is so large the TDS and ion concentrations are much lower than the smaller sites. The Hudson starts in the Adirondacks and flows south over its granites and metamorphic formations and then draws in sub watersheds underlain by glacial till, limestones and shales. Of the ions present, the most interesting is the elevated level of ammonia. It is the highest out of all the watersheds and there is no geologic or land use practice exerting influence on its concentration. This could be an indicator of an anthropogenic source of pollution in the river coming from septic leakage, or contamination from surface runoff. Interestingly, Hudson was the only river that increased in total concentration from baseflow to high flow. The increase in concentration stems from Cl, Na, K, and bicarbonate.

Caroga Creek is distinct from the other watersheds in its lithology and land use practices. CC has almost no agricultural land and is made up of mostly forested land, wetlands, and developed areas. In addition to this CC is underlain by a mixture of metamorphic and crystalline lithology. These factors result in Caroga having the lowest concentration of ions out of all of the watersheds (Figure 16). The major constituents of Caroga are calcium, bicarbonate, chloride, and sodium. The elevated levels of Cl and Na we believe are linked to road salt pollution because CC has the highest percentage of developed land and does not weather its geology a great deal. The

concentration decreases slightly from baseflow to high flow and this comes from a small shift in the concentration of calcium and bicarbonate, as well as sodium and chloride. These constituents decreased at relatively the same level as their paired ion, such as Ca and HCO_3 , and Na and Cl. When looking at the percentages of cations and anions between baseflow and high flow, they look essentially the same, which indicated that the decrease in concentration is just partial dilution from the same sources.

Figure 17
A



B

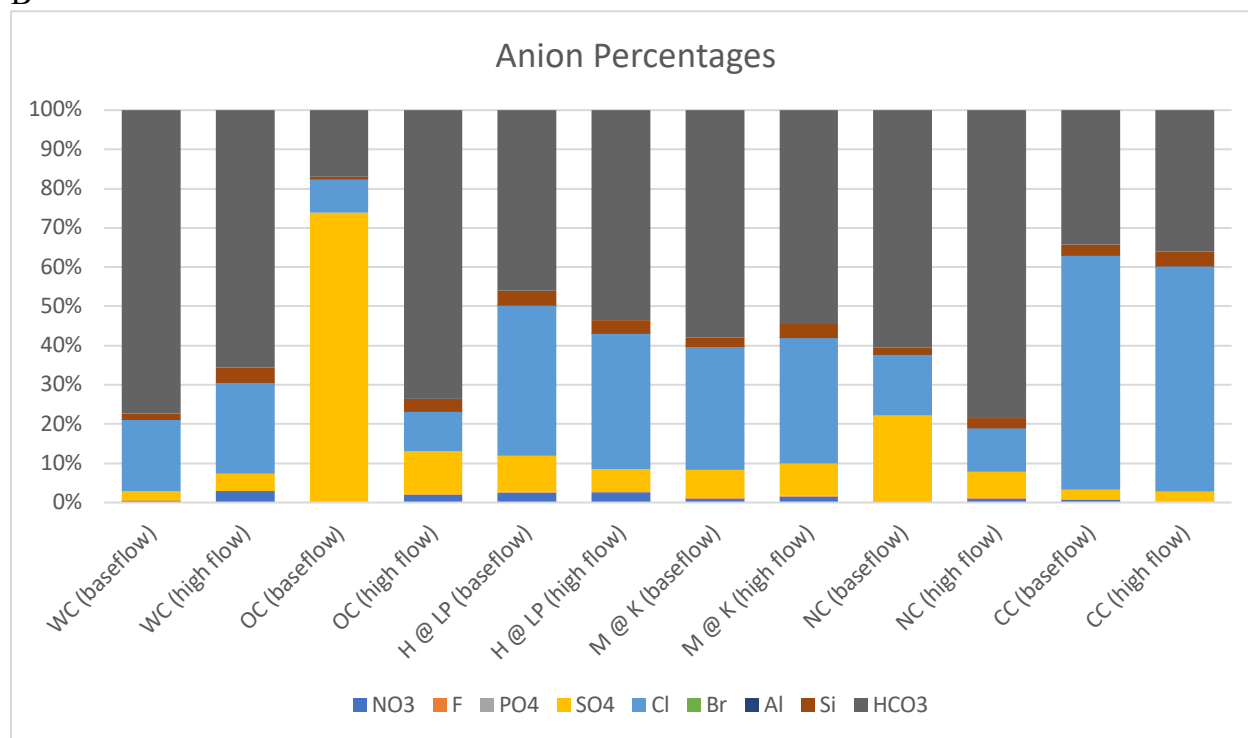


Figure 16: The percentages of each cation (A) and anion (B) makes up of the total concentration for each river for the baseflow and high flow samples.

Historic Stream Chemistry and Concentration Discharge Curves

Having collected and analyzed our own samples we are able to get an idea of the stream chemistry of today, but this is only a snap shot. By looking back on historic stream chemistry and stream flow, we are able to get much more representative data than two sampling events. Historic stream data was collected from the USGS on gauges and sampling events on the rivers of interest. We then compared the historic record with the hydrograph analysis done in this project and see how the chemistry responds to shifts in land use and anthropogenic activity in the watersheds. The USGS data gathered included measurement taken for discharge and a number of chemical constituents such as Mg, Na, Ca, K, Cl, Si, nitrate, sulfate, and bicarbonate. We then used this data to construct concentration discharge curves which are used to tease out possibly hydrochemical processes that control runoff water quality. Concentration discharge curves are

created by plotting the concentration of ions against the discharge of a river on logarithmic scales. This allows for the relationship of an ion has and its response to changes in discharge to be observed and to then gain explanatory power to sourcing of the ions and the load that they will have. It can be seen that the majority of the ions display a near chemostatic behavior, meaning that their concentration is not influenced or changed based on variable discharge rates (Figure 18). This is where the slope of the line is near 0, where a slope of -1 would indicate the concentration of the chemical constituent would vary inversely with the level of discharge indicating that the controlling process would be dilution (Godsey, Kirchner, and Clow 2009). Our concentration discharge curves indicate that there is a power-law relationship ($C = a \cdot Q^b$) between concentration and discharge which is embodied in the slope of these relationship between the concentration of a particular ion in a stream to that streams discharge. To better see this power-law relationship we fit a line to the log transformed concentration and flow data for each ion of interest grouped by each watershed so that trends can be seen across constituents and watersheds (Figure 19). In doing this we are able to gain a great deal of explanatory power of the controls on the chemistry in the rivers.

Figure 18

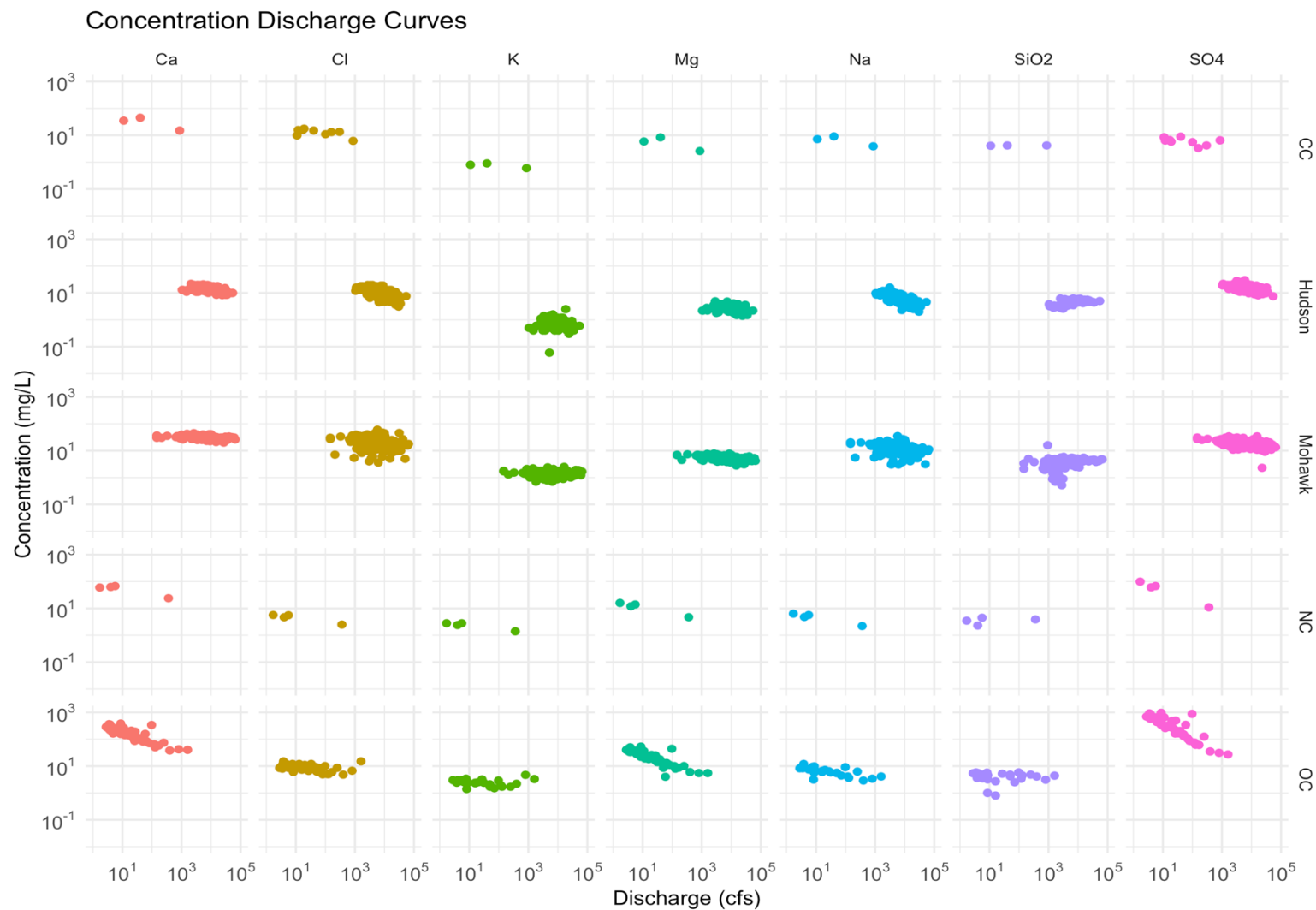


Figure 18: Concentration discharge curves for the constituents of major concern for each river. Data was collected from USGS stream gauges

Figure 19

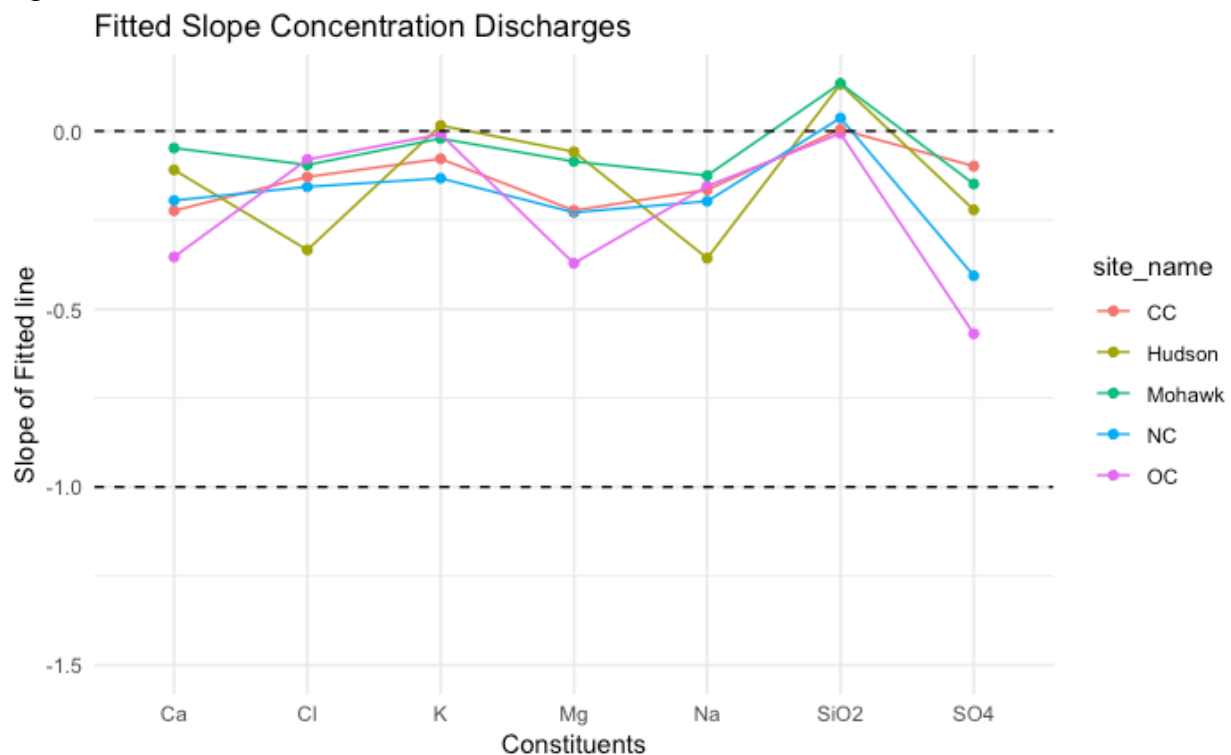


Figure 19: The concentration discharge data grouped by river, with the slope of the discharge curve fitted to each chemical constituent. This allows for sources of ions to be identified and to see to what extent the concentrations are changing with discharge.

The fitted slope graphic nicely highlights geologic controls on the water quality as watersheds with similar lithologies like those of NC and OC as well as the size and mixedness of Hudson and Mohawk, are grouped closely and follow the same trends over ions. In Otsquago and Nowadaga we can SO₄, Ca and Mg show a more negative slope and are clustered near each other. The similarity in the dilution behavior of these three constituents suggest that they may be derived from the same mineral source. This finding is consistent with the source of the elevated levels of sulfate under baseflow conditions is sourced by pockets of gypsum and anhydrite. This helps to explain the elevated levels of sulfate under base flow conditions and a significantly lower concentration under high flow conditions. SiO₂ appears to be acting chemostatic and even increasing as concentration with discharge in watersheds like Hudson, Mohawk, and Nowadaga.

This is consistent with other studies as in general Si and its other dissolved silica compounds tend to have slopes closer to zero than other ions (Godsey, Kirchner, and Clow 2009). We also see near chemostatic behavior from potassium which other studies have shown can be possibly attributed to leaching from organic soils during high flow (Walling and Webb 1986; Godsey, Kirchner, and Clow 2009). Additionally, we see the paring of sodium and chloride in their slopes across their watersheds indicating a link between the two from possible road salt pollution. This information is critical to constructing the controls on the geochemistry and how these controls are affected by changes in discharge. This needs to be put into historical context by looking at how the concentrations of the ions have changed over time.

To investigate how stream chemistry has change over time I compiled historic datasets on stream chemistry easements to establish the record. The historic data was also joined by the data from the field samples we collected to place todays concentrations into the picture. When comparing the time series of these ion with the concentrations of the samples we collected and analyzed, we find that most constituents have remained relatively constant, with the notable exceptions of sodium and chloride. The concentration of these elements that we measured are significantly elevated compared to the historic measurements. The other ions stayed at or around the same level of concentration as their historic values, while Na and Cl were the only ones increase significantly. All of the watersheds display increases in concentrations of Cl over time (Figure 21). None of the lithologies of the watersheds contain formations that would be responsible for the concentrations we see in the samples today. We believe the most likely source of the chloride and sodium levels is road salt pollution. Salt is placed on roadways in order to de-ice them make them safer for travel in winter conditions. With our watersheds being located in Upstate New York where there are cold winters and heavy snow fall, road salt it placed down generously. Since the 1940s road salting began and since then it increased in its intensity and has

become the standard practice for de-icing roads (Dugan et al. 2017). The level of road salting is reflected in the increase in mean daily yields of Na and Cl being 130 and 243 % respectively from 1950 to 1990 in the Mohawk river basin. This extreme increase is the opposite of other constituents like Ca, Mg, and K which all changed less than 10% (Godwin, Hafner, and Buff 2003). Since this time period road salting has increased, and in 2005 the use of salt for de-icing roads passed the chlor alkali industry, which is the industry that produces chloride, hydrogen and sodium hydroxide solutions, for the most consumption of salt (R.Mullaney, L.Lorenz, and D. Arntson 2009, Figure 20). This practice has drastically increased and its impacts are beginning to be seen. Elevated Cl and Na concentrations in waterways in consistent with the finding of numerous other studies in the Northeast (Thunqvist 2004; Kelly et al. 2008; Kaushal et al. 2005). For the watersheds of interest there were elevated chloride and sodium levels from their historic levels, and a sharp increase can be seen in the past 20-30 years for streams that have measurements from that period (Figure 21 D and E). The elevated levels of Cl and Na are seen in both baseflow and high flow conditions. The samples taken during high flow conditions generally display slightly lower concentrations than the low flow samples across all of the sites except for the Hudson. This trend is supported by the concentration discharge curves that we generated, in which all rivers showed roughly chemostatic behavior. This is represented by roughly the same concentration as discharge increases, with some decrease but not dilution inversely related to discharge. Having higher levels of Cl and Na in baseflow fed conditions than high flow conditions can be a sign of more serious issues. The fact that the concentrations of these constituents are so elevated in groundwater show, indicates the level to which the road salting pollution has reached. Having impacted groundwater means that it will take years and decades to flush and replenish groundwater if road salting were to stop immediately, groundwater is formed over long temporal scales and do not shift or change drastically. The

elevated levels of Cl and Na that we see have been deposited consistently over time and they will take a long time to get out. The elevated levels are not coming in the spring during a large surface runoff event that brings a great deal of road salt into the stream, but during the summer when the flow generated from groundwater that has been stored for a long period of time. We see the elevated levels in the fall under high flow conditions when there is no road salting taking place and any remnants have been washed away. This means that consistently throughout the year, Cl and Na are entering the rivers at concentrations that are different than the levels that would reflect the hydrology, geology, and land use. This results in the concentration discharge curves displaying nearly chemostatic behavior of sodium and chloride therefore giving us a greater flux of Na and Cl in our rivers. This has broader implications given the hydrologic characterizations of the watersheds done in this study. We have established that precipitation and runoff across our watersheds is increasing based on the hydrograph analysis. When coupled with the concentration discharge curves and increased chloride and sodium concentration from road salting, the total flux of these constituents could be seen to continually increase in the coming years. This increase in Cl and Na concentrations will have immense consequences on the ecosystems and aquatic life of the impacted streams (Corsi et al. 2015). Road salting is the best-known practice for de-icing roads and for reducing the hazards to human health associated with dangerous roads. Finding the nexus between human health safety and environmental health is a tough one, but something needs to be done about the impact road salting is having on watershed chemistry and health.

Figure 20

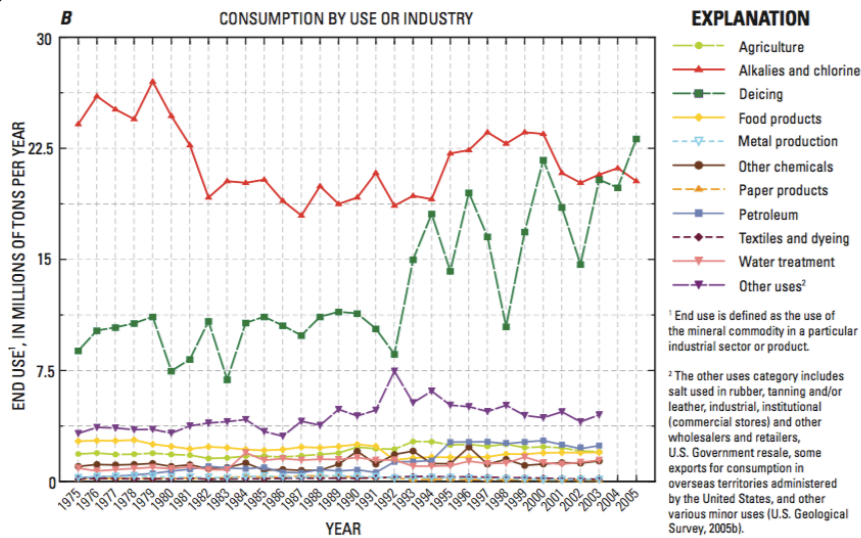
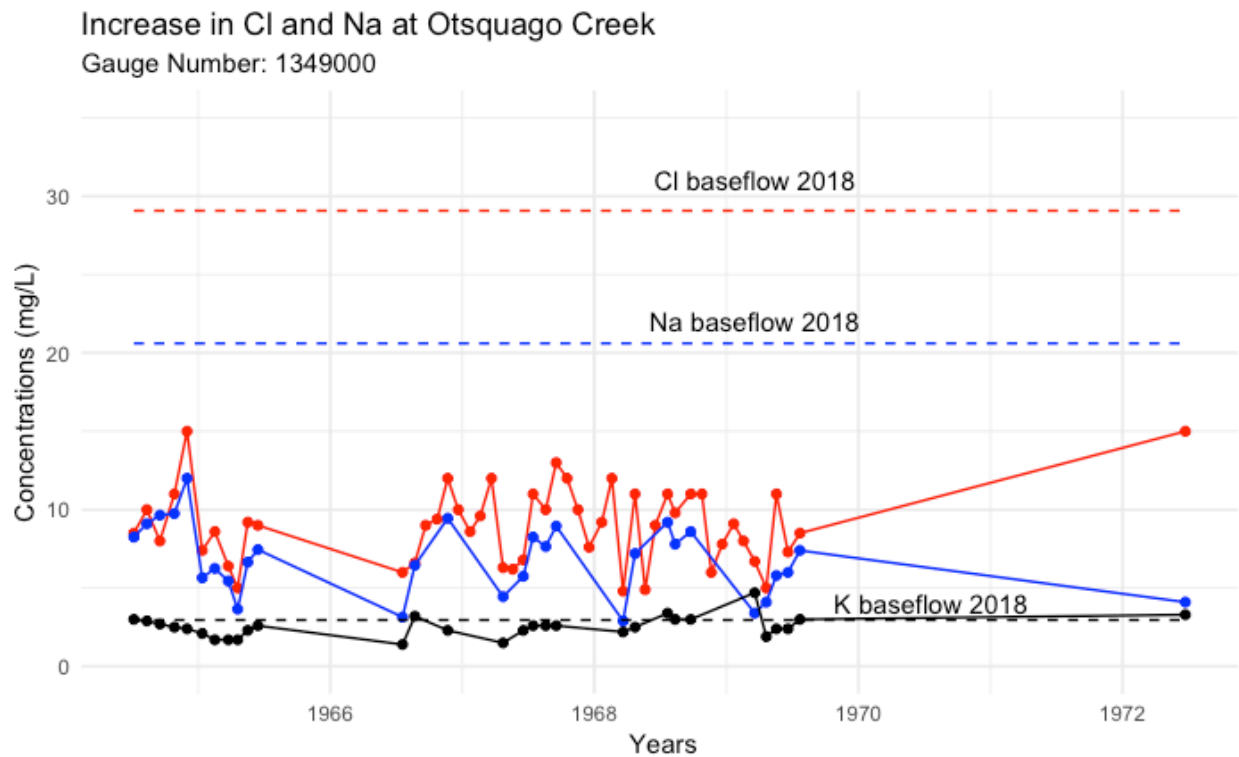


Figure 1. Salt use and consumption in the United States by (A) all end users, 1975–2003 (data from U.S. Geological Survey, 2005b), and (B) consumption by use or industry, 1975–2005 (data from U.S. Geological Survey, 2005b; Kostick and others, 2007).

Figure 20: Taken from a USGS report by Mullaney, the figure shows consumption of salt broken up by industry over time

Figure 21

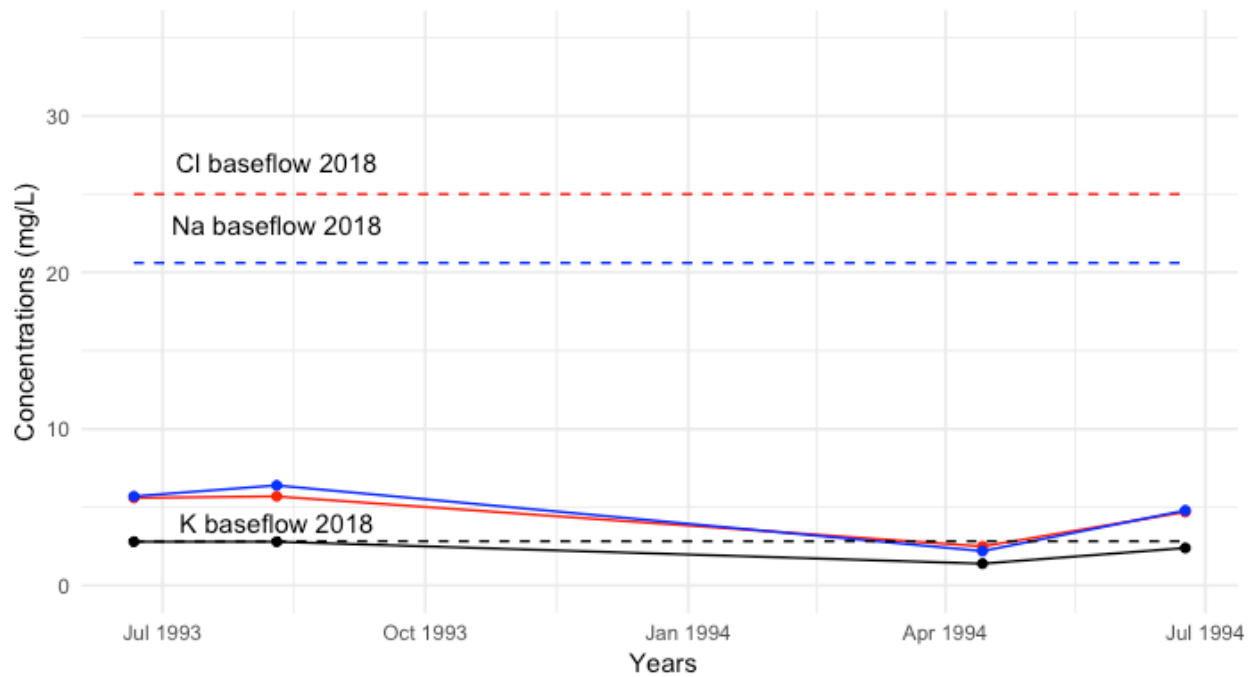
A



B

Increase in Cl and Na at Nowadaga Creek

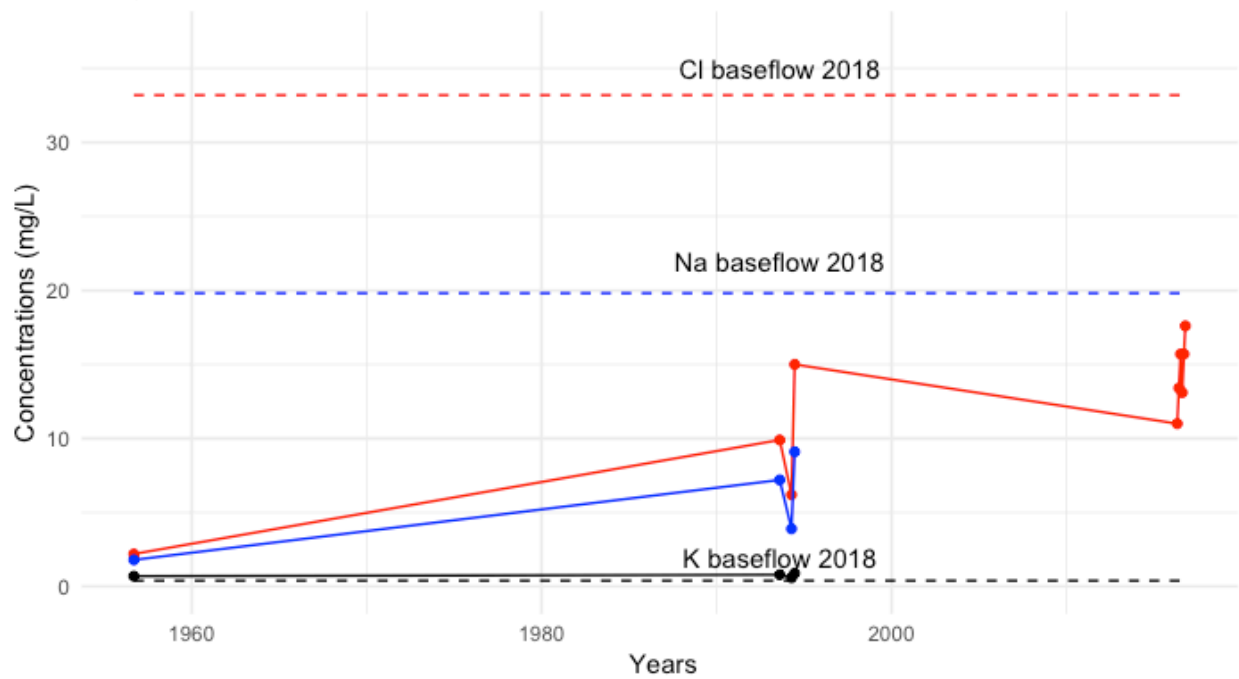
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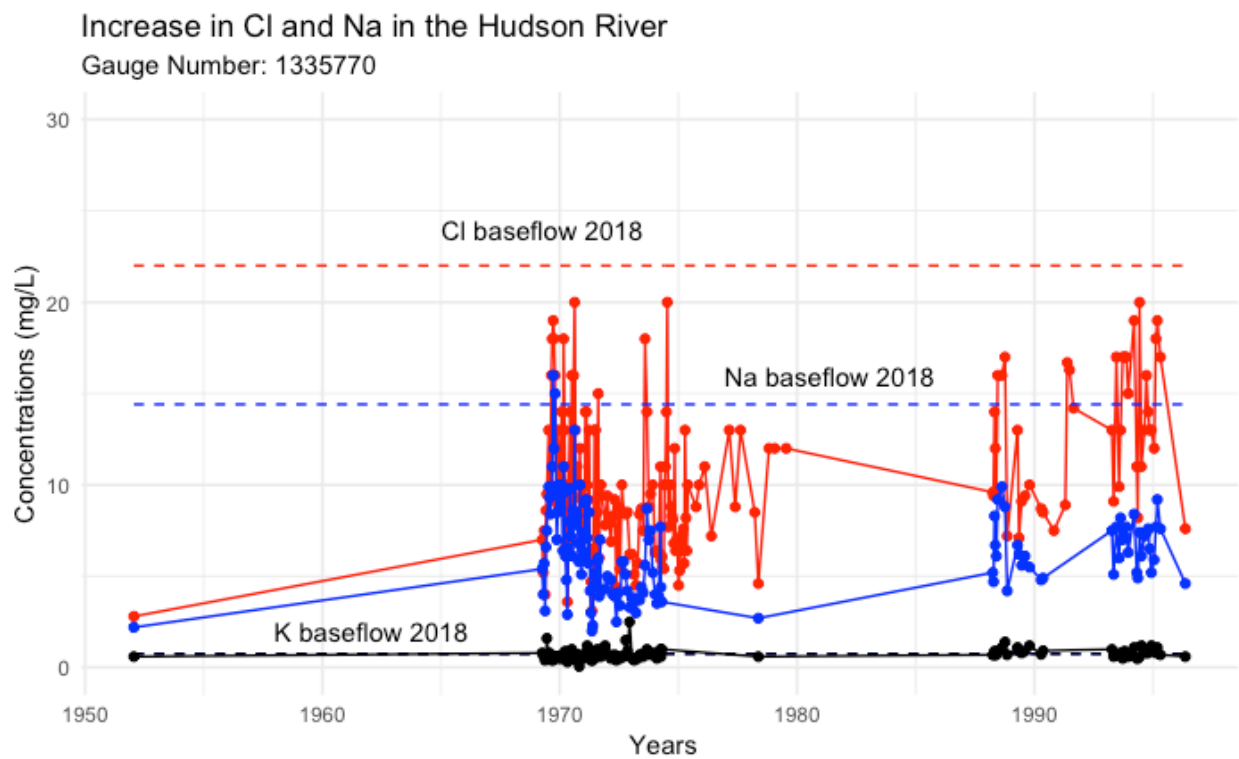
C

Increase in Cl and Na at Caroga Creek

Gauge Number: 1346865



D



E

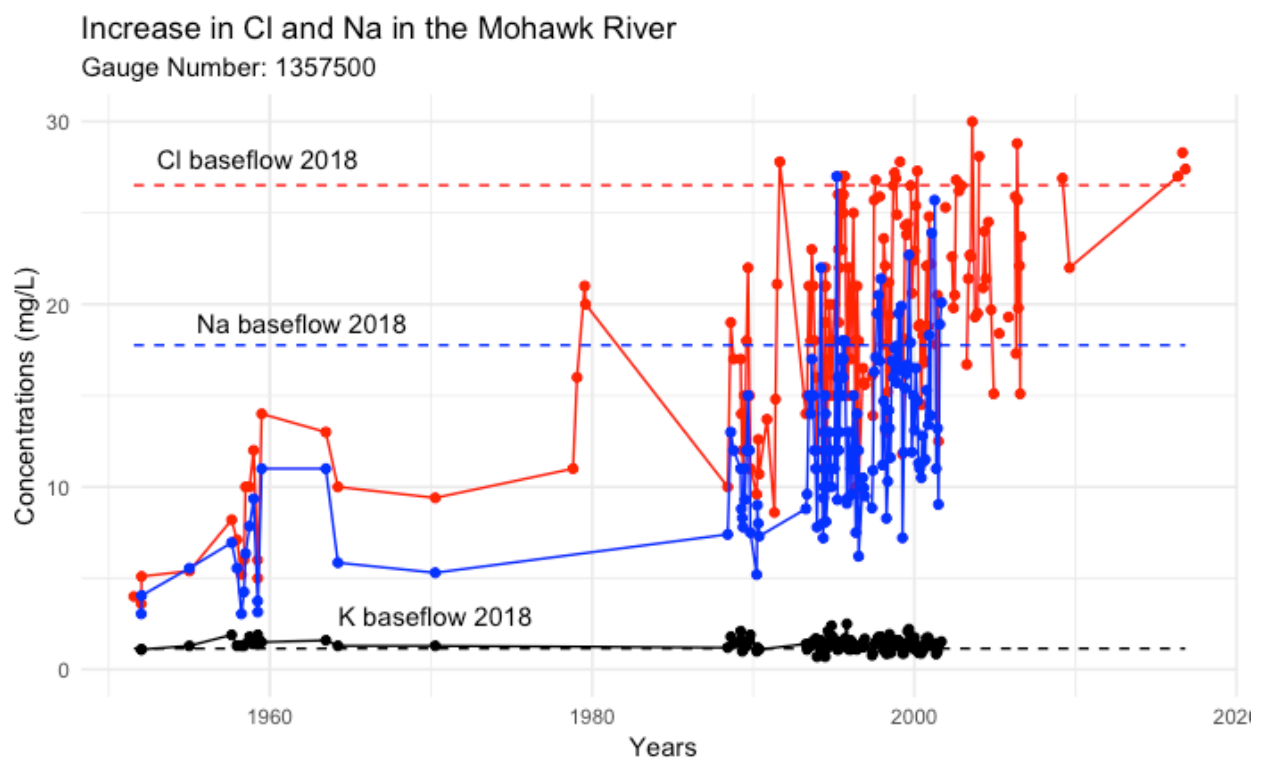


Figure 21: The historic measured levels of Cl (red), Na (blue), K (black), with the concentrations we measured under baseflow conditions plotted along the dashed lines.

Conclusions

This thesis aimed at taking a holistic approach to characterizing 6 watersheds to further understand and investigate their physical hydrology and how the dynamics between hydrology, geology and land use control water quality. It is essential to understand how watersheds function because of human's reliance on them. This research hoped to create a model which can be translated to other watersheds across the northeast. By combining collected samples under both baseflow and high flow, with modeled data, and historic measurements, we identified shifts in flow timing, flow levels, and in geochemistry. These were all used to help identify sources for geochemical signatures and fluxes. The most predominant finding from this research, was the pronounced increase in sodium and chloride levels from road salt pollution. All of our studied rivers displayed elevated sodium and chloride levels, whose source could only be explained by road salting. Moreover, these elevated concentrations were found in samples taken under baseflow conditions meaning that the groundwater has been affected. This is worrisome because the groundwater reservoirs will take years to decades to be flushed and replenished if road salting stopped now, which is not going to happen. Road salting is critical to human health and safety, especially in the Northeast, and that is why it will not be stopped. What we need to determine is to what level are we willing sacrifice environmental health, for road safety. We have gone above and beyond with the level of road salting in the past 30 years and we can now see the effect that it is having on our water resources. What needs to be further investigated is how different road salt application practices can affect the level of pollution in watersheds. Looking at different salting practices in different watersheds could provide a possible way to keep road safe, while mitigating the environmental harm. This could be done by looking at two similar watersheds in size, lithology and hydrology like those of Otsquago and Nowadage Creek and compare the level of road applied, and how it is applied to see if there is a difference made.

Additionally, if there are more resources and time than this thesis, to expand this study to other watersheds in Upstate New York and across the Northeast to develop a record to see regional trends in hydrologic and geochemical parameters.

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