

NEW ENGLAND WATERSHEDS

A Data Driven Portrait of Water Pollution in the North Eastern United States

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THIS PAPER EXAMINES THE DIFFERENCE BETWEEN A RIVER THAT HAS HAD NO HUMAN INTERVENTION AND RIVERS WITH VARIOUS AMOUNTS. HUMAN INFLUENCE WAS EVALUATED THROUGH STREAM CHEMISTRY TO DETERMINE EACH ONE'S OVERALL WATER QUALITY. WATER'S COMPOSITION CHANGES AS IT FALLS FROM THE SKY AND FLOWS OVER GROUND. THIS RESEARCH MAKES USE OF THE WATER CHEMISTRY DATA PROVIDED BY THE HUBBARD BROOK EXPERIMENTAL FOREST AS WELL AS FROM THE NEW ENGLAND COSTAL BASIN NATIONAL WATER QUALITY ASSESSMENT. THE DATA WAS USED TO COMPUTE MONTHLY AVERAGES OF IONS SUCH AS SODIUM, CHLORIDE, CALCIUM AND MAGNESIUM. THESE AVERAGES WERE GRAPHED AND THE TRENDS ANALYZED. DATA ABOUT EACH RIVER'S DRAINAGE AREA, SURROUNDING POPULATION DENSITY, AND LAND USAGE LEND INSIGHT TO THE REASON FOR EACH RIVER'S CHEMICAL COMPOSITION. THE STUDY CONCLUDED THAT THE LAND USAGE AROUND A RIVER HAS AN EFFECT ON THE CHEMICAL COMPOSITION OF THE WATERS. THE RIVERS SURROUNDED BY URBAN AREAS HAD SIGNIFICANTLY MORE TOTAL DISSOLVED SOLIDS AND HIGH LEVELS OF DISSOLVED SODIUM CHLORIDE, ESPECIALLY DURING THE WINTER MONTHS. THIS IS EVIDENCE THAT ANTHROPOGENIC EFFECTS CONTROLLED THE STREAM CHEMISTRY.

INTRODUCTION

Earth is uniquely suited to have liquid water. This liquid—the basis for all life—covers nearly 70% of the planet's surface. Of that, only about 3% is natural freshwater, and most of it is inaccessible, as it is frozen into ice caps. A large portion of freshwater is below the surface in groundwater, and a mere .03% of Earth's freshwater is found at the surface. It is this water though that gives the human race life. Clearly, it is crucial that we protect this water to allow for the human race to flourish. It is estimated that over \$450 billion worth of foods, fiber, manufactured goods and tourism depend on clean, healthy, natural waters. But these waters often fall victim to anthropogenic pollution. The resulting chemical imbalances not only alter the water's natural state, but also affect the surrounding soil, vegetation, and their chemical compositions.

It is important to study the hydrologic chemistry of natural water to have a baseline by which to evaluate polluted water. Understanding the chemical processes and interactions will also aid in developing comprehensive methods through which humans can correct the problems caused in these waters. Water's chemical composition changes depending on its environment. These changes occur as the waters run through the land surface and take on the chemical signature thereof. A study of the stream waters of a watershed is the best indicator for a general outlook of the health of the surrounding environment. This paper will aim to discuss how anthropogenic land use affects the water quality of local stream waters as non-pristine water versus natural forest water without anthropogenic influences as a baseline.

BACKGROUND

The Hubbard Brook Ecosystem Study pioneered evaluations of small watersheds under differing conditions. Its original purpose was studying the effects of acid rain on stream waters and their surrounding terrestrial environments. The study was expanded to include the hydrology, biology, geology and chemistry of a forest and its associated aquatic ecosystems. Hubbard Brook is broken up into ten different watersheds, each of which is its own experiment. As seen in Figure 1, watersheds 1-6 are southern facing slopes while watersheds 7-9 are northern facing slopes. The sixth watershed in the experiment (WS6) was the control; it is considered to be a benchmark of pristine water, with data extending back to 1964. This breadth of about five decades allows for the data to be analyzed for

trends over long periods of time. Hubbard Brook located in New Hampshire consists mainly of a forest ecosystem that provides the area with a variety of vegetation as well as stable water flow and some of the purest water qualities. It is important to note that because there is limited vehicle access to the Hubbard Brook Experimental Forest, anthropogenic effects are negligible on the control of WS6. This exemplifies why WS6 is the closest extant data to what a pre-colonial forest would look like and what its stream chemistry would be. The Hubbard Brook forest has thrived without the effects of humans.

The New England Coastal Basin (NECB) National Water Quality Assessment (NAWQA) data spans a variety of rivers throughout the region. NAWQA assembled for a national water quality database in 1997-2002, with lesser activity continuing through present day. The NECB shown in Figure 2 is one of the 62 regions of water studies across the United States. The NECB was created to aid in understanding of water quality and hydro-chemical reaction between soil and water. Each of the rivers was studied and data was collected for a two-year span. This does not give the same depth as the Hubbard Brook data, but rather offers glimpses into the stream water chemistry of different rivers that are under different levels of anthropogenic influences. The streams vary in surrounding land use from forestry and agriculture, to urban areas more densely populated by humans. These anthropogenic effects negatively affect streams by disrupting the balance between the stream and its surrounding land area.

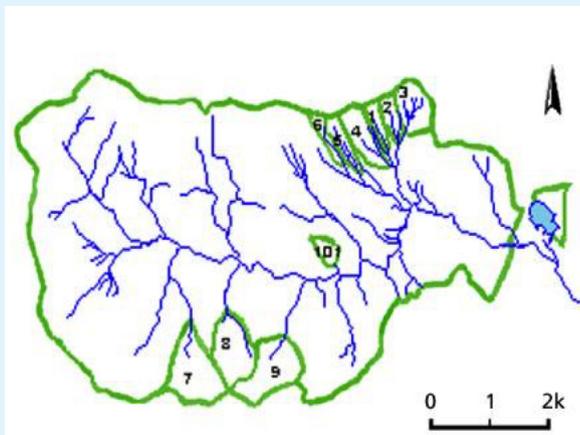


Figure 1. Map of the Hubbard Brook Experimental Forest with watersheds numbered sequentially throughout.

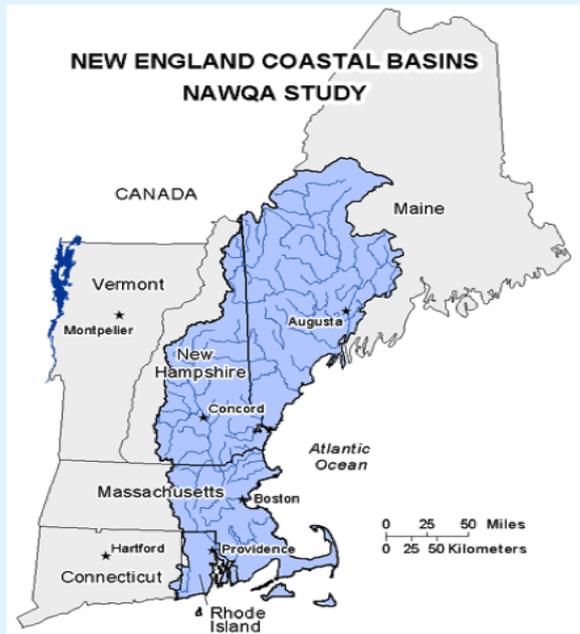


Figure 2. Map of the region covered by the New England Coastal Basin National Water Quality Assessment Study.

Station Name	Drain Area
KENNEBEC RIVER AT NORTH SIDNEY, ME	5411.44
STILLWATER RIVER NEAR STERLING, MA	30.38
MERRIMACK RIVER BL CONCORD RIVER AT LOWELL, MA	4626.85
IPSWICH RIVER AT SOUTH MIDDLETON, MA	44.51
SAUGUS RIVER AT SAUGUS IRONWORKS AT SAUGUS, MA	23.31
ABERJONA RIVER AT WINCHESTER, MA	25.15
CHARLES RIVER AT WATERTOWN, MA	268.16
NEPONSET RIVER AT NORWOOD, MA	32.77
WADING RIVER NEAR NORTON, MA	43.77

Figure 3. Chart of the 9 NECB NAWQA sites being assessed and their drainage sizes.

OBJECTIVE

The goal of this study is to examine the relationship between stream water quality and land use within the watershed area. A combination of the long-running Hubbard Brook data set and the NECB NAWQA data provides a useful data set that shows both a pristine watershed as well as watersheds that reflect anthropogenic effects. The NECB NAWQA data provides small two-year glimpses into the water quality of multiple sites in the region. The available data allows a comprehensive view of the effects of land use on stream water quality as well as the undeniable connection between the two.

METHODS

Once the sites had been chosen, the next step was to obtain the actual collected data set. From their respective websites <hubbardbrook.org> and <http://nh.water.usgs.gov>, the data was downloaded (last accessed on 11/10/16) under the agreement that the result of such analysis would only be used for post-secondary educational purposes. With a basic knowledge of chemistry, inferences could be made of trends and relationships between certain constituents. Data points could then be plotted on graphs both against time and against other data sets.

Aside from Excel, another program used in the methods of this analysis was the standard student edition of Geochemists Work Bench (GWB). It was used in conjunction with Excel because it allowed varying plots to be created, for instance it allowed for thermodynamic assessment (saturation indices and fugacities) of aqueous equilibrium. A fugacity is a partial pressure that relates to a real gas instead of an ideal gas. Fugacities must often be determined via experiments and then collected in databases. GWB has access to all of these databases and can calculate fugacities. Fugacities are useful in showing how saturated a gas is in a water. Saturation indices are similar except they show the saturation of a mineral in water.

DATA

Hubbard Brook

Data displayed for major ions (i.e. Sodium, Calcium, Silica, etc.) was collected weekly and then averaged monthly. Therefore analysis of the stream water chemistry at Hubbard Brook could show seasonal variations and trends. The data was divided by month and by ion, and then averaged to generate a value for each month. It was useful to plot the data onto an XY Scatter Plot to visualize trends or variations over the seasons.

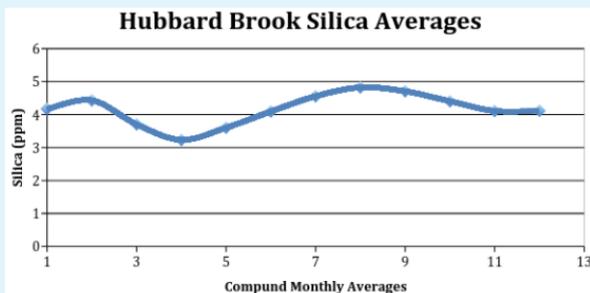


Figure 4. A line plot of average monthly silica levels in Hubbard Brook stream water from WS6.

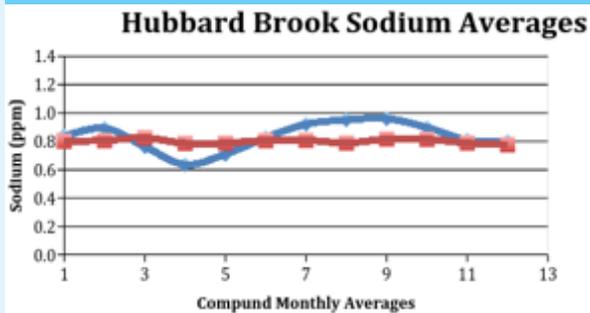


Figure 5. A line graph of average monthly sodium levels in the stream waters of WS6 at Hubbard Brook Forest (dot line). Also shows that data normalized to the silica content of that month (square line).

The Hubbard Brook site is determined to be in equilibrium of Silica with the surrounding bedrock as the only source of silica nearby. This equilibrium is 4 ppm and deviation from this value either means a dilution or a concentration. Therefore, all data trends across the monthly averages are normalized to the silica equilibrium to either amplify or weaken some trends. This varied according to whether there was more or less water entering the watershed. The seasonal trend for silica shows that during the early months (January, February) there is an increase in the concentration of silica in the waters mainly due to water being withheld in snow and ice. Through the later winter and spring, there is dilution of silica as all the ice and snow melts, while rain increases. Then throughout the summer and early fall the concentration increases as water is being used extensively for the growth of vegetation and throughout the ecosystem. In fall and early winter, an equilibrium of 4 ppm is reached once again, as vegetation dies and all water flows to the stream. The only ion to track a near identical pattern is sodium. When normalized to

silica the resulting plot is nearly a straight line. Due to a lack of anthropogenic additions of sodium to this environment it is shown that sodium naturally tracks about the same pattern as silica does throughout the seasons.

Potassium dissolved from rocks and the surrounding soil has a pattern of two peaks and a valley. The first peak of potassium concentration is observed in the late winter to early spring. The valley is found when potassium is taken up in the soils to provide nutrients to vegetation. The second peak of potassium comes in the fall. As trees begin to lose their leaves, their leaves release plentiful potassium back into the soils and in turn can dissolve into the stream waters. As the dissolved potassium washes out of the watershed and the dead plant matters stops decaying, the potassium levels return to equilibrium with the soil and surrounding rock.

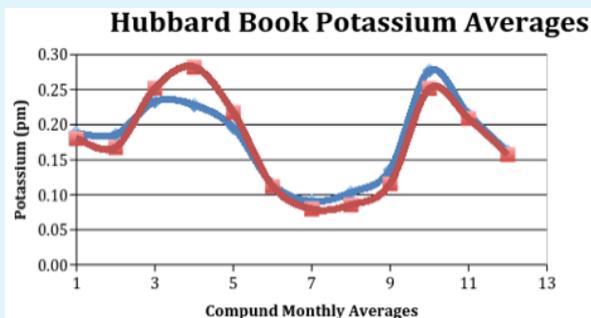


Figure 6. A line graph of average monthly potassium levels in the stream waters of WS6 at Hubbard Brook Forest (dotline). Also shows that data normalized to the silica content of that month (square line).

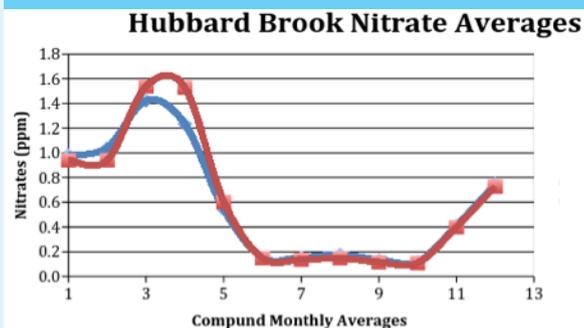


Figure 7. A line graph of average monthly nitrate levels in the stream waters of WS6 at Hubbard Brook Forest (dot line). Also shows that data normalized to the silica content of that month (square line).

Nitrates trend such that there is a large increase in their concentration during the early spring as soil thaws and release the nitrates from the previous year's decay of vegetation. Nitrogen, a limiting nutrient, is quickly taken up throughout the ecosystem both by plants as well as algae. From June until October there are almost no nitrates left in the stream waters as they are all being used for organismal growth. As winter begins again, the productivity of vegetation ends and waters become too cold for algae to bloom. The significant decay of plant material results in a steady climb of nitrates in the stream waters and thereby in the soils throughout the watershed as well.

Calcium and magnesium follow similar paths throughout the seasons. Both calcium and magnesium are nutrients indispensable for the proper growth of vegetation. Therefore their seasonal variations are largely dependent on the growth and decay of plants. From February to May calcium

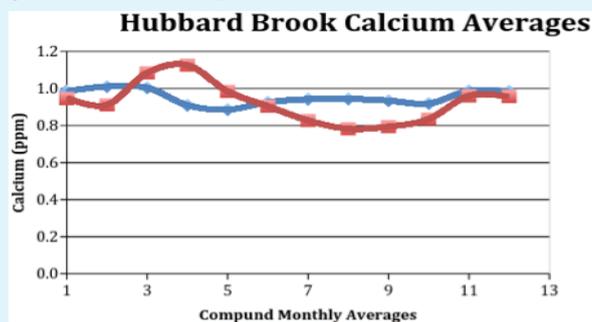


Figure 8: A line graph of average monthly calcium levels in the stream waters of WS6 at Hubbard Brook Forest (dotline). Also shows that data normalized to the silica content of that month (square line).

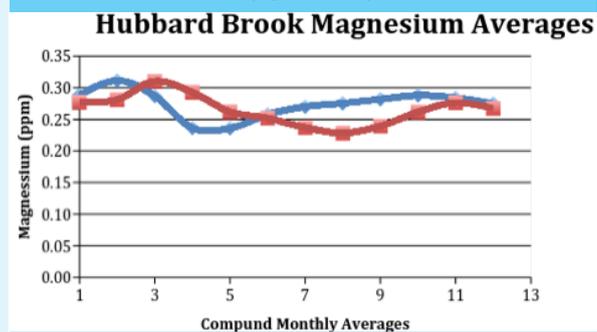


Figure 9. A line graph of average monthly magnesium levels in the stream waters of WS6 at Hubbard Brook Forest (dot line). Also shows that data normalized to the silica content of that month (square line).

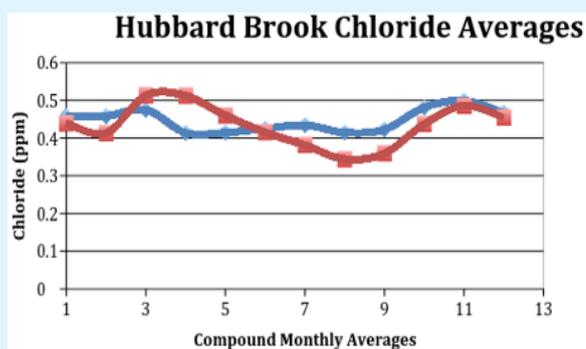


Figure 10: A line graph of average monthly chloride levels in the stream waters of WS6 at Hubbard Brook Forest (dot line). Also shows that data normalized to the silica content of that month (square line).

and magnesium surges into the stream waters. This surge is due to snowmelt that carries these cations into the waters as the soils are already saturated and plants are not ingesting the nutrients yet as they have not begun to grow. During the growing season, summer and fall, there are low concentrations of these nutrients in the stream waters as they are being taken up by vegetation. When normalized to silica, the trend becomes even more apparent as the concentrations are lower, despite the fact that according to silica, they should be. From October into the winter the growing in concentrations again begin to increase as the vegetation is no longer using these nutrients.

Chloride is an anion that balances out some of the cations found in the stream waters. Chloride, therefore, is controlled by the presence of these cations; the chlorides of calcium, magnesium, and sodium are very soluble in water. The trend of chloride is proportional to that of calcium, magnesium, and with some regards, to sodium as well. As these ionic compounds dissolve in water they release the chloride and cation, creating a more amplified version to the trends of the cations individually.

The inter-component plot of Chloride vs sodium exhibits that at Hubbard Brook there is no correlation between sodium and chloride. The R^2 value is far too low for the data to be reliable; there is too much variation in the points to say that either sodium or chloride has a controlling effect on the other. On the other hand, the Mg vs Ca diagram has a much higher R^2 value showing that there is most likely a correlation between calcium and magnesium in the stream waters.

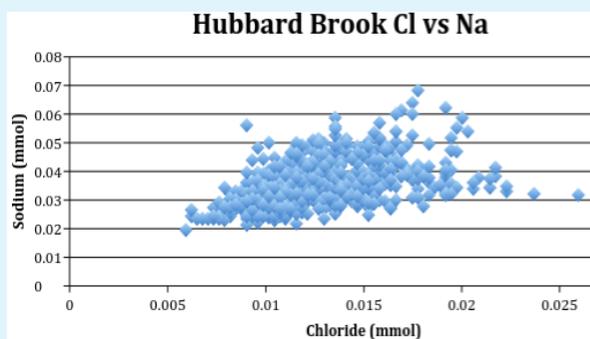


Figure 11. The inter-component relationship between chloride and sodium at the Hubbard Brook forest, accompanied by the trend line with its equation and the R^2 value.

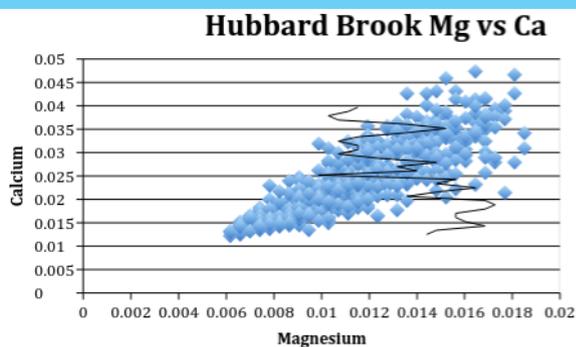


Figure 12. The inter-component relationship between magnesium and calcium at the Hubbard Brook forest, accompanied by the trend line with its equation and the R^2 value.

NECB NAWQA

Of the NECB NAWQA sites, the Kennebec River is the least impacted by humans, with nearly 80% of its land use being forestry. It has the largest drainage area of these 9 sites therein having the most soil to naturally filter the water before it enters the stream. Its silica levels also fall in line with the benchmark of Hubbard Brook levels with a maximum at 5 ppm and a minimum at 2.5 ppm. Chloride levels at the Kennebec River are the lowest amongst all the testing sites, amounting to an overall lower total dissolved solids (TDS) content of its stream waters. The magnesium to calcium ratio at the Kennebec River falls in line with the levels observed at the other nine sites. Its R^2 value lends a reasonable evidence for a correlation between the two components. However, the chloride and sodium ratio does

not fall within error of the other observed ratios. It is much lower with nearly no correlation confidence between the two components having such a low R^2 value.

The Merrimack River and its watershed have a population density ten times that of the Kennebec watershed. Its main land use is forestry followed by urban development and agriculture. The inter-component diagrams depict a clear

Station Name	Drain Area	Pop Density	Precipitation	Main Land Use	Main LU %	Second LU	Second LU %	Third LU	Third LU %
KENNEBEC RIVER AT NORTH SIDNEY, ME	5411.4	26	43.52	Forested	79.6	Water	6.4	Agriculture	5.9
STILLWATER RIVER NEAR STERLING, MA	30.38	166	49.34	Forested	75.2	Agriculture	10	Wetlands	8.1
MERRIMACK RIVER BL CONCORD RIVER AT LOWELL, MA	4626.8	278	44.55	Forested	73.6	Urban	8.5	Agriculture	7.6
IPSWICH RIVER AT SOUTH MIDDLETON, MA	44.51	1175	45.20	Forested	39.4	Urban	38	Wetlands	16.2
SAUGUS RIVER AT SAUGUS IRONWORKS AT SAUGUS, MA	23.31	2291	45.10	Urban	55.9	Forested	26.9	Wetlands	9.1
ABERJONA RIVER AT WINCHESTER, MA	25.15	3010	45.73	Urban	67.3	Forested	23.8	Wetlands	4.3
CHARLES RIVER AT WATERTOWN, MA	268.16	1345	46.46	Forested	53	Urban	29.8	Agriculture	7.5
NEPONSET RIVER AT NORWOOD, MA	32.77	1078	47.17	Forested	52.9	Urban	30.1	Wetlands	9.6
WADING RIVER NEAR NORTON, MA	43.77	533	47.04	Forested	63.5	Urban	18.4	Wetlands	8.8

Figure 13. Each NECB site's location, drainage area, population density, precipitation, and three major land uses.

Column1	Aberjona.	Charles	Ipswich	Stillwater	Merrimack
Mg#s#Ca	5.1857	4.4217	4.5595	5.6297	5.1736
R^2	0.9743	0.9027	0.9129	0.9661	0.9742
AtomicMg#s#Ca	3.5267	2.6814	2.7651	3.4139	3.1373
R^2	0.9743	0.9028	0.9129	0.9661	0.9742
Cl#s#Na	0.5496	0.5613	0.5571	0.5549	0.6076
R^2	0.9826	0.9862	0.9805	0.8694	0.9646
AtomicCl#s#Na	0.8476	0.8655	0.8591	0.8557	0.937
R^2	0.9826	0.9862	0.9805	0.8694	0.9647
Cl#Max	259	216	98.7	34.3	62.4
Max#Silica	10.3	10.7	14.3	9.1	7
Min#Silica	2.7	1.3	1.6	3.8	1.4
Column1	Kennebec	Neponset	Wading.	Saugus	
Mg#s#Ca	4.7777	3.5554	4.2918	2.7139	
R^2	0.8485	0.8723	0.9011	0.5787	
AtomicMg#s#Ca	2.897	2.1562	2.6027	1.6457	
R^2	0.8487	0.872	0.9008	0.5787	
Cl#s#Na	1.1533	0.5666	0.589	0.5368	
R^2	0.4709	0.9146	0.9197	0.9806	
AtomicCl#s#Na	1.7785	0.8739	0.9084	0.8278	
R^2	0.4712	0.9146	0.9199	0.9806	
Cl#Max	8.4	63.6	63.7	197	
Max#Silica	5	10.2	9.5	13.9	
Min#Silica	2.5	3.1	1.3	3.3	

Figure 14. The 9 NECB NAWQA sites and a summary of the ratios of Magnesium vs Calcium level and R^2 as well as sodium to chloride levels with their R^2 values. The maximum chloride levels are also displayed as well as both the maximum and minimum silica levels.

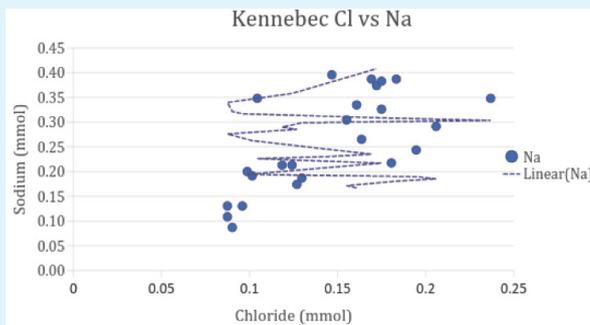


Figure 15. Sodium vs Chloride levels at Kennebec as well as the trend line, its equation, and R² value.

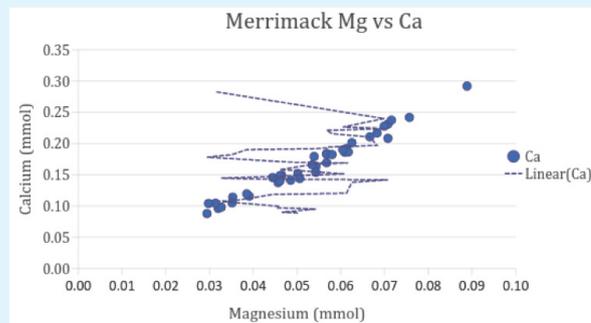


Figure 18. Magnesium vs Calcium levels at Merrimack as well as the trend line, its equation, and R² value.

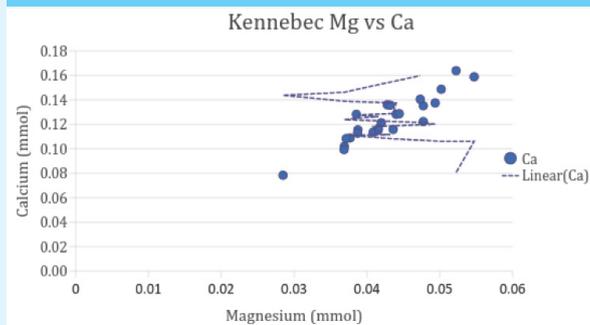


Figure 16. Magnesium vs Calcium levels at Kennebec as well as the trend line, its equation, and R² value.

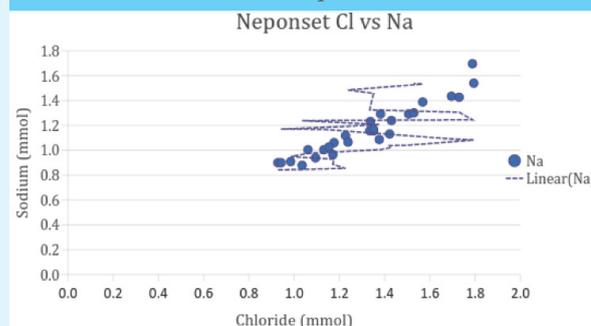


Figure 19. Sodium vs Chloride levels at Neponset as well as the trend line, its equation, and R² value.

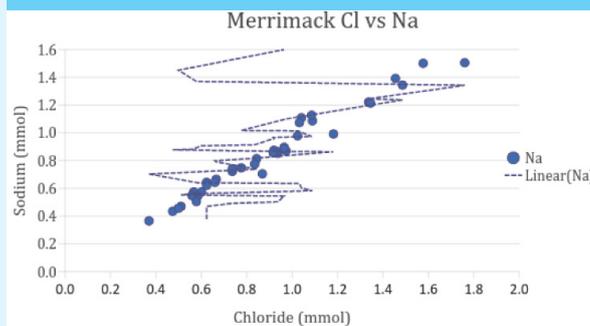


Figure 17. Sodium vs Chloride levels at Merrimack as well as the trend line, its equation, and R² value.

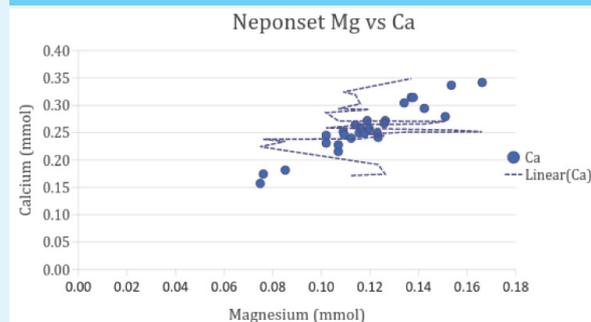


Figure 20. Magnesium vs Calcium levels at Neponset as well as the trend line, its equation, and R² value.

correlation between chloride and sodium with the atomic ratio being one to one. This suggests the concentration of the two constituents is controlled by salt (NaCl). The concentrations of chloride and sodium at the Merrimack River are eight times higher than they are at the Kennebec River. There is more variation in the silica levels at the Merrimack River with the minimum being at 1.4 ppm while the

maximum is 7 ppm. The magnesium to calcium ratio indicates a correlation within a range of error in the other rivers, suggesting chemical weathering of surrounding bedrock controls the trend.

The Neponset River is a small watershed with a high population density. The main land use is forestry but a fair

amount of the land is also urban. The chloride – sodium inter-component diagram shows there is a correlation between the two about equal with the average levels of the other rivers. Therefore the sodium levels are lower than the chloride levels, which reach a maximum of 64 ppm. The data is reliable such that there is an R^2 value of over 0.90. Overall the silica levels of the Neponset River are higher than that of Kennebec ranging between 3.1 ppm and 10.2 ppm. The magnesium to calcium ratio is 2.15 with a R^2 value of nearly 0.90, the second lowest magnesium to calcium ratio of all of the test watersheds.

In the Saugus watershed the land is over 50% urban, followed by 27% forested. The watershed is very small with a high population density. In Saugus the chloride to sodium ratio is 0.80 with a very high R^2 value of 0.98. The ratio of is slightly lower but still in line with the average values of the rest of the sites, with slightly elevated levels of chloride over sodium. The chloride level reaches a maximum of 197 ppm. The silica levels are the second highest maxi-

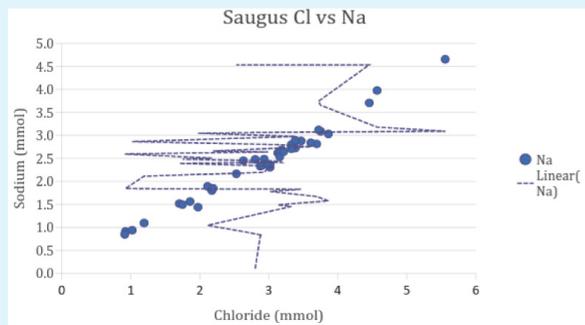


Figure 21. Chloride vs Sodium levels at the Saugus River as well as the trend line, its equation, and R^2 value.

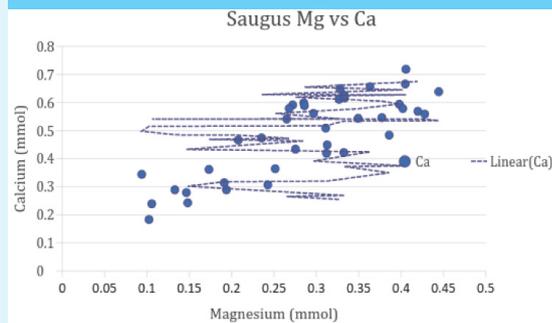


Figure 22. Magnesium vs Calcium levels at the Saugus River as well as the trend line, its equation, and R^2 value.

um and minimum silica values of all of the rivers. The magnesium to calcium ratio is not conclusive with a variation wide enough to have an R^2 value of less than 0.60.

Stillwater is a relatively small watershed with a low population density. The land use is primarily forested at 75%, followed by agriculture at 10%. The chloride to sodium ratio at Stillwater is slightly below a one to one ratio. With chloride slightly higher than sodium, the R^2 value at 0.87 percent depicts a fairly reasonable correlation. The chloride maximum at Stillwater was 34.3 ppm, which is the second lowest observed level over all of the rivers. The magnesium to calcium ratio of 3.41 has a strong correlation with a R^2 value of 0.96. The silica ranged from 3.8 ppm to 9.1 ppm.

Wading River is a relatively small watershed with a median population density amongst the NECB Rivers. Its mainly forested at 63.5% followed by urban at 18.4%. The chloride to sodium ratio is 0.90. There is a strong correlation in this ratio with a R^2 value of 0.91. The maximum chloride

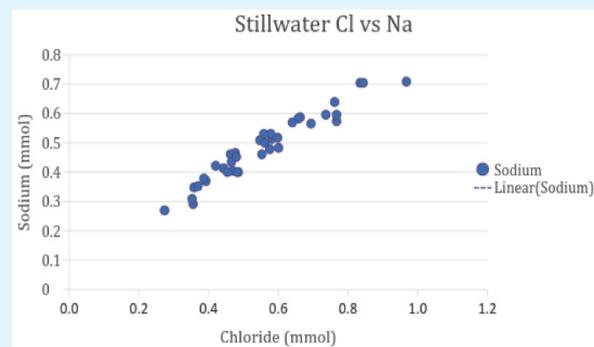


Figure 23. Chloride vs Sodium levels at Stillwater as well as the trend line, its equation, and R^2 value.

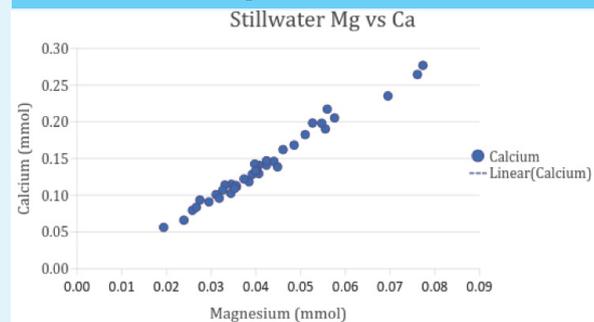


Figure 24. Magnesium vs Calcium levels at Stillwater as well as the trend line, its equation, and R^2 value.

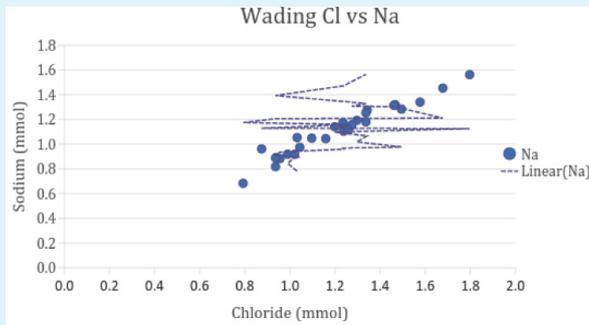


Figure 25. Chloride vs Sodium levels at Wading as well as the trend line, its equation, and R^2 value.

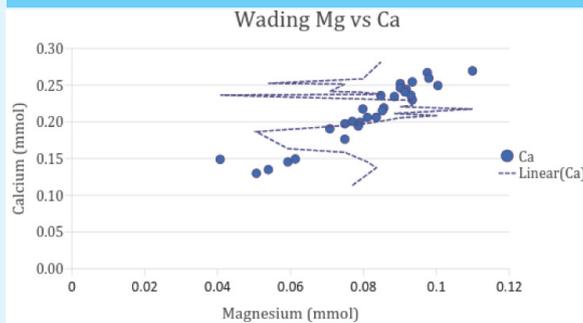


Figure 26. Magnesium vs Calcium levels at Wading as well as the trend line, its equation, and R^2 value.

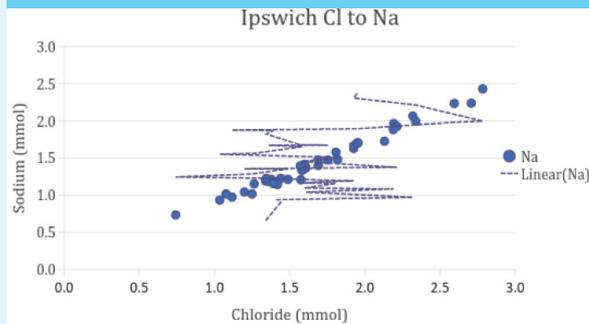


Figure 27. Chloride vs Sodium levels at Ipswich as well as the trend line, its equation, and R^2 value.

level recorded at Wading River was 63.7ppm. The magnesium to calcium ratio of 2.6 has a strong correlation with a R^2 value of 0.90. The silica values ranged from 1.3 ppm to 9.5 ppm.

The Ipswich watershed is fairly small but has a relatively high population density. Its main land uses are 39.4% forested and 38% urban. The chloride to sodium ratio is 0.86

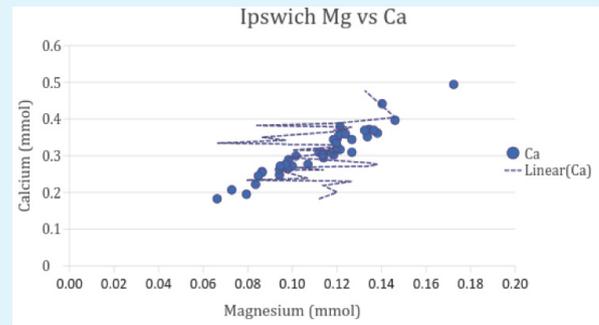


Figure 28. Magnesium vs Calcium levels at Ipswich as well as the trend line, its equation, and R^2 value

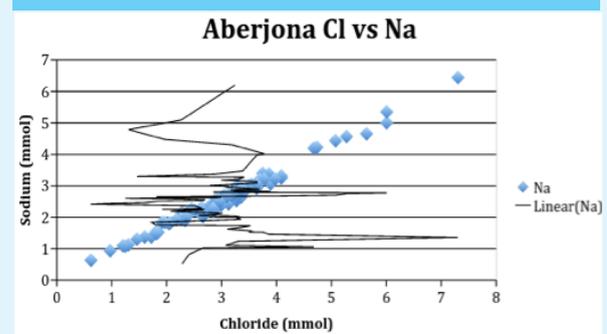


Figure 29. Chloride vs Sodium levels at Aberjona as well as the trend line, its equation, and R^2 value. Figure 28: Plot showing Magnesium vs Calcium levels at Ipswich as well as the trend line, its equation, and R^2 value

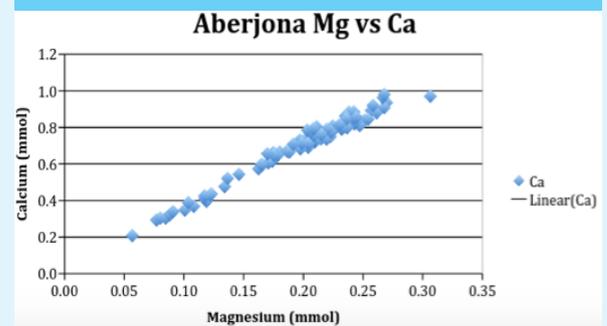


Figure 30. Magnesium vs Calcium levels at Aberjona as well as the trend line, its equation, and R^2 value.

with a strong correlation of an R^2 value of 0.90. The slightly higher levels of chloride reach a maximum of 98.7 ppm. The magnesium to calcium ratio is 2.76 with a strong correlation of 0.91. The silica levels at the Ipswich River range from 1.6 ppm and 14.3 ppm.

The Aberjona watershed is small but has a high population density. Its main land use is 67.3% urban followed by forestry at 23.8%. The chloride to sodium ratio is 0.85 with a strong correlation of an R^2 value of 0.98. The slightly higher levels of chloride reach a very high maximum of 259 ppm. The magnesium to calcium ratio is 3.35 with a strong correlation of 0.97. The silica levels at the Aberjona River range between 2.7 ppm and 10.3 ppm.

The Charles watershed is midsize with a high population density. Its main land use is 53% forestry with its second land use as urban at 29.8%. The chloride to sodium ratio is 0.86 with a strong correlation of a 0.98 R^2 value. The slightly higher levels of chloride reach a very high maximum of 216 ppm. The magnesium to calcium ratio is 2.68 with a strong correlation of 0.90. The silica levels at the Charles River range between 1.3 ppm and 10.7 ppm.

DISCUSSION

In the data of the pristine waters of Hubbard Brook there are relatively low concentrations of each of the chemical components in the water. It can be deduced that without

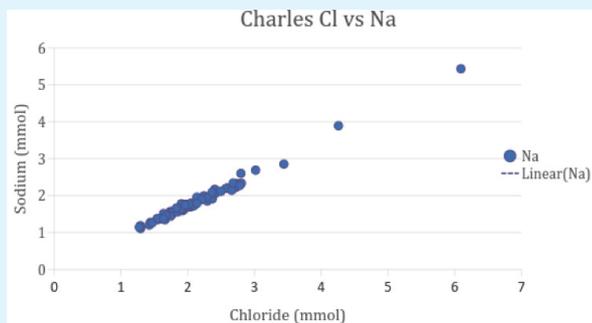


Figure 31. Chloride vs Sodium levels at Charles as well as the trend line, its equation, and R^2 value.

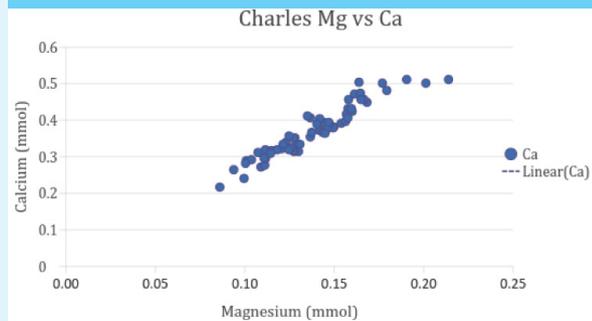


Figure 32. Magnesium vs Calcium levels at Charles as well as the trend line, its equation, and R^2 value.

anthropogenic effects, natural waters, precipitation, and chemical weathering control the water's composition. At Hubbard Brook, the precipitation volume has not changed significantly over the six decades of data. Therefore Hubbard Brook is a good indicator of what pre-colonial water quality would be, as well as an overall environment. In the steep slopes of Hubbard Brook, the residence time of water is fairly fast, flushing out into the stream.

The stark difference in the composition of the majority of the NECB NAWQA sites can be attributed to the land use in those areas. The more urban sites such as Aberjona show how polluted stream waters can become due to anthropogenic effects. Altering the landscape from forested areas changes the natural nutrient cycling characteristically found in environments less impacted by human activity such as the Hubbard Brook forest. The stream waters are no longer controlled by chemical weathering, but by anthropogenic runoff and other human-caused imbalances.

One of the primary discrepancies between the baseline Hubbard Brook data and the NECB data is that the sodium chloride levels are much higher in urban areas than in forested areas. This problem is most prevalent throughout the winter months. Road salts distribute large amounts of added sodium chloride into the environment. This added sodium chloride runs off the roads and enters the stream waters. The slightly higher levels of chloride in the waters suggest some of the sodium is not making it to the water, but is caught up in the soil replacing calcium chloride.

When comparing the effect of land use on water chemistry and quality there are a multitude of different sites that can be used as markers. Hubbard Brook is an example of pristine, untouched natural waters and is used as a benchmark for comparing the NECB NAWQA data. The area that remains most untouched is the Kennebec River. With silica levels that are very close to one another, it is possible that the composition of the Kennebec River is still mostly controlled by chemical weathering rather than anthropogenic effects. Kennebec's main land use being forested land would support the claim that while humans do live on the surrounding land, the Kennebec is still a healthy river when being compared to Hubbard Brook. One similarity is that neither stream naturally has a trend in the relationship between chloride and sodium. Another similarity is how low the levels of both sodium and chloride are both being well under 1 mmol. The correlation between the magnesium and calcium in both is fairly strong and the

slope of the trend line is within error bars of one another at 2.2-2.8.

Stillwater is a suburban area that is a main contributor of the drinking water to the greater Boston Area. When comparing the chloride-sodium ratios, it is apparent there is a much stronger trend between the two components, and that the ratio is approaching 1 with a slightly higher level of chloride than sodium. The interesting factor is the lowest levels of both sodium and chloride at Stillwater are right in line with the highest levels of these elements found at the Kennebec River, and much higher than those found at Hubbard Brook. The Merrimack River, found in a suburban area, has a strong correlation between sodium and chloride with the ratio between the two virtually being 1. The lowest observed levels of the constituents are even higher than those found at Stillwater. This is cause to believe the similar land use of these two suburban areas has transformed the stream chemistry from where it otherwise would be.

The most urban area by far is Aberjona with a land use of over 67% urban. The sheer volume of dissolved solids in the water is much higher than any of the rivers that are less urban. With regard to the ratio chloride to sodium, there is one of the strongest correlations of any of the observed sites. The lowest values for both chloride as well as sodium are well above the very low values found at Hubbard Brook. In the transformation from forested to urban areas, the concentration of these components continues to increase to levels that are excessive in comparison to the concentration at sites that have little to no anthropogenic effects. Thus land use has a direct effect on the composition of the stream water chemistry.

CONCLUSION

Water takes on the chemistry of surrounding soils, thus land use has an effect on local stream water chemistry. Thus sodium chloride is a stream water constituent that is highly impacted by anthropogenic activities. In the pristine, untouched waters of Hubbard Brook or the remote waters of the Kennebec River, levels of sodium chloride are very low. Areas such as Aberjona or the Saugus Rivers, according to the USGS have urbanization percentages of 67% and 56% respectively, are the two highest amongst the rivers in this study. In turn the levels of sodium chloride are much higher in these rivers. Throughout the rivers there is a correlation between increased sodium chloride concentration and urbanized areas.

Hubbard Brook WS6 data is an example of a pristine watershed that can be used as a reference to judge the NECB Rivers. This data gives insight as to what water chemistry looked like in pre-colonial times as the constituent levels as well as the precipitation amounts have remained virtually the same over the past 60 years when data has been collected. Here, water quality is mostly determined by the weathering of rocks, creating equilibria with the stream waters. This is displayed through the silica saturation index that was calculated using the GWB software where the equilibria point with the weathering rock was determined to be a consistent 4 ppm. Variations in concentrations seen in the data are examples of dilutions of the silica in the water after a snowmelt, or due to evaporation during the summer.

Seasonally there are variations in the levels of the stream chemistry constituents. Throughout the winter much of the water is frozen in snow and ice and then during the spring the snowmelt causes a dilution of all of the constituents. This dilution is contrasted by a concentration due to an increase in evapotranspiration during the summer. For constituents that are also limiting nutrients, the growing season causes them to be taken up by plants rather than run into the stream water. This is why the levels of calcium, magnesium, sulfates, and nitrates lower in concentration during the warmer months, despite the expected increase in concentration due to evapotranspiration.

In the multicomponent diagrams, the sodium to chloride ratio approaches a one to one ratio in most of the watersheds tested with slightly elevated chloride levels compared to sodium. This would suggest dissolved sodium chloride is the controlling factor in the levels of these components in stream waters. However, some of the sodium ions get trapped in soils through a cation exchange relationship with calcium. The lack of correlation in the watersheds that are primarily forested as well as the much lower levels show that the sodium to chloride relationship is not sodium chloride controlled in more pristine watersheds.

All of the waters analyzed in this paper are in equilibrium with the atmosphere and the earth. In terms of the atmosphere, it would be remiss to not consider the fugacity of oxygen and carbon dioxide. Oxygen is widely under saturated in these stream systems while carbon dioxide is more often oversaturated in the waters. While under saturation of oxygen impacts the ability of organisms to live in the waters, especially fish, oversaturation of carbon dioxide can be an indicator of anthropogenic effects. On the other

hand, dissolved nitrogen plays little to no part in the biologic cycles as opposed to its counterpart NO_3 , which is a very important contributor to plant cycles. Regarding equilibrium with the earth, saturation indices of the waters with silica derived from quartz commands that there is about 4 ppm of silica coming from dissolving quartz consistently. Variations from this concentration can be attributed to changes in the amount of water present in the streams at a given time.

Being able to quantify the chemistry changes in watersheds that interact with humans is evidence that anthropogenic activities have a significant impact on the surrounding environment. This reality instills an important responsibility onto humans to use rivers and the land surrounding them with prudence. Therefore it is necessary to make use of the information acquired in studies such as this one to make informed decision regarding the protection of waterways and their shorelines. Creating policy that ensures their protection is integral to solving the problem of water pollution. Anyone can help by knowing the status of pollution in waterways near them, and urging local government to allocate funding to environmental projects that promote sustainability.

REFERENCES

Likens, G. E. (n.d.). Chemistry of Streamwater at the Hubbard Brook Experimental Forest, Watershed 6, 1963 - present. *Hubbard Brook Ecosystem Study*.

Robinson, K. W., Flanagan, S. M., Ayotte, J. D., Campo, K. W., Chalmers, A., Coles, J. F., & Cuffney, T. F. (2016). Water Quality in the New England Coastal Basins. U.S. Geological Survey Circular , (1226).