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Surface Water Geochemical Characteristics near Historical Distillery Locations in Tennessee and Kentucky

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Abstract

Kentucky and Tennessee has been the primary region in which whiskey has been produced in the United States for the last 200+ years. The locations of Kentucky and Tennessee whiskey distilleries in the pre-industrial era appear to be constrained by the geochemistry of natural waters, stratigraphy, geomorphology, and the average ambient temperatures of fermentation. Distilleries are located near first-order streams where the groundwater surfaces, indicating there was little to no manipulation of these local water sources used in the distilling process during pre-industrial America. These groundwater sources flow through heavily dominated limestone and/or Mg-rich limestone (dolostone), adjusting the geochemistry of the first-order streams creating an optimal Ca-Mg-Fe concentration ratio to create high quality 'tasting' whiskey. Collection of water samples in these areas suggest that Kentucky and Tennessee both hold ideal physiographic and hydrologic terrains, as well as the naturally occurring ideal Ca-Mg-Fe concentration ratios in the waters to create high quality 'tasting' whiskey. The question of why most American whiskey distilleries has endured prior to the industrial revolution are confined to a small region of Kentucky and Tennessee. No further areas of the southern U.S. with suitable climates or geochemistry for whiskey feedstock productions will be discussed.

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Introduction

The Knobs and Inner Bluegrass geomorphic provinces of Kentucky and the Highland Rim geomorphic province of Tennessee are the location of the longest-lived whiskey distilleries in the United States and are the most popular American-made whiskies in the world. Bourbon and Tennessee Whiskey are made from primarily corn. To efficiently make whiskey from corn requires mash water to have dissolved iron content lower than 25 ppm, so that amylase enzymes that convert starch from corn into fermentable sugar are not denatured (Smiley, 1999 and Miller, 2016). Shallow groundwater and streams in the Knobs, Inner Bluegrass, and Highland Rim regions typically have dilute, Ca-Mg-bicarbonate-type compositions with circumneutral pH, which limits dissolved Fe and also promotes growth of bacteria involved in fermentation. These specific chemical characteristics would have been difficult to manipulate in pre-industrial, rural America and therefore are attributed to the Ordovician and Mississippian bedrock of the Cincinnati Arch and the Lexington Dome.

The locations of the oldest distilleries in the U.S. are found in regions with average temperatures above 14.44°C (58°F) (Figure 1). Some distilleries in Kentucky used local stream water for distilling due to the relatively uniform temperatures in the Bluegrass region (Fryar 2009). The phenomenon of whiskey being produced in these regions can also be attributed to the average temperatures of fermentation (Smiley, 1999). Bacteria thrive in warmer fermentations and can produce organic acids which can esterify in the maturation process of whiskey and produce desirable flavors. Additionally, physiography appears to play a strong role in the location of Bourbon and Tennessee Whiskey distilleries. Specifically, topography, location within the watershed, and stratigraphy have striking similarities at the locations of 12 unique whiskey distilleries in pre-industrial America (Figure 2), of which 10 are in operation today. The physiographic similarities between whiskey distillery sites suggest that pre-industrial distillers had a geo-centric ‘search image’ for locations that would efficiently result in commercially superior beverages.

Historical, commercial production of whiskey in Tennessee, prior to modern water treatment, was an is confined to four distilleries in the Highland Rim physiographic province of Tennessee, very close to the contacts between the Mississippian Fort Payne Formation, the Ordovician Leipers, Inman, and Catheys, Formations, and Ordovician Bigby-Cannon Formation (Figure 3). The Jack Daniel Distillery (1866-present), the George Dickel (Cascade Hollow Distillery, 1877-present), the Farrar Distillery (1875-1902), and the Nelson’s Greenbrier Distillery (1870-1909) produced whiskey made from corn. In Kentucky, distilleries such as, the Atherton Distillery (1967-1972), Barton Distillery (1879-present), Maker’s Mark Distillery (Burk’s Distillery 1889), Woodford Reserve Distillery (1812-present), Four Roses Distillery (1910-present), Old Pepper Distillery (1862-present), Castle and Key (Cold Taylor Distillery 1887-present), and Buffalo Trace Distillery (1792-present) all use local groundwater sources from the Knobs and Inner Bluegrass regions (Fryar 2009).

The production of distilled spirits in pre-Industrial America was based largely on the types of feedstocks available to distillers (Carson 2010). Feedstock and ambient temperature of the region in which the fermentation was conducted were key considerations in the particular type of fermented beverage produced. The type of beverage consumed, generally, were of local origin and were either products that required little processing to be consumed after fermentation, such as beer and wine in northern US, or distilled spirits in the southern U.S. In climates where fruit production was viable, fruit brandies were the preferred distilled spirit. On the western frontier of Tennessee and Kentucky, homemade whiskies from local feedstocks of corn, rye, and barely were commonly consumed. In the hollows comprising the dissected escarpment of Tennessee's Highland Rim, corn was a common cereal crop and corn whiskey was the most commonly available alcoholic beverage (Carson, 2010).

When corn is used to make commercial whiskey, ground corn kernels are cooked in hot water near boiling temperature to disperse the starches in the corn kernel into the mash water. The temperature of the mash is allowed to cool to 158°F (70°C) and malted grains, such as rye and barley, are added as a source of amylase enzyme. These amylase enzymes from the malted grains convert the starch from the corn into fermentable sugar which yeasts convert into ethanol and CO2 during fermentation (Smiley, 1999). Dissolved $CaCO_3$ may also promote fermentation by maintaining elevated pH, favoring growth of bacteria that produces lactic acid in yeast mashes (Fryar 2009). Water chemistry suitable for amylase enzyme conversion of starch into fermentable sugar is central to commercially successful whiskey production where corn is used. It is also believed that having mash water slightly elevated in dissolved calcium is beneficial to the mashing process and to the final taste of the whiskey (Smiley, 1999, and Miller, 2016). In pre-industrial Kentucky, distilleries would have needed low-Fe and high-Ca concentration waters to achieve this as well as the natural waters of Tennessee's Highland Rim to allow commercial production of corn-based whiskey (Carson 2010). The location of commercial distilleries in this region is likely to be the result of environmental factors associated with the geology, geomorphology, and geochemistry of groundwater available.

Stratigraphy

The stratigraphy of the Highland Rim is comprised mainly of Mississippian-age formations of abundant limestone which dip east and outcrop on most of the cuesta. At the western edge of the eastern Highland Rim the oldest Mississippian units' outcrop in the dissected escarpment where

Tennessee's oldest distilleries are located. The Fort Payne and Chattanooga Formations contact one another along the hillsides of the hollows, of the dissected escarpment. The Ordovician-aged Leipers, Inman, and Catheys, Formations and the Bigby-Cannon Formations comprise the valley floors of the hollows where the distilleries are located. The Fort Payne Formation appears to be the uppermost strata in the groundwater recharge area of the streams next to the distilleries. The Fort Payne Formation is described by Chowns and Elkins (1974) as being a limestone with up to 30% silica with abundant chert nodules. The Chattanooga Shale is a dark black, organic shale that comprises the basil unit of the Fort Payne Formation. It is the impermeability of the Chattanooga Shale that causes the emergence of springs and artisan wells at the contact with overlying the Fort Payne Formation (Figure 3). Both the Cascade Hollow Distillery, Farrar Distillery, and Nelson's Greenbrier Distillery are located in terrains with these characteristics. The Jack Daniel Distillery is adjacent to two springs which emerge from the Leipers, Inman and Catheys formation near to the contact with the Bigby-Cannon Formation. The hillsides surrounding the area are feasibly within the recharge area of these springs and are topped by the Fort Payne Formation and the Chattanooga Shale (Wilson, 1969). The Mississippian-aged Fort Payne Formation seems to be the source of natural waters used by historical Tennessee distilleries in the area.

Kentucky's stratigraphy of the Inner Bluegrass region is primarily dominated by weathered carbonate rocks in karst topography (McDowell, 1986) and is encompassed by the Outer Bluegrass Region. Different erosional rates create an abrupt change in slope on the outskirts of the Outer Bluegrass, creating many escarpments that separate physiographic regions, including the Knobs located on the southwest boundary. Headward-eroding streams heavily incise these escarpments, and as they erode and retreat, erosional remnants or 'knobs' form. Kentucky whiskey distilleries are located within the eroded escarpment remnants of the Knobs and the karst terrain of the Inner

Bluegrass regions. The Inner Bluegrass is primarily composed of the middle Ordovician-aged Lexington Limestone, and underlain by the High Bridge Group. Weir and others (1978) describe a lateral gradational sequence of shale and limestone, where shale is predominant in the north, and limestone in the center and south. The primary members of the Lexington Limestone described by Cressman (1973) include the Curdsville Limestone and Logana, the Grier Limestone, and the Tanglewood Limestone and Sulphur Well. The Upper Ordovician-age Garrard Siltstone and Kope and Clays Ferry Formations, made up of equal interbedded limestone and shale, inter tongues with primarily the Tanglewood Limestone and Sulphur Well members where the distilleries are located. Similar to the Chattanooga and Fort Payne in Tennessee, the impermeability of the northern shales in Kentucky causes emergence from groundwater into the southern and central limestones creating karst terrain characteristics around the distilleries. Similar to the Highland Rim in Tennessee, the stratigraphy in the Knobs in Kentucky also includes the Fort Payne Formation overlain the Chattanooga Shale. This again, creates a terrain with similar characteristics of dissected escarpments near hollows in both the Knobs geomorphic province in Kentucky and the Highland Rim geomorphic province in Kentucky.

Groundwater Flow Models

Groundwater flow models throughout the Highland Rim show variation in localized flow across the major physiographic subdivision of the Highland Rim cuesta (Wolfe et al., 1997) (Figure 3). In general, surface streams in the dissected escarpment are the result of localized surface flow and emergence of groundwater from Mississippian limestone bedrock, which is the Fort Payne Formation in the hollows of the escarpment of the Highland Rim (Brahana and Bradley, 1986). First-order streams of the dissected escarpment of the Highland Rim are fed by ground water emerging from the contact between the Fort Payne Formation and the Chattanooga Shale (Figures

3 and 4). The unconfined Fort Payne Formation serves as the recharge area for the aquifer of the Highland Rim, though ground water and streams in the dissected escarpment can be recharged from as far as the eastern half of the Barrens physiographic subdivision (Figure 4). These recharge zones contain active dissolution as slightly acidic water reacts with the limestone to create larger openings (Brahana 1986). Groundwater is generally modeled as flowing to lower elevation in the Highland Rim in the Mississippian formations. Flow from the water table is on steep gradients, resulting in quick movement towards areas of discharge (Brahana 1986). The aquifer system has low intergranular porosity and permeability, resulting in groundwater flow mostly along joints, fractures, and bedding planes (Brahana 1986). Ground water flow in the Ordovician units is primarily facture flow (Broshears, 1986). The historical whiskey distilleries of Tennessee are located near the contacts of the strata where groundwater emerges at the surface. The Jack Daniel distillery is located at the western base of a hill, at the spring emerging from the Leipers, Inman, and Catheys Formation, near the contact with the underlying Bigby-Cannon Formation; the Fort Payne Formation sits atop the hill (Wilson, 1969). The Cascade Hollow distillery is situated on the north side of a stream, which begins in the Fort Payne and crosses the Leipers, Inman, and Catheys formation contact (Wilson, 1970). The site of the Farrar distillery is on the north side of a stream which begins in the Fort Payne Formation and crosses the Leipers, Inman, and Catheys contact. Nelson's Greenbrier Distillery is situated near the west side of a stream beginning in the Fort Payne Formation, and crosses through the Chattanooga shale near the Northwest side of the Highland Rim. The geochemistry of the strata of the Highland Rim seems to be the dominant factor in geochemistry of groundwater in the aquifers in the eastern Highland Rim (Broshears, 1986).

Groundwater aquifers in karst terrain can be described as 'shallow conduit-flow (SCF) carbonate aquifers' (Thrailkill 1991). Significant portion of recharge of SCF aquifers comes from surface water flow diverting underground through discrete openings called 'swallets' along surface streams and underground sinkholes (Thrailkill 1991). Combined with the efforts of soil infiltration, this creates a dendritic flow system within the underlying limestone that discharges at a spring. Groundwater flow in this area is very shallow and widespread, and follows the gradient of surface streams. Distilleries are located along these surface streams and springs within the Lexington Limestone strata.

Aquifer Geochemistry

Published geochemical analyses of groundwater from aquifers in the eastern Highland Rim and Inner Bluegrass region are scarce. Aggregate geochemical data from the aquifers of the Highland Rim are available (Broshears, 1986) (Figure 5) and show that the water is hard with an average calcium carbonate concentration of 200 mg/L in Mississippian aquifers, and 250 mg/L in Ordovician aquifers. The iron content of Mississippian aquifers is 300 ug/L and Ordovician aquifers contain and average of 100 ug/L (Broshears, 1986). Ambient temperatures of groundwater are between 16.6 – 17.7°C (Johnson, 2016). It is the goal of this research to provide geochemical data of the natural waters in historically important whiskey-making regions in Kentucky and Tennessee to determine their role in the location of these industries.

Methodology

Over the fall of 2020, data collection of river water in the Highland Rim as well as the Knobs and Inner Bluegrass physiographic regions were taken at First-Order streams that fed into the hollows where pre-industrial Tennessee and Kentucky era whiskey distilleries are located. Four of the samples were collected in the Highland Rim, and eight of the samples were in the Knobs or Inner Bluegrass regions (Figure 2). These samples were collected in 125mL polyethylene plastic bottles, acidified using Nitric Acid for storage and transportation, refrigerated till analysis, and were analyzed using an ICP-MS at Hazan Huffman Labs in Golden CO. The ICP-MS tested for trace elements of Calcium (Ca), Magnesium (Mg), and Iron (Fe). Data collection of pH and temperature (°C) were also taken at the collection sites (Table 1) from the source itself using Milwaukee Instruments MW102 pH and Temperature Meter and was calibrated using General Hydroponics pH 4.01 & pH 7.0 Calibration Solution Kit (8 oz).

Results

The pH of surface waters in the locations ranges from 7.7 – 8.28 while temperature ranged from 7.6 – 16.6 °C (Table 1). The data findings from the ICP-MS analysis showed absolute Ca and Mg concentrations high, while Fe concentrations exceptionally low (Table 2). After normalization of the data for ternary diagram analysis, Ca concentration % in surface waters of KY ranged from 65% - 93%, Mg concentration % ranged from 6% - 34% and Fe concentration % ranged from 0.05% - 0.3%. Waters tested in TN had Ca concentration % ranging from 82% - 94% while Mg concentration % ranging 5% - 17% and Fe concentration % ranging from 0.01% - 0.4 %. Note that Fe's concentration % was adjusted by a magnitude of 2 for graphical representation. The ternary diagrams show the concentration % relative to each other, showing the Ca-Mg-Fe concentration ratios in the water samples (Figure 6) which show that Ca-Mg-Fe concentration ratios in TN and KY are consistent with one another.

Athertonville, KY yielded a concentration of 40.800mg/L Ca, 10.600mg/L Mg, and 0.051mg/L Fe with an average pH of 7.94 and ambient temperature of 10.5 °C. Athertonville yielded the smallest ratio concentration % Ca in all samples collected. Bardstown, KY showing 69.900mg/L Ca, 36.100mg/L Mg and 0.156mg/L Fe, with the highest pH value of 8.28 and temperature 9.4 °C. It should be noted that Bardstown contained the highest Mg ratio concentration %. Castle and Key, KY had concentrations with 93.500mg/L Ca, 7.100mg/L Mg, and 0.166mg/L Fe with a pH of 7.94

and temperature 9.7 °C. Four Roses, KY included 88.700mg/L Ca, 8.500mg/L Mg, and 0.243mg/L Fe, however due to complications, no pH or temperature readings were collected. Frankfort, KY water samples have 103.000mg/L Ca, 10.800mg/L Mg, and 0.342mg/L Fe with a pH of 7.9 and temperature 9.6 °C. Grassy Spring (Woodford), KY yielded 94.400mg/L Ca, 6.420mg/L Mg, and 0.184mg/L Fe with a pH of 7.86 and temperature of 11°C. Lexington, KY samples have concentrations of 96.200mg/L Ca, 10.500mg/L Mg, and 0.082mg/L Fe with a pH of 7.7 and temperature 11.1 °C. Loretto, KY included of 90.700mg/L Ca, 23.200mg/L Mg, and 0.045mg/L Fe with pH of 8.18 and the lowest collected temperature of 7.6 °C.

Cascade Hollow, TN yielded 19.900mg/L Ca, 3.640mg/L Mg, and 0.038mg/L Fe with pH 8.04 and temperature 15.2°C. Greenbrier, TN have the lowest % Fe ratio concentration which included 68.500mg/L Ca, 14.600mg/L Mg, and 0.007mg/L Fe as well as the lowest collected pH of 7.08 and ambient temperature of 15.5 °C. Lynchburg, TN yielded the highest recorded % Fe ratio concentration at 0.39% Fe, including 40.100mg/L Ca, 4.890mg/L Mg and 0.175mg/L Fe. The highest collected temperature at 16.6 °C with a pH of 7.92. Noah, TN yielded the highest % ratio concentration of Ca, 94.496%, as well as the lowest % Mg, 5.410%, and included: 26.200mg/L Ca, 1.500mg/L Mg and 0.026mg/L Fe, as well as a pH of 7.72 and temperature of 13 °C.

Discussion

Geologic study done in the Knobs and Inner Bluegrass of Kentucky as well as the Highland Rim of Tennessee show widespread limestone sedimentary deposits creating karst terrains within and around dissected escarpments. This terrain creates a suitable environment to change the geochemistry of the groundwater such that it will be enriched in Ca and Mg. Limestone being primarily composed of Calcite, $CaCO_3$, and Mg being easily interchangeable with Ca, inclusion of High Mg Calcite and Dolomite within these karst terrains are common. So, the raw data came as no surprise seeing Ca and Mg concentrations much higher than Fe concentrations in this limestone dominated area (Figure 2 showing widespread sedimentary carbonate). These groundwater sources have proven to produce quality tasting corn whiskey, so overtime the continuation and location for distilleries has been controlled by the economic efficiency for quality whiskey making. With groundwater chemistry being the result of natural sources, these karst or hollow terrains make for excellent distillery locations due to the geochemical ratio of Ca-Mg-Fe in the water used during the production of whiskey. The ratios of Ca-Mg-Fe of TN's Highland Rim first-order streams are consistent with ratios of KY's Knobs and Inner Bluegrass first-order streams, suggesting the physiographic regions of the Knobs and Inner Bluegrass are consistent with the Highland Rim of TN.

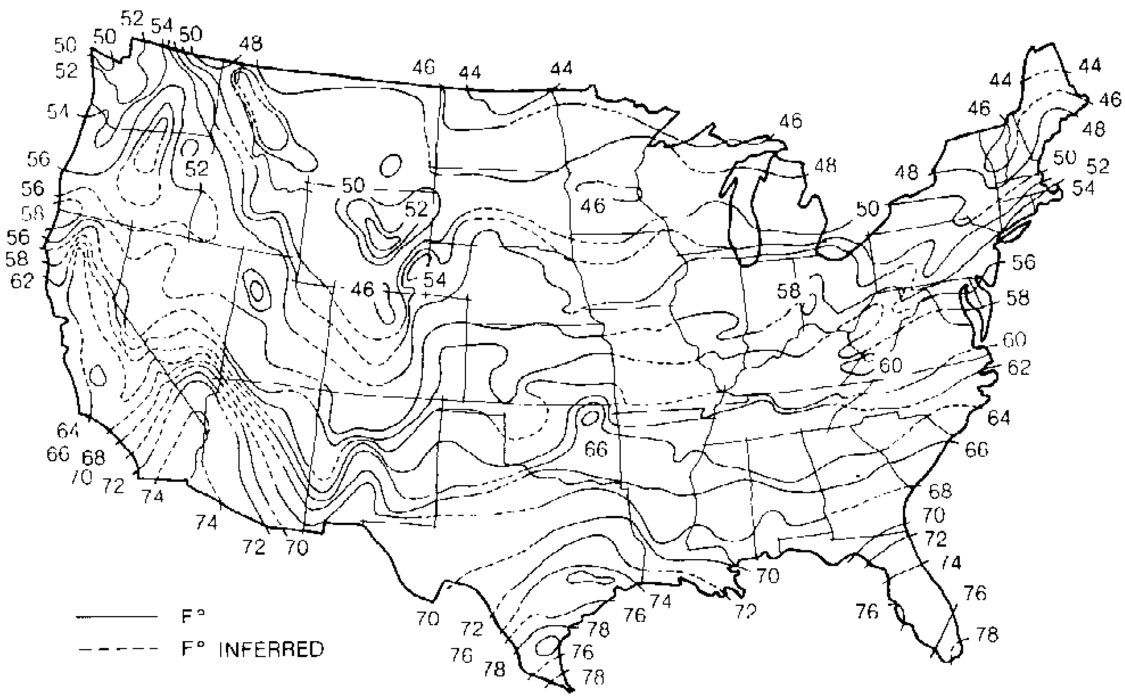
Average groundwater geochemical data from Mississippian and Ordovician aquifers and the first use of water in the watershed suggest that chemical conditions of the water available for mashing meet the requirements for efficient use of corn as source of fermentable sugar at Tennessee Whiskey distillery locations in the dissected escarpment of the eastern Highland Rim. Specifically, iron content of 300 ug/l (0.3ppm) in Mississippian groundwater and 100 ug/l (0.1 ppm) in Ordovician groundwater are well below the 25ppm threshold for iron content in mash water to prevent denaturing of amylase enzymes. The role of Ca in 'improving the flavor' of finished whiskey is not well understood at this time.

However, there seems to be ample Ca in the form of calcium carbonate in both Mississippian and Ordovician groundwater sources in TN and KY according to geochemical analysis of the aquifers of the eastern Highland Rim (Figure 5) and related strata of the Knobs and Inner Bluegrass. It is possible that Ca (and to some extent Mg) could be important factors in esterification of acids and aldehydes in the distilled spirit. Calcium and magnesium oxides are known to be catalysts in esterification in biodiesel production (Lee et al., 2014). If Ca and Mg ions at low temperature serve a similar function in distilled spirits during dilution and barreling as calcium and magnesium oxides do in esterification at high temperature in biodiesel it is possible that high Ca waters improve the finished 'taste' of whiskey. Further investigation of The Knobs and Inner Bluegrass regions stratigraphy and aquifers should provide further insight on ideal locations for making corn whiskey as well as the geochemical differences between them.

Conclusion

Whiskey production and location of distilling in pre-industrial Tennessee and Kentucky can be traced back to the physiography, hydrology, and stratigraphy of the surrounding area. The data collected of water concentrations of important ions in Kentucky and Tennessee First-Order streams yielded results that can compare similar hydrology, stratigraphy, and physiography between the Highland Rim of TN, and the Knobs and Inner Bluegrass of KY. The geochemical change in these locally collected water sources originate from the groundwater of karstified limestone terrain and creates an optimal Ca-Mg-Fe ratio to make a better 'tasting' whiskey that propelled the continuation of whiskey distilling in theses terrains throughout the duration of America's whiskey distilling history.

Figures and Tables



Ground water temperatures. Map courtesy of National Water Well Association.

Figure 1.)
Taken from www.ngwa.org

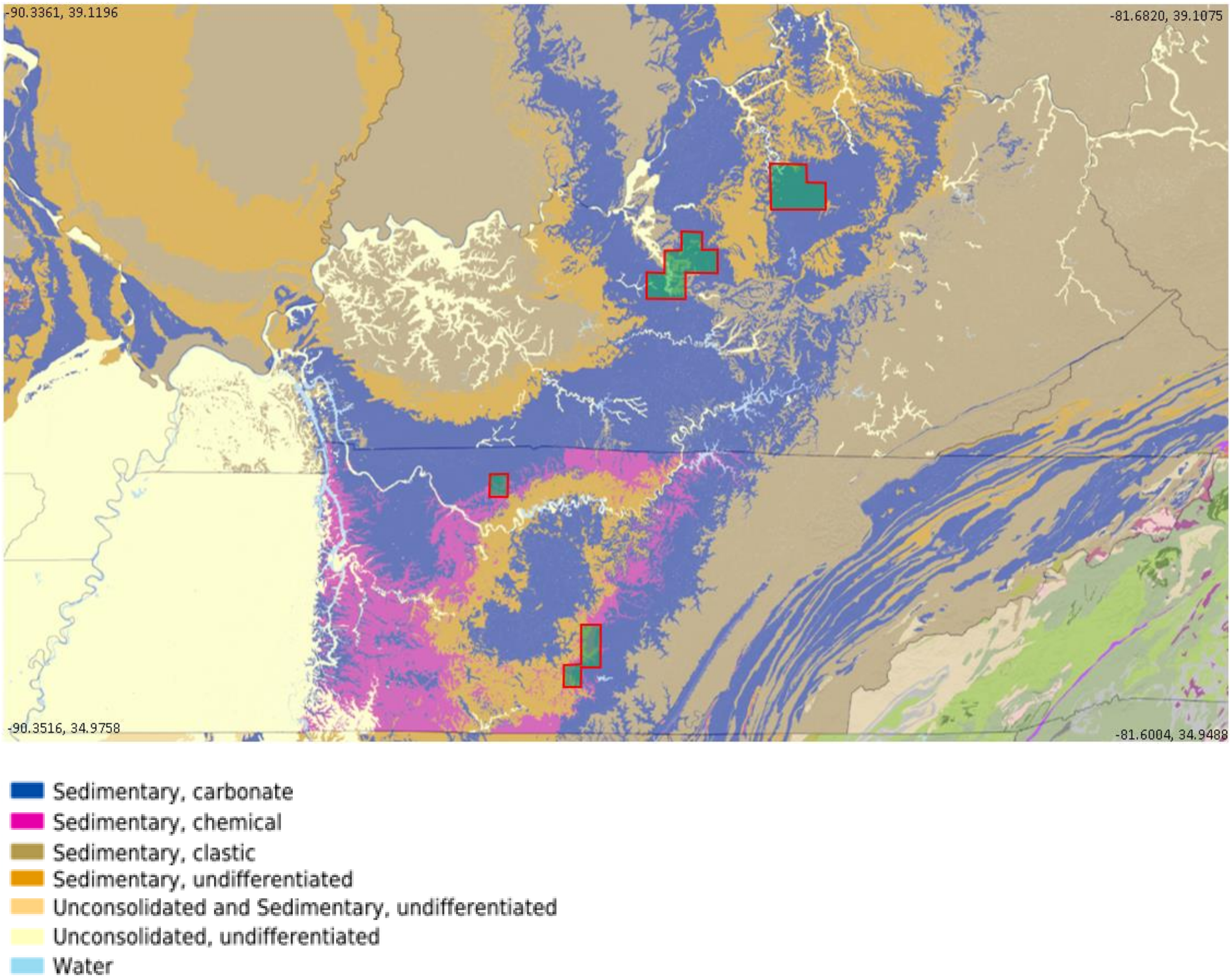


Figure 2.)
Geologic Map of KY and TN
Figure shows a geologic map of KY and TN, including units of sedimentary carbonate, chemical, clastic, and undifferentiated, as well as unconsolidated, undifferentiated material. Highlighted in green are locations of where data samples were taken (Horton et. al. 2017).

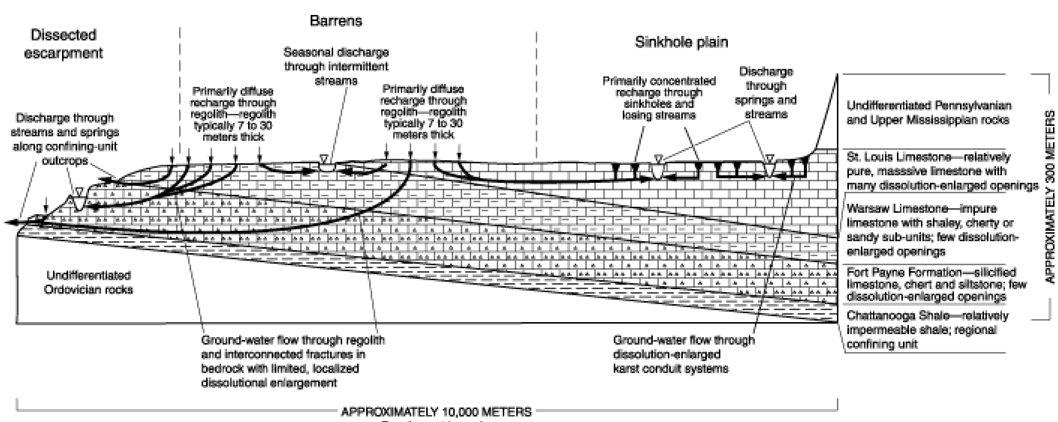


Figure 3.)
Generalized hydrogeologic section through the Eastern Highland Rim in Tennessee (Brahana 1986).

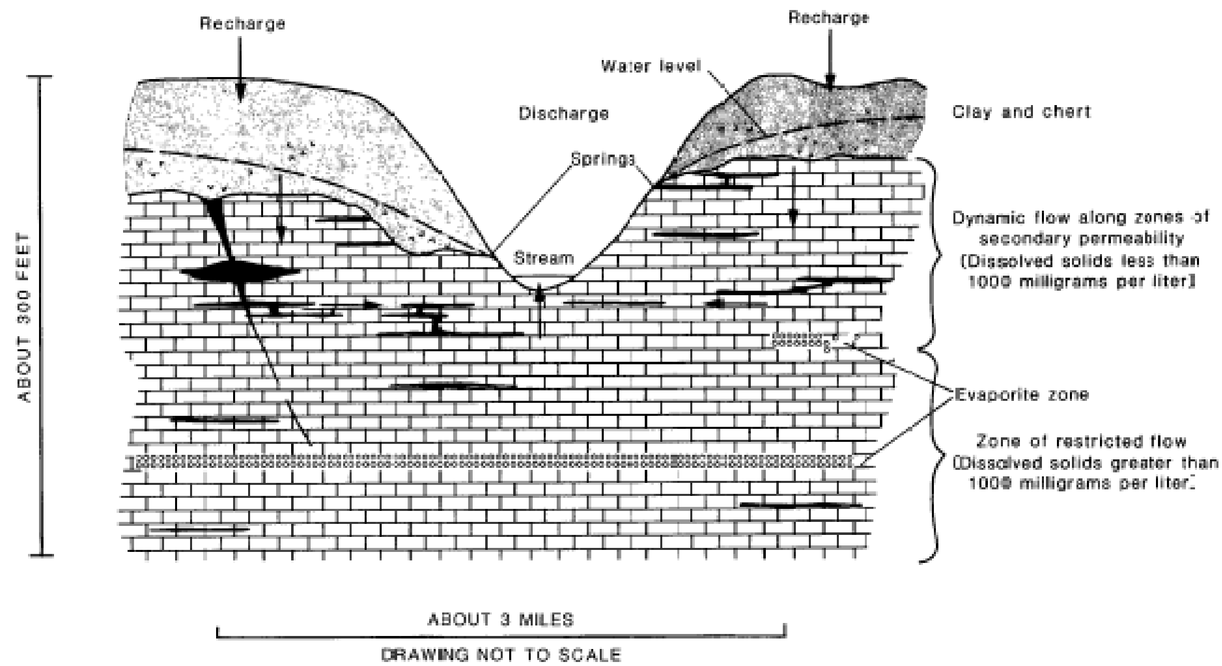


Figure 4.)
Conceptual model of ground-water occurrence in the limestones of the Highland Rim aquifer system (Brahana 1986).

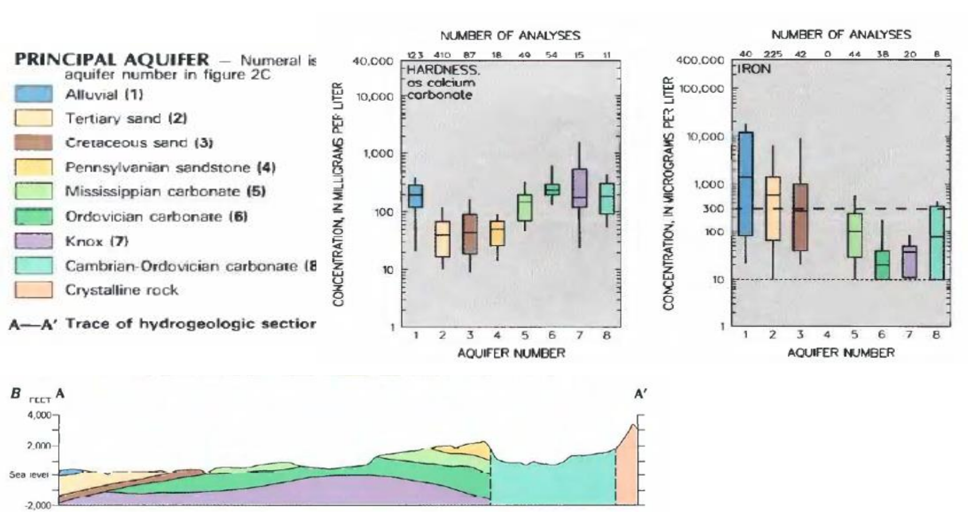


Figure 5.)
Aggregate geochemical data from the aquifers of the Highland Rim (Broshears 1986).

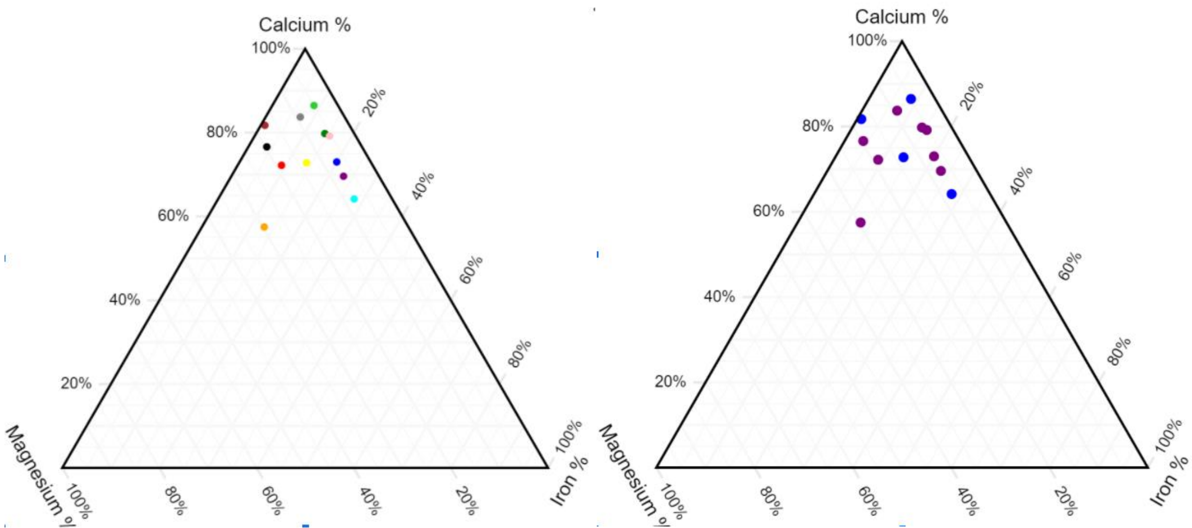


Figure 6.)
Ternary Diagrams
Ternary diagrams comparing Ca-Mg-Fe concentration against each other in collected water samples. Note that Fe's % was adjusted for comparison's sake, as Fe was too small to be seen using its absolute concentration. Key is located in Table 1 comparing by state, and by actual collected site.

pH and Tempertaure Data from Water Sampling Locations			
Location	**pH**	**Temperature (°C)**	**Date**
Athertonville	7.94	10.5	11/17/2020
Bardstown	8.28	9.4	11/17/2020
Cascade Hollow	8.04	15.2	11/15/2020
Castle & Key	7.94	9.7	11/18/2020
Four Roses	not collected	not collected	11/18/2020
Frankfort	7.9	9.6	11/18/2020
Grassy Spring (Woodford)	7.86	11	11/17/2020
Greenbrier	7.08	15.5	11/16/2020
Lexington	7.7	11.1	11/18/2020
Loretto	8.18	7.6	11/17/2020
Lynchburg	7.92	16.6	11/16/2020
Noah	7.72	13	11/16/2020

Table 1.)
Table of pH and Temperature (°C) of collected data sites.

Lab Sample ID	Customer Sample ID	Calcium mg/L	Magnesium mg/L	Iron mg/L	Sum	Calcium % (100/Sum)*mg/L	Magnesium % (100/Sum)*mg/L	Iron % (100/Sum)*mg/L	Iron Adjusted % x100		Ternary Legend	
20H01923-001	Blank Standard (Nitric Acid+ Distilled Water)	0.036	0.157	0.002	0.195	18.462	80.513	1.026	102.5641		**did not plot standard**	
20H01923-002	Athertonville	40.8	10.6	0.051	51.451	79.299	20.602	0.099	9.9123		KY	Red
20H01923-003	Bardstown	69.9	36.1	0.156	106.156	65.846	34.007	0.147	14.6954		KY	Orange
20H01923-004	Cascade Hollow	19.9	3.64	0.038	23.578	84.401	15.438	0.161	16.1167		TN	Yellow
20H01923-005	Castle & Key	93.5	7.1	0.166	100.766	92.789	7.046	0.165	16.4738		KY	Green
20H01923-006	Four Roses	88.7	8.5	0.243	97.443	91.028	8.723	0.249	24.9377		KY	Blue
20H01923-007	Frankfort	103	10.8	0.342	114.142	90.238	9.462	0.3	29.9627		KY	Purple
20H01923-008	Grassy Spring (Woodford)	94.4	6.42	0.184	101.004	93.462	6.356	0.182	18.2171		KY	Pink
20H01923-009	Greenbrier	68.5	14.6	0.007	83.107	82.424	17.568	0.008	0.8423		TN	Brown
20H01923-010	Lexington	96.2	10.5	0.082	106.782	90.09	9.833	0.077	7.6792		KY	Gray
20H01923-011	Loretto	90.7	23.2	0.045	113.945	79.6	20.361	0.039	3.9493		KY	Black
20H01923-012	Lynchburg	40.1	4.89	0.175	45.165	88.786	10.827	0.387	38.7468		TN	Cyan
20H01923-013	Noah	26.2	1.5	0.026	27.726	94.496	5.41	0.094	9.3775		TN	Limegreen

Table 2.)
Table of collected water samples
Table shows Ca, Mg, and Fe concentrations in mg/L for each water sample collected in this study. The absolute concentrations are on the left, and then normalization done on the right showing % of each element compared to each other. To the far right, shows the state, either KY or TN for each sample as well as Figure 6.'s legend for the Ternary diagrams below.

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