CHEMICAL WEATHERING YIELDS IN RELATION TO LAND USE IN THE CUYAHOGA AND MAUMEE WATERSHEDS

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ABSTRACT

Data obtained from the National Center for Water Quality Research database at Heidelberg University are used to look at two steams, the Maumee River and the Cuyahoga River. Data from a wet year, 2009, and from 2011, a dry year, are used to determine the relationship between river discharge (Q), with the concentration of dissolved silicon (Si), or reactive silicate in both rivers. Log vs log plots show that, except at low discharge rates, both rivers behave chemostastically in that there is little change of dissolved Si concentration with discharge. With data from both years, the silicate chemical weathering yields were calculated for both rivers. Because of the tillage, fertilizer, and tile drainage, it was initially hypothesized, that the agriculturally dominated Maumee would have higher weathering yields that the more natural dominated watershed of the Cuyahoga River. Calculations demonstrated the opposite, with the Cuyahoga yields being 2.76 and 4.79 tons Si/km^2/yr and the Maumee being 1.76 and 2.45, for 2009 and 2011, respectively.

ACKNOWLEDGEMENTS

First and foremost, I want to thank Dr. Lyons for the opportunity he provided me to work with him on this project. I also want to thank him for not only caring about me in an academic sense but also in the personal world too. Dr. Lyons and Dr. Carey both welcomed me into their home on multiple occasions for gatherings with the research group, for that I am thankful as well.

Though Dr. Lyons I connected with Dr. Sarah Fortner, Wittenberg University. Information provided by her in combination with Heidelberg University made this entire project possible.

I want to thank Alex Smith for being the first person in the School of Earth Science I connected with and making we feel welcome from the start and remaining friends throughout our time in school together.

I want to thank those in the Lyons research group for all the assistance they provided me throughout this process. Melisa Diaz in particular was extremely helpful and always willing to make time to talk.

Another person who deserves thanks is my academic adviser Dr. Karen Royce. She helped me stay on track to graduate and helped me remedy all the curve balls I could've possibly thrown at her. She is a true blessing and I am grateful for all she did for me.

Lastly but not least I want to thank The School of Earth Sciences for making this all possible and providing me with lots of great experiences I will keep as memories forever. Thank you.

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INTRODUCTION

Quantification of the relationships between stream flow and dissolved chemical concentrations has been an important research activity in both hydrology and geochemistry. Concentration vs. discharge relationships compare the concentration of solutes produced primarily by mineral weathering products, the dissolution of soluble salts and the solubilization of inorganic matter in rivers compared to the discharge of the river. These relationships have been used as clues to the hydrochemical and biogeochemical processes that control the dissolved chemistry in rivers and streams. River discharge is defined as the volume of water passing a point in a river in a given time. The relationships between discharge and solute concentration have been used to suggest that many rivers in the US display chemostatic behavior, where chemostatic behavior is defined as when the concentration of a stream solutes vary little, while the discharge of said stream may vary greatly. Previous thought had suggested that the dilution effect of increased discharge should dominate solute concentrations. The work of Godsey et al. (2019) suggested that this paradigm needed revisal.

Godsey et al. (2009) demonstrated that the log-log plots of these two parameters (i.e., stream discharge and solute concentration) follow a power law relationship or C=aQ^b, where C equals the dissolved concentration, Q is the discharge, a is a constant, and b is the slope of the log-log plot. When the slope is at or near zero, chemostatic behavior of the particular solute exists (Godsey et al., 2009; Maher, 2011), and that pre-event water must be a major component in streams during storm or high flow events (i.e., little to no dilution occurs) (Clow and Mant, 2010). Subsurface flow depth, along with the sources of water may have great influence on controlling chemostatic behavior (Kroger et al., 2017). More recent work by Godsey's group has suggested that these initial conclusions about concentration – discharge relationships were generally correct for dissolved weathering derived products, and this chemostatic behavior was due in part to groundwater buffering and rapid reactions controlling solute geochemistry (Godsey et al. 2019). Over the past decade numerous studies have determined that for chemical weathering products, such as dissolved Si or H_4SiO_4, behave chemostatically (Musolff et al., 2015). However, variation in concentrations of weathering derived solutes are negatively related to long term climate variables such as precipitation (Godsey et al., 2019). It has also been hypothesized that dissolved Si chemostatic behavior in streams may be related to its interactions with biological forms of Si which are controlled by temperature and the amount of suspended material present in the water (Godsey et al., 2019). Therefore, differences in watershed location and hydrology effected by land use may have important consequences in this relationship (Godsey et al., 2019)

In this study, two Ohio river locations are investigated: the Cuyahoga River and the Maumee River. These two rivers were chosen based on their differences in land use and lithologic composition, but similarity of climate. In addition, this study was focused on two different years, 2009 and 2011, which reflect very different flow conditions in the rivers.

STUDY LOCATIONS

Cuyahoga River

The Cuyahoga River watershed drains a total of 2,103 total square kilometers in northeastern Ohio. The eastern portion of the watershed is a mixture of agricultural land uses such as cultivated crops and forest. The western portion of the watershed predominantly comprises urban development, including Cleveland and some of its suburbs, Akron, and Kent. Geologically, the Cuyahoga is a very young river compared to many of the other glacially formed rivers in the Great Lakes region. During the most recent glacial retreat, more than 12,000 years ago, the upper Cuyahoga was redirected north into the uncovered vestiges of a pre-glacial valley, which today comprises Cuyahoga Valley National Park. (ODNR). Prior to development, the mouth of the Cuyahoga was a minor stream with an extensive flood plain reaching 2 kilometers in width. The river's mouth was frequently blocked by sand and the floodplain consisting of wetlands and narrow beaches split the city's 10 to 15-meter-high bluffs. However, in recent history the river's floodplain and shore have been altered significantly due to the placement of fill north of the bluffs in Lake Erie along with the channelization of portions of the river for economic development purposes.

Maumee River

The Maumee River drains approximately 13,012 total square kilometers in northwestern Ohio. The Maumee is a major tributary to the western Lake Erie Basin and its watershed is composed of forests, cultivated crops, and some urban development, including Toledo, Findlay, Lima, etc. The upper portion of the river drains agricultural lands while the upper Maumee is used as a major transportation corridor for commercial freight entering and leaving the Port of Toledo which has led to concerns in the past that too much industrial and waste water contaminants had been discharged into the lower portion of the river.

Land Use

The land uses of the two watersheds are very different. The Cuyahoga is 34% forest, 39.5% urban and 9% agriculture, of which 12% is pasture (Baker et al. 2014). The Maumee on the other hand is 73% agricultural of which 74% is in row crops such as corn and soybeans (Baker et al. 2014, Fitzgibbon et al., 2008). Vandeveene et al. (2012) have suggested that agricultural practices can have a great disruption on the naturally occurring Si cycle in that the uptake of Si into agricultural biomass such as corn, can remove large amounts of Si from the soil-water system. In addition, because much of the row crop landscape has drain tiles associated with it, it was thought that this would affect hydrological flow paths and hence dissolved Si fluxes and yields. In previous work on the maximum dissolved Si yields was found to be substantially lower in watersheds where corn was grown compared to other nearby land uses watersheds of similar geology and soil type (Fortner et al., 2012). These lower yields were assumed to be due to lower contributions of Si-enriched base flow and the previous loss of easily weathered dissolved Si due to fertilizer-enhanced weathering (Fortner et al., 2012). Therefore, I hypothesize that given the differences in land use between these two watersheds, the dissolved Si chemical weathering yields are lower in the agriculturally dominated Maumee River system.

METHODS

The data in this study are from the National Center for Water Quality Research (NCWQR) database at Heidelberg University, https://ncwqr.org/monitoring/. The database is a tributary loading program that measures the amount of components that move down stream past a sampling station on these rivers each year. The tons of constituents moving past a sampling station represent the loading to downstream receiving waters. Accurate loading measurements require information on stream flows and frequent concentration measurements in the water flowing past the sampling station. NCWQR measurements of many constituents, were recorded daily since roughly 1975. These solutes include ammonium, chloride, sulfate, and dissolved reactive silica. For my purposes the data were condensed to two full calendar years, 2009 and 2011. These two years were chosen because one is considered a wet year, 2011, and 2009 being a dry year in relation to the average precipitation. For me, doing this will allow another point of comparison, not only when comparing to each other, but also comparing data within the same location.

In order to determine if these two river systems were behaving chemostatically with regard to dissolved Si, the individual daily discharges were plotted vs dissolved Si for both rivers for both years. This was done as a log-log relationship as detailed by Godsey et al. (2009).

With these data, all of the components to calculate silicate chemical weathering yields are available. The Si-chemical weathering yield is the rate at which dissolved Si is produced per watershed area on an annual basis, or the geochemical flux divided by the area of the watershed. The assumption is that little to no dissolved Si is introduced via precipitation (Welch et al., 2010). To do the calculation one must obtain the average discharge throughout the stream for the entire year. That is then multiplied by the average concentration of dissolved Si in the stream over the same time period. The resulting value is then divided by the total watershed area, which then gives you the weathering rate of the watershed in relation to dissolved Si. The units of discharge are cubic feet per second (values later converted to liters per year), the concentration is in mg/L and the watershed area is in square km.

RESULTS AND DISCUSSION

Figure 1 represents the concentration of dissolved Si in the river versus the discharge for both rivers and both the wet and dry years (2011, 2009, respectively). Basic but useful information found on these graphs show that the maximum discharge, in cubic feet per second (CFS), was around 90,000 in both 2009 and 2011 for the Maumee river. However, in the Cuyahoga, the maximum discharge was 11,000 CFS in 2009 and 19,000 in 2011. For the Maumee river as the discharge decreases and approaches zero, the greater the variability in the concentration of dissolved Si concentration.

In figures 7 and 8, the Cuyahoga River data clump more closely together in 2011, than 2009, showing more of a linear trend in the data. Some clumping of data can be seen in 2009, but the concentration range varies much more than that of 2011 showing more data variability especially at the lower discharges. The Maumee river plots (Figure 5 and 6), on the other hand, show a different trend. There is a distinct upwards trend at lower discharges but, the data almost reaches a maximum. It finally levels out as it approaches log Si = 1.

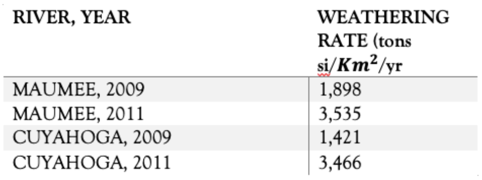
Recent more detailed work in the relationship between discharge and geogenic produced solutes, such as dissolved Si, strongly suggest that the major sources of higher concentrations to streams is from groundwater, but these higher concentrations can be diluted by sources of lower Si concentration water as the event proceeds (Rose et al. 2017). Thus, flow path connectivity and how it varies in both time and space can greatly affect the shapes of concentration-discharge relationships. The large variation in concentrations at lower discharges in both of my data sets, but particularly the Maumee data probably reflects this behavior. At these lower flows there may be different water source contributions to these baseflow contributions. This large variation in dissolved Si could possibly reflect the various stages, and locations, of agriculturally dominated tile drainage discharge. As flows measured above Q=log 3-3.5, the concentrations of dissolved Si are well-mixed with all the major water sources within the watershed system (i.e., event water, groundwater, soil water, and tile drain water), and become chemostatic in behavior. Because of the smaller amount of watershed area in the Cuyahoga that is of agricultural land use, the low discharge scatter within the dissolved Si data is less.

The main difference between the two watersheds, as stated earlier, is that the Maumee watershed is generally composed of a landscape dominated by agriculture. Hydrologically speaking, the biggest impact is the use of tile drainage, in these agricultural lands. Tile drainage is a type of drainage system that removes excess water from soil just below the surface. The phrase tile drainage derives from its original composition from tiles of fired clay. Today tile drainage is commonly corrugated and PVC slotted subsurface pipes which discharge water into surface ditches that it sends into streams to control the depth of water table and minimized recharge and water logging (Sheler et al. 2013). This rapid movement of the water should have a serious effect on the chemical weathering within the watershed. The original path water would take to get to the river would be close to or on the surface, instead of most of the water infiltrating into the ground and traveling through the porous soil. When traveling through the soil, water would pick up various minerals that may influence the weathering of the riverbed. When this stage of water connectivity through the deeper soil is passed over, water is transported directly to the stream rather than flowing into the deeper groundwater systems leading to increased water-rock interaction and potential chemical weathering.

Much work has been done using dissolved Si and the sum of Na+K+Mg-Ca-Ca_{carb} to determine the watershed weathering yields of aluminosilicate minerals and it all will not be repeated here. The dissolved Si values in rivers (and hence the Si weathering rates) are primarily controlled by the lithology of the catchment and the mean annual temperature at that location (Meybeck, 1980). Lyons et al. (2005) have suggested that chemical weathering in closely tied to physical erosion as well so that topography in also an important factor in general. Volcanic rocks weather faster than more felsic lithologies which in turn weather faster or equal to the rates of silicate-rich sedimentary rocks (Berner and Berner, 1996).

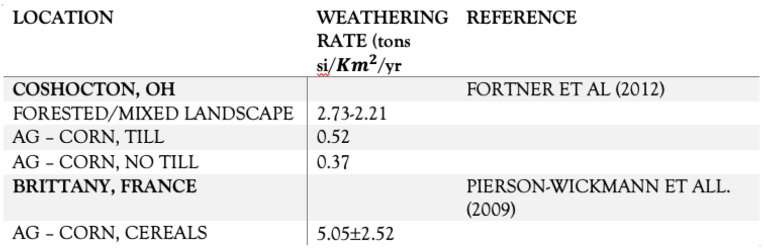
Others have suggested that agricultural activity could increase chemical weathering rates in part due to the tilling of soil, the addition of fertilizer, and the replumbing of the near sub-surface hydrological system. This has certainly been established in the upper Mississippi River drainage where increased fertilizer use, liming (i.e., addition of calcite/dolomite to increase soil pH) and the use of tile drainage have increased the fluxes and yields of dissolved bicarbonate (Raymond et. al., 2008).

In order to asses the impact of agricultural activities on the aluminosilicate mineral chemical weathering rates in these two watersheds, using the method of Lyons et al. (2005) I have calculated dissolved Si weathering yields in both watersheds during both 2009 and 2011 (the dry" and the wet years, respectively) The Cuyahoga watershed yields were 2.76 and $4.79 (Tons\ Si/Km^2/yr)$, respectively, which the Maumee yields were 1.76 and 2.45 $(Tons\ Si/Km^2/yr)$respectively. Clearly the Cuyahoga yields were 1.6 and 2 times higher than the agricultural dominated Maumee, and of course, the rainier years had higher yields by factors of 1.7 and 1.4, respectively.



RIVER, YEAR	**WEATHERING RATE (tons si/Km^2/yr**
MAUMEE, 2009	1,898
MAUMEE, 2011	3,535
CUYAHOGA, 2009	1,421
CUYAHOGA, 2011	3,466

Table 1: The calculated weathering rate for each stream in each year.



LOCATION	**WEATHERING RATE (tons si/Km^2/yr**	**REFERENCE**
COSHOCTON, OH		FORTNER ET AL (2012)
FORESTED/MIXED LANDSCAPE	2.73-2.21	
AG – CORN, TILL	0.52	
AG – CORN, NO TILL	0.37	
BRITTANY, FRANCE		PIERSON-WICKMANN ET ALL. (2009)
AG – CORN, CEREALS	5.05±2.52	

Table 2: Weathering rates from other papers for comparison.

These calculated yields are similar to those determined for other, smaller watersheds in Ohio (Fortner, et al., 2012), and the small, granitic agricultural watersheds in NW France (Table 2). All this previous work as well as what I have presented here suggest that agricultural activities do not necessarily lead to increased aluminosilicate mineral weathering above that of non-agricultural watersheds of similar age and soil. The uptake and removal of agricultural biomass may buffer any enhanced solubility of Si in agricultural landscapes as suggested by Vandevenne et al. (2012).

CONCLUSIONS

Data from the National Center for Water Quality Research Center, Heidelberg University were used to value the relationship between river discharge (Q) and the dissolved silicon (Si) concentrations for the Maumee and Cuyahoga Rivers, Ohio. This was done for both a'wet year (compared to the mean) in 2011 and a dry year in 2009. When I compared this relationship both rivers generally demonstrated chemostatic behavior at higher discharges. There was much more scatter in the data at low concentrations indicating different sources of water over time, and less connectivity within the various water flow paths in the watersheds. The Cuyahoga River data suggest there may be dilution of dissolved Si during the highest flows.

In addition, aluminosilicate chemical weathering yields were calculated for both watersheds for both years by using the mean dissolved Si concentrations and the total discharge for the respective years. It was expected that the rivers would have different values due to their great difference in land-use characteristics. The Maumee watershed is greatly dominated by row-crop agriculture and was hypothesized to have higher yields due to tillage and abundant tile drainage which has been demonstrated to decrease water recharge. Yields in both rivers were higher during the wetter year, strongly indicating the importance of increased precipitation and water flux to the process of chemical weathering. However, the Cuyahoga dissolved Si yields were higher than those of the Maumee in both years, and almost a factor of 2 higher during the wetter year of 2011. The calculated yields for both rivers are similar to what has been previously determined.

RECOMMENDATIONS FOR FUTURE WORK

With these data being limited to 2 years, one thing that could be done is to complete the same calculations with more years from the same database. The data used were also narrowed down to 2 river locations. The same calculations from other river data could also be compared to add information to this topic.

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APPENDIX A

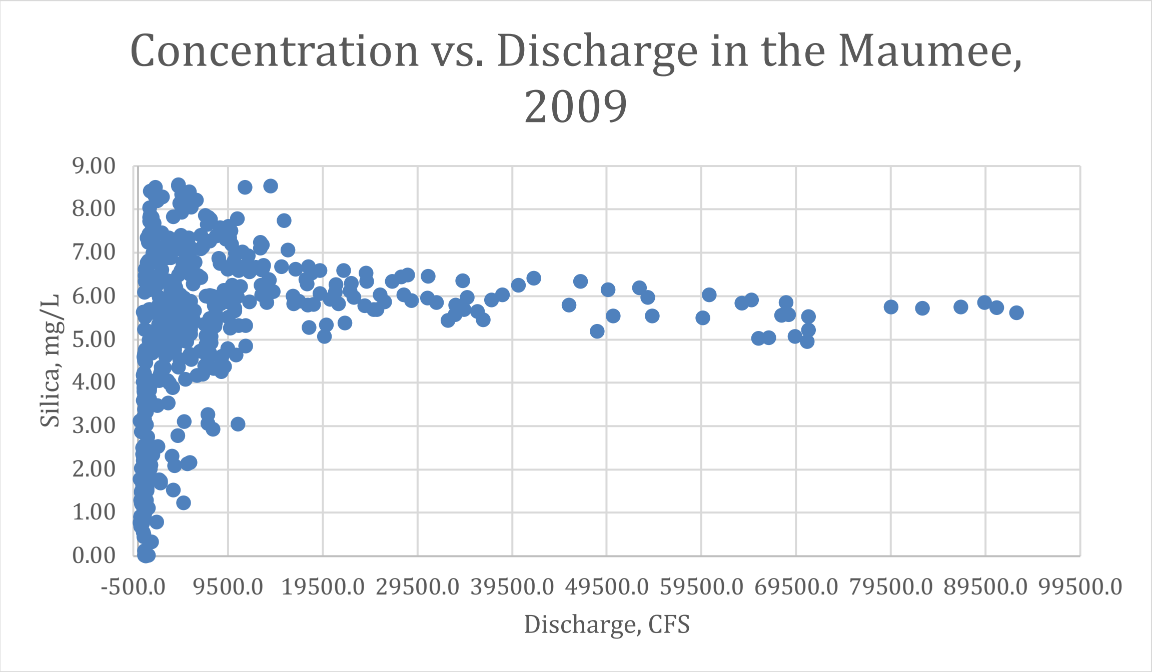


Figure 1: NCWQR data formed into C-D graph in relation to Silica, from 2009 in the Maumee watershed.

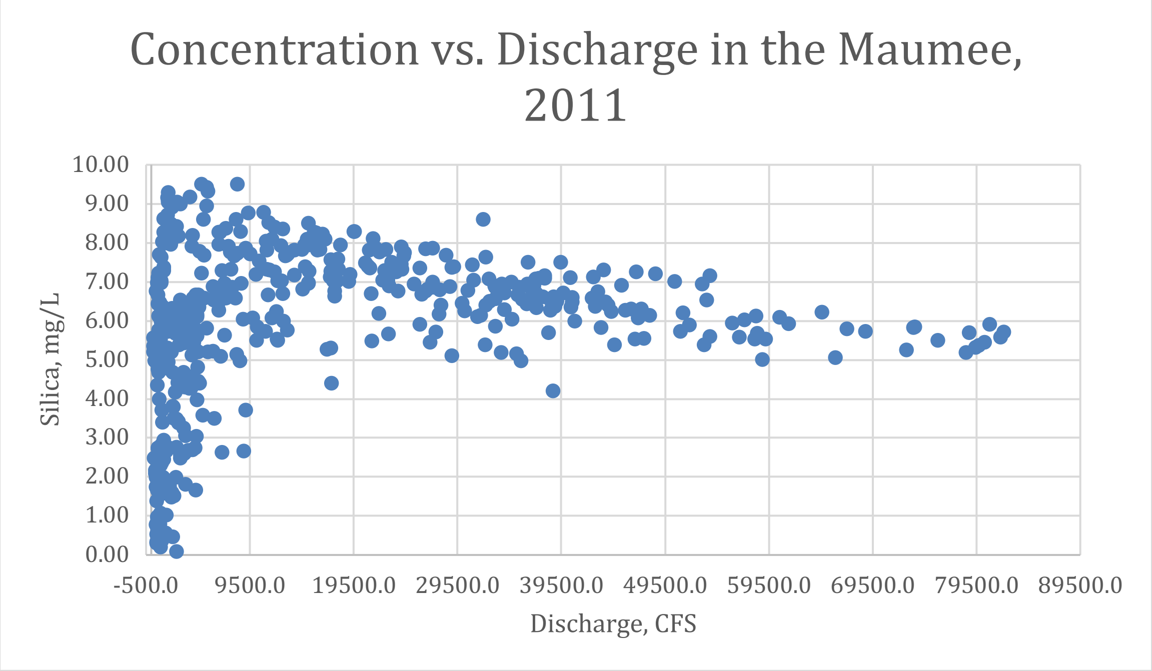


Figure 2: NCWQR data formed into C-D graph in relation to Silica, from 2011 in the Maumee watershed.

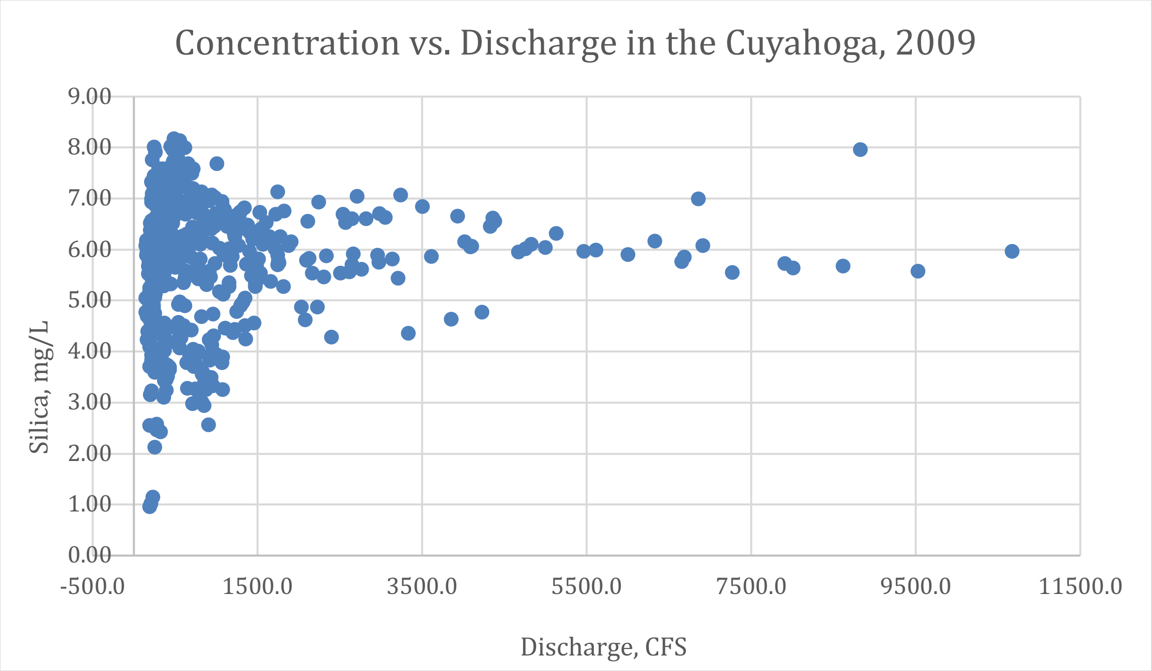


Figure 3: NCWQR data formed into C-D graph in relation to Silica, from 2009 in the Cuyahoga watershed.

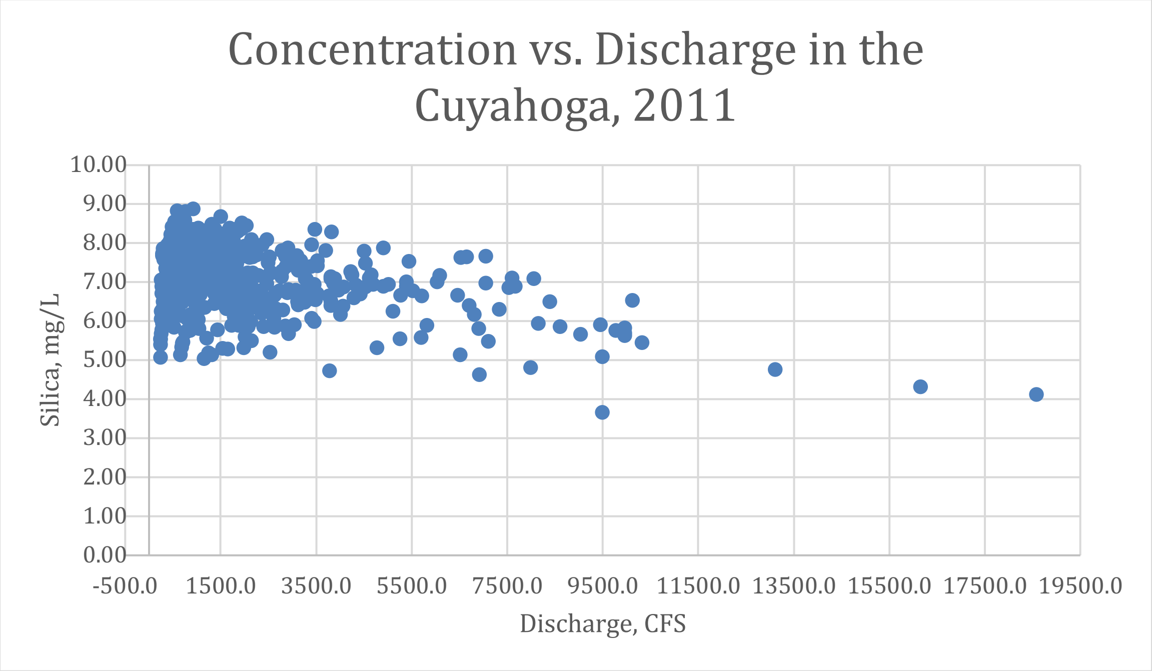


Figure 4: NCWQR data formed into C-D graph in relation to Silica, from 2011 in the Cuyahoga watershed.

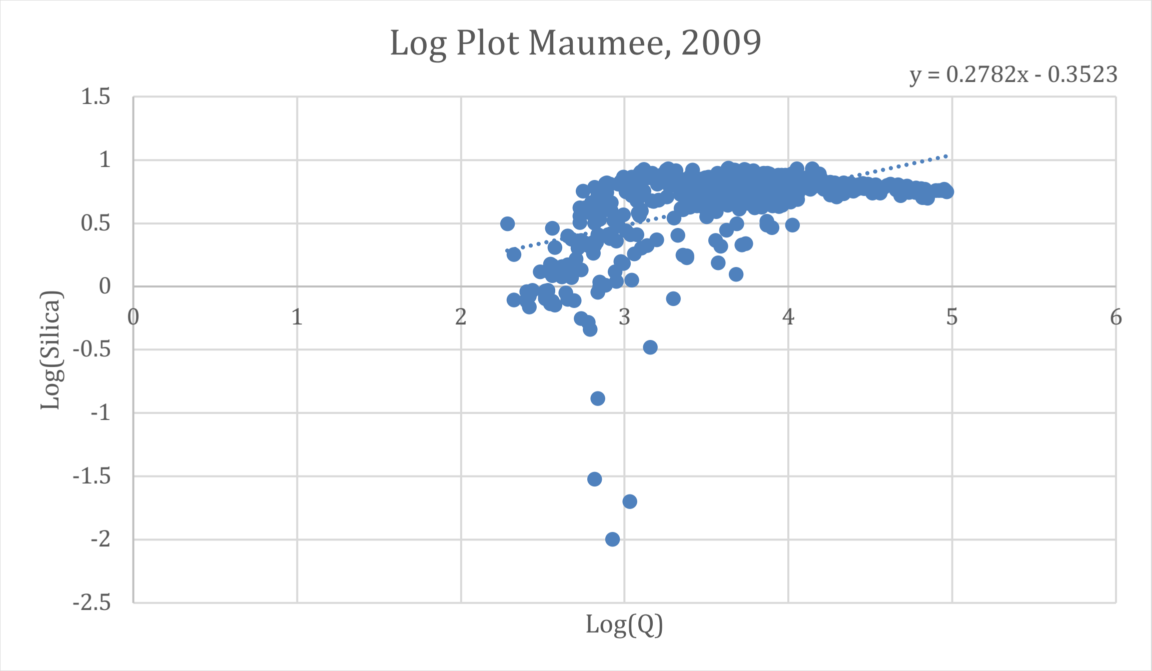


Figure 5: NCWQR data formed into Log (Si) vs. Log (CFS) from 2009 in the Maumee watershed.

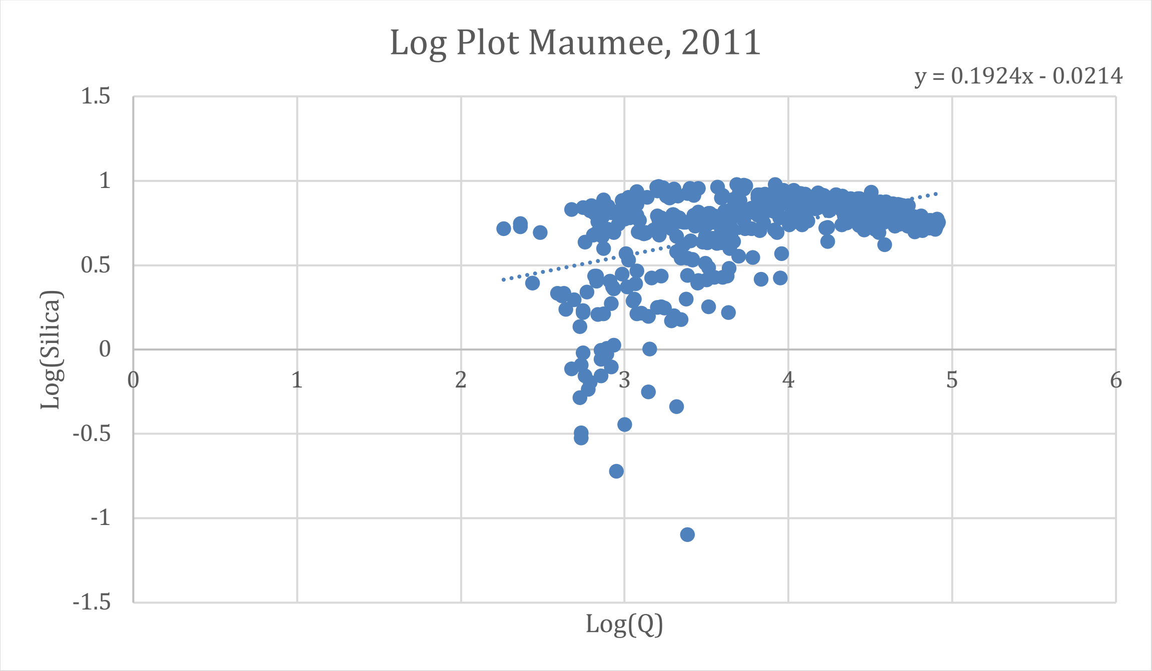


Figure 6: NCWQR data formed into Log (Si) vs. Log (CFS) from 2009 in the Maumee watershed.

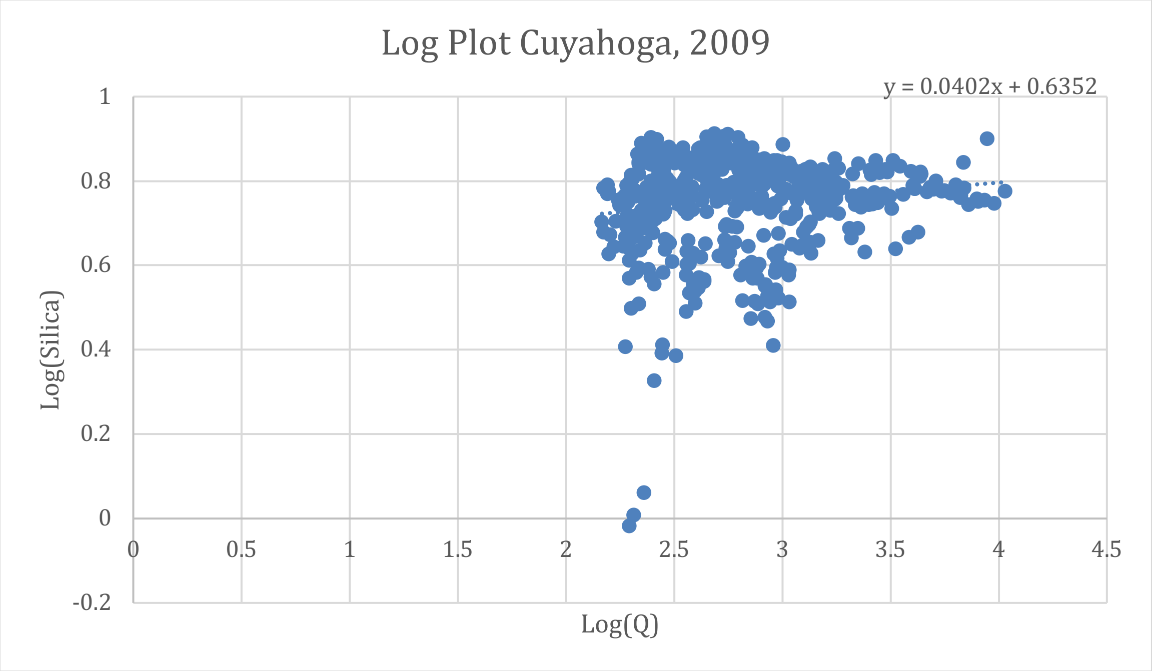


Figure 7: NCWQR data formed into Log (Si) vs. Log (CFS) from 2009 in the Cuyahoga watershed.

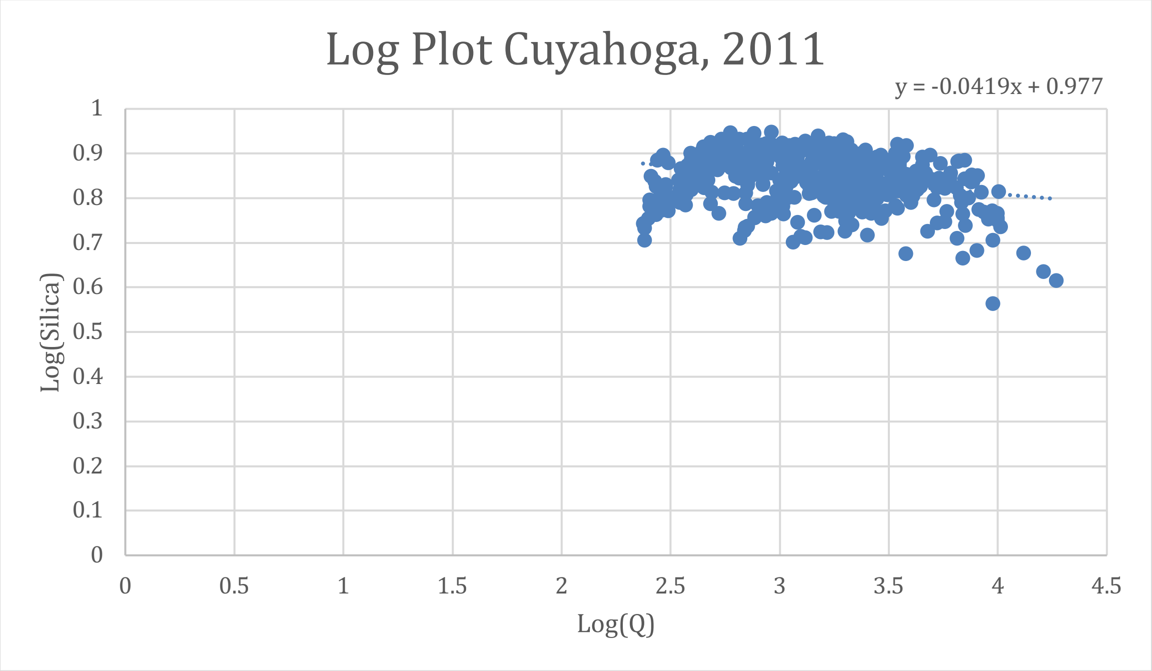


Figure 8: NCWQR data formed into Log (Si) vs. Log (CFS) from 2011 in the Cuyahoga watershed.

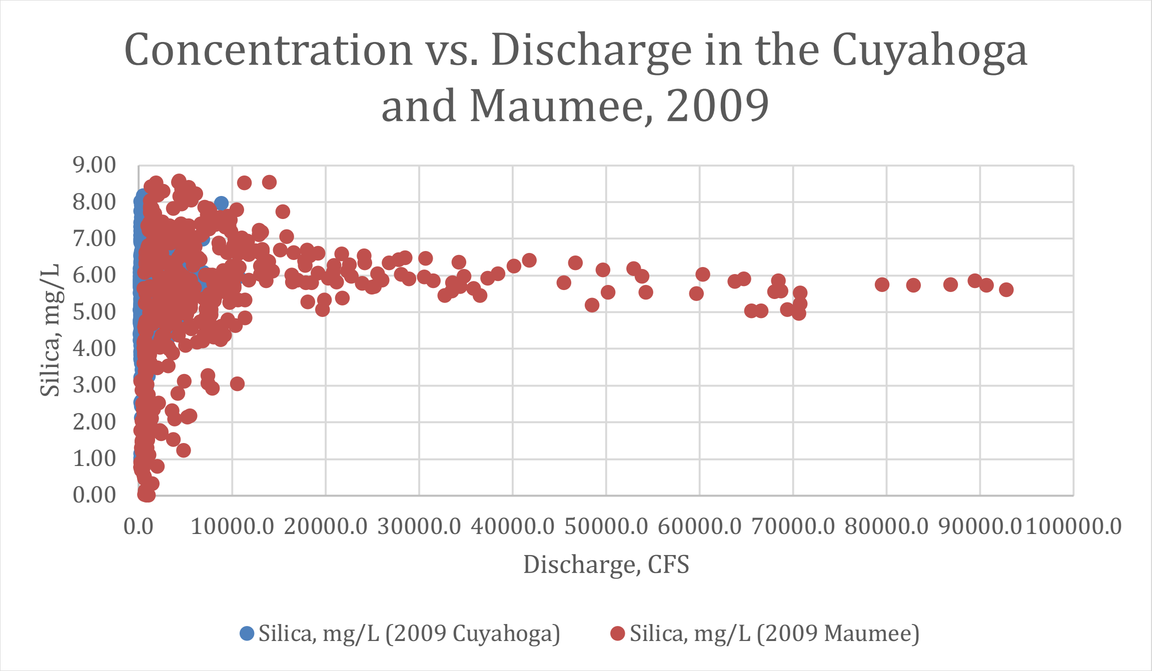


Figure 9: NCWQR data formed into C-D graph in relation to Silica, from 2009 in the Maumee and Cuyahoga watersheds together.

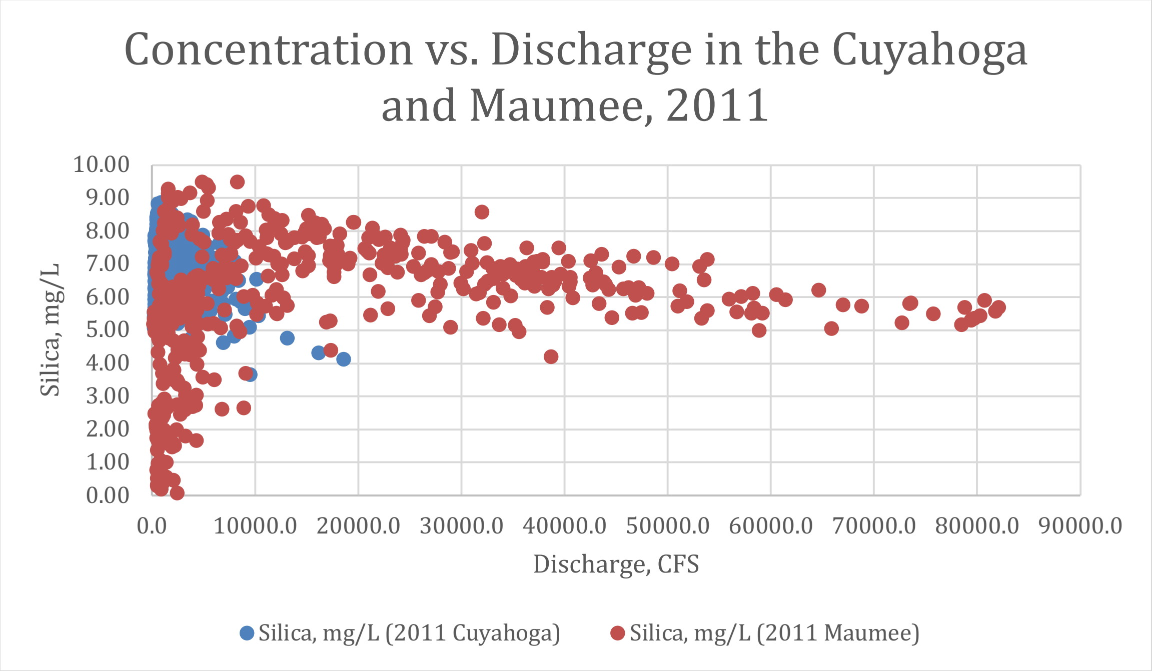
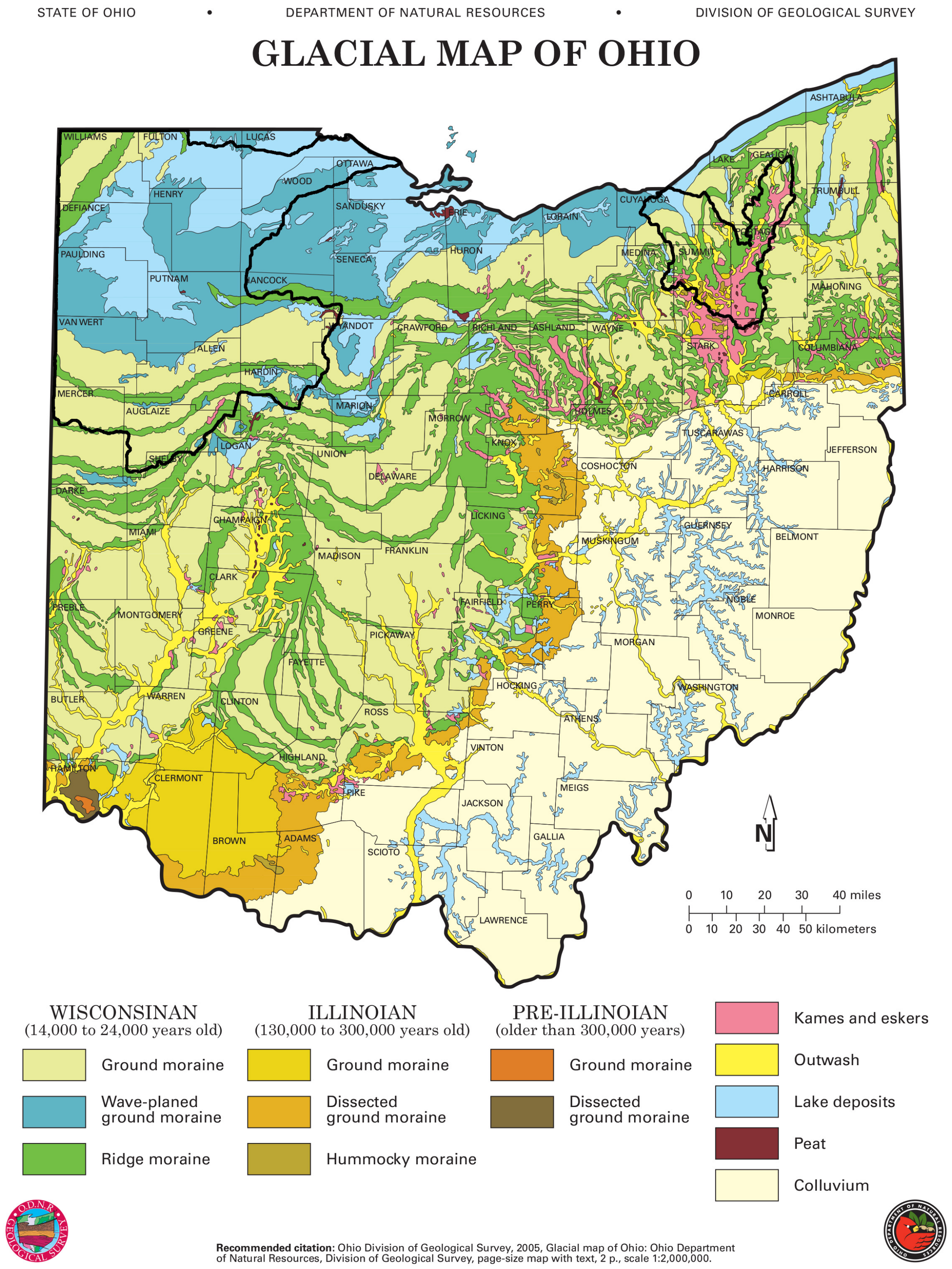


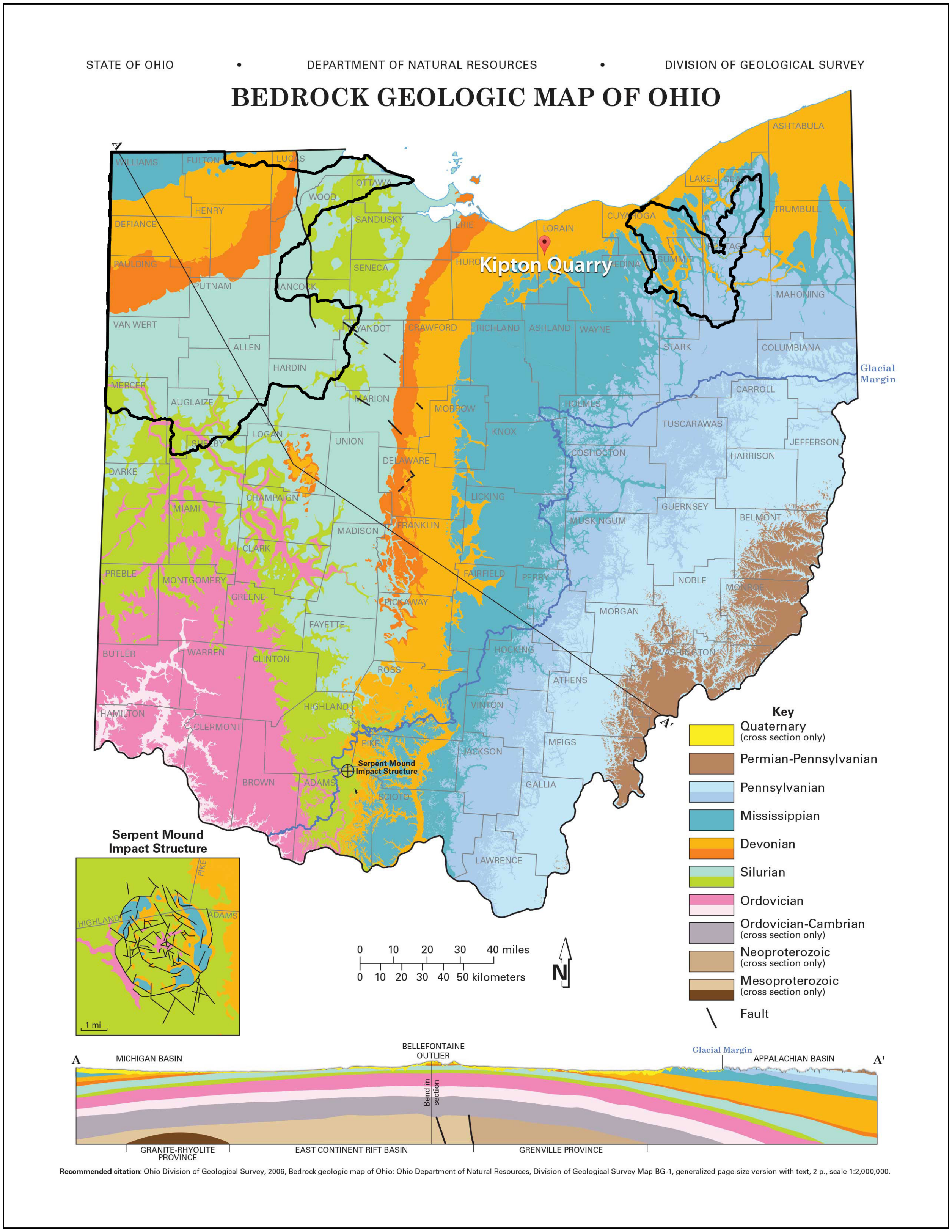
Figure 10: NCWQR data formed into C-D graph in relation to Silica, from 2011 in the Maumee and Cuyahoga watersheds together.

APPENDIX B



Recommended citation: Ohio Division of Geological Survey, 2005, Glacial map of Ohio: Ohio Department of Natural Resources, Division of Geological Survey, page-size map with text, 2 p., scale 1:2,000,000.

Figure 12: This figure shows surficial geology underlaying the watersheds outlined.



Recommended citation: Ohio Division of Geological Survey, 2006, Bedrock geologic map of Ohio: Ohio Department of Natural Resources, Division of Geological Survey Map BG-1, generalized page-size version with text, 2 p., scale 1:2,000,000.

Figure 13: This figure shows bedrock geology underlaying the watersheds outlined.