Correlating Trends of Silica Concentrations within a Subalpine Watershed Using Long Term Data

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Silica is the second most abundant element in the Earth's crust, and cycles through the Earth system through weathering (Struyf et al. 2009). Silica (SiO_2) is an important mineral found in terrestrial and aquatic ecosystems and supports a wide range of species. Silica is introduced into an ecosystem from mineral weathering. The silicate weathering process consumes CO_2 and thus plays a major role in climate regulation on the geological time scale (Hilley and Porder 2008, Struyf et al. 2009, Conley and Carey 2015). Silica is a critical element for the survival of many terrestrial and aquatic species, such as grasses and diatoms.

It is estimated that 1,142–2,764 Tg SiO_2 are weathered from rocks and soils globally every year (Hilley and Porder 2008). Grasses and diatoms have dominated the biological silica cycle for the past 65 million years (Conley and Carey 2015). As silicates enter the system, they move through the terrestrial biogeochemistry cycle through uptake, storage and recycling (Struyf et al. 2009). Terrestrial plants uptake silica through active mechanisms, or passively through the mass flow of water (Struyf et al. 2009). The terrestrial demand for silica comes primarily from grasses, and varies between species. Species such as horsetails and wetland reeds (*Phragmites*) have a higher uptake of silica, while sugarcane and dryland grasses have a lower uptake (Struyf et al. 2009). Silica is an important structural component of cell walls and supports plant growth. If silica is limited, plants are structurally weaker, exhibit abnormal seedling growth, and are more susceptible to biotic and abiotic stresses (Struyf et al. 2009). Silicates reach aquatic ecosystems through erosion of soil, where it is taken up primarily by sponges and diatoms to be used for structural components (Struyf et al. 2009). Because silica is a necessary nutrient for many species, it has a critical role in primary productivity and carbon cycling on the continents and in the oceans. (Conley and Carey 2015). The silica cycle has been significantly altered in the anthropocene due to increased CO_2 concentrations, construction of dams and reservoirs, deforestation and agriculture (Struyf et al. 2009, Seitzinger et al. 2010, Garnier et al. 2010, Harrison et al. 2012).

Diatoms (*Bacillariophyceae*) are single celled algae that use silica to form ornate siliceous shells called frustules (Struyf et al. 2009, Gross 2012). Diatoms are primary producers, converting solar energy to chemical energy through photosynthesis. Through this, CO_2 is fixed and O_2 is released into the atmosphere. It has been estimated that marine diatoms produce ~20% of global oxygen (Alverson 2014). Diatoms have a higher demand for silica than other types of phytoplankton, as it is required to form frustules (Harrison et al. 2012). Hundreds of species of diatoms have been identified in North America (diatoms.org), all of which have different silica requirements, and the silica content can vary greatly within a species (Garnier et al. 2010). Silica uptake by diatoms is dependent on the residence time, and if it is compatible with their growth rates (Garnier et al. 2010).

Anthropogenic changes to the environment are affecting the movement of silica throughout terrestrial and aquatic ecosystems. Disruption to the terrestrial silica cycle is caused by human activities, such as agriculture and deforestation. This has resulted in changes of silica inputs from terrestrial to aquatic ecosystems (Harrison et al. 2012). Multiple studies have found that human constructed dams and reservoirs are retaining silica, and subsequently limiting the amount of silica that is transported downstream (Seitzinger et al. 2010, Garnier et al. 2010, Harrison et al. 2012). At the end of a diatom's life cycle, it sinks to the bottom of the water body, and the silica is then incorporated in the sediment, where it is then remobilized by a slow dissolution process (Garnier et al. 2010). Reservoirs trap sediment, thus retaining the sedimented silica and other elements such as phosphorus. Additionally, increased loading of nitrogen (N) and phosphorus (P) may also lead to increased production, and thus sedimentation, of diatoms in reservoirs (Garnier et al. 2010). It has also been found that small lakes act as a silica sink in watersheds (Harrison et al. 2012). Small lakes (< 50 km^2) process 257% more silica than large lakes, on a per unit basis. Each year, small lakes remove around 46.9 Tg SiO_2 compared to 11.2 Tg SiO_2 for large lakes, emphasizing the importance of small reservoirs ability to remove silica throughout flow paths within watersheds (Harrison et al. 2012).

When N and P are available in excess over silica, diatoms will become limited, and other, often undesirable, algal species will develop instead (Garnier et al. 2010). In downstream ecosystems, such as coastal zones, increases in anthropogenic N and P loading limits silica, which may lead to harmful algal blooms, hypoxia and negative impacts on fisheries (Garnier et al. 2010). As human populations expand, we are continuing to build dams and altering the hydrology of our global river systems. As a result, silica river export will decrease due to retention and eutrophication (Garnier et al. 2010). Because of this, it is important to consider the impact on silica river export and eutrophication when planning construction of water diversion for domestic, industrial and agricultural use, as well as dam construction for hydroelectric power development. (Garnier et al. 2010)

As we continue to alter our environment and experience climate change, one may wonder if this will have an impact on the global silica cycle. A study conducted by White and colleagues (1999), found that temperature does significantly impact natural silicate weathering rates. It has been documented that temperatures around the globe are increasing, so we may expect to see an increase in silicates entering ecosystems.The weathering of silica is not directly affected by human activities, but is indirectly affected by climate change and dam construction (Harrison et al. 2012). The weathering of silicates is influenced by concentrations of CO_2, which data shows is increasing (Struyf et al. 2009). Climate has the potential to alter the balance of evapotranspiration and runoff, significantly altering the silica transfer to surface waters (Harrison et al. 2012). Given the complex, interacting controls on silica mobilization, transport, uptake and burial, it is difficult to predict the direction and magnitude of these effects (Harrison et al. 2012).

This study aims to determine the SiO_2 trends in the Loch Vale watershed (LVWS), Rocky Mountain National Park, from 1982 - 2017, and the direct and indirect relationships between SiO_2 concentrations, hydrological patterns, and aquatic algae, especially diatoms. Loch Vale is a good place to explore trends in silica dynamics over time because it is undisturbed with respect to major land uses such as forest harvest or agriculture. Its high elevation location in Rocky Mountain National Park protects it from direct human interference, but influences from climate change and atmospheric deposition may have altered silica dynamics (Oleksy et al. 2020). Specific questions I asked of the data were: If and how are silica concentrations over the specified timeframe changing? What are the drivers of change for silica concentrations? What is the relationship between discharge and silica? Is there a relationship between silica concentrations and diatoms during the open water season?

Loch Vale Watershed

The Loch Vale Watershed is an alpine-subalpine drainage basin located in Rocky Mountain National Park, Colorado (Figure 1). The watershed covers 660 hectares and ranges in elevation from 3,110 m at the Loch Outlet to 4,009m at Taylor Peak (Heath and Baron 2014).

Rocky Mountain National Park rests upon igneous (granite) and metamorphic (schist and gneiss) formations. The major minerals present are quartz, An_{27} plagioclase, microcline, biotite, and sillimanite (Mast et al. 1990). The average annual precipitation is 110 cm, over 50% originating as snow (Baron 1992).

Loch Vale was instrumented in 1983 to understand watershed-scale ecosystem processes. Research questions in Loch Vale ask how alpine and subalpine ecosystems respond to climate variability and atmospheric deposition (www2.nrel.colostate.edu/projects/lvws/site_description.html). Water sampling during the open water seasons for chemical analysis began in the summer of 1983. A Parshall flume and stilling well were installed at the watershed outlet in 1983, collecting continuous stream discharge data through present (Mast et al. 1990). Beginning in 1991, weekly year-round sampling of surface waters was taken at The Loch outlet and continues to present (Heath and Baron 2014). There are many publications about this long-term research and monitoring program, some of which have looked at mineral weathering, diatoms, and the changes in lake primary productivity. Heath and Baron (2014) observed statistically significant increases in concentrations and fluxes of weathering products, such as SiO_2 over the period 1983-2010. They suggest that the rapid change in the flux of weathering products is the direct and indirect result of warming temperatures and a thawing cryosphere.

Methods

To examine how SiO_2 concentrations have changed over time, silica data from 1982-2017 was extracted from the Loch Vale database. The most complete data set is from The Loch Outlet, but data that were collected over time from other locations in LVWS were also used (Table 1).

Silica and discharge data were collected as part of the LVWS program using standard protocols (https://www2.nrel.colostate.edu/projects/lvws/data.html#Methods_manual). Weekly SiO_2 measurements were taken beginning in 1991 and discharge beginning in 1983. I worked with a data set that included samples collected for quality assurance, including duplicate, blank, and split samples. In order for me to analyze silica trends, these samples were removed from the dataset. I then sorted the data into water years, starting October 1 of each year, and ending September 30, to observe the trends that take place during spring runoff, summer, and fall seasons until ice-on. The analysis was then expanded to observe the SiO_2 monthly and annual means throughout time. A Seasonal Kendall test was performed to determine the trends in silica data from the Loch Outlet. A Seasonal Kendall test is a nonparametric test that analyzes the data for monotonic trends in seasonal data. Because the SiO_2 concentrations vary throughout the year, the Seasonal Kendall was used to eliminate the seasonality and identify a positive or negative trend in the data.

Discharge data from the Loch Outlet were analyzed to determine the relationship with silica concentrations. After calculating monthly means, a time series of silica and discharge data was created. Precipitation data from 1983 - 2017 for the watershed was obtained from the National Atmospheric Deposition Program website (http://nadp.slh.wisc.edu/data/) to determine if precipitation had an impact on silica concentrations. I calculated both monthly and annual averages. I created a time series of precipitation, discharge, and SiO_2 data to observe the relationship.

To get a better understanding of silica concentrations over a larger area of LVWS, I used SiO_2 data from a longitudinal transect beginning at the highest sample location, Sky Inlet, and moving downstream to Sky Outlet, Loch Inlet, Andrews Creek, and The Loch outlet sites. I then took all of the data for each month of the year for each site and calculated the means, minimum and maximum values and standard deviation. This analysis allowed me to observe mean concentrations for each month at each site to see how silica concentrations are changing spatially and temporally.

Results

There was a positive trend in silica concentrations for the period 1983-2017 (Figure 2). The mean for SiO_2 at the Loch outlet in 1984 was 1.992 mg/L (n=57) and in 2017 it was 2.395 mg/L (n=47). The results from the Seasonal Kendall Test (Table 1) supports this, showing that there was a slight significant increase in SiO_2 over time (p-value= 1.763E-11). The Seasonal Kendall Test accounted for auto-correlation, which automatically detected seasons and tested if there was a significant seasonal trend in the data, which the p-value supports (p-value= 2.473E-11). The Z value is an assumption of the analysis and indicates that all of the trends run in the positive direction (z-value= 6.675).

From observing the time series of discharge and silica, it was determined that there is indeed an inverse relationship between the two (Figure 3). Concentrations of silica increase as flow decreases and remains high during the winter months. There is a slight decrease in concentrations in early spring from March-April. We observe a sharp decrease concurrent with the beginning of snowmelt, typically around late May. This trend is apparent in the water-year time series of discharge and silica (Figure 3).

After calculating the average silica concentrations for each month for each location within LVWS (Table 3), I created a series of box plots to understand how silica concentrations move from the top of the watershed to the bottom over the course of the summer (Figure 4). At the top of the watershed at Sky inlet, the mean for June was 1.525 (n=26), July was 1.474 (n=29), August was 1.810 (n=31), September was 2.148 (n= 25) and October was 2.514 (n=6). At the Sky outlet, the mean for June was 1.205 (n=26), July was 1.097 (n=26), August was 1.485 (n=26), September was 1.605 (n=21) and October was 1.745 (n=10). In June-October, we observe a decrease in silica from the Sky inlet to the outlet.

Moving to The Loch inlet, we can see a slight increase in silica compared to the Sky outlet throughout the months. During May and June, The Loch outlet (2.984 n=32, 1.999 n=33) has slightly higher silica concentrations than the inlet (2.684 n=9, 1.753 n=29). In July, the Loch outlet (1.404 n=33) and inlet (1.365 n=29) have similar concentrations. During August, September, and October, the Loch inlet (1.83 n=28, 2.138 n=26, 2.361 n=11) has higher concentrations than the outlet (1.697 n=34, 1.915 n=33, 2.178 n=31). Andrews Creek has higher concentrations throughout the season. In general, the silica concentrations are lowest in June and July, and increase through August, September, and October.

Discussion

The time series and Seasonal Kendall test demonstrate that silica concentrations in LVWS have been increasing throughout the 1983 - 2017 time period (Figure 2, Table 2). The cause for this trend could be due to a shift in species composition or increased weathering rates. The box plots allow us to understand how on average, the silica concentrations change through the seasons throughout the Loch Vale watershed (Table 3, Figure 4). Starting from the top of the watershed in Sky Pond, we can see a decrease in silica from the inlet to the outlet during June through October. This suggests that there is diatom uptake of silica. Sky Pond is the most productive lake in LV, with summer chlorophyll A values of 5.3 ug/L and 2.2 ug/L for Sky Pond and The Loch, respectively (Oleksy et al. 2020, supplementary materials). As we move downstream to the Loch inlet, there is a slight increase in silica. These results suggest that Andrews Creek is a source of silica entering The Loch. Throughout the months, we can observe a shift in silica concentrations in the Loch inlet and outlet. In May and June, the outlet has higher concentrations, suggesting that there is minimal diatom uptake. This shifts throughout the rest of the months resulting in the outlet having lower concentrations than the inlet. These results suggest that there is an increase in diatom uptake of silica as The Loch becomes more productive during the warmer months. It is important to consider the amount of data available at each site

Diatom uptake influences the SiO_2 concentrations in the Loch Vale watershed, but discharge from the lakes also has a key role. The trend is easy to observe seasonally (Figure 3). Silica concentrations increase during the winter months, with a slight decrease in the early spring months, most likely due to an under-ice algal bloom as the sun starts to shine on the lake (Baron 1992). Higher discharge results in lower concentrations of silica, which influences the amount of available silica for diatom uptake.

The results from this analysis are important because the Loch Vale watershed may serve as a source of nutrients for ecosystems downstream. Studies have shown that lakes and terrestrial ecosystems influence the silica cycle and the amount of silica that is transported downstream (Struyf et al. 2009, Garnier et al. 2010). Harrison and colleagues (2012) demonstrated that there is a relative importance of small reservoirs controlling silica removal along flow paths within watersheds. They suggest that future research will aid in understanding the spatial distribution and biogeochemical role of these systems. Understanding how silica moves throughout a subalpine watershed can be important in understanding the impacts it has downstream. As lakes control the amount of elements transported, LV has the potential to influence downstream productivity and species composition. The results of this analysis and further research can aid in achieving a better understanding of the lake productivity in the Loch Vale watershed.

In the future, I recommend conducting additional analyses that compare other mineral concentrations to narrow the causes of the silica trends. Since silica is a result of weathering, it could be compared to an element that is also only introduced through weathering, such as Chloride (Cl) or Sodium (Na). If there is an increase in the comparison element that is not found in silica, then one can assume that the silica loss is due to biological uptake. If there is no increase in the comparison element, that would suggest that there is a decrease in biological uptake.

Comparison of silica concentrations to existing diatom and chlorophyll data in LV or a similar watershed could help one understand their relationship and explain the silica trends. An in-depth analysis of temperature trends could be compared to the silica data to help determine if temperature has an influence on weathering rates. This would be an important analysis due to the disputed effect of temperature on mineral weathering (White et al. 1999). Increases in available silica can influence the species composition and primary productivity of aquatic ecosystems. If the trend in Loch Vale continues, we may expect to see a shift in diatom species.

Conclusion

Silica is an important weathering product derived from minerals that is used by many species, predominantly grasses, and diatoms. Silica plays a role in the global carbon cycle as it has the ability to influence primary productivity. Monitoring silica concentrations allows us to understand what the species composition may be of an ecosystem and how it contributes to primary productivity. Understanding silica concentrations in an alpine aquatic ecosystem can lead us to understanding the biological uptake from diatoms. As we experience climate change, we may expect to see an increase in silica concentrations. The long-term data analysis in the Loch Vale Watershed supports this theory as we can observe a slight increase of concentrations in the outlet over a 30-year period.

Figures

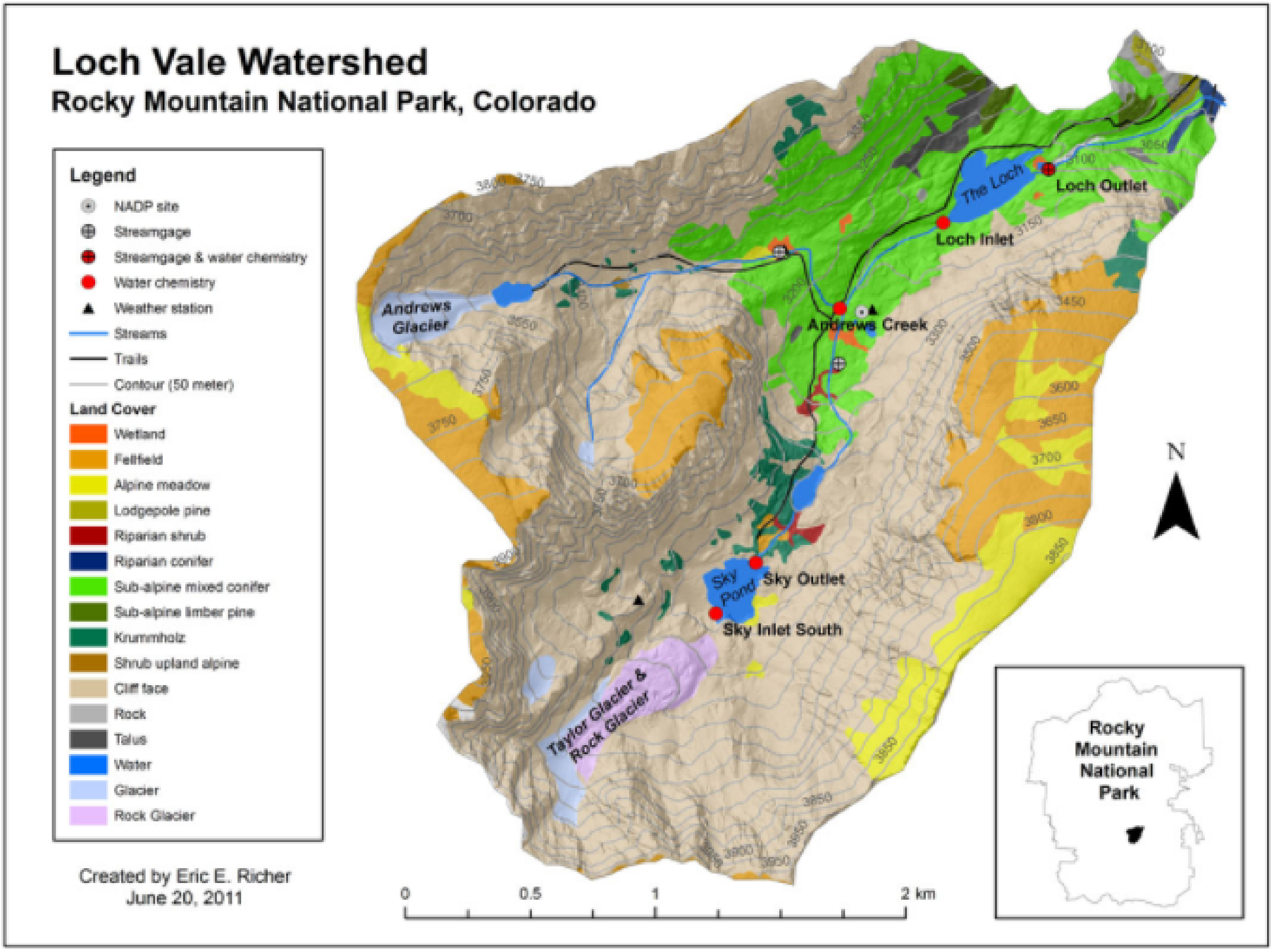


Figure 1: The Loch Vale Watershed lies within Rocky Mountain National Park, Colorado, USA. Water chemistry data is collected at five locations (red dots): Sky Inlet, Sky Outlet, Andrews Creek, Loch Inlet, and Loch Outlet. The Loch Outlet has the most continuous data, as well as being the location of the stream gage.

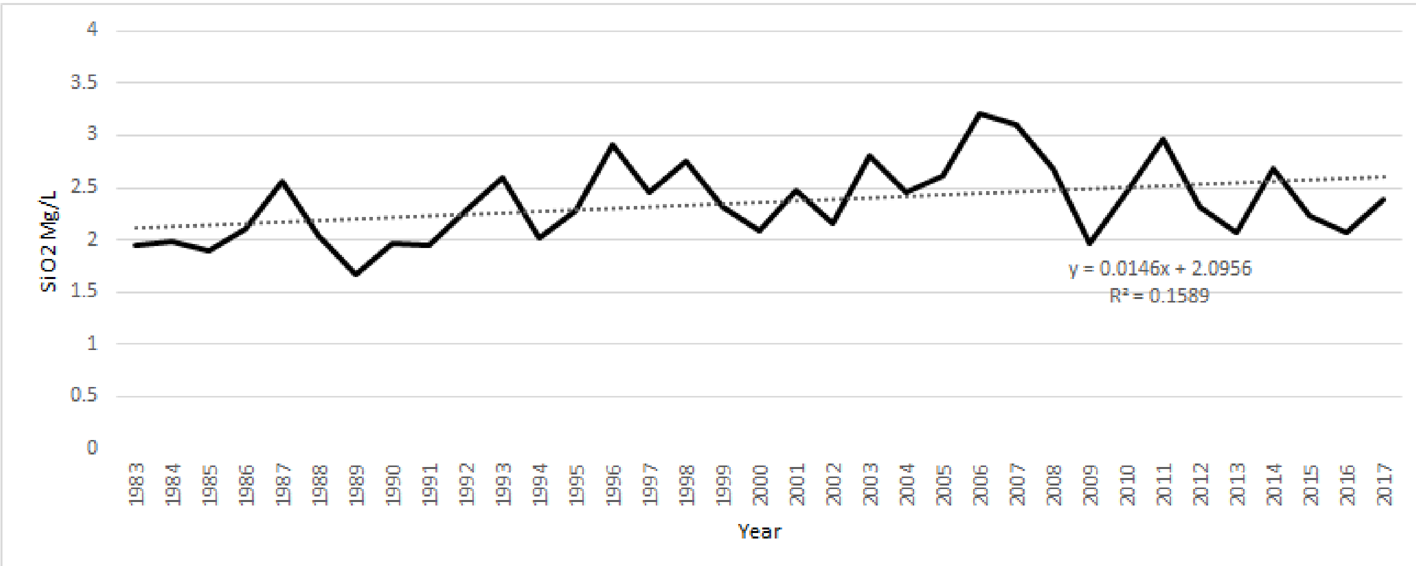


Figure 2a: Annual average silica concentrations at The Loch outlet from 1983 – 2017. The highest concentration is in 2006 and the lowest concentration is in 1989. The trendline shows a slight increase in silica over time.

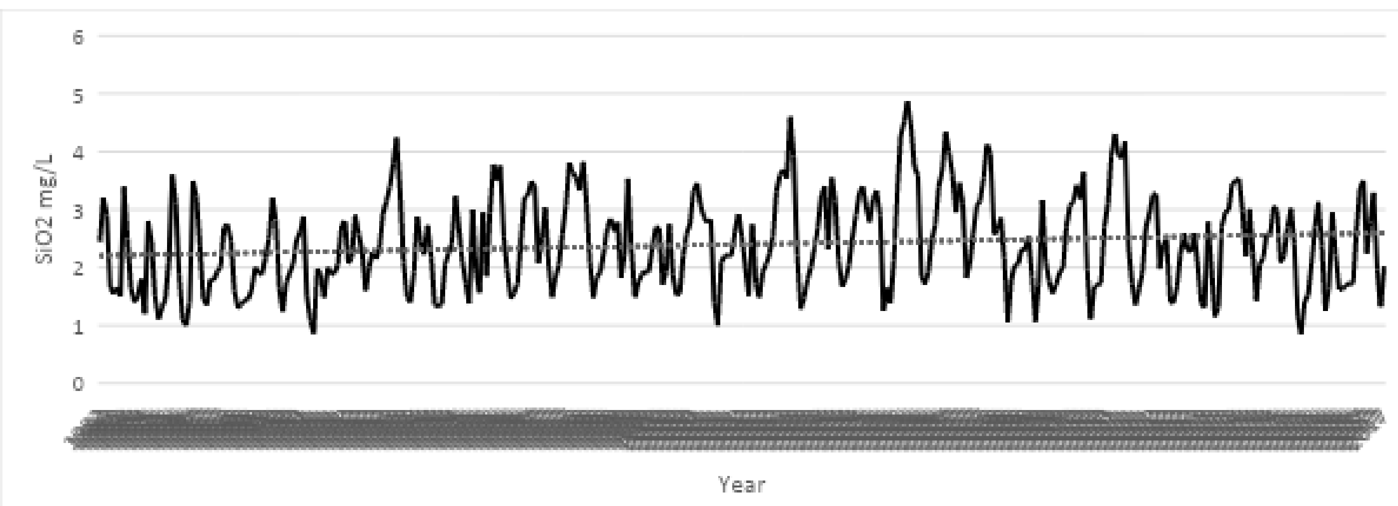


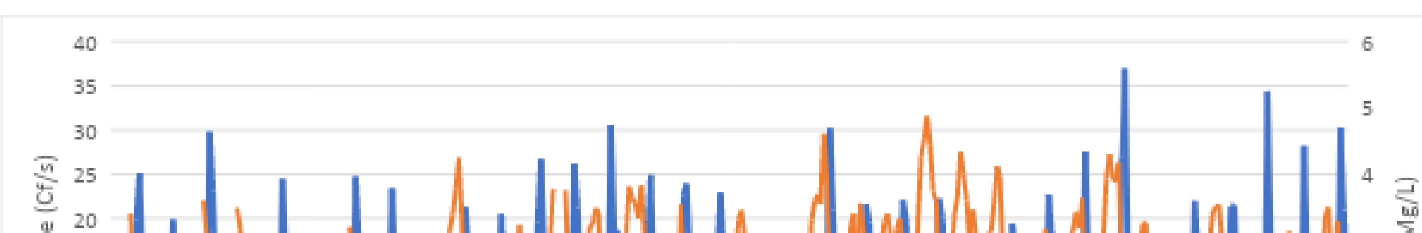
Figure 2b: Monthly average silica concentrations at The Loch outlet from 1983 - 2017

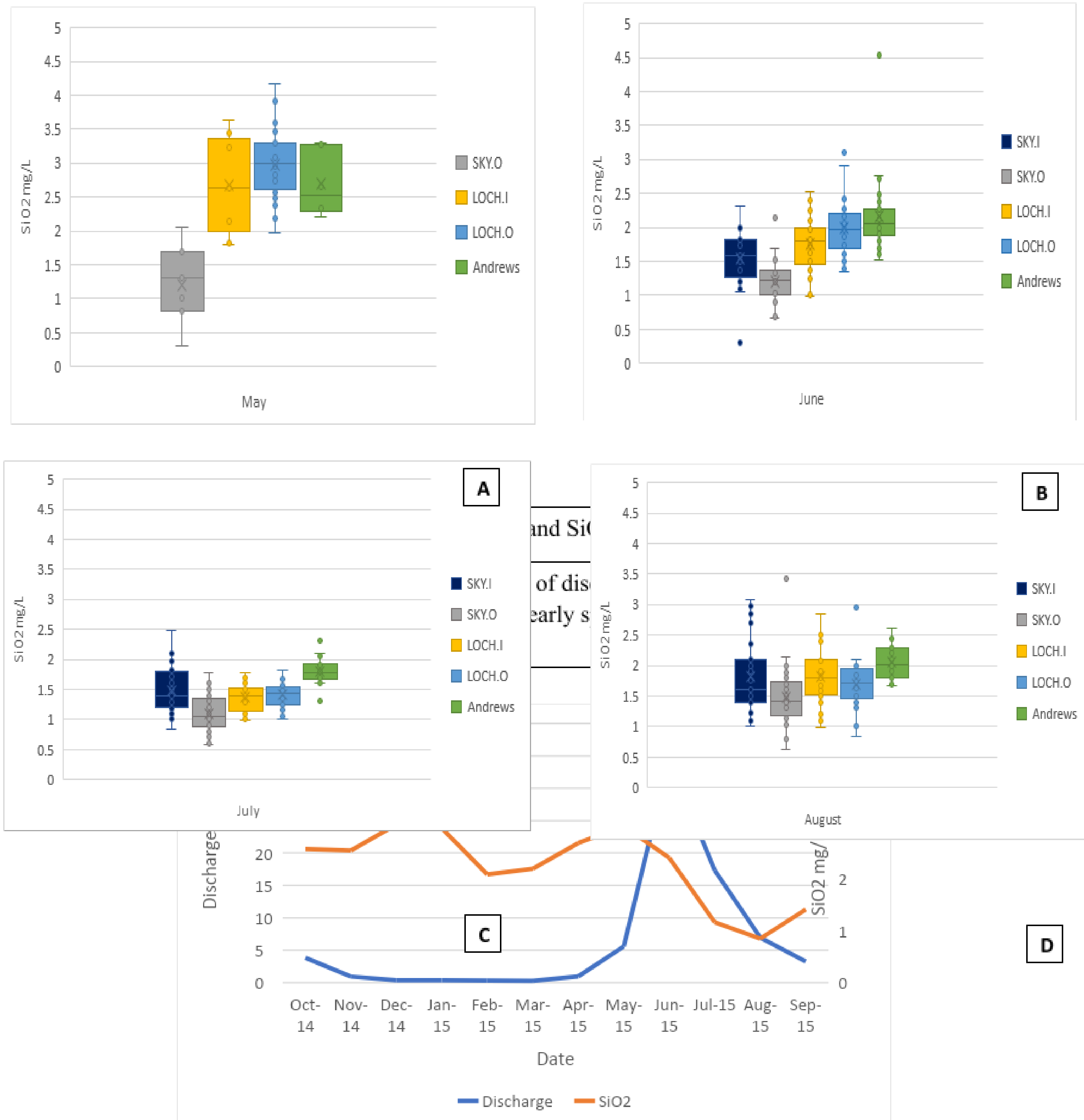
	SKY.I	SKY.O	LOCH.I	LOCH.O	ANDREWS
# of samples	185	155	253	1554	132

Table 1: The number of SiO_2 samples taken at each location in LVWS from 1983-2017

Z (Trend)	P-value	Slope	Tau	P-value (auto-correlation)
6.675	1.76E-11	0.009	0.098	2.47E-11

Table 2: The results from the Seasonal Kendall Test, performed in R. The z score demonstrates that all of the trends are in a positive direction. The P-value shows that the results are statistically significant, confirming that there is a trend. The slope shows that there is a small, but significant increase in silica over time.




Si O2 mg/L
May
June
July
August
SKY.I
SKY.O
LOCH.I
LOCH.O
Andrews
A
B
C
D
Discharge
SiO2 mg/
Date
Oct-14
Nov-14
Dec-14
Jan-15
Feb-15
Mar-15
Apr-15
May-15
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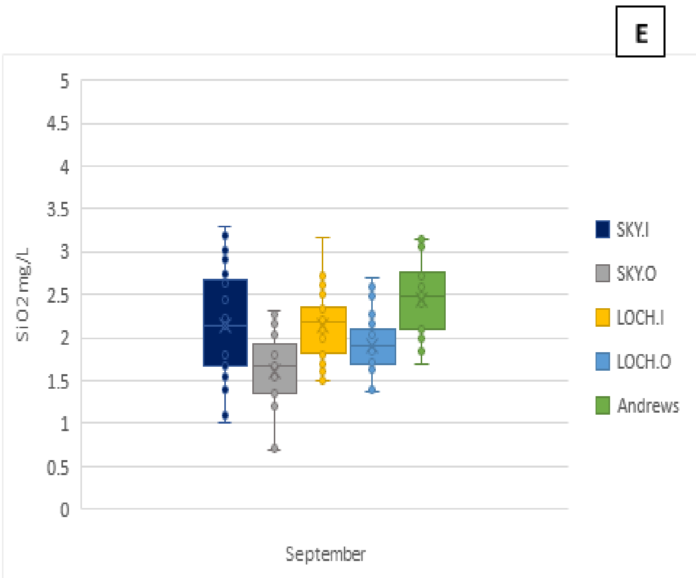
Jul-15
Aug-15
Sep-15
Discharge
SiO2



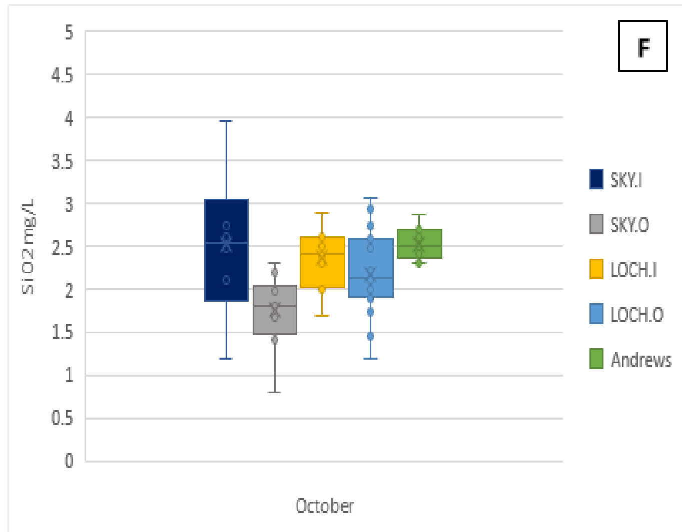


Figure 4: Overall mean for each month for each site in LV. **A**. May **B.** June **C.** July **D.** August **E.** September **F.** October

	Sky.I						Sky.O					
Month	Mean	Std. Dev	Median	Min	Max	n	Mean	Std. Dev	Median	Min	Max	n
1												
2												
3												
4												
5	1.833					1	1.205	0.573	1.300	0.300	2.045	7
6	1.545	0.419	1.580	0.300	2.304	26	1.205	0.324	1.225	0.670	2.133	26
7	1.474	0.404	1.400	0.840	2.484	29	1.097	0.325	1.060	0.580	1.768	26
8	1.810	0.583	1.606	1.000	3.075	31	1.485	0.533	1.408	0.625	3.420	26
9	2.148	0.622	2.140	1.000	3.300	25	1.605	0.446	1.680	0.684	2.304	21
10	2.514	0.900	2.540	1.200	3.960	6	1.745	0.434	1.800	0.800	2.290	10
11												
12												

	Loch.I						Loch.O					
Month	Mean	Std. Dev	Median	Min	Max	n	Mean	Std. Dev.	Median	Min	Max	n
1	3.510					1	3.268	0.528	3.248	2.533	4.526	27
2	2.530					1	3.022	0.826	3.110	1.500	4.871	26
3	3.019					1	2.561	0.941	2.276	1.062	4.426	28
4	4.285					1	2.753	0.876	2.773	0.860	4.602	33
5	2.684	0.725	2.630	1.800	3.632	9	2.984	0.492	3.004	1.975	4.172	32
6	1.753	0.373	1.793	0.995	2.517	29	1.989	0.392	1.965	1.350	3.094	33
7	1.365	0.218	1.400	0.980	1.785	29	1.404	0.216	1.426	1.002	1.821	33
8	1.830	0.432	1.805	0.986	2.840	28	1.697	0.375	1.706	0.848	2.950	34
9	2.138	0.398	2.177	1.500	3.162	26	1.915	0.330	1.900	1.382	2.702	33
10	2.361	0.341	2.400	1.700	2.880	11	2.178	0.447	2.130	1.200	3.071	31
11							2.539	0.530	2.475	1.620	3.775	29
12	3.300					1	2.987	0.489	2.915	2.274	4.260	27

	Andrews					
Month	Mean	Std. Dev.	Median	Min	Max	n
1						
2						
3						
4						
5	2.692	0.481	2.530	2.200	3.297	6
6	2.157	0.572	2.060	1.522	4.525	26
7	1.801	0.203	1.775	1.300	2.315	28
8	2.052	0.276	2.010	1.662	2.610	28
9	2.443	0.433	2.492	1.696	3.136	23
10	2.524	0.188	2.486	2.300	2.860	10
11						
12						

Table 3: Mean, median, minimum, maximum and standard deviation values for each month at each site.

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