

Eliza Cranston, Mehek Singh, Meghan Stasko, Maddy Wilson
26 July 2019

The Correlation Between Calcium, Sulfate, and pH in RPCS Soil

Abstract

When looking at pH in soil, two common elements that impact its level are calcium and sulfate. While sulfate makes pH more acidic, the properties of calcium carbonate have the ability to neutralize this acidity to create a more balanced pH in soils (Parnes 2013). Prior research has shown that the minimum ratio of calcium to sulfur needed to balance the pH in acidified soils is 3 parts calcium to 1 part sulfur (Oldham 2019). The results from E.S.S.R.E 2019 Biota Survey showed that in Microclimate site 4, the sulfur level was high but the pH was natural. We hypothesized that the limestone bedrock above Site 4 was leaching carbonate leading to more neutral pH values down the hill as the carbonate reacted with the sulfate in the soil. 15 soil samples 2 cm in diameter and 30cm deep were taken from 5 different elevations on the hillside, and 3 negative control samples were taken from Site 4 over the course of 4 days in July, 2019. All the samples were tested for calcium, sulfate, and pH levels using the LaMotte STH-14 chemical kit. Our data showed that the pH was not more neutral towards the bottom of the hill, that the calcium levels actually decreased down the hill, and that the sulfate was not having a significant impact on the pH level in the soil. Further research would be to apply a controlled amount of rainwater from the retaining tank above Site 4 down the limestone hill in order to identify if it was a possible cause for the pH level changes observed down the hill.

Introduction

The pH of a given soil is extremely important in ensuring that plants have a nutrient-rich growing environment and that macro and microorganisms living there have a stable habitat. pH measures the acidity or alkalinity in the water content of soil (Lake 2000) and has an indirect relationship with the growth and health of plants in the area as it impacts the amounts and type of biological matter in the soil and the availability of other elements that are vital to plant survival (Parnes 2013).

Two common soil chemicals strongly associated with soil pH are calcium and sulfate. Calcium, in the form of the compound Calcium Carbonate, can neutralize acidic soils; while sulfate acidifies soils (Parnes 2013). Therefore, soils that are saturated in sulfate, which is anionic, tend to be more acidic, and, in fact, as little as 250 ppm of sulfur per 1 acre of sandy soil can reduce the pH of that soil from 7.5 to 6.5. Because calcium and sulfate have opposite impacts on soil pH, when there is as little as a 3-to-1 ratio that exists between the calcium and sulfur levels in the soil, the calcium can neutralize the acidifying effects of the sulfur, and thus, a higher level of calcium, paired with a corresponding amount of sulfur, should cause the soil acidity to equalize to a more neutral pH (Oldham 2019).

In addition to impacting soil pH, calcium and sulfate play critical roles in the life of plants. Calcium and sulfate are two minerals that are essential to the maintenance of healthy natural life, and in plants, calcium is used to regulate the movement of particles across the cell wall, as well as being present in the root systems (Parnes 2013). Through the roots, calcium allows the plant to absorb necessary nutrients and water from the soil, and by aiding in the intracellular communication process (through the cell walls), it helps the plant react to environmental stimulation (White, Broadley 2003). Sulfur (in its sulfate form) is used by plants for protein synthesis, as well as by rhizobacteria in the nitrogen fixation process (Oldham 2019). These bacteria are in a symbiotic relationship with plants, as they utilize the sulfate in the soil to transform nitrogen, which is an essential nutrient for plants, into a form that is usable by both groups of organisms.

After an initial data collection from E.S.S.R.E. Microclimate Site 4 (N 39.35733; W 076.63840) during the 2019 E.S.S.R.E. Biota Survey (E.S.S.R.E. 2019), it was observed that the sulfur levels were high, but the pH level was neutral. The hill that was used for experimental purposes is exposed limestone; thus the soil that is created from it should be high in calcium. As rainwater and runoff flow down the hill, calcium should leach down along with the water, thus hypothetically raising the calcium levels at the base of the hill. As the calcium levels increase, it may interact with the sulfur found in the soil, potentially causing the pH level to neutralize. Therefore, at the base of the hill, the pH should theoretically be more balanced than at the peak of the hill. Based on this data, we predicted that the balanced pH level observed in Microclimate Site 4 was due to the high levels of calcium in the soil. This high level of calcium may be the result of rain runoff coming down from the nearby hill.

Methods

15 plots on a hillside adjacent to the north of E.S.S.R.E Microclimate 4 (N 39.35733; W 076.63840) were created perpendicular to the slope of the hill. 3 of the plots were located at the bottom of the hill 4 meters apart horizontally along the contour of the hill. An additional 3 plots were created 7.5 meters perpendicular up the hill from the first 3 plots, and this process was repeated in 7.5 meter increments until each row of plots up the hill contained 5 plots (see Table 1). Negative control plots were created 4 m apart in a separate location at the base of the hill in Quadrants 3 and 4 in Microclimate 4. At each location, leaves and/or ground cover were brushed away so that the soil was directly exposed. A 2 cm diameter soil core 30 cm deep was extracted at each location and this process was repeated at the same time at each location daily, for a total of 4 days (7/18,7/19,7/22,7/23). Each days' collection of soil samples were tested simultaneously for pH, calcium (ppm), and sulfate (ppm) levels using the LaMotte STH-14 kit.

Table 1	
Soil Sample Plots	GPS Coordinates
1A	N 79°, 21.516' W 076°, 38.321'
1B	N 39°, 21.493' W 076°, 38.352'
1C	N 39°, 21.494' W 076°, 38.333'
2A	N 39°, 21.505' W 076°, 38.350'
2B	N 39°, 21.490' W 076°, 38.241'
2C	N 39°, 21.490' W 076°, 38.341'
3A	N 39°, 21.506' W 076°, 38.336'
3B	N 39°, 21.480' W 076°, 38.341'
3C	N 39°, 21.508' W 076°, 38.334'
4A	N 39°, 21.484' W 076°, 38.345'
4B	N 39°, 21.476' W 076°, 38.340'
4C	N 39°, 21.485' W 076°, 38.342'
5A	N 39°, 21.473' W 076°, 38.345'
5B	N 39°, 21.487' W 076°, 38.341'
5C	N 39°, 21.480' W 076°, 38.335'
NCA	N 39°, 21.473' W 076°, 38.325'
NCB	N 39°, 21.470' W 076°, 38.326'
NCC	N 39°, 21.468' W 076°, 38.328'

Results

Figure 1: Correlation Between pH and Calcium Levels

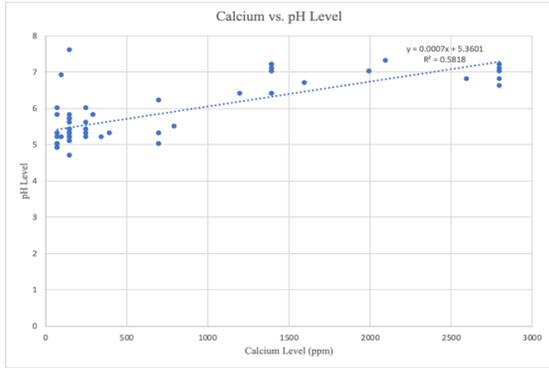


Figure 2: Correlation Between pH and Sulfate Levels

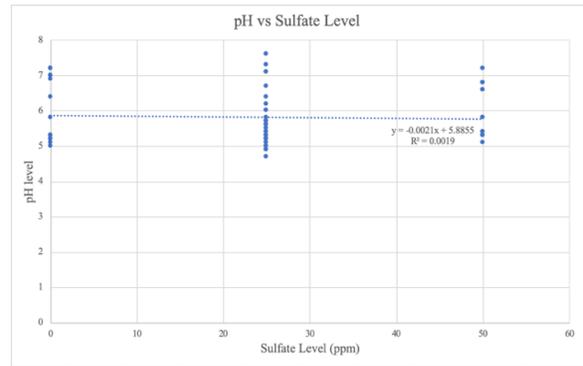


Figure 3: The Impact of Elevation on Soil Calcium Levels

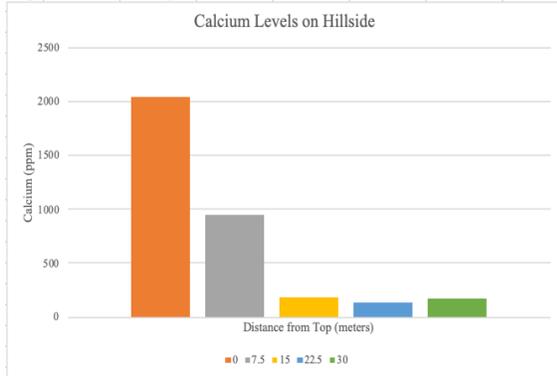


Figure 4: The Impact of Elevation on Soil pH

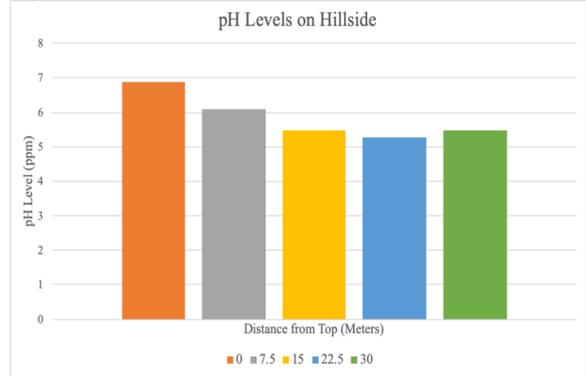


Table 1: Sulfate T-Test Results

Samples Compared	P-Value
0 vs. 7.5	0.79
0 vs. 15	0.79
0 vs. 22.5	0.57
0 vs. 30	0.57
0 vs. Negative Control	0.28

Table 2: pH T-Test Results

Samples Compared	P-Value
0 vs. 7.5	0.0029
0 vs. 15	0.0000134
0 vs. 22.5	0.000000155
0 vs. 30	0.0000000946
0 vs. Negative Control	0.639

Table 3: Calcium T-Test Results

Samples compared	P-Value
0 vs. 7.5	0.00257
0 vs. 15	0.00000165
0 vs. 22.5	0.00000147
0 vs. 30	0.0000017
0 vs. Negative Control	0.000245

Discussion

As Figure 1 shows, the expected relationship between calcium and pH was observed in the research site. However, as Figure 2 indicates, the expected impact that sulfate would have on soil pH was not observed, and a statistical analysis revealed that it was not the sulfate that decreased the pH along the hillside (see Table 1; $p=0.57-0.79$). Thus, our hypothesis was incorrect.

What was observed was that calcium levels had a negative trendline as the distance from the top of the hill increases (see Fig. 3), which does correlate with the pH data that was collected (see Fig.4), both trends being the opposite of what we anticipated. Furthermore, the correlation between these trend lines is highly significant (see Tables 2 and 3; $p=9.46 \times 10^{-8}-0.0029$ for pH; $p=1.47 \times 10^{-6}-0.00257$ for calcium), and as Figure 1 clearly shows, the expected positive correlation between calcium and pH was observed throughout our research site ($r^2=0.5818$).

However, we did not anticipate that the calcium levels would be highest and the pH the most neutral at the top of the hill, and vice versa at the bottom of it. We had originally thought that calcium would leach down the hill from the exposed limestone at the top, releasing the carbonate ions from the limestone to react with any sulfate in the soil, thereby neutralizing the soil's pH further down the hill. However, as seen in Fig. 5, the sulfate level had no clear correlation with where on the hill the soil was tested. Furthermore, as seen in Fig. 2, the known correlation between sulfate and pH was not found ($r^2=0.0019$), and when the sulfate data was analyzed statistically, no statistical significance was found (see Table 1; $p=0.57-0.79$). Therefore, we can conclude that sulfate was not playing any role in the pH of the soil in the research site, and that there must, as a consequence, be an alternate explanation for the observed correlation between calcium, pH, and the slope of the hill.

One possibility is rainwater. Rainwater is slightly naturally acidic and has a pH level between 5-7. This is due to the fact that as rainwater falls down from the atmosphere, it collects many impurities such as atmospheric carbon dioxide. It may combine with other acidic substances in the atmosphere, making the water slightly more acidic (Balun 2017). Hence, it is possible that acid in rainwater reacts with the calcium carbonate in the limestone at the top of the hill, dissociates, and creates calcium and carbonic acid in the soil. As the carbonic acid travels down the hill, it could then cause the pH levels to become more acidic. As shown in Fig. 4, the pH levels decrease as the distance from the top increases. In fact, there was an 11% decrease in pH level between the soil collected from the top of the hill when compared to the soil collected from the bottom of the hill.

A possible source of excess rainwater and increased acidity at the base of the hill is the retaining tank that collects runoff from the RPCS tennis courts and then slowly releases rainwater into the surrounding hillside where our research was done. Therefore, for further research, we would include releasing a controlled amount of rainwater in an area with limestone and collecting the soil to analyze the pH values. This would show whether or not the acidic rainwater is having an effect on the pH value. If the pH value decreased as the distance from the top of the hill increased, it would indicate that the carbonic acid is traveling down the hill and decreasing the pH in the soil.

References

- Balun, R. (2017, April 24). Why is rain naturally acidic? Retrieved July 25, 2019, from Sciencing website: <https://sciencing.com/rain-naturally-acidic-6475032.html>
- The Environmental Literacy Council. (n.d.). Sulfur Cycle. Retrieved July 21, 2019, from The Environmental Literacy Council website: <https://enviroliteracy.org/air-climate-weather/biogeochemical-cycles/sulfur-cycle/>
- Environmental Science Summer Research Experience for Young Women. (2001). General Description of the ESSRE Survey Sites. Retrieved July 24, 2019, from ESSRE website: <http://essre.rpcs.org>
- Lake, B. (2000, June). Understanding Soil pH. Retrieved July 21, 2019, from NSW Agriculture website: https://www.dpi.nsw.gov.au/__data/assets/pdf_file/0003/167187/soil-ph.pdf
- Oldham, D. L. (2014, April 14). Secondary Plant Nutrients: Calcium, Magnesium, and Sulfur. Retrieved July 21, 2019, from Mississippi State University website: <http://extension.msstate.edu/publications/secondary-plant-nutrients-calcium-magnesium-and-sulfur>
- Parnes, R. (2013). Calcium and Soil pH. Retrieved July 21, 2019, from North Organic Farming Association website: <http://www.nofa.org/soil/html/calcium.php>
- Parnes, R. (2013). A guide to organic and inorganic soil amendments: Soil Fertility. Retrieved from <https://nofa.org/soil/pdf/book.pdf>
- soil Ph. (n.d.). Retrieved July 21, 2019, from United States Department of Agriculture website: https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_053293.pdf
- Spectrum Analytic Inc. (n.d.). Agronomic Library. Retrieved July 21, 2019, from Spectrum Analytic website: https://www.spectrumanalytic.com/support/library/ff/S_Basics.htm
- White, P. J., & Broadley, M. R. (2003, October). Calcium in Plants. Retrieved July 23, 2019, from PMC website: <https://www.ncbi.nlm.nih.gov/pmc/articles/>

Acknowledgments

We would like to thank David L. Brock and Cheryl Carmona for helping us throughout this entire experiment and all of the data collection leading up to it, as well as giving us the opportunity to participate in E.S.S.R.E. We would also like to thank Larry & Kathy Jennings and the VWR Charitable Foundation for sponsoring this program and allowing us to learn through this experience.