JOURNAL OF
EMERGING INVESTIGATORS

Article

Reduce the harm of acid rain to plants by producing nitrogen fertilizer through neutralization

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SUMMARY

The phenomenon of dying trees and plants in areas affected by acid rain has become increasingly problematic in recent times. Is there any method to efficiently utilize the rainwater and reduce the harmfulness of acid rain or make it beneficial to plants? This study aimed to investigate the potential of neutralizing acid rainwater infiltrating the soil to increase soil pH, produce beneficial salts for plants, and support better plant growth. To test this hypothesis, precipitation samples were collected from six states in the U.S. in 2022, and the pH of the acid rain was measured to obtain a representative pH value for the country. Experiments were then conducted to simulate the neutralization of acid rain and the subsequent change in soil pH levels. To evaluate the effectiveness and feasibility of this method, cat grass was planted in pots of soil soaked with solutions mimicking acid rain, with control and experimental groups receiving neutralizing agents (ammonium hydroxide) or not. Plant growth was measured by analyzing the height of the plants. Results demonstrated that neutralizing agents were effective in improving soil pH levels and that the resulting salts produced were beneficial to the growth of the grass. The findings suggest that this method could be applied on a larger agricultural scale to reduce the harmful effects of acid rain and increase agricultural efficiency.

INTRODUCTION

Acid deposition, commonly referred to as acid rain, refers to the deposition of acidic substances from the atmosphere to the earth's surface in the form of wet or dry precipitation. This type of precipitation can take many forms, including rain, snow, fog, hail, and even dust particles that have acidic components (1). In the United States, the majority of precipitation has a pH lower than 5.7, which is indicative of acid deposition. This acidic condition arises from the high concentration of nitric and sulfuric acids in the atmosphere that reacts with water molecules in the air, and subsequently, falls to the ground with precipitation. The widespread occurrence of acid deposition is due to the fact that the primary constituents of acid precipitation are acidic sulfur and nitrate compounds, which can be carried over long distances, up to 1000-2000 km (2-5).

Human activities, such as the expansion of production and consumption, as well as natural processes, have a significant impact on the pH value of precipitation. The growing emissions of various air pollutants from these activities are leading to an increase in acidic precipitation (6). The *National Atmospheric Deposition Program* has produced maps that indicate a wide range of pH patterns in precipitation across the United States. The most recent data on precipitation pH at field sites is from 2002 (4). Analysis of the "*Hydrogen ion concentration as pH of precipitation*" map shows a correlation between the acidity trend levels in the U.S., air pollution, and industrial pollution. The pH of precipitation tends to increase from the southwest to the northeast of the country (5).

Over time, acid precipitation can alter the soil pH in which plants grow by dissolving and binding vital minerals and then carrying them away. This leads to a decrease in soil pH, which can result in plants becoming more susceptible to diseases or nutrient deficiencies (7). Acid rain can have detrimental effects on trees, freshwater, and soil, and can even cause the destruction of insects and aquatic life. In addition, it can cause corrosion to steel structures, such as bridges, and weathering of stone buildings and sculptures. Furthermore, exposure to acid particles can pose health risks to humans, including respiratory problems and diseases such as asthma, chronic bronchitis, and pneumonia (2, 5, 8, 17).

Acid deposition can have significant impacts on agricultural activities, including altering soil microbial biomass and community networks, reducing methane flux from agricultural soil, disrupting plant metabolism, and inhibiting agricultural growth (9, 10). Recent research indicates that acid deposition can also react with other chemical elements and compounds to create combined pollution, the effects of which depend on the concentration of the elements and the pH of the acid precipitation (11).

While society can promote lifestyle changes to reduce the formation of acid rain, such as reducing the use of fuel-consuming vehicles, finding ways for farmers and planters to mitigate or utilize acid rain is crucial.

Using an alkaline solution to neutralize the pH of acid deposition is one method to reduce the harm of acid rain on agricultural activities. Ammonium hydroxide (NH_4OH), a colorless liquid chemical solution in the class of caustics, is formed when ammonia dissolves in water. Ammonium hydroxide can react with sulfuric and nitric acid to form ammonium sulfate and ammonium nitrate, which are beneficial fertilizers for plants (12, 13).

Ammonium sulfate, one of the two salts formed in this experiment, is primarily used as a fertilizer for alkaline soils. In the soil, the ammonium ion is released and forms a small amount of acid, lowering the pH of the soil while providing essential nitrogen for plant growth. It is also used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. Ammonium sulfate functions to bind iron and calcium cations present in both well water and plant cells, making it particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Another salt fertilizer, ammonium nitrate (NH_4NO_3), is a white crystalline solid consisting of ions of ammonium and nitrate. It is highly soluble in water and hygroscopic as a solid, although it does not form hydrates. It is predominantly used in agriculture as a high-nitrogen fertilizer.

In conclusion, acid rain has harmful effects on both plants and animals, and a prompt solution is needed to reduce the acidity of precipitation. Alkaline solutions, such as ammonium sulfate and ammonium nitrate, can neutralize natural acid rain, produce salts to fertilize the soil, and benefit agricultural products. By using these salts, we can neutralize acid rain through a "titration-like" method.

RESULTS

We conducted a study to determine the actual pH value of acid deposition in six different regions in the United States. Two different methods were used to collect precipitation samples. The first method involved the direct use of pH testing paper to determine the acidity of the samples, while the second method used the app SPARKvue to directly measure the pH of the rainwater samples collected from the ground. To verify the effectiveness of our methods, we compared our results to those of previously published work. Our measurements showed that the mean pH value of the samples from different regions was 4.6, which is significantly lower than the standard pH value of acid rain, which is 5.7 (**Figure 1**) (1).

To eliminate uncertainties due to differences in soil, we measured the pH of the regular soil available in the school garden. We neutralized acid rain simulations with ammonium hydroxide to achieve a pH of approximately 7. To maintain the soil and distilled water as controlling factors in this experiment, we added only acidic and alkaline solutions to the soil. The soil sample was divided into five pots, with four experimental groups and one control group. We rinsed the pots with distilled water to determine that 200 mL of acid solutions were needed to saturate the soil. We calculated the required volume of ammonium hydroxide, using molarity, to neutralize 200 mL of sulfuric and nitric acid solutions with a pH of 4.6 in place of natural acid rain. For the experimental groups, we added 12.62 mL and 25.24 mL of ammonium hydroxide, respectively, to the acidic solutions to form salt fertilizers. The ammonium hydroxide used had a pH of 10.4.

We recorded the change of pH value of the liquid in the tray of the three groups every ten minutes for 60 minutes, which allows the soil sample to be completely infiltrated by and reacted with the acidic and alkaline solutions. We measured the pH of the collection tray and recorded it every 10 minutes for an hour (**Figure 2**). The experiment demonstrated that the reaction can occur within an hour and that the pH of the solution that penetrated the soil can be neutralized at the end. The collected data supported the hypothesis that the alkaline solution is capable of neutralizing the acid solution, even if it penetrates through the soil. The delay in the change of the pH value can be attributed to the time required for the acidic and alkaline solutions to completely infiltrate the soil and react fully in the tray.

Two key characteristics emerged from the relationship between pH values and time. Firstly, a longer reaction time between the infiltrated solutions and soil led to a more neutralized solution in the tray prior to reaching equilibrium. Secondly, the reaction was completed within 60 minutes and the solutions in the tray eventually reached a fixed equilibrium. (**Figure 3**).

The procedure above demonstrates the effects of acid rain on soil pH and tests the feasibility of using the procedure to reduce the harm of acid precipitation and produce salt fertilizer. To make sure this method can be put into real-life cultivation and can be beneficial to plants, we designed an experiment to elucidate the benefits of this method by watering cat grass with the acid and alkaline solutions mentioned above.

We compared the growth of four groups of cat grass with different levels of acidity in the soil. The results showed that the maximum heights of the groups were 17.4 cm, 9.3 cm, 9.8 cm, and 11.7 cm, indicating that the growth rate varies

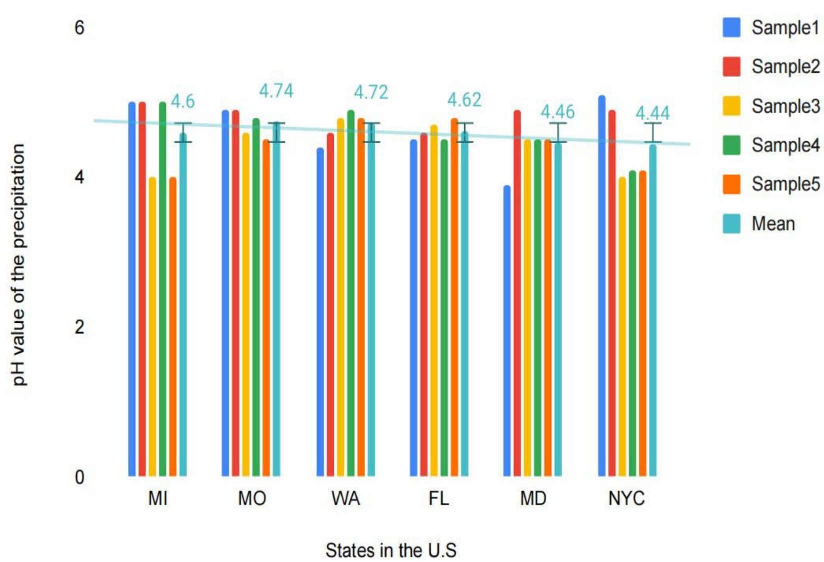

Figure 1: pH value of the precipitate of the six regions in the US in 2022. Collected pH value and the means of the precipitation collected in Michigan (MI), Missouri (MO), Washington (WA), Florida (FL), Maryland (MD), and New York City (NYC) in the U.S. in 2022. The means are 4.6, 4.74, 4.72, 4.62, 4.46, and 4.44 respectively.

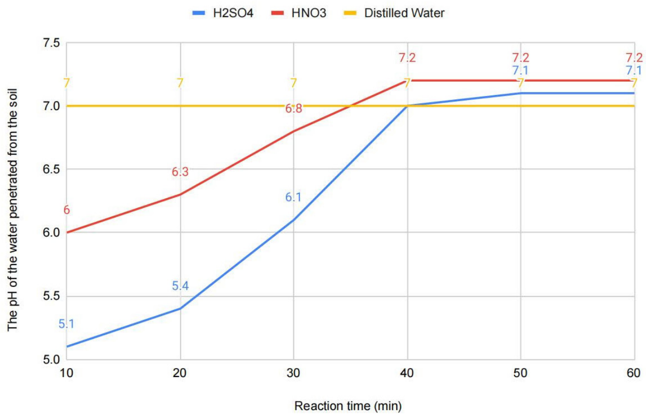

Figure 2: The rate of the reaction between alkaline solution and acid solution. The experimental groups (groups 2-5) show the rate of the reaction between alkaline solution and H_2SO_4 and HNO_3 solution, comparing them with the control group graph which shows the rate of reaction between alkaline and distilled water. The acids neutralized the alkaline solution and brought the pH level near 7 after 60 min.

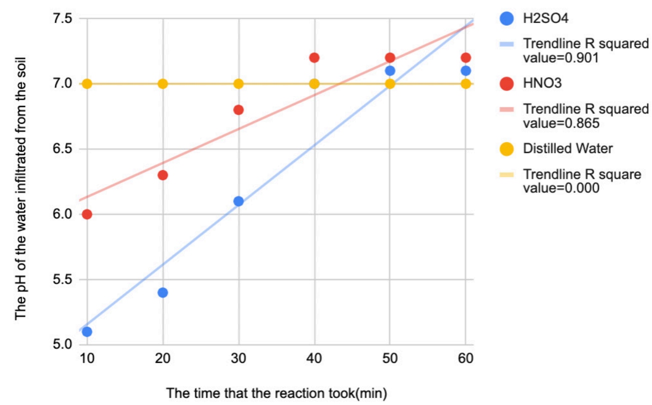

Figure 3: Relationship between the pH value and time. Change in pH value on a time scale of 60 minutes. The graph shows the trend line of neutralization.

depending on the acidity level (**Figure 4**). Therefore, the experiment demonstrated that the acidity of the soil affects the growth of plants. In the experiment, Control group 1 was used as a control while Groups 2 and 3 were used to demonstrate the negative effects of acidic precipitation on plants without any alkaline solution to mitigate harm. On the other hand, Groups 4 and 5 showed the benefits of using NH_4NO_3 solution to neutralize the soil pH. The observation of grass color and shape indicated that the grass in Groups 4 and 5 had a more vibrant color and straighter shape than the other groups. These results support the hypothesis that using alkaline solutions to neutralize acidic precipitation can reduce harm to plants and benefit agricultural products by producing salts to fertilize the soil.

DISCUSSION

In this experiment, we reduced the harm of acid rain to agricultural activities, fertilized the soil, and nourished the plants while neutralizing the acid deposition. This treatment for acid rain proved to be feasible and easy to access in the experiment as well. However, several points can be improved or can be expanded to construct research in the future. First, we assumed that people would know the volume of the precipitation through the weather forecast or the precipitation detector they had on their farm, but that is not always the case. The deficiency mentioned above could be expanded into a new experiment, determining another way to neutralize the acid deposition and avoid using volume as a trait of measurement.

Secondly, some factors can influence the accuracy of this experiment. The difference between the soil from the school garden and the soil from the box of the cat grass could've caused concerns and inaccuracy. Different soil might have different characteristics and require different volumes of alkaline solution to be neutralized after the acidic precipitation. To deal with this unavoidable error, the experiment can be improved to apply all kinds of soil. By testing all the soil samples in the world using the methods in this research, a mathematical formula determining the volume of the needed alkaline solution could be found.

Also, the color and the strength of the grass mentioned in the result are judged and measured by human eyes which is not objective and precise. In the future, with better experimental labs and equipment, spectrophotometers can be used to detect color differences more precisely and measure the strength of the grass by measuring the diameter of the stalk.

Moreover, for irrigation, the acid and alkaline solution are poured into the grass without designing the best way. There must be a better way to rain the grass with chemical solutions. According to the research result, the acid rain absorbed by the leaves of the plants is also harmful, so spraying the alkaline solution onto the plants and pouring the solution directly onto the soil may be more beneficial. Future experiments can be designed to determine the efficiency difference between spraying the alkaline solution and pouring the alkaline solution.

Even though a method is developed to reduce the harm of acid rain, it is still best if the natural precipitation can be reversed back to normal pH (**Figure 4**). People can do many things such as turn off lights, computers, televisions, video games, and other electrical equipment when they are not in use all to use less fuel energy since fossil fuels contain high levels of sulfur and nitrogen compounds, such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x), which are released into the atmosphere when these fuels are burned. These compounds can react with water, oxygen, and other atmospheric chemicals to form sulfuric acid and nitric acid, which then fall to the ground as acid rain.

While nitrogen fertilizer is generally advantageous for plant growth, it's important to consider the amount of fertilizer used in agriculture. Excessive use of chemical fertilizers can have negative consequences on plant health, so it's necessary to use an appropriate amount. Usually, nitrogen fertilizer can nourish the grass and make the grass appear green and strong by helping to create chlorophyll and stimulating root growth. It can also help turf recover from environmental stresses and injury (15). However, over-fertilization hurts the plants by causing plants to develop shallow roots, which impedes their ability to withstand drought and other stresses (16). Over-fertilization can also cause serious environmental problems such as the greenhouse effect. Some soil microorganisms

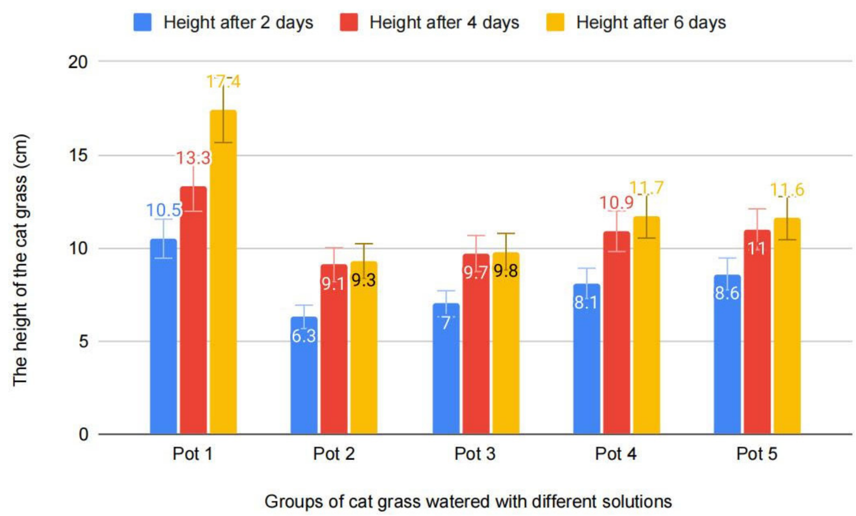

Figure 4: The rate of the growth of cat grass in different groups. The growth trends of different groups are reflected by the different heights of the cat grass. By watering the grass with different solutions with different pH levels, the growth rate is changed.

can transform nitrogen into nitrogen-containing gasses, which get released into the atmosphere in the form of nitrous oxide, a greenhouse gas (15). Therefore, a balance is needed between the positive benefits and negative effects of nitrogen fertilization. In the future, experiments can be designed to determine in what amount and frequency people and farmers should use the method that we developed to maximize the benefits of neutralization to plants without affecting the environment.

Human activities that release sulfur dioxide and nitrogen oxides into the atmosphere are responsible for the increased occurrence of acidic precipitation, commonly known as acid rain (1). Although natural sources such as rotting vegetation and volcanoes also contribute, human activities like coal-burning power plants, factories, and automobiles are the primary cause. Instead of solely focusing on reducing the harm caused by acid rain, it's important for individuals and society to prioritize protecting the environment through sustainable practices and a low-carbon lifestyle. This experiment is a meaningful and necessary step toward addressing the harmful effects of acid rain on agriculture by determining the appropriate volume of ammonium hydroxide needed to neutralize the acidity caused by acid rain for agricultural purposes.

To mitigate the negative effects of acid rain on the environment, it's crucial to reduce the emission of pollutants such as sulfur dioxide and nitrogen oxides by adopting cleaner energy sources and more sustainable land-use practices (17). As the biosphere is the shared home of all living creatures, it's our responsibility to protect it by combining scientific knowledge with individual action.

MATERIALS AND METHODS

We collected rainwater from six states (Michigan, Missouri, Washington, Florida, Maryland, and New York City) in the U.S. to determine the average pH level of precipitation nationwide. We then removed the soil on the surface and dug below the soil surface to obtain a soil sample after we got the rainwater sample from different states. We then dug in several locations in the school garden bed to obtain an average soil sample representative of the area. We also removed stones, sticks, and other debris from the soil and broke up large clumps. After that, we ground the soil into very tiny particles and try to make it soluble in the water solution using a mortar and pestle. Placing the soil into a clean glass container, we added distilled water to turn the soil into a muddy liquid (14). Finally, we measured the soil pH using a pH meter connected to SPARKvue software and record the obtained data.

To test if the alkaline solution can be used to neutralize the soil, we set up three identical soil pots with the same amount of soil inside. Next, we rinsed the soil with distilled water first to estimate how much acid solution was needed to completely infiltrate the soil and eventually flow into the collection tray. We estimated that 200 ml of water could irrigate the soil based on the infiltration we tried with distilled water, therefore 200 ml of acid solutions would be suitable for the experiment. The volume of ammonium hydroxide required to neutralize both 200 mL sulfuric and nitric acid can be calculated using molarity. Since the region (St. Louis) does not have constant rainwater support, 200 ml sulfuric and nitric acid solutions were made with a pH of 4.6 to replace the natural acid rainwater that is needed in the experiment. According to the calculations, we made 12.62 ml and 25.24 ml of ammonium hydroxide. The two experimental groups used the ammonium hydroxide that is already prepared to neutralize the two acids forming salt fertilizer. We made ammonium hydroxide with a pH of 10.4 for this part of the experiment. The setup of three mocking groups enables our experiment to test if the solution can neutralize even penetrated soil: Water the soil with 200 ml distilled water to build a control group, which is Group 1. Water the soil in group 2 with 200 ml sulfuric acid to build an experimental group which then added 25.24 ml ammonium hydroxide into the pot. Water the soil in group 3 with 200 ml nitric acid to build an experimental group which then added 12.62 ml ammonium hydroxide into the pot.

To ensure that the method could be applied to real-life cultivation and benefit plants, an experiment was designed and carried out. Firstly, the box containing dried soil and seeds was opened, and the soil was watered to germinate the seeds. After the grass had grown to a height of 2 cm, the

	Solution added first	Solution added Second
Group 1	Distilled water	Distilled water
Group 2	H_2SO_4	Distilled water
Group 3	HNO_3	Distilled water
Group 4	H_2SO_4	HN_4NO_3
Group 5	HNO_3	HN_4NO_3

Table 1: The setup of the experimental groups. We set up five groups, including one control group (group 1) and four experimental groups. By changing the solutions added to the group first and secondly, we altered the pH of the soil, simulating the different levels of soil contaminated by acid rain.

box of soil and grass was divided into six equal parts of the same shape and size, with one part remaining unused. The five parts of the soil and plants were set into five clay pots of the same shape and size to prevent the acidic or alkaline solution from reacting with plastic. The setup of the control group and experimental groups is shown in **Table 1**. Group 1, the control group, was irrigated with only water. Group 2 was irrigated with 200 ml H_2SO_4 and then distilled water was added to the pot after most of the H_2SO_4 infiltrated the soil and was collected in the tray. Group 3 was irrigated with 200 ml HNO_3 and then distilled water was added to the pot after most of the HNO_3 infiltrated the soil and was collected in the tray. Group 4 was irrigated with 200 ml H_2SO_4 and then NH_4NO_3 was added to the pot after most of the H_2SO_4 infiltrated the soil and was collected in the tray. Group 5 was irrigated with 200 ml HNO_3 and then NH_4NO_3 was added to the pot after most of the HNO_3 infiltrated the soil and was collected in the tray. Finally, the height of the grass in each group was recorded every two days. The pH of the soil was measured using a pH meter connected with SPARKvue, and the data was recorded.

ACKNOWLEDGEMENTS

We express our gratitude to the Lutheran High School South Science Department for providing the necessary materials to conduct this experiment. We extend our appreciation to Mr. Brian Lind for the provision of the Pasco pH meter, and Mr. Steve Schmid for supplying the soil and equipment required for this study. Additionally, we extend our special thanks to the students who participated in the Future Science Scholar Organization (FuSSO) and collected the pH value data of the precipitation in 2022 in their respective states. We acknowledge the support of their schools, which provided them with pH testing paper and pH meters. We would like to specifically acknowledge Sharon Yang from Haslett High School, Tina Zhou from North Broward Prep School, Nancy Chen from Brooklyn Technical High School, and an unnamed student from Maryland for their contributions to the study.

Received: May 19, 2022
Accepted: December 12, 2022
Published: April 25, 2023

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