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Phosphate in Soils: An Undergraduate Exploration of Soil Texture, Chemistry, and Amendment

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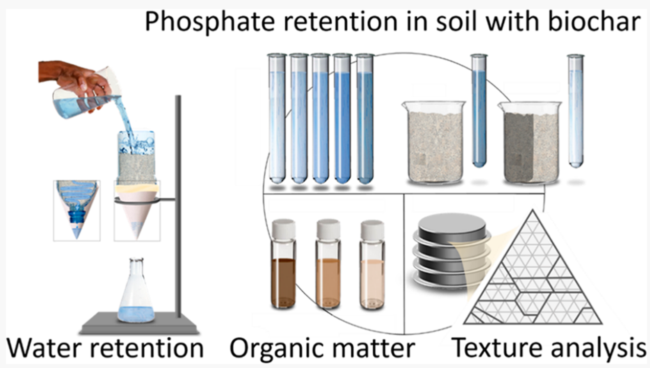
ABSTRACT: This paper presents an experimental lab designed for undergraduate students which focuses on soil science and chemistry. Students perform a series of tests to classify soil's phosphate retaining characteristics, texture, pH, organic matter content, and permeability with the addition of a novel soil amendment, Al Mg biochar. This lab has minimal cost as most chemicals are inexpensive and a soil column is crafted from a used water bottle, filter paper, and masking tape. Students apply their measurements to understand how agriculture plays a role in ocean and watershed health and how soil-testing, soil amendments, and responsible farming practices can minimize agriculture's footprint. It is important for agriculturally focused students to understand how soil chemistry relates to crop yields, and the importance of responsible agricultural practices. Learning outcomes and student attitudes from this experiment were assessed to evaluate the experiment.



KEYWORDS: *High School/Introductory Chemistry, Interdisciplinary/Multidisciplinary, Hands-On Learning/Manipulatives, Analytical Chemistry, Environmental Chemistry, Agricultural Chemistry, Geochemistry, First-Year Undergraduate/General, Applications of Chemistry, Quantitative Analysis*

■ INTRODUCTION

Agricultural runoff water containing phosphates is an area of concern given environmental implications. Phosphorus-containing fertilizers (often in the form of orthophosphates) are applied to farmlands to support the world's current and growing population.[1,2] Phosphorus not taken up by crops is available to runoff in stormwater to nearby bodies of water and cause eutrophication. In many cases, this runoff makes its way to large bodies of water such as oceans where they cause dead zones and drastically impact marine life. To combat this, responsible agricultural practices are necessary.[3]

Undergraduate student exposure to soil properties and amendments enhance their understanding of important environmental issues and stress the importance of responsible agricultural practices of farmland. Students learn firsthand how responsible soil management can vary depending on soil properties such as texture, pH, water permeability, and organic matter content. A novel Al/Mg biochar adsorbent is also used in this experiment to measure its impact on phosphate retention in varying soils.

To date, limited activities are developed for hands on learning with agriculturally focused students. This experiment was designed to focus on important soil chemistry for students in a survey-level organic chemistry class. Important concepts merged in this lab include Beer's Law,[3−10] pH analysis,[11−16] phosphate's conjugate acid/base behavior,[17−19] and the characterization of soil's physical and chemical properties such as soil water retention[20,21] and texture as they relate to the retention of phosphate.[11,12,16,18,22]

Biochar is a low cost adsorbent formed by heating organic biomass such as leaves, wood, or manure in a limited oxygen environment.[23] The result is a highly aromatic carbonaceous material with many oxygen groups, namely hydroxyl, carboxylic acid, ketone, and ether functional groups. Biochar's high surface area, low cost, and usefulness to soil and water systems makes it an attractive material.[24] Although biochar alone does not have an affinity for phosphates, a low cost modification allows it to remove phosphate ions from aqueous environments. In soil systems, phosphate can be adsorbed onto the modified Al/Mg biochar surface and retained in the soil, remaining available for plant uptake.[25,26] Figure 1 shows

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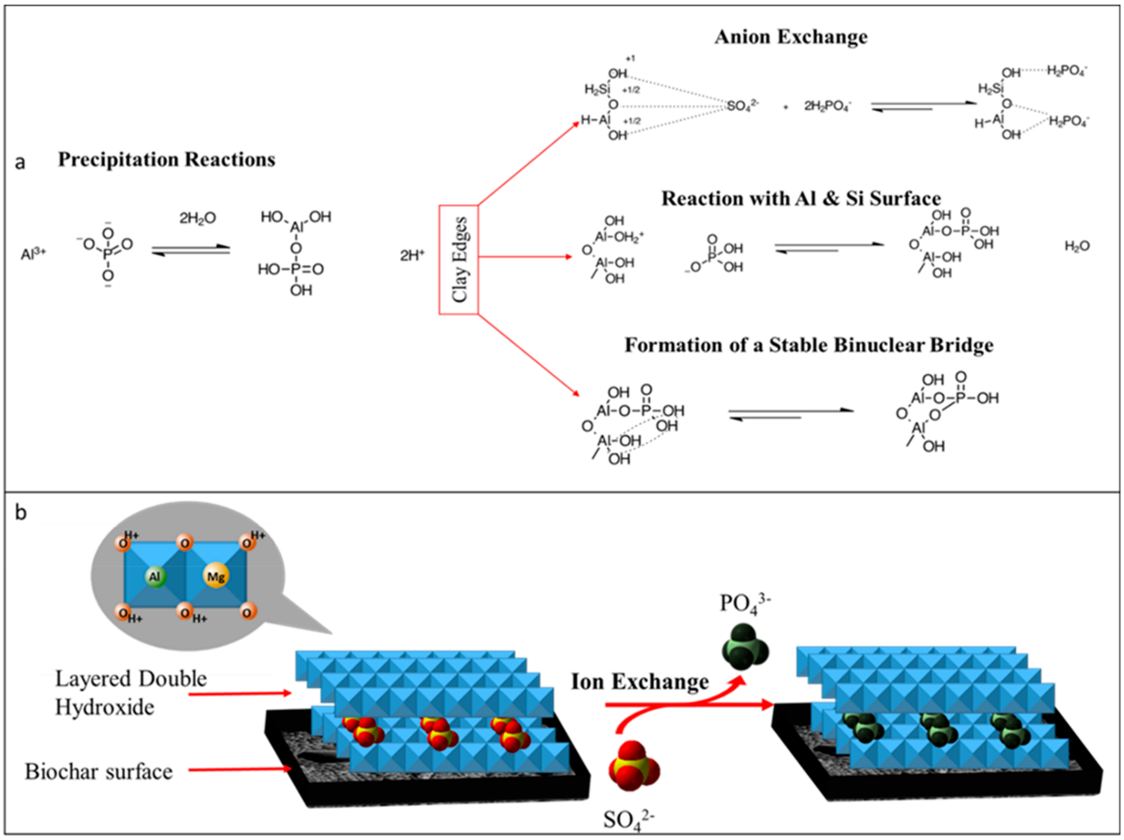

Figure 1. Mechanisms of phosphate retention by (a) clay edges and (b) Al/Mg modified biochar. Phosphate ions bind with Al/Mg biochar through ion exchange. Because phosphate ions make stronger electrostatic interactions with Al^{3+} than with water molecules, phosphate reduces its water solubility and retains in soil.

phosphate retention on (a) clay edges and (b) Al Mg modified biochar.

This applied chemistry undergraduate laboratory is designed for majors such as plant and soil science, soil chemistry, turf grass management, and environmental science. Although undergraduates are the primary audience, this laboratory also works well for high school students as the learning objectives support younger students as well. Depending on the audience and the amount of time available, the instructor has the option of allowing students to use Beer's law to quantitate phosphate using UV−vis, or allowing students to estimate the amount of phosphate using colored solutions. Either pH strips or a pH probe can be used to determine soil pH. Additionally, the materials for the lab are inexpensive; including a soil filtration column constructed from a recycled plastic water bottle and soil samples obtained from the local environment.

Students in agriculturally focused majors may have been introduced to concepts such as anionic exchange capacity, soil pH, and soil texture. This lab combines all these concepts and allows students to characterize a regional soil. This lab experiment is designed to be completed within 3 h. Twenty-four students would be ideal for one set of experiment to work as 2 or 3 students in a group. Student learning reinforces the need for responsible agriculture and the necessity of soil testing.

■ LEARNING OBJECTIVES

With this experiment, the student learning objectives were for the student to

(1) understand how clay content affects soil phosphate retention
(2) relate soil texture to water drainage and water retention
(3) understand how the addition of soil amendments such as Al/Mg biochar would affect soil phosphate retention
(4) understand how soil pH is modulated by phosphate speciation within that specific soil

■ SAFETY HAZARDS

Students will work with caustic chemicals including reagents containing sodium hydroxide and sulfuric acid. Students should wear goggles and gloves during the entirety of this experiment. EDTA, organic matter extraction solution, and any unused sodium hydroxide solution is to be disposed of in the basic waste. Reducing solution, unused phosphate standards, and any spent reducing solution should be disposed on in the acidic waste. Further details regarding waste disposal is detailed in the Supporting Information.

■ EXPERIMENT OVERVIEW

Preparation of Al/Mg Biochar, Reagents, Standards, And Procurement of Various Soil Types

Black Owl Premium Organic Biochar was purchased from Millipore Sigma, St. Louis, MO, and modified into Al/Mg biochar following the method proposed by Ronghua. Al/Mg biochar was prepared by soaking aluminum sulfate (Millipore Sigma, St. Louis, MO) and magnesium sulfate salts (Millipore Sigma, St. Louis, MO) into biochar and exposing this slurry to sodium hydroxide.[27] The complete instructions for biochar production is given in the notes for stockroom preparation in the Supporting Information. Al/Mg biochar was prepared by the instructor before the experiment. The prepared biochar can be stored indefinitely and used for multiple lab sections. Standard solutions of phosphate were prepared via serial dilution. These solutions can be prepared ahead of time by instructor or prepared by students prior to start of soil testing if it is extended to a 2-week lab. Reducing solution (an acidic solution of ammonium molybdate) should be prepared the week of lab and not stored any longer as it has a short shelf life. Ammonium molybdate was purchased from Millipore Sigma, St. Louis, MO. Reducing solution was stored in a 4 °C refrigerator and equilibrated to room temperature prior to the lab. Soil samples can be chosen by the instructors to obtain different effects depending on the type of soil. The National Resources Conservation Service (NRCS) soil survey for a state can be found by visiting the USDA governmental website.[28] This resource can assist the instructor/student in procuring soil types for this undergraduate laboratory experiment.

Students first created a soil filtration column by unscrewing and discarding the top of an empty used water bottle. The bottom of the water bottle was cut away using scissors and discarded. A piece of filter paper was folded into a tight cone and secured onto the water bottle where the cap was located using masking tape. This water bottle-column was inverted over a flask and secured to a ring stand. The student then added 50 g soil to this column along with deionized water. Soil was allowed to drain for 1 h.

While constructing this column, students made a hot water bath by heating a beaker of water to 55 °C. In a separate container, students shook phosphate (Millipore Sigma, St. Louis, MO) containing solution through soil and soil + Al/Mg biochar. The solutions were filtered and analyzed for phosphate content using reducing solution (colorimetrically or with UV−vis absorbance). While waiting for the color to develop, students analyzed soil organic matter content using EDTA (Millipore Sigma, St. Louis, MO) and sodium hydroxide (Millipore Sigma, St. Louis, MO) organic extraction solution. The organic content was approximated using a comparison chart, with organic content scores ranging low, medium, and high. Students additionally performed a soil texture analysis by sieving their soils to separate soil components by size.

Sized components include sand, silt, and clay. The percentages of each were used in tandem with a soil texture triangle to determine the texture and classification of the students' specific soil. Soil pH was determined by taking the pH of solution obtained by mixing soil and deionized water. At this point, the students constructed a calibration curve using the phosphate standards and the experimental solutions at 830 nm using a UV−vis spectrometer and disposable cuvettes. Students revisited their water column, and the amount of water that sits atop of the soil (runoff), drained through the soil (percolated), and held by the soil (retained) was calculated.

■ RESULTS AND DISCUSSION

Students determined the retention of phosphate colorimetrically or by using Beer's law with a UV−vis spectrometer. The ammonium molybdate mixed with phosphate solution led to a strong blue colored complex. When students observed their soil and amended soil filtrate, they could clearly see that the soil filtrate had a blue color whereas the amended soil filtrate was almost completely clear. Students could visually discern that the soil + Al/Mg biochar retains phosphate better than soil without this amendment. Figure 2 shows a student's

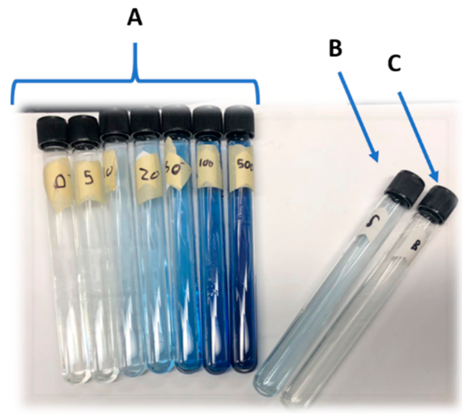

Figure 2. Student colorimetric results: (A) standard series, (B) soil filtrate, and (C) soil and Al/Mg biochar filtrate. The blue color of sample B soil filtrate is due to phosphate washed out of the soil. In contrast, sample C soil and Al/Mg biochar filtrate is pale in color or almost colorless. The Al/Mg biochar amendment allows soil to retain more phosphate ions.

phosphate standard series as well as their soil filtrate and amended soil filtrate. Table 1 presents washed out phosphorus concentrations by different soils with and without biochar.

Table 1. Comparison of Phosphate Drainage Results Obtained by Students for Different Soils

Location with Some Soil Type Characterizations	Phosphate Drainage, ppm Biochar Absent	Biochar Present[a]
Pontotoc Ridge	24.9	0.26
Black Prairie Topsoil	10.3	3.24
North Farm Soils:		
Sand	83.7	3.24
Silt/Loam	27.3	2.77
Clay	13.0	3.24
Black Prairie Subsoil	11.8	3.24
North Central Hills	45.8	3.88
Flatwoods	29.2	4.12

[a]Results show that soils treated with Al/Mg biochar have retained more phosphate and consequently have smaller amounts of phosphate in drainage.

Table 1. Phosphate drainage results obtained by students for different soils. The results show that soils treated with Al/Mg biochar have retained more phosphate and consequently have smaller amounts of phosphate in drainage.

Students determined the soil composition (% clay, % silt, % sand) through sieving of soil samples through sieves of varying size. The smallest particle sizes represent clay and are collected by the collection pan (<125 μm). The next smallest particles are representative of silt. These particles are of sizes (125−250 μm). The largest soil component is sand (250 μm−2 mm). Water that was percolated through the soil was collected and tested for pH via a pH meter or pH strip. Figure 3 shows how a student would determine the species of phosphate that dominates at their specific soil's pH. Instructors emphasized the buffer capacity of the conjugate acid/base pair determined

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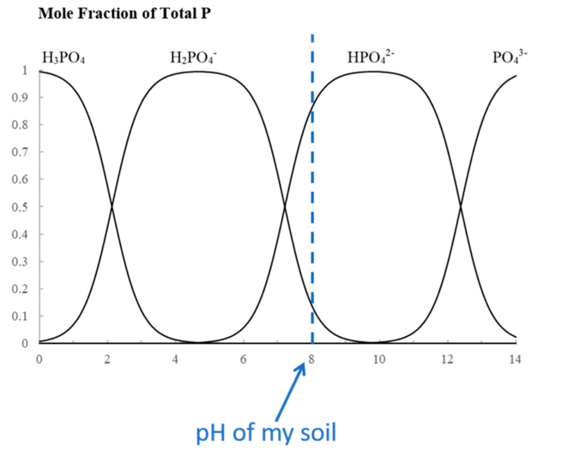

Figure 3. Example student results for soil pH. Student understanding of pH and buffer capacity is supported through analysis of the conjugate acid/base pair.

through this analysis and supported students to understand how soil pH is regulated.

Students determined the soil's ability to retain water using a recycled water bottle column. The step by step procedure for constructing a soil column from a used water bottle is shown in Figure 4. This approach allowed students to visually assess how much water drains through their soil. Students calculated the amount of retained water held within the soil. Water retention is directly related to soil texture, which allows students to understand the impact soil texture has on nutrient retention or water runoff. Students rated their soil's organic matter content by using an EDTA/NaOH extraction solution and comparing the color of filtered solution with a standard.

■ EVALUATION OF LEARNING OUTCOMES

This laboratory experiment was presented to a total of 68 students in a survey of organic chemistry lab course. The majority of the students in this course were agriculturally focused majors including agronomy, plant and soil science, poultry and dairy science, turf grass management, nutrition, and biomedical and agricultural engineering. Many of these students have been exposed to soil chemical properties such as pH but lack detailed understanding of how soil chemical and physical properties are related.

In general, this lab was a success in that most students successfully accomplished the defined learning objectives. The learning objectives were analyzed using post-laboratory questions. Objective 1 was analyzed by asking students how efficiently their soil retained phosphate. They were asked to relate this to clay percentage. The majority of students (97%) were able to understand how phosphate retention was impacted by their soil composition. Students were asked to relate how the clay content of their soil impacted the water fraction that would likely percolate through their soil as well as how that would affect the amount of runoff a particular soil would experience. Seventy-six percent (76%) of students demonstrated mastery of this objective. Objective 3 was measured by asking students how their observed phosphate retention in soil was impacted when biochar is added. Eighty-eight percent (88%) of students correctly reported that biochar increased phosphate retention in their soil. In addition, 88% of students were able to correctly identify which phosphate species was present in their soil, and were able to describe how the pH is buffered. A student survey (in form of a Likert Scale) was administered upon the completion of the laboratory. Upon looking at the results of these surveys and reading student written comments, it is clear that the major appeal of this lab is its relevance to the students taking the course. With Mississippi State University being a land-grant institution, most students enrolled in this survey of organic course are agronomy majors. The application of this lab to the students' area of interest was clear. Some written student comments included, "It was actually [relevant] towards my degree" and "It is a real-life issue and topic." Other students stated that "This is my favorite lab as it relates to the outside world," and "Great lab for MSU with agriculture being our top major." The student surveys showed that the lab worked as expected (4.0/5.0), and students were able to see clear results (4.4/5.0).

■ CONCLUSIONS

Recently, this lab received much positive attention by various departments including the Mississippi State University Department of Landscape Architecture which wants to modify this laboratory procedure to be portable so that it can be readily applied out in the field. As well, MSU Department of Biochemistry is interested in using this exercise as part of their outreach efforts with local high school students and 4-H participants, and it has been recommended for inclusion as part of an MSU extension workshop on agriculture for adult learners. These would all be a direct expansion of the audience for this experiment as described in this paper.

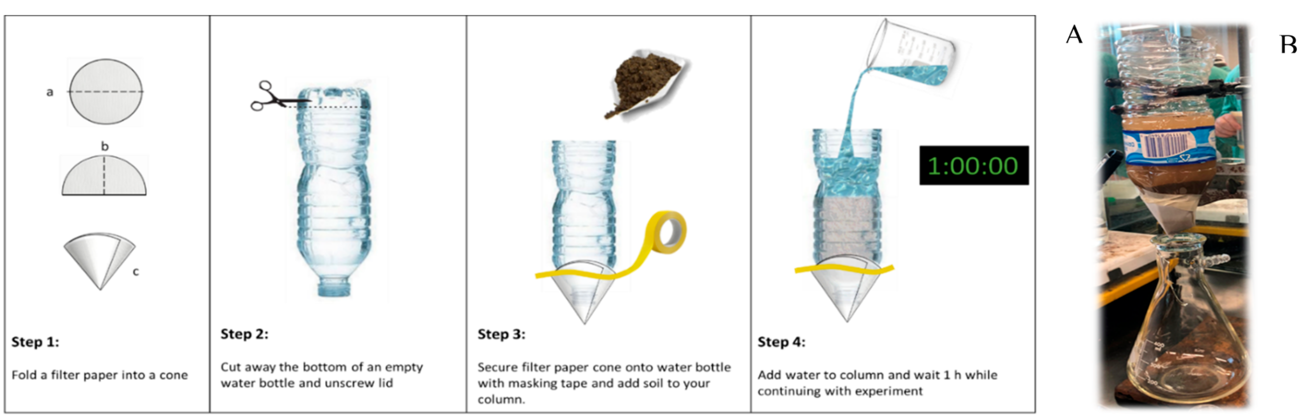

Figure 4. (A) Step by step procedure for constructing the soil column from the used water bottle; (B) the prepared soil water column.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.9b00529.

Equipment, chemicals, detailed experimental procedure, notes for the instructor, and typical student data (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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