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Seth Boles

University of Arkansas, Fayetteville

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Effect of Incubation Temperature on Phosphorous Release from Soils to Water

Seth Boles

Biological Engineering Program

Biological and Agricultural Engineering Department

College of Engineering

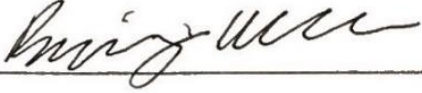
University of Arkansas

ADVISORY AND COMITEE SIGNATURE PAGE

This thesis has been approved by the Biological and Agricultural Engineering Department for submittal to the College of Engineering and Honors College at the University of Arkansas



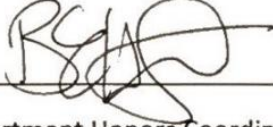
Signature 04/30/2018 Date
Dr. Brian E. Haggard



Signature 4-30-18 Date
Dr. Benjamin R. Runkle



Signature 4/30/18 Date
Dr. David M. Miller



Signature 04/30/2018 Date
Department Honors Coordinator

Abstract

In recent years, nutrient release into flood waters and runoff has been a major concern within the Illinois River watershed, as well as nationwide. This study investigated whether there was a change in the release rate of soluble reactive phosphorous (SRP) into overlying water from soil cores incubated at different temperatures. Soil cores were incubated at 4.4°C, 20°C, and 32°C. After inundation, water samples were taken periodically over a seven-hour period and SRP measured. Following the drainage of the water, the upper 5 cm soil from each core was dried and analyzed for Mehlich III-extractable and water-extractable P. The results showed that SRP release at 32°C ($63.5 \text{ mg m}^{-2} \text{ h}^{-1}$) was significantly greater ($p < 0.01$) than those at 4.4°C ($18.4 \text{ mg m}^{-2} \text{ h}^{-1}$) and 20°C ($24.1 \text{ mg m}^{-2} \text{ h}^{-1}$). The equilibrium SRP concentration seen in the flood water was also 2.5 times greater in the 32°C (0.54 mg L^{-1}) treatment group ($p < 0.01$). The SRP concentrations and flux were not related to extractable P in the soil, which did not vary across treatment groups ($p > 0.05$). The study found that an increase in temperature can lead to higher SRP concentrations and a faster SRP flux. Based on these results, soil amendments to mitigate P release would be the most effective if applied before the increased rainfall typical of the spring and rise in temperature of the late spring and summer months.

Introduction

Anthropogenic nutrient loading from the landscape to aquatic systems is an environmental problem on a global scale. For example, every summer a hypoxic dead zone forms in the Gulf of Mexico near the mouth of the Mississippi River due to nutrient inputs; the dead zone was 22,720 km² in 2017 (USEPA, 2017). The source of nutrients to water bodies in the watershed include direct discharges and diffuse sources across the watershed (Kiedrzyńska et al., 2014).

The diffuse nutrient sources are spread across the landscape and include agriculture and urban development. The application of fertilizers and manures to the landscape is an important nutrient source. Fertilizer and animal manures are typically applied to meet plant needs, but manure application is guided by a nutrient management tool (P index; Sharpley et al., 2010). When animal manure, such as poultry litter, is used, the nutrient composition is not proportional to plant needs; there is more phosphorous (P) relative to nitrogen (N) (Lory, 1999). This excess P applied can build up over time in the soil (Sharpley et al. 1993).

Phosphorous molecules bind to soil through what is known as adsorption or may even be precipitated in solids. During periods of inundation, P can either dissolve into the overlying water or it can be carried on eroded soil particles (Daniel et al. 1998). Once the P enters the overlying water, it will then be carried in the runoff to nearby waterbodies. The amount of P stored in the soil is positively correlated to runoff P concentrations (Schroeder et al. 2004) and P release rates during inundation (Reavis and Haggard, 2016).

Several other factors, such as pH, dissolved oxygen (DO), and temperature, could also have a correlation to P release rates during inundation (Wu et al., 2013). Temperature is a common factor influencing chemical reaction rates. Typically, an increase in temperature will result in an increase in the rate at which a chemical reaction proceeds if all other factors are held constant. This relationship is expressed by the Arrhenius equation, which determines chemical rate constants based on temperature

and activation energy of the reaction in question. If the mechanism of P release into overlying water is a de-sorption reaction than it is expected that the reaction would follow the Arrhenius relation and SRP release rates would increase as temperature increases.

The goal of this research was to look at how the release rate of soluble reactive P (SRP) changes due to the temperature. The specific objective was to evaluate P release rates from soil incubated and flooded at 4.4°C, 20°C, and 32°C. This research will help us understand if temperature is an important factor in release from soil, and it might help inform how temperature variability in between seasons might influence P release from soils.

Methods

Soil cores were taken from the flood plain of the Watershed Research and Education Center (WREC) in Fayetteville, Arkansas (36° 5'23.33"N/ 94°11'6.27"W), for the simulated flood experiments. The soil at this site was a Pickwick silt loam with a 1-3% slope (USDA-NRCS, 2017). The Pickwick series is taxonomically classified as a Fine-silty, mixed, semiactive, thermic Typic Paleudult. This soil series forms from an alluvial parent material on stream terraces, has a low clay content, and is well drained. The field in question has been historically fertilized with poultry litter and at the time of core extraction was an actively grazed cattle pasture.

Soil samples were taken from across a five-foot by five-foot area along a one-foot grid. Cores were taken using plexiglass cylinders with an inside diameter of 6.3 cm. These cylinders were driven about 10 cm into the ground then carefully removed to keep the soil column intact within the tube. Following removal, each core was capped and wrapped with electrical tape to prevent soil loss. In total, 18 soil cores were taken for the experiments.

After samples were brought back to the lab, they were numbered and separated into 3 test groups. The first set was left out in the lab to stay at 20°C, the second set was placed in a refrigerator at

4.4°C, and the third set was placed in a warm water bath set to 32. The cores were then left in these conditions for 10 days to acclimate to the desired temperatures.

To allow for testing of temperatures above room temperature, a circulating warm water bath was constructed. This involved placing a stand, holding soil core tubes, into a water tank. An aquarium heater was inserted into the tank to control the temperature. A submersible pump was also included to circulate water, improving mixing and heat transfer.

After the acclimation period, each core was artificially flooded with water to a volume of 1 L (32.1 cm) above the soil surface. Tap water was used because its conductivity ($171 \mu\text{s cm}^{-1}$; Beaver Water District, 2016) is similar to that of flood waters within local watersheds (Haggard, unpublished data). The overlying water in each core was aerated during the entire inundation to replicate the oxygenated conditions of typical flood waters.

A syringe was used to take 20 mL samples from the overlying water of the cores. These samples were then passed through $0.5 \mu\text{m}$ glass fiber filters. Initial water samples were taken immediately after flooding and additional samples were then taken at hours 1, 2, 4, and 7. After each sampling, water was then added back into each core to maintain the 1 L water level above the soil surface.

Water samples were then acidified using hydrochloric acid to lower the pH below 2 for storage. Following acidification, samples were taken to the Arkansas Water Resource Center water quality lab for analysis. There the certified water quality lab performed SRP analysis using the modified ascorbic acid method (Murphey and Riley, 1962).

The top 5 cm of each core was then collected and dried before being taken to the Agricultural Diagnostic Lab for P analysis in the soil. This lab measured water-extractable P (WEP) and Mehlich-3 extractable P (M3P) in the soils (Arkansas Agricultural Experiment Station, 2018). These values will be used to determine if soil P properties were not different among treatment groups.

The total mass of P released into the overlying water was needed to determine SRP flux. P concentrations (mg L^{-1}) at each sample time were multiplied by the 1 L volume maintained above the soil surface to give mg of SRP. A correction was made for the mass of P removed from each core during previous samplings. Finally, the SRP mass was divided by the surface area of the soil cores (mg m^{-2}).

The adjusted mass per unit area was then plotted against the time after the initial flooding. Initially, linear regression was going to be used to estimate the flux ($\text{mg m}^{-2} \text{hr}^{-1}$). Due to the non-linear nature of this data the regressions generally had low coefficients of determination (R^2) and were not representative of the flux rates. After attempting several methods to linearize the data, we decided to determine rate by taking the mass release determined for the 3rd sample and divide that by the inundation time to estimate the flux ($\text{mg m}^{-2} \text{hr}^{-1}$) to the overlying water. These rates were then compared using the Analysis of Variance (ANOVA) with a single factor analysis in Microsoft Excel and means were separated using least significant difference (LSD).

By the final water sample, the P concentration had plateaued or had begun to plateau for most of the cores. This is a result of the P concentration in the water reaching an equilibrium with the P concentration within the soil. For this reason, we also compared the concentrations from the samples taken at the 7th hour for each core using ANOVA LSD.

Results

The WEP content varied across the cores taken from the field at the WREC, ranging from 2.87 mg kg^{-1} to 12.3 mg kg^{-1} . However, the mean WEP content was not significantly different between treatment groups ($p > 0.05$, Figure 1). The means range from 4.99 mg kg^{-1} in the 4.4°C treatment group to 6.75 mg kg^{-1} in the 20°C treatment group. The WEP content was strongly correlated ($R = 0.85$, $P < 0.01$) to M3P content across the cores.

The M3P content also varied in the collected cores. The optimum M3P content for agronomic crops is from 36 to 50 mg/kg (Sharpley et al. 2013). The M3P content of the collected cores ranged from 46.7 mg kg⁻¹ to 98.3 mg kg⁻¹ and are therefore at or above the upper limits of the recommended M3P range. Like WEP, the mean M3P content was not significantly different across treatment groups ($p > 0.05$, Figure 1). The M3P treatment means varied from 59.7 mg kg⁻¹ in the 4.4°C treatment group to 77.8 mg kg⁻¹ in the 32°C treatment group.

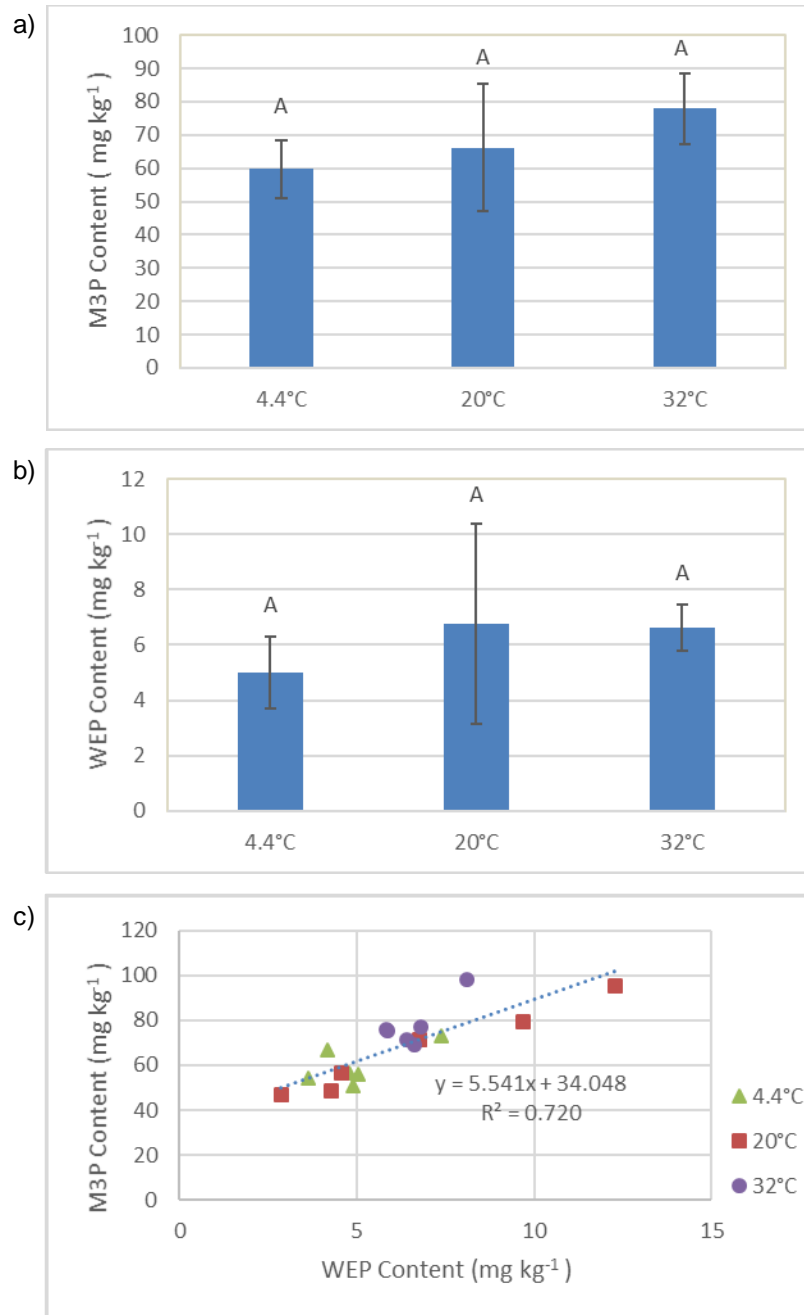


Figure 1. a) Comparison of mean Mehlich III phosphorous (M3P) content at each temperature; b) comparison of mean water extractable phosphorous (WEP) content at each temperature; and, c) scatter plot of M3P content versus WEP content with line of best fit

SRP release rates varied across cores and ranged from 7.87 mg m⁻² h⁻¹ to 110 mg m⁻² h⁻¹. The SRP flux in core 2 (110 mg m⁻² h⁻¹) appeared to be an outlier when compared to other fluxes within that treatment and across all cores (Figure 2). This value was about 22.5 mg m⁻² h⁻¹ greater than the next highest flux and the 5 values closest to the value in question were in the test group maintained at the highest temperature. The flux rate (110 mg m⁻² h⁻¹) was outside the 99% confidence interval (± 81.1 mg m⁻² h⁻¹) about the treatment mean (24.1 mg m⁻² h⁻¹) when excluding the data point. Therefore, it was decided not to include this data point in the statistical analysis.

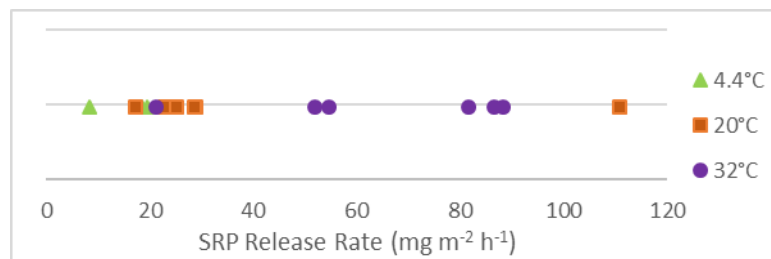


Figure 2. Distribution of soluble reactive phosphorous (SRP) flux across all treatments

The SRP release rates were then grouped by incubation temperature. The ANOVA analysis showed a significant difference between the incubation groups ($p < 0.05$, Figure 3). The mean SRP flux at 32°C (63.5 mg m⁻² h⁻¹) was significantly greater than that observed at 4.4°C (18.4 mg m⁻² h⁻¹) or at 20°C (24.1 mg m⁻² h⁻¹). There was not a significant difference between the mean SRP flux rates in the 4.4°C and 20°C treatments. The SRP flux across the cores and treatments was not correlated to M3P or WEP content in the soil (Figure 3, $p > 0.05$).

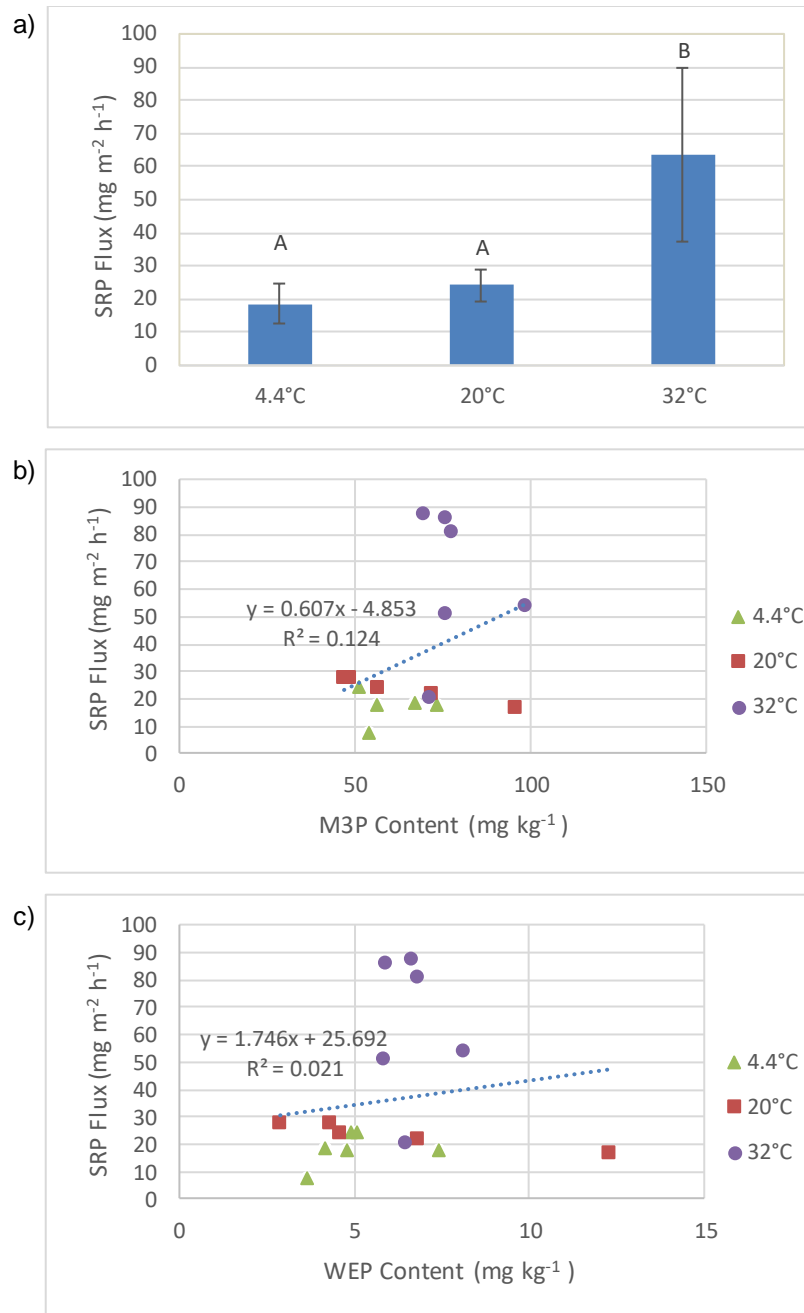


Figure 3. a) Mean soluble reactive phosphorous (SRP) flux rates for each temperature with error bars of one standard deviation; b) scatter plot of SRP flux versus Mehlich III phosphorous (M3P) content with line of best fit; and, c) scatter plot of SRP flux versus water extractable phosphorous (WEP) content with line of best fit

The mean SRP concentrations across the treatment groups increased during the incubation (Figure 4). By the end of sampling, SRP concentrations in the overlying water had begun to stabilize to an equilibrium with the P within the soil cores. The seventh hour samples had SRP concentrations that ranged from 0.097 mg L⁻¹ to 0.769 mg L⁻¹. ANOVA analysis showed a significant difference between treatments ($p < 0.05$, Figure 5) where the mean P concentration at 32°C (0.54 mg L⁻¹) was significantly greater than the mean at 4.4°C (0.20 mg L⁻¹) and the mean at 20°C (0.22 mg L⁻¹). However, the difference in the mean SRP concentration at 4.4°C and 20°C was also not large enough to be significant. The equilibrium SRP concentration across the cores and treatments was not correlated to M3P or WEP content in the soil (Figure 5, $p > 0.05$).

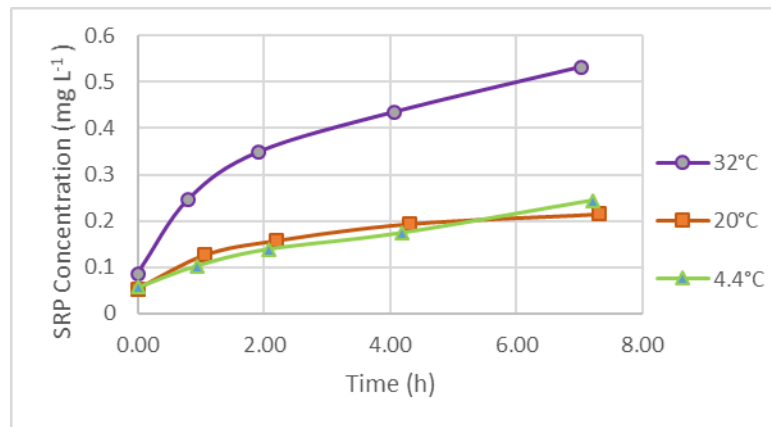


Figure 4. Mean of soluble reactive phosphorous (SRP) for each treatment and sample time

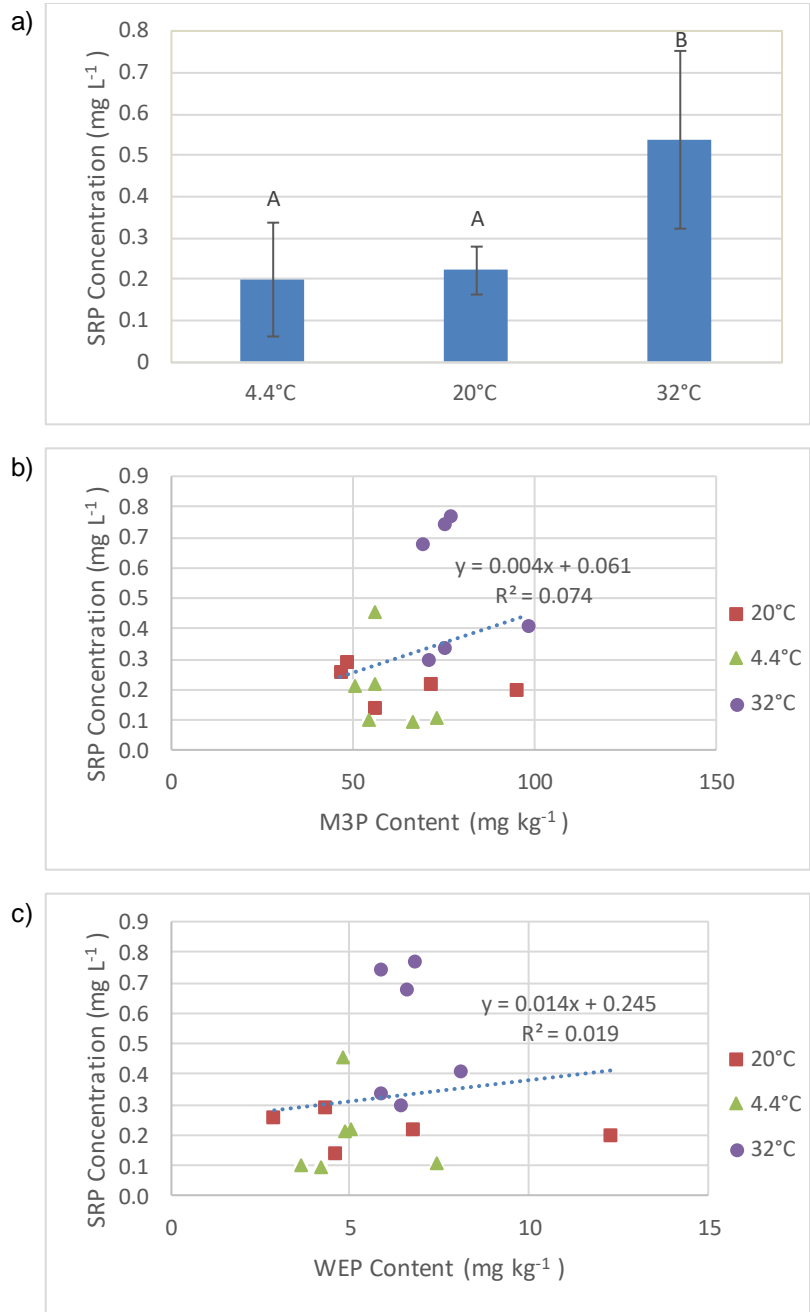


Figure 5. a) Mean equilibrium soluble reactive phosphorous (SRP) concentration of each temperature with error bars of one standard deviation; b) SRP concentration versus Mehlich III phosphorous (M3P) content; and, c) Equilibrium SRP concentration versus water extractable phosphorous (WEP) content

Discussion and future opportunities

The data suggests that the rate of SRP release does increase as ambient soil temperature increases, which is consistent with similar studies. For example, Holdren and Armstrong (1980) found that an increase in the water temperature resulted in increased P release rates from lake bottom sediments, this was seen between cores held at several temperatures between 2°C and 23°C. The implications for such an increase are important during runoff events where a greater mass of P could be transferred to the water during the short period of contact. Therefore, large rainfalls in the summer months will have a greater potential to release large amounts of P than similar storms in the cooler winter months.

The data also suggests that the equilibrium SRP concentration will increase with an increase in temperature. This is supported by multiple studies which determined that the mass of P released was greater in the soils incubated at higher temperatures (Koerselman et al., 1993; Wu et al., 2013). This shows that in times of extended flooding, the overlying water has the potential to reach a greater P concentration when the water and ambient temperatures are higher. When this water finally drains from the area, this will lead to more P being carried to the surrounding streams and lakes.

Global warming could have an impact on water quality and ecological stability due to the potential increases in temperature and the frequency and intensity of rainfall events. The temperature has been estimated to rise anywhere from 1.4°C to 5.8°C by 2100 (IPCC, 2000). If left unmanaged this temperature increase could contribute to increases in the P released into water bodies. A study on the effect of global warming by Wang et al. (2013) showed that a five degree increase in water temperature led to a 25% increase of the SRP flux seen in small scale tests, while this study saw a 163% (or 2.63 times) increase with a 12°C increase. A three-point fit was used to find an exponential temperature effect equation to estimate the increase seen for a 5°C increase. Following this curve, a 24.3% increase would be seen for an increase of 5°C. This same temperature effect equation showed that a 1°C increase

led to an 4.4% increase in SRP flux which suggest that an increase of a few degrees, like the estimated increase, can lead to a significant increase of the SRP release rate.

The results from this study could likely benefit work to reduce P release into flood waters. Soil amendments, such as water treatment residuals (WTRs), have been shown to immobilize P and to significantly reduce SRP flux (Reavis and Haggard, 2016). By understanding the effect of temperature on P release and the local climatic patterns (Figure 6.), application of soil amendments could be planned for the optimum time to mitigate the release of P. This optimum time would be before the large increases in average temperatures seen in late spring and summer months and before the heavy spring rains.

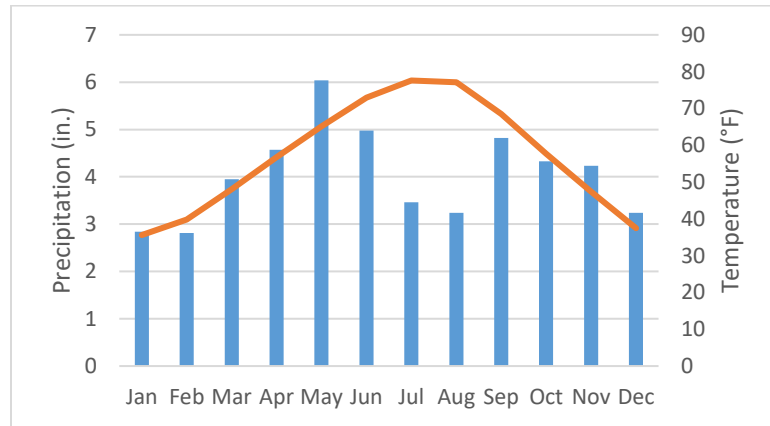


Figure 6. Monthly mean precipitation (bars) and monthly mean Temperature (line) for Fayetteville, AR (NWS, 2018)

Future work in this area would be very beneficial to better understand this trend. The simplest way to do this would be to repeat the process of this project to create larger sample sizes while using the same temperatures. The tests could also be redone at several temperatures within the 20°C to 32°C range in order to better understand the relation leading to the significant difference seen.

These tests could be done in conjunction with tests comparing several other soil characteristics such as texture, organic matter, drainage, pH, and mineral contents. The data from such experiments could then be used to determine a general temperature effect equation that can predict P-release from

a soil based on soil test P (STP), the temperature, and various other characteristics. This equation could then be used to estimate the SRP flux from a soil from field data and common lab tests.

A field scale experiment could also be a good pathway for furthering this research. Runoff at a selected sight could be sampled, along with soil, air, and water temperatures, over an extended period. This could be done by sampling runoff during natural rainfall events, or in a more controlled setting where water is applied by an artificial rainfall system or by uniform surface flooding. A large-scale experiment such as this could be used to determine if there is a temporal variation of SRP release over the course of the year, and if so, when the seasonal peaks of SRP concentration in runoff water occur. This type of test would be more representative of the entire watershed.

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