

Runoff-Water Properties from Various Soils as Affected by Struvite-Phosphorus Source and Water Type

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Abstract

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) can be produced from municipal wastewater and has been shown to be an alternative fertilizer-phosphorus (P) source for various crops, but little is known about the runoff-water-quality implications from soil-applied struvite. The objective of this study was to evaluate the effects of soil [Crelton (Oxyaquic Fragluudalfs), Dapue (Fluventic Hapludolls), Roxana (Typic Udifluvents), and Calloway (Aquic Fraglossudalfs) series], fertilizer-P source [synthetically produced electrochemically precipitated struvite (ECSTsyn), real-wastewater-derived ECST (ECSTreal), chemically precipitated struvite (CPST), and monoammonium phosphate (MAP)], and water source (rainwater, groundwater, and struvite-removed real wastewater) over time on runoff-water-quality parameters from laboratory-conducted, rainfall-runoff simulations. Mesh tea bags containing each soil-fertilizer treatment combination were rained on with each water source (Trial 1), incubated for 6 months, and rained on again (Trial 2) to evaluate runoff-water quality. Struvite fertilizers had similar runoff-water-quality properties to those from MAP. In Trial 1, runoff total P (TP) concentration differences (*i.e.*, soil-fertilizer-water-type response minus control response minus blank response) from ECSTsyn or ECSTreal were 1 to 5 times larger than MAP and CPST for all water-soil-fertilizer-P source treatment combinations, except for the Crelton-groundwater and Roxana-wastewater combinations. In both trials, runoff TP decreased over time in all water-soil and soil-fertilizer-P source treatment combinations, except for the Roxana-CPST combination where TP increased over time by 46%. The similar water-quality responses from the struvite fertilizers among the various soils and water types compared to MAP suggest that struvite has similar runoff-water-quality implications as at least one widely used, commercially available fertilizer-P source.

Keywords

Rainfall Simulation, Runoff, Struvite, Phosphorus, Water Quality

1. Introduction

Widespread use of phosphorus (P) fertilizers in agricultural systems has been documented since the 1940s, when exponential population growth in the United States (US) created a demand for increased food production [1]. Since P is a limiting, plant-essential nutrient in many soils, the addition of P fertilizers into agricultural systems allowed for a large increase in crop production and yield. The incorporation of synthetic fertilizers into crop systems is estimated to have increased worldwide yield by over 50% [2].

Currently, most fertilizer-P sources are derived from phosphate rock (PR). Phosphate rock is mined from deposits worldwide, but the majority is controlled by Morocco, China, and the US [3]. There is an estimated 5×10^{12} kg P present in mineable phosphate rock in North America [4]. However, PR does not contain pure phosphate. Apatite is the most common phosphate mineral in PR, and the majority of PR is mined from sedimentary deposits. After processing, the concentration range of actual phosphate derived from PR is 5% to 40% [5]. In the US, more than 95% of the PR-derived phosphate goes to agricultural use, namely fertilizer production. Fifty percent of the phosphate goes directly to commercially available fertilizer-P production, specifically diammonium phosphate (DAP) and monoammonium phosphate (MAP) [6]. Fertilizer derived directly from PR, known as superphosphate, contains ~10% P [4].

Crop yield demands are expected to increase annually by approximately 2.5% [5]. In 2020, the demand for fertilizer-P increased by 7% [7]. However, demand for all fertilizer is expected to increase at an annual rate of only 0.9% [7]. Phosphate rock reserves and demand for fertilizer-P fluctuate year to year. Depending on demand, economic viability, and P concentrations, current PR reserves are likely to be depleted in the next 30 to 150 years [8]. Therefore, it is necessary to establish sustainable, alternative fertilizer-P sources for the future of agricultural production.

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is a crystalline mineral, containing a 1:1:1 equimolar ratio of magnesium (Mg^{2+}), ammonium (NH_4^+), and phosphate (PO_4^{3-}), that is minimally soluble in neutral and alkaline conditions, but more readily soluble in acidic conditions [9]. The solubility of struvite in water is generally low, around 1% to 5%, but research shows that the low solubility of struvite does not decrease its effectiveness as a fertilizer-P source for plants [10]. Struvite has been characterized as a slow-release fertilizer due to its low water solubility, although more recent research shows that struvite in powder form has a similar dissolution rate in soil as MAP [11]. However, struvite's reported slow-release properties may benefit crops, as the P becomes available to crops in a con-

trolled-release manner as the rhizosphere develops and slightly acidifies over time [12]. Although struvite has been shown to be an effective, potential fertilizer-P source [13] [14] [15], struvite's composition is somewhat variable depending on method of creation and source material.

The addition of compounds such as MgCl_2 or MgO allow for struvite crystallization once the solution becomes supersaturated with Mg^{2+} , NH_4^+ , and PO_4^{3-} [16]. The process of adding chemicals to an aqueous solution to precipitate struvite out of solution is known as chemical precipitation. There is a commercially available, chemically precipitated struvite (CPST) fertilizer known as Crystal Green, which is produced by Ostara Nutrient Technologies, Inc. (Vancouver, British Columbia). According to Ostara [17], Crystal Green is a slow-release fertilizer in pellet form with a fertilizer grade of 5-28-0 and 10% Mg and low heavy metal and salt concentrations.

A more recently developed technique for precipitating struvite from wastewaters is electrochemical precipitation. Electrochemical precipitation of struvite is achieved by electrochemically releasing Mg via sacrificing a Mg anode plate [18]. Electrochemical precipitation avoids the chemical dosing that chemical struvite precipitation requires and instead requires only an energy input for Mg dissolution. Kékedy-Nagy *et al.* [19] used electrochemical precipitation to more efficiently recover P from synthetic wastewater compared to chemical precipitation.

Struvite formation and purity can also be affected by solution pH and/or the presence of calcium (Ca^{2+}) ions or heavy metals in solution. Struvite generally precipitates out of solution at about pH 7.5 and increases in precipitation rate until pH 10.5 [20]. The optimum pH for struvite purity > 90% is from 7.5 to 9 [21]. Hao *et al.* [21] also discovered that precipitating struvite out of solution with a lower pH can result in differential phosphate forms, such as HPO_4^{2-} instead of PO_4^{3-} formation. Wastewater normally has a low Mg concentration; thus, Mg typically needs to be added as a Mg salt for chemical struvite precipitation to occur. In many cases, the Mg is added in the form of magnesium chloride (MgCl_2), magnesium oxide (MgO), or magnesium hydroxide [$\text{Mg}(\text{OH})_2$], all of which also increase the solution pH [22].

Since struvite formation relies on the solution pH, struvite solubility will depend on the soil pH once land-applied as a fertilizer-P source [23] [24]. Acidic soils enhance struvite solubility, while alkaline soils lower struvite solubility [23] [24]. As soil pH affects struvite solubility, the struvite itself can also change the soil pH, as well as the soil-P concentration.

Various studies have been conducted to evaluate the extractable nutrient concentrations of struvite compared to other commercially available fertilizers, such as triple superphosphate (TSP), MAP, DAP, and rock phosphate (RP) [25] [26] [27]. In a flooded-soil incubation experiment, Anderson *et al.* [27] reported the pH of an initially acidic silt-loam soil increased significantly after struvite application. Anderson *et al.* [27] also reported that the soil pH increased with time incubated. The change in water-soluble (WS)-P concentrations in struvite-treated soils were reported to be double the change in WS-P concentrations under any

other fertilizer treatment (*i.e.*, TSP or MAP) [27]. The change in WS-P concentrations decreased with time, while the same trend was reported with Mehlich-3 (M3)-extractable P concentrations [27]. Nongqwuegna *et al.* [28] performed a similar soil-struvite incubation study with soils wetted to 50% of their water-holding capacity instead of being under flooded conditions. Like Anderson *et al.* [27], Nongqwuegna *et al.* [28] reported an increase in extractable-P concentration over time in both fertilizer treatments [*i.e.*, struvite and single superphosphate (SSP)].

Similar to being incubated with various moisture contents, rainfall onto and runoff from fertilized soils can also affect soil-P concentrations, both by water interaction and nutrient runoff. Shigaki *et al.* [29] performed a small-scale tray rainfall-runoff study to evaluate various rainfall intensities (*i.e.*, 25, 50, and 75 mm·h⁻¹), fertilizer-P sources (TSP, SSP, RP, and swine manure), and their effects on runoff-P concentration from the soil. In all fertilizer-P treatments, the runoff-P concentration exponentially increased with an increase in rainfall intensity [29]. However, if rainfall occurred days or weeks after the fertilizer application, the runoff-P concentration exponentially decreased [29]. Smith *et al.* [30] reported similar results, where runoff-P concentration decreased over time. Consequently, the longer the time that passed between fertilizer application and the rainfall event, the lower the runoff-P concentration [29] [30].

Currently, agriculture depends heavily on PR as the main source for P fertilizers. However, PR is a non-renewable resource, and the world's minable PR deposits will likely be depleted within 150 years. Therefore, the objective of this study was to evaluate the effects of soil [*i.e.*, Crelton (Oxyaquic Fragiudalfs), Dapue (Fluventic Hapludolls), Roxana (Typic Udifluvents), and Calloway (Aquic Fraglossudalfs) series], fertilizer-P source [*i.e.*, synthetically produced ECST (ECSTsyn), real-wastewater-derived ECST (ECSTreal), CPST, and MAP)], and water source (*i.e.*, rainwater, groundwater, and struvite-removed wastewater) over time on the change in runoff-water quality parameters from small-scale, laboratory-conducted, rainfall-runoff simulations. It was hypothesized that the change in runoff-water quality parameters will differ among soils, fertilizer-P sources, and water sources over time. More specifically, it was hypothesized that the largest runoff-P concentration from the ECST treatments will occur in the soil with the lowest-pH soil treated with water with the lowest pH due to struvite's larger solubility in low-pH solutions. It was also hypothesized that all struvite treatments will, in general, have the lowest runoff-P concentrations among the fertilizer-P treatments due to struvite's reported slow-release nature [10]. However, it was hypothesized that struvite (*i.e.*, ECSTsyn, ECSTreal, and CPST) runoff-water quality parameters, in general, will be similar to MAP.

2. Materials and Methods

2.1. Soil Collection

Soil was collected from agriculturally managed areas of southwestern Missouri

and western and eastern Arkansas for use in a laboratory rainfall-runoff simulation study. Bulk soil was collected from the 0- to 15-cm depth at all locations. A Roxana fine sandy loam (coarse-silty, mixed, superactive, nonacid, thermic Typic Udifluvents) [31] was collected from a row-crop-cultivated field at the University of Arkansas, Division of Agriculture's Vegetable Research Station near Kibler, AR (35°22'50"N; 94°14'01"W) [32]. A Calloway silt loam (fine-silty, mixed, active, thermic Aquic Fraglossudalfs) [33] was collected from within an approximate 3-m² area from the edge of a row-crop-cultivated field at the University of Arkansas, Division of Agriculture's Pine Tree Research Station near Colt, AR (35°07'23"N; 90°55'46"W). The Roxana soil was collected in December 2017 and the Calloway soil was collected in early spring 2021. Two soils were also collected from managed pasturelands at the University of Missouri's Southwest Research Center near Mount Vernon, MO in June 2021. One soil was a Creldon silt loam (fine, mixed, active, mesic Oxyaquic Fragiudalfs; 37°04'45"N; 93°52'17"W) [34] and the second soil was a Dapue silt loam (fine-silty, mixed, active, mesic Fluventic Hapludolls; 37°05'07"N; 93°52'17"W) [35]. All four soils represented various typical agricultural areas in the mid-Southern US.

2.2. Soil Processing and Analyses

After collection, all moist soil was gently, manually pushed through a 6-mm sieve to remove large plant or/and rock debris and to unify the aggregate-size distribution to facilitate use in the rainfall-runoff simulation tests. Sieved soil was then air-dried in a greenhouse for approximately one week at approximately 37.8°C and stored in 20-L plastic buckets. Three soil sub-samples were gathered from each of the four air-dried bulk soils. Soil sub-samples were oven-dried at 70°C for 48 hours to determine gravimetric water content, manually crushed using a mortar and pestle, and sieved through a 2-mm sieve before performing chemical analyses.

Soil pH and electrical conductivity (EC) were measured potentiometrically in a 2:1 water volume: soil mass slurry. Soil organic matter (SOM) concentration was determined gravimetrically through weight-loss-on ignition after 2 hours of combustion at 360°C in a muffle furnace [36]. Total N (TN) and C (TC) were determined by high-temperature combustion with a VarioMAX CN analyzer (Elementar Americas Inc., Mt. Laurel, NJ). Particle-size analyses were conducted using a modified 12-hr hydrometer method [37] to determine sand, silt, and clay fractions and confirm soil textural classes.

Extractable soil nutrient concentrations were also determined for each of the four soils. A water extraction was performed with a 1:10 soil mass: water volume ratio, where the soil suspensions were agitated for 1 hour, filtered through a 0.45- μ m filter, and analyzed by inductively coupled, argon-plasma spectrometry (ICAPS; Spectro Arcos ICP, Spectro Analytical Instruments, Inc., Kleve, Germany) [38] to determine WS element (*i.e.*, P, K, Ca, Mg, S, Na, Fe, Mn, Zn, and Cu) concentrations. A M3 extraction [39] was conducted with a 1:10 (mass: volume) soil: extractant solution ratio to determine weak-acid-extractable nutrient

(*i.e.*, P, K, Ca, Mg, S, Na, Fe, Mn, Zn, and Cu) concentrations. A strong-acid digestion was conducted using the Environmental Protection Agency (EPA) method 3050B [40] and analyzed by ICAPS to determine total-recoverable element (*i.e.*, P, K, Ca, Mg, S, Na, Fe, Mn, Zn, and Cu) concentrations. All measured initial soil physical and chemical properties are summarized in **Table 1**.

2.3. Fertilizer Treatments

The fertilizer-P treatments used in the rainfall-runoff simulation were CPST (*i.e.*, Crystal Green) [17], MAP, ECSTreal, ECSTsyn, and an unamended control (UC). The CPST material is pelletized and has nutrient concentrations of 11.7% P, 6% N, and 8.3% Mg [32]. Monoammonium phosphate is a pelletized, commonly used, commercially available P and N fertilizer that has a reported fertilizer grade of 11-52-0 and contains 20.9% P, 11% N, and 1.5% Mg [27]. Both ECSTsyn and ECSTreal were electrochemically precipitated struvite materials, but ECSTsyn was precipitated from a synthetic wastewater source, produced to have a similar average P and N composition as typical municipal wastewater [19]. The nutrient composition of ECSTsyn was 18.5% P, 3.3% N, and 13.3% Mg [13]. Using similar methods as for the creation of the ECSTsyn material, the ECSTreal material was created from an actual municipal wastewater source collected from the West Side Wastewater Treatment Facility in Fayetteville, AR and contained 15.4% P, 3.3% N, and 13.6% Mg.

Chemical analyses had been previously performed on the ECSTsyn, CPST, and MAP fertilizer-P sources by Anderson *et al.* [13], and similar procedures were used to chemically characterize the ECSTreal fertilizer-P source. Since both the ECSTsyn and ECSTreal materials were electrochemically precipitated, the material produced was a crystalline-flake powder. Since CPST and MAP were originally in pellet form, both were finely ground to match the powder consistency of the ECSTsyn and ECSTreal materials for more valid fertilizer comparisons.

2.4. Water Collection and Processing

Three water sources were used for the rainfall-runoff simulations. Rainfall was collected in July 2021 from a single rainfall event. The rainwater used in the rainfall-runoff simulation was to mimic natural rainfall events on the soil. Groundwater was obtained from an existing well in July 2021 from the Savoy Research Center west of Fayetteville, AR (36°07'52"N; 94°18'54"W) to represent an irrigation-water source. The third water source was struvite-removed wastewater (SRW) produced in July 2021 as a result of the precipitation of the ECSTreal material described above. The purpose of using the SRW was to evaluate its effectiveness as a potential irrigation-water source after struvite removal. All water sources were refrigerated at 4°C until used. Chemical characterization of the three water sources occurred from the analyses of blanks as part of the rainfall-runoff simulations described below.

Table 1. Summary of soil physical and chemical property differences among the Calloway, Roxana, Creldon, and Dapue soil series used in the rainfall-runoff simulations.

Soil property	<i>P</i>	Calloway	Roxana	Dapue	Creldon
Sand (g·g ⁻¹)	<0.01	0.09d [†]	0.44a	0.20c	0.24b
Silt (g·g ⁻¹)	<0.01	0.79a	0.47d	0.74b	0.67c
Clay (g·g ⁻¹)	<0.01	0.12a	0.10b	0.07c	0.09b
pH	<0.01	7.46a	6.17b	5.77d	6.03c
Electrical conductivity (dS·m ⁻¹)	<0.01	0.17b	0.11d	0.19a	0.13c
Total C (%)	<0.01	1.14c	0.28d	2.57a	1.65b
Total N (%)	<0.01	0.11c	0.03d	0.2a	0.1b
C:N ratio	<0.01	10.0c	10.5b	11.8a	11.5a
Soil organic matter (%)	<0.01	2.6c	0.7d	4.2a	3.4b
NO ₃ -N (mg·kg ⁻¹)	<0.01	10.6c	9.0d	35.8a	15.3b
NH ₄ -N (mg·kg ⁻¹)	<0.01	5.3c	6.4b	17.9a	19.5a
Water-soluble concentrations (mg·kg ⁻¹)					
P	<0.01	1.8d	11.9a	5.7b	3.5c
K	<0.01	6.2c	44.8a	19.7b	20.3b
Ca	<0.01	58.8b	34.0d	83.0a	43.7c
Mg	<0.01	8.9c	21.7a	16.7b	16.3b
S	<0.01	12.0a	4.9c	12.2a	9.5b
Na	<0.01	19.5a	4.1d	4.8c	5.9b
Fe	<0.01	1.5d	49.7a	1.9c	12.6b
Mn	<0.01	0.12d	0.57c	2.2a	1.7b
Zn	<0.01	0.52b	0.33c	0.90a	0.47bc
Cu	<0.01	0.03c	0.08a	0.06b	0.04c
Mehlich-3-extractable concentrations (mg·kg ⁻¹)					
P	<0.01	11.4d	93.3a	41.7b	17.0c
K	<0.01	46.1d	145.3a	102.0c	113.0d
Ca	<0.01	2006a	933d	1601b	1115c
Mg	<0.01	276.3b	194.3d	216.0c	328.0a
S	<0.01	12.0b	5.7c	17.0a	13.0b
Na	<0.01	29.8a	10.0b	7.7c	10.4b
Fe	<0.01	303.8a	200.7b	139.3c	112.0d
Mn	<0.01	244.3a	32.9c	98.7b	101.3b
Zn	<0.01	2.6c	2.4c	30.9a	4.2b
Cu	<0.01	1.6b	1.1c	2.6a	1.2c

Continued

	Total-recoverable concentrations (mg·kg ⁻¹)					
P	<0.01	342.9c	370.7b	426.3a	248.0d	
K	<0.01	597d	1730a	1436b	1160c	
Ca	<0.01	2424a	1440c	2251b	1494c	
Mg	<0.01	1318c	2433a	1202d	1372b	
S	<0.01	137.2c	42.3d	245.7a	154.0b	
Na	<0.01	61.6a	52.7b	26.7c	25.7c	
Fe	<0.01	16705a	8340c	11059b	18023a	
Mn	<0.01	1337a	177d	687c	1163b	
Zn	<0.01	32.9b	22.3c	97.0a	31.3b	
Cu	<0.01	6.3b	4.2d	9.0a	4.7c	

[†] Means in a row with different letters are different at $P < 0.05$.

2.5. Rainfall-Runoff Simulation Experiment

Due to the experimental nature of ECSTsyn and ECSTreal, only small quantities of both ECST materials were able to be produced for testing. Consequently, despite abundant runoff-water-quality studies using simulated rainfall onto field plots $> 1 \text{ m}^2$, to accomplish the objective of the current study required a much smaller scale in terms of soil and fertilizer mass used, treatment area exposed to stimulated rainfall, and the rainfall-simulation apparatus itself.

To simulate rainfall onto fertilizer-soil mixtures and generate runoff, a wooden rainfall-runoff simulator was constructed measuring 91.1-cm tall by 87.0-cm wide by 73.7-cm deep. A frame containing four sets of seven, 31.5-mL·min⁻¹ drip emitters (MLD-AAD, Mister Landscaper Inc., Dundee, FL), separated by approximately 15.9 cm, rested parallel to one another on top of the simulator. For each of the four rows of emitters, three drip emitters were installed in a row 10 cm apart starting at 10.8 cm from the water-source end of the series of emitters and four additional drip emitters were installed 5 cm apart 10.5 cm from the third emitter. All emitters were connected with 4.8-mm-inside-diameter plastic tubing. Tapered, plastic trays (*i.e.*, short sections of rain gutters for houses), 62-cm long by 12-cm wide at the top by 7-cm wide at the base, were manually placed free-standing at a slope of 22.1% below each row of drip emitters to contain the soil-fertilizer mixtures and collect runoff.

On a day of a set of rainfall-runoff simulations, water stored in a 20-L plastic carboy was removed from the refrigerator approximately 1 hr prior to use. The carboy was set on top of a ladder 176.5 cm above and immediately adjacent to the rainfall simulator. The carboy's spigot was connected to 6.4-mm-inside-diameter plastic tubing to gravity-flow to and through the drip emitters. The water delivery rate was approximately 3.5 cm·hr⁻¹ to represent a substantial, high-intensity storm event.

Tea bags (TamBee, B07TCDT76Q), 15-cm wide by 20-cm long, made from a synthetic fiber, were filled with 175 g of air-dried soil that had previously been sieved through the 6-mm mesh screen. An agriculturally relevant fertilizer-P rate (56 kg P₂O₅ ha⁻¹) was determined based on the fertilizer-P recommendation for soybeans (*Glycine max* L. [Merr.]) grown on a loamy Arkansas soil [41]. The appropriate mass of each fertilizer material (*i.e.*, CPST, ECSTsyn, ECSTreal, and MAP) was added to the soil-filled tea bags to deliver the fertilizer-P rate of 56 kg P₂O₅ ha⁻¹ based on the air-dry mass of soil added to the tea bag, but the nitrogen rate was not balanced among fertilizer treatments since the objective of the study did not include evaluating any plant response. The tea bags were then gently, manually massaged to mix the fertilizer with the soil. Since air-dried soil was initially used, once fertilizers were mixed with the soil, each tea bag was pre-wet using a squirt bottle with 20 mL of the appropriate water source (*i.e.*, rainwater, groundwater, or SRW) one week before conducting the rainfall simulation to increase the soil moisture content and to minimize potential soil and fertilizer loss through the tea bags upon handling. Three replications of each soil-fertilizer combination were prepared for a total of 60 tea bags for each of the three water sources, totaling 180 tea bags.

Rainfall simulations were performed on 21, 22, and 23 July 2021 (Trial 1). Each day, a single water source was used for rainfall simulations. The sequence of tea bags containing each soil-fertilizer combination was randomized within each water source. Prior to any rainfall simulations, the plastic tubing was primed with the water source to be used for raining on treatment-filled tea bags. Prior to raining on each set of four treatment-filled tea bags, rainfall was simulated onto the four empty trays and then rainfall was simulated into the four trays with an empty, dry tea bag in the tray to serve as two sets of blanks. Treatment-filled tea bags were placed four at a time directly under the four drip emitters that were closest together and near the down-slope end of the tray to simulate raindrops impacting the soil and water moving underneath and through the soil from up-slope. Each set of four rainfall simulations were conducted for 6 minutes. Pre-trial tests were conducted to determine that 6 minutes of rainfall would yield an estimated 220 mL of runoff water for conducting all planned chemical analyses.

Runoff water from each tray was collected in 2400-mL, rectangular containers at the end of each tray and poured into 250-mL plastic cups for immediate processing for water quality attributes. The process was repeated until each sample was rained on and all runoff water samples were collected.

After raining on each set of four tea bags, tea bags were laid out on plastic bags to air-dry at room temperature (~22°C) for one week. Each day the tea bags were gently, manually turned over to facilitate uniform drying on each side of the tea bag. Once air-dried, the three replications of each treatment-filled tea bag were placed into its own separate plastic bag for incubation for approximately six months when a second rainfall-runoff simulation was performed. The incu-

bated samples for the rainwater and groundwater water sources were wetted using a beaker with 5 to 10 mL of each appropriate water source once a month.

Following the procedures described above, the second rainfall-runoff simulation experiment was conducted on 15 and 16 December 2021 (Trial 2). Only the rainwater and groundwater sources were used in the second rainfall-runoff simulation experiment due to insufficient quantity of the SRW source.

2.6. Water Sample Processing and Analyses

Runoff-sample pH and EC measurement, filtering, and acidification were conducted immediately after sample collection. For pH and EC measurements, approximately 25 mL of each sample were poured into a 50-mL glass beaker. A combination pH/EC probe (Orion StarTM A215 pH/Conductivity Benchtop Multiparameter Meter, Thermo Scientific, Beverly, MA) was placed in the runoff sample for 30 seconds, after which pH and EC readings were recorded. The pH/EC probe was rinsed with distilled water between each individual runoff sample. The pH and EC for all runoff samples were measured within seven minutes of sample collection.

Following pH/EC measurements, approximately 100 mL of each runoff water sample were poured into a small plastic vessel (UC475, Ultimate Clean Environmental Express, Charleston, SC) and filtered through a 0.45- μ m filter (SC0409, FilterMate, Environmental Express, Charleston, SC) attached to the bottom of a plunger. Approximately 20 mL of filtered runoff sample were poured into four, 20-mL, plastic scintillation vials. Two of the four vials were acidified with two drops of concentrated hydrochloric acid for preservation and analysis for total soluble elemental concentrations [*i.e.*, total P (TP), Ca, Mg, and Fe], while the other two vials were left unacidified for nitrate + nitrite ($\text{NO}_3 + \text{NO}_2$), NH_4^+ , and soluble-reactive P (SRP; primarily orthophosphates) concentration analyses. Nitrate + nitrite was measured using the salicylate method (EPA 351.2) [42], NH_4^+ was measured using the cadmium-reduction method (EPA 353.2) [43], and SRP was measured using the acid-molybdate method (EPA 365.1) [44]. Blanks were also analyzed for total soluble S, Na, Mn, Zn, and Cu in acidified runoff samples. When a measured concentration was below the instrument's detection limit (DL), the value used was one-half of the instrument's DL.

To prepare the resulting runoff-water data for statistical analyses, separately for each water source, the average of all eight measured blank values for a water quality parameter was subtracted from the raw water quality parameter measurement to create a blank-corrected value. Since each of the four soils used had somewhat differing initial soil properties, to eliminate potential data bias from dissimilar initial properties, the average was calculated for the UC replications for each water-source-soil-fertilizer-treatment combination and was also subtracted from the blank-corrected value. Correcting the raw water quality parameter measurements for blanks and subtracting the average UC value resulted in

a final water quality parameter data set. The final data set varied from negative to positive values for all measured water quality parameters, which is hereafter referred to as the change in water quality data, to better address actual soil-fertilizer interactions without being skewed by dissimilar initial soil properties.

2.7. Statistical Analyses

Based on a completely random design, a one-factor analysis of variance (ANOVA) was conducted in SAS (version 9.4, SAS Institute, Inc., Cary, NC) using PROC GLIMMIX to evaluate the differences in initial soil properties among the four soils used and the differences in initial water properties among the three water sources used. A gamma distribution was used for analyses of initial soil and water data.

It was impractical to randomize the water sources for the rainfall-runoff simulations, but the soil-fertilizer treatment combinations were randomized within a water source. Therefore, a randomized block design was assumed for the purposes of statistical analyses of runoff-water-quality data. Consequently, a three-factor ANOVA was performed using PROC GLIMMIX in SAS to evaluate the effects of water source, soil, fertilizer-P source, and their interactions on the change in runoff water pH, EC, total soluble P, K, Ca, Mg, Fe, $\text{NO}_3 + \text{NO}_2$, NH_4 , and SRP separately for the first rainfall-runoff trial. Since the change in water quality parameters varied between negative and positive values, a normal distribution was used for statistical analyses of water-quality-change data.

To evaluate treatment effects for Trial 2 and changes over time (*i.e.*, results from the first compared to the second rainfall-runoff trial) on the soil-fertilizer treatment combinations for the rainwater and groundwater sources only, a four-factor ANOVA was performed using PROC GLIMMIX in SAS evaluate the effects of water source, soil, fertilizer-P source, time (*i.e.*, trial), and their interactions on the change in runoff water pH, EC, total soluble P, K, Ca, Mg, Fe, $\text{NO}_3 + \text{NO}_2$, NH_4 , and SRP. Since the change in water-quality parameters over time varied between negative and positive values, a normal distribution was also used for analyses of water-quality data. For all data analyses, significance was judged at $P < 0.05$. When appropriate, means were separated by the least significant difference at the 0.05 level.

3. Results and Discussion

3.1. Initial Soil Property Differences

All initial soil properties evaluated differed ($P < 0.01$) among soils (**Table 1**). Percent clay was largest in the Calloway soil, smallest in the Dapue soil, and was intermediate for the Roxana and Creldon soils, which did not differ (**Table 1**). Similar to percent clay, soil pH was most alkaline in the Calloway soil, most acidic in the Dapue soil, and was intermediate for the Roxana and Creldon soils (**Table 1**). Total C, TN, SOM, and $\text{NO}_3\text{-N}$ were largest in the Dapue soil and smallest in the Roxana soil (**Table 1**).

Water-soluble P, Ca, Mg, and Fe concentrations differed ($P < 0.01$) among all soils (**Table 1**). Water-soluble P, Mg, and Fe were numerically largest in the Roxana soil and numerically smallest in the Calloway soil (**Table 1**). However, unlike P and Fe, Mg did not differ between the Calloway and Creldon soils. Water-soluble Ca was largest in the Dapue soil and smallest in the Roxana soil (**Table 1**).

Mehlich-3-extractable P, Mg, Ca, and Fe concentrations differed ($P < 0.01$) among all soils (**Table 1**). Mehlich-3 Ca and Fe were largest in the Calloway soil, but M3 Ca was smallest in the Roxana soil, while M3 Fe was smallest in the Creldon soil (**Table 1**). Mehlich-3 P was largest in the Roxana soil and smallest in the Calloway soil, while M3 Mg was largest in the Creldon soil and smallest in the Roxana soil (**Table 1**).

Total-recoverable P, Ca, Mg, and Fe concentrations differed ($P < 0.01$) among all soils (**Table 1**). Total-recoverable Fe and Ca were largest in the Calloway soil, but TR Fe was smallest in only Roxana, whereas TR Ca was smallest in both Roxana and Creldon, which did not differ (**Table 1**). Total-recoverable P was largest in the Dapue soil and smallest in the Creldon soil, while TR Mg was largest in the Roxana soil and smallest in the Dapue soil (**Table 1**). Differences in initial soil pH and nutrient concentrations necessitated inclusion of the UC treatment and subtraction of the mean water-quality response for the UC treatment from the water-quality response from each replicate soil-fertilizer treatment combination.

3.2. Initial Water Property Differences

All initial water properties evaluated (*i.e.*, pH, EC, and TP, K, Ca, Mg, S, Na, Fe, Mn, Zn, Cu, B, $\text{NO}_3 + \text{NO}_2$, NH_4 , and SRP concentrations), except Fe, differed ($P < 0.01$) among water types (**Table 2**). Initial water pH was most alkaline for the SRW and least alkaline for rainwater (**Table 2**). Of the initial nutrient concentrations evaluated, most were largest in the SRW, except for Ca and $\text{NO}_3 + \text{NO}_2$, which were largest in groundwater (**Table 2**). Initial Ca, Mg, and $\text{NO}_3 + \text{NO}_2$ were numerically smallest in rainwater, while TP, NH_4 , and SRP were numerically smallest in groundwater (**Table 2**). The alkalinity differences among initial water types likely affected elemental and compound solubilities, particularly after 6 months of incubation for Trial 2.

3.3. Initial Treatment Effects on Runoff Water Quality (Trial 1)

With the exception of runoff EC, every other measured water quality parameter (*i.e.*, pH, TP, Ca, Mg, Fe, $\text{NO}_3 + \text{NO}_2$, NH_4 , and SRP) change was affected ($P < 0.05$) by a combination of two or more treatments (*i.e.*, water type, soil, and/or fertilizer-P source; **Table 3**). Runoff water quality changes are being presented where responses from blanks without soil and the UC were both subtracted so that the change results isolate the actual effect of the fertilizer addition rather than being complicated by the inherent differences among initial soil (**Table 1**) and water (**Table 2**) properties.

Table 2. Summary of water chemical property differences among the rainwater, groundwater, and struvite-removed wastewater sources used in the rainfall-runoff simulations.

Water property	<i>P</i>	Rainwater	Groundwater	Wastewater
pH	<0.01	7.22c [†]	7.89b	9.77a
Electrical conductivity (dS·m ⁻¹)	<0.01	14.8c	461b	578a
P (mg·kg ⁻¹)	<0.01	0.14b	0.01c	1.25a
K (mg·kg ⁻¹)	<0.01	0.41c	1.17b	20.2a
Ca (mg·kg ⁻¹)	<0.01	0.37c	77.9a	27.2b
Mg (mg·kg ⁻¹)	<0.01	<0.01c	1.05b	35.6a
S (mg·kg ⁻¹)	<0.01	0.16c	0.92b	12.1a
Na (mg·kg ⁻¹)	<0.01	0.41c	13.2b	35.8a
Fe (mg·kg ⁻¹)	0.38	0.18a	0.15a	0.19a
Mn (mg·kg ⁻¹)	<0.01	<0.01b	<0.01b	<0.01a
Zn (mg·kg ⁻¹)	<0.01	0.06b	0.11a	0.05c
Cu (mg·kg ⁻¹)	<0.01	<0.01b	<0.01b	<0.01a
NO ₃ + NO ₂ (mg·kg ⁻¹)	<0.01	<0.01c	5.79a	3.05b
NH ₄ (mg·kg ⁻¹)	<0.01	0.27b	0.03c	7.83a
Soluble-reactive P (mg·kg ⁻¹)	<0.01	0.05b	<0.01c	1.17a

[†] Means in a row with different letters are different at $P < 0.05$.

Table 3. Analysis of variance summary of the effects of water type (W), soil (S), fertilizer (F), and their interactions on the change (Δ) in runoff-water quality properties for Trial 1 of the rainfall-runoff simulation experiment.

Source of variation	Δ pH	Δ EC [†]	Δ [TP] [†]	Δ [Ca] [†]	Δ [Mg] [†]	Δ [Fe] [†]	Δ [NO ₃ + NO ₂] [†]	Δ [NH ₄] [†]	Δ [SRP] [†]
Water type	0.01	0.09	<0.01	<0.01	<0.01	<0.01	0.16	<0.01	<0.01
Soil	<0.01	0.07	<0.01	<0.01	<0.01	0.14	<0.01	<0.01	<0.01
Fertilizer	0.99	0.74	<0.01	0.36	0.55	0.31	0.40	0.02	<0.01
W × S	<0.01	0.19	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
W × F	0.14	0.35	0.05	0.41	0.47	0.04	0.53	0.22	0.01
S × F	0.33	0.23	<0.01	0.15	0.58	0.35	0.49	0.27	<0.01
W × S × F	0.11	0.12	<0.01	0.10	0.88	0.28	0.04	0.29	0.02

[†] Electrical conductivity, EC; total phosphorus, TP; calcium, Ca; magnesium, Mg; iron, Fe; nitrate + nitrite, NO₃ + NO₂; ammonium, NH₄; soluble-reactive phosphorus, SRP.

Averaged across fertilizer-P sources, runoff-water pH, NH₄, Ca, Mg, and Fe concentration changes differed ($P < 0.05$) among water type-soil combinations (Table 3). Water pH influences the fraction of soluble nutrients compared to what might remain sorbed to soil solids. Of the three water types, runoff-water pH changes in response to rainwater differed from zero in all soils, except for Creldon where runoff pH decreased in the Dapue and Calloway soils, but increased in the Roxana soil (Figure 1). In addition, runoff-pH changes decreased

from zero in the Dapue soil-wastewater treatment combination (**Figure 1**). Runoff-pH changes from all other water type-soil combinations did not differ from zero or from each other (**Figure 1**). The runoff-pH decrease among the Dapue- and Calloway-rainwater and Dapue-wastewater combinations, which did not differ, was lower than the runoff pH increase from rainwater in the Roxana soil (**Figure 1**). It is likely that the runoff pH response in the Dapue soil was dominated by the lowest initial soil pH and largest initial soil TC and SOM concentrations that imparted an acidifying effect to the runoff water. The runoff pH increase from rainwater in the Roxana soil was likely related to low buffer capacity from the coarsest soil texture so that the alkaline rainwater dominated the response. For the Calloway soil, the decreased runoff pH from rainwater was likely due to the lower initial rainwater pH compared to the initial soil pH, whereas the initial pH for the groundwater and wastewater were both greater than the initial soil pH.

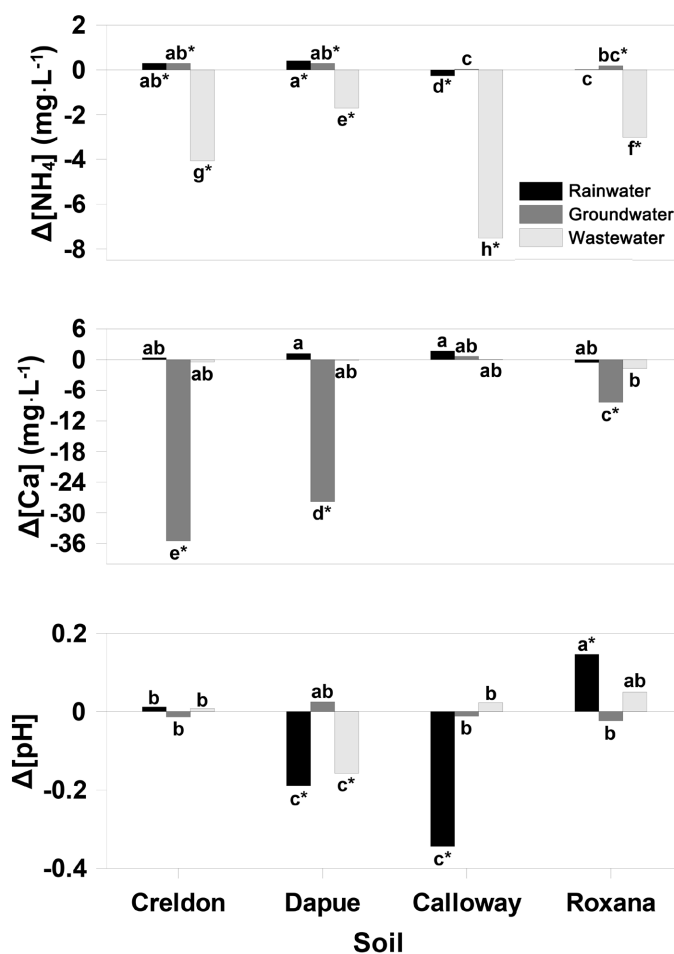


Figure 1. Summary of changes (Δ) in runoff-water ammonium (NH_4), calcium (Ca), and pH concentrations among water type (*i.e.*, groundwater, rainwater, and struvite-removed wastewater)-soil series (*i.e.*, Credlon, Dapue, Calloway, and Roxana) combinations for Trial 1. Bars with different lower-case letters across within a panel are different at $P < 0.05$. Asterisks (*) indicate the change is significantly different from zero at $P < 0.05$.

Excluding the groundwater-Calloway and rainwater-Roxana combinations, runoff-water NH_4 concentration changes for all other water type-soil combinations differed ($P < 0.05$) from zero (**Figure 1**). The greatest runoff-water NH_4 concentration decrease occurred from the wastewater treatment within each soil (**Figure 1**), in which all runoff-water NH_4 concentration changes for the wastewater-soil combinations also differed from each other (**Figure 1**). The wastewater-soil combinations had the greatest decrease in NH_4 . The large initial NH_4 concentration in the wastewater was likely retained in the soil during rainfall and was responsible for the runoff NH_4 decrease.

In addition, averaged across water types and soils, runoff-water NH_4 concentration changes differed ($P = 0.02$) among fertilizer treatments (**Table 3**). Runoff-water NH_4 concentration changes for all four fertilizer treatments (*i.e.*, CPST, MAP, ECSTreal, and ECSTsyn) differed from zero (*i.e.*, -1.35 , -1.14 , -1.28 , and $-1.25 \text{ mg}\cdot\text{L}^{-1}$, respectively). The MAP treatment had the numerically smallest runoff-water NH_4 concentration change, which differed from ECSTreal and CPST, while CPST had the numerically largest runoff-water NH_4 concentration change (**Table 3**). Runoff-water NH_4 concentration differences from ECSTsyn did not differ from any other fertilizer treatment (**Table 3**). Added NH_4 from the fertilizers was retained by the soils, likely due to cation exchange sites from clays, TC, and/or SOM.

In contrast to NH_4 , runoff-water Ca concentration changes differed from zero in three of four groundwater-soil combinations (*i.e.*, Creldon, Dapue, and Roxana), but did not differ from zero for any of the rainwater- or wastewater-soil combinations (**Figure 1**). However, runoff-water Ca concentration changes did not differ from each other in the groundwater-Calloway combination or among any other rainwater-soil combination (**Figure 1**). In addition, in contrast to NH_4 , runoff-water Ca concentrations decreased the most in the groundwater-soil combinations, which was a 5 to 30 times greater decrease in runoff-water Ca concentration compared to all other water type-soil combinations (**Figure 1**). Groundwater had a large initial pH (7.9) in addition to having the largest initial Ca concentration (**Table 2**). The combination of large initial pH and large initial Ca concentration likely facilitated the precipitation of a portion of the Ca as Ca-P compounds to retain Ca and result in lower runoff Ca for the Creldon, Dapue, and Roxana soils. However, the Calloway soil was unaffected by all three water types, possibly due to its large initial pH leading to no additional precipitation of Ca.

Similar to NH_4 , runoff-water Mg concentration changes differed from zero in all wastewater-soil combinations and in the groundwater-Roxana combination (**Figure 2**). Runoff-water Mg concentration changes in all rainwater- and groundwater-soil combinations did not differ from each other. Runoff-water Mg concentration changes in the wastewater treatment across the four soils decreased 5 to 25 times more than any other water type-soil combination (**Figure 2**). Wastewater had the largest initial pH of the three water types (9.8; **Table 2**),

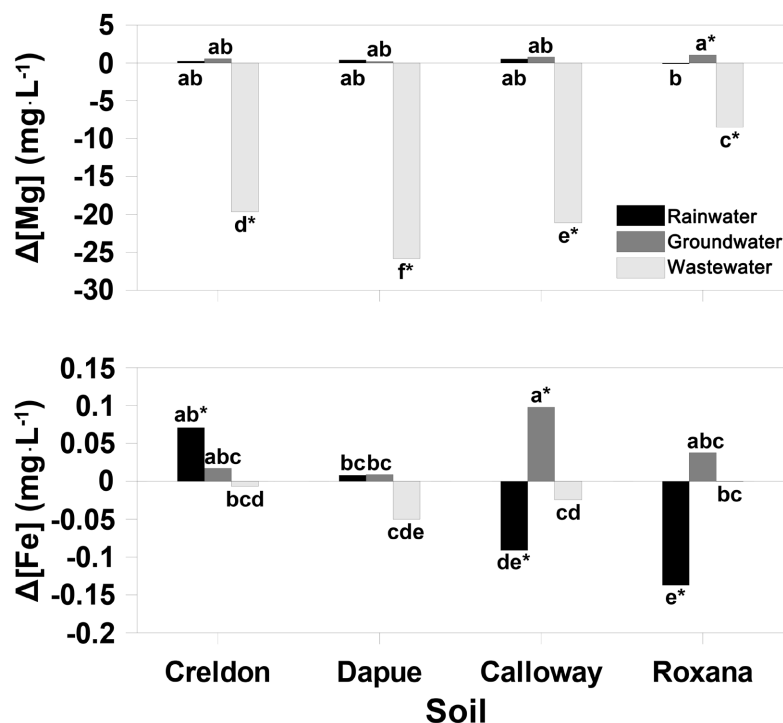


Figure 2. Summary of changes (Δ) in runoff-water magnesium (Mg) and iron (Fe) concentrations among water type (*i.e.*, groundwater, rainwater, and struvite-removed wastewater)-soil series (*i.e.*, Crelton, Dapue, Calloway, and Roxana) combinations for Trial 1. Bars with different lower-case letters within a panel are different at $P < 0.05$. Asterisks (*) indicate the change is significantly different from zero at $P < 0.05$.

which likely caused a fraction of the Mg to precipitate as Mg-P and/or Ca-Mg-P compounds in all four soils, resulting in the runoff-Mg decrease from zero. The runoff-Mg concentration change was also positive in the groundwater-Roxana combination, but the positive change was small.

Runoff-water Fe concentration changes differed from zero in three of four rainwater-soil combinations, excluding the Dapue soil, and was greater than zero for the groundwater-Calloway combination (Figure 2). Runoff-water Fe concentration from all water type-soil combinations, except for those that differed from zero and the wastewater-Dapue combination, did not differ from each other (Figure 2). Of the water type-soil combination whose runoff-water Fe concentration change differed from zero, the rainwater-Calloway and -Roxana combinations did not differ from each other and both changes decreased from zero (Figure 2). Similarly, runoff-water Fe concentration change for the rainwater-Crelton and groundwater-Dapue combinations did not differ from each other, but both changes were greater than zero (Figure 2). The decrease in runoff Fe in the Calloway- and Roxana-rainwater combinations was likely due to the relatively large initial soil and water pHs, as Fe solubility in soil decreases as pH increases. For similar reasons, in combination with the low initial Fe in the Calloway and Crelton soils (Table 1), there was an increase in runoff Fe in the Crelton-rainwater and Calloway-groundwater combinations.

Averaged across soils, runoff-water Fe concentration changes also differed ($P = 0.04$) among water type-fertilizer-P source combinations (Figure 3). Runoff-water Fe concentration changes differed from zero in three of four rainwater-fertilizer-P source combinations, excluding CPST (Figure 3). Runoff-water Fe concentration changes were less than zero in all wastewater-fertilizer-P source combinations, but were greater than zero in all groundwater-fertilizer-P source combinations (Figure 3). In general, the rainwater treatment caused the greatest runoff-water Fe concentration change from zero among all water sources (Figure 3). In all rainwater-fertilizer-P source combinations, except for ECSTreal, the runoff-water Fe concentration change was less than zero (Figure 3). Similarly, the runoff-water Fe concentration change from rainfall for CPST and ECSTsyn was similar to MAP, except for the rainwater-ECSTreal combination (Figure 3). All treatment combinations did not differ from each other, except for the rainwater-CPST, -MAP, and -ECSTsyn and wastewater-ECSTsyn combinations, which did not differ from each other (Figure 3). The increase in runoff Fe from only ECSTreal in the rainwater treatment was likely due to the original conditions under which the ECSTreal was formed. Unlike ECSTsyn, ECSTreal was precipitated from a real municipal wastewater source, while CPST and MAP were also created from a source with known composition. There could

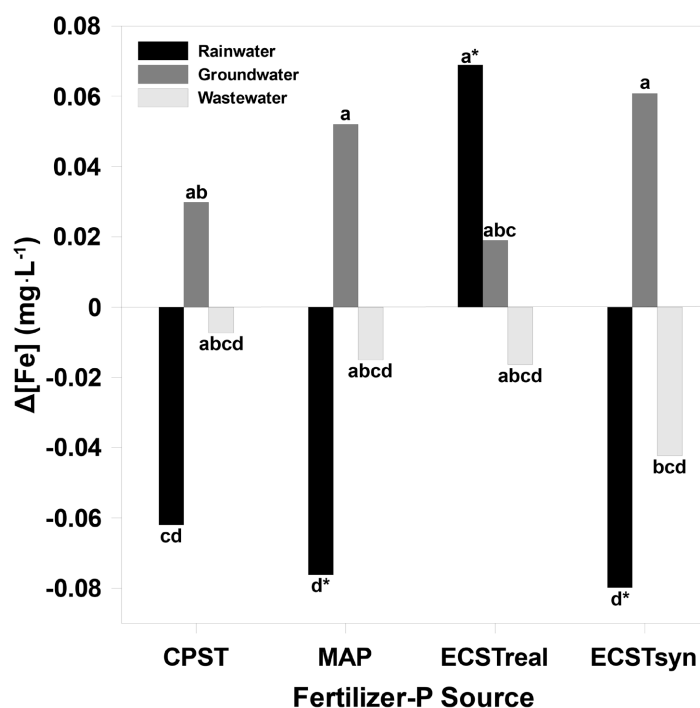


Figure 3. Summary of changes (Δ) in runoff-water iron (Fe) concentrations among water type (*i.e.*, groundwater, rainwater, and struvite-removed wastewater)-fertilizer-phosphorus (P) source [*i.e.*, chemically precipitated struvite (CPST), monoammonium phosphate (MAP), real-wastewater-derived electrochemically precipitated struvite (ECSTreal), and synthetic electrochemically precipitated struvite (ECSTsyn)] combinations for Trial 1. Bars with different lower-case letters within a panel are different at $P < 0.05$. Asterisks (*) indicate the change is significantly different from zero at $P < 0.05$.

have been unknown or unexpected elemental concentrations within the wastewater from which ECSTreal was originally created. Because Fe is more available at more acidic pHs, the non-significant runoff Fe change that occurred in the groundwater and wastewater treatments was likely due to the groundwater's and wastewater's initial pHs > 7.8 (Table 2).

Runoff-water TP, NO₃ + NO₂, and SRP concentration changes differed ($P < 0.05$) among water type-soil-fertilizer-P source treatment combinations (Table 4). There were few consistent trends among water type-soil-fertilizer-P source treatment combinations, and most were complex. Most runoff-water TP concentration changes differed from zero among treatment combinations, particularly within the wastewater treatment (Table 4). All runoff-water TP concentration changes from wastewater were negative in three of four soil-fertilizer-P source combinations, excluding the Roxana soil (Table 4). The numerically largest runoff-water TP concentration changes were in the rainwater-Roxana combination, excluding the CPST fertilizer-P source. The numerically smallest runoff-water TP concentration changes occurred in the wastewater-Calloway combinations (Table 4). Few runoff-water TP concentration changes differed from each other among fertilizer-P sources within water type-soil combinations (Table 4). In most treatment combinations, runoff-water TP concentration changes from the struvite-P sources (*i.e.*, CPST, ECSTsyn, and ECSTreal) were similar to MAP (Table 4). However, within the rainwater-Creldon and groundwater-Dapue combinations, runoff-water TP concentration changes from ECSTsyn differed from all other fertilizer treatments. Within the rainwater-Roxana combination, runoff-water TP concentration changes did not differ among MAP, ECSTreal, or ECSTsyn (Table 4).

The negative runoff-TP concentration changes in the wastewater-soil-fertilizer treatment combinations could have been caused by the large initial wastewater Ca and Mg concentrations binding with P due to the wastewater's alkaline pH (Table 2). Phosphorus solubility in the soil is largely dictated by pH, where phosphate forms poorly soluble Fe³⁺ and Al³⁺ compounds at low pH, readily soluble Ca²⁺ and Mg²⁺ compounds at pH near neutrality, and poorly soluble Ca²⁺ compounds at greater pH [45]. However, in the wastewater-Roxana combination, the TP concentration change was positive. The positive TP concentration change, in contrast to the other three soils' negative TP concentration change, was likely due to the large initial TP, but small initial Ca (Table 1), causing little to no precipitation of Ca-P compounds. In every water-soil-fertilizer combination but one (*i.e.*, wastewater-Roxana), either ECSTsyn or ECSTreal consistently had the largest runoff-TP concentration (Table 4). The large runoff-TP concentration of ECSTreal and ECSTsyn was unexpected since the initial P concentration of the ECST fertilizers was the intermediate among the four fertilizer treatments, but the initial Mg concentration for ECSTsyn and ECSTreal was the largest (*i.e.*, 13.3% and 13.6%, respectively). The large runoff-TP concentration in the ECSTsyn and ECSTreal treatments, in contrast to CPST and MAP, may

Table 4. Summary of mean changes (Δ) in water-quality parameters among water type-soil-fertilizer-phosphorus-(P)-source treatment combinations from rainfall-runoff simulation in Trial 1.

Water type	Soil	Fertilizer-P source [†]	Δ [TP] ^{†*} (mg·L ⁻¹)	Δ [NO ₃ + NO ₂] ^{†*} (mg·L ⁻¹)	Δ [SRP] ^{†*} (mg·L ⁻¹)
Groundwater	Crelton	CPST	0.16 ^{*e-k}	0.91c-h	0.15 ^{*e-k}
		MAP	0.06jk	-0.52e-i	0.06jkl
		ECSTreal	0.09h-k	-0.60e-i	0.08ijk
		ECSTsyn	0.23 ^{*d-j}	2.48 ^{*b-e}	0.14 ^{*e-k}
	Dapue	CPST	0.11g-k	0.83c-h	0.09 ^{*ijk}
		MAP	0.12 ^{*g-k}	0.51c-i	0.10 ^{*h-k}
		ECSTreal	0.15 ^{*e-k}	-2.52 ^{*i}	0.14 ^{*e-k}
		ECSTsyn	0.30 ^{*cde}	-0.59e-i	0.26 ^{*cde}
	Calloway	CPST	0.06k	-0.08d-i	0.03kl
		MAP	0.12 ^{*g-k}	-0.98f-i	0.07i-l
		ECSTreal	0.12g-k	1.08c-h	0.08ijk
		ECSTsyn	0.12 ^{*g-k}	-0.31d-i	0.08ijk
	Roxana	CPST	0.14 ^{*e-k}	0.73c-i	0.12 ^{*g-k}
		MAP	0.16 ^{*e-k}	1.91b-g	0.14 ^{*e-k}
		ECSTreal	0.30 ^{*c-f}	0.64c-i	0.25 ^{*c-f}
		ECSTsyn	0.23 ^{*d-i}	-0.36d-i	0.19 ^{*d-j}
Rainwater	Crelton	CPST	0.07ijk	-0.52e-i	0.06jkl
		MAP	0.15 ^{*e-k}	0.63c-i	0.14 ^{*e-k}
		ECSTreal	0.14 ^{*e-k}	0.98c-h	0.18 ^{*e-k}
		ECSTsyn	0.37 ^{*bcd}	-0.80e-i	0.36 ^{*abc}
	Dapue	CPST	0.24 ^{*d-i}	0.98c-h	0.20 ^{*d-i}
		MAP	0.11g-k	-1.04f-i	0.12 ^{*g-k}
		ECSTreal	0.26 ^{*d-g}	2.08c-f	0.25 ^{*c-g}
		ECSTsyn	0.20 ^{*d-k}	-0.60e-i	0.23 ^{*d-h}
	Calloway	CPST	0.12 ^{*g-k}	3.53 ^{*abc}	0.11 ^{*h-k}
		MAP	0.12g-k	5.08 ^{*ab}	0.13 ^{*f-k}
		ECSTreal	0.04k	1.44c-h	0.13 ^{*e-k}
		ECSTsyn	0.13 ^{*f-k}	2.88 ^{*bcd}	0.14 ^{*e-k}
	Roxana	CPST	0.09h-k	-1.16f-i	0.04kl
		MAP	0.48 ^{*ab}	-0.75e-i	0.40 ^{*ab}
		ECSTreal	0.59 ^{*a}	1.03c-h	0.47 ^{*a}
		ECSTsyn	0.45 ^{*abc}	-0.19d-i	0.43 ^{*a}

Continued

Struvite-removed wastewater	Credon	CPST	-0.79*n	0.01d-i	-0.87*no
		MAP	-0.64*lmn	-0.08d-i	-0.74*mn
		ECSTreal	-0.68*mn	-1.39ghi	-0.77*mn
		ECSTsyn	-0.50*l	-1.03f-i	-0.71*m
	Dapue	CPST	-0.72*mn	0.17d-i	-0.77*mn
		MAP	-0.58*lm	0.75c-i	-0.72*m
		ECSTreal	-0.66*lmn	0.32c-i	-0.73*m
		ECSTsyn	-0.56*lm	0.59c-i	-0.73*m
	Calloway	CPST	-1.22*o	6.43*a	-1.19*q
		MAP	-1.19*o	0.43c-i	-1.07*pq
		ECSTreal	-1.15*o	0.46c-i	-1.10*pq
		ECSTsyn	-1.11*o	-0.34d-i	-0.98*po
	Roxana	CPST	0.16*e-k	-1.84hi	-0.06l
		MAP	0.52*ab	-0.62e-i	0.28*bcd
		ECSTreal	0.11g-k	-0.95f-i	0.11*h-k
		ECSTsyn	0.25*d-h	-1.17f-i	0.19*d-j

[†] Means in a column with different letters are different at $P < 0.05$. * An asterisk (*) indicates the mean change differs from zero at $P < 0.05$. [‡] Chemically precipitated struvite, CPST; monoammonium phosphate, MAP; real-wastewater-derived electrochemically precipitated struvite, ECSTreal; synthetic electrochemically precipitated struvite, ECSTsyn; total phosphorus, TP; nitrate + nitrite, $\text{NO}_3 + \text{NO}_2$; soluble-reactive phosphorus, SRP.

have been due to the timing of when each fertilizer material solubilized and subsequently ran off during the rainfall event. Being readily soluble, MAP may have dissolved within the first few days of pre-wetting and had sufficient time for Ca-Mg-P compounds to form, lowering the runoff-TP concentration. In contrast, ECST's slow-release nature, as reported by Anderson *et al.* (2021c), could have led to the simulated rainfall promoting ECST solubilization, increasing runoff-TP concentrations.

Runoff-water SRP concentration changes were similar to runoff-water TP concentration changes in terms of which treatments differed from zero and which treatments differed from each other (Table 4). Similar to runoff-water TP, runoff-water SRP concentration changes differed from zero in almost all water type-soil-fertilizer-P source combinations, except for the groundwater-Calloway combination (Table 4). Also similar to runoff-water TP, the numerically largest runoff-water SRP concentration changes occurred for the rainwater-Roxana treatment combination, excluding CPST (Table 4). The numerically smallest runoff-water SRP concentration changes occurred for the wastewater-Calloway combinations (Table 4). Few runoff-water SRP concentration changes differed from each other among fertilizer-P sources within water

type-soil combinations (**Table 4**). In general, except for the rainwater-Calloway and -Credon and wastewater-Dapue combinations, runoff-water SRP concentration changes were numerically smaller than runoff-water TP concentration changes. In most treatment combinations, runoff-water SRP concentration changes from the struvite-P sources were similar to MAP (**Table 4**).

Runoff-SRP concentration responses were likely the result of reasons similar to that for runoff-TP responses. The negative runoff-SRP concentration changes in the wastewater-soil-fertilizer combinations could have been caused by the large initial wastewater Ca and Mg concentrations binding with P due to the wastewater's alkaline pH. However, in the wastewater-Roxana combination, the SRP concentration change was generally positive. The positive TP concentration change, in contrast to the other three soils' negative SRP concentration change, was likely due to the large initial TP, but small initial Ca causing no precipitation of Ca-P compounds. Runoff-SRP concentration changes were smaller than for runoff TP in almost all instances, which was consistent with TP measuring all P forms and SRP only measuring plant-available P forms.

In contrast to runoff-water TP and SRP, most runoff-water $\text{NO}_3 + \text{NO}_2$ concentration changes did not differ from zero (**Table 4**). Runoff-water $\text{NO}_3 + \text{NO}_2$ concentration changes differed from zero in three of four rainwater-Calloway-fertilizer-P source combinations, excluding ECSTreal (**Table 4**). Runoff-water $\text{NO}_3 + \text{NO}_2$ concentration changes for most treatment combinations also did not differ from each other, except the numerically largest and smallest runoff-water $\text{NO}_3 + \text{NO}_2$ concentration changes (**Table 4**). The largest runoff-water $\text{NO}_3 + \text{NO}_2$ concentration changes occurred for the wastewater-Calloway-CPST and the rainwater-Calloway-CPST and -MAP combinations (**Table 4**). The smallest runoff-water $\text{NO}_3 + \text{NO}_2$ concentration change occurred for the groundwater-Dapue-ECSTreal combination (**Table 4**). In most treatment combinations, runoff-water $\text{NO}_3 + \text{NO}_2$ concentration changes for the struvite-P sources were similar to MAP (**Table 4**). Complex interactions between soil, water type, and fertilizer properties made it challenging to explain runoff $\text{NO}_3 + \text{NO}_2$ concentration changes, as there were no consistent patterns among treatment combinations. In contrast to all other measured water-quality parameters, runoff-EC changes were unaffected by water type, soil, or fertilizer-P source (**Table 3**) and averaged $4.32 \text{ dS}\cdot\text{m}^{-1}$ across all treatments.

3.4. Treatment Effects on Runoff-Water Quality over Time (Trial 2)

After a 6-month period of incubation between rainfall simulations, with monthly wetting and in contrast to Trial 1, every measured water quality parameter, with the exception of runoff-Mg concentration changes, differed ($P < 0.05$) over time (**Table 5**). For Trial 2, SRW was not used, thus the water types only consisted of rainwater and groundwater. The remainder of the results in this section will focus on changes over time and differences among treatment combinations from Trial 2 results only.

Table 5. Analysis of variance summary of the effects of water type (W), soil (S), and fertilizer (F) over time (T) and their interactions on the change (Δ) in runoff-water quality properties for Trial 2 of the rainfall-runoff simulation experiment.

Source of variation	Δ [pH] [†]	Δ [EC] [†]	Δ [TP] [†]	Δ [Ca] [†]	Δ [Mg] [†]	Δ [Fe] [†]	Δ [NO ₃ + NO ₂] [†]	Δ [NH ₄] [†]	Δ [SRP] [†]
Water type	<0.01	0.66	0.02	<0.01	0.05	0.42	0.80	0.16	0.01
Soil	0.10	0.12	<0.01	<0.01	0.79	<0.01	0.06	<0.01	<0.01
W * S	<0.01	<0.01	0.16	<0.01	0.02	0.15	0.01	<0.01	0.91
Fertilizer	0.03	0.48	0.01	0.73	0.87	0.15	0.92	0.04	<0.01
W * F	0.03	0.29	0.81	0.33	0.59	0.07	0.43	0.22	0.11
S * F	<0.01	0.35	0.35	0.13	0.97	0.04	0.95	0.92	0.08
W * S * F	0.12	0.79	0.38	0.71	0.73	0.20	0.40	0.62	0.01
Time	<0.01	0.46	<0.01	<0.01	0.85	0.12	0.06	<0.01	<0.01
W * T	<0.01	0.06	0.01	<0.01	0.81	0.98	0.08	0.17	<0.01
S * T	<0.01	0.19	0.02	<0.01	0.39	<0.01	0.13	<0.01	<0.01
W * S * T	<0.01	0.01	0.02	<0.01	0.17	0.32	<0.01	0.82	<0.01
F * T	0.37	0.71	<0.01	0.33	0.83	0.40	0.71	0.12	<0.01
W * F * T	0.99	0.96	0.51	0.66	0.91	0.26	0.83	0.07	0.15
S * F * T	0.28	0.67	<0.01	0.60	0.76	0.07	0.60	0.88	<0.01
W * S * F * T	0.89	0.03	0.09	0.07	0.55	0.85	0.02	0.27	0.16

[†]Electrical conductivity, EC; total phosphorus, TP; calcium, Ca; magnesium, Mg; iron, Fe; nitrate + nitrite, NO₃ + NO₂; ammonium, NH₄; soluble-reactive phosphorus, SRP.

Changes in runoff-pH, which partially dictates the fractionation between WS and sorbed nutrient concentrations, and runoff-TP, -Ca, and -SRP concentration changes differed ($P < 0.02$; **Table 5**) among water type-soil combinations over time (**Table 5**). Averaged across fertilizer-P sources, runoff-pH changes decreased over time in all water type-soil combinations, where the decrease was larger for rainwater-compared to groundwater-soil combinations (**Table 6**). In response to rainwater and groundwater, after 6 months of incubation (Trial 2), all runoff-pH changes differed from zero (**Table 6**). Runoff-pH changes in groundwater-soil combinations did not differ from each other in Trial 2 (**Table 6**). In contrast, runoff-pH changes in all rainwater-soil combinations differed from each other in Trial 2, except for the Roxana soil which did not differ from the Dapue or Creldon soils (**Table 6**). The decrease in runoff pH over time was likely due to the nitrifying processes that occurred during incubation, producing H⁺ ions, thus lowering runoff pH [46]. The general temporal decrease in runoff pH was similar to the results of Anderson *et al.* [27], who reported a decrease in soil pH over time in a silty clay loam soil with large initial SOM and clay concentration.

Table 6. Summary of mean changes (Δ) in water-quality parameters among water type-soil combinations over the 6-month period from rainfall-runoff simulation Trial 1 to Trial 2.

Water type	Soil	Trial	Δ pH ^{†*}	Δ [TP] ^{†*} (mg·L ⁻¹)	Δ [Ca] ^{†*} (mg·L ⁻¹)	Δ [SRP] ^{†*} (mg·L ⁻¹)
Groundwater	Creldon	1	-0.01b	0.14*bcd	-35.5*g	0.11*de
		2	-1.95*e	<0.01e	1.18bc	<0.01gh
	Dapue	1	0.03ab	0.17*bc	-27.8*f	0.15*bcd
		2	-1.89*e	<0.01e	0.08bcd	-0.01gh
	Calloway	1	-0.01b	0.10*cd	0.64bcd	0.07*ef
		2	-1.90*e	<0.01e	1.45*abc	-0.03h
	Roxana	1	-0.02b	0.21*b	-8.34*e	0.18*bc
		2	-1.96*e	0.10*cd	0.33bcd	0.07*ef
Rainwater	Creldon	1	0.01b	0.18*b	0.40bcd	0.18*bc
		2	-2.58*g	0.01e	0.39bcd	0.04*fg
	Dapue	1	-0.19*c	0.20*b	1.21bc	0.20*b
		2	-2.73*h	<0.01e	3.45*a	0.02fgh
	Calloway	1	-0.34*d	0.10*cd	1.68*ab	0.13*cd
		2	-2.33*f	<0.01e	-0.98d	0.01gh
	Roxana	1	0.15*a	0.40*a	-0.58cd	0.34*a
		2	-2.66*gh	0.07*ed	-0.16bcd	0.02fgh

[†] Means in a column with different letters are different at $P < 0.05$. * An asterisk (*) indicates the mean value differs from zero at $P < 0.05$. [‡] Total phosphorus, TP; calcium, Ca; soluble-reactive phosphorus, SRP.

Similar to runoff-pH, runoff-TP concentration changes also decreased over time in all water type-soil combinations, with the larger decreases over time generally occurring in the rainwater-soil combinations (Table 6). In six of the eight water type-soil combinations in Trial 2, with the exception of the groundwater- and rainwater-Roxana soil combinations, runoff-TP concentration changes were small and did not differ from zero and did not differ among themselves (Table 6). However, runoff-TP concentration changes the groundwater- and rainwater-Roxana combinations were larger than for the other six water-type combinations and differed from zero, but did not differ from one another. Soluble P may have reacted with Ca and/or Mg to form Ca- and/or Mg-P compounds, partially explaining the decrease in runoff TP over the 6 months from Trial 1 to Trial 2. However, due to the decrease in runoff pH, it was more likely that soluble P forms were adsorbed onto soil particles over the 6-month incubation period. Shigaki *et al.* [29] and Smith *et al.* [30] reported a similar decrease in WS P over time in a loam and silt loam soil, respectively.

In contrast to runoff-pH and -TP, runoff-water Ca concentrations at least numerically increased over time in all groundwater-soil and two of four rainwater-soil combinations, excluding the rainwater-Creldon, which did not change

over time, and the rainwater-Calloway combination, which significantly decreased over time (**Table 6**). For Trial 2 only, the largest runoff-water Ca concentration increase occurred in the rainwater-Dapue, while the largest decrease occurred in the rainwater-Calloway combination (**Table 6**). The increase in runoff Ca concentration over time was likely due to the decrease in runoff pH and Ca being released from cation exchange sites. The runoff pH of the rainwater-Dapue combination was already low, likely resulting in no change of the cation exchange site components and explaining the decrease in runoff Ca in the rainwater-Dapue combination.

Similar to runoff-water TP, runoff-water SRP concentration changes also decreased significantly over time in all water type-soil combinations, with the larger decreases generally occurring in response to rainwater compared to groundwater combinations (**Table 6**). Similar to runoff-water TP, in Trial 2, runoff-water SRP concentration changes were generally small, where most did not differ from a change of zero and many did not differ from one another (**Table 6**). For Trial 2 only, the largest runoff-water SRP concentration increases occurred in the groundwater-Roxana and rainwater-Creldon combinations, which differed from zero, but did not differ from one another (**Table 6**). The explanation for changes in runoff SRP is likely similar to that of runoff TP, where it was likely that SRP adsorbed onto soil particles over time. Runoff-SRP was lower than runoff-TP concentration changes in almost all instances, which was consistent with TP measuring all P forms and SRP only measuring plant-available P forms.

Averaged across water type, runoff-water TP and SRP concentration changes also differed ($P < 0.01$; **Table 5**) among soil-fertilizer-P source combinations over time (**Table 7**). Treatment combination effects on runoff-TP and -SRP concentration changes over time were the same (**Table 7**). Runoff-TP and -SRP concentration changes were generally small for Trial 2, where, with the exception of the same two treatment combinations, most changes did not differ from zero, and decreased over time in all soil-fertilizer-P source treatment combinations (**Table 7**). The largest runoff-TP and -SRP concentration changes from Trial 2 occurred in the Roxana-CPST and -ECSTsyn combinations, which were both larger than zero, but did not differ from one another, and both were larger than the changes measured in all other soil-fertilizer-P source combinations (**Table 7**). Runoff-TP and -SRP concentration changes for Trial 2 did not differ between the three struvite-P sources in the Creldon, Dapue, or Calloway soils and behaved similarly to MAP (**Table 7**). However, runoff-TP and -SRP concentration changes for Trial 2 from the Roxana-CPST and -ECSTsyn were both greater than changes from Roxana-ECSTreal and -MAP combinations, which did not differ (**Table 7**).

The explanation for changes in runoff-SRP and -TP concentration changes was likely similar, as both SRP and TP measure soil-P pools that were likely adsorbed to soil particles over time. In most instances, runoff-TP and -SRP concentration changes were largest in the ECSTsyn or ECSTreal combinations in Trial 1. The large runoff-TP and -SRP concentration changes were unexpected

Table 7. Summary of mean changes (Δ) in water-quality parameters among soil-fertilizer-phosphorus-(P)-source treatment combinations over the 6-month period from rain-fall-runoff simulation Trial 1 to Trial 2.

Soil	Fertilizer	Trial	Δ [TP] ^{†‡} (mg·L ⁻¹)	Δ [SRP] ^{†‡} (mg·L ⁻¹)
Credon	CPST	1	0.12*efg	0.10*efg
		2	<0.01kl	0.02j-m
	MAP	1	0.11*e-k	0.10*e-h
		2	<0.01kl	0.04g-m
	ECSTreal	1	0.12*e-h	0.13*def
		2	0.01jkl	0.01j-m
ECSTsyn	1	0.30*bc	0.25*bd	
	2	0.01h-l	0.02j-m	
Dapue	CPST	1	0.17*def	0.15*de
		2	<0.01kl	0.01j-m
	MAP	1	0.12*e-h	0.11*efg
		2	<0.01kl	0.02i-m
	ECSTreal	1	0.21*cde	0.19*cd
		2	<0.01kl	0.02j-m
ECSTsyn	1	0.25*bcd	0.24*bc	
	2	0.01jkl	<0.01klm	
Calloway	CPST	1	0.09*f-l	0.07*e-k
		2	<0.01kl	<0.01j-m
	MAP	1	0.12*efg	0.10*e-h
		2	<0.01lk	-0.01lm
	ECSTreal	1	0.08*f-l	0.11*efg
		2	0.01i-l	-0.01lm
ECSTsyn	1	0.13*efg	0.11*efg	
	2	<0.01l	-0.02m	
Roxana	CPST	1	0.11*e-j	0.08*e-j
		2	0.16*def	0.07*e-l
	MAP	1	0.32*b	0.27*bc
		2	0.03g-l	0.01j-m
	ECSTreal	1	0.44*a	0.36*a
		2	0.04g-l	0.02h-m
ECSTsyn	1	0.34*ab	0.31*ab	
	2	0.10*f-l	0.06*f-l	

[†] Means in a column with different letters are different at $P < 0.05$. * An asterisk (*) indicates the mean value differs from zero at $P < 0.05$. [‡] Chemically precipitated struvite, CPST; monoammonium phosphate, MAP; real-wastewater-derived electrochemically precipitated struvite, ECSTreal; synthetic electrochemically precipitated struvite, ECSTsyn; total phosphorus, TP; soluble-reactive phosphorus, SRP.

since the initial P concentration of the ECST fertilizers was intermediate among the four fertilizer treatments, but the initial Mg concentration for ECSTsyn and ECSTreal was the largest (*i.e.*, 13.3% and 13.6%, respectively). As previously, the large runoff-TP concentration change in the ECSTsyn and ECSTreal treatments, in contrast to CPST and MAP, may have been due to the timing of when each fertilizer material solubilized and subsequently ran off during the rainfall event. Being readily soluble, MAP may have dissolved within the first few days of pre-wetting and had sufficient time to form Ca-Mg-P compounds, lowering the runoff-TP concentration. The increase in runoff-TP concentration for ECST may have been due to the slow-release nature of ECST (Anderson *et al.*, 2021c) and the promotion of ECST dissolution by rainfall. After the 6-month incubation period, there was likely sufficient time for Ca-Mg-P compounds to form in all fertilizer treatment combinations. Anderson *et al.* (2021c) reported that CPST, not ECST, had the greatest increase in WS-P concentration over nine months of plant-less soil incubation. However, Anderson *et al.* [27] also reported that, in general, there was a decrease in WS-P concentration after the initial wetting event, which was similar to the results of the current study.

In contrast to the other soluble nutrients, averaged across water type and fertilizer-P source, runoff-Fe and -NH_4 concentration changes differed ($P < 0.01$; Table 5) among soils over time (Figure 4). For three of the four soils (*i.e.*, Creldon,

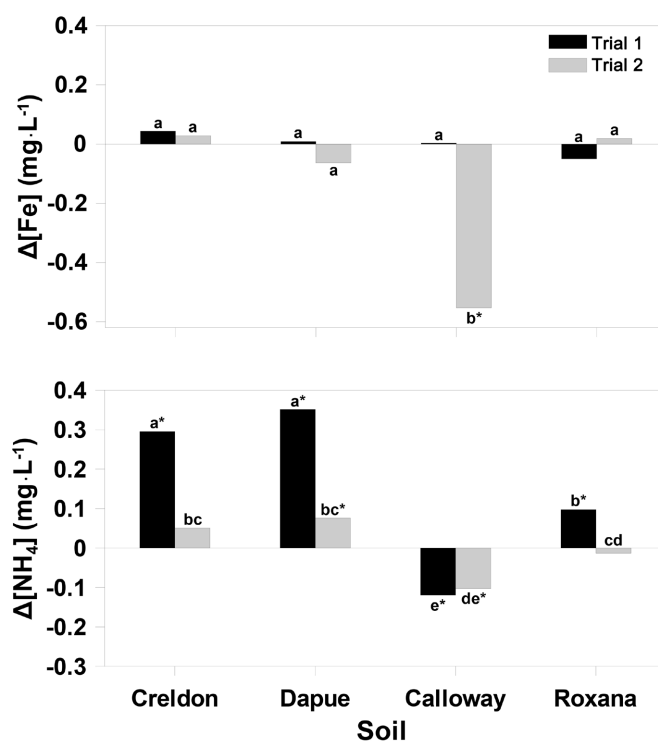


Figure 4. Summary of changes (Δ) in runoff-water iron (Fe) and ammonium (NH_4) concentrations among soil series (*i.e.*, Creldon, Dapue, Calloway, and Roxana) over the 6-month period from rainfall-runoff simulation Trial 1 to Trial 2. Bars with different lower-case letters within a panel are different at $P < 0.05$. Asterisks (*) indicate the change is significantly different from zero at $P < 0.05$.

Dapue, and Roxana), runoff-Fe concentration changes did not differ over time, changes for Trial 2 did not differ from zero, and changes were all similar to one another (**Figure 4**). However, for the Calloway soil, runoff-Fe concentration changes decreased $> 0.5 \text{ mg}\cdot\text{L}^{-1}$ over the six months between trials, in which the decrease differed from zero and differed from all other soil-time combinations (**Figure 4**). The decrease in runoff Fe over time was likely due to the large initial pH of the Calloway soil (**Table 1**), where Fe availability decreased at the large pH.

In contrast to Fe, averaged across water type and fertilizer-P sources, runoff-NH₄ concentration changes decreased over time for the Creldon, Dapue, and Roxana soils, where the change for Trial 2 only was greater than zero for the Dapue soil, but did not differ from the change in the Creldon or Roxana soils (**Figure 4**). However, for the Calloway soil, the runoff-NH₄ concentration change remained similar over time, while the change for Trial 2 only was less than zero, which also did not differ from the change in the Roxana soil, but was smaller than the change in the Creldon and Dapue soils (**Figure 4**). The decrease in runoff-NH₄ concentrations over time was likely due to nitrification occurring during the 6-month incubation period. There was no change over time in runoff-NH₄ concentration in the Calloway soil, but the Calloway soil had the smallest initial NH₄ concentration and largest initial pH (**Table 1**), which may have contributed to an increased nitrification rate and the runoff NH₄ decrease from zero. In contrast to all other measured water-quality parameters, runoff-EC and -NO₃ + NO₂ concentration changes were complex and differed ($P < 0.03$; **Table 5**) among water type-soil-fertilizer-P source combinations over time (**Table 8**). Runoff-EC changes for Trial 2 did not differ from zero, except for the groundwater-Calloway-MAP and -ECSTsyn, rainwater-Dapue-MAP, -ECSTreal, and -ECSTsyn combinations, where all changes were greater than zero (*i.e.*, an increase in runoff EC; **Table 8**). Similarly, most runoff-EC changes did not change over time, except for the groundwater-Calloway-MAP, rainwater-Dapue-MAP, and -ECSTsyn combinations that increased over time, where the Trial 2 change did not differ among themselves, and the rainwater-Calloway-CPST and -MAP combinations that decreased over time, where the Trial 2 changes did not differ between them (**Table 8**). Runoff-EC changes for most other water type-soil-fertilizer-P source combinations did not differ among themselves (**Table 8**). Most of the changes and interactions in runoff EC among treatment combinations were likely due to the initial EC differences among the soils (**Table 1**) and water types (**Table 3**).

Similar to EC, runoff-NO₃ + NO₂ concentration changes for Trial 2 did not differ from zero, except for the groundwater-Calloway-MAP, -ECSTreal, and -ECSTsyn, and rainwater-Dapue-MAP, ECSTreal, and -ECSTsyn combinations, where all Trial 2 changes were greater than zero (*i.e.*, an increase in runoff-NO₃ + NO₂ concentration; **Table 8**). Similarly, most runoff-NO₃ + NO₂ concentration changes did not change over time, except for the groundwater-Calloway-MAP and rainwater-Dapue-MAP and -ECSTsyn combinations that increased over

Table 8. Summary of mean changes (Δ) in water-quality parameters among water type-soil-fertilizer-phosphorus-(P)-source treatment combinations over the 6-month period from rainfall-runoff simulation Trial 1 to Trial 2.

Water type	Soil	Fertilizer-P source	Trial	Δ [EC] ^{†‡} (dS·m ⁻¹)	Δ [NO ₃ + NO ₂] ^{†‡} (mg·L ⁻¹)	
Groundwater	Credon	CPST	1	6.66d-k	0.91d-l	
			2	12.3b-j	1.41d-k	
		MAP	1	-5.00g-k	-0.52g-l	
			2	18.7a-g	1.73c-j	
		ECSTreal	1	7.66d-k	-0.60g-l	
			2	18.7a-g	1.57c-j	
		ECSTsyn	1	4.00e-k	2.48a-i	
			2	10.7c-k	2.12a-j	
		Dapue	CPST	1	-13.0ijk	0.83d-l
				2	-5.67g-k	0.45e-l
			MAP	1	-7.67g-k	0.51d-l
				2	-15.7jk	-2.07kl
	ECSTreal		1	-10.0h-k	-2.52l	
			2	0.33e-k	0.38e-l	
	ECSTsyn	1	-5.67g-k	-0.59g-l		
		2	10.7c-k	1.73c-j		
	Calloway	CPST	1	3.00e-k	-0.08e-l	
			2	18.7a-g	0.64d-l	
		MAP	1	8.67d-k	-0.98i-l	
			2	38.7*abc	5.71*a	
		ECSTreal	1	11.0c-k	1.08d-l	
			2	13.7a-i	2.83*a-h	
		ECSTsyn	1	12.0c-j	-0.31g-l	
			2	24.7*a-f	3.35*a-f	
Roxana		CPST	1	10.0d-k	0.73d-l	
			2	0.83e-k	0.70d-l	
		MAP	1	9.00d-k	1.91b-l	
			2	4.17e-k	0.38e-l	
	ECSTreal	1	6.33d-k	0.64d-l		
		2	-4.83g-k	-0.12f-l		
	ECSTsyn	1	6.66d-k	-0.36g-l		
		2	3.17e-k	1.37d-k		

Continued

Rainwater	Credon	CPST	1	4.60e-k	-0.52g-l
			2	12.4b-j	1.34d-k
		MAP	1	16.2a-h	0.63d-l
			2	7.23d-k	0.40e-l
		ECSTreal	1	13.6a-i	0.98d-l
			2	0.93e-k	0.05e-l
	ECSTsyn	1	-6.07g-k	-0.80h-l	
		2	3.60e-k	0.47d-l	
	Dapue	CPST	1	16.0a-h	0.98d-l
			2	-1.70f-k	0.09e-l
		MAP	1	-1.40f-k	-1.04i-l
			2	40.6*ab	5.43*ab
		ECSTreal	1	34.3*a-d	2.08a-j
			2	28.6*a-e	4.10*a-d
	ECSTsyn	1	-0.27f-k	-0.60g-l	
		2	28.4*a-e	4.09*a-d	
	Calloway	CPST	1	19.7*a-g	3.52*a-e
			2	-5.03g-k	0.12e-l
MAP		1	41.7*a	5.08*abc	
		2	-2.53f-k	-0.24f-l	
ECSTreal		1	-4.44g-k	1.44d-k	
		2	0.03f-k	0.01e-l	
ECSTsyn	1	6.96d-k	2.88*a-g		
	2	-16.4k	-1.21jkl		
Roxana	CPST	1	-13.8ijk	-1.16jkl	
		2	6.70d-k	0.94d-l	
	MAP	1	-3.47f-k	-0.75g-l	
		2	-2.47f-k	-0.37g-l	
	ECSTreal	1	15.8a-h	1.03d-l	
		2	-1.97f-k	-0.29g-l	
ECSTsyn	1	1.66e-k	-0.19f-l		
	2	-3.07f-k	-0.56g-l		

† Means in a column with different letters are different at $P < 0.05$. * An asterisk (*) indicates the mean value differs from zero at $P < 0.05$. ‡ Chemically precipitated struvite, CPST; monoammonium phosphate, MAP; real-wastewater-derived electrochemically precipitated struvite, ECSTreal; synthetic electrochemically precipitated struvite, ECSTsyn; electrical conductivity, EC; nitrate + nitrite, $\text{NO}_3 + \text{NO}_2$.

time, where the Trial 2 change did not differ among themselves, and the rainwater-Calloway-MAP and -ECSTsyn combinations that decreased over time, where the Trial 2 changes did not differ between them (**Table 8**). Runoff-NO₃ + NO₂ concentration changes for most other water type-soil-fertilizer-P source combinations did not differ among themselves (**Table 8**). The change in runoff-NO₃ + NO₂ concentrations over time was likely due to the mineralization of organic matter, nitrification of NH₄⁺, and/or the denitrification of fertilizer-N additions, especially in the Calloway soil, which had the largest pH and largest runoff-NO₃ + NO₂ changes among the four soils.

3.5. Implications

On a global scale, capturing and reusing P from wastewater instead of converting mined PR into fertilizer could potentially lead to an increase in global food security due to lowered reliance on a decreasing, finite resource. Struvite also has the potential to maintain or increase crop yields, potentially further increasing food production and security. On a regional scale, struvite could lower nutrient loads to already sensitive aquatic environments and resources. Recovery of struvite from wastewater also leads to a reduction of nutrients in wastewater effluent and sewage sludge. Furthermore, as results of the current study show, nutrient runoff concentrations are not substantially different from runoff concentrations from a widely used, commercially available fertilizer-P source (*i.e.*, MAP). However, as there is not yet a pelletized form of ECST, this study showed that the timing of ECST application may influence runoff water quality. Furthermore, as there were few differences between runoff nutrient concentrations from MAP and ECST, the application of and potential runoff from ECST would not appear to exacerbate current environmental, nutrient-input issues. Because of reduced nutrient loads to receiving waters from nutrient recovery and having similar nutrient concentrations as MAP, struvite appears to be an alternative fertilizer-P source that may help minimize eutrophication of surface receiving waters, without negatively affecting runoff water quality in areas where struvite (*i.e.*, ECSTreal or ECSTsyn) may be land-applied and incorporated.

Currently, it is too expensive to produce ECST on a commercial scale. Struvite is more costly than traditional fertilizers to produce, partially due to the experimental state of ECST materials and the lack of commercial-scale cost information [47]. However, struvite generally contains more N than many traditional fertilizer-P-only sources, such as TSP, which can reduce the need to purchase and apply additional fertilizer-N inputs in some cropping systems [48]. Furthermore, struvite also has the potential to outperform traditional fertilizer-P sources in terms of crop yield [48] [49]. Continued research is needed to compare the cost of struvite, particularly ECST, production to the production of traditional, commercially available fertilizer-P sources, but, as more research is conducted, there will be the opportunity to increase the efficiency and decrease the cost of struvite production.

4. Conclusions

This study evaluated the effects of soil, fertilizer-P source, and water source over a 6-month period on runoff-water quality parameters from small-scale, laboratory-conducted, rainfall-runoff simulations. The small-scale nature of this study was necessitated by the small quantity of experimental ECST materials produced and provided a unique methodology to help improve understanding of interactions between fertilizer-P sources and various soils.

Somewhat similar to that hypothesized, numerous runoff-water-quality parameters changed differently among soil-fertilizer-P-source and soil-water-type combinations, but, in contrast, numerous runoff-water-quality parameters also changed among soil-fertilizer-P-source- water-type combinations. However, in contrast to that hypothesized, runoff-P changes from ECST materials were not consistently largest in the soil and water type with the lowest initial pH and were not consistently smallest among fertilizer-P sources. Furthermore, runoff-P changes from the struvite fertilizers (*i.e.*, CPST, ECSTreal, and ECSTsyn) were often similar to MAP in many treatment combinations, which was similar to that hypothesized.

To date, the environmental impacts of struvite, as a relatively new, potential alternative fertilizer-P source, generated from recycled nutrients in simulated and real wastewaters, have been under-studied. The similar water-quality responses of the struvite fertilizers among the various soils and water types compared to MAP suggest that struvite has similar runoff-water-quality implications as at least one widely used, commercially available fertilizer-P source. However, more long-term soil and field studies are needed to fully understand the environmental and agronomic implications of using struvite as an alternative fertilizer-P source to commonly used, commercially available fertilizer-P sources.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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