PREDICTING PHOSPHORUS RETENTION IN TWO HAPLOHUMULT FOREST SOILS OF NORTHERN CALIFORNIA

by

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ABSTRACT

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Plant available phosphorus (P) occurs in anionic forms which become unavailable (retained) when iron and aluminum oxides form insoluble phosphate complexes. P-retention is especially likely to occur under acid conditions in soils containing short range order (SRO; poorly crystalline) materials, namely allophane and imogolite. This set of characteristics is common in volcanic-derived forest soils in Pacific Northwest timber regions. P-retention was investigated in Powellton (Fine-loamy, parasesquic, mesic Andic Haplohumults) and Aiken (Fine, parasesquic, mesic Xeric Haplohumults) soil series from Feather Falls and Whitmore "Garden of Eden" sites, respectively. Some soils received heavy fertilization over multiple years; another set of unfertilized soils were compared as a control. Results show that $\mathrm{pH_{NaF}}$ (indicator of SRO materials), soil carbon, and New Zealand P-retention decreased with soil depth in both soils. In near-surface horizons, Feather Falls soil had higher $\mathrm{pH_{NaF}}$, carbon content, and P-retention than the Whitmore soil. Unexpected high P-retention at Feather Falls is probably due to the presence of P-fixing organo-metal complexes in Feather Falls surface horizons. The

Whitmore soil shows higher pH_{NaF} and P-retention than Feather Falls in deep horizons. At Whitmore, the drop in P-retention with depth is attributed to decreasing SRO minerals deeper in the profile; at Feather Falls, a simultaneous drop in carbon and SRO minerals contributes to the pattern of P-retention with depth. Fertilized surface soils at Feather Falls showed ten percent less P-retention than unfertilized soils at that site. Fertilization did not affect P-retention at Whitmore. pH_{NaF} was the single best predictor of P-retention, with other important factors including depth, soil carbon, and soil “redness” (a quantitative measure representing iron content) in a mixed-effects regression of P-retention for these soils.

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INTRODUCTION

In acidic forest soils the majority of inorganic phosphorus (P) is chemically or physically bound, with varying degrees of permanence, to soil minerals. Phosphate (dissolved P) is chemically reactive, prone to precipitation reactions and adsorption to soil particles—these processes are collectively referred to as “phosphorus retention” (Richardson and Simpson, 2011). Phosphorus retention (P-retention) can be defined as the phenomenon whereby contact with the soil results in removal of phosphate from soil solution; no particular mechanism is implied (Wild, 1950).

Soil chemical environments promoting P-retention include 1) acidic conditions with high aluminum (Al) and iron (Fe) content; 2) soils with andic (volcanic) soil properties and amorphous Al compounds; 3) alkaline soils rich in carbonates; and 4) soils with high clay content (Wood et al., 1984; Brady and Weil, 2008). In general, P is chemically fixed by Al- and Fe-oxides under acid conditions, and by calcium carbonates under alkaline conditions (Batjes, 2011; Figure 1). A certain amount of P-retention also occurs on “organo-metal complexes” of Al and Fe (Beck et al., 1999). Retention by soil organic matter is considered insignificant (Wild, 1950) or may reduce P-retention directly (Palm et al., 1997). However, recent reviews have painted a more complex picture of soil organic compound/ phosphorus interactions which may influence P-retention in either direction (Guppy et al., 2005).

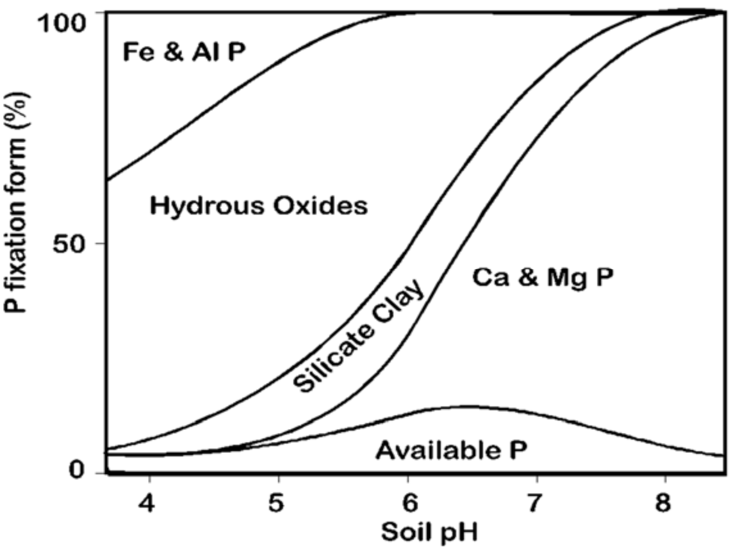

Figure 1. Representation of phosphate retention mechanisms over a range of soil pH. Only a small fraction of soil phosphorus is readily bioavailable.

Soils with special characteristics of volcanic-derived soils are said to have andic soil properties in the U.S. system of Soil Taxonomy (Soil Survey Staff, 2014b). Andic properties develop as a function of volcanic parent materials which weather to form short range order (SRO; amorphous, non-crystalline) minerals such as allophane, imogolite, ferrihydrite and metal-humus complexes. These substances have disproportionately high surface area, providing many exchange sites capable of adsorbing both cations and anions (such as phosphate, HPO_4^{2-}). Volcanic-derived soils are notorious for their high P-retention capacity (Soil Survey Staff, 2014b; Imai et al., 1981).

Allophane is the main component in the clay fraction of many volcanic soils. Its chemical formula is mSiO$_2$, Al$_2$O$_3$, nH$_2$O, where m = 1 to 2, with varying chemical composition and structure (Imai et al., 1981). Studies by Imai and others (Rajan, 1975; Imai et al., 1981) suggest there are two to three types of exchange sites, therefore several adsorption processes, which may occur on allophane particles. These can be understood as one instantaneous process (seconds to minutes) and two slow processes (hours to days or years). Evidence suggests the instantaneous reaction is linked to surface adsorption while the slower reactions represent adsorption on internal surfaces and on new surfaces that become exposed over time. Slower reactions are especially important in acidic soils and when high concentrations of phosphate become available (i.e. during fertilization).

Soil phosphorus *not* fixed by volcanic-derived SRO minerals is scarce. Only a small amount of soil P (0.01%) is generally available for plant uptake at one time—that is, dissolved in soil solution, immediately available to be transported into roots (Brady and Weil, 2008). Bioavailable orthophosphate occurs mainly as HPO_4^{2-} under acidic conditions ($pH < 7.2$) and as $H_2PO_4^-$ under basic conditions ($pH > 7.2$). The optimum pH for P-availability is about 6.5—at this pH, phosphate is least likely to become fixed (Foth, 1990; Figure 1). The concentration of phosphate in soil solution ranges from 0.001 mg/L in infertile soils to 1 mg/L in heavily fertilized soils (Brady and Weil, 2008). The flux (retention and release) of phosphate is a pH-dependent process intertwined with complex interacting biogeochemical processes (Giardina et al., 1995).

Additionally, soil biota compete with plants for the limited amount of bioavailable P; a significant pool of phosphorus is contained within microbial cells. Yet microbial immobilization protects P from other soil chemical reactions that could make it permanently unavailable and ultimately provides a steady release of P to soil solution via microbial turnover (Foth, 1990; Richardson and Simpson, 2011).

Even so, low solubility and slow release of bioavailable forms restrict plant access to soil P, so that many soils have insufficient amounts to meet biological demands (D'Angelo et al., 2003). P-limitation (and co-limitation along with nitrogen) is widespread across all major habitat types of the biosphere (Elser et al., 2007; Richardson and Simpson, 2011). Soil phosphorus retention is a naturally occurring phenomenon which, when paired with inappropriate management, may lead to P-limitation and ecosystem change. The combination of volcanic derived soils and biomass removal can amplify P-retention, causing quantitative changes in production and qualitative shifts in nutrient cycling (Vitousek et al., 2010). In forests, P-deficiency may limit growth, restrict reproductive success and lead to low survival rates of trees (Fisher and Binkley, 2000). As a consequence, competition and community structure of forests may be altered (Elser et al., 2007) and economic value may decrease. Additionally, fertilization of soils with high P- retention capacity can be financially inefficient since the soil will absorb most of the phosphorus, leaving little available for trees.

Despite the co-occurrence of intensively managed forests and volcanic soils in the Pacific Northwest (Appendix A), biogeochemical and anthropogenic influences on P-retention are not well understood by most forest managers. This is in part because the chemical "behavior" of acidic forest soils can defy classical (familiar) principles of soil chemistry, which often come from a context of agricultural soils (Grand and Lavkulich, 2013). Currently fertilization is used to avoid P-limitation, yet this is only a temporary solution to nutritionally deficient soil and may become economically infeasible as the price of P-containing soil amendments rise (Brady and Weil, 2008). This will become especially problematic as phosphate rock, a non-renewable resource from which P-containing fertilizers are made, becomes depleted over the next century (Cordell et al., 2009).

To summarize the points discussed so far:

1) Phosphorus has naturally low availability in soils.
2) P is often a limiting/co-limiting element to growth.
3) The chemical environment of volcanic soils makes them particularly prone to P-retention.
4) P-scarcity can be amplified by poor or misinformed forest management techniques.
5) P-retention and related processes are not particularly well-understood by forest managers in the Pacific Northwest, where volcanic-derived forest soils are common.

For these reasons, a study of the mechanisms behind phosphorus retention in volcanic-derived forest soils of northern California seemed warranted. This study addressed a limited understanding of P-retention in such soils, providing general background to managers and a useful tool for predicting P-retention on their own lands. A main goal of this study was to use common soil assays to model presence/absence and relative degree of P-retention. Utilizing soils collected from two Garden of Eden U.S. Forest Service long-term experimental sites (Powers and Ferrell, 1996; Appendix B) leveraged previous soil sampling and analysis to study the phenomenon of P-retention with minimal cost.

Liles (2013) increased our understanding of the soil processes supporting tree growth in volcanic-derived soils at two Garden of Eden sites, Whitmore and Feather Falls. Previously collected data include soil carbon, nitrogen, iron, and quantitative measurements of soil color (Liles, unpublished data, 2013)—tests that are common and informative in and of themselves, but which also have the potential to predict P-retention. For example, iron and carbon are used to infer relative amounts of volcanic-derived SRO materials and metal-humus complexes (Soil Survey Staff, 2014b). In turn, soil color has been correlated with soil properties such as carbon and iron content (Gunal et al., 2008). Liles (2013) also investigated the mineral component of Whitmore and Feather Falls sites through x-ray diffraction, which describes degree of crystallinity of soil minerals and allows for the identification of certain soil constituents (Appendix C). These data were made available to us for the examination of phosphorus retention at Whitmore and Feather Falls.

In addition, a few specific assays were evaluated in this thesis to test and improve our ability to predict P-retention. Sodium fluoride pH (hereafter $\mathrm{pH_{NaF}}$) is a simple test which indicates the amount of SRO materials in soil. $\mathrm{pH_{NaF}}$ is used to identify andic soil properties as either a simple field test (Gardner, 2007) or a more exacting laboratory procedure (Soil Survey Staff, 2014a). pH_{NaF} is an indicator of SRO material presence and relative amount. Another key aspect of this project is to measure P-retention with the New Zealand Phosphorus Retention method. New Zealand Phosphorus Retention was used to directly measure P-retention at various depths throughout the soil profile. Bioavailable phosphorus was measured with the Bray/Kurtz P1 method (Pierzinski, 2000). Mixed-effects regression analysis was used to investigate relationships between P-retention and combinations of variables measured by Liles and the author of this paper (Table 1).

Table 1. Summary of soil properties measured by collaborator Liles and author Besyk for use in the prediction of soil P-retention capacity

Liles	**Besyk**
Soil carbon & nitrogen content	pH_{NaF} – field method
Pyrophosphate-extractable iron	pH_{NaF} – laboratory method
Quantitative color	New Zealand Phosphorus Retention
X-ray Diffraction mineralogical assessment	Bray/Kurtz P1 soil phosphorus

The strongly contrasting mineralogy of the two sites—one fertile site with crystalline soil minerals (Feather Falls), and one infertile with abundant SRO material (Whitmore)—allowed us to approach this general question with two virtual end members. Further, comparing heavily fertilized with untreated soils provides assessment of the most common silvicultural treatment associated with P-deficiency. These contrasts allowed us to make inferences about the mechanisms of P-retention, while the experimental design supported an approach where simple metrics and resultant models have broad applicability across volcanic soils.

Better understanding of a site's nutritional stock will lead managers to more effective treatments that optimize growth and return on investment. D'Angelo et al. (2003) recognize that few studies have taken into account classical measurements of soil phosphorus *and* retention characteristics in order to make P-recommendations. The need for increased understanding of nutrient retention and bioavailability in non-agricultural soils is more important than ever in the face of changing climate, new demands on forest soils, and increasing cost of soil amendments (Cordell et al., 2009; Grand and Lavkulich, 2013). Batjes (2011) identifies topsoil P-retention as a research priority, particularly in certain soils such as allophanic volcanic soils.

In summary, P-availability has strong implications for productivity of forest ecosystems. This study provides a better picture of covariates in phosphorus availability and develops tools which can be used by managers to assess the P-status of their soils. With a deeper understanding of forest soils in California which are prone to P-retention/P-limitation, managers can plan for productive forests which provide crucial ecosystem services and products.

Hypotheses

Hypotheses are presented below along with the data which were used to prove/disprove each prediction. Alternative hypotheses are presented in the format "H*n*" and null hypotheses in the format "Hn_0".

H1: Aiken soil (Whitmore site) will have higher P-retention and pH_{NaF} than Powellton soil (Feather Falls site) due to higher amorphous material content in the former.

$H1_0$: There is no difference in P-retention nor pH_{NaF} between Aiken and Powellton soils.

Data: A depth function showing P-retention (or pH_{NaF}) with depth in the soil profiles will visually separate patterns of P-retention (or pH_{NaF}) by site.

H2: Fertilized plots will exhibit lower P-retention than unfertilized plots.

$H2_0$: Treatment will have no effect on P-retention.

Data: A depth function showing P-retention with depth in the soil profiles will visually separate patterns of P-retention by treatment and site.

H3: pH_{NaF} (both laboratory and field method), as an indicator of SRO materials, will correlate strongly and positively with P-retention.

$H3_0$: There is no relationship between pH_{NaF} and P-retention.

Data: Simple correlation and regression analyses will determine the relationship between pH_{NaF} and P-retention.

H4: Soil carbon content will have little influence over P-retention, as SRO content is the main driver of this phenomenon.

$H4_0$: Soil carbon will have a significant effect on P-retention.

Data: Simple correlation and regression analyses will determine the relationship between soil carbon and P-retention.

H5: Soils with higher concentration of iron-oxides will exhibit more P-retention

$H5_0$: There is no relationship between Fe-oxide content (pyrophosphate-extractable Fe) and P-retention.

Data: Simple correlation and regression analyses will determine the relationship between pyrophosphate-extractable iron and P-retention.

H6: Quantitative soil color will be a good predictor of C content (i.e. dark soils have more C) and Fe-oxide content (i.e. red soils have more Fe-oxides). In turn, quantitative color will be as good a predictor of P-retention as are its related characteristics (C and Fe).

$H6_0$: There is no relationship between quantitative soil color, C, Fe or P-retention.

Data: Simple correlation and regression will determine relationships among soil carbon and "darkness", extractable iron and "redness", and P-retention and soil color.

H7: SRO content is the main driver of P-retention in both soils.

$H7_0$: P-retention is controlled by soil characteristics other than SRO content.

Data: pH_{NaF} and its relationship to P-retention will be examined via correlation, regression, and mixed-effects modeling.

H8: Some combination of pH_{NaF} with other soil parameters such as carbon, iron, and color can act as variables in a mixed-effects model to predict P-retention.

$H8_0$: P-retention cannot be reliably predicted with these metrics.

Data: The whole dataset will be used in building a model for P-retention including any significant relationships (and interactions between variables) from the investigations mentioned above. “Random effects” will be employed within the model to account for the nested experimental design.

MATERIALS AND METHODS

Study Area

Two sites in northern California, “Whitmore” and “Feather Falls” are compared in this study (Appendix D). Both sites occur on privately owned timber land and were planted in ponderosa pine (*Pinus ponderosa*) in 1986 (Whitmore) and 1988 (Feather Falls). The sites were originally chosen as part of the Garden of Eden experiments (Powers and Ferrell, 1996) and represent, along with six other sites not studied here, the range of pine plantation conditions across California (Appendix B). Both Whitmore and Feather Falls fall within a Mediterranean climate, but Whitmore is warmer and drier while Feather Falls is cooler and wetter (Wei et al., 2013).

While the soils at Whitmore and Feather Falls are both derived from volcanic parent materials, they have developed into different soils (Table 2). Whitmore represents a low- to mid-quality plantation, while Feather Falls is a highly productive site. This difference is attributed to higher precipitation and greater organic matter accumulation at Feather Falls.

Another notable difference is the contrasting mineralogy of these two sites. Short range order (SRO) minerals lacking repeating structure, such as allophane, imogolite and gibbsite dominate Whitmore’s mineralogy. The mineral component of Feather Falls, in contrast, is made up of more crystalline materials including a quartzite-dominated subsoil. The evidence for mineral crystallinity at these sites comes from X-ray

Diffraction analysis by Liles (2013; Appendix C) as well as inferences from past work on the Aiken soil series associated with the Whitmore site (Ulrich et al,. 1947).

Together, Feather Falls and Whitmore sites act as virtual end-members allowing for the comparison of a low organic matter/high SRO soil with a high organic matter/low SRO soil. Soil texture is similar at both sites (Whitmore 31% clay, 42% sand; Feather Falls 27% clay, 41% sand) as is surface soil pH (Whitmore 6.2 ± 0.1, Feather Falls 6.0 ± 0.1) (McFarlane et al., 2009).

Table 2. Site characteristics for Whitmore and Feather Falls Garden of Eden sites in northern California, U.S. MAT = Mean Annual Air Temperature. MAP = Mean Annual Precipitation.

	Whitmore Site	**Feather Falls Site**
Soil Series	Aiken	Powellton
Soil Classification	Fine, parasesquic, mesic Xeric Haplohumults	Fine-loamy, parasesquic, mesic Andic Haplohumults
Parent Material	Volcanic Mudflow	Tephra over Metadiorite
Elevation (m)	790	1220
MAP (mm)	1100	2000
MAT (^{o}C)	15	11
Site Index 50 (m)	23	30
Mineralogy	Lower crystallinity Less Felsic	Higher crystallinity More Felsic

Treatments – Fertilized and Control

At both sites, two treatment types were studied: Fertilized and Control. Fertilized sites received heavy application of all essential elements during the Garden of Eden experiments. The fertilization treatment followed a "ramp" schedule where increased nutrient application matched increased physiological demand. In years one, three, and five, commercial dry salts of phosphorus and other essential nutrients were applied to four holes around each seedling. In year seven, larger quantities of fertilizer were applied in parallel bands between tree rows. Each fertilized plot received a grand total of 530 lbs of phosphorus over six years (Powers and Ferrell, 1996). Control sites were unfertilized and undisturbed for 25 years after planting, representing the natural soil condition.

Experimental Design

A randomized block design was implemented so that treatment types were replicated three times in an identical grid pattern at each site (Figure 2). There were three replicate treatment plots per site; two soil cores were collected per plot (Figure 3).

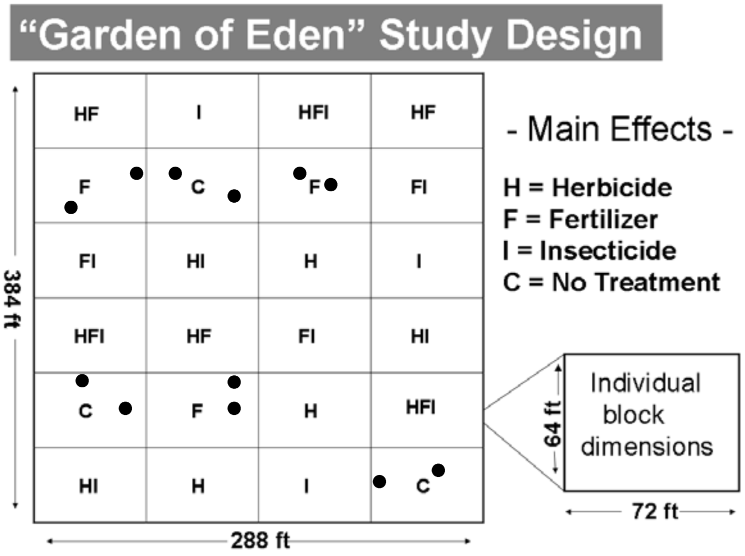

Figure 2. Completely randomized block design common to Whitmore and Feather Falls sites, inherited from the "Garden of Eden" study. Control (C) and Fertilized (F) plots were examined in this study. Black dots represent two randomly located soil cores (two meter depth) taken from each plot.

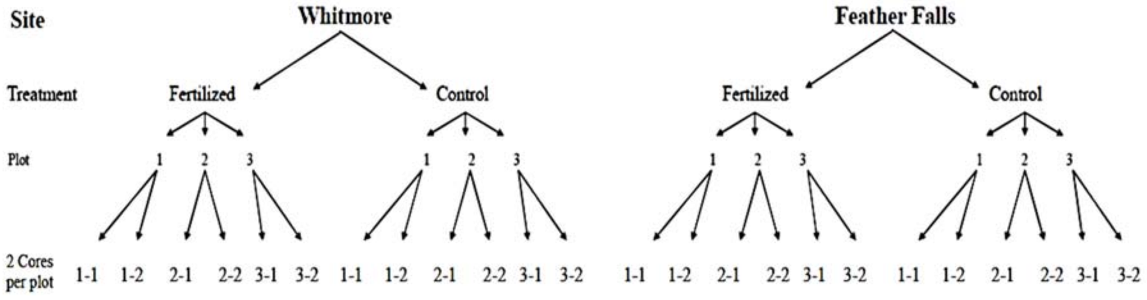

Figure 3. Nested sampling design including two sites, two treatments per site, three plots per treatment, and two cores per plot. In other words, six cores were collected from four site/treatment combinations: Whitmore fertilized, Whitmore control, Feather Falls fertilized, Feather Falls control.

Sample Collection

Soil samples were collected in 2010 with a hydraulic geoprobe. Two randomly located cores were taken from each plot, representing a continuous sample of the soil profile extending two meters below the soil surface. Cores were broken up into ten-centimeter increments for analysis. Two cores from the same plot were analyzed as one composite sample, assuming little variation between cores. Put another way, two cores were treated as one assuming low variation within plots.

Soil samples near the soil surface (≤ 30 cm) were resampled by hand in June 2014 to supplement missing archived samples. Again, two random locations throughout the plot were chosen and a continuous sample was taken down to 30 cm depth. Then those samples were separated into ten-cm depth increments and composited for analysis.

Soil samples were air dried and stored at room temperature until analysis.

Data provided by Liles comes from the originally sampled and archived soils. Assays by Besyk were either performed on the originally sampled, archived soils (depths 40, 100, 150, and 170 cm) or from soils sampled in June 2014 (depths 0, 10, and 20 cm).

Collaborative Timeline

Various parts of this research were implemented by multiple parties including Robert F. Powers, the lead researcher behind the Garden of Eden study; Garrett Liles, who studied soil at the Whitmore and Feather Falls sites; and the author of this project, Nichole

Besyk. Table 3 clarifies which parts of this collaborative project were completed by each party.

Table 3. Summary of researchers contributing to the study of Whitmore and Feather Falls sites (with dates). Includes Powers, designer of the Garden of Eden experiment; Liles, who studied mineralogical and nutritional aspects of the soils; and Besyk, investigating phosphorus retention.

Powers	**Liles**	**Besyk**
1986 – 2012 - Experimental Design - Tree Planting (Whitmore 1986, Feather Falls 1988) - Fertilization (Spring of years one, three, and five after planting; Autumn of year six) - Repeatedly measured aspects of stand development, tree growth and nutrition	2010 – 2012 - Collected geoprobe soil cores - Soil C, N, Fe assays - Quantitative color - X-ray diffraction	2014-2015 - Collected supplementary samples from top 30 cm soil - pH_{NaF} (laboratory method, field method) - Phosphorus retention - Available soil phosphorus

Sodium Fluoride pH (pH_{NaF})

Sodium fluoride (NaF), when added to soil solution, releases OH^- ions that are bound to aluminum (Al) and silica (Si) at a potential exchange-site for P- retention. This is illustrated by the following reactions:

$Al\,(OH)_3 + 3\,F^- \rightarrow AlF_3 + 3\,OH^-$

$Si\,(OH)_4 + 4\,F^- \rightarrow SiF_4 + 4\,OH^-$

Increased OH^- in solution causes pH to rise. The maximum pH reached depends on the amount of short range order (SRO; high surface-area, many exchange-sites) materials in the soil (Soil Survey Staff, 2014a). The more SRO materials in soil, the higher pH rises when NaF is added.

Two methods of pH_{NaF} were tested in this study; a crude field method and a more refined laboratory method. The purpose was to determine the reliability of the cheaper, easier field method; is this method of pH_{NaF} equally as predictive of P-retention as is the pH_{NaF} laboratory method?

pH_{NaF} – Laboratory Method

The laboratory method involved preparation of one normal (1 N) NaF solution; 41.99 g solid NaF dissolved in 1 L reverse osmosis deionized water (Soil Survey Staff, 2014a). The starting pH of the NaF solution was adjusted to 7.5 – 7.8 with NaOH or HCl if necessary. Fifty mL NaF solution was added to the soil sample (5 g soil). After two minutes of agitation, the pH was read with an electrode in the upper 1/3 of the suspension (above the sediments). pH_{NaF} was reported to the nearest 0.01 pH unit.

Our method differed slightly from the standardized NRCS method in that we used five grams of soil whereas one gram is usually used. The use of a larger soil sample means that our pH_{NaF} values are higher than would be obtained for the one gram quantity. To explore this issue, 32 one gram samples were analyzed for pH_{NaF} and compared with respective five gram results. Using simple linear regression, we compared pH_{NaF} from 1g vs 5g samples then calculated root mean square error (RMSE) based on observed and predicted 1g pH_{NaF} values. RMSE was calculated to be 0.44, indicating the five gram samples generally had pH_{NaF} values higher than would be expected, too high to assume no difference between 1g and 5g pH_{NaF} values. Therefore, while our results are comparable to each other within the study, direct comparison with pH_{NaF} from other studies should be avoided (Z. Libohova, personal communication, 2014). However, the trends and relationships discovered in this study are still meaningful.

pH_{NaF} – Field Method

This less standardized test is used for field identification of andic soil properties using transportable materials for quick in-situ analysis. A $pH_{NaF} \geq 9.4$ is considered an indicator of significant amounts of amorphous Al- and Fe-oxides (SRO materials) and likely phosphorus retention (Gardner, 2007).

Porcelain spot plate pools were filled ¾ full with soil. A solution of one normal (1 N) NaF was added to each pool with a dropper until sample was saturated (five to ten drops). After two minutes, three drops of Thymol Blue pH indicator were added to the spot plate and pH determined by the solution's color change. If the pH was greater than 9.6 (the upper limit of Thymol Blue pH indicator), the pH_{NaF} field method was repeated with a high-range pH strip and this higher pH_{NaF} was recorded. Spot plates were washed with deionized water between each test.

New Zealand Phosphorus-Retention

The New Zealand Phosphorus-Retention test directly measures the ability of soil to fix dissolved phosphate (remove P from solution). A soil with high P-retention (i.e. high New Zealand P-Retention values) leaves little P available for plants. This method is based on Method 4D8 in the Soil Survey Lab Methods Manual (Soil Survey Staff, 2014a).

Soil samples were passed through a two millimeter (2 mm) sieve and dried at 105°C for eight hours. Then five grams (5 g) of soil were transferred to a 50-mL falcon tube. Twenty-five (25) mL of "P-retention solution" (PRS) were added to the falcon tube, and the mixture was shaken for 24 hours. PRS is a 1000 mg L^{-1} P solution prepared as follows: 35.2 g potassium phosphate [KH_2PO_4, dried two hours at 110°C] + 217.6 g sodium acetate trihydrate [$CH_3COONa \cdot 3H_2O$] + 92 mL glacial acetic acid, diluted to 8 L with reverse osmosis deionized water, pH adjusted to 4.55 – 4.65. After shaking, the mixture (PRS + soil) was centrifuged at 2000 rpm for 15 minutes, filtered through No. 42 Whatman filter paper, and then stored at 4˚C for up to 72 hours before colorimetric analysis.

P-standards were made to represent zero (0), 200, 400, 600, 800, and 1000 ppm (mg L^{-1}) by diluting PRS with "diluent solution" (54.4 g $CH_3COONa \cdot 3H_2O$ + 23 mL glacial acetic acid, brought to two [2] L with reverse osmosis deionized H_2O) .

For colorimetric analysis, we used a commercially prepared solution of ammonium molybdate-vanadate (hereafter, "AMV") (Ricca Chemical Company, Cat. No. 677-32). The filtrate or standard was diluted 1:20 with AMV (0.2 mL filtrate + 3.8 mL AMV) in a plastic cuvette. Color was left to develop for 32 minutes, then read at 466 nm with a spectrophotometer (we used a Beckman DU-640 in the HSU CORE facility). Three to four replicate filtrate samples were colorimetrically analyzed per soil sample.

Available Soil Phosphorus

The "Bray and Kurtz P1" soil phosphorus method is suitable for acid and neutral soils. This test estimates available soil P, with a value of 25-30 mg P/kg soil (equivalently, ppm) considered optimum for plant growth (Pierzynski, 2000). The Bray/Kurtz P1 extracting solution was prepared by dissolving 11.11g ammonium fluoride (NH_4F) in distilled water, adding 250 mL 1M hydrochloric acid (HCl), and bringing to 10 L with distilled water. The pH was adjusted to 2.6 using HCl and ammonium hydroxide

(NH_4OH) as needed. The detection limit of the Bray/Kurtz P1 test is 1 ppm (Watson and Mullen, 2007).

P-extraction was accomplished as follows:

1. Two g of dry soil (previously passed through two mm sieve) were added to 15 mL Bray/Kurtz P1extracting solution.
2. The mixture was shaken at 200 revolutions per minute for five minutes at room temperature.
3. Extracts were filtered through Whatman No. 42 filter paper and stored in the refrigerator for up to 72 hours.
4. Extracts were analyzed colorimetrically (see "Colorimetric Phosphorus Analysis").
5. Bray/Kurtz P1 Extractable P (mg P/ kg soil) was calculated with Equation 1.

Equation 1: Extractable P (mg P / kg soil) = Cp x [Liters of extract] / [kg soil]
where Cp = Concentration of P in Bray/Kurtz P1 extract (mg/L)

Colorimetric Phosphorus Analysis

This procedure was based on the method by K.P. Moore (in Plank, 1992). Acid molybdate stock solution was prepared by dissolving 125 g ammonium molybdate $(NH_4)_6Mo_7O_{24} \circ 4H_2O]$ in 400 mL reverse osmosis deionized water, heating to 60°C. After cooling, 2.9 g antimony potassium tartrate $[K(SbO)C_4H_4O_6 \circ 1/2H_2O]$ was added to solution. The mixing flask was placed in an ice bath while 1500 mL concentrated sulfuric acid (H_2SO_4) was added, then finally brought to volume (2 L) with reverse osmosis deionized water. Ascorbic acid stock solution was prepared by dissolving 211.2 g ascorbic acid ($C_6H_8O_6$) in 2 L water. Working solution was prepared fresh daily by combining 20 mL acid molybdate stock solution with 10 mL ascorbic acid stock solution in 800 mL reverse osmosis deionized water, then bringing to volume (1 L) with reverse osmosis deionized water.

Extracts were diluted 1:1 with working solution and left to develop for 30 minutes before reading absorbance in the spectrophotometer at 660 nm.

Soil Carbon

Soil carbon (C) content was determined for archived soil samples from the top 30 cm of soil only (Liles, unpublished data). Samples from 10 cm depth increments were air dried, mixed, and passed through a 2 mm sieve. Visible roots were removed by hand then samples were crushed to a fine powder with a ball mill. C was analyzed by direct combustion on a Costech CHN elemental analyzer.

Pyrophosphate-Extractable Iron

Iron (Fe) content of the soil was analyzed using sodium pyrophosphate selective dissolution (Method 4G3; Soil Survey Staff, 2014a) (Liles, unpublished data). Pyrophosphate fails to dissolve amorphous Fe compounds, so this pool of Fe is distinct from the allophane and imogolite fraction. The method involves overnight shaking of the soil sample with 0.1 M $Na_4P_2O_7$, then analyzing the filtrate with an atomic absorption spectrophotometer.

Quantitative Color

Quantitative soil color was determined for soil samples from Whitmore and Feather Falls sites (Liles, unpublished data). Sieved and dried samples were measured with a handheld Minolta CR-400 chromameter with C65 internal standard light (Liles et al., 2013). Color is expressed in quantitative values of darkness (L), redness (A), and yellowness (B).

Depth Functions

At times we use soil “depth functions” to display trends of changing soil characteristics with depth (Figures 4, 6, and 9). This is a tool often used in soil science which may be unfamiliar to some readers. It is important to note that, on our depth function graphs, actual measurements were taken only at certain depths represented by nodes (i.e. squares and X’s) along the smoothed line. The smoothed line itself is an interpolation of the change between our actual measurements; the line represents our ‘best guess’ of the pattern between measured values, and is meant more as a visual aid rather than a true representation of the values at depths in-between actual measurements.

Statistical Analysis

The variables in this study are depth interval, treatment, plot, and site. We were interested in analyzing the difference in P retention between the two sites, between treatments within sites, and between depths. Each variable combination is replicated three to four times (Table 4).

Table 4. Replication of New Zealand Phosphorus Retention analyses. Since some samples were replicated three times and others four times, the "Grand Total" comes out to 256 phosphorus-retention data points.

	Treatments (control, fertilized)	**Number of plots**	**Number of 10-cm depth intervals analyzed**	**Replicates of P-retention test**	**Total number of analyses (multiply across row)**
Whitmore	2	3	6	3 to 4	108 to 144
Feather Falls	2	3	6	3 to 4	108 to 144
Total					**256**

Relationships between variables were explored via basic correlation and regression techniques. Correlation coefficients (r, r^2) and significance of model parameters (p-values) are at times reported to describe these relationships. Microsoft Excel® and statistical software R (R Core Team, 2013) were used to analyze data and create figures. Mixed-effects models were built under R package "lme4" (Bates et al., 2014).

Due to the nested nature of variables, mixed-effects regression was used to model P-retention. This approach accounts for pseudoreplication within the nested experimental design, focusing instead on variability caused by treatments (fixed effects) while accounting for natural variability between plots (random effects).

RESULTS

Phosphorus Retention – Site Differences

P-retention generally decreases with depth in the soil profile (Figure 4). At the surface Feather Falls has higher P-retention than Whitmore; deep in the soil profile the trend is reversed, with Whitmore showing higher P-retention. At medium depths (around 40 cm) P-retention becomes similar at both sites (Table 5). At Whitmore, P-retention drops slowly between 0 and 30 cm, quickly between 30 and 40 cm, then changes little below 40 cm depth. P-retention at Feather Falls decreases quickly between 0 and 30 cm, drops steadily until 100 cm, then increases slightly between 100 and 170 cm.

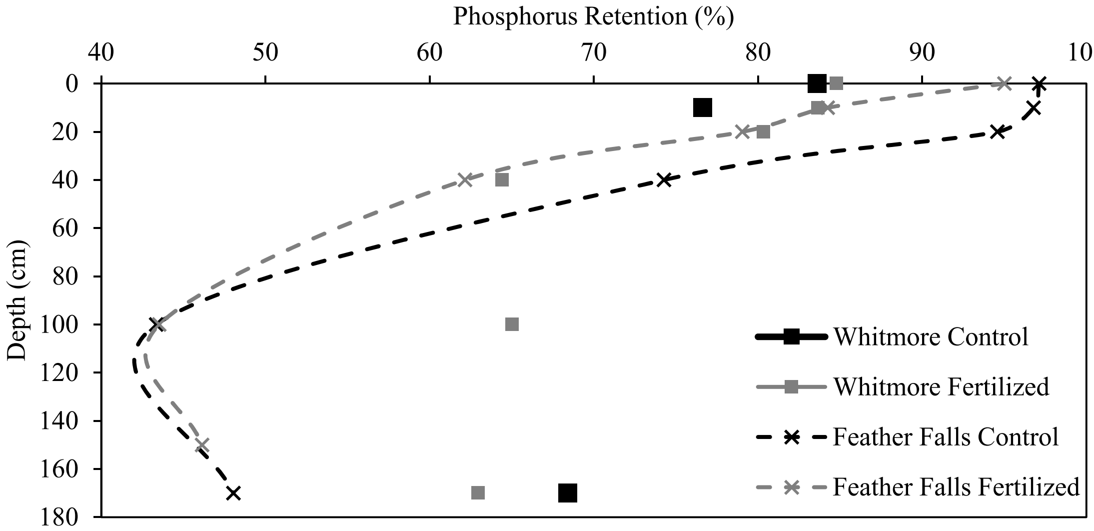

Figure 4. Depth function showing mean phosphorus retention by site and treatment. P-retention decreases with depth and shows different patterns at each site. See Appendix E for error distribution and sample sizes.

Table 5. Mean phosphorus retention (%) by site and depth increment. Surface = 0 to 30 cm, Medium = 40 to 50 cm, Deep = 170 to 180 cm beneath soil surface (150 to 160 cm for Feather Falls Fertilized). These are site averages and do not include treatment effects. See Appendix F for sample sizes.

	P-retention (%)		
	Surface	**Medium**	**Deep**
Whitmore	81.0	64.9	63.8
Feather Falls	91.2	68.2	47.1

Phosphorus Retention – Treatment Effects

At the soil surface (0 to 30 cm), mean P-retention for fertilized plots did not differ from that of control plots at Whitmore (Figure 5). At Feather Falls (surface, 0 to 30 cm), mean P-retention of fertilized soils was ten percent less than control. P-retention was not affected by treatment in any other part of the soil profile neither at Whitmore nor Feather Falls. In Table 6, mean P-retention is summarized by site, treatment, and depth.

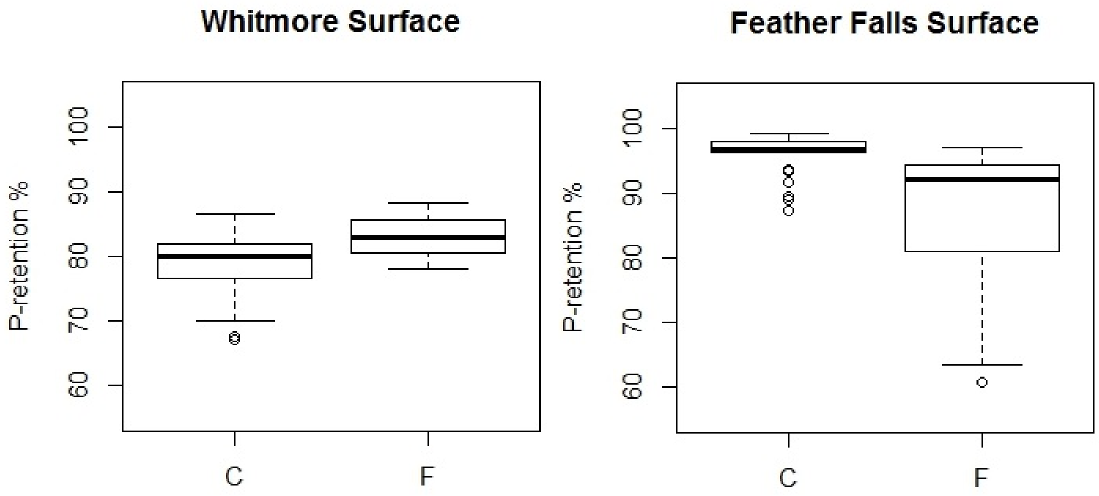

Figure 5. Boxplot of phosphorus retention (%) in the top 30 cm of soil at Whitmore and Feather Falls sites. The box represents the middle 50% of the data distribution, while the “whiskers” represent 25th and 75th percentiles. The thick line in the middle of the box is the median. C = Control, F = Fertilized. See Appendix F for sample sizes.

Table 6. Mean phosphorus retention (%) by site, treatment, and depth increment. Surface = 0 to 30 cm, Medium = 40 to 50 cm, Deep = 150 to 160 or 170 to 180 cm beneath soil surface. Standard Deviation appears in parentheses. See Appendix F for sample sizes.

	Mean P-Retention % (Std. Dev.)		
	Surface	**Medium**	**Deep**
Whitmore Control	79.1 (5.1)	65.5 (5.0)	64.6 (5.0)
Whitmore Fertilized	82.9 (3.1)	64.4 (11.9)	63.0 (4.2)
Feather Falls Control	96.2 (2.9)	74.3 (12.0)	48.1 (4.8)
Feather Falls Fertilized	86.0 (12.2)	62.2 (7.7)	46.1 (3.6)

pH_{NaF} – Laboratory Method

Mean laboratory-derived pH_{NaF} (indicator of SRO materials) shows a very similar pattern with depth as does P-retention (Figure 6). The portion of the soil profile around 30 to 40 cm deep seems to represent a transitional zone where P-retention patterns are shifting; likewise, SRO content also drops significantly within this zone (as indicated by decrease in pH_{NaF}). pH_{NaF} patterns at Feather Falls are similar to those found in the associated Powellton soil series (Soil Survey Staff, Official soil series descriptions). pH_{NaF} data for the Aiken soil series (corresponding to Whitmore site) are not available for comparison.

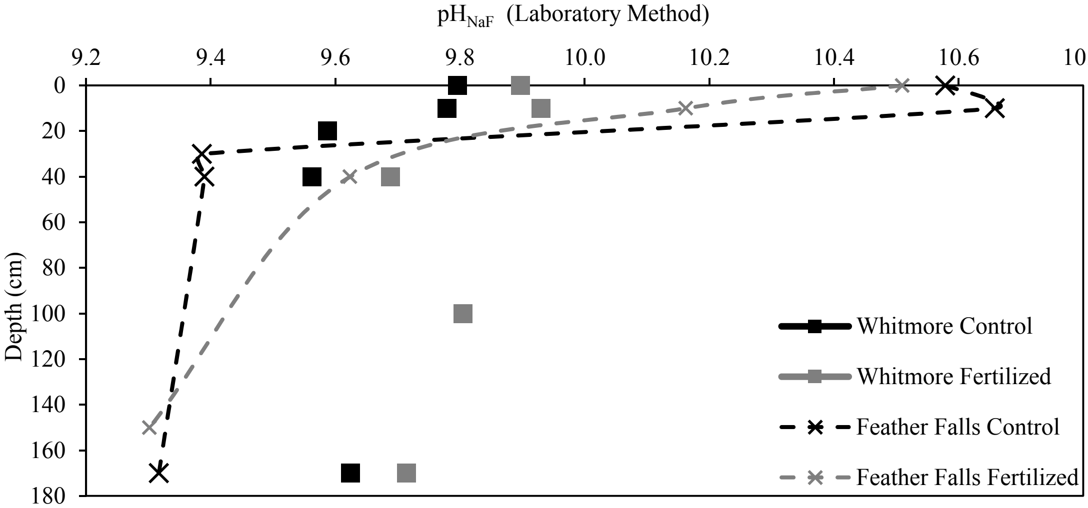

Figure 6. Depth function showing mean pH$_{NaF}$ (determined via laboratory method) by site and treatment. pH$_{NaF}$, an indicator of SRO materials, decreases with depth and shows different trends at the surface versus deep in the soil profile. See Appendix E for error distribution and sample sizes.

There is a strong positive relationship between pH$_{NaF}$ and P-retention (Figure 7). Feather Falls has a wider range of P-retention and pH$_{NaF}$ values, while Whitmore values are visually distinct in a central cluster with a smaller range of P-retention and pH$_{NaF}$ values. The range of pH$_{NaF}$ values is 9.08 to 10.72 (mean = 9.58, median = 9.68).

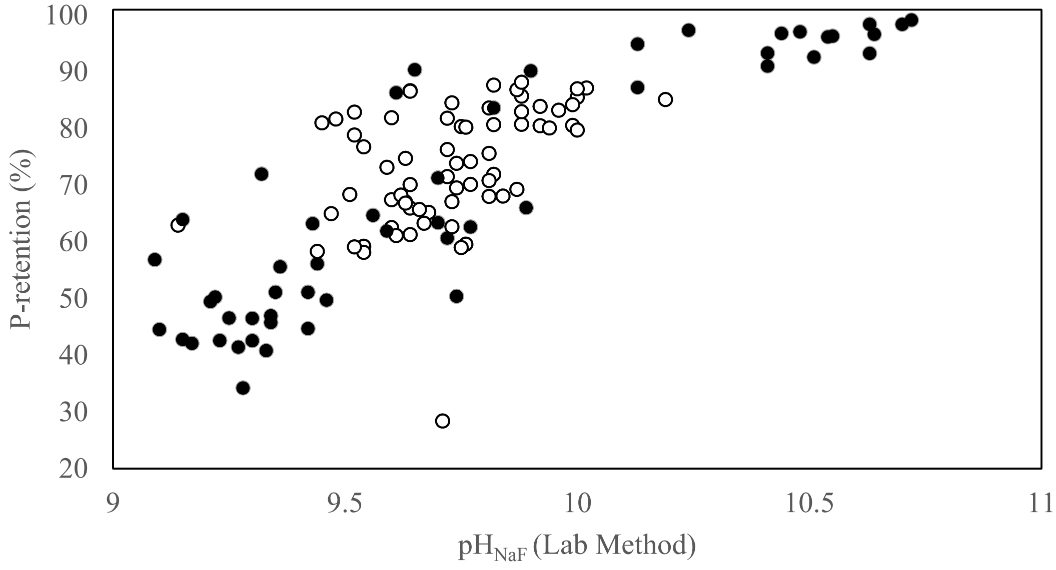

Figure 7. Phosphorus retention (%) versus pH_{NaF} (laboratory method). Black dots represent Feather Falls, open circles represent Whitmore. N = 121 data points

pH_{NaF} – Field Method

There is a weak positive relationship between field-determined pH_{NaF} and P-retention (Figure 8). Results from the field pH_{NaF} show a weaker relationship to P-retention than the laboratory pH_{NaF} ($R^2 = 0.17$ and 0.65, respectively). For the field pH_{NaF} test, pH_{NaF} ranges from 8.0 to 9.6 (mean = 9.2, median = 9.2) with a few data points (N = 6) ranging between 10.0 and 11.0. There is significant overlap of data points in Figure 8 and poor distinction between Feather Falls and Whitmore data points at the upper limits of P-retention/pH_{NaF}. In other words, the laboratory test is more sensitive than the field method, especially at the upper range of pH_{NaF} and P-retention values observed in this study.

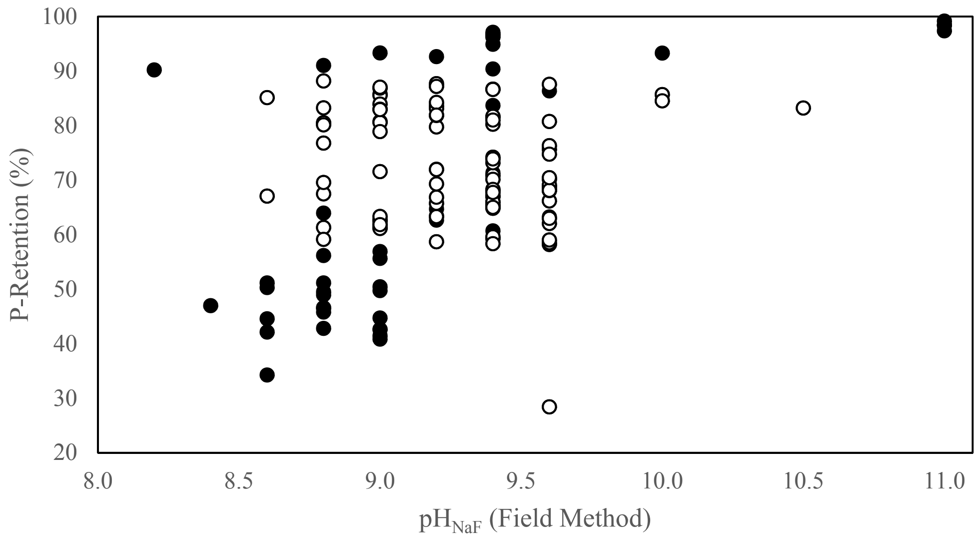

Figure 8. Phosphorus retention (%) versus pH_{NaF} (field method). Black dots represent Feather Falls, open circles represent Whitmore. N = 149 data points.

Available Soil Phosphorus

Measurements indicate that bioavailable soil phosphorus occurs at very low concentrations in both Whitmore and Feather Falls soils. All measured samples fell below the limit of detection for the Bray-Kurtz P-1 method (1 ppm; Watson and Mullen, 2007). Professional laboratory analysis showed similar results for phosphorus: Whitmore Control, Feather Falls Control, and Feather Falls Fertilized all came out to 1 ppm, while Whitmore Fertilized had 3 ppm (Appendix H).

Soil Carbon

Mean soil carbon content (g C per 100 g soil, %) shows a similar pattern with depth as does P-retention and pH_{NaF} (Figure 9). The portion of the soil profile around 30 to 40 cm deep seems to represent a transitional zone where P-retention patterns are shifting; likewise, soil carbon and SRO content drop significantly within this zone. There is a positive logarithmic relationship between soil carbon and P-retention (Figure 10).

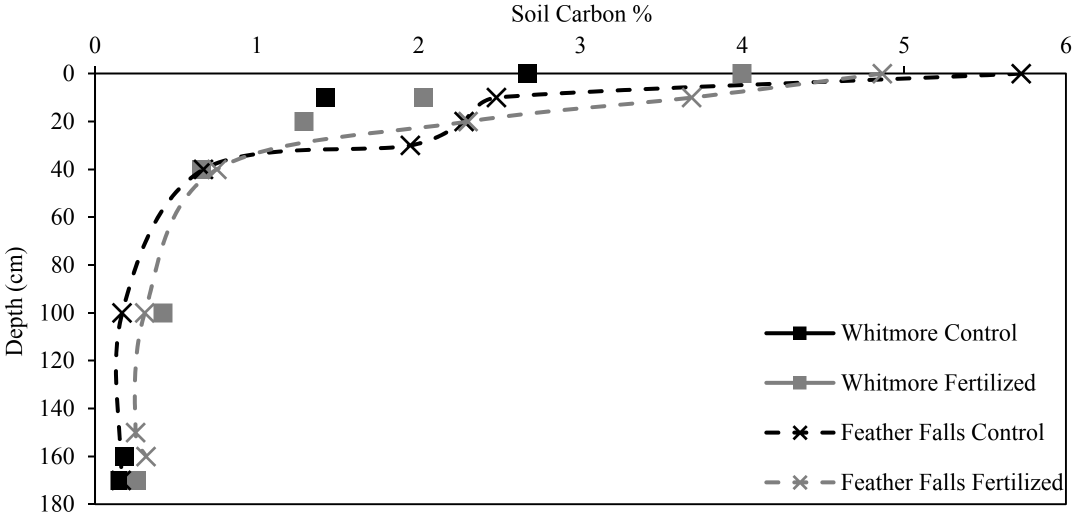

Figure 9. Depth function showing mean soil carbon (g C per 100 g soil, %) summarized by site and treatment. Significant differences in soil C are only apparent near the surface. Soil C decreases with depth, with concentrations becoming similar across sites and treatments deep in the soil profile. See Appendix E for error distribution and sample sizes.

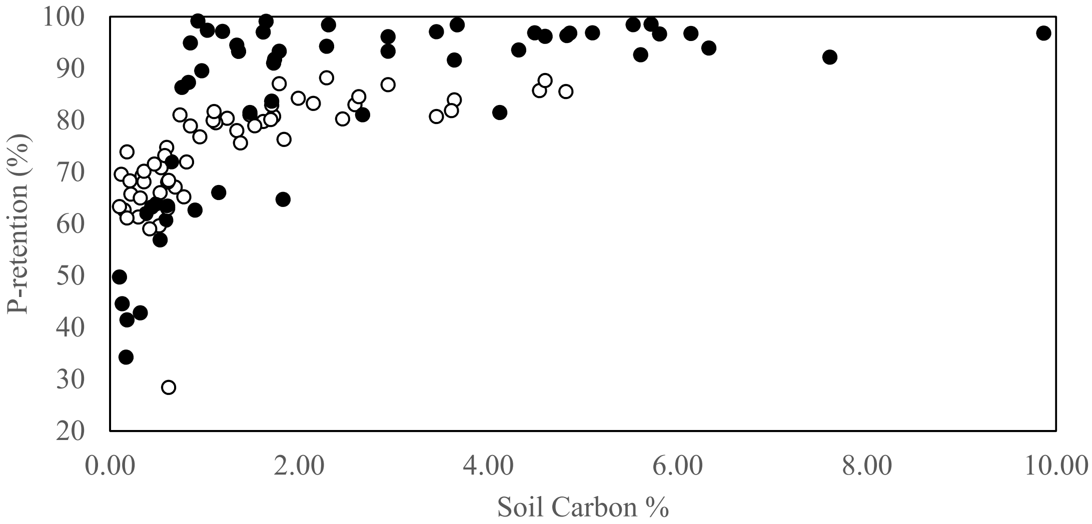

Figure 10. Phosphorus retention (%) versus soil carbon (g C per 100 g soil, %). Black dots represent Feather Falls, open circles represent Whitmore. N = 122 data points.

The relationship between soil C and P-retention (Figure 10) looks very much like the graph of P-retention versus pH_{NaF} (Figure 7). High C samples tend to have high pH_{NaF} and high P-retention. The correlation between C and pH_{NaF} (laboratory method) is high (r = 0.58).

Pyrophosphate-Extractable Iron

Pyrophosphate-extractable Iron (Fe) data are only available for the top 30 cm of soil (N=36 observations). Yet there exists a positive relationship between extractable iron and P-retention (Figure 11).

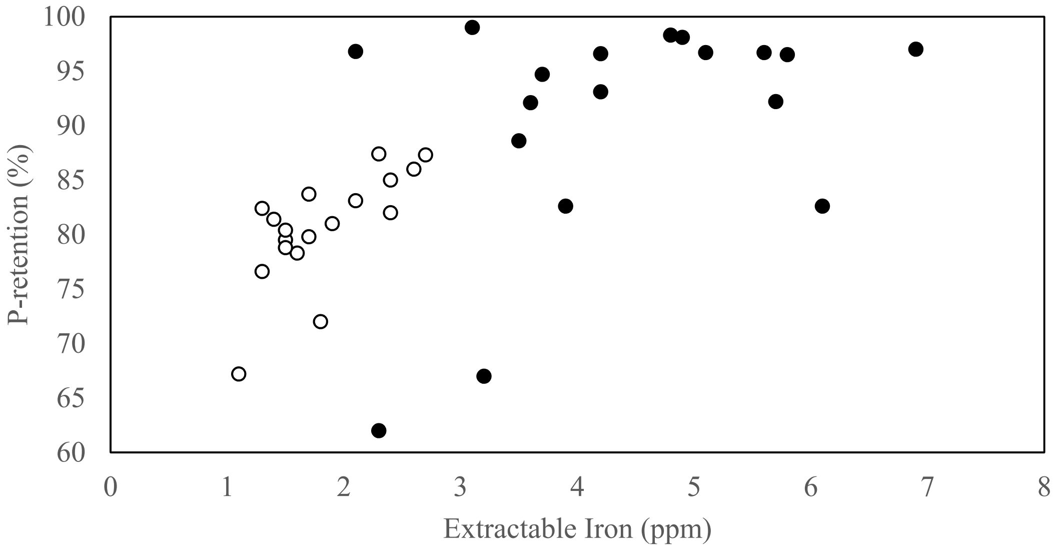

Figure 11. Phosphorus retention (%) versus pyrophosphate-extractable iron (ppm). Black dots represent Feather Falls, open circles represent Whitmore. Soil iron data are for top 30 cm of soil only. N = 36 data points.

Quantitative Color

Quantitative color is related to pyrophosphate-extractable iron (quantitative redness, "A") and carbon (quantitative darkness, "L"). The carbon/darkness relationship is more variable than the iron/redness relationship here. The A and L variables generally underestimate extractable iron and carbon for Whitmore and overestimate iron and carbon for Feather Falls. A similar trend is apparent when using "A" or "L" for P-retention prediction; these variables have distinct relationships with each site (Figure 12 and 13). These site-specific relationships are not seen with direct measurements of carbon and extractable iron (Figure 10 and 11).

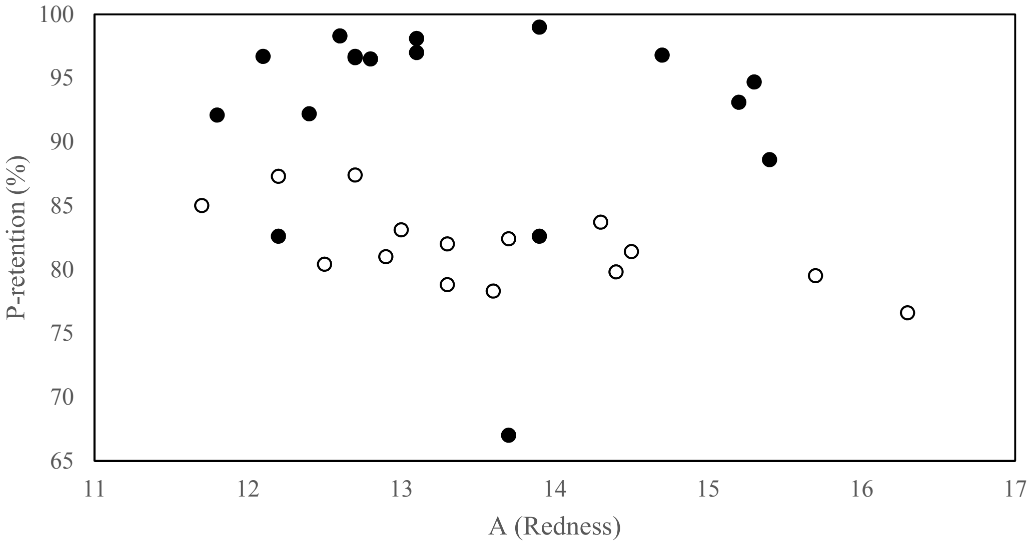

Figure 12. Quantitative color (A, “redness”) versus phosphorus retention (%). Lower A values represent “more red” soil color. Black dots represent Feather Falls, open circles represent Whitmore. N = 32 data points.

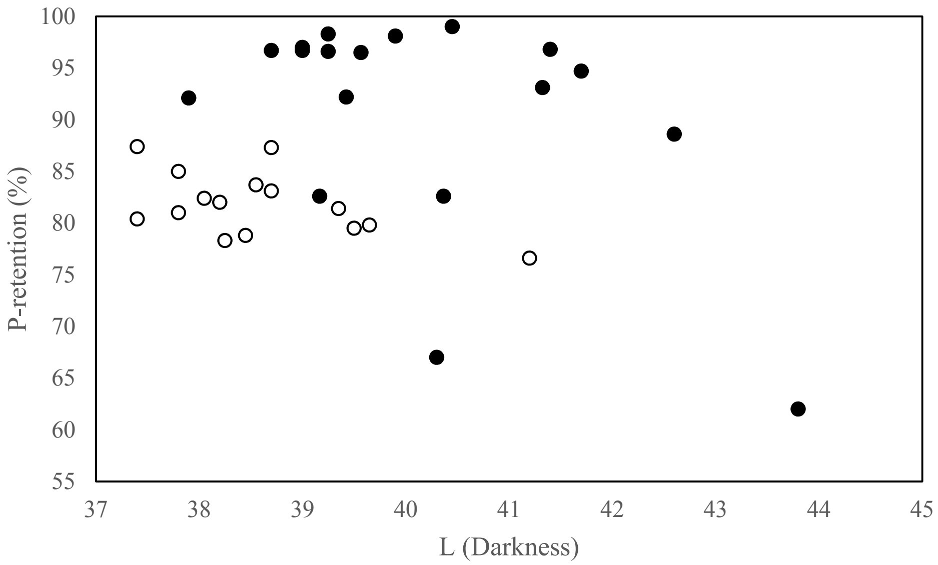

Figure 13. Quantitative color (L, “darkness”) versus phosphorus retention (%). Lower L values represent “darker” soil color. Black dots represent Feather Falls, open circles and dashed line represent Whitmore. N = 33 data points.

Modeling P-retention

Two mixed-effects models are presented here for the prediction of phosphorus retention. The first represents a larger dataset for depths 0 to 170 cm below the soil surface. The second model only includes depths 0 to 30 cm below the soil surface, but incorporates additional chemical tests such as extractable iron. See Appendix G for model parameter estimates and a summary of the variables used in the two models.

Model 1, all depths: P-retention ~ pH_{NaF} + log(Carbon+1) + pH_{NaF}*log(Carbon+1) + Treatment + (1|Plot/Site)

The term “P-retention ~ ...” should be read as “P-retention is a function of…” Where “pH_{NaF}*log(Carbon+1)” represents a statistical interactions between these factors and “1|Plot/Site” represents “Plot nested within Site” as a random effect. The random effects term takes into account the nested nature of the experimental design and accounts for pseudoreplication. Random effects are those model parameters that are not manipulated or measured, but are part of the natural variability (i.e. randomly located plot within a site). Mixed effects models separate variability in this way to reveal relative strengths of contributors to variability. In Model 1, the parameter “percent soil carbon” was log-transformed (log[soil carbon % + 1]) to achieve a better fit.

Many different models were constructed, attempting to cover all possible combinations of variables, and then compared in a pairwise fashion with Analysis of Variance (ANOVA) to select the best one. The model with the lowest Akaike Information Criterion (AIC), in combination with other statistical measures such as log likelihood and deviance, was chosen as the best representation of the data. For Model 1, AIC = 576.5, log likelihood = -281.3, and deviance = 562.5.

For Model 1, there is much higher variation associated with the residual error (variance = 58.7) than the random effect (variance = 0.9). This means there was little variation within plots; most of the error in the model is due to random noise.

Figures 14a-b show the relationship between pH_{NaF}, soil carbon, and predicted P-retention from our linear mixed-effect model for the whole soil profile (Model 1). To isolate the effect of one fixed effect at a time, we held one variable constant while varying the other across its range of values (Figure 14a-b).

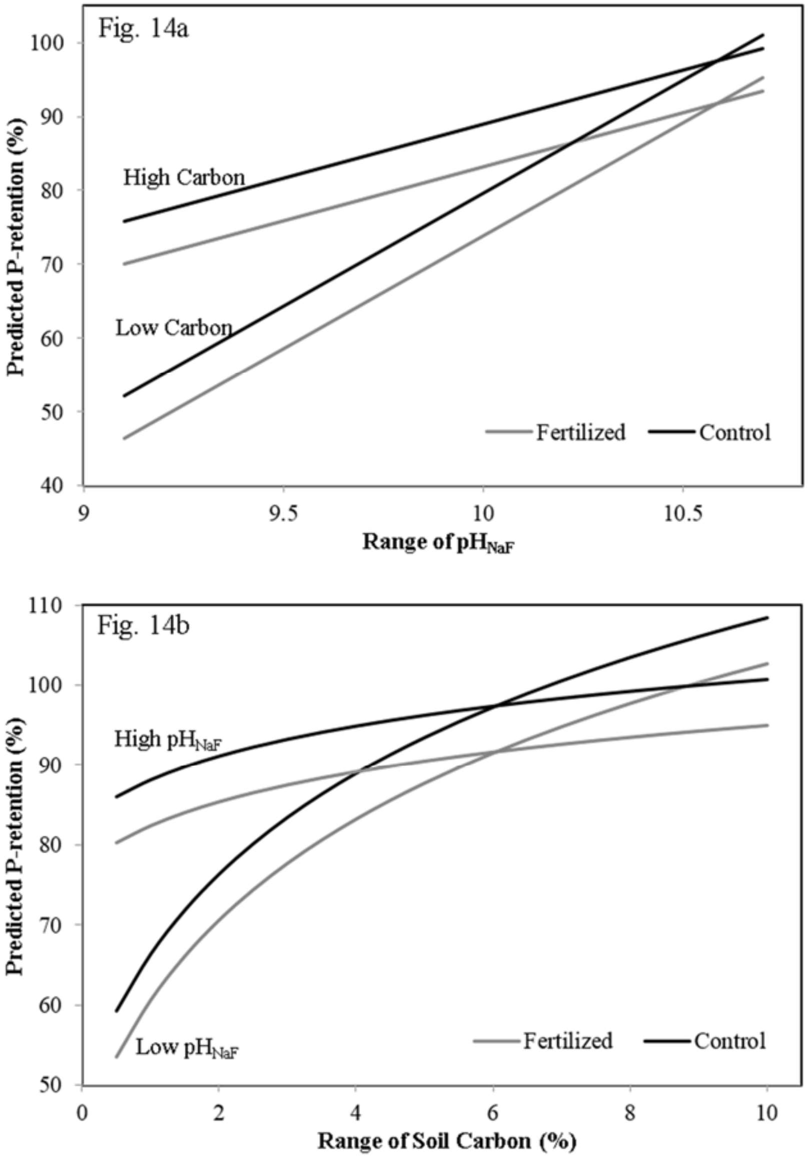

Figure 14. Predicted phosphorus retention based on two interacting fixed effects (pH$_{NaF}$ and soil carbon) from Model 1. Figure 14a focuses on the effect of pH$_{NaF}$ at high and low levels of soil carbon (0.44 and 2.3%, respectively). Figure 14b shows the effect of soil carbon at high and low levels of pH$_{NaF}$ (9.3 and 10.2, respectively). pH$_{NaF}$ values come from the laboratory method.

Figure 14a shows the range of pH_{NaF} values plotted against predicted P-retention, while holding soil C constant at a representative low and high values (corresponding to about the 25th and 75th percentile of the range of soil C). The reason for doing this was to show the interactive effects of soil C and pH_{NaF}. Interpreting Figure 14a, it is evident that at low pH_{NaF}, soil C has a larger influence on the predicted P-retention. Conversely, at high pH_{NaF} the soil C parameter affects P-retention less; if a soil has a high pH_{NaF}, no matter the C content, it is likely to have high P-retention. This interactive effect is illustrated by the divergent "Low C" and "High C" trends at low pH_{NaF} (left side of the figure), but convergent "Low C" and "High C" trends at high pH_{NaF} (right side of the figure).

Likewise, the interaction between C and pH_{NaF} can be observed in Figure 14b. Figure 14b shows the range of soil C values plotted against predicted P-retention, while holding pH_{NaF} constant at representative low and high values (corresponding to about the 25th and 75th percentile of the range of pH_{NaF}). The lines in Figure 14b are curved because soil C was log-transformed in Model 1. Interpreting Figure 14b, at low soil C pH_{NaF} has a larger influence on the predicted P-retention. At high soil C, however, the pH_{NaF} parameter is less influential; if a soil has high C content, no matter the pH_{NaF}, it is likely to have high P-retention. This is illustrated by the divergent "Low pH_{NaF}" and "High pHNaF" trends at low soil C (left side of the figure), but convergent "Low pH_{NaF}" and "High pHNaF" trends at high soil C (right side of the figure). At very high carbon contents (6-10%) Model 1 tends to overestimate P-retention, especially for fertilized soils.

Model 2, 0 to 30 cm: P-retention ~ pH_{NaF} + A (Redness) + Carbon + Treatment + Site + Treatment*Site + (1|Plot/Site)

Where "Treatment*Site" represents a statistical interaction between these factors and "1|Plot/Site" represents "Plot nested within Site" as a random effect. Model 2 uses grams of soil carbon per kilogram of soil, and it is *not* log-transformed as in Model 1.

This model had the lowest AIC, log likelihood, and deviance values of all models tried. For Model 2, AIC = 195.9, log likelihood = -89.0, and deviance = 177.9.

For Model 2, there is much higher variation associated with the residual error (variance = 16.23) than the random effect (variance = 4.85).

Figures 15a-c show the relationship between pH_{NaF}, soil redness (A), soil carbon and predicted P-retention from our linear mixed-effect model for the top 30 cm of soil (Model 2). To isolate the effect of one fixed effect at a time, held two variables constant at their average values while varying the other across its range of values (Figure 15a-c).

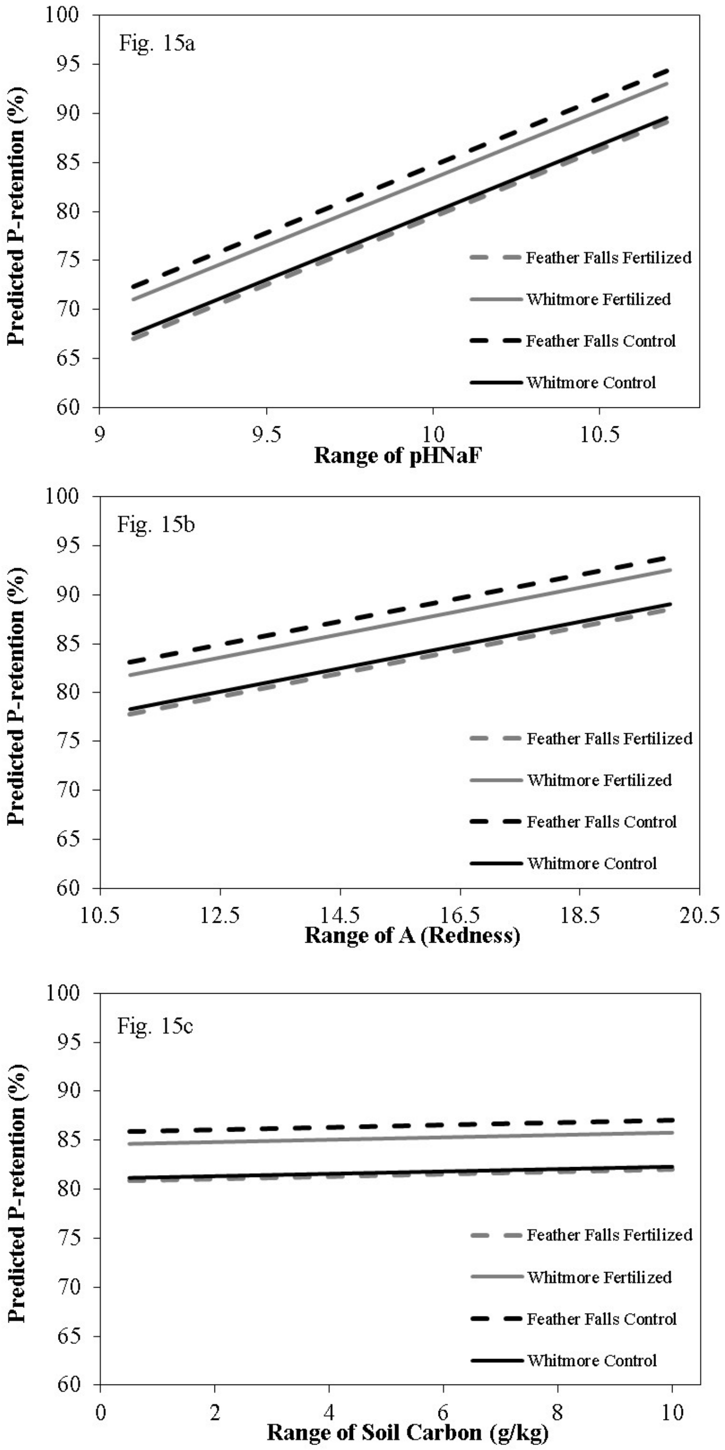

Figure 15. See page 45 for complete description.

Figure 15. Predicted phosphorus retention based on three fixed effects: pH_{NaF}, soil redness (A), and soil carbon (g/kg) from Model 2. Figure 15a focuses on the effect of pH_{NaF} while A (Redness) and soil C are held constant at their average values (A = 13.5, C = 1.7). Figure 15b shows the effect of soil redness (A) at average values of pH_{NaF} and soil C (pH_{NaF} = 10.1, C= 1.7). Figure 15c demonstrates the effect of soil C while redness (A) and pH_{NaF} are held constant at average values (pH_{NaF} = 10.1, A = 13.5). pH_{NaF} values come from the laboratory method.

From Figures 15a-c, it is clear that pH_{NaF} has the strongest effect on predicted P-retention (Figure15a) while soil carbon has the weakest (Figure 15c). All three variables (pH_{NaF}, A, C) are significant model parameters in a linear mixed effects model, but in the top 30 cm of soil they are non-interacting (Model 2, Appendix G).

DISCUSSION

Overview

The inclusion of two contrasting soils in this study has allowed us to build a model of P-retention which captures various properties of volcanic-derived forest soils. This is important, as similar parent materials can produce quite different soils over time. Acting as virtual end-members, the soil at the Whitmore site (Aiken soil series) provides insight into the role of SRO minerals (allophane, imogolite, gibbsite) in P-retention while the soil at the Feather Falls site (Powellton soil series) highlights the importance of organo-metal complexes (humus with various iron and aluminum oxides) to P-retention. The most important factors in P-retention prediction are SRO mineral content, soil carbon, soil iron, and depth. The laboratory method pH_{NaF} performed better than the field test pH_{NaF} as a predictor of P-retention; values from the laboratory method are used throughout the rest of this paper unless otherwise noted.

In these two soils, P-retention decreases strongly with depth, similar to findings by Barreal et al. (2001). Conspicuously, pH_{NaF} (indicator of SRO materials) and carbon (C) content follow a very similar pattern, often tracking site and treatment patterns of P-retention.

SRO - Carbon Interactions

Hypotheses about the mechanisms of P-retention predicted that SRO content would be the main driver of P-retention while soil carbon would have little effect. If this were true, Whitmore, with low organic matter and high SRO content should have greater P-retention than Feather Falls, with high organic matter and low SRO content. These predictions were made because amorphous materials are notorious for P- retention while soil organic matter (directly related to soil carbon) is generally thought not to cause P-retention on its own (Wild, 1950; Saunders 1965). In fact, organic matter may directly reduce soil P-retention by i) complexing with Fe and Al ions, preventing their reaction with [retention of] phosphate, ii) competing with P for exchange sites, or iii) solubilizing P from Ca/Fe/Al phosphates (Palm et al., 1997). However, findings from recent studies, as well as the results of this project, are beginning to uncover a more complex role played by soil organic compounds and P-retention (Guppy et al., 2005).

Our results indicate the highest P-retention occurs with highest carbon content. Feather Falls surface soils, with up to 9.9 % carbon (range 0.6-9.9%), have mean P-retention capacity over 90% (Figure 16). These same surface soils also had the highest pH_{NaF} values (9.7 to 10.7); X-ray diffraction readings (Appendix C) led us to believe Whitmore would have greater pH_{NaF} throughout due to comparatively less-crystalline minerals (thus higher surface area) than Feather Falls. In summary, while we expected high pH_{NaF} and P-retention at Whitmore, we found the highest pH_{NaF} and P-retention in surface soils at Feather Falls.

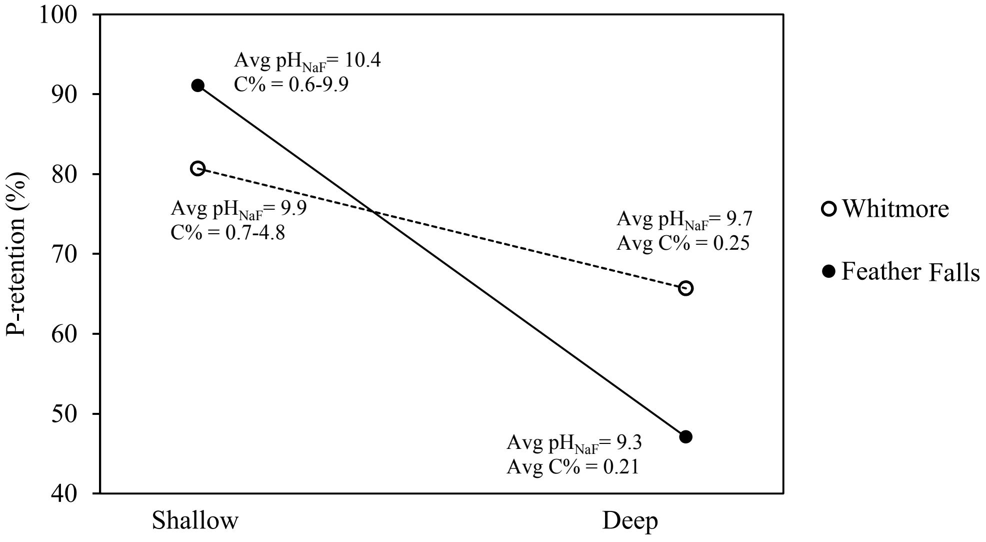

Figure 16. Summary of mean phosphorus retention, pH$_{NaF}$, and soil carbon (C%) at shallow (0 to 30 cm) and deep (either 150 to 160 or 170 to 180 cm) depths at Whitmore and Feather Falls sites. The straight lines are for visualization of difference between two points; P-retention and other soil characteristics did not drop linearly with depth (see Figures 5, 8, and 11). Laboratory-determined pH$_{NaF}$ is used here.

One possible explanation is a chemical interaction between SRO and organic materials. Allophane is known to react easily with humic acid (Imai et al.,1981), and considerable P-retention has been attributed to organo-metal (Fe, Al) complexes (Ahenkorah, 1968; *in allophanic soils specifically* Borie and Zunino, 1983; Barreal et al., 2001; Guppy et al., 2005). The significant statistical interaction between pH$_{NaF}$ and soil C indicates this may be happening in our study (Table 7). High P-retention in carbon-rich surface soils at Feather Falls is likely attributable to organo-metal complexes, while P-retention in carbon-poor surface soils at Whitmore probably reflect P-retention by SRO minerals.

Lower P-retention in deep horizons is attributable to lower amounts of SRO minerals, carbon, and organo-metal complexes.

Table 7. Correlation between pH_{NaF}, soil carbon and phosphorus retention. pH_{NaF}, soil carbon (g C per 100 g soil, %), and their interaction are all significant predictors of P-retention (Model 1, Appendix G. Laboratory-determined pH_{NaF} is used here.

	Correlation with P-retention
Soil Carbon	0.65
pH_{NaF}	0.79
Carbon x pH_{NaF} *interaction*	0.62

It should be noted that pH_{NaF} is a strong predictor of P-retention. So while hypotheses about the importance of SRO materials to P-retention were not wrong, they did not tell the whole story. Compounds released during decomposition of soil organic matter may each interact differently with soil phosphate (Guppy et al., 2005) and such compounds have complicated the story of P-retention at Feather Falls especially. Some organic-derived compounds reduce P-retention while others, especially those containing Fe and Al, actually fix phosphate themselves (Guppy et al., 2005).

Parent Materials

Another key difference playing a role in site-specific P-retention patterns here is parent materials. Feather Falls has a tephra cap of variable thickness across the site which is underlain by quartzite parent material. Whitmore is derived from a lahar parent material which is consistent throughout the profile. P-retention is significantly less in crystalline quartzite compared to poorly crystalline (SRO) volcanic materials. This explains the dramatic drop-off of P-retention with depth at Feather Falls, compared to the relatively gradual decrease in P-retention with depth at Whitmore.

Iron and P-retention

The relationship between P- retention and iron can be more closely examined in the top 30 cm of soil, where pyrophosphate-extractable Fe was measured. Amorphous iron compounds, such as imogolite and gibbsite, do not dissolve in pyrophosphate (Birkeland, 1999; Soil Survey Staff, 2014a). Therefore, pyrophosphate-extractable Fe represents a pool of Fe which is strongly correlated with, but theoretically distinct from, the SRO materials (Fe vs pH_{NaF}, $r = 0.80$). Though pyrophosphate-Fe is a significant predictor of P-retention by itself, the pyrophosphate-Fe*Carbon interaction is not significant. This could mean that Fe-oxides represent one distinct source of P- retention while organo-metal complexes involving SRO minerals represent another source of P- retention.

Effect of Fertilizer

Fertilized plots were expected to have significantly lower P-retention than unfertilized (control) plots. We hypothesized that heavy fertilization would saturate P-fixing soil exchange sites so that less and less P- retention would occur with each subsequent fertilization. Yet results indicate that fertilization did little to affect long-term P-retention except in Feather Falls surface soil (0 to 30 cm) where fertilized plots had about ten percent less P-retention than unfertilized plots. This pattern has led to a statistically significant interaction between treatment and site, meaning fertilization treatments did not affect both sites in the same way (with respect to P-retention).

What could this site-treatment interaction mean? Why do fertilized plots at Feather Falls exhibit lower P-retention, while fertilized and control plots at Whitmore do not differ (Figure 5)? In the Garden of Eden experiments, the idea was to provide trees with enough fertilizer to effectively rule out nutrient limitation. The drop in P-retention of fertilized Feather Falls surface horizons may be due to a) saturation of P-fixing exchange sites, b) fertilizer boosting organic matter, reducing P-retention via mechanisms from Palm et al. (1997; mechanisms listed on page 43 of this paper), or c) Type I error.

Fertilization boosted total C and N pools of the forest floor by 82% and 200% at Whitmore, 48% and 75% at Feather Falls respectively (McFarlane et al., 2009; Table 8); evidence that fertilized plots could have built up higher organic matter content, thereby decreasing P-retention. Mineral soil C and N pools, however, were not very responsive to fertilization treatment (McFarlane et al., 2009; Table 8). It is not clear whether fertilization's effects on C and N pools (reflecting organic matter content) caused P-retention to be lower in fertilized than control plots. The reason for this difference could simply be the large error associated with Feather Falls fertilized plots (see large whiskers of "FF" in Figure 5), resulting in a Type 1 error.

Table 8. Forest floor (organic horizon above mineral soil) and surface soil (0 to 15 cm) C:N ratios from McFarlane et al. (2009). Forest floor C:N ratios were taken from the text, surface soil ratios were estimated from a graph.

	C:N Ratio	
	Control	**Fertilized**
Whitmore Forest Floor	71	65
Feather Falls Forest Floor	65	54
Whitmore Surface Soil	31	28
Feather Falls Surface Soil	31	30

Beck et al. (1999) note that Al-humus complexes react more strongly with phosphate as the concentration of P in solution increases. Heavy fertilization at Feather Falls, where soil C concentration and pH_{NaF} are high, could have caused strong reactions between organo-metal complexes and phosphate, resulting in highly elevated P-retention. Though Whitmore soils received the same large addition of P, low organo-metal content (indicated by lower soil C concentration and pH_{NaF}) would have excluded these strong reactions. This could help explain why P-retention of fertilized and control plots was similar at Whitmore but different at Feather Falls.

Long-Term P-cycling

We measured P-retention on soils about 20 years after the last fertilization treatment. It would be valuable to investigate how fertilization affects P-retention in the short-term. Findings from Richter et al. (2006) point to a significant buffering capacity of soil where slowly cycling soil P (both organic and inorganic forms) provides trees with a steady P-supply over a timeframe of decades—the timeframe of this study. Slow release of soil P may further explain why fertilizer did not appear to affect long-term P-retention at Whitmore or below 30 cm at Feather Falls.

Whatever the mechanism, it is evident that some form of slow-release P-source is acting at Feather Falls, a very productive site which produced significantly more biomass than Whitmore (Powers and Reynolds, 1999; Wei et al., 2013; Table 9) despite having 10% higher mean P-retention in surface horizons (Table 7).

Table 9. Standing bole volume (m^3 / ha) of trees at age 10 years for Whitmore and Feather Falls sites, fertilized and control treatments. Different lowercase letters denote statistically differing means by Tukey's Honest Significant Difference test ($p<0.05$). Volumes are estimated from a figure in Powers and Reynolds, 1999.

	Bole volume at age 10 years (m^3 / ha)	
	Fertilized	**Control**
Whitmore	9 ^{a}	6 ^{a}
Feather Falls	58 ^{b}	33 ^{c}

Support for Model Parameters

Our findings are consistent with published studies on P-retention and related soil characteristics. D'Angelo et al. (2003) called oxalate-extractable Al and Fe strong predictors of soil P-requirements and found amorphous oxides of those elements to be primarily responsible for P-sorption in four soils of three soil orders (Alfisol, Ultisol, Entisol). Oxalate extracts allophane, imogolite, and Al-humus complexes (Birkeland, 1999). Gunal et al. (2008) found the quantitative color parameters L (Darkness) and A (Redness) to be adequate for predicting organic matter and red iron oxide content, especially when grouped by parent material; Liles et al. (2013) had similar success in northern California soils specifically. Depth is clearly an important variable with respect to P-retention. Grand and Lavkulich (2013) say that a good predictor for surface soils is not necessarily a good predictor for deeper horizons, since different parts of the soil profile are subject to different pedogenic processes. This is very applicable to the Feather Falls soil which has a lithologic discontinuity consisting of a tephra cap with higher P-retention over a quartzite parent material with low P-retention (see discussion on page 46). Ahenkorah (1968) described a good relationship between soil organic C and P-retention (r = 0.89) and between the C*Fe interaction and P-retention (r = 0.88). Singh and Gilkes (1981; and later Gilkes and Hughes, 1994) found a tight correlation between pH_{NaF} and P-retention, suggesting that it might be a quick predictor of P-retention.

pH_{NaF} and P-retention

The field test does not appear to be an adequate substitute for the laboratory method. The latter is a more accurate predictor of P-retention, though it requires more time and effort to perform. The field test could be improved to attain more accurate results by standardizing the materials used. For example, one tablespoon of soil and ten drops of indicator could be used each time, instead of haphazardly choosing any amount of soil and adding indicator until saturation, as is often done in a field setting. However, at this time we recommend the field pH_{NaF} test only be used for presence/absence indicator of SRO materials. If pH_{NaF} is found to be ≥9.4 in the field, we recommend performing the laboratory pH_{NaF} to make any inferences about degree of P-retention.

Available Soil Phosphorus

Results from Bray-P1 phosphorus readings show very low P-concentrations in Feather Falls and Whitmore soils, less than one part per million. The Bray-P1 method uses an acidic solution to simulate the pH of root exudates. Other researchers have found similar phosphorus concentrations in Whitmore, Feather Falls, and similar soils. Powers and Reynolds (1999) reported 1.88 mg/kg bicarbonate-soluble P (a pool of readily bioavailable soil P) for Feather Falls and 1.12 mg/kg for Whitmore. The method used by Powers and Reynolds employed a bicarbonate extractant with near-neutral pH, while the Bray-P1 extracting solution was much more acidic (pH 2.6). Palmer et al. (2005) most commonly found 3 to 6 ppm by the Bray-P2 Method (which uses a stronger extractant than Bray-P1) for a similar soil.

Surface soil samples (0 to 30 cm) were sent to a professional soil laboratory for confirmation of phosphorus and other tests of soil nutritional status (Appendix H). Bray-P was reported as 1 ppm for Whitmore Control, Feather Falls Control, and Feather Falls Fertilized. Whitmore Fertilized had 3 ppm phosphorus.

The concentration of readily available phosphate in Whitmore and Feather Falls is very low, below the threshold considered adequate for plant nutrition. Critical values are 12 ppm for seedling establishment (Palmer et al., 2005) and 25 to 30 ppm for optimal plant growth (Pierzynski, 2000).

Management Perspectives

Although no single in-the-field measurement provided a precise determination of soil P-retention, the basic models we generated using commonly measured soil characteristics provides a starting point to develop a better understanding of P-retention in volcanic-derived forest soils. The overlap between Pacific Northwest timber regions and the range of volcanic-derived soils with potentially high P-retention (Appendix A), along with projected increase in price / decrease in availability of inorganic phosphate fertilizer in the coming decades (Cordell et al., 2009) constitute a need for our models. To validate and improve these models, other long-term forest research projects should incorporate P-retention/availability (and its response to management) into the experiments. Further development of these models could lead to recommendation of fertilizer application rates. For now, the models act as proof-of-concept that P-retention can be predicted based on related soil characteristics, particularly by pH_{NaF} and soil carbon.

The results of this research also have applications to mapping and classification of volcanic soils. Phosphorus retention ≥ 85% (or ≥ 25%, depending on other soil properties) is a diagnostic andic soil property (Soil Survey Staff, 2014b). But forest soils with andic soil properties still grow trees; it is unclear to what magnitude P-retention actually affects tree growth and timber production. In our study, the soil with the surface soil P-retention ~90% produced significantly more tree biomass than the site with ~80% surface P-retention (Table 6).

Research has showed that slowly cycling P can provide nutrients to trees over decades (Richter et al., 2006). But the effect of P-retention on annual and perennial crops, where significant phosphate in/outputs occur every year, is probably more pronounced than for timber. Soil disturbance such as tillage can break up established mycorrhizal mycelia, which must then re-grow in order to recover their ability to provide P to the next round of crops. Such disturbance delays mycorrhizal colonization of roots (therefore delaying the benefits of augmented P-uptake to the next crop), though the magnitude of effects of disturbance on mycorrhizae are inconsistent (Brundrett, 1991; McGonigle and Miller, 2000; Garcia et al., 2007).

Schachtman et al. (1998) note that even in fertilized agricultural soils crops may recover only a small amount of applied P, as ≥ 80% of may be subject to P-retention. If this is true, farmers who fertilize every year are paying the price of P-inefficiency in their annual budgets (as 80% of applied P may not go to crops). Forest managers, on the other hand, generally apply fertilizer only once or twice per rotation, meanwhile leaving long periods of time without soil disturbance during which mycorrhizal associations can develop. The mycorrhizae (or other slow-cycling mechanism) may then recover some of the phosphate fixed by soil at the time of fertilization. In this way, fertilization of P-retaining forest soils may be more efficient than yearly fertilization of agricultural soils.

Soils with the capacity for high P-retention occur in the Pacific Northwest and southeastern United States, as well as internationally in northern South America, sub-Saharan Africa, south and southeast Asia (Batjes, 2011). No doubt a significant portion of crops come from these widespread areas. It may be more important to distinguish between significantly P-retaining and non-P-retaining soils in these areas than forestland.

Further Study

A powerful addition to this research would be separating out the effect of carbon and organo-metal complexes on phosphorus retention. Measuring P-retention before and after loss-on-ignition carbon removal could be an easy way to begin on the archived soil samples at Humboldt State University.

Another part of this story is the role of mycorrhizal fungi-plant symbioses. Roots colonized by mycorrhizae may have 300-500% higher P-influx than uncolonized roots (Smith and Read, 1997; Schachtman et al., 1998). These specialized fungi can release P from mineral and organic soil phosphorus sources, thereby partially counteracting P-retention. Most tree species in temperate forest ecosystems form these symbioses (Duĉić et al., 2009). Ponderosa pine, growing in the Sierra Nevada foothills at our study sites, formed symbioses with ectomycorrhizal fungi *Rhizopogon occidentalis* and *Suillus grandulcatus* in a Sierra Nevada forest stand (Walker et al., 2010). Although the role of mycorrhizae at these sites has not been investigated, it is likely an important agent regulating P-uptake.

Further, P-retention models could be improved by using *non-linear* mixed effects models. These data were challenging to model due to substantial nonlinear patterns with depth and complex interacting factors.

Conclusions

By building on extensive past research, this effort has succeeded in building models of phosphorus retention in volcanic-derived soils of the Pacific Northwest, U.S. Variables used to predict P-retention such as pH_{NaF}, soil carbon and iron are supported by the literature. The statistically powerful experimental design has allowed for a repeatable approach to future research, which will be necessary to validate and improve the models. Currently, the models are intended to be used for predicting degree of phosphorus retention and to help decide whether fertilization will be a profitable investment.

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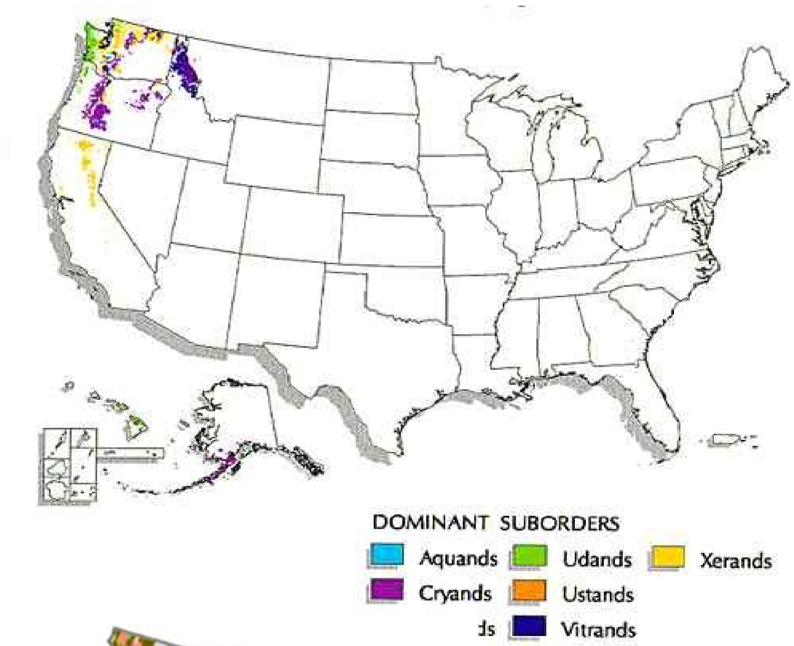
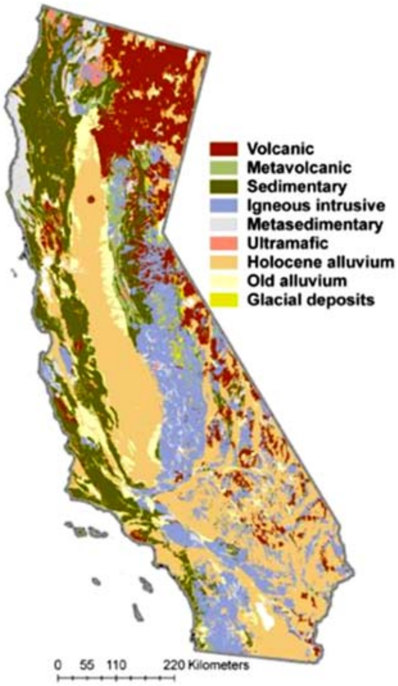
Appendix A. Distribution of Andisols in the United States and volcanic parent materials in California, U.S. Volcanic-derived soils, notorious for high P-retention, are common in timber regions of the Pacific Northwest.



Appendix A Figure 1. Distribution of Andisols, soils dominated by special properties of volcanic parent materials, in the U.S (Soil Survey Staff, Andisols Map).

www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/ class/maps



Appendix A Figure 2. Distribution of parent materials in California, U.S.A. Volcanic parent materials are shown in red (O’Geen and Arroues, 2015).

Note: The extent of Andisols and Volcanic Parent Materials in California do not completely overlap because some soils formed on volcanic surfaces have weathered enough so that andic soil properties no longer dominate. This is the case for soils at the Whitmore and Feather Falls sites, which are derived from volcanic materials but classify as Ultisols, not Andisols.

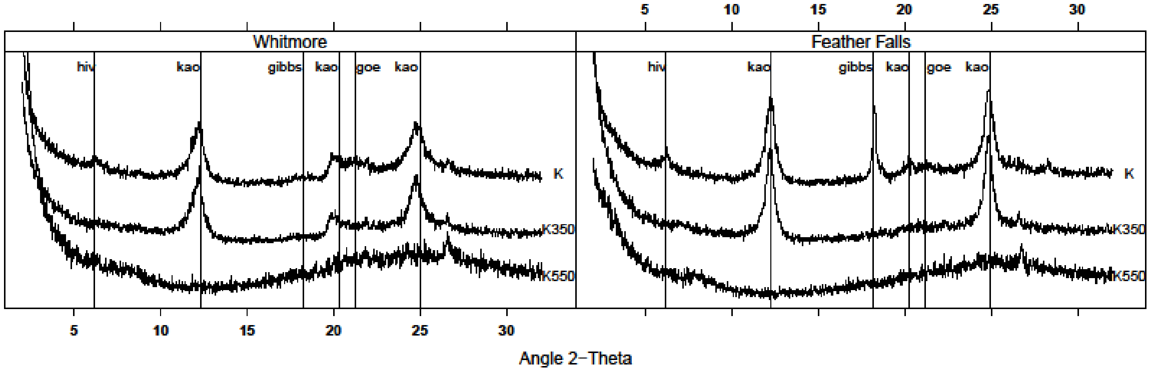
http://californiarangeland.ucdavis.edu/Soils/

Appendix B. Summary of U.S. Forest Service long-term forest productivity "Garden of Eden" experiment

This study builds on the long-term Garden of Eden experiment implemented by USFS scientist Robert Powers beginning in 1985 (Powers and Ferrell, 1996). In the Garden of Eden experiments, factorial combinations of common silvicultural practices (fertilizer, weed control, and insecticide) were implemented across a range of sites in northern California. Insecticide had no effect at any Garden of Eden site. Effects of other treatments on ponderosa pine productivity were found to be additive and to vary with site quality (Powers and Ferrell, 1996). Trees at droughty, infertile sites (i.e. Whitmore) benefitted primarily from weed control and secondarily from fertilizer treatments. Productivity at the most fertile sites (i.e. Feather Falls) responded only to weedy vegetation control. Removal of strong weed competitors from the understory increased tree access to moisture and nutrients, though moisture ultimately imposed the limit to growth on all sites (Powers and Reynolds, 1999). It is noted that Aiken soil at the Whitmore site is notorious for its high P-retention by "oxides of polyvalent cations" (Ulrich et al., 1947). Nothing is explicitly said about P-retention capacity of Powellton soil (Feather Falls site).

Liles (2013) continued the study of soils from two Garden of Eden sites (Whitmore and Feather Falls), as have others (most recently, McFarlane et al., 2009 and Wei et al., 2013). Now, almost thirty years after the Garden of Eden experiment's inception, an opportunity to expand the scope of this research by including phosphorus analysis has presented itself, resulting in this thesis project.

Appendix C. X-Ray Diffraction mineralogical assessment of Whitmore and Feather Falls soils (Liles, 2013). Higher, more pronounced peaks at Feather Falls indicate presence of identifiable, crystalline minerals. Lower, more rounded peaks at Whitmore indicate that hard-to-identify amorphous (short range order) compounds predominate. X-Ray Diffraction analysis provides evidence for claims about crystallinity/SRO content throughout this paper.

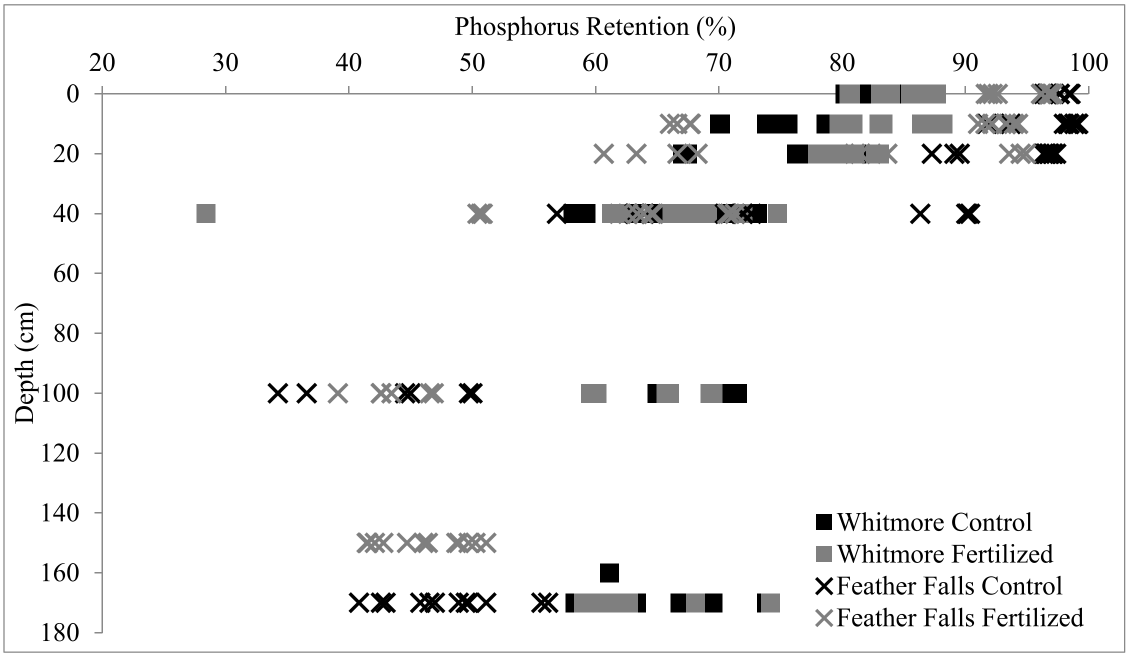


Appendix D. Location of study sites Whitmore and Feather Falls in northern California, U.S.

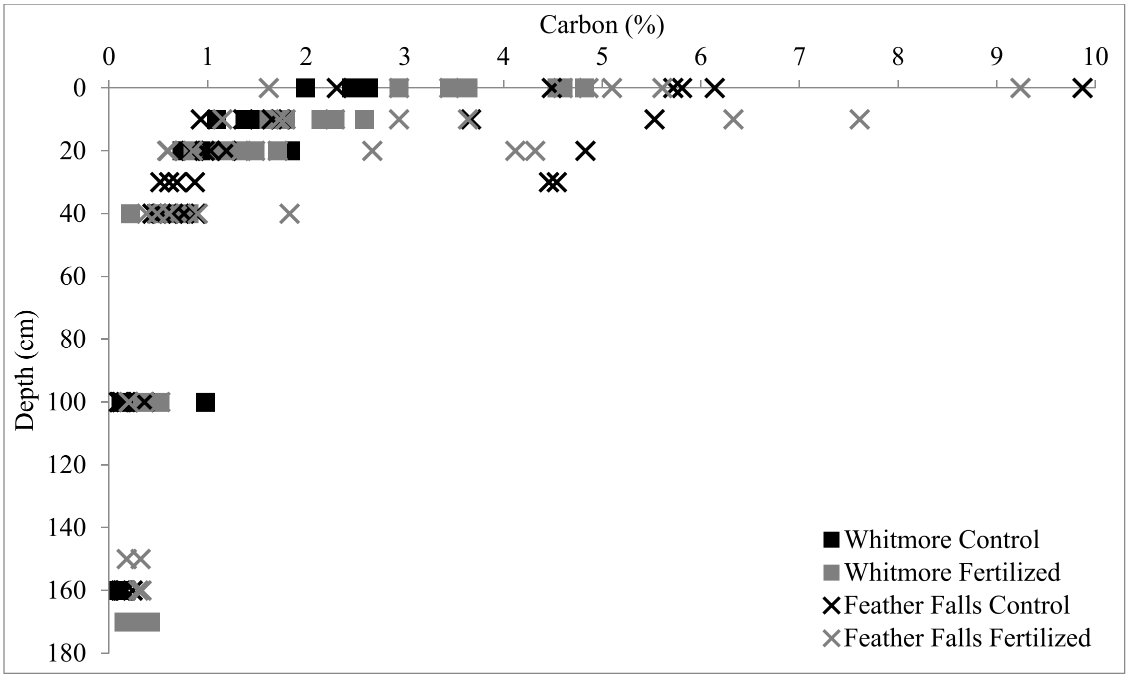
Source: Esri, DigitalGlobe, GeoEye, i-cubed, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community, Esri, HERE, DeLorme, TomTom, MapmyIndia, © OpenStreetMap contributors, and the GIS user community

Feather Falls	39° 37’ 10.15” N	121° 11’ 46.43” W
Whitmore	40° 37’ 32.44” N	121° 53’ 55.90” W

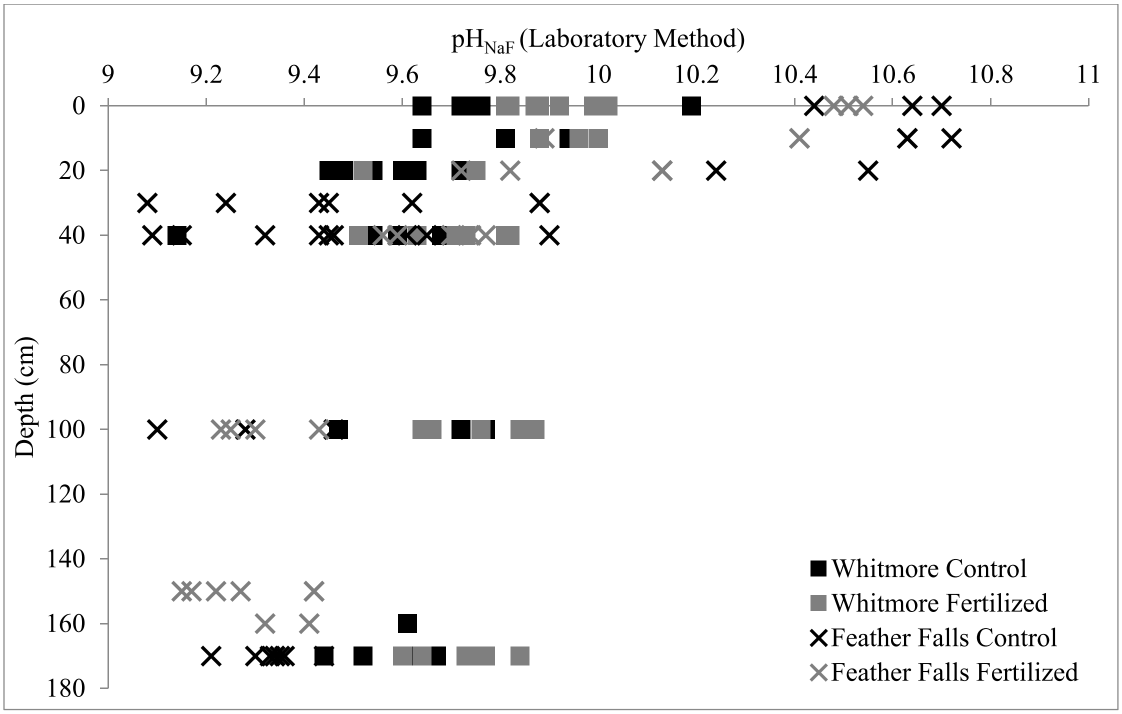
Appendix E. Distribution of depth-function data for phosphorus retention, soil carbon, and $\mathrm{pH_{NaF}}$ (laboratory method).



Appendix E Figure 1. Whitmore Control n = 62, Whitmore Fertilized n = 65, Feather Falls Control n = 65, Feather Falls Fertilized n = 64.



Appendix E Figure 2. Whitmore Control n = 27, Whitmore Fertilized n = 36, Feather Falls Control n = 40, and Feather Falls Fertilized n = 37.



Appendix E Figure 3. Whitmore Control n = 35, Whitmore Fertilized n = 35, Feather Falls Control n = 36, Feather Falls Fertilized n = 26.

Appendix F. Sample sizes for summaries of phosphorus retention at various levels of resolution.

Sample sizes (n) for Table 5.

	Surface	**Medium**	**Deep**
Whitmore	69	24	23
Feather Falls	69	24	24

Sample sizes (n) for Figure 5

	Control	**Fertilized**
Whitmore	34	35
Feather Falls	35	34

Sample sizes (n) for Figure 6

	Surface	**Medium**	**Deep**
Whitmore Control	34	12	11
Whitmore Fertilized	35	12	12
Feather Falls Control	35	12	12
Feather Falls Fertilized	34	12	12

Appendix G. Parameter estimates for two mixed-effects models of phosphorus retention.

Model 1 predicts phosphorus retention for the entire soil profile. Model 2 predicts phosphorus retention for the top 40 cm of soil. In both models, pH_{NaF} values from the laboratory method are used. The symbol "*" represents a statistical interaction.

Model 1 Fixed Effects

	Estimate	**Standard Error**	**t-value**	**p-value**
Intercept	-299.93	46.23	-6.49	< 0.001
pH_{NaF} ǂ	37.55	4.49	7.85	< 0.001
Log (Soil Carbon + 1)	203.47	44.49	4.57	< 0.001
$Treatment_{Fertilized}$	-5.72	1.85	-3.10	0.002
*pH_{NaF} * Log (Soil Carbon + 1)* ǂ	-19.23	4.46	-4.31	< 0.001

ǂ pH_{NaF} values come from laboratory method

Model 1 Random Effects

	Variance	**Standard Deviation**
Plot within Site (Intercept)	0.86	0.93
Residual	58.71	7.66

Model 2 Fixed Effects

	Estimate	**Standard Error**	**t-value**	**p-value**
Intercept	-69.19	53.44	-1.30	0.19
pH_{NaF} ǂ	13.76	4.41	3.12	< 0.01
A (Redness)	1.19	1.06	1.12	0.19
Carbon (g C / kg soil)	0.12	0.06	1.94	0.01
$Site_{Whitmore}$	-4.75	4.03	-1.18	0.14
$Treatment_{Fertilized}$	-5.03	3.02	-1.67	0.03
$Treatment_{Fertilized}$ * $Site_{Whitmore}$	8.51	4.47	2.04	0.01

ǂ pH_{NaF} values come from laboratory method

Model 2 Random Effects

	Variance	**Standard Deviation**
Plot within Site (Intercept)	4.85	2.20
Residual	16.23	4.03

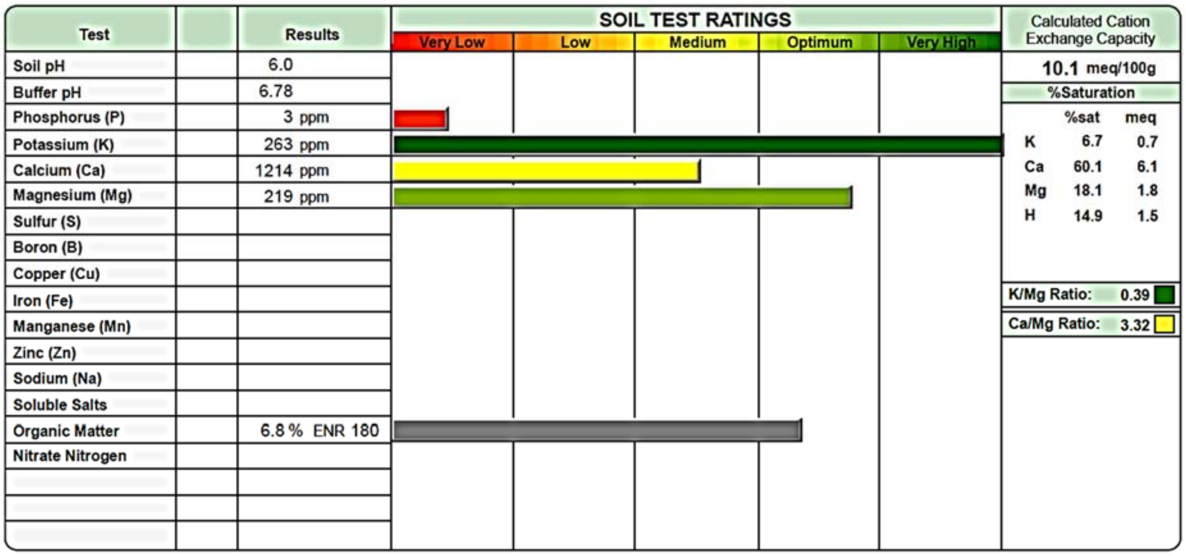
Summary of model parameters

	Minimum	**Maximum**	**Median**	**Mean**
Depth	0	170	30	--
Soil Carbon (%)	0.10	9.87	0.92	1.74
pH_{NaF} ǂ	9.08	10.72	9.68	9.71
A (Redness)	11.33	20.08	14.79	14.74
Carbon (g C / kg soil)	7.50	80.00	22.00	29.01

ǂ pH_{NaF} values come from laboratory method

Appendix H. Professional soil analysis results. Results are for a composite sample of 0 to 30 cm depth from each of four groups: Whitmore Fertilized, Whitmore Control, Feather Falls Fertilized, and Feather Falls Control.

Whitmore Fertilized



SOIL TEST RATINGS

Very Low | Low | Medium | Optimum | Very High

Test		Results
Soil pH		6.0
Buffer pH		6.78
Phosphorus (P)		3 ppm
Potassium (K)		263 ppm
Calcium (Ca)		1214 ppm
Magnesium (Mg)		219 ppm
Sulfur (S)		
Boron (B)		
Copper (Cu)		
Iron (Fe)		
Manganese (Mn)		
Zinc (Zn)		
Sodium (Na)		
Soluble Salts		
Organic Matter		6.8 % ENR 180
Nitrate Nitrogen		

Calculated Cation Exchange Capacity

10.1 meq/100g

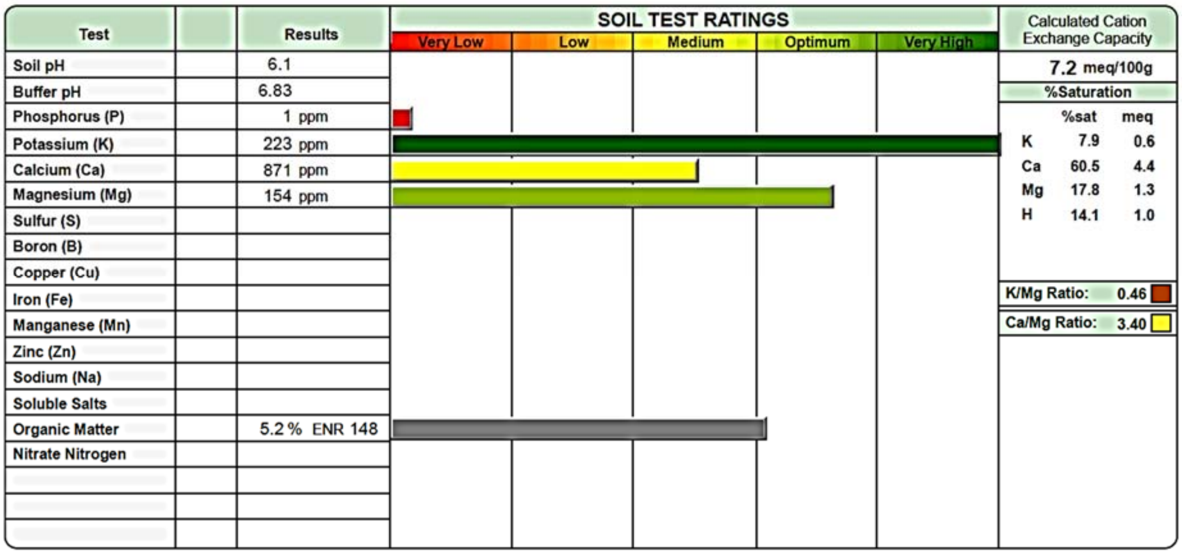
%Saturation

	%sat	meq
K	6.7	0.7
Ca	60.1	6.1
Mg	18.1	1.8
H	14.9	1.5

K/Mg Ratio: 0.39 🟩

Ca/Mg Ratio: 3.32 🟨

Whitmore Control



SOIL TEST RATINGS

Very Low | Low | Medium | Optimum | Very High

Test		Results
Soil pH		6.1
Buffer pH		6.83
Phosphorus (P)		1 ppm
Potassium (K)		223 ppm
Calcium (Ca)		871 ppm
Magnesium (Mg)		154 ppm
Sulfur (S)		
Boron (B)		
Copper (Cu)		
Iron (Fe)		
Manganese (Mn)		
Zinc (Zn)		
Sodium (Na)		
Soluble Salts		
Organic Matter		5.2 % ENR 148
Nitrate Nitrogen		

Calculated Cation Exchange Capacity

7.2 meq/100g

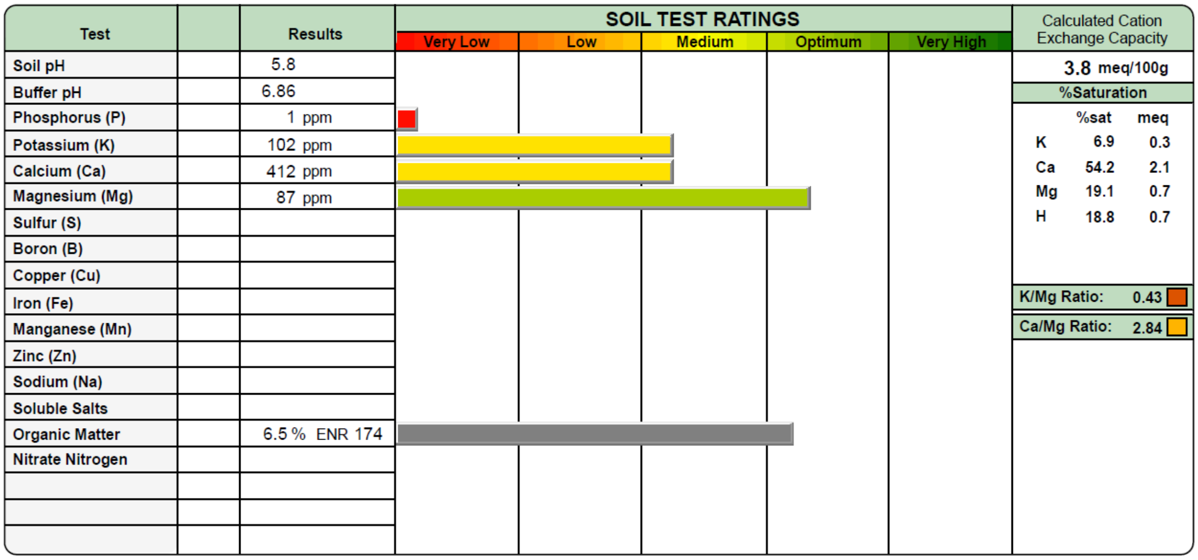
%Saturation

	%sat	meq
K	7.9	0.6
Ca	60.5	4.4
Mg	17.8	1.3
H	14.1	1.0

K/Mg Ratio: 0.46 🟥

Ca/Mg Ratio: 3.40 🟨

Feather Falls Fertilized



Test		Results
Soil pH		5.8
Buffer pH		6.86
Phosphorus (P)		1 ppm
Potassium (K)		102 ppm
Calcium (Ca)		412 ppm
Magnesium (Mg)		87 ppm
Sulfur (S)		
Boron (B)		
Copper (Cu)		
Iron (Fe)		
Manganese (Mn)		
Zinc (Zn)		
Sodium (Na)		
Soluble Salts		
Organic Matter		6.5 % ENR 174
Nitrate Nitrogen		

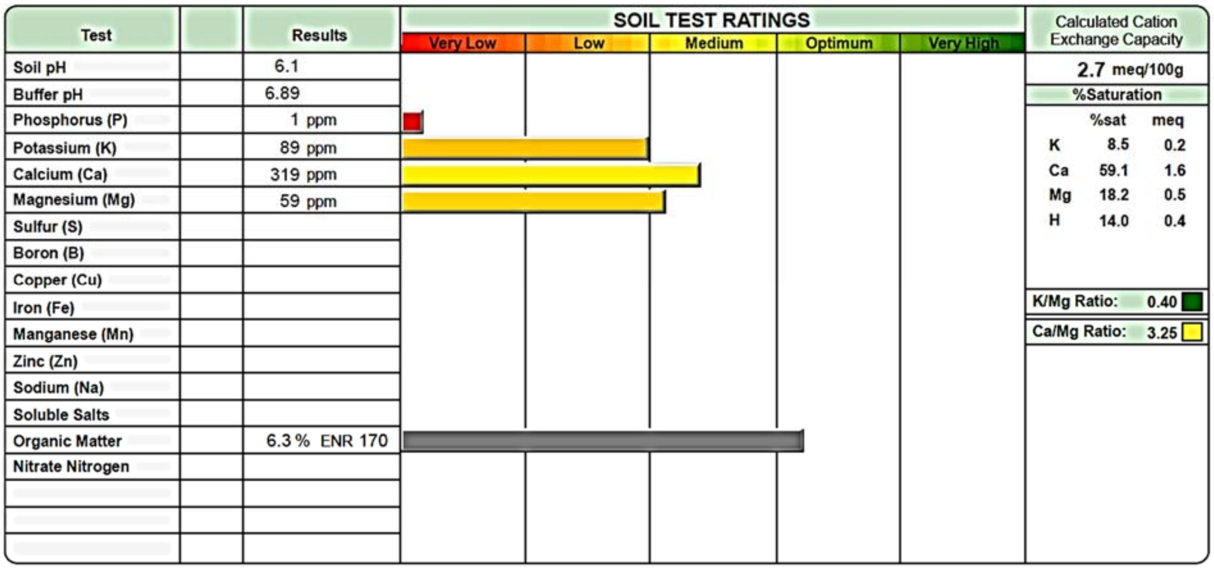
Calculated Cation Exchange Capacity
3.8 meq/100g

%Saturation

	%sat	meq
K	6.9	0.3
Ca	54.2	2.1
Mg	19.1	0.7
H	18.8	0.7

K/Mg Ratio: 0.43 🟧
Ca/Mg Ratio: 2.84 🟨

Feather Falls Control



Test		Results
Soil pH		6.1
Buffer pH		6.89
Phosphorus (P)		1 ppm
Potassium (K)		89 ppm
Calcium (Ca)		319 ppm
Magnesium (Mg)		59 ppm
Sulfur (S)		
Boron (B)		
Copper (Cu)		
Iron (Fe)		
Manganese (Mn)		
Zinc (Zn)		
Sodium (Na)		
Soluble Salts		
Organic Matter		6.3 % ENR 170
Nitrate Nitrogen		

Calculated Cation Exchange Capacity
2.7 meq/100g

%Saturation

	%sat	meq
K	8.5	0.2
Ca	59.1	1.6
Mg	18.2	0.5
H	14.0	0.4

K/Mg Ratio: 0.40 🟩
Ca/Mg Ratio: 3.25 🟨

Soil analysis by A&L Heartland Laboratories, Inc.

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