Topographic influence on phosphorus forms after 30 years of soil development

on a Mount St. Helens pyroclastic flow

by

Melissa M. Knudson

Abstract

In terrestrial ecosystems, nitrogen (N) and phosphorus (P) are two essential elements influencing primary production. Both N and P are essential nutrients used for synthesis of protein and nucleic acids in all organisms. However, P differs from N in that it has no gaseous input that continuously contributes to its availability in soils. In contrast to N, nearly all P present in terrestrial ecosystems is derived from the weathering of the primary mineral apatite whose supply is initially fixed and can only decrease over time. Walker and Syers (1976) have proposed a conceptual model of P dynamics in an ecosystem based on such a fixed supply. Their model predicts that as P is released from weathering it is stored in plant and bioavailable soil pools, before it is made locally unavailable through occlusion or lost from the system by leaching. Although considerable work has been done investigating this model in very old or humid systems (Vitousek et al. 1993, Crews et al. 1995, Vitousek and Farrington 1997, Hedin et al. 2003, Turner et al. 2007) and little empirical work exists for arid and semi-arid ecosystems (Carreira et al. 1997, Selmants and Hart 2010) to the best of our knowledge, no work exists examining this model in very young temperate systems. The young soils developing near Mount St. Helens, Washington provide a rare opportunity to examine the Walker and Syers (1976) model and other P dynamics such as accumulation and availability more closely as P dynamics in very young, temperate systems remains poorly understood. This study investigates effects of topography and soil development on bioavailable and total P by examining soils from depressions and surrounding uplands and relates these results to historical data in an attempt to reveal how relative P amounts and forms have changed in these topographic sites since the 1980 eruption. Our results indicate a potentially significant relationship between topography and total and available P and support the theoretical model proposed by Walker and Syers (1976) that total

P in this developing temperate system decreases with time due to varying combinations of weathering, uptake and occlusion.

Introduction

The catastrophic lateral blast of the May 18th, 1980 eruption of Mount St Helens devastated more than 500-km^2 of forestlands a portion of which was completely sterilized by pyroclastic flows that effectively removed all biological components (Franklin et al., 1988). Pyroclastic flows are hot, often incandescent mixtures of volcanic fragments and gases that sweep along close to the ground often reaching extremely high temperatures and velocities (Tilling et al., 1990). This catastrophic eruption formed at least 17 separate pyroclastic flows creating 60 square km region of primary successional habitat are now in the earliest stage of ecosystem recovery (Fagan et al. 2004).

Research for this study and the historical data referenced was conducted on the Spirit Lake Pyroclastic Flow (SLPF). The topography of this site following the eruption was described as having a fan-like pattern of overlapping sheets, tongues, and lobes (Tilling et al. 1990) creating a heterogeneous and patchy landscape that persists today. The soils developing on the SLPF are in the very earliest stages of soil formation and have been subject to continuous weathering, shifting topography, and changes in vegetation since the 1980 eruption resulting in a landscape dotted with depressed areas of deposition and moisture accumulation bordered by small arid upland ridges of slightly higher elevation. The distinctive topography created by the SLPF provides a unique opportunity for scientists to study the role topography plays in the early stages of soil development and its influence P dynamics during primary succession.

Soil is a dynamic system and its development is often expressed in terms of soil forming factors including: climate (cl), relief or topography (r), organisms (o), parent material (p), and

time (t) (Jenny, 1941). This approach allows researchers to assemble soil data numerically using the state-factor equation (1), where $s = f(cl, o, r, p, t...)$ (Jenny, 1941). This equation implies that soil is the result of parent material being acted on by climate and organisms, all influenced by topography, over time (Nuhn 1987). It should be noted that while this equation suggests the relationship between soil-forming factors and soil properties is causal, this is not the case as every soil property may be considered both a cause and an effect (Jenny, 1941). Essentially, the soil-forming factors described by Jenny (1941) control the state of the system, which in turn, influences but are not the cause of soil development (Jenny 1958).

In order to conduct a thorough examination of the role one state factor plays in soil development, all others must be kept constant. For example, the soil-topography relationship can only be accurately discussed if comparisons are restricted to soils of similar origin, climate, biotic assemblages, etc. The soils forming on the SLPF fit these criteria as the 1980 eruption of Mount St. Helens effectively reset soil development creating a potentially ideal system for examining the effect of topography on P dynamics and soil development in a very young system.

Phosphorus (P) is unique among the major elements present in soil organic matter in that it lacks a significant gaseous component and so must be supplied almost entirely by the weathering of parent material (Walker and Syers, 1976). Unlike other major soil elements such as carbon, nitrogen, and sulphur, P is cycled mainly on a geologic timescale and is not cycled through the atmosphere (Walker and Syers 1976). As described by Walker and Syers (1976) the general pattern of P availability at the onset of soil development consists of high rates of weathering and high amounts of total P at the onset of primary succession giving way to increasing occlusion and a decrease on total P over time (fig 1). The Walker and Syers (1976) model of P availability over time can be further refined by dividing P cycles into biological or

geochemical components (Olander and Vitousek 2004). However, these cycles are not mutually exclusive and in fact, interact in a number of ways. Phosphorus traveling in the geochemical cycle is released from apatite and initially held in bioavailable (non-occluded) form. This bioavailable P can either enter the biological cycle through uptake or immobilization or it can remain in the geochemical cycle through occlusion (Schlesinger, 1997). Occlusion can occur when available P is not taken up by biota and slowly becomes surrounded by secondary minerals and is no longer available to biota on a biologic timescale (Schelsinger, 1997). This pattern of weathering, P release, and movement between biological and geochemical cycles essentially controls how much P is available for uptake by biota and how much is geochemically retained in the soil (Olander and Vitousek 2004).
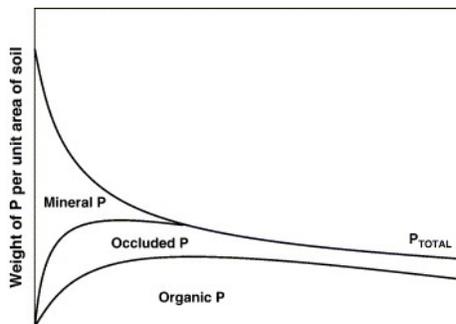

Fig. 1 Walker and Syers (1976) conceptual model of P evolution over time

The soils developing on the SLPF are in the very earliest stages of soil formation and are therefore experiencing rapid rates of change and development (Schlesinger et al. 1998). While these young soils are low in bioavailable P (Bishop et al. 2010), appreciable amounts of P bound with calcium in the form of mineral apatite are present (Nuhn, 1987). Therefore, we expect that since depressions are areas of deposition and moisture accumulation, these areas will have more bioavailable P than the surrounding uplands, which are areas of moisture runoff and thus lower moisture accumulation. Additionally, we expect that available P weathered out of apatite but not

5

taken up by plants or immobilized by soil organisms will become occluded by other soil

minerals, such as aluminum (Al) or iron (Fe) oxides rendering them essentially unavailable to

biota (Crews et al. 1995). Since the soils developing on the SLPF have experienced constant

weathering since the 1980 eruption we hypothesize there will less total P present in the upper 15

cm of the soil profile today than was present shortly after the eruption.

Our objective was to investigate the significance of topography and time on P dynamics

by analyzing soils from depressions and the surrounding uplands for total and available P and

relating these results to historical data. In doing so, we intend to elucidate how topographic

characteristics such as elevation, relief, and moisture accumulation interact to influence the rate

of availability and loss of soil P over time. The results of this study will contribute to a better

understanding of P dynamics and ecosystem recovery in very young disturbed systems, an area

of research that remains poorly understood.

Methods

Site Description
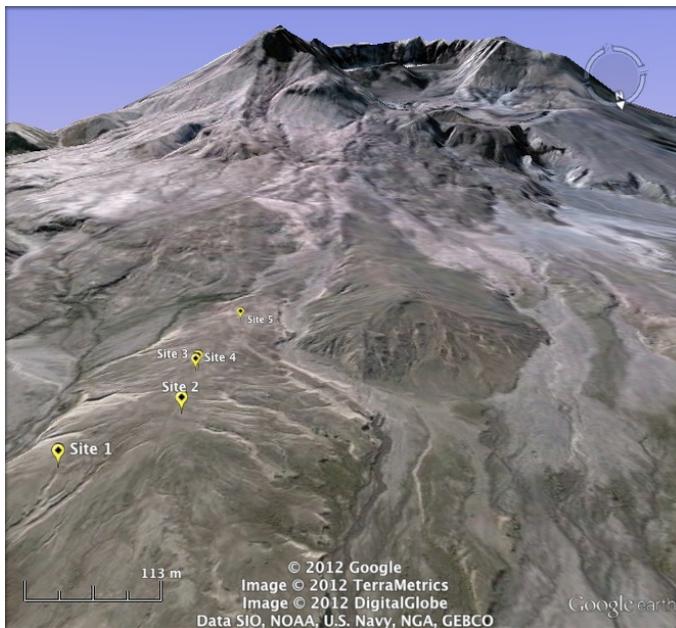
This research and the historical data referenced were conducted on the Spirit Lake Pyroclasitic Flow (N 46 degrees 14.8' W 122 degrees 9.9'). Soil samples were collected in July 2012 from five depression sites on the SLPF with depression sites defined as areas of deposition bordered by small upland ridges of slightly higher elevation. This type of topography can be thought of in terms of knobs (uplands) and basins (depressions) where uplands are areas of local aridity and depressions are areas of local humidity (Jenny 1941). This distinction between upland and depression moisture regimes arises from the assumption that the amount of moisture experienced by a flat parcel of land is considered "normal" for the region (Ellis as cited in Jenny 1941). Therefore, uplands are considered areas of local aridity because they essentially experience less moisture than what is "normal" for the region due to runoff. In contrast to uplands, depressions are areas of local humidity because, due to lower elevation and moisture accumulation, they experience more moisture than normal.
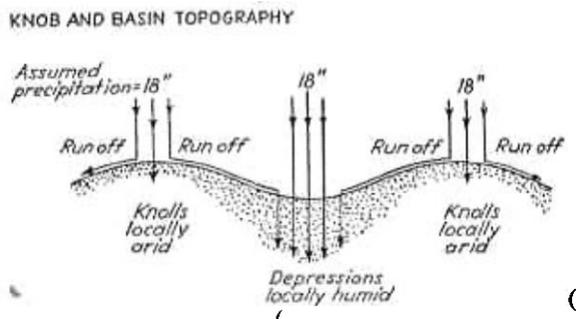
Depression and upland topography Jenny (1941)

Sample collection

Sample plots consisted of depressed zones of deposition surrounded by upland ridges of slightly higher elevation. The total area of each sample plot varied from $81m^2$ to $225m^2$. Within each plot, three subsamples were collected from three upland regions and three depositional regions

7

from two depths, 0-5 cm (surface) and 5-15 cm (subsurface), for a total of 60 samples (5 sample sites x 6 subsamples x 2 depths = 60 total samples). Samples were placed into plastic bags and kept cool for transport back to the lab.

Sample preparation and analysis

In the lab, samples were dried at 65 degrees C with three days of collection and passed through a 2-mm sieve (Soil Survey Investigations Report (SSIR) 2004). Both fractions were weighed in order calculate the percent >2-mm. Water content was obtained by weighing samples prior to and after oven drying. Soil pH was measured 1:1 in distilled water, 1:2 in 0.01 M $CaCl_2$ (pH_{H2O}, pH_{CaCl2}) using an Oakton pH meter with a glass electrode (SSIR 2004).

Available P was determined using the Olsen method (SSIR 2004). For Olsen available P, 1.0 g of soil (two replicates) was shaken with 20 mL of 0.5 M $NaHCO_3$ (pH 8.5) for 30 min. at 24 degrees C and 250 orbits min^{-1}. Extracts were filtered using a Whatman no.42 filter paper then stored at 4 degrees C and analyzed within 72 hours (Soil Survey Staff, 2004). Extracts were analyzed for P on a nutrient analyzer SmartChem 200 (Westco Scientific Instruments Inc, Brookfield, CT) using SmartChem 200 method 420-365. Results are expressed on an oven-dry (65 degree C) soil basis.

Samples for total P analysis were ground to between 0.15 – 0.18 mm on a Pica Blender Mill (Cianflone Scientific Instruments Corp, Pittsburg, PA). Total P was determined using a modified Kjeldahl digest method (Turner and Vitousek n.d.) where ~150 mg of finely ground soil was digested with 5 mL digest solution consisting of concentrated sulfuric acid (H_2SO_4), cupric sulfate ($CuSO_4$), potassium sulfate (K_2O_4S), and hydrogen peroxide (H_2O_2). The samples were processed for 2 hours at 400˚ C on a SmartDigest block digester (Westco Scientific Instruments Inc, Brookfield, CT). Digested samples were diluted to 75 mL with deionized H_2O

and were analyzed colorimetrically on the SmartChem 200 as described above . Figures 3 – 7 were generated using the statistical program R (2012 ver. 2.15.1).

Results

Topography had a significant effect on the mean plant available P (Olsen) with more available P measured in the depression sites than in the surrounding uplands (fig. 3). Although the depression sites had more available P overall, different depths within the depression sites were almost identical while the mean available P in the upland sites was much lower at 10-15cm depth than the 0-5cm. Within site pH varied between topographic features with the lowest values recorded for shallow depression sites and the largest values recorded for deep upland sites (fig. 4). Additionally, there is a negative correlation between pH and available P across topographic features (fig. 5).

My comparison of total P between 1986 and 2012 in depression sites indicate a decrease in P over the ensuing 25 year period at both depths (fig. 6).
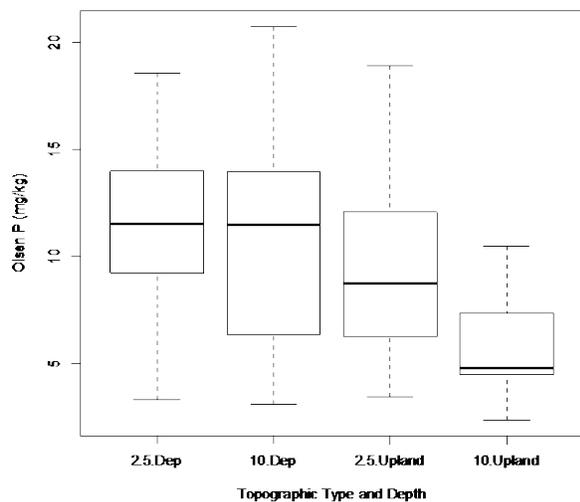

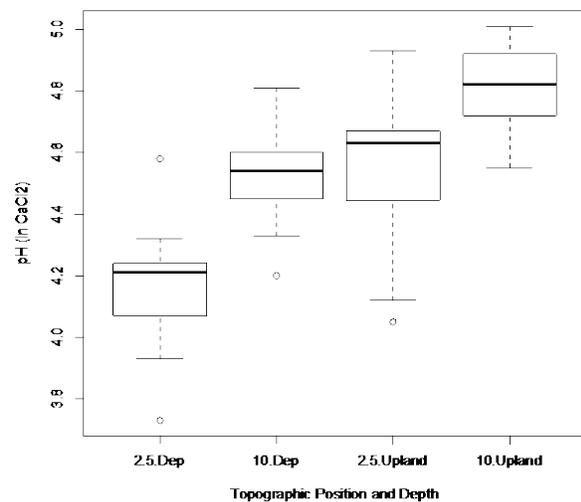Fig. 3 Available P between depths and topographic Features (2012 data)
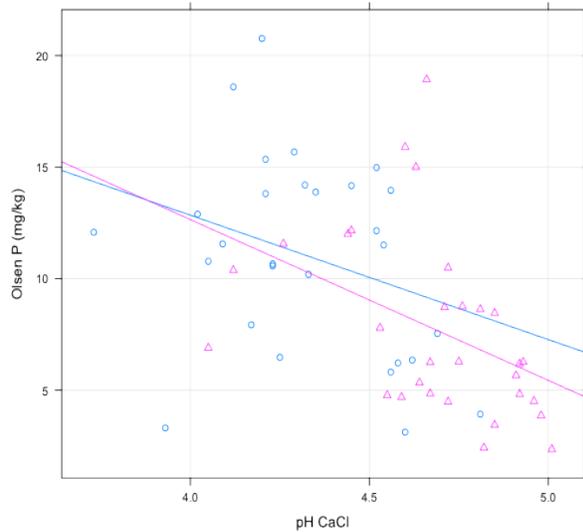
Fig. 4 pH measured in $CaCl_2$ (2012 data)

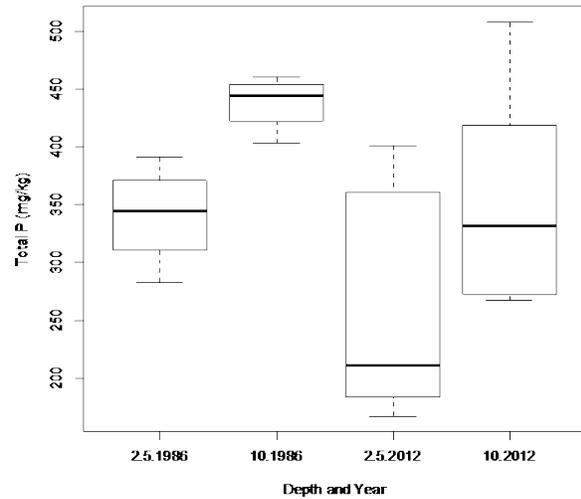Fig 5. Relationship between pH and available P by topographic type.

Fig. 6 Comparison of total P present in depression sites between 1986 and 2012.

Discussion

Topographic influence on pH and available P

The Olsen bicarbonate method (Olsen 1954) was used to determine the amount of P that is easily extracted from soil colloids via biological processes. This method utilizes a sodium bicarbonate solution to extract P from both acidic and calcareous soils (Tiessen and Moir 1993). While this method is commonly used as an index of soil P that is either readily available in solution or can be easily desorbed from soil particles it should be noted that, unlike total P, available P is a functional concept rather than a measurable quantity (Tiessen and Moir 1993). In other words, the size of the available P pool is in constant flux due to rapid geochemical and biological processes such as uptake, sorption, immobilization, and mineralization, which makes quantifying the available P pool difficult (Olander and Vitousek 2004, Vandecar 2009). Although simple and direct measurements of the available P pool are not yet possible, the Olsen (1954) method provides a snapshot of available P at any given point in time by utilizing sodium bicarbonate

10

($NaHCO_3$) to decrease the concentration of Ca^{2+} and Al^{3+} in the soil sample thus increasing P solubility allowing it to be measured colorimetrically in solution (Kuo 1996).

The data represented in figure 3 indicate available P varies across topographic features with more available P present in depression sites than in upland sites. This observed variation in available P between depressions and uplands is possibly a result of depression sites being zones of accumulation due to their lower elevation relative to surrounding uplands. Moisture from rain and snow melt accumulates in the depression sites possibly resulting in higher rates of weathering and more P release from parent material than occurs in the arid uplands. However, while moisture in general does influence the rate of mechanical and chemical weathering of minerals (Schlesinger 1997) moisture present in the soil may only become an important regulator of P availability on a seasonal timescale when moisture becomes limiting or wetting and drying cycles are present (Vandecar 2009). Therefore evaluating the significance of seasonal moisture accumulation on P availability is beyond the scope of this study.

In addition to moisture, depression sites are zones of accumulation for particulate deposition via wind and runoff from surrounding uplands, which suggests available forms of P may be deposited from surrounding areas possibly contributing to the higher available P values observed in depressions. While topographic features appear to affect available P concentration in SLPF soil, there are no doubt other contributing factors as well.

Biotic and abiotic activities within and above the soil surface such as decomposition, immobilization, mineralization, and factors that influence pH play an important role in the availability of all soil nutrients including P (Schlesinger 1997). Soil pH is probably the most informative measurement that can be made with regard to nutrient availability because of the control it exerts over fundamental soil reactions such as ion exchange, dissolution and

11

precipitation, reduction and oxidation, and adsorption (McBride 1994). Our results indicate a

significant relationship between pH and available P across topographic features (fig. 5). A $CaCl_2$

solution was used to measure pH because it dampens seasonal variability that is common in

temperate systems (Soil Survey Staff 1999). The seasonal variation reflected in pH

measurements using H_2O is a result of the loss, formation, or accretion of salts during the various

times of the year (Thomas 1996). The $CaCl_2$ method corrects for this effect by providing Ca^{2+}

ions that displace the hydronium and aluminum ions from the colloid surfaces resulting is a more

accurate representation of pH values across seasons.

In general, P availability is strongly influenced by soil pH with the maximum level of P

available in solution P at a pH of ~7 (Schlesinger 1997). Two cations, hydrogen (H^+) and

aluminum (Al^{3+}), are largely responsible for soil acidity, however the influence these cations

have on soil function depends on the degree of soil acidity and the source and nature of the soil

colloids (Brady 1990). Under very acidic conditions aluminum becomes highly soluble and is

either tightly bound to organic matter or becomes oxidized and remains in solution as Al oxide

$(Al(OH)^2)$ (Brady 1990). According to figures 4 and 5, the overall pH in SLPF soil across

topographic features is low (<5.2) partially due to the fact that these soils have low organic

matter stemming from their young age (Halvorson 2009) and the rain that falls on these sites may

be acidic due to the continued outgassing of the volcano as has been reported in the past (Nuhn

1986). While the overall connection between H^+ concentration and pH is relatively

straightforward it is less clear how pH influences specific soil reactions, specifically the amount

and form of P present in the soil.

Nearly all P taken up by plant roots is either in the form of the primary orthophosphate

anion H_2PO_4 or the secondary form of HPO_4^{-2} (Brady 1990). In low pH soils, such as those

developing on the SLPF, the dominant ionic form of P is H_2PO_4. Although P in this form is relatively plant available, other elements present at low pH tend to interfere with plant uptake mechanisms (Brady 1990). For example, the dominant form of P present on the SLPF is in the form of apatite, which weathers rather rapidly especially at low pH (Schlesinger 1997). Rapid weathering increases the amount of Al^{3+} present, which reacts strongly with H_2PO_4 creating insoluble hydroxy phosphates ($Al(OH)_2H_2PO_4$). This leaves relatively little H_2PO_4 available for plants growing in low pH soils, which agrees with observations made by other researchers in regards to Mount St. Helens soil (Bishop et at, 2010).

The negative correlation between pH and available P across topographic features (fig. 5) suggests topography influences pH and thus may play a significant role in the amount of available P present in these sites. However, as mentioned previously, available P is a functional concept rather than a quantifiable substance and Lambers et al. (2012) has hypothesized that some plants may posses specialized uptake mechanisms that allow them to liberate P that is largely unavailable to other organisms. Therefore, more detailed information regarding plant community characteristics, mineral weathering rates, and the amount of aluminum oxide present in these sites is necessary to develop a more precise explanation of the possible relationship between topography and available P in SLPF soil.

Historical comparison of total P change over time

As described by Walker and Syers (1976) the general pattern of P availability during the weathering of parent material containing apatite consists of high rates of weathering and high amounts of total P at the onset of soil development giving way to increasing occlusion and a decrease in total P over time (fig 1). Based on this model we hypothesized that due weathering since the eruption less total P will be present in the upper 15 cm of the soil profile today than was

present shortly after the eruption, and, indeed, this is what we observed. Figure 6 represents the total P contained in depression sites from shortly after the eruption (1986) compared to total P values from similar depression sites at present (2012). This observation based on our experimental design suggests the Walker and Syers model (1976) holds true for this temperate system during the earliest years of soil development. Furthermore, less total P was present in the upper profile for both 1986 and 2012 samples (fig. 6) suggesting soils at shallower depths are possibly subject to more rapid weathering due to increased moisture content and lower pH values, which may be related to topography. Although it appears as if these temperate soils follow the general P transformation pattern explained by Walker and Syers (1976) more work is needed in order to elucidate the overall rate of these P transformations and its movement between pools.

Conclusion

The distinctive topography of the SLPF has clearly resulted in a heterogeneous landscape with varying amounts and forms of P present within and between depression and upland sites. The results of this study fulfill our objective to investigate the significance of topography on bioavailable and total P both spatially and temporally and support our hypotheses that depressions will have more bioavailable P than the surrounding uplands. Furthermore, our results support the general P transformation model proposed by Walker and Syers (1976) by revealing a significant decrease in the total amount of P present in depression sites today than was present shortly after the 1980 eruption. Although our study clearly suggests soil development and P availability on the SLPF is complex and cannot be explained by topography alone, it provides a useful starting point for future research focused on gaining a better understanding of P dynamics, including availability, weathering rates, and losses, in this and other young temperate systems.

References

Bishop J.G., O'Hara N.B., Tutus J.H., Apple J.L., Gill R.A., Wynn L. 2010. N-P co-limitation of primary production and response of arthropods to N and P in early primary succession on Mount St. Helens Volcano. *PLoS One.* 5(10):e13598.

Brady N.C. 1990. The nature and properties of soils. Tenth edition. MacMillan Publishing Co., New York, New York.

Carreira J.A., Lajtha K., Niell, F.X. 1997. Phosphorus transformations along a soil/vegetation series of fire-prone, dolomitic, semi-arid shrublands of southern Spain – soil P and Mediterranean shrubland dynamic. *Biogeochemistry.* 39(1):87 – 120.

Crews T.E., Kitayama K., Fownes J.H., Riley R.H., Herbert D.A., et al. 1995. Changes in soil phosphorus fractions and ecosystem dynamics across a long chronosequence in Hawaii. *Ecology* 76:1407 – 1424.

Escudey M., Galindo G., Forster J., Briceno M., Diaz P., and Chang A. 2001. Chemical forms of phosphorus of volcanic ash-derived soils in Chile. *Commun. Soil Sci. Plant Anal.* 32(5&6):601 – 616.

Franklin J.F., Frenzen P.M., and Swanson F.J., Re-Creation of Ecosystems at Mount St. Helens: Contrasts in Artificial and Natural Approaches. Rehabilitating Damaged Ecosystems. Volume II. CRC Press, Inc., Boca Raton Florida. 1988. p 1-37, 17 fig, 5 tab, 48 ref.

Hedin L.O., Vitousek P.M., and Matson P.A. 2003. Nutrient losses over four million years of tropical forest development. *Ecology.* 84(9):2231 – 2255.

Jenny H. 1941. Factors of soil formation: a system of quantitative pedology. Dover Publications, Inc. New York, New York.

Jenny H. 1958. Role of the plant factor in the pedogenic functions. Ecology, 39:5 – 16.

Kuo S. 1996. Phosphorus. p. 869 – 919. In D.L. Spark D. (ed.). Methods of soil analysis: Part 3—chemical methods. Soil Science Society of America Book Series No. 5. Soil Science Society of America and American Society of Agronomy, Madison, WI.

Lambers H., Bishop J.G., Hopper S. D., Laliberte E., Zuniga-Feest A. 2012. Phosphorus-mobilization ecosystem engineering: the roles of cluster roots and carboxylate exudation in young P-limited ecosystems. *Annals of Botany* 110:329 – 348.

Nuhn W. W. 1987. Soil Genesis on the 1980 pyroclastic flows of Mount Saint Helens. Thesis, University of Washington, Seattle

Olander L.P. and Vitousek P.M. 2004. Biological and geochemical sinks for phosphorus in soil from a wet tropical forest. *Ecosystems.* 7:404 – 419.

Olsen S.R., Cole C.V., Watanabe F.S., and Dean L.A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S. Dep. of Agric. Circ. 939.

Satti P., Mazzarino M.J., Roselli L., and Crego P. 2007. Factors affecting soil P dynamics in temperate volcanic soils of southern Argentina. *Geoderma.* 139:229 – 240.

Schlesinger W.H. 1997. Biogeochemistry: an analysis of global change. Second edition. Academic Press, San Diego, California, USA.

Schlesinger W.H., Bruijnzeel L.A., Bush M.B., Klein E.M., Mace K.A., et al. 1998. The biogeochemistry of phosphorus after the first century of soil development on Rakata Island, Krakatau, Indonesia. *Biogeochemistry* 40:37 – 55.

Soil Survey Investigations Report. 2004. Soil Survey Laboratory Methods Manual No. 42:4.0. United States Department of Agriculture.

Soil Survey Staff. 1999. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. 2nd ed. Natural Resources Conservation Service. United States Department of Agriculture Handbook 436.

Thomas, G.W. 1996. Soil pH and soil acidity. p. 475-490. In J.M. Bigham (ed.). Methods of soil analysis: Part 3—chemical methods. Soil Science Society of America Book Series No. 5. Soil Science Society of America and American Society of Agronomy, Madison, WI.

Tiessen H. and Moir J.O. 1993. Characterization of available P by a sequential extraction. In Soil Sampling and Methods of Analysis (ed. M.R. Carter). *Canadian Society of Soil Science*, Lewis Publishers, Boca Raton.

Tilling R.I., Topinka L., and Swanson D.A., 1990, Eruptions of Mount St. Helens: Past, Present, and Future, U.S. Geological Survey Special Interest Publication, 56p.

Turner D. and Vitousek P.M. n.d. Vitousek lab method for acid digests. Available from http://www.stanford.edu/group/Vitousek/kjeldahl.html.

Vandecar K.L., Lawrence D., Wood T., Oberbauer S.F., Das R., Tulley K., and Schwendenmann L. 2009. Biotic and abiotic controls on diurnal fluctuations in labile soil phosphorus of a wet tropical forest. *Ecology.* 90(9):2247 – 2555.

Vitousek P.M., Walker L.R., Whiteaker L.D. et al. 1993. Nutrient limitations to plant-growth during primary succession in Hawaii Volcanos National Park. *Biogeochemistry.* 23(3):197 – 215.

Walker T.W. and Syers J.K. 1976. The fate of phosphorus during pedogenesis. *Geoderma* 15:1 – 19.