

Chemical and textural controls on phosphorus mobility in drylands of southeastern Utah

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Abstract We investigated several forms of phosphorus (P) in dryland soils to examine the chemical and textural controls on P stabilization on a diverse set of substrates. We examined three P fractions including labile, moderately labile, and occluded as determined by a modified Hedley fractionation technique. The P fractions were compared to texture measurements and total elemental concentrations determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Labile P related to the absence of materials involved in P sorption. Moderately labile P was most strongly associated with high total Al & Fe content that we interpret to represent oxides and 1:1 clay minerals. The occluded P fraction was strongly associated with low total Al & Fe environments and interpreted to represent 2:1 clay minerals where ligand exchange tightly sequesters P. The results indicate that the controls on P fraction distribution are initially closely tied to the chemical and physical properties of the bedrock units that contribute to soil formation. Further, these results suggest that the progression of

stabilized P forms in dryland areas differs from the progression observed in mesic environments. Soil development in dryland settings, such as the formation of pedogenic carbonates, may lead to differing controls on P availability and the proportional size of the moderately labile fraction.

Keywords Available phosphorus · Canyonlands National Park · Hedley fractions · Occluded phosphorus · Soil biogeochemistry · P stabilization

Introduction

Phosphorus (P) is an essential, and sometimes limiting, element for plant growth (Carreira and Niell 1992; Crawford and Gosz 1982; Skujins 1991; Tiessen 1995). Phosphorus is found in multiple forms in soil, each of which plays a distinct function in soil-nutrient cycling. The plant-available forms of P in soils are typically very limited because some forms of dissolved P rapidly sorb onto different soil constituents. Phosphorus sorbs to organic matter, oxides, clays, or carbonates; however, the rate and reversibility of sorption vary with each material. Under certain conditions, P can become permanently bound to soil particles; under other conditions, P is present in exchangeable forms that allow for potential plant use (Tiessen and Moir 1993). Researchers generally

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describe the degree of functional stabilization between P and soil particles as: (1) *labile* when P is free in the soil, weakly associated with surfaces, or in readily mineralizable organic compounds, thus generally available for plant uptake; (2) *moderately labile* when P is reversibly bonded to mineral surfaces; or (3) *occluded* when P is stabilized in forms that resist most short and mid-term physical and chemical changes in soils.

In dryland soils, the ability of P to move from one fraction to another is largely controlled by mineralogy (Cross and Schlesinger 2001; Lajtha and Schlesinger 1988a; Neff et al. 2006), and a number of different minerals can play important roles in the stabilization and release of P. For example, the positive electrostatic charge of carbonates sorbs P moderately, but that association can be reversed by changes in pH (Tiessen and Moir 1993). In contrast, a mineral such as goethite quickly sorbs P through ligand exchange until the sorption capacity of the mineral is met. Neither chemical nor physical alterations will easily reverse those bonds when surface coverage of sorption sites is low (Goldberg and Sposito 1985). Despite a clear role for minerals in the determination of P fraction distributions, mineralogy alone is not sufficient to predict P-stabilization mechanisms because some minerals may stabilize P through more than one mechanism. Al & Fe oxides may absorb P on mineral surfaces in a way that is reversible, or may exchange ligands which sequester P into the physical structure of the oxides (Sollins et al. 1988). Finally, sorption is complicated by other factors, such as particle size and structure. Smaller particles form tighter bonds with P because they have more surface area (Carreira et al. 2006). Amorphous minerals tend to sorb P more rapidly than crystalline material for similar reasons (Ryan et al. 1985). Distinctions concerning the type and intensity of P bonding are important because these issues address the mobility and plant availability of P in dryland soil.

Controls on dryland soil P mobility are complex and may involve several factors, including substrate composition, soil age, and degree of weathering. Dryland soils have a wide range of P concentrations but typically have very small amounts of organic P (Cross and Schlesinger 1995; Cross and Schlesinger 2001; Neff et al. 2006; Tiessen et al. 1984). In the absence of a large organic P fraction in soils, variation in P content can be closely related to the inorganic P content of parent materials (Neff et al.

2006). In addition to substrate chemistry, soil age appears to be a primary factor in P mobility (Lajtha and Schlesinger 1988b; Lilienfein et al. 2004; Tiessen et al. 1984; Walker and Syers 1976). As soils age, they weather and are exposed to a variety of chemical alterations that ultimately change the constraints on P mobility (Cross and Schlesinger 1995; Roberts et al. 1985; Walker and Syers 1976).

Past research in soil P cycling and stabilization has relied frequently on incubation studies to identify the soil constituents responsible for P sorption. In several studies, oxide abundance strongly correlates with the amount of P that soils are able to sorb during exposure to dissolved P (Agbenin and Tiessen 1994; Hamad et al. 1992; Pena and Torrent 1984; Ryan et al. 1985; Samadi and Gilkes 1999; Solis and Torrent 1989; Zhou and Li 2001). Several other incubation studies show that carbonate content determines sorption capacity (Bertrand et al. 2003; Carreira and Lajtha 1997; Carreira et al. 2006; Cross and Schlesinger 2001; Lajtha and Bloomer 1988; Lajtha and Schlesinger 1988a). This incubation approach is important for identifying the soil constituents that will take up P when P is supplied in abundance (e.g., in agricultural settings); however, these studies neither identify the minerals sorbing P in natural settings nor identify the mechanisms stabilizing P.

Identifying the role P plays in dryland ecosystems is difficult due to the multiplicity of factors involved in P sorption. Across highly heterogeneous landscapes, the controls on P mobility may be closely tied to variation in substrate geochemistry and soil properties. To examine this variability and to develop a clearer understanding of the controls on P stabilization in a southeastern Utah (USA) dryland, we examined a set of young, immature soils on different lithic types. Parent materials include limestones, eolian sandstones, alluvial sandstones, lagoonal siltstones, and volcanic ash mudstones. We investigated P mobility in these materials by evaluating statistically the relations among chemistry, texture, and soil P fractions.

Methods

Study area

We selected a geologically diverse dryland on the Colorado Plateau located in the southeastern corner

of Utah, near Canyonlands National Park (CNP). In this region, elevation ranges from 1400 to 2000 meters. Climate is generally cool and semiarid, with an average 215 mm of annual precipitation. Temperatures range from an average 3°C in winter to 23°C in summer (Western Regional Climate Center 2009). Vegetation communities include grasslands, juniper woodlands, and shrublands. We investigated soils developed on 17 different bedrock units representing a variety of depositional environments between about 300 and 180 million years ago.

Diversity of parent materials

Different bedrock types in the study area represent sediment deposited in many different marine and non-marine environments. Sediment origin, depositional environment, and post-burial conditions influence P concentrations, mineralogy and sorption dynamics of the subsequent soils formed on these bedrock types. The chemical and textural features of the sampled soils are largely controlled by the depositional environments of sediments that now compose bedrock (Table 1). Several previous published works will provide additional details and references for Table 1 (Baars 2003; Barr 1983; Campbell 1987; Doelling et al. 2003; Morris et al. 2003; Stokes 1988).

Sampling design

We sampled immature soils near bedrock outcrops to analyze the primary geochemical mechanisms controlling P fraction distributions. The sample design addressed two specific aims. The first aim was to sample from chemically- or mineralogically-distinct lithologies. Analysis performed on a broad diversity of substrates provided the sufficient breadth required for landscape-scale observations. We collected 21 soil samples associated with most of the geologic units shown in Table 1. In some cases, a single lithology could be separated into two chemically- or mineralogically-distinct subtypes. For example, the soils on the Navajo Sandstone are white in some areas and red, hematite-bearing in other areas. Several researchers have suggested that the white sandstone resulted from removal of the hematite grain coatings by hydrocarbon migration (Beitler et al. 2003; Chan et al. 2000). Ferric iron (Fe^{3+}) is insoluble and must be reduced to Fe^{2+} for transport.

Thus the areas of hydrocarbon flow may have altered the species of iron oxides. Iron oxide species have varying capacity to sorb P; consequently, the final soil sample list includes samples from both white and red Navajo soils.

The second aim of our sampling design was to sample physically weathered soils near bedrock outcrops. Previous P cycling studies (e.g., (Lajtha and Bloomer 1988; Samadi and Gilkes 1998)) examined surficial deposits where advanced pedogenesis and variations in substrate composition may confound the interpretations. These challenges make it difficult to scale observations from a local to a landscape level. Therefore, this sampling design excluded areas of surficial deposits, such as colluvial and alluvial sediment, as well as soils where advanced pedogenesis may have altered soil chemistry. Although we cannot strictly rule out dust inputs or other pedogenic effects (Reynolds et al. 2006), sites were selected to exclude areas where dust accumulation might be significant (Reynolds et al. 2001). Generally, sites were selected on the basis of their presumed similarity to substrate chemistry. The composite sampling was conducted on areas that were generally flat to slightly convex surfaces where substrates formed regolith and soils. Soil sampling depth was also limited to the top 3 cm to further minimize the effects of pedogenic processes.

Chemical and mineralogical analyses

Each soil sample was subjected to chemical and mineralogical testing. Bulk soil (measure of total elements) chemistry was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) by the USGS laboratories in Denver. All samples were ground and 0.2-g aliquots were dissolved using a four-acid (HF , HCl , HNO_3 , HClO_4) total digestion procedure (Lichte et al. 1987). An S20 SevenEasy meter was used to measure pH. Calcium carbonate percent was measured on a percent basis using a Chittick apparatus (Machette 1986). The method combines ground sample with 6N HCl and measures the volume of liquid displaced by evolved gas. Each sample was replicated three times and the results were averaged.

Soil mineralogy was measured on the clay fraction with standard X-ray diffraction (XRD) techniques in USGS laboratories in Denver. In this analysis,

Table 1 Summary of substrates within Canyonlands National Park

Period	Group Formation	Unit Name	Geologic Description
JURASSIC	Glen Canyon Group	Navajo sandstone*	Red sandstone formed from eolian dunes
		Kayenta Formation*	Discontinuous layers of red sand, silt and mudstone deposited by shifting streams
TRIASSIC	Chinle Formation	Wingate Sandstone	Orange to brown colored eolian sandstone
		Church Rock Member	Reddish-brown iron-rich sandstone
		Owl Rock Member	Green and orange limestone with sandstone interbeds
		Petrified Forest Member*	Multicolored volcanic ash deposited on overbank and lacustrine surfaces—bentonitic rich mudstones
		Moss Back Member	Stream eroded channels within the Shinarump infilled with sand and gravel
		Monitor Butte Member*	Nodular brown limestone of sand and mud facies rich in bentonitic clays
		Shinarump Member*	Calcareous fluvial conglomerate with sandstone facies
	Moenkopi Formation	Moody Canyon Member*	Dark brown lagoonal deposit with silt and mudstone facies and green bands of reduced iron sediments
		Torrey Member*	Red tidal flat deposit of iron-rich sediments with silt and mudstone facies
		Sinbad Limestone Member*	Oolitic yellow carbonate with both siltstone and sandstone facies
PERMIAN	Cutler Group	Black Dragon Member*	Conglomerate transitioning to iron- rich sandstone
		White Rim Sandstone*	Calcareous cemented white sandstone with marine and eolian facies
		Organ Rock Formation*	Dark reddish-brown arkosic sediments with both shale and sandstone facies
		Cedar Mesa Sandstone*	Coastal dune complex of white calcareous sandstone interbedded with arkosic -rich sediment
		Elephant Canyon Formation*	Limestones with interbedded sandstones and shales

Soils sampled for this study are marked with an asterisk

oriented samples were subjected to three treatments: air-dry, glycolated, and heat-treated (550°C).

Particle-size measurements and soil-texture classification

Soil texture was measured on a volume percentage basis using a laser-light scattering method. The Mastersizer 2000 has an accuracy and reproducibility of $\pm 1\%$. Soil samples were split to 100 g and then sieved with an 850- μm sieve. Prior to analysis, all samples were prepared by digesting organic matter

and CaCO_3 using 30% H_2O_2 and 15% HCl , respectively, and sodium hexametaphosphate was added to each sample to de-flocculate clays.

We evaluated textural variation with two different classification schemes. We grouped the continuous soil-texture data provided by the laser method into classes of sand, silt, and clay using the standard Wentworth scale. The analysis of the data, however, suggested that another approach might better capture the natural groupings of textural classes in these diverse soils; therefore, we applied a natural-breaks algorithm to establish a second grouping for textural

classes. The natural-breaks algorithm parses textural data based on the spread of data points represented in the entire data set. Four breaks were designated: (1) coarse (2000–210 μm); (2) intermediate (210–156 μm); (3) fine (156–0.58 μm); and (4) very fine (all particles less than 0.58 μm .)

Hedley fractionation

We measured P fractions using the modified Hedley fractionation method (Tiessen and Moir 1993), which characterizes P mobility into three separate categories of labile, moderately labile, and occluded (Tiessen et al. 1984). Hedley fractionation is a sequential leaching process to evaluate the location and bonding type of P within a soil matrix. Labile P was measured by extracting phosphates from the soil solution using resin exchange strips followed by the elution of resins using sodium bicarbonate (NaHCO_3). Moderately labile P refers to chemically (but reversibly) bound P. Moderately labile P exists in several forms, including on soil particles surfaces, microorganisms, and stable calcium P minerals (e.g., secondary calcium carbonates). Sodium hydroxide (NaOH) was used to extract both inorganic and organic P forms, whereas hydrochloric acid (HCl) mainly extracted calcium phosphates and sesquioxides held in inorganic P forms. The final Hedley step measured occluded P residing in stable bonds that are generally non-reversible. These bonds include inner sphere complexes with PO_4^{3-} replacing the surface hydroxyls of clays (Sollins et al. 1988). Measurement of occluded P included a two-step process involving sonic and fusion fractions. The remaining P in the sample was considered residual P. After leaching, the supernatant from each step was analyzed using the molybdate-ascorbic method on a Lachat QuickChem, 2000 analyzer at the University of Denver. Each sample was replicated three times and results were averaged.

Statistical design

We used regression analysis to identify chemical and textural factors that uniquely contributed to the prediction of the percentage of P measured in each fraction. Predictive regression modeling systematically removes each observation, recalculates the regression, and then determines how well the regression predicts the removed data point. In this text, we

use the specific term “predicted R^2 value” to reference the result of predictive regression modeling and a simple “ R^2 ” for the coefficient determined by a standard regression. The predictive regression modeling method provides a quantitative assessment of how well the regression formula can predict data points as opposed to a simple R^2 that describes the degree to which the regression formula can describe the full dataset. Predictive regression modeling typically produces smaller R^2 values than linear regression because, in addition to explaining variance, the formula is assessed for its ability to predict new data. We selected the most robust equations based on the predictive R^2 value but report both values in this study. All calculations were performed using Minitab statistical package Release 14.

Multicollinearity (highly correlated variables) among variables required that we develop an additional set of variables beyond the initial set of independent variables, which included cations from ICP (Al, Fe, K, Mg, Na, Ca, and Mn), carbonate percentage, and textural classes. We addressed issues of multicollinearity by creating composite scores for variables showing high collinearity. For example, Al, Fe, and K were highly correlated. The Z score for each element was determined, and then Z scores were multiplied together to create a single variable representing all three elements.

Moderator variables were developed to capture specific interactions of texture and chemistry. For example, Fe has a strong relation to P sorption; however, that relation can be strengthened or weakened by the effect of textural classes. Whereas sand-size fractions of Fe are unlikely to have any direct effect on P mobility, clay-sized fractions of Fe should because of their high surface area and the electronic affinity of phyllosilicates. The application of moderator variables is a statistical approach, called mediated moderation (Baron and Kenny 1986). Each element is multiplied by a texture group producing variables such as “Al sand” and “Al silt”. These variables isolate the effect of Al in cases of specific texture classes. In some cases, these combined factors likely represent specific mineralogies within the soil sample. For example, “Al & Fe clay” represented the product of the percentage of aluminum concentration multiplied by the percentage of iron and the percentage of clay. Soil samples with large “Al & Fe clay” factors likely represent samples rich in 1:1 clays.

Regressions were developed using an iterative process that identified and compared the amount of variance explained by each predictor variable. We began by locating three or four single terms that generated the highest predicted R^2 values. After the first term was selected, we tested additional terms in an attempt to increase the predicted R^2 value. Additional variables were included only if their correlation to other variables was less than 0.70 (Tabachnick and Fidell 1996). The variable selection process was repeated until either no additional term enhanced the regression model or the effects of the additional terms were small compared to an increase in the Mallow's Cp value.

We compared regression models with similar predicted R^2 values using several other statistical factors representing model accuracy. The Mallow's Cp statistic was examined to determine how suitable the independent variables were in predicting the dependant variable, given issues of multicollinearity. The prediction sum of squares (PRESS) value was used as an accuracy indicator because it is the sum of squares of the prediction errors. In addition, we considered the Durbin-Watson Statistic because it measures the auto correlation in the residuals. Finally the variance inflation factor (VIF) was used to examine the correlation between predictors.

This regression approach was used to identify unique contributors to the dependant outcome, thereby pointing to mechanisms that may affect P mobility. Multicollinearity issues can obscure mechanisms; therefore, each regression term was limited to those variables that contribute uniquely to the

outcome. Only variables significant at $P < 0.05$ were included in the final models.

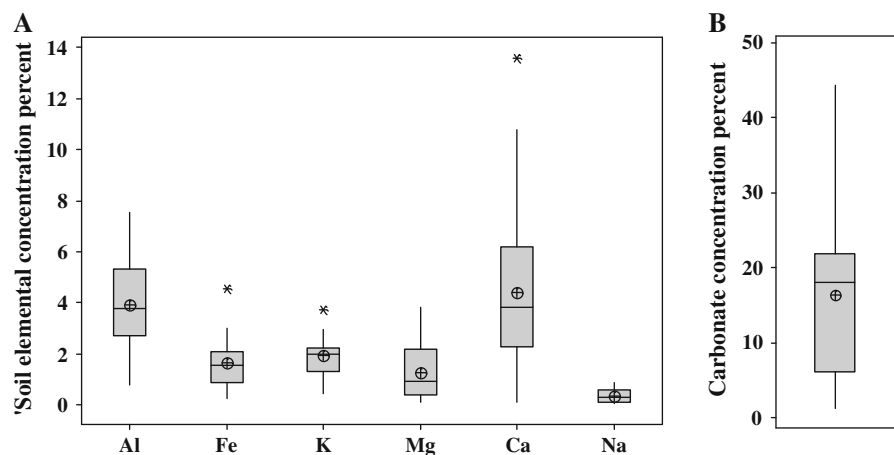
Results

Chemical and textural distributions

The chemical and textural data indicate that the soil samples represent a wide variety of soil environments. The cation and carbonate concentrations suggest that mineral compositions among the 17 substrates vary considerably; this mineralogic variability is shown also by variable concentrations of Al, Ca and Mg (Fig. 1). Median carbonate values are high, but several samples have very low percentages (Fig. 1). Soil P fraction variability provides a natural gradient to evaluate variations in P fractions. The labile P values are consistently low across all samples; however, the amount of moderately labile P and occluded P is variable (Fig. 2).

The Hedley results (Table 2) are similar to values generated for Entisols and Aridisols determined in other studies (Cross and Schlesinger 2001; Neff et al. 2006). The percentage of labile P is extremely low. Values for moderately labile P represent a large portion of the total P, typically a half to a third of the total P. Residual P values are also large and comparable in amount to moderately labile P. In these samples, organic P is often less than 1% of total P, in contrast with higher values from other published data from drylands (Cross and Schlesinger 2001; Neff et al. 2006).

Fig. 1 Box plots of soil chemistry across all the study sites. The gray box demarcates the 25–75 percentile values while the whiskers locate the 0 and 100th percentile. Outliers are noted with stars above the whiskers. Mean data values are noted with a circular target symbol. Panel A shows Al, Fe, K, Mg Ca and Na concentrations, panel B shows soil carbonate concentrations



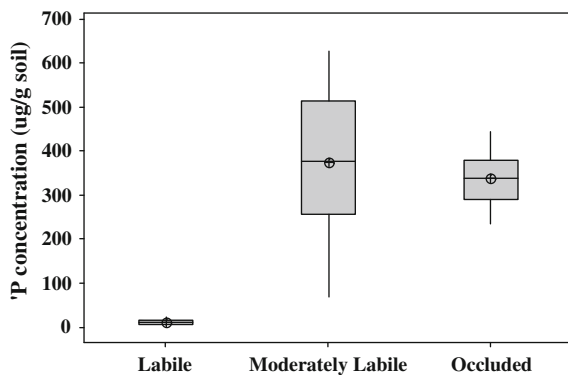


Fig. 2 Box plots of soil concentration of P fractions across all the study sites. The gray box demarcates the 25–75 percentile values while the whiskers locate the 0 and 100th percentile. Outliers are noted with stars above the whiskers. Mean data values are noted with a circular target symbol

XRD results indicate that the clay-size fraction represents different clay minerals within each sample (Table 3). The results confirm the presence of 2:1 and 1:1 clays in most samples.

Descriptive statistics: zero order correlations

The highest concentration of Al, Fe, K, and Mg are found in the fine and very fine particle-size fractions (Table 4). In most cases, correlations between texture classes and chemistry show strong negative correlations of these elements with coarse size fractions and strong positive correlations with fine and very fine size fractions, indicating the presence of most elements in these small size fractions (Table 4). Notably, the intermediate size fraction has a low correlation with elemental abundances and is significantly correlated only with Fe and Mn. Correlations using the Wentworth scale show a similar pattern of high correlations of Al, Fe, K, and Mg in the silt and clay fraction.

Simple regression

Neither elemental chemistry nor texture alone explains a large amount of variance in P fractions across sites. Both Al and Fe independently predict slightly more than 25% of the labile P values; however, when combined, they provide the highest predicted R^2 value (Table 5). Fe poorly predicts the percentage of moderately labile P and occluded P, and Al produces the highest predicted R^2 values for

both categories. The highest predicted R^2 values for moderately labile P include variables Al, Al & Fe, and sand (Al: $R^2 = 41\%$, Al & Fe: $R^2 = 31\%$, and sand: $R^2 = 27\%$; Table 5). The best models for occluded P also included variables Al, Al & Fe and sand (Al: $R^2 = 37\%$, Al & Fe: $R^2 = 27\%$, and Sand: $R^2 = 24\%$; Table 5).

Predictive regressions using textural moderators

Moderator variables (combined chemistry and texture variables) produce more robust models of P fractions across soils from varied lithologies. Each moderator term represents an interaction where the texture condition specifies the relation between the phosphorus fraction and the elemental variable. These relations are shown in interaction graphs that demonstrate a two factor interaction of high versus low chemical variable values and high versus low texture condition values (Fig. 3).

Modeled regression for labile P

The best model for labile P consists of three moderator terms: K sand, Na coarse, and Al intermediate (Table 6). Together, these terms create a model with a predicted R^2 value of 54.5% ($R^2 = 71.5\%$), $P < 0.001$, $F = 14.19$, PRESS value of 0.0007, and Durbin-Watson Statistic of 1.97. The additional terms, Mn coarse and Ca coarse, increase the predicted R^2 by only about 1%. Models applying a fourth term are virtually indistinguishable from each one another and the best three-term model. These terms were excluded from the final model because their P values exceeded 0.05.

The labile P model consists of three combined chemical-textural terms to create a much stronger model of labile P than chemistry alone. K sand has the largest beta and explains more about the labile P than any other factor (Table 6). The flat black line in Fig. 3 indicates that, in very sandy soils (high sand texture), the concentration of K has little influence on the percentage of labile P. In contrast, the gray line indicates that when soils contain little sand (i.e., soils enriched in silt or clay) high concentrations of K are associated with small percentage of labile P, whereas low concentrations of K are associated with larger percentage of labile P. The magnitude of this relation can be approximated by the slope of the gray line.

Table 2 Results from Hedley fractionation

Soil samples	pH	Resin Pi	HCO ₃ ⁻ Pi	HCO ₃ ⁻ Po	NaOH Pi	NaOH Po	HCl Pi	Sonic Pi	Sonic Po	Residual P	Total P	Labile (%)	Moderately Labile (%)	Occluded (%)
Elephant Canyon	7.78	12.22	9.20	1.47	2.99	6.99	515.68	4.25	4.79	367.07	924.65	2.5	56.9	40.7
Cedar Mesa (white)	7.94	8.20	6.13	3.00	2.25	0.94	296.51	3.12	2.19	333.54	655.87	2.6	45.7	51.7
Cedar Mesa (red)	7.96	2.66	2.36	1.15	2.35	0.00	148.53	1.07	4.29	271.58	433.98	1.4	34.8	63.8
Organ Rock (red)	8.03	2.09	1.60	6.44	2.34	0.00	298.96	0.23	5.49	229.36	546.51	1.9	55.1	43.0
Organ Rock (purple)	7.94	1.26	1.16	5.25	1.47	1.54	419.07	0.35	5.71	256.17	691.97	1.1	61.0	37.9
Organ Rock (chocolate)	8.04	3.50	2.56	4.42	1.37	0.18	375.17	0.56	6.05	289.04	682.84	1.5	55.2	43.3
White Rim	7.75	4.16	3.80	1.32	2.73	1.63	212.35	1.69	2.49	286.96	517.13	1.8	41.9	56.3
Black Dragon	7.96	0.99	1.74	3.14	1.54	2.21	167.16	1.00	2.93	305.25	485.97	1.2	35.2	63.6
(conglomerate)														
Black Dragon (siltstone)	8.02	0.72	2.25	4.16	3.42	0.08	437.18	1.02	3.30	285.92	738.06	1.0	59.7	39.3
Sinbad	7.82	1.15	1.66	9.13	2.02	0.78	596.07	2.53	5.21	270.29	888.83	1.3	67.4	31.3
Torrey	7.92	0.76	2.60	2.66	2.18	1.23	624.63	1.61	2.25	346.04	983.95	0.6	63.8	35.6
Moody Canyon	8.14	0.00	1.69	1.24	1.74	0.00	592.04	1.49	2.00	441.43	1041.64	0.3	57.0	42.7
Shinarump	7.88	3.11	3.03	0.00	2.84	0.00	558.52	3.39	0.00	384.32	955.21	0.6	58.8	40.6
Monitor Butte	7.93	9.45	9.33	0.00	4.56	0.00	501.39	4.51	0.00	421.87	951.11	2.0	53.2	44.8
Petrified Forest (red)	8.06	7.30	5.65	0.43	3.83	0.00	437.18	3.72	0.00	370.38	828.48	1.6	53.2	45.2
Petrified Forest (purple)	8.20	2.03	1.61	4.19	1.49	0.00	341.33	1.82	0.11	378.68	731.26	1.1	46.9	52.1
Monitor Butte/Shinarump mix	7.75	2.59	5.00	2.65	2.07	0.00	366.72	9.38	0.00	391.40	779.81	1.3	47.3	51.4
Kayenta (North)	7.69	8.71	8.46	0.00	4.70	0.57	400.70	14.42	0.00	359.29	796.83	2.2	51.0	46.9
Kayenta (South)	7.53	9.27	3.19	2.85	6.02	3.98	292.86	12.29	0.00	366.48	696.96	2.2	43.5	54.4
Navajo (red)	7.61	13.02	2.60	5.81	7.02	6.01	137.58	7.80	0.00	311.08	490.92	4.4	30.7	65.0
Navajo (white)	7.74	8.10	0.95	1.35	13.61	1.54	54.76	3.93	3.55	329.49	417.27	2.5	16.8	80.8

“Pi” represents the inorganic P fraction and “Po” the organic P fraction in micrograms per gram

Table 3 Summary of X-ray diffraction (XRD) results

Soil	Illite	Chlorite	Smectite	Kaolinite
Elephant Canyon	X	X	X	X
Cedar Mesa (white)	X		X	X
Cedar Mesa (red)	X		X	X
Organ Rock (red)	X		X	X
Organ Rock (purple)	X		X	X
Organ Rock (chocolate)	X	X	X	X
White Rim	X		X	X
Black Dragon	X	X	X	X
(conglomerate)				
Black Dragon (siltstone)	X		X	X
Sinbad	X			X
Torrey	X	X		X
Moody Canyon	X	X		X
Shinarump	X	X	X	X
Monitor Butte	X	X	X	X
Petrified Forest (Red)	X	X	X	X
Petrified Forest (Purple)	X			
Monitor Butte/ Shinarump mix	X	X	X	X
Kayenta (North)	X	X		X
Kayenta (South)	X	X	X	X
Navajo (red)	X	X	X	X
Navajo (white)	X	X	X	X

X indicates mineral identification from XRD of clay fraction

Table 4 Correlation table for elements that have statistically significant correlation to texture classes

Variable	Coarse	Intermediate	Fine	Very fine
Al	−0.717		0.806	0.756
Fe	−0.703	−0.44*	0.935	0.862
K	−0.771		0.812	0.735
Mg	−0.581		0.794	0.698
CaCO ₃			0.481*	
Mn		−0.44*		

P value less than 0.01; * indicates P values less than 0.05

The combination of Na and coarse texture explain the second largest amount of variance in the pattern of labile P in our soil set (Table 6). In sandy soils (high coarse texture), low concentrations of Na yielded the largest percentage of labile P (Fig. 3). In contrast, in finer grained soils (low coarse texture), high concentrations of Na are associated with the largest

Table 5 Simple regression of variables and P fractions percentiles and their respective predicted R^2 values

Variable	Labile P	Moderately Labile P	Occluded P
Al	26**	41**	37**
Fe	29**	16**	12**
K	7*	21**	19**
Al & Fe	30**	31**	27**
Al & Fe & K	23**	29**	25**
CaCO ₃	8*	0	0
% Sand	6*	27**	24**
% Silt	25**	24**	21**
% Clay	6*	13**	11*

** $P \leq 0.01$, * $P \leq 0.05$

percentages of labile P. Small percentage of labile P occur when the soil is either very sandy with high concentration of Na or when loamy soils have very little Na. Comparisons of the lines' slopes indicate that sandy soils have a greater influence on labile P than loamy or clay-rich soils. Low concentrations of Al are associated with larger percentages of labile P in both low and high intermediate texture groups (Fig. 3). Under conditions of high Al concentration, texture plays no role in labile P.

Modeled regression for moderately labile P

The best model for predicting moderately labile P consists of two terms: Al & Fe intermediate and Mg (Table 6). These terms create a model with a predicted R^2 value of 61% ($R^2 = 74.7\%$), $P < 0.001$, $F = 26.61$, PRESS value of 0.117, and Durbin-Watson Statistic of 1.73. The use of the textural moderator with Al & Fe produces the highest predictive R^2 value of 58%. Only one term—Mg—significantly increases predicted R^2 values when applied to the single moderator term. Mg without any textural moderator yields a very large negative beta (−0.41).

Combined variables of Al, Fe, and intermediate texture strongly predict the percentage of moderately labile P. In both sandy and loamy soils, high concentrations of Al & Fe predict the largest percentages of moderately labile P (Fig. 3). Moderately labile P in sandier soils is less affected by Al & Fe concentrations than in finer grained soils. In the presence of high concentrations of Al & Fe,

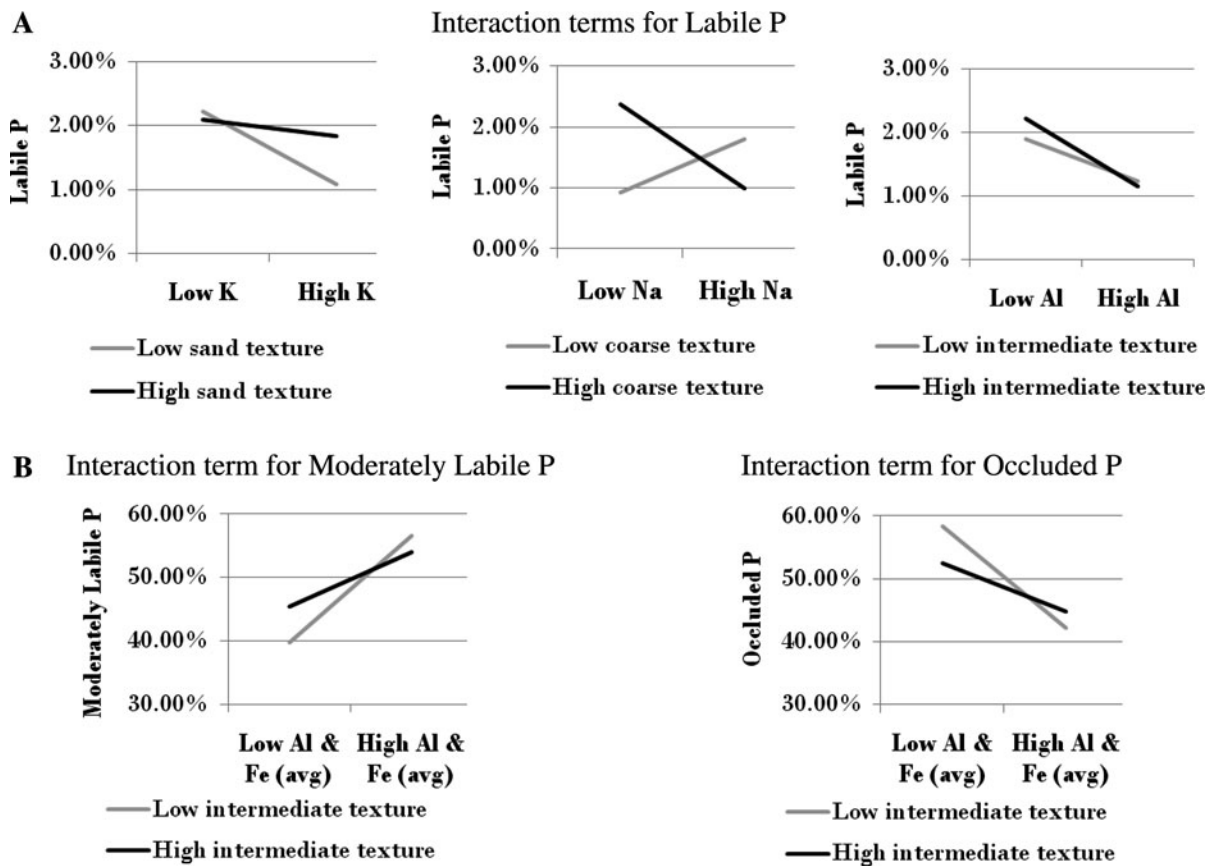


Fig. 3 Interaction graphs for moderator variables demonstrating a two-factor interaction of high versus low chemical variable and high versus low texture condition Panel A shows

labile P interaction terms, Panel B shows terms for moderately labile P and occluded P

Table 6 Predictive regressions developed for each P fraction

Model type	Variable	SE (B)	P	T	VIF
% Labile P	K Sand	1.03	0.000	5.94	1.8
	Na Coarse	−0.61	0.002	−3.73	1.6
	Al intermediate	−0.61	0.000	−4.33	1.2
% Moderately Labile P	Al & Fe intermediate	1.11	0.000	6.51	2.1
	Mg	−0.41	0.027	−2.40	2.1
% Occluded P	Al & Fe intermediate	−1.12	0.000	−6.30	2.1
	Mg	0.44	0.022	2.51	2.1

SE (B) is the standardized error, (*P*) is the significance level, (*T*) is the *T*-value and (VIF) is the variance inflation factor

texture has a small effect on percentages of moderately labile P.

Modeled regression for occluded P

The model that best explained the variance in occluded P included two terms: Al & Fe intermediate

and Mg (Table 6). The best model resulted in a predicted R^2 value of 58.3% ($R^2 = 72.8\%$), $P < 0.001$, $F = 24.10$, PRESS value of 0.116, and Durbin-Watson Statistic of 1.80. A single variable, Mg, added to Al & Fe intermediate raised the R^2 predicted values by approximately 4%. Additional models with % clay, % very fine, % coarse, Mn fine,

or Mn silt add less than 1% to the predicted R^2 . Each of these models was examined using Normal Probability, Residuals vs. Fitted, and Histograms of Residuals. Although predicted R^2 values were similar among these three-term models, the best graphical results were created with the three-term model of Al & Fe intermediate, Mg, and % clay. Yet, the simpler two-term model was chosen as the most suitable model for occluded P because the clay variable did not contribute uniquely to the equation.

High concentrations of Al & Fe result in low percentages of occluded P across all soil types. The interaction term for occluded P is almost the exact opposite of the interaction term for moderately labile P. Low concentrations of Al & Fe produced the largest percentages of occluded P in both sandy and loamy soils (Fig. 3). Sandier soils are also associated with far less occluded P percentage than finer soils under low Al & Fe conditions. Under high Al & Fe conditions, textural differences resulted in very small variation in occluded P.

Discussion

Labile P

The results of this study support Samadi and Gilkes' (1999) argument that labile P is not the consequence of a single soil property, but of a combination of characteristics that describe sorption of P. We found very little labile P as is typical of dryland soils (Carreira et al. 1997; Cross and Schlesinger 1995; Lajtha and Schlesinger 1988a; Neff et al. 2006; Tiessen et al. 1984). Labile P is scarce because parent material commonly has very little P and/or is poorly weathered, and because few organic sources contribute labile P through decomposition. In our study, amounts of labile P are especially low due to sampling between plants on immature soils. Nevertheless, the use of moderator variables and interaction graphs offer insights into the complexities of labile P by describing chemical and textural conditions under which labile P is either highly available or alternatively made unavailable through mineral sorption. We interpret the first interaction term of K sand to represent the influence of 2:1 clays on labile P. The K interaction graph shows low labile P percentages when K is high and sand is low (enrichment of fines),

implying that 2:1 clays stabilize P and decrease the percentages of labile P (Fig. 3). When K-enriched materials are absent, labile P is high. High concentrations of K are indicative of illite, a 2:1 expanding clay common in sedimentary rocks (Brady and Weil 2002). XRD results positively identify illite clays in every soil sample (Table 3). Phosphorus is sorbed by 2:1 clays through the exchange hydroxyl ions, and these bonds are considered irreversible (Baryosef et al. 1988; Kasama et al. 2004; Traina et al. 1986). The Na coarse term represents the complex interaction of high Na concentration in the diffuse double layer of clay, separating the surface of the clay particle and the soil solution. Under the condition of high Na concentrations, finer texture soils have higher percentages of labile P (Fig. 3). The width of the double layer has been shown to expand in high Na concentration; this effect blocks P anions from accessing the clay surface and limits the sorption of P (Blackmore 1980; Elmahi and Mustafa 1980; Rimmer et al. 1992). Increases in sodium concentration increase labile P, but have no effect on moderately labile P (Curtin et al. 1992). The Al intermediate term may represent the influence of clays and oxides on the percentage of labile P. The interaction graph demonstrates that labile P is high when Al is low and that labile P is low when Al is high. This interaction suggests that Al strongly influences sorption. Incubation studies commonly show that sorption is highly correlated to extractable or exchangeable Al (Parfitt 1978). However, our results for Al (Fig. 3) represent the total bulk concentration of Al rather than exchangeable; thus, we cannot compare sorption correlations of extractable or exchangeable Al discussed in other studies.

Moderately labile P

In this study, moderately labile P was predicted by Al, Fe, and Mg concentrations. We interpret the first term in the regression (Al & Fe Intermediate) to indicate the presence of secondary mineral oxides along with kaolinite that formed by alteration in the bedrock or by weathering before deposition. High concentrations of Al & Fe are associated with relatively high percentages of moderately labile P (Fig. 3). In clays, high concentrations of Al & Fe indicate deeply weathered materials. Although weathered products are not generally considered

components of Aridisols and Entisols, the sedimentary bedrock units, which now produce the young soils examined here, contain minerals that formed under intense weathering conditions or other types of post-depositional alteration.

Al and Fe oxides may be present in the soil samples, but their controls on moderately labile P may differ. Other researchers working in this study area have identified hematite mostly as coatings on silt- and sand-sized particles (Goldstein et al. 2005; Reynolds et al. 2006). Hematite coatings sorb far less P than discrete particles of hematite (Hamad et al. 1992), perhaps explaining why Al is a much better predictor for the moderately labile fraction. Al-rich materials may include silicates, such as allophane or phyllosilicates, such as kaolinite. Several members of the Chinle Formation contain volcanic ash deposits that weather into allophane (Benson et al. 1952). Allophanes ultimately weather into aluminosilicate clay materials, such as kaolinite (Parfitt 1990).

The association of oxides with the moderately labile P fraction suggests that the size of the fraction is dependant, at least in part, on pH values. The pH controls the capacity of oxides to sorb P as well as the types of bonds that are formed (Subramanian et al. 1988; Van Emmerik et al. 2007). Oxides tend to form outer sphere complexes under higher pH conditions, and inner sphere complexes under low pH conditions (Van Emmerik et al. 2007). Ligand exchange and precipitation reactions are generally irreversible; therefore, all moderately labile P held by oxides must be held in an outer sphere complex. The pH values of our soils are close to, or below, the point of zero charge (PZC) expected in a mixed oxide soil (Parks and Bruyn 1962; Subramanian et al. 1988).

In addition to oxides, kaolinite may stabilize P in the moderately labile fraction. High concentrations of Al and Fe are associated with kaolinite, as there is very little isomorphic substitution in the clay matrix. XRD confirms the presence of kaolinite in all soil samples except one (Table 3). Similar to oxides, sorption by kaolinite is heavily influenced by pH, but several other factors affect sorption. Kaolinite may absorb P or form inner sphere complexes with the Al–OH sites available at the edges of crystals. The bonding mechanism is influenced by pH such that inner sphere complexes increase as pH decreases (Baryosef et al. 1988; Van Emmerik et al. 2007). Sorption capacity of kaolinite is limited by the

surface area of the crystal edges and the number of Al–OH sites (Van Emmerik et al. 2007); thus, finer particle sizes increase sorption capacity (Black 1943). Hematite coatings on kaolinite decrease sorption as the coatings increase flocculation (Ioannou et al. 1996). Finally divalent exchange ions (e.g., Ca^{2+}) create higher sorption maxima (Baryosef et al. 1988; Pissarid et al. 1968).

The results for moderately labile P point to the influence of Mg that we interpret as an indicator for 2:1 silicates (i.e., smectites). Magnesium correlates highly with fine textures, suggesting that the bulk of Mg may be found in clay-sized particles. The presence of Mg in clays indicates relatively unweathered soils in which isomorphic substitution is still prominent (Brady and Weil 2002). Magnesium could be part of the clay lattice structure or represent ions in the diffuse double layer outside the clay-particle surface. Magnesium concentration as an exchange ion increases the sorption maximum for kaolinites (Pissarid et al. 1968). The Mg term is negative in the regression, and it thus does not likely represent Mg as an exchange ion but rather Mg in the clay lattice.

Occluded P

The results suggest that the occluded P fraction is initially dominated by 2:1 clays (illites, or smectites), which we found in every soil. Occluded P values were strongly predicted by low Al & Fe concentrations and high Mg concentrations. In clays, low percentages of Al and Fe are associated with 2:1 minerals either due to isomorphic substitution or high levels of cations adsorbed to the surface of the particle. In several other dryland soils, sorption capacity was highly predicted by clay concentration (Samadi and Gilkes 1999; Solis and Torrent 1989), although the clay species were not identified. Sorption of phosphates by 2:1 materials is well established (Baryosef et al. 1988; Ioannou et al. 1994; Kasama et al. 2004; Traina et al. 1986). We suspect that several samples may represent mixed-layer clays or interlayered clays. In these cases, P may be bonding with Al interlayers. XRD results suggest the presence of interlayers in some samples, but results were not conclusive.

Controls on P sorption in 2:1 materials include pH, exchange ion, and ion strength. As pH decreases, sorption of P increases (Baryosef et al. 1988). Like

kaolinites, 2:1 materials have greater sorption capacity when the exchange ion is divalent (Pissarid et al. 1968). When the exchange ion is dominantly Mg, illite sorption capacity is almost twice that of sorption capacity by smectite (Pissarid et al. 1968). When surrounded by monovalent ions, smectites exhibit negative adsorption, whereas illite clays sorb P anions (Pissarid et al. 1968). Unlike kaolinites, 2:1 materials do not desorb P when conditions change. Although P develops bonds to these materials that are irreversible, 2:1 materials are inherently unstable and therefore likely to degrade through time.

Implication for landscape scale P

The Walker and Syers (1976) general model of pedogenic changes in P transformations may not reflect the gradations of P forms observed in some dryland areas or in soils derived from sedimentary bedrock. Walker and Syers suggested that moderately labile P fractions dwindle as soils weather and that oxide concentrations eventually dominate the pool of occluded P (Cross and Schlesinger 1995; Walker and Syers 1976). Our data suggest a different pattern in P transformations where oxides may weather directly from sedimentary rocks along with P, as opposed to developing as a result of pedogenesis. We found that oxides and 1:1 phyllosilicates were associated with the moderately labile P fraction as opposed to the occluded P fraction. This is an important deviation from the Walker and Syers model because our study focused on immature soils that represent the initial condition of P fractions prior to extensive pedogenesis.

The soils of southeastern Utah (and other dryland settings) differ functionally from the wetter environments where the general Walker and Syers model has been tested. In the Walker and Syers model, leaching diminishes soil carbonates through time and soils become more acidic. In contrast, semiarid areas tend to accumulate carbonate over time and form distinct horizons known as caliche (Schlesinger 1985). Our results suggest that moderately labile P is initially stabilized by oxides and 1:1 clays; however, these bonds will destabilize as carbonates accumulate and pH increases (Baryosef et al. 1988). Moderately labile P may gradually become associated with carbonate as pedogenesis progresses and as fine-grained secondary carbonates build up in the soil profile. We theorize that pedogenic carbonates may ultimately serve as the

reservoir for moderately labile P (Carreira et al. 2006). In several dryland studies, carbonates are associated with moderately labile P (Bertrand et al. 2003; Carreira and Lajtha 1997; Carreira et al. 2006; Lajtha and Bloomer 1988; Lajtha and Schlesinger 1988b). In contrast to previous studies (Lajtha and Schlesinger 1988a), however, we found that carbonate values are poor predictors for all P fractions illustrating the importance of understanding bedrock chemistry and mineralogy for predictions of soil P availability. Though several of our soils weathered from carbonate materials, we suspect that large particle sizes in these soils prevented P from developing calcium phosphates (Carreira et al. 2006).

Finally, the Walker and Syers model may not accurately assess the trajectory of the moderately labile P fractions in drylands. They suggest that the moderately labile P fraction diminishes over time while the occluded P fraction increases (Walker and Syers 1976). However, several dryland studies show that the size of the moderately labile P fraction is similar to, if not larger, than that of the occluded P fraction further emphasizing the importance of this pool in arid soils. (Carreira et al. 1997; Cross and Schlesinger 1995; Lajtha and Schlesinger 1988a).

Conclusion

We examined P fractionation in a diverse set of young, poorly developed soils and applied chemical and textural statistical analysis to determine the minerals associated with each fraction. The results suggest that P fractionation in these soils differs from previously published results. We find that labile P concentrations are determined by the absence of specific minerals or groups of minerals that would otherwise stabilize PO_4^{3-} . Moderately labile P fractions are associated with Al and Fe oxides and minerals, such as kaolinite. Although oxides are typically associated with stronger ligand exchange bonds, the moderately labile fraction is apparently held with weaker chemical associations and is, therefore, susceptible to changes in pH. Occluded P is associated with 2:1 clays. Some of these materials may represent mixed-layer clays with Al interlayers.

On the landscape scale, the mechanisms involved in P stabilization vary with pedogenesis (Smeck 1985; Walker and Syers 1976). In drylands, the

stabilized P transitions may differ from transitions observed in mesic environments. Based on literature about dryland settings (Lajtha and Schlesinger 1988a), we theorize that as pedogenic carbonate develops, soil pH will increasingly destabilize oxide-P associations and will facilitate P sorption onto pedogenic carbonates. These changing conditions may explain the importance of carbonate in stabilizing soil P in some dryland settings (Lajtha and Bloomer 1988; Lajtha and Schlesinger 1988a). Occluded P, initially associated with 2:1 clays, will likely destabilize and may release P or may decompose into P-bearing oxide minerals. Collectively, these complex and variable relations among P forms, soil mineralogy, and soil chemistry highlight the diversity of potential P stabilization mechanisms in dryland soils. The study area in southwestern Utah is well-suited to this analysis because of the high degree of substrate variation in small areas that are otherwise similar in ecological and physiographic characteristics. In this sense, this study area represents a microcosm of the range of potential soil P stabilization mechanisms that control the cycling of this important element in dry, temperate ecosystem.

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