



Biological and geochemical controls on phosphorus fractions in semiarid soils

ANNE FERNALD CROSS^{1,3*} and WILLIAM H. SCHLESINGER^{1,2}

¹Department of Botany, Duke University, Durham, NC 27708; ²Nicholas School of the Environment, Duke University, Durham, NC 27708; ³Current address: Department of Botany, Oklahoma State University, Stillwater, OK 74078, U.S.A.

(*author for correspondence, e-mail: afcros@okstate.edu)

Key words: desert soils, New Mexico, sequential P fractionation, soil organic phosphorus, soil phosphorus

Abstract. This study examined the concentration of organic and inorganic phosphorus in surface soils of a *Bouteloua gracilis*-*Bouteloua eriopoda* grassland, and a *Larrea tridentata* shrubland, in the northern Chihuahuan Desert, New Mexico, USA. In this desert where the grassland vegetation has a uniform spatial distribution and individual shrubs have a patchy spatial distribution across the landscape, vegetation strongly influences the distribution of soil nutrients. Most studies of soil phosphorus fractions in desert soils have focused primarily on inorganic P fractions and have demonstrated the importance of geochemical controls on soil P cycling. The research presented here addressed the question of whether organic phosphorus, determined by the presence of different vegetation types, also contributes to soil P cycling. Within soils of similar age, topography, parent material, and climatic regime, samples were collected under and between vegetation and analyzed for P fractions following a modified sequential fractionation scheme. Most soil inorganic P was found in the HCl- and cHCl-extractable forms in both the grassland and shrubland soils, indicating CaCO₃ control over phosphorus availability. In contrast, most soil organic P was bound to Al and Fe minerals. Labile, plant-available P fractions summed to 9.5% of total P in the grassland and 6.1% in the shrubland. Organic P comprised 13.3% of the total phosphorus pool in the grassland and 12.0% in the shrubland. Our results show that the organic P pool may represent an important, yet often overlooked, source of P in semiarid ecosystems.

Introduction

In desert ecosystems, phosphorus limits net primary production after plant requirements for water and nitrogen have been satisfied (Crawford & Gosz 1982; Skuijins 1991; Tiessen 1995). Lajtha and Schlesinger (1988) showed that geochemical processes dominate P cycling in semiarid soils when calcium carbonate (CaCO₃) is abundant in the soil profile. Ligand exchange between P and carbonate minerals limits P availability in desert soils, and

the precipitation of phosphate with calcium establishes the upper limit for the availability of P (Lajtha & Bloomer 1988). Competition from organic anions for adsorption sites on calcite may increase the availability of P in the soil solution (Holford et al. 1990); but, semiarid soils lack appreciable levels of organic matter. Thus, while geochemical controls probably restrict the pool of labile, biologically-available phosphorus in desert soils, biological influences, such as the distribution of vegetation, may also contribute to P cycling, particularly of organic P in semiarid soils.

Our previous research in the Chihuahuan Desert of New Mexico indicates that plants have a uniform spatial distribution in semiarid grasslands and a heterogeneous spatial distribution in shrublands (Cross 1994; Cross & Schlesinger 1999). In desert shrublands, biological activity tends to be concentrated under the canopy of individual shrubs, rather than in the spaces between shrubs (Schlesinger & Pilmanis 1998). 'Islands of fertility' form under individual shrubs by the accumulation of wind-blown materials and nutrients recycled from plant litter, creating local hotspots of biological activity (Garcia-Moya & McKell 1970; Charley & West 1975, 1977; Burke 1989). Geostatistical analyses reveal that the distribution of vegetation in desert shrublands influences the scale of soil nutrient heterogeneity (Schlesinger et al. 1996). For P, water-extractable forms exhibit near-random distribution in semiarid grasslands, but high degrees of spatial autocorrelation in shrublands (Schlesinger et al. 1996). Creosotebush (*Larrea tridentata*) creates favorable conditions for microorganisms under its canopy by protecting understory soils from high temperatures and desiccation, and by retaining soil nitrogen and organic matter (Garcia-Moya & McKell 1970; Kieft et al. 1998). Greater microbial biomass and activity is found under shrubs (Rostagno 1989; Gallardo & Schlesinger 1995; Zaady et al. 1996). These islands may also influence the biogeochemical cycle of organic P in semiarid ecosystems.

Organic P (Po) influences P availability by contributing to the labile inorganic P pool, which is important to net primary production in many ecosystems (Tate & Salcedo 1988). Bowman and Cole (1978) and Stewart and Tiessen (1987) suggest that organic P fractions may be important pools of biologically-available P in grasslands, because Po is more mobile than inorganic P, which is readily fixed by mineral surfaces (Frossard 1989). The purpose of our research was to characterize biological influence on soil P fractions, estimate labile phosphorus pools, and quantify the organic phosphorus content of soils – of similar age, topography, climatic regime, and parent material. Because our previous research in the Chihuahuan Desert (Cross & Schlesinger 1999) showed higher levels of organic matter in grassland sites and under creosotebush shrubs, we expected that concentrations of labile and

Table 1. Vegetation and soil characteristics in the grassland and shrubland plant communities. Significant differences for a pairwise *t*-test ($P = 0.05$) between grassland and shrubland are indicated by the different superscript letters (modified from Cross & Schlesinger 1999)

Site	Plant cover %	Plant biomass (g m ⁻²)	pH	CEC (cmol _c kg ⁻¹)	Sand %	Silt %	Clay %
Grassland	58.46 ^a	405.03 ^a	7.5	10.0 ^a	83.28 ^a	8.05 ^a	8.68 ^a
Shrubland	41.55 ^b	252.56 ^b	7.8	13.3 ^b	63.95 ^b	26.10 ^b	10.70 ^b

organic P would be greatest in grassland soils, and localized under individual plants in the shrubland.

Methods

Field collections

We established four 10 × 10-m plots in grassland and shrubland habitats near the Five Points area of the Sevilleta Long Term Ecological Research Site (LTER) in the northern Chihuahuan Desert, New Mexico, USA. All plots were located several kilometers west of the Los Pinos Mountains – an isolated fault block derived from metasedimentary rocks of Precambrian origin (Johnson 1988). Alluvial materials from the Los Pinos have contributed to soil development along the desert piedmont underlying these plant communities. Haplargid soils containing a calcic horizon within 1 meter of the surface and a 15-cm thick argillic horizon, which has developed through illuviation of silicate clay, underlie the grassland sites (Gile et al. 1981; Southard & Southard 1985). Calciorthid soils, where the pedogenic calcic horizon is at or near the surface as result of loss of surface horizons by erosion, following shrub invasion, underlie the shrubland sites (Kieft et al. 1998). The Calciorthids originated from rhyolitic tuff and lava, exhibited a gravel-like sandy loam texture, and had a carbonate content of 10–20% (Johnson 1988). Soil properties differ between the grassland and shrubland sites (Table 1). Additional information on local environmental conditions and other soil attributes may be found in Cross (1994) and Cross and Schlesinger (1999).

In the grassland, paired plots (two plots separated by 50-m) were located at sites where *Bouteloua eriopoda* (Torr.) Torr. (Black grama) and *B. gracilis* (H.B.K.) Lag. ex Steud. (Blue grama) dominate. In the shrubland, paired plots were located in areas dominated by *Larrea tridentata* D.C. (Cov.) (creosote-bush). In 1989, we collected a total of 40 soil samples to 10-cm depth in

grassland and shrubland plots following a random stratified design and noted whether samples were taken under or between vegetation. All soil samples were air-dried and sieved through a 2-mm sieve prior to analysis. Although Lajtha and Schlesinger (1988) reported significant differences in phosphorus values from unground and ground samples, they suggested that using ground samples for the fractionation may overestimate labile fractions by exposing the phosphorus held in the internal structure of crystalline minerals. Thus, we used unground soils for the fractionation.

Laboratory analyses

Phosphorus was extracted using a modified sequential Hedley fractionation (Tiessen et al. 1984; Tiessen & Moir 1993). A 2-g soil sample was placed in a 50-ml plastic centrifuge tube with 30 ml of deionized water and a 2.5-cm² anion exchange membrane (AR-204UZR-412 Ionics, Watertown, MA) (Abrams & Jarrell 1993; Cooperbrand & Logan 1994). Samples were shaken end-over-end for 16 hours at 25 °C. The anion-exchange membrane was removed and phosphorus retained on the membrane was eluted by shaking the strip with 30 ml of 1M HCl for 4 hours (resin-extractable P). Subsequently, the remaining soil sample was extracted with 30 ml of 0.5M NaHCO₃ (pH 8.5) in the 50-ml centrifuge tube (bicarbonate-extractable P). This process was repeated with increasingly stronger reagents to remove the more tightly bound P using NaOH (hydroxide-extractable P), HCl (HCl-extractable P), cHCl (concentrated HCl P), and H₂SO₄-H₂O₂ (residual P). The NaHCO₃, NaOH, and cHCl extracts were divided and half of the sample was digested with H₂SO₄-H₂O₂ in order to determine total P. For these extracts, organic P was calculated by subtraction. All extracts were analyzed for orthophosphate with the Total Phosphorus procedure for the TRAACS 800 Autoanalyzer (Murphy & Riley 1962; Technicon Bran-Luebbe 1987). Recovery of organic P from standards mixed with fructose-6-phosphate was (78–95%) ($r^2 = 0.997$). Total P values calculated from the sum of the individual fractions following Tiessen and Moir (1993), averaged 4.5% less than total P values for a subset of samples digested for only total P.

Unlike the chemistry of other soil nutrient elements, descriptions of soil P chemistry rely on operational definitions. We follow the current practice of distinguishing P fractions by the extract. Correspondence between current and traditional terminology – labile, non-occluded, occluded, and residual – is discussed by Cross and Schlesinger (1995). Resin P represents P that is both readily exchangeable inorganic P (Pi) and P that is easily dissolved from solid phases in the soil (Tiessen & Moir 1993). The bicarbonate-P extract is thought to simulate the action of plant roots in dissolving P minerals and to give an index of plant-available P (Olsen et al. 1954). Both the resin- and

bicarbonate-extractable P are considered to be plant- and microbe-available in the short-term. The hydroxide-P extract is thought to remove P that is associated with the surface of amorphous and some crystalline Al and Fe minerals and is probably available in the intermediate-term. Organic P (Po) in the bicarbonate extract is thought to be derived from organic compounds that are readily mineralized by microbes, while Po in the hydroxide extract represents more stable P that is involved in the intermediate-term P transformations in soils. The remaining P extracts (HCl, cHCl, and $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$) represent P that is available over long time periods (Cross & Schlesinger 1995). The HCl fraction represents P associated with calcium carbonate minerals, and the cHCl extract removes Pi and Po that is bound in the interior of Fe and Al minerals and apatite (Tiessen & Moir 1993). The residual P represents the most stable form of P that is available only in the long term, if at all (Cross & Schlesinger 1995).

We also analyzed all soil samples for total N, total organic C, K, Ca, Mg, $\text{SO}_4\text{-S}$, Na, and Cl. We considered N, P, and K to be plant-limiting, essential elements, Ca, Mg, and $\text{SO}_4\text{-S}$ to be non-limiting but essential elements, and Cl and Na to be non-essential, non-limiting elements. Sulfate and Cl were extracted by shaking a 6-g soil sample in 30-ml of deionized H_2O for 30 minutes (Schlesinger et al. 1996). The extract was filtered through a $0.45\text{-}\mu\text{m}$ Millipore filter, and analyzed with a Dionex 2010i ion chromatograph. Cations were extracted by shaking a 10-g soil subsample with 50 ml of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (ammonium acetate) at pH 7.0 (Schlesinger et al. 1996). The extract was filtered gravimetrically through a #40 Whatman filter and analyzed with a Perkin Elmer 3100 Atomic Absorption Spectrophotometer. Ground soil samples were analyzed for total organic carbon, following the removal of CaCO_3 , and total nitrogen at the Chemical Analysis Laboratory at the University of Georgia, Athens, GA, using a Carlo-Erba CHN Analyzer and for soil texture by the Soils Testing Laboratory at Colorado State University, Ft. Collins, CO (Jackson 1958). All soil element data are reported as μg element / g soil.

Statistical analyses

Data were analyzed with a pairwise *t*-test to compare P fractions in the grassland and shrubland soils, using soil samples as replicates. *A priori* tests showed no statistically significant differences between plots within each plant community. An additional pairwise *t*-test was conducted to determine whether vegetative cover in the two plant communities influenced soil P distribution. Because organic P content may be related to the concentrations of other elements and to soil texture, we conducted a Spearman Rank correlation of total Po against concentrations of other elements. We also conducted cor-

Table 2. Mean soil phosphorus concentrations by fraction in grassland and shrubland soils listed as $\mu\text{g P/g soil}$. Means were averaged from 20 soil samples in each vegetation type. A pairwise *t*-test was conducted with 19 degrees of freedom. S/G indicates the ratio of each P fraction in the shrubland to that in the grassland. Fractions are listed in order of fractionation scheme (after Tiessen & Moir 1993). Descriptions of traditional P fractions may be found in Cross & Schlesinger (1995)

P extract	Grass	Shrub	S/G	<i>t</i> -statistic	<i>P</i> value	Fraction
Resin Pi	13.2	6.1	0.5	5.707	0.0001	soil solution
Bicarb Pi	3.5	10.8	3.1	-17.28	0.0001	labile
Bicarb Po	1.3	3.2	2.5	-10.00	0.0001	labile
NaOH Pi	11.1	9.8	0.9	2.535	0.0202	non-occluded
NaOH Po	3.8	3.4	1.0	-0.1879	0.8529	non-occluded
HCl	79.3	196.1	2.5	-13.50	0.0001	non-occluded
cHCl Pi	32.3	35.0	1.1	-2.814	0.0111	non-occluded
cHCl Po	20.3	33.5	1.7	-9.207	0.0001	non-occluded
Residual P	26.7	39.1	1.5	-6.246	0.0001	occluded
Total P	191.5	337.5	1.8	-15.14	0.0001	
Total Pi	166.1	296.8	1.8	-12.25	0.0001	
Total Po	25.5	40.6	1.6	-14.33	0.0001	

relations of bicarbonate-, NaOH-, and cHCl-extractable Po against total N, C, K, Ca, Mg, $\text{SO}_4\text{-S}$, Na, and Cl separately for the grassland and shrubland samples. We conducted a correlation of total Po versus the percentages of sand, silt, and clay. *T*-tests and correlation analyses were conducted with DataDesk 6.0 (DataDescription, Ithaca, NY).

Results

For these semiarid soils, the labile P fractions – resin Pi, and bicarbonate Pi and Po – summed to 9.4% of total P in the grassland and 6.0% in the shrubland (Table 2; Figure 1). The hydroxide fractions accounted for 7.8% of total P in the grassland and 4.0% of total P in the shrubland. The largest fraction in both vegetation types was the CaCO_3 -bound, HCl-extractable P (Table 2; Figure 1), which comprised 41.4% of the total phosphorus pool in the grassland and approximately half of the total phosphorus pool in the shrubland (58.1%). The more recalcitrant forms, cHCl Pi, cHCl Po, and residual P, accounted for 41.4% of total P in the grassland and 31.9% in the shrubland (Table 2; Figure 1). The sum of organic fractions made up only a

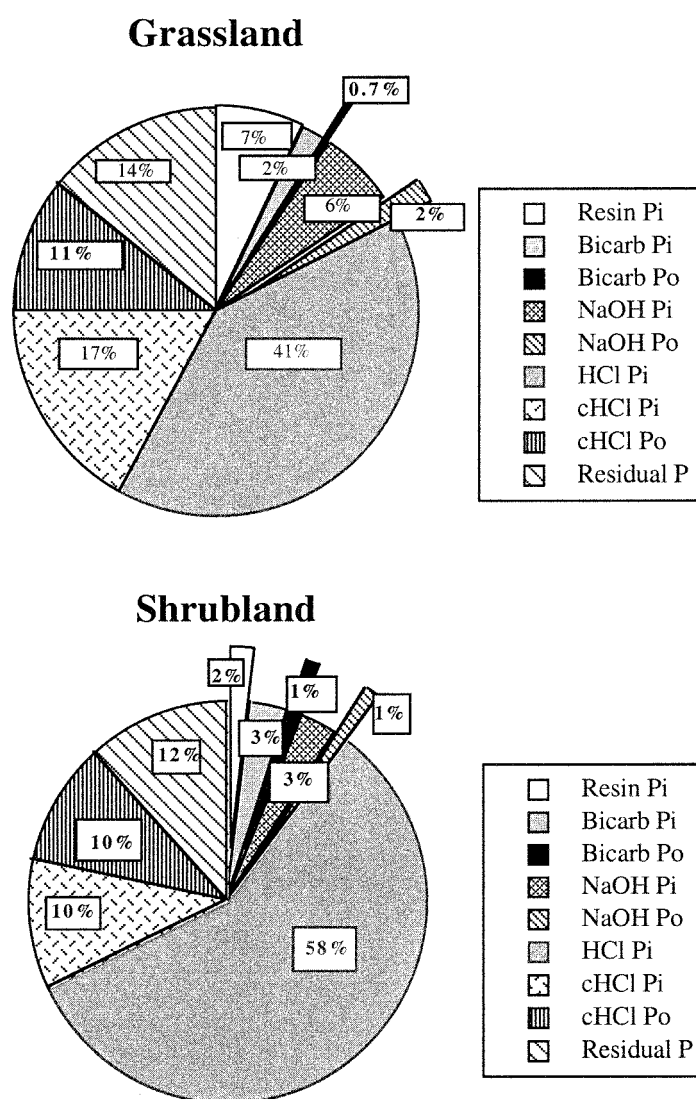


Figure 1. Soil phosphorus fractions in grassland and shrubland soils (N = 20 soil samples / vegetation type).

small portion of the total phosphorus pool, comprising 13.3% in the grassland and 12.0% in the shrubland.

Pairwise *t*-tests indicated a marked difference between grassland and shrubland communities for most P fractions, with the exception of NaOH-extractable organic P (Table 2). Most fractions, except resin-extractable P

Table 3. Influence of plant cover on soil phosphorus fractions under and between grasses and shrubs. Averages were calculated on 10 soil samples in each vegetation class. Superscript letters that are the same for each extract indicate a lack of significant difference between mean values within each vegetation type (paired *t*-test, *P* = 0.05). All values are reported as $\mu\text{g P / g soil}$

P extract	Grass under	Grass between	Shrub under	Shrub between	Fraction
Resin Pi	11.37 ^a	14.94 ^a	7.19 ^b	4.95 ^b	soil solution
Bicarb Pi	3.50 ^a	3.53 ^a	11.53 ^b	10.13 ^b	labile
Bicarb Po	1.42 ^a	1.25 ^a	3.68 ^b	2.79 ^c	labile
NaOH Pi	10.90 ^{ab}	11.32 ^a	9.95 ^{bc}	9.67 ^c	non-occluded
NaOH Po	4.39 ^a	3.11 ^b	5.16 ^{ab}	2.63 ^b	non-occluded
HCl	82.99 ^a	75.62 ^a	188.01 ^b	204.12 ^b	non-occluded
cHCl Pi	32.52 ^{ab}	32.08 ^a	33.96 ^{ab}	35.98 ^b	non-occluded
cHCl Po	20.30 ^a	20.48 ^a	31.21 ^b	35.84 ^b	non-occluded
Residual P	26.00 ^a	27.34 ^a	36.31 ^b	41.89 ^c	occluded
Total P	193.98 ^a	189.66 ^a	327.00 ^b	349.99 ^b	
Total Pi	167.28 ^a	164.83 ^a	286.96 ^b	306.73 ^b	
Total Po	26.10 ^a	24.84 ^a	40.05 ^b	41.27 ^b	

and NaOH-extractable Pi, showed greater concentrations in the surface soils of the shrubland than in the grassland. The HCl-extractable fractions (HCl-extractable Pi + cHCl-extractable Pi and Po), which made up approximately 78% of the total P pool in both vegetation types, showed the strong control that geochemical reactions exert on soil P availability in this desert (Table 2; Figure 1). The small pools of biologically-available P – resin-extractable P, bicarbonate-extractable Pi and Po, and NaOH-extractable Po – clearly differed between vegetation types (Table 2), but showed little influence of plant cover in each community (Table 3; Figure 2).

In the grassland, all fractions, except for NaOH-extractable Po, were equally distributed under and between vegetation (Table 3; Figure 2). Only one fraction showed a significant difference between under and between vegetation in the shrubland – bicarbonate Po (Figure 2). This labile P fraction was positively associated with the higher concentrations of organic carbon and total N content under shrubs. The more stable P fractions, which were associated with CaCO_3 and Al- and Fe minerals (HCl-extractable and cHCl-extractable P), were equally distributed under and between shrubs.

The relationship between soil chemistry and total Po was shown by correlation analysis of total organic P (bicarbonate-extractable Po + NaOH-

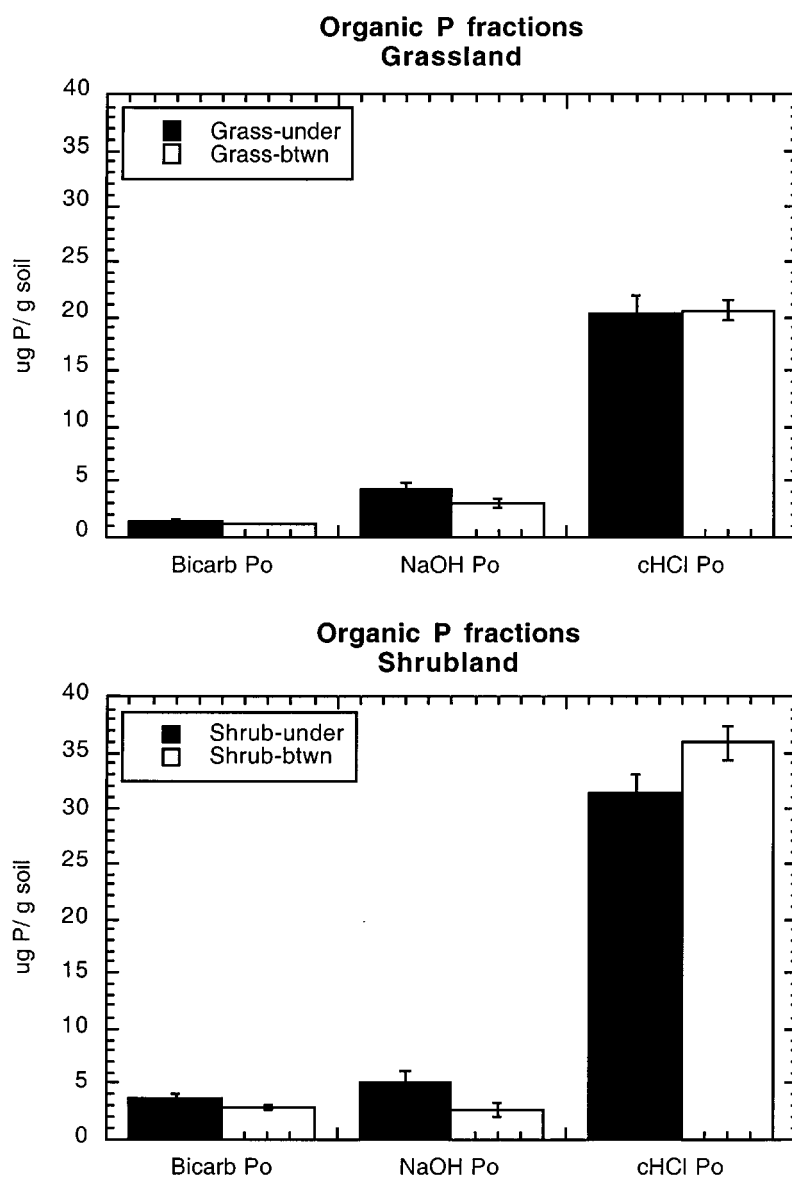


Figure 2. Organic P fractions distribution in grassland and shrubland soils (N = 10 soil samples / location). Location signifies under or between individual grassland or shrubland plants.

Table 4. Spearman Rank correlation coefficients between fractions of organic P, individual soil elements, and soil texture. TPo = total Po

Po fraction	% of TPo	N	C	K	Ca	Mg	SO ₄	Cl	Na	Sand	Silt	Clay
Grass and Shrub												
Total Po	100	0.646	0.534	0.700	0.902	0.285	0.675	0.154	-0.253	-0.908	0.904	0.692
Grass												
Bicarb Po	5	0.552	0.379	0.350	0.258	-0.0505	0.254	0.400	0.011			
NaOH Po	15	0.404	0.456	-0.112	0.314	0.2121	-0.007	-0.220	0.460			
cHCl Po	80	0.651	0.502	-0.019	0.652	0.0311	-0.129	0.050	0.657			
Total Po	100	0.723	0.555	0.326	0.589	0.0820	-0.027	0.071	0.488			
Shrub												
Bicarb Po	8	0.478	0.492	0.301	-0.280	-0.078	0.062	0.488	-0.197			
NaOH Po	8.5	0.519	0.359	0.334	-0.532	-0.275	-0.051	0.387	-0.300			
cHCl Po	83.5	-0.073	-0.105	0.033	0.796	0.772	0.449	0.052	-0.104			
Total Po	100	0.124	0.089	0.317	0.631	0.833	0.458	0.138	-0.311			

extractable Po + cHCl-extractable Po) and other soil elements in the grassland and the shrubland soils (Zar 1984) (Table 4). Exchangeable Ca was the element most highly correlated with total Po, but other biologically important elements – those often found in relatively constant ratios with P in soil organic matter (N, C, and S) – were also positively correlated with soil Po concentrations (Table 4). In contrast to K, which is strongly associated with Po, other highly mobile elements (e.g. Na, Cl) were not strongly associated with soil organic matter and showed little relation to soil Po (Table 4). These data suggest that available Ca may be associated with organic P, as well as inorganic P fractions (Lajtha & Schlesinger 1988). In soils under both vegetation types, Po extractable with concentrated HCl comprised approximately 80% of total soil Po; whereas, the labile Po (bicarbonate-extractable) made up between 5 and 8 percent, and the Al- and Fe-associated (NaOH-extractable) Po made up 8.5 to 15 percent of total soil Po (Table 4).

Correlation analysis showed relationships between the percentages of sand, silt, and clay in the soils and total Po content (Table 4). Grassland values were sand (79–90%), silt (4–11%), and clay (7–11%) and shrubland values were sand (61–75%), silt (21–31%), and clay (4–13%). Total Po was negatively correlated with sand content and positively associated with both clay and silt levels.

Discussion

The availability of P in most ecosystems depends on soil properties that regulate P availability, such as mineralogy of the parent material, leaching rates, and soil texture (Tiessen et al. 1984; Roberts et al. 1985; Stewart & Tiessen 1987; Anderson 1988). In desert soils, phosphorus availability to plants and microbial biomass is determined by the labile, surface-adsorbed phosphate, rather than the CaCO₃-bound, crystalline forms (Murrman & Peach 1969). The availability of crystalline forms is minimal owing to the low surface area of calcium phosphates, which are mainly present as sand and silt-sized particles (Chu & Chang 1966; Stewart & Tiessen 1987). In most soils, soil texture is central to soil phosphorus availability (Roberts et al. 1985; Anderson 1988). Often, clay content correlates with soil organic carbon and phosphorus, because a high sand content allows a higher rate of phosphate leaching as water percolates through the soil (Jenny 1980; Nichols 1984; Anderson 1988).

The percentages of phosphorus that reside in the inorganic fractions in the Aridisols of the Chihuahuan Desert are similar to those found in other Mollisols and Aridisols with similar vegetation (Table 5; Sharpley et al. 1987; Lajtha & Schlesinger 1988). Surface soils contain small pools of

Table 5. Percentage Pi and Po of total P values for various Mollisols and Aridisols from the U.S. and Canada

Soil Class	Species	Resin Pi	Bicarb Pi	Bicarb Po	NaOH Pi	NaOH Po	HCl Pi	Resid P	cHCl Pi	cHCl Po	Study*
Haploboroll	<i>B. gracilis</i>	3.2	1.2	1.7	3.9	7.9	41.7	40.2	•	•	[1]
Haploboroll	<i>B. gracilis</i>	2.7	1.3	2.1	3.8	7.9	35.0	47.3	•	•	[1]
Mollisol	<i>B. gracilis</i>	• [†]	•	5.0	•	33.1	•	12.3	•	49.6	[2]
Mollisol	<i>B. gracilis</i>	•	•	7.8	•	44.4	•	11.0	•	36.8	[2]
Haplargid	<i>B. eripoda</i>	2.1	0.4	•	1.1	•	73.2	23.2	•	•	[3]
Haplargid	<i>L. tridentata</i>	3.6	0.5	•	0.7	•	69.0	20.2	•	•	[3]
Mollisol	<i>B. gracilis</i>	8.1	4.4	4.2	6.9	11.6	28.5	0.0	9.1	25.5	[4]
Mollisol	<i>B. gracilis</i>	1.5	2.0	0.9	2.0	11.6	34.3	45.6	•	•	[5]
Mollisol	<i>B. gracilis</i>	3.6	1.9	1.4	2.1	6.9	37.2	45.4	•	•	[5]
Mollisol	<i>B. gracilis</i>	3.5	2.3	1.3	2.7	10.8	33.2	44.2	•	•	[5]
Haplargid	<i>B. gracilis</i>	7.0	1.9	0.7	5.9	2.0	40.5	14.3	17.1	10.8	[6]
Calciorthid	<i>L. tridentata</i>	1.9	3.3	1.0	3.0	1.2	54.6	10.5	11.3	10.0	[6]

*Study authors [1] Schoenau et al. 1989, [2] Bowman & Cole 1978, [3] Lajtha & Schlesinger 1988, [4] Tiessen & Moir 1993, [5] Roberts et al. 1985, [6] This study.

[†]Data were not included in the original data set in the literature.

labile P (resin- and bicarbonate-extractable) and non-occluded P (NaOH-extractable), and large pools of occluded and carbonate-bound P (cHCl- and HCl- extractable and residual) (Figure 1). In these soils, the largest pool of P is the CaCO_3 -bound, acid-extractable P. This fraction reflects the geochemical influence on P cycling that is dominated by high concentrations of calcium carbonate minerals in the surface soils. Comparisons of P pools in the grassland and shrubland, show greater concentrations of NaOH-extractable forms in the grassland, and higher levels of the acid-extractable forms in the shrubland. This reflects the greater abundance of Al- and Fe-rich minerals in the argillic horizon of the grassland, and the abundance of calcite in the surface soils of the shrubland.

The presence of organic P in desert soils is well established (Jenny 1941). Certain fractions of organic P represent relatively labile pools of phosphorus that are accessible to plant and microbial populations (Haas et al. 1961; Wild & Oke 1966; Dormaar 1972; Halm 1972; Dalal 1977). Organic P may be mineralized to inorganic P by simple autolysis or enzymatic phosphorylation, and become plant-available (Cosgrove 1977). Mineralization of organic P provides a large portion of the plant-available P in most soils; however, field or laboratory measurements of this pool are difficult because microbial mineralization and immobilization of organic P typically occur simultaneously (Halstead & McKercher 1975; Dalal 1977; Stewart & Tiessen 1987). The availability of P in soil organic matter depends primarily on seasonal patterns of precipitation and temperature, which affect microbial activity and mineralization (Eid et al. 1951; Dormaar 1972; Westin 1978; Magid & Neilsen 1992).

The propensity for inorganic phosphorus (P_i) to form insoluble compounds in soils renders it highly immobile and largely unavailable to biota (Johnson & Cole 1980; Bolin et al. 1983; Ramirez and Rose 1992). By releasing organic acids (e.g., oxalate) from roots and mycorrhizae, plants can increase the rate at which phosphorus is derived from soil minerals by chemical weathering (Jurinak et al. 1986; Fox & Comerford 1992; DeLucia et al. 1997). Phosphate is then available for uptake by vegetation, but the transformations of P from soluble to solid forms and uptake by microorganisms often limit P supply (Oglesby & Bouldin 1984). Thus, the availability of inorganic P to plants largely depends on two factors – microbial decomposition of plant litter (Parton et al. 1987), and the pools of exchangeable and organic P in the soil (Tate and Salcedo 1988).

Overall, the Chihuahuan Desert soils of the Sevilleta have extremely low contents of organic phosphorus (Table 5). In other Mollisols and Aridisols, bicarbonate-extractable P_o concentrations average 2.9% of total P, but this fraction accounts for 0.7% of total P in grassland soils at the Sevilleta

and 1.0% of total P in the shrubland. Bicarbonate-extractable Po represents phosphorus that is held in the soil by adsorption to soil particles or soil organic matter (Bolan 1991). A more striking difference is seen in the NaOH-extractable Po, which averages 15.4% of total P in many soils (Table 5), whereas in Sevilleta soils this fraction is 2.0% of total P in the grassland and 1.2% in the shrubland. NaOH-extractable Po is bound to Al or Fe minerals, which are found in the surface horizons of the grassland and likely transported by wind to the shrubland, where they accumulate under individual shrubs (Cross & Schlesinger 1999). The CHCl -extractable organic P averages 10% of total P at the Sevilleta, but can comprise up to nearly 50% in other similar soils (Table 5). The Po extracted with CHCl is thought to be tightly bound to Fe and Al minerals (Tiessen & Moir 1993), and perhaps is unavailable to plants. Traditionally the Hedley fractionation has not analyzed the 1M HCl extract for Po. Future work should evaluate this fraction to determine whether Po is bound to CaCO_3 minerals in arid soils.

Potential controls on the concentrations of soil organic P are best seen by examining the individual fractions of organic P, rather than their total. In the grassland, bicarbonate- and NaOH-extractable organic P show a strong positive relationship with organic C, which averages $92 \mu\text{g C/g soil}$ (Cross & Schlesinger 1999). In the shrubland, higher levels of organic C are found under shrubs ($166 \mu\text{g C/g soil}$), than between shrubs ($137 \mu\text{g C/g soil}$) (Cross & Schlesinger 1999). This distribution of organic C may explain the higher concentrations of bicarbonate- and NaOH-extractable organic P fractions under shrubs. Indirect evidence also suggests that Al- and Fe mineralogy may influence the availability of organic P in both vegetation types (Tables 3 and 4). In the grassland, the positive relationship between $\text{SO}_4\text{-S}$ and NaOH- and CHCl -extractable Po, implicates soil mineralogy, because sulfate may also bind to Al and Fe minerals. Perhaps similar to its role in controlling the availability of inorganic P, calcium appears to play a role in the dynamics of organic P in the shrubland, and associations of Po with carbonate minerals should be examined in more detail.

Shrubs influence the spatial distribution of some labile fractions of organic and inorganic P at the Sevilleta (Table 3). The high concentrations of labile organic and inorganic P (resin- and bicarbonate-extractable) that accumulate under shrubs are most likely the result of microbial decomposition of plant litter and mineralization of organic P (Table 3). The non-occluded, NaOH-extractable inorganic P most likely accumulates under shrubs as a consequence of wind- or rain droplet-borne Al- and Fe particulates that originate from the argillic horizon of the adjacent grassland soils (Cross & Schlesinger 1999). In contrast, NaOH-extractable Po, also held by Al- and Fe minerals, shows a higher concentration between shrubs. More research is required to

fully understand the controls on this relatively large, pool of organic P. The uniform distribution of the refractory, acid-extractable forms of inorganic P and organic P result from the widespread distribution of CaCO_3 and Al- and Fe minerals, that overwhelms patchy distribution of shrubland vegetation.

Recently we proposed an index of biologically-available phosphorus in soils under various weathering regimes (Cross & Schlesinger 1995) – the bicarbonate Po divided by the total of resin Pi , bicarbonate Pi , and bicarbonate Po . Values for this index of biologically-available P in soils at the Sevilleta fall at the upper end of those predicted for Aridisols – 15.9% under grasses and 19.7% under shrubs – showing the importance of biological processes in desert soil P cycling. Although geochemical factors dominate the soil phosphorus pool in arid ecosystems (Lajtha & Schlesinger 1988), the small, often overlooked pool of organic phosphorus, may determine the availability of P to plants and its biogeochemical cycle in deserts.

Acknowledgements

I appreciate comments provided by Dan Richter, Boyd Strain, and the late W. Dwight Billings. Statistical advice was provided by Michael Palmer. Jim Gosz, Bob Parmenter, and Doug Moore generously provided lodging and logistical support at the Sevilleta LTER site. Anion exchange membranes were graciously provided by Andrew Sharpley. The manuscript was improved by the comments and editorial remarks of Robert S. Cross, and three anonymous reviewers. This research was supported in part by an Explorer's Club Research Grant, a Sigma Xi Grant-in-Aid-of-Research, a NASA Graduate Student Fellowship for Global Change Research, and an NSF Doctoral Dissertation Improvement Grant (#BSR-91-01248) to AFC and WHS. This publication is number 167 in the Sevilleta LTER Research Series.

References

- Abrams MM & Jarrell WM (1992) Bioavailability index for phosphorus using ion exchange resin impregnated membranes. *Soil Sci. Soc. Amer. J.* 56: 1532–1537
- Anderson DW (1988) The effect of parent material and soil development on nutrient cycling in temperate ecosystems. *Biogeochemistry* 5: 71–97
- Bolan NS (1991) A critical review on the role of mycorrhizal fungi in the uptake of phosphorus by plants. *Plant Soil* 134: 189–207
- Bolin B, Crutzen PJ, Vitousek PM, Woodmansee RG, Goldberg ED & Cook RB (1983) Interactions of biogeochemical cycles. In: Bolin BG & Cook RB (Eds) *The Major Biogeochemical Cycles and their Interactions* (pp 1–39). Wiley, New York
- Bowman RA & Cole CV (1978) Transformations of organic phosphorus substrates in soils as evaluated by NaHCO_3 extractions. *Soil Sci.* 125: 49–54

- Burke IC (1989) Control of nitrogen mineralization in a sagebrush steppe landscape. *Ecology* 70: 1115–1126
- Charley JL & West NE (1975) Plant-induced chemical patterns in some shrub-dominated semi-desert ecosystems of Utah. *J. Ecol.* 63: 945–963
- Charley JL & West NE (1977) Micropatterns of N-mineralization activity in soils of some shrub-dominated semidesert ecosystems of Utah. *Soil Biol. Biochem.* 9: 357–365
- Chu W & Chang S (1966) Surface activity of inorganic soil phosphorus. *Soil Sci.* 101: 459–464
- Cooperbrand LR & Logan TJ (1994) Measuring *in situ* changes in labile soil phosphorus with anion-exchange membranes. *Soil Sci. Soc. Amer. J.* 58: 105–114
- Cosgrove DJ (1977) Microbial transformations in the phosphorus cycle. *Adv. Microb. Ecol.* 1: 95–134
- Crawford CS & Gosz JR (1982) Desert ecosystems: their resources in space and time. *Envir. Conserv.* 9: 181–194
- Cross ASF (1994) Biogeochemistry at the grassland-shrubland boundary: a case study of desertification in the northern Chihuahuan Desert of New Mexico. PhD Dissertation, Duke University, Durham, NC
- Cross AF & Schlesinger WH (1995) A literature review and evaluation of the Hedley fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma* 64: 197–214
- Cross AF & Schlesinger WH (1999) Plant regulation of soil nutrient distribution in the northern Chihuahuan Desert. *Plant Ecol.* 145: 11–25
- Dalal R (1977) Soil organic phosphorus. *Adv. Agron.* 29: 83–117
- DataDescription (1992) DataDesk V. 4.0, Ithaca, NY
- DeLucia EH, Callaway RM, Thomas EM & Schlesinger WH (1997) Mechanisms of P acquisition for ponderosa pine seedlings under different climatic regimes. *Ann. Bot.* 79: 111–120
- Dormaar J (1972) Seasonal patterns of soil organic phosphorus. *Can. J. Soil Sci.* 52: 107–112
- Eid M, Black C & Kempthorne O (1951) Importance of soil organic and inorganic phosphorus to plant growth at low and high soil temperatures. *Soil Sci.* 51: 361–370
- Fox TR & Comerford NB (1992) Rhizosphere phosphatase activity and phosphatase hydrolyzable organic phosphorus in two forested Spodosols. *Soil Biol. Biochem.* 24: 579–583
- Frossard E, Stewart JWB & St. Arnaud RJ (1989) Distribution and mobility of phosphorus in grassland and forest soils of Saskatchewan. *Can. J. Soil Sci.* 69: 401–416
- Gallardo A & Schlesinger WH (1995) Factors determining soil microbial biomass and nutrient immobilization in desert soils. *Biogeochemistry* 28: 55–68
- Garcia-Moya E & McKell CM (1970) Contribution of shrubs to the nitrogen economy of a desert-wash plant community. *Ecology* 51: 81–88
- Gile LH, Hawley JW & Grossman RB (1990) Soils and geomorphology in the Basin and Range Area of southern New Mexico: a guidebook to the desert project. New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico
- Haas HJ, Grunes DL & Reichman GA (1961) Phosphorus changes in Great Plains soils as influenced by cropping and manure applications. *Soil Sci. Soc. Amer. Proc.* 25: 214–218
- Halm BJ, Stewart JWB & Halstead RL (1972) The phosphorus cycle in a native grassland ecosystem. In: International Atomic Energy Agency (Ed.) *Isotopes and Radiation in Soil-Plant Relationships Including Forestry* (pp 571–586). Vienna, Austria
- Halstead RL & McKercher RB (1975) Biochemistry and cycling of phosphorus. In: Paul EA & McLaren AD (Eds) *Soil Biochemistry* (pp 31–63). Marcel Dekker, New York

- Holford IC, Chater R & Mattingly GEG (1990) Effects of decalcification on the phosphate sorption characteristics of eight calcareous soils. *Austral. J. Soil Res.* 28: 919–928
- Jackson ML (1958) *Soil Chemical Analysis*. Prentice-Hall, Englewood Cliffs, NJ
- Jenny H (1941) *Factors of Soil Formation*. McGraw Hill, New York
- Jenny H (1980) *The Soil Resource*. Springer-Verlag, New York
- Johnson DW & Cole DW (1980) Anion mobility in soils: relevance to nutrient transport from forest ecosystems. *Environ. International* 3: 79–90
- Johnson RW (1988) *Soil Survey of Socorro County area, New Mexico*. United States Department of Agriculture, Soil Conservation Service, United States Government Printing Office, Washington, DC
- Jurinak JJ, Dudley LM, Allen MF & Knight WG (1986) The role of calcium oxalate in the availability of phosphorus in soils of semiarid regions: a thermodynamic study. *J. Soil Sci.* 24: 512–522
- Kieft TL, White CS, Loftin RS, Aguilar R, Craig JA & Skaar DA (1998) Temporal dynamics in soil carbon and nitrogen resources at a grassland-shrubland ecotone. *Ecology* 79: 671–683
- Lajtha K & Schlesinger WH (1988) The biogeochemistry of phosphorus cycling and phosphorus availability along a desert chronosequence. *Ecology* 69: 24–39
- Lajtha K & Bloomer SH (1988) Factors affecting phosphate sorption and phosphate retention in a desert ecosystem. *Soil Sci.* 146: 160–167
- Magid J & Nielsen NE (1992) Seasonal variation in organic and inorganic phosphorus fractions of temperate climate sandy soils. *Plant Soil* 144: 155–165
- Murphy J & Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. *Annals Chemica Acta* 27: 31–36
- Murrman RP & Peech M (1969) Relative significance of labile and crystalline phosphates in soil. *Soil Sci.* 107: 249–255
- Nichols JD (1984) Relation of organic carbon to soil properties in the southern Great Plains. *Soil Sci. Soc. Amer. J.* 48: 1382–1384
- Oglesby RT & Bouldin DR (1984) Phosphorus in the environment. In: Nriagu JO & Moore PB (Eds) *Phosphate Minerals* (pp 400–423). Springer-Verlag, New York
- Olsen SR, Cole CV, Watanabe FS & Dean LA (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA circ. 939. Washington, DC
- Parton WJ, Schimel DS, Cole CV & Ojima DS (1987) Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Sci. Soc. Am. J.* 51: 1173–1179
- Ramirez AJ & Rose AW (1992) Analytical geochemistry of organic phosphorus and its correlation with organic carbon in marine and fluvial sediments and soils. *Am. J. Sci.* 292: 412–454
- Roberts TL, Stewart JWB & Bettany JR (1985) The influence of topography on the distribution of organic and inorganic soil phosphorus across a narrow environmental gradient. *Can. J. Soil Sci.* 65: 651–665
- Rostagno CM (1989) Infiltration and sediment production as affected by soil surface conditions in a shrubland of Patagonia, Argentina. *J. Range Manag.* 42: 382–385
- Schlesinger WH & Pilmanis AM (1998) Plant-soil interactions in deserts. *Biogeochemistry* 42: 169–187
- Schlesinger WH, Raikes J, Hartley AE & Cross AF (1996) On the spatial pattern of soil nutrients in desert ecosystems. *Ecology* 77: 364–374
- Sharpley AN, Tiessen H & Cole CV (1987) Soil phosphorus forms extracted by soil tests as a function of pedogenesis. *Soil Sci. Soc. Amer. J.* 5: 362–365
- Skujins J (1991) *Semiarid lands and deserts: soil resources and reclamation*. Marcel Dekker, New York

- Southard RJ & Southard AR (1985) Genesis of cambic and argillic horizons in two northern Utah Aridisols. *Soil Sci. Soc. Amer. J.* 49: 167–171
- Stewart JWB & Tiessen H (1987) Dynamics of soil organic phosphorus. *Biogeochemistry* 4: 41–60
- Tate KR & Salcedo I (1988) Phosphorus control of soil organic matter accumulation and cycling. *Biogeochemistry* 5: 99–107
- Technicon Bran-Luebbe (1987) Total phosphorus method. Bran-Luebbe Analyzing Technologies. Elmsford, NY
- Tiessen H, Stewart JWB & Cole CV (1984) Pathways of phosphate transformations in soils of differing pedogenesis. *Soil Sci. Soc. Amer. J.* 48: 853–858
- Tiessen H & Moir JO (1993) Characterization of available P by sequential fractionation. In: Carter MR (Ed.) *Soil Sampling and Methods of Analysis* (pp 75–86). Lewis Publishers, Boca Raton
- Tiessen H (1995) *Phosphorus in the Global Environment*. John Wiley & Sons, New York
- Westin FC (1978) Organic phosphorus changes over a growing season in some borolls and associated aquolls of South Dakota. *Soil Sci. Soc. Amer. J.* 42: 472–477
- Wild A & Oke OL (1966) Organic phosphate compounds in calcium chloride extracts of soils: identification and availability to plants. *J. Soil Sci.* 17: 356–371
- Zaady E, Groffman PM & Shachak M (1996) Litter a regulator of N and C dynamics in macrophytic patches in Negev Desert soils. *Soil Biol. Biochem.* 28: 39–46
- Zar JH (1984) *Biostatistical Analysis*. Prentice-Hall, New York