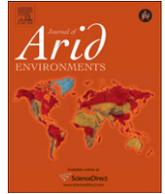




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Phosphorus biogeochemistry across a precipitation gradient in grasslands of central North America

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ABSTRACT

Soil P transformations and distribution studies under water limited conditions that characterize many grasslands may provide further insight into the importance of abiotic and biotic P controls within grass-dominated ecosystems. We assessed transformations between P pools across four sites spanning the shortgrass steppe, mixed grass prairie, and tallgrass prairie along a 400-mm precipitation gradient across the central Great Plains. Pedon total elemental and constituent mass balance analyses reflected a pattern of increased chemical weathering from the more arid shortgrass steppe to the more mesic tallgrass prairie. Soil surface A horizon P accumulation was likely related to increased biocycling and biological mining. Soluble P, a small fraction of total P in surface A horizons, was greatest at the mixed grass sites. The distribution of secondary soil P fractions across the gradient suggested decreasing Ca-bound P and increasing amounts of occluded P with increasing precipitation. Surface A horizons contained evidence of Ca-bound P in the absence of CaCO₃, while in subsurface horizons the Ca-bound P was associated with increasing CaCO₃ content. Calcium-bound P, which dominates in water-limited systems, forms under different sets of soil chemical conditions in different climatic regimes, demonstrating the importance of carbonate regulation of P in semi-arid ecosystems.

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1. Introduction

Grasslands ecosystems are characteristically water limited and have evolved under highly variable rainfall and temperature regimes (Kelly et al., 1998). The literature is replete with studies that identify and quantify the fundamental controls on organic matter accumulation (e.g. Aguilar and Heil, 1988; Burke et al., 1989; Parton et al., 1987) and the cycling of C and N in grassland ecosystems (e.g. Honeycutt et al., 1990; McCulley et al., 2005). As P transformations are predominately regulated by weathering processes, little attention has been directed towards identification and quantification of P pools in water limited grassland ecosystems.

Understanding phosphorus transformations in water limited ecosystems of temperate climates can provide insight into the relative importance of abiotic versus biotic controls on the availability of this essential nutrient (Cross and Schlesinger, 2001; Lajtha

and Schlesinger, 1988; McCulley et al., 2004; Titus et al., 2002). Though inorganic fractions tend to dominate total soil P in arid systems, biologic P cycling plays an important role in maintaining available P (Chadwick et al., 2007; Cross and Schlesinger, 2001; Lajtha and Schlesinger, 1988) and may help explain to some degree the high P accumulations in surface layers of soils across ecosystems (Jobbagy and Jackson, 2001).

Pioneering work from Smeck (1973) and Walker and Syers (1976) provided a look at biogeochemical P transformations as a function of time or the duration of weathering processes. Climatic controls, such as precipitation and temperature, regulate the intensity of weathering and biological activity and are fundamental in determining P transformations and distribution within ecosystems (Chadwick et al., 2007). Theoretically, the weathering of primary apatitic and other P-bearing minerals leads to the initial release of P into the soil solution. Once in solution, the fate of soluble P depends on a variety of physical and biological processes. Solution P can be assimilated and biocycled by plants and microorganisms and enter the organic-P pool, sorbed to soil particles, or precipitated as secondary mineral phases such as Al- and Fe-oxyhydroxides or Ca-phosphates. Over time, both organic and

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inorganic P pools are predicted to decline as primary P-bearing minerals are depleted and P is lost through leaching and erosion (Walker and Syers, 1976).

Shifts in the control of P availability, from reactions with Ca in drier climates to Al and Fe in wetter climates, is a common occurrence observed in diverse ecosystems (Carreira et al., 1997; Vitousek et al., 2004) where transformations result from increased weathering intensity. Calcium-bound P phases typically dominate all soil fractions and control P availability in arid climates given the limited chemical weathering in these systems; Fe- and Al-bound P often comprise very small fractions (Cross and Schlesinger, 2001; Lajtha and Bloomer, 1988; Lajtha and Schlesinger, 1988). Tyler (2002) showed that Ca-phosphate phases dominated the inorganic P fraction of high-pH soils (~90%), were reduced in moderate-pH soils (60–70%), and were highly variable in low-pH soils (10–40%). That study also indicated increasing Fe- and Al-phosphate phases with decreasing pH.

Redistribution of soil P within soils through leaching or plant uptake also impacts soil P fractions and depth distribution. In arid to semi-arid grasslands, maximum concentrations of total P

were found either in or immediately above the horizon with maximum carbonate concentrations (Honeycutt et al., 1990), demonstrating that downward P movement may be limited by the mean depth of water movement and further impeded by precipitation of Ca-phosphates (Runge and Riecken, 1966; Smeck and Runge, 1971). Biocycling can increase P concentrations in the soil surface as plants access nutrients from deeper horizons (Carreira et al., 1997; Chadwick et al., 2007; McCulley et al., 2004).

Our objectives in this study were to identify and quantify P pools in water limited grassland ecosystems along a precipitation gradient in the central Great Plains of North America, and to assess the relative importance of different biogeochemical controls on P availability within and among soil pedons. Studies of soil C and N dynamics in grasslands along this climate gradient suggest that microclimatic controls and plant productivity are important determinants of C and N accumulation rates and turnover (McCulley and Burke, 2004; McCulley et al., 2005; Vinton and Burke, 1997), while we speculate that P availability will be strongly influenced by geochemical differences in soils.

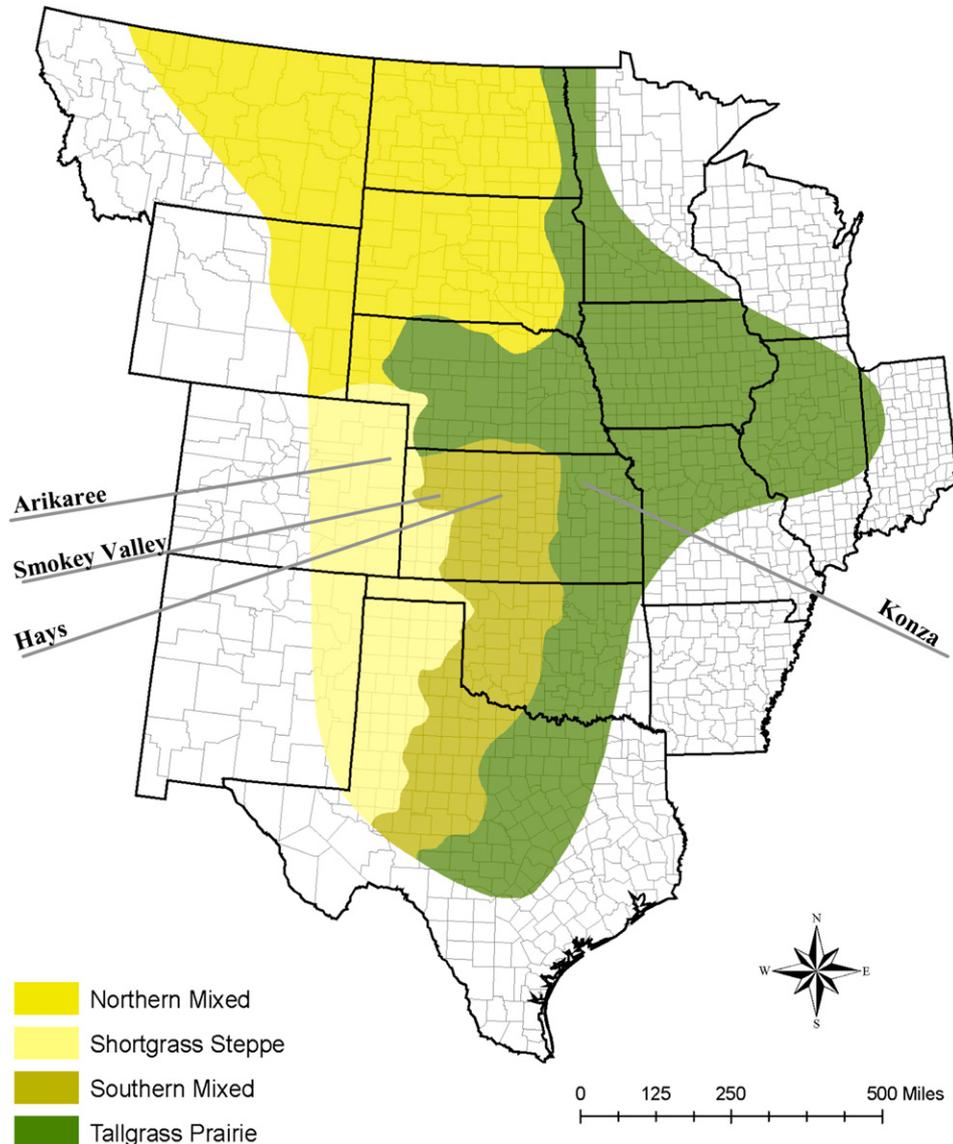


Fig. 1. Grassland regions of the United States illustrating the Central Great Plains Arikaree, Smokey Valley, Hays, and Konza research sites.

Table 1

Characteristics for the 4 sites comprising the Great Plains climosequence: AK – Arikaree River Ranch, owned by The Nature Conservancy (TNC), SV – Smokey Valley River Ranch owned by the TNC, HR – Hays Range Area, owned by Ft. Hays State University, KP – Konza Prairie Research Natural Area and LTER site. MAP = mean annual precipitation, MAT = mean annual temperature, MPMPE = mean annual precipitation minus mean annual potential evapotranspiration.

	AK Arikaree – TNC	SV Smokey Valley – TNC	HR Ft. Hays State Univ.	KP Konza Prairie – LTER
Latitude	39° 45.0 N	38° 53.1 N	38° 52.4 N	39° 05.5 N
Longitude	102° 28.7 W	100° 57.6 W	99° 23.2 W	96° 34.1 W
Elevation (m)	1220	879	610	406
MAP ^a (mm)	462	502	575	884
MAT ^a (°C)	9.7	10.8	11.9	12.7
MPMPE ^b (mm)	–600 to –200	–600 to –200	–200 to 200	–200 to 200
Vegetation type	Shortgrass steppe	Mixed grass	Mixed grass	Tallgrass
Soil classification ^c	Aridic argiustoll	Typic argiustoll	Typic argiustoll	Udic argiustoll

^a U.S. Dept. of Commerce (2002) compiled data from 1971 to 2000.

^b McCabe and Wolock (2002) compiled data from 1961 to 1990.

^c Soil Survey Staff (2006).

2. Materials and methods

2.1. Site description

Four sites spanning a 400 mm precipitation gradient across US central Great Plains grasslands were sampled: Arikaree (AK; shortgrass steppe, eastern CO), Smokey Valley (SV; mixed grass prairie, western KS), Hays Range Area (HR; mixed grass prairie, central KS) and Konza Prairie (KP; tallgrass prairie, eastern KS) (Fig. 1). Water balance was estimated as the mean annual precipitation minus mean annual potential evapotranspiration (McCabe and Wolock, 2002; Table 1). Increasing precipitation, temperature and available water along the transect suggest greater weathering intensity across the climosequence. Additional site characteristics are listed in Table 1. Soils at these sites were primarily derived from

local sedimentary rock and, although located outside the boundaries of mapped loess deposits (Mason et al., 2003; Roberts et al., 2003), local loess sources cannot be entirely ruled out as a component of the parent material.

All sites were uncultivated and located on nearly level landscape positions. The dominant grass species included *Bouteloua gracilis* and *Buchloe dactyloides* (AR), *Bouteloua gracilis*, *Buchloe dactyloides*, *Festuca* sp. (SV, HR), and *Andropogon gerardii*, *Sorghastrum nutans*, and *Panicum virgatum* (KP).

2.2. Soil analyses

Soils were described and sampled by genetic horizon to unweathered C or Cr horizons from hand-dug pits. Samples were passed through a 2-mm sieve and air-dried for subsequent

Table 2

Soil characteristics for the four sites comprising the Great Plains grassland climosequence.

Site/Horizon	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Texture	pH	Total N (%)	Total C (%)	Inorganic C (%)	Organic C (%)	Bd (g cm ⁻³)
<i>Arikaree</i>											
A	0–9	52.3	28.9	18.8	sl ^a	5.68	0.140	1.464	0.000	1.464	1.49
BAt	9–22	55.1	19.3	25.7	scl	6.37	0.083	0.834	0.000	0.834	1.48
Bt	22–51	52.3	22.1	25.7	scl	6.65	0.067	0.683	0.000	0.683	1.39
Btk	51–72	62.3	14.1	23.6	scl	7.82	0.035	0.491	0.277	0.214	1.67
BCK	72–91	55.8	21.8	22.4	scl	8.01	0.012	0.351	0.212	0.139	1.52
Ck1	91–184	73.1	15.1	11.8	sl	8.42	0.006	0.213	0.169	0.044	1.62
Ck2	184–221+	87.0	2.5	10.5	ls	8.38	0.001	0.101	0.094	0.007	1.77
<i>Smokey valley</i>											
A	0–8	13.8	57.5	28.6	si cl	5.66	0.207	2.119	0.000	2.119	1.21
ABt	8–21	13.1	54.7	32.2	si cl	6.30	0.133	1.325	0.000	1.325	1.37
Bt	21–32	11.6	56.1	32.3	si cl	6.43	0.105	1.051	0.003	1.048	1.36
Btk	32–62	3.2	63.4	33.4	si cl	7.45	0.083	1.604	0.930	0.674	1.26
BCK1	62–81	2.5	68.8	28.7	si cl	7.74	0.043	1.656	1.316	0.340	1.24
BCK2	81–103	5.6	67.2	27.3	si cl	7.69	0.033	1.302	1.093	0.209	1.30
Ck1	103–192	9.6	68.9	21.5	si l	7.90	0.027	1.122	0.944	0.178	1.35
<i>Hays</i>											
A	0–8	5.9	69.1	25.0	si l	5.88	0.276	2.823	0.000	2.823	1.24
ABt	8–28	7.1	56.7	36.2	si cl	5.72	0.142	1.434	0.000	1.434	1.22
Bt	28–46	4.9	56.1	39.0	si cl	6.72	0.061	0.572	0.000	0.572	1.46
Btk1	46–71	3.1	60.5	36.3	si cl	8.07	0.044	0.518	0.261	0.257	1.30
Btk2	71–101	8.1	51.1	40.8	si c	8.15	0.049	0.424	0.093	0.331	1.23
Btk3	101–161	7.1	50.4	42.5	si c	7.75	0.055	0.605	0.218	0.387	1.32
Bk	161–186	26.6	38.1	35.3	cl	7.91	0.042	0.879	0.552	0.327	1.47
BCK	186–198+	5.6	31.1	63.3	c	7.96	0.014	3.812	0.962	2.850	1.27
<i>Konza</i>											
A	0–16	8.0	60.0	32.0	si cl	5.25	0.298	3.424	0.000	3.424	1.37
ABt	16–29	4.0	46.0	50.0	si c	4.89	0.147	1.623	0.000	1.623	1.49
Bt1	29–39	3.3	44.2	52.6	si c	5.05	0.114	1.254	0.000	1.254	1.49
Bt2	39–52	7.7	43.5	48.8	si c	5.12	0.113	1.089	0.000	1.089	1.46
Btg1	52–60	5.1	45.5	49.4	si c	5.21	0.079	0.864	0.000	0.864	1.46
Btg2	60–81	5.4	45.6	49.0	si c	5.43	0.073	0.690	0.000	0.690	1.61

^a sl = sandy loam, scl = sandy clay loam, ls = loamy sand, si cl = silty clay loam, si l = silt loam, si c = silty clay, cl = clay loam, c = clay.

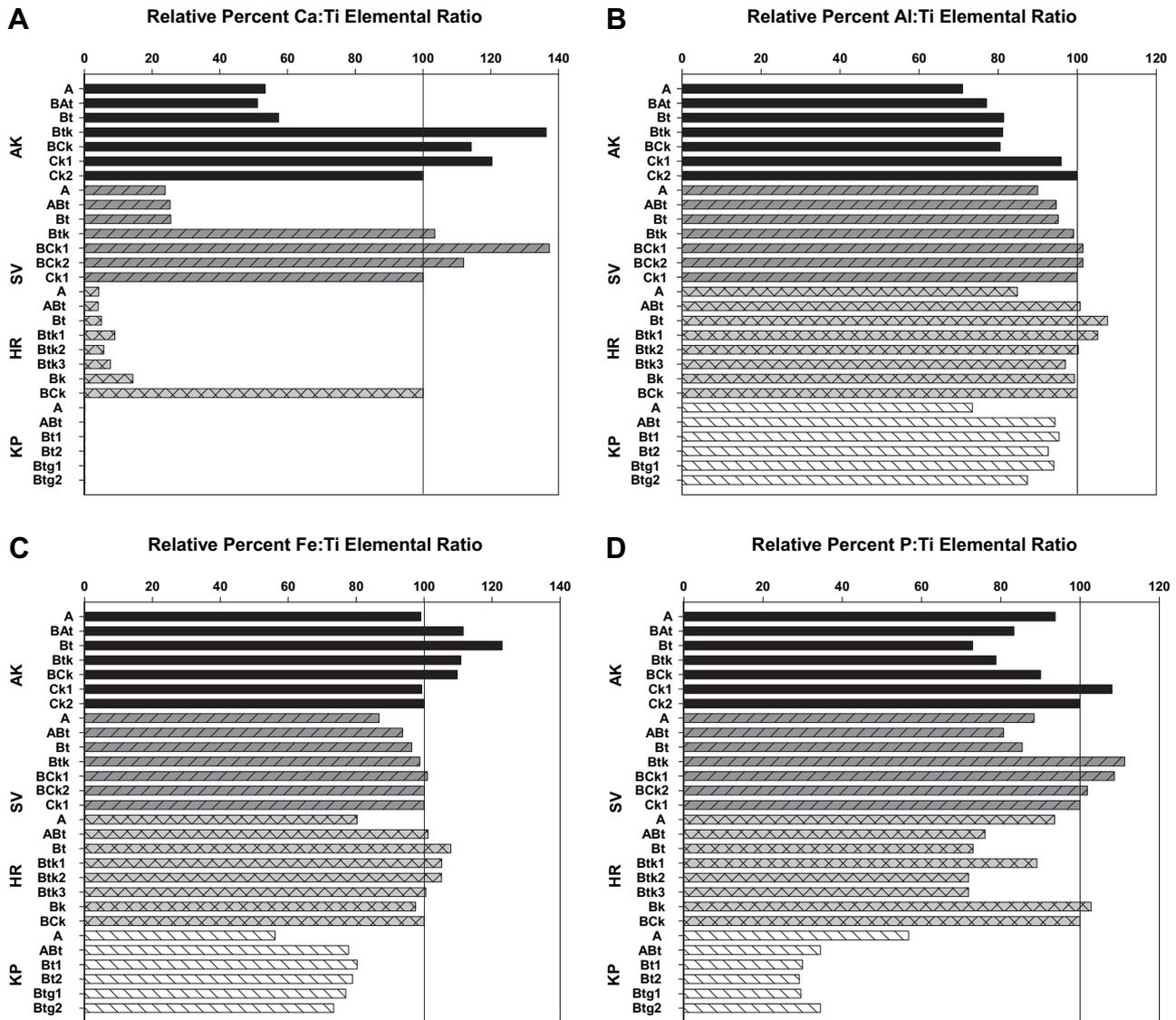


Fig. 2. Relative percent of elements as indexed to the immobile element, Ti, across all sites (AK, Arikaree site – shortgrass steppe; SV, Smokey Valley site – mixed grass prairie; HR, Hays Range site – mixed grass prairie; KP, Konza Prairie site – tallgrass prairie) and horizons. A) Ca remaining; B) Al remaining; C) Fe remaining; D) P remaining. Vertical lines represent the molar ratio in the parent material at each site.

analyses. Soil separates and texture were determined by hydrometer method (Gee and Bauder, 1986). Soil pH was determined using a 2:1 water:soil extract (Thomas, 1996). Soil bulk density was determined by either the core or clod method (Blake and Hartge, 1986), where soil structure and consistency determined the method used. On pulverized soil samples, total soil N and C were determined using a LECO-1000 CHN auto-analyzer (Nelson and Sommers, 1996) and soil inorganic C (consisted mostly of CaCO_3) using a pressure transducer method (Sherrod et al., 2002). Organic C was determined by the difference between total and inorganic C.

To assess weathering losses and gains of major elements during pedogenesis, oven-dried, pulverized soil and rock samples were ashed at 500 °C to remove organic matter, fused with Li-metaborate, dissolved in dilute HNO_3 , and analyzed by inductively coupled plasma atomic emission spectroscopy (Hossner, 1996). Proportions of major elements remaining in the sample were indexed relative to an “immobile” element (Kurtz et al., 2000). Mass balance calculations of major elements were conducted according to procedures outlined by Chadwick et al. (1990) and

Brimhall et al. (1991) with Ti chosen as the immobile element since the Ti content can be assumed to not change with weathering in soils with pH > 4.5 (Carreira et al., 1997). The percentage of an element remaining in a soil horizon, relative to parent material, was calculated as:

$$L_{ij} = 100(C_{i,j}/(C_{Ti,j}(C_{i,pm}/C_{Ti,pm}))) \quad (1)$$

where L_{ij} is the percentage of element i remaining in soil horizon j , $C_{i,j}$ and $C_{Ti,j}$ are the molar concentrations of element i and Ti in soil horizon j , and $C_{i,pm}$ and $C_{Ti,pm}$ are element i and Ti molar concentrations in the parent material (Vitousek et al., 2004). It is important to note that the potential confounding impact of re-worked regional loess and more recent dust deposits were not resolved in this study; i.e. bedrock or C horizon material was used as the unweathered parent material end member since mineralogical composition of soils suggested loess was derived from local sedimentary materials (Blecker, 2005). Unfortunately time and resources did not permit the sampling or analysis of field replicates. However, given intra-site similarities between soil profile

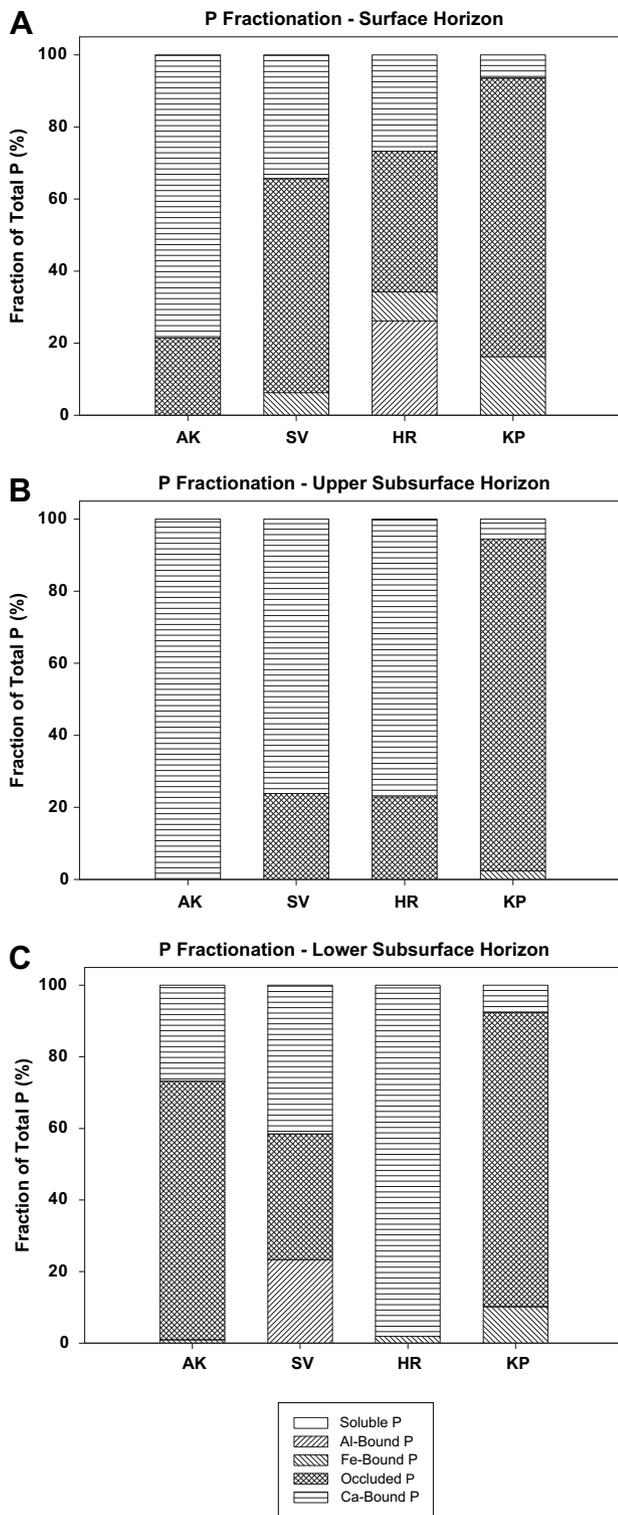


Fig. 3. Phosphorus fractions of A) A horizon, B) upper subsurface, and C) lower subsurface horizons across sites (AK, Arikaree site – shortgrass steppe; SV, Smokey Valley site – mixed grass prairie; HR, Hays Range site – mixed grass prairie; KP, Konza Prairie site – tallgrass prairie).

descriptions and surface clay and organic C concentrations from previous research (McCulley et al., 2004), we believe the differences in parameters across the transect are greater than any intra-site variability. Thus despite not having field replicates we believe the trends across the transect are valid.

2.3. Identification of soil phosphorus fractions

A five-step or three-step sequential inorganic P extraction procedure was utilized on all genetic horizons from non-calcareous and calcareous soils, respectively, based on procedures outlined by Kuo (1996). The non-calcareous extraction procedure identified soluble and loosely bound, Al oxyhydroxide-surface bound, Fe oxyhydroxide-surface bound, occluded (within the matrices of retaining components/minerals (Evans and Syers, 1971)), and Ca-bound mineral P fractions. The calcareous extraction procedure identified soluble and loosely bound/Al-bound/Fe-bound, occluded, and Ca-bound mineral P fractions. Extracts were filtered through a 0.2 μm membrane prior to colorimetric P determination by spectrophotometer (882 nm wavelength), following a modified ascorbic acid procedure (Rodriguez et al., 1994). Modifications based on previous research by Weaver (1974) were made to the occluded P fraction due to insufficient color development, whereby a 2.5 mL aliquot was transferred to a 25 mL volumetric flask. Then, 1.5 mL of 5% ammonium molybdate solution, 15 mL of deionized water (DI), and 2.5 mL of color developing reagent (Rodriguez et al., 1994) were added, and the solution brought to a final volume using DI. The final solution was allowed to stand for 30 min prior to P analysis. For the non-calcareous (five-step extraction procedure) horizons, data from the soluble, Al-bound, and Fe-bound phases were combined for comparison with data from the calcareous (three-step extraction procedure) horizons.

3. Results and discussion

3.1. Soil physical and chemical properties

Characterization data along the precipitation gradient presents a broad array of soil physical and chemical properties (Table 2). These data support general soil development trends across the climosequence that are consistent with increasing rates of soil weathering (e.g. Franzmeier et al., 1985; Honeycutt et al., 1990; Jenny, 1941). The clay content of soils increased from the shortgrass steppe (AK) to the tallgrass prairie (KP) while soil pH decreased with increasing precipitation. As reported elsewhere, surface soil total C and N increased from AK to KP, and decreased with depth within all sites (McCulley and Burke, 2004). In general, subsurface horizons contained greater amounts of inorganic C (IC), which decreased with increasing precipitation although IC was absent throughout the KP soil profile.

3.2. Mobility and transfers of key elements

Quantities of key elements in the parent material and overlying soil were compared to Ti in order to assess weathering gains or losses within and among soils. The percent of Ca, Al, Fe, and P remaining or enriched throughout each profile, as determined by equation (1), are presented in Fig. 2.

Ca is more mobile than Al, Fe or P (Fig. 2A). All sites, regardless of precipitation and grassland system, experienced some redistribution, or a net loss, of Ca relative to the parent material. At the wettest site (KP), all Ca has been leached from the soil profile. At the intermediate rainfall sites (HR and SV) only 5–20% of the original Ca remains in the upper portions of the soil. In contrast, most all of the Ca remains in the soil profile at the most water-limited site (AR).

The geochemical behavior of Al and Fe is quite similar across all sites (Fig. 2B and C). The insoluble nature of these elements in alkaline to slightly acidic soils (Table 2) is evident. Aluminum and Fe are relatively conserved at all sites with net gains/losses ranging from +20 to –35% at the drier site (AR) in the upper portions of the profile, and 15–40% losses in the higher rainfall soil (KP). The

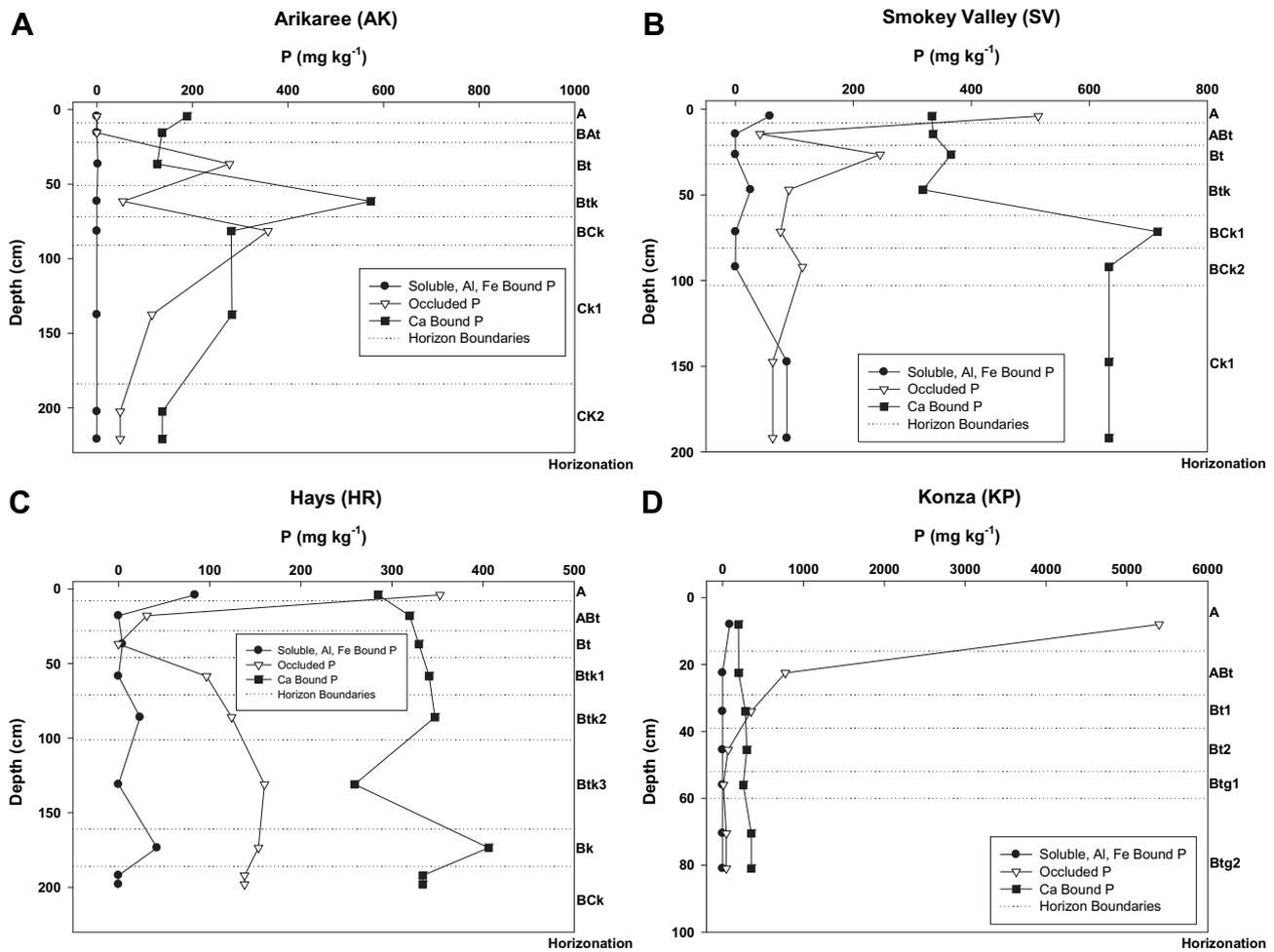


Fig. 4. Phosphorus fractions across sites. A) Arikaree (AK) shortgrass steppe site; B) Smokey Valley (SV) mixed grass prairie site; C) Hays Range (HR) mixed grass prairie site; D) Konza (KP) tallgrass prairie site.

intermediate rainfall sites (SV, HR) show relative preservation of Fe and Al compared to the other sites.

Phosphorus has minimal solubility in soil because it participates in a number of secondary reactions after release from primary minerals. Phosphorus has been depleted at KP but elsewhere there is approximately 60–80% P remaining in the soil profiles (Fig. 2D). The KP also had the greatest surface horizon P loss relative to the other sites, yet it is the only site where the maximum P in the profile is in the surface layer. By contrast, the drier sites have maximum P retention in subsurface horizons. Overall, Ca losses were greatest, P intermediate, and Fe and Al losses the lowest. This weathering trend of $\text{Ca} > \text{P} > \text{Fe} \geq \text{Al}$ was similar to that found by Carreira et al. (1997) and other studies relating time and/or weathering intensity to cation loss (e.g. Campbell, 1975; Chadwick et al., 1990).

In addition to losses of P due to weathering, Fig. 2D suggests possible redistribution of P to the soil surface at all sites relative to the immediately subjacent horizons. At KP for example, P concentration was greater in the A horizon and lower in all subsurface horizons as compared to the parent material, suggesting possible biological accumulation. As suggested by others (Smeck and Runge, 1971; Walker and Syers, 1976), soil surface P accumulation can be related to plant uptake, subsequent degradation, and organic-P accumulation. Honeycutt et al. (1990) showed that total P accumulation in the soil surface of three Great Plains locations was similar, and a greater amount of total P was present as organic P.

3.3. Phosphorus fractionation in soils

The dominant soil cation (Ca, Al or Fe) at each site should exert strong control over the mobility and retention of P in that system. The relative fractions of P in the soluble, Al-bound, Fe-bound, occluded, and Ca-bound phases, as compared to the total of all fractions within the upper portions of the soil profiles across all sites, are shown in Fig. 3. At all sites regardless of depth, soluble P was a negligible fraction of total P, likely due to rapid uptake by plants and microorganisms or due to formation of secondary mineral phases. In the soil surface horizons (Fig. 3A), Ca-bound P decreased while Fe-bound and occluded P generally increased from AR to KP. Aluminum-bound P was only observed at HR. In the upper subsurface horizons (Fig. 3B), Ca-bound and occluded P phases followed similar trends as compared to the A horizons, with other P fractions being minor constituents. In the lower subsurface horizon (Fig. 3C), Ca-bound P increased from the AR to HR sites and then declined at KP; occluded P followed an opposite trend. Aluminum-bound P comprised ~20% of the total P at SV site and was minimally important at all other sites. Iron-bound P comprised ~10% of the total P at KP with minor amounts present at all other sites.

Even in these water limited grassland ecosystems the observed chemical transformations and weathering patterns across this precipitation gradient mirror conceptual presentations reported in other more geochemically dynamic ecosystems. Syers et al. (1970)

demonstrated that the total amount of P associated with Ca phases decreased across a weathering gradient of New Zealand pasture soils. Filippelli and Souch (1999) noted that mineral P transformations were more complete in warm/humid compared to cool/humid systems, progressing towards a system dominated by organic and occluded P fractions. Lindsay (1979) reported that a decrease in soil pH coupled with a loss of basic cations (e.g. from the shortgrass steppe to tallgrass prairie) shifted systems dominated by Ca-phosphates to Fe- and Al-phosphates. The observed P weathering patterns across the semi-arid US central Great Plains also compared well with findings of Carreira et al. (1997), who studied P transformations across semi-arid lands in Spain. They found that under conditions of low, intermediate, and high weathering most inorganic soil P was Ca-bound, Al- and Fe-bound, and occluded, respectively. Concomitant with this decrease occluded P increased along the weathering sequence, which is consistent with our observations of the highest proportion of occluded P at KP. Walker and Syers (1976) suggested that P associated with Ca will decrease with time, with decreases occurring more rapidly in the soil surface due to increased weathering. Non-occluded (i.e. Al- and Fe-bound) as well as occluded phases initially increase during pedogenesis. Eventually these secondary mineral phases are predicted to decrease to a steady state concentration where system inputs equal losses. Given the weathering intensity in our central Great Plains sequence it is unlikely the steady state conditions proposed by Walker and Syers (1976) have been achieved.

The concentration of the various P pools for each site over the entire soil depth is shown in Fig. 4. At AR (Fig. 4A), the soluble + Al-bound + Fe-bound P pool changed little with depth, with concentrations at or below detection. Occluded P varied with depth, containing 270–350 mg P kg⁻¹ in the Bt and BCK horizons; lesser amounts were found above and below these horizons. The soils at AR were dominated by Ca-bound P throughout the profile. The soluble + Al-bound + Fe-bound P pool at the SV (Fig. 4B) site was relatively small but did increase with depth. The occluded phase contained the greatest P concentration in the soil surface and decreased with depth. The HA (Fig. 4C) P pools followed trends similar to SV, although occluded phases tended to increase with depth. The upper horizons at KP (Fig. 4D) were dominated by occluded P and decreased rapidly with depth. The soluble + Al-bound + Fe-bound P pool and the Ca-bound P phase concentrations remained relatively constant with depth.

The important role Ca plays in P fractionation across this landscape cannot be discounted. Several reports state that Fe- and Al-oxyhydroxides can overwhelm the role of carbonate minerals in forming P precipitates (Carreira and Lajtha, 1997; Pena and Torrent, 1990) even in soils with a basic pH. However, other authors (Cross and Schlesinger, 2001; Roberts et al., 1985; Schoenau et al., 1989) have noted a greater percentage of Ca-bound P phases in Mollisols as compared to other soil inorganic P phases, as we found with the AR, SV, and HR sites. Within the upper soil horizons at AR, SV, and HR, Ca-bound P dominates all fractions yet inorganic C content (Table 2), or CaCO₃, is low or absent. These findings support the contention that secondary precipitation of Ca–P minerals has broad ecosystem implications for the retention of P (Carreira et al., 2006). Although not present in the soil surface, this trend continues with depth at the KP site. Phosphorus retention altered between secondary and primary mineral precipitates in the surface and subsurface at AR, SV, and HR. Subsurface Ca-bound P compares well with inorganic C, supported by findings of Lajtha and Bloomer (1988) and Carreira et al. (2006) which showed the importance of carbonate P controls in arid ecosystems.

4. Summary and conclusions

The range and variability in P transformations, transfers and losses from the soil profiles in these grass-dominated ecosystems is instructive. A greater understanding of P biogeochemistry under current climate/grassland associations is important in light of potential climate-driven changes in these associations and subsequent control on P cycling and availability. Understanding current P biogeochemical transformations in these systems could aid land managers if global climate change affects the central Great Plains of the U.S. In drier areas of the precipitation gradient, P is depleted somewhat relative to the parent material, although there is slightly more P remaining in the surface horizons than there is in the immediately subjacent horizons. This suggests translocation of P within plants and subsequent deposition at the soil surface is a likely mechanism for the long-term pattern of P accumulation. The net loss of P in the more arid ecosystems is more difficult to explain, as loss by leaching is unlikely given that Al and Fe show little loss from those sites and given the fact that the water balance is mostly negative for these ecosystems (Pardo et al., 1999). It is plausible that the losses of P at the shortgrass and mixed grass sites are due to biocycling of P to the surface followed by erosion of the surface material. The erosion could be affected by either water or wind, but in this instance we believe wind erosion of soil and organic material (dead and partly decomposed leaves) is likely. At the wettest end of this precipitation gradient P is leached to a greater extent, but retained somewhat in the surface horizons and depleted in the subsurface horizons. These patterns suggest that different pedogenic and biologic processes are intensified within the three dominant grassland systems.

Our results further suggest that increased plant productivity, increased mineral weathering intensity, and organic P mineralization occurred concurrently and to a significant extent in the surface horizon at KP. Barrett et al. (2002) studied N mineralization across the transect utilized in our current study, and showed that mineralizable pools of N correlate with greater N demand due to increased plant productivity at the wetter sites (i.e. KP). We did not measure organic P in our study, but if mineralization were occurring at an increased rate in the A horizon across sites as a function of precipitation, this would potentially release more soluble P to the soil solution. This soluble P fraction could then be adsorbed by plants or contribute to the increased P content within each inorganic P fraction.

In addition to chemical transformations of P from weathering reactions, some redistribution to the soil surface occurred at all sites suggesting biological cycling or eolian input. Soluble P was a minor fraction of total P within all soil profiles, most likely due to this phase being quickly utilized by plants or microorganisms, or precipitated as secondary mineral phases. The greatest percentage of inorganic P was bound to Ca phases in the shortgrass steppe (AR) and mixed grass prairie (SV and HR). As observed in other weathering sequences, the total amount of P associated with Ca phases decreased with a concomitant increase in occluded P, following increased weathering intensity along the climosequence.

Previous research has suggested that the effect of Fe- and Al-oxyhydroxides can overwhelm the role of carbonate minerals in forming P precipitates; however, Al- and Fe-bound phases are quite low across the semi-arid US central Great Plains. The soil horizons in the upper portions of the soil profile at the shortgrass steppe (AR) and mixed grass prairie (SV and HR) contain Ca-bound P. Within these upper horizons inorganic C content is absent and Ca-bound P trends within these horizons do not appear to follow that of organic C, suggesting that secondary Ca–P minerals most likely control P availability in the upper horizons. Subsurface Ca-bound P compares well with inorganic C content at these sites, further

supporting evidence of the important role of carbonate-bound P controls in semi-arid ecosystems.

References

- Aguilar, R., Heil, R.D., 1988. Soil organic carbon, nitrogen, and phosphorus quantities in northern Great Plains rangelands. *Soil Sci. Soc. Am. J.* 52, 1076–1081.
- Barrett, J.E., McCulley, R.L., Lane, R.L., Burke, I.C., Lauenroth, W.K., 2002. Influence of climate variability on plant production and N-mineralization in Central US grasslands. *J. Veg. Sci.* 13, 383–394.
- Blake, G.R., Hartge, K.H., 1986. Bulk density. In: Klute, A. (Ed.), *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*. Soil Science Society of America, Madison, Wisconsin, USA, pp. 363–375.
- Blecker, S.W., 2005. *Silica Biogeochemistry Across the Great Plains*. Dissertation, Colorado State University, Fort Collins, CO, USA.
- Brimhall, G.H., Lewis, C.J., Ford, C., Bratt, J., Taylor, G., Warin, O., 1991. Quantitative geochemical approach to pedogenesis: importance of parent material reduction, volumetric expansion, and eolian influx in lateritization. *Geoderma* 51, 51–91.
- Burke, I.C., Reiners, W.A., Schimel, D.S., 1989. Organic matter turnover in a sagebrush steppe landscape. *Biogeochem* 7, 11–31.
- Campbell, A.S., 1975. *Chemical and Mineralogical Properties of a Sequence of Soils Near Reefton, NZ*. PhD thesis, Lincoln College, University of Canterbury, New Zealand.
- Carreira, J.A., Lajtha, K., 1997. Factors affecting phosphate sorption along a Mediterranean, dolomitic soil and vegetation chronosequence. *Eur. J. Soil Sci.* 48, 139–149.
- 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. *Biogeochem* 39, 87–120.
- Carreira, J.A., Vinegla, B., Lajtha, K., 2006. Secondary CaCO₃ and precipitation of P–Ca compounds control the retention of soil P in arid ecosystems. *J. Arid Environ.* 64, 460–473.
- Chadwick, O.A., Brimhall, G.H., Hendricks, D.M., 1990. From a black to a gray box – a mass balance interpretation of pedogenesis. *Geomorph* 3, 369–390.
- Chadwick, O.A., Kelly, E.F., Hotchkiss, S.C., Vitousek, P.M., 2007. Precontact vegetation and soil nutrient status in the shadow of Kohala volcano, Hawaii. *Geomorph* 89, 70–83.
- Cross, A.F., Schlesinger, W.H., 2001. Biological and geochemical controls on phosphorus fractions in semiarid soils. *Biogeochem* 52, 155–172.
- Evans, T.D., Syers, J.K., 1971. An application of autoradiography to study the special distribution of ³³P-labelled orthophosphate added to soil crumbs. *Soil Sci. Soc. Am. Proc.* 35, 906–909.
- Filippelli, G.M., Souch, C., 1999. Effects of climate and landscape development on the terrestrial phosphorus cycle. *Geology* 27, 171–174.
- Franzmeier, D.P., Lemme, G.D., Miles, R.J., 1985. Organic carbon in soils of North central United States. *Soil Sci. Soc. Am. J.* 49, 702–708.
- Gee, G.W., Bauder, J.W., 1986. Particle-size analysis. In: Klute, A. (Ed.), *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*. Soil Science Society of America, Madison, Wisconsin, USA, pp. 383–411.
- Honeycutt, C.W., Heil, R.D., Cole, C.V., 1990. Climatic and topographic relations of three Great Plains soils: II. Carbon, nitrogen, and phosphorus. *Soil Sci. Soc. Am. J.* 54, 476–483.
- Hossner, L.R., 1996. Dissolution for total elemental analysis. In: Bartels, J.M. (Ed.), *Methods of Soil Analysis. Part 3. Chemical Methods*. Soil Science Society of America, Madison, Wisconsin, USA, pp. 49–64.
- Jenny, H., 1941. *Factors of Soil Formation: A System of Quantitative Pedology*. McGraw-Hill, Mineola, New York, USA.
- Jobbagy, E.G., Jackson, R.B., 2001. The distribution of soil nutrients with depth: global patterns and the imprints of plants. *Biogeochem* 53, 51–77.
- Kelly, E.F., Chadwick, O.A., Hilinski, T.E., 1998. The effect of plants on mineral weathering. *Biogeochem* 42, 21–53.
- Kuo, S., 1996. Phosphorus. In: Bartels, J.M. (Ed.), *Methods of Soil Analysis. Part 3. Chemical Methods*. Soil Science Society of America, Madison, Wisconsin, USA, pp. 869–919.
- Kurtz, A.C., Derry, L.A., Chadwick, O.A., Alfano, M.J., 2000. Refractory element mobility in volcanic soils. *Geology* 28, 683–686.
- Lajtha, K., Bloomer, S.H., 1988. Factors affecting phosphate sorption and phosphate retention in a desert ecosystem. *Soil Sci.* 146, 160–167.
- Lajtha, K., Schlesinger, W.H., 1988. The biogeochemistry of phosphorus cycling and phosphorus availability along a desert soil chronosequence. *Ecology* 69, 24–39.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. John Wiley & Sons, New York, USA.
- Mason, J.A., Jacobs, P.M., Hanson, P.R., Miao, X., Goble, R.J., 2003. Sources and paleoclimatic significance of Holocene Bignell loess, central Great Plains, USA. *Quat. Res.* 60, 330–339.
- McCabe, G.J., Wolock, D.M., 2002. Trends and temperature sensitivity of moisture conditions in the conterminous United States. *Clim. Res.* 20, 19–29.
- McCulley, R.L., Burke, I.C., 2004. Microbial community composition across the Great Plains: landscape versus regional variability. *Soil Sci. Soc. Am. J.* 68, 106–115.
- McCulley, R.L., Burke, I.C., Nelson, J.A., Lauenroth, W.K., Knapp, A.K., Kelly, E.F., 2005. Regional patterns in carbon cycling across the Great Plains of North America. *Ecosystems* 8, 106–121.
- McCulley, R.L., Jobbagy, E.G., Pockman, W.T., Jackson, R.B., 2004. Nutrient uptake as a contributing explanation for deep rooting in arid and semi-arid ecosystems. *Oecologia* 141, 620–628.
- Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter. In: Bartels, J.M. (Ed.), *Methods of Soil Analysis. Part 3. Chemical Methods*. Soil Science Society of America, Madison, Wisconsin, USA, pp. 975–977.
- Parton, W.J., Schimel, D.S., Cole, C.V., Ojima, D.S., 1987. Analysis of factors controlling soil organic matter level in Great Plains grasslands. *Soil Sci. Soc. Am. J.* 51, 1173–1179.
- Paruelo, J.M., Lauenroth, W.K., Burke, I.C., Sala, O.E., 1999. Grassland precipitation-use efficiency varies across a resource gradient. *Ecosystems* 2, 64–68.
- Pena, F., Torrent, J., 1990. Predicting phosphate sorption in soils of Mediterranean regions. *Fert. Res.* 23, 173–179.
- Roberts, H.M., Muhs, D.R., Wintle, A.G., Duller, G.A.T., Bettis III, E.A., 2003. Unprecedented last-glacial mass accumulation rates determined by luminescence dating of loess from western Nebraska. *Quat. Res.* 59, 411–419.
- Roberts, T.L., Stewart, J.W.B., Bettany, J.R., 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.
- Rodriguez, J.B., Self, J.R., Soltanpour, P.N., 1994. Optimal conditions for phosphorus analysis by the ascorbic acid-molybdenum blue method. *Soil Sci. Soc. Am. J.* 58, 866–870.
- Runge, E.C.A., Riecken, F.F., 1966. Influence of natural drainage on the distribution and forms of phosphorus in some Iowa prairie soils. *Soil Sci. Soc. Am. Proc.* 30, 624–630.
- Schoenau, J.J., Stewart, J.W.B., Bettany, J.R., 1989. Forms and cycling of phosphorus in prairie and boreal forest soils. *Biogeochem* 8, 223–237.
- Sherrod, L.A., Dunn, G., Peterson, G.A., Kolberg, R.L., 2002. Inorganic carbon analysis by modified pressure-calcimeter method. *Soil Sci. Soc. Am. J.* 66, 299–305.
- Smeck, N.E., 1973. Phosphorus: an indicator of pedogenetic weathering processes. *Soil Sci.* 115, 199–206.
- Smeck, N.E., Runge, E.C.A., 1971. Phosphorus availability and redistribution in relation to profile development in an Illinois landscape segment. *Soil Sci. Soc. Am. Proc.* 35, 952–959.
- Soil Survey Staff, 2006. *Keys to Soil Taxonomy*, tenth ed. USDA-Natural Resources Conservation Service, Washington, DC, USA.
- Syers, J.K., Williams, J.D.H., Walker, T.W., Chapman, S.L., 1970. Mineralogy and forms of inorganic phosphorus in a graywacke soil-rock weathering sequence. *Soil Sci.* 110, 100–106.
- Thomas, G.W., 1996. Soil pH and soil acidity. In: Bartels, J.M. (Ed.), *Methods of Soil Analysis. Part 3. Chemical Methods*. Soil Science Society of America, Madison, Wisconsin, USA, pp. 475–490.
- Titus, J.H., Nowak, R.S., Smith, S.D., 2002. Soil resource heterogeneity in the Mojave Desert. *J. Arid Environ.* 52, 269–292.
- Tyler, G., 2002. Phosphorus fractions in grassland soils. *Chemosphere* 48, 343–349.
- U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, National Climatic Data Center, 2002. U.S. Monthly Climate Normals 1971–2000. Asheville, NC. Electronic resource. Available at: <http://lwf.ncdc.noaa.gov/oa/climate/normals/usnormals.html> Verified 11 February 2009.
- Vinton, M.A., Burke, I.C., 1997. Contingent effects of plant species on soils along a regional moisture gradient in the Great Plains. *Oecologia* 110, 393–402.
- Vitousek, P.M., Ladefoged, T.N., Kirch, P.V., Hartshorn, A.S., Graves, M.W., Hotchkiss, S.C., Tuljapurkar, S., Chadwick, O.A., 2004. Soil, agriculture, and society in precontact Hawai'i. *Science* 304, 1665–1669.
- Walker, T.W., Syers, J.K., 1976. The fate of phosphorus during pedogenesis. *Geoderma* 15, 1–19.
- Weaver, R.M., 1974. A simplified determination of reductant-soluble phosphate in soil phosphate fractionation schemes. *Soil Sci. Soc. Am. Proc.* 38, 153–154.