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PROCEEDINGS OF THE TWENTY-FOURTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

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FORMATION OF BASEMENT-INVOLVED FORELAND ARCHES: INTEGRATED STRUCTURAL AND SEISMOLOGICAL RESEARCH IN THE BIGHORN MOUNTAINS, WYOMING
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INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO
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EOCENE TECTONIC EVOLUTION OF THE TETONS-ABSAROKA RANGES, WYOMING
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Students: *JESSE GEARY*, Macalester College, *KATHERINE KRAVITZ*, Smith College, *RAY MCGAUGHEY*, Carleton College.

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Short Contributions— Front Range, CO

INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO
Project Faculty: DAVID P. DETHIER: Williams College, WILL OUIMET: University of Connecticut

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Research Advisor: Anna Martini

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Research Advisor: David P. Dethier

THE DISTRIBUTION OF PHOSPHORUS IN ALPINE AND UPLAND SOILS OF THE BOULDER CREEK, COLORADO CATCHMENT
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USING POLLEN TO UNDERSTAND QUATERNARY PALEOENVIRONMENTS IN BETASSO GULCH, COLORADO
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Research Advisor: Carl Mendelson

STREAM TERRACES IN THE CRITICAL ZONE – LOWER GORDON GULCH, COLORADO
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METEORIC ^{10}BE IN GORDON GULCH SOILS: IMPLICATIONS FOR HILLSLOPE PROCESSES AND DEVELOPMENT
CIANNA E. WYSHNYSZKY, Amherst College
Research Advisor: Will Ouimet and Peter Crowley

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THE DISTRIBUTION OF PHOSPHORUS IN ALPINE AND UPLAND SOILS OF THE BOULDER CREEK, COLORADO CATCHMENT

HAYLEY CORSON-RIKERT, Wesleyan University
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INTRODUCTION

Biological growth within terrestrial ecosystems is generally limited by the concentration of nitrogen, phosphorus, or both (Sato et al., 2009). Investigation into the availability of both these macronutrients in modern day alpine environments is important as N + P availability determines how such ecosystems will respond to climatic changes and anthropogenic alterations of soil chemistry (Wu et al., 2006). Recent studies have shown that enhanced rates of nitrogen deposition can force alpine systems that are typically N-limited to become P-limited, especially when P is efficiently cycled, making investigation into soil P dynamics yet more important (Sievering et al., 1996; Hedin et al., 2003; Vitousek et al., 2010).

Distribution of soil P occurs through geochemical and biochemical pathways, and is controlled by the demand for and supply of P in soil horizons (McGill and Cole, 1981). Crystalline or primary mineral P in deeper soils represents a long-term soil P reservoir, whereas secondary mineral forms and in particular labile forms are cycled more rapidly in upper and/or surface horizons (Walker and Syers, 1976). On short timescales, the availability of labile soil P to plants is dependent on a number of factors, including temperature, moisture, aeration, and soil microorganism activity (Tate & Salcedo, 1988). In the long term, labile P availability is dependent on the state of soil development, which in turn is determined by soil residence time and the rate of chemical and physical weathering (Walker and Syers, 1976; Porder et al., 2007).

In this study, I examine the soil P reservoirs of four soil profiles across an elevation gradient in Boulder County, Colorado, in order to better understand the patterns of and controls on soil P distribution in alpine environments. The four selected profiles are a subset of a broader set of studied soils in the Boulder Creek NCZO, and represent a range of elevations and climatic conditions. From greatest to least elevation, the sites are GLV, in the Green Lakes Valley; SLM, at the moraine below Silver Lake; UGG, in upper Gordon Gulch; and Betasso, in the Betasso Preserve (Table 1). The soils at GLV and SLM are relatively stable, with minimal soil movement, while the UGG and Betasso profiles are marked by buried horizons, which represent discontinuities in the soil sequence. Mean annual temperature near the highest site averages -3.7ºC, while average annual temperature at Betasso are about 10ºC (Niwot Ridge LTER; NOAA). Annual precipitation at this lower altitude is about 40 cm, while precipitation at the continental divide above GLV can amount to more than 100 cm annually (Table 1; Birkeland et al., 2003).

METHODS

In July and August 2010, soils from 31 sites were collected from newly scraped exposures or fresh soil pits. Collected samples were stored in plastic bags vacated of air in order to best preserve field moisture. Soil pH in water and soil moisture were determined by standard methods (Carter and Gregorich, 2008). Total carbon and nitrogen concentrations were determined on a Thermo Flash 1112 Elemental Analyzer. Given the lack of carbonate minerals in these soils, total carbon (TC) is assumed to equal total organic carbon (TOC). Bulk chemistry analysis for metals was determined by ICP-OES techniques at SGS Mineral Services, after dissolving soils in a four-acid digest ($HCl/HNO_3/HF/HClO_4$). The digestion may not have completely dissolved very recalcitrant mineral phases. On 21 samples, soil P pools were determined by a modified Hedley sequential extraction procedure (Figure 1; Hedley et al., 1982; Ruttenberg, 1992; Tiessen and Moir, 1993). Inorganic (Pi) and total phosphorus (Pt) concentrations were determined by spectrophotometry methods of Murphy and Riley (1962) using a Beckman Coulter DU5300 at a wavelength of 885 nm. Organic phosphorus (Po) concentrations were determined by subtraction of Pi from Pt.

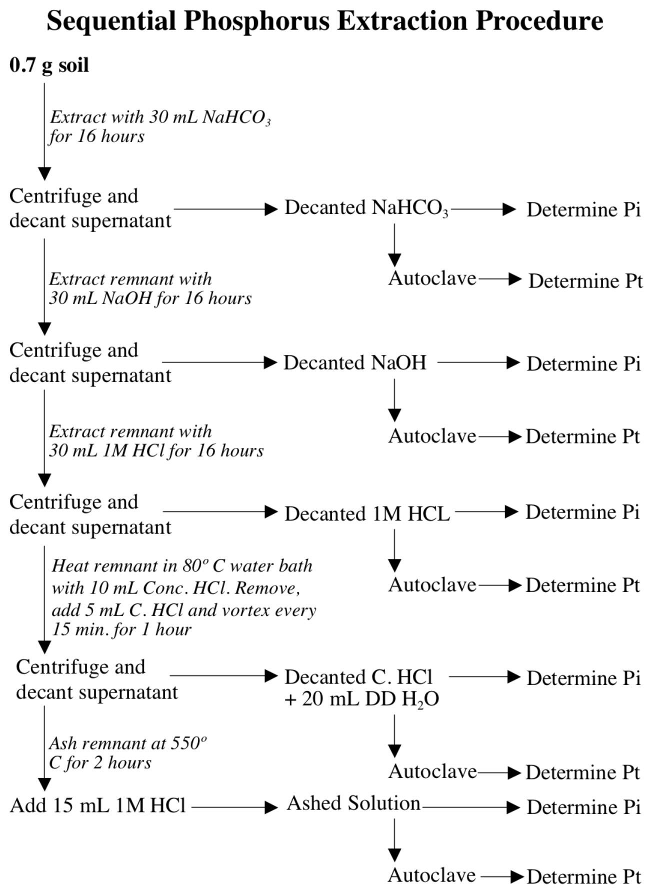

Figure 1. Flowchart of sequential phosphorus extraction methodology. The procedure is a modification of Tiessen and Moir (1993), with the ashing step of Ruttenberg (1992). Pi = inorganic phosphorus, and Pt = total phosphorus. Autoclaving conditions were 121ºC, 17 psi, for 50 minutes.

Measured extractable P fractions were grouped to obtain operationally-defined soil pools: Exchangeable P (NaHCO3 Pi); Organic P ($NaHCO_3$ Po + NaOH Po + C. HCl Po); Fe-bound P (NaOH Pi); Ca-bound P (1M HCL Pi + 1M HCl Po); Recalcitrant P (C. HCl Pi); and Highly Recalcitrant P (Ashed Pi + Ashed Po) (Tiessen and Moir, 1993). The percentage of initial total P remaining in individual horizons was calculated relative to Al as follows, where X = sample horizon and Y = parent material (or deepest available horizon): Initial total P concentration equals [Al]X x ([Pt]Y/[Al]Y). The % of initial total P remaining equals 100 x ([Pt]X/[Pt]Y) (Vitousek et al., 2004, Supp. Mat.). The percent of initial Ca-bound Pi was calculated in the same manner.

RESULTS AND DISCUSSION

General soil properties

A summary of results is shown in Table 1. In these four soil profiles, soil pH increases with depth, with surface horizons displaying pH ranging from 4.43 to 5.61 and base horizons pH ranging from 5.51 to 6.05. The greater acidity of surface horizons is typically the result of organic matter decay, which lowers the pH of soil pore waters (Twidale, 1990). This assumption is supported by the consistently high TOC concentrations in surface horizons (Figure 2). As expected, TOC is correlated with organic N throughout all horizons, and C:N, C:P_0, N:P_0, and soil moisture values decrease with depth (Table 1; Figure 2). P organic:P inorganic decreases with depth, demonstrating the transition from surface horizons rich in organic and plant available P to deeper horizons dominated by primary and secondary mineral P (Figure 2). Soil concentrations of Al increase with depth at all sites (Table 1).

Site Elevation (Annual Precip.)	Site Location	Horizon	Horizon Age (in years)	Horizon Depth (cm)	pH	Water (wt.%)	C (wt.%)	C/N (molar)	Al (wt.%)	Total P (ug/g)
1951 m *(≤44.5 cm)*	Betasso Preserve	O		0 - 4	4.44	17.9	47.4	31.5	0.6	660
		A		4 - 12	5.57	5.7	2.22	20.5	6.8	662
		Bw	5,400*	12 - 40	5.85	4.2	0.48	6.4	7.3	855
		bA	6,200*	40 - 93	6.18	9.3	0.77	13.3	7.6	879
		bBt	12,200*	93 - 145+	6.05	9.6	0.32	6.9	7.7	991
2700 m *(~44.5 cm)*	Upper Gordon Gulch (Pit 2)	A		0 - 6	5.61	24.9	7.15	27.5	5.8	322
		Bw		6 - 19	5.39	4.7	0.80	12.9	6.4	262
		Cox	2,000*	19 - 34	5.40	11.0	0.46	10.5	7.1	273
		bBt		34 - 50	5.89	7.7	0.21	6.8	7.7	279
		bBt2	26,200*	50 - 69	5.96	10.1	0.20	6.5	7.4	2302
		CRt		69 - 100	5.87	9.0	0.18	6.2	8.4	2853
3097 m *(~82.6 cm)*	Silver Lake Moraine	Ej		9 - 15	4.51	1.7	1.22	18.7	5.6	198
		B1		15 - 32	4.40	3.1	1.10	17.9	6.4	614
		B2		32 - 48	4.86	6.1	1.19	22.2	6.7	744
		B3		48 - 66	4.89	4.9	0.82	16.5	6.1	615
		B4		66 - 102	5.05	4.0	0.40	22.2	6.0	732
		Cu	14,500†	102+	5.84	1.9	0.06	-----	6.4	982
3440 m *(~95.3 cm)*	Green Lakes Valley (b/t lakes 1 & 2)	O		0 - 2	4.43	31.7	10.6	27.3	5.5	605
		A		2 - 11	5.06	16.4	3.97	26.0	6.3	367
		Bwh		11 - 25	5.05	20.2	1.27	16.0	6.5	238
		Bw2		25 - 45	4.79	20.3	1.66	18.7	7.5	420
		Cox		45 - 70	5.65	9.8	0.61	13.3	7.2	632
		Cu	14,000†	70+	5.51	10.0	0.21	6.8	7.5	663

*Table 1. Table of study site information and soil properties. Soil ages from Dethier et al., unpublished data -- * denotes exposure ages measured by OSL techniques, † denotes age based on CRN techniques.*

Total Soil P

Total P concentration profiles are presented in the right-hand column of Figures 3 and 4. Total soil P concentration varies from 198 to 2853 ug/g across all horizons. These values are comparable to those of other alpine soil studies, which were generally be

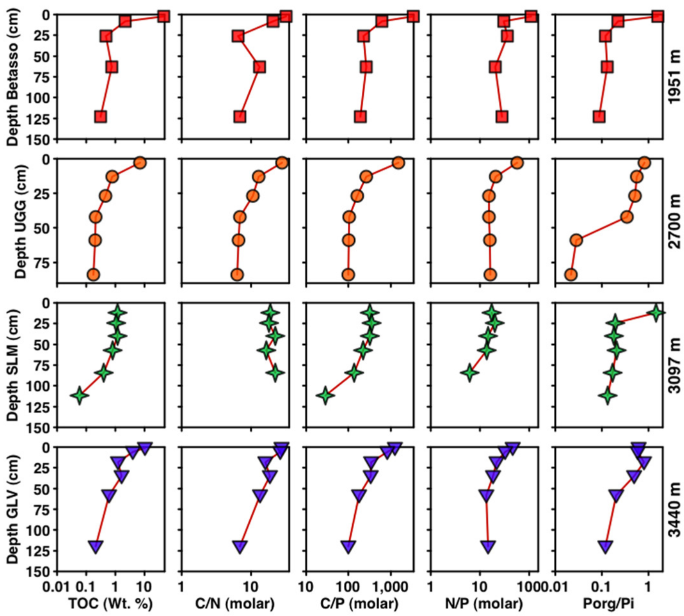

Figure 2. Soil depth vs. TOC, C:N. C:P_o, N:P_o, and P organic:P inorganic. Note log scale on x-axis.

tween 121 to 2540 ug/g (Table 1; e.g. Makarov et al., 1997). Total soil phosphorus concentrations show no discernable correlation with elevation. It is assumed that the variation in moisture regimes, parent material, soil residence time, and weathering rates is too great for a clear pattern to emerge.

The Development of Soil P Reservoirs

Soil P is widely held to exist in three main pools: primary inorganic P, secondary inorganic P, and organic P. Walker and Syers (1976) presented a model in which primary inorganic P (mineral P) is abundant in early stages of soil development and, as weathering progresses, is transformed into organic forms and sorbed to secondary minerals. Thus, the primary mineral P fraction becomes depleted as the organic P and secondary mineral P fractions are enriched. At first, a portion of this sorbed inorganic secondary mineral P is exchangeable, or plant available, but this labile fraction is later diminished with the exhaustion of the primary mineral P reservoir. In more highly weathered profiles, labile P is further depleted due to the progressive transformation of the secondary mineral P into occluded, or recalcitrant, forms that are biologically unavailable. Within soil profiles, horizon development progresses vertically, with upper horizons originating from parent material. Each horizon, therefore, represents a stage and/or type of soil development, and soil P distribution within these horizons should reflect their position on the continuum. In effect, primary mineral P is expected to decrease from deeper to surface horizons, while organic, secondary mineral, and labile P are expected to increase (Walker and Syers, 1976; Stewart and Tiessen, 1987; Crews, 1995; Porder et al., 2007). In stable soils, this increase in plant-available P and decrease in primary mineral P occurs as total P is diminished due to net P removal by weathering. This pattern is most visible in sites that experience high annual levels of precipitation, due to the enhancement of soil redox processes and thus the quickening of mineral P dissolution and removal (Miller et al., 2001; Hedin et al., 2003).

Distribution of Soil P Pools in the Boulder Creek Catchment

Figures 3 and 4 show the distribution of P fractions, total P, and calculated values of % P remaining at the four study sites. The importance of various soil P transformation processes is reflected in the distribution of these soil P pools, and is impacted by the extent to which the soil profile has been disturbed during development (Beck and Elsenbeer, 1999). Buried horizons at UGG and Betasso indicate that these soils have experienced more soil movement than the more stationary profiles of GLV and SLM. At GLV and SLM, Ca-bound Pi generally increases with depth and exchangeable P decreases with depth. The O and A horizons at GLV are the exception to this pattern, as they have proportionally greater concentrations of Ca-bound P than the horizons immediately below. These elevated levels of primary mineral P, coupled with the concomitant rise of remaining initial total P to percentages greater than 100, points to an external input of comparatively unweathered hillslope colluvium or eolian material. This is supported by the P organic:P inorganic ratios of the O and A horizons (Figure 2), which are slightly lower than in the horizons immediately below, suggesting that these upper horizons are less weathered than the B horizons below (Tate and Salcedo, 1988). Soil P distribution within these GLV B horizons instead appears to be the result of continued weathering, as a net loss of total P due to mineral dissolution is apparent from the Cu to Bw1 horizon.

Site SLM, due to its stability, has the most standard distribution of soil P fractions, with a clear inverse

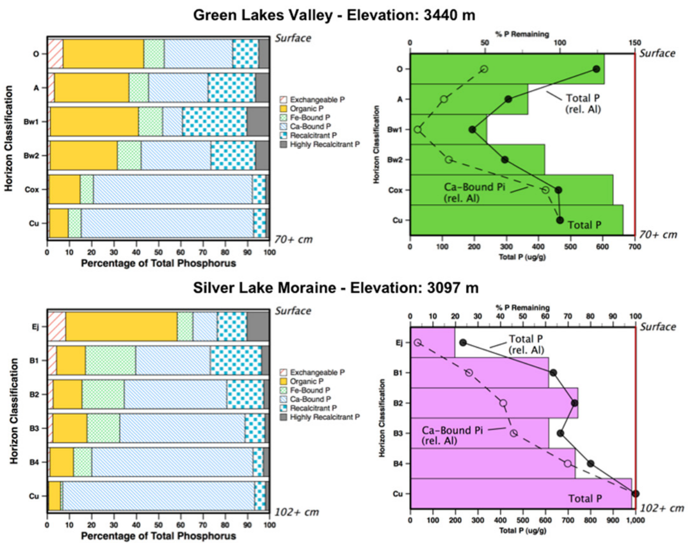

Figure 3. GLV and SLM Soil P reservoirs, with the left-hand chart depicting the relative percentage of each P-reservoir per soil horizons, and the right-hand chart illustrating total P (bars, lower x-axis) and the % of initial total P and Ca-bound Pi remaining in each horizon, relative to Al (upper x-axis).

relationship between the organic P and Ca-bound P fractions. This clean pattern indicates that soil surface horizons are developed almost entirely from the parent material, though some eolian deposition may have altered surface horizon composition. Here, like in the lower GLV horizons, total soil P is highest at depth and decreases above the parent material horizon. Measurements of % initial total P remaining also decrease, suggesting that P is consistently being removed from the soil system throughout all horizons, leading to a decrease in Ca-bound P and a subsequent enrichment of the organic P fraction.

The lower two studies sites, UGG and Betasso, have a more complex history than GLV and SLM, as both contain buried horizons. At UGG, though organic P content decreases with depth, as expected, and Ca-bound P concomitantly increases, there is a clear difference between buried and current soil horizons. Total P decreases sharply between the lower bBt2 and the bBt above it. Similarly, Ca-bound P is at least 70% of total P in the lowermost horizons, but only ~7% of total P in the Bt1, Cox, and Bw horizons. This low total P content in these middle three horizons, coupled with their corresponding low percentage of primary mineral P, and high percentage of organic P and recalcitrant P indicate that these horizons are highly weathered, despite their relatively young exposure age (Table 1). This conclusion, in turn, suggests that that these upper horizons have either experienced intense and rapid weathering, or formed from already weathered material that was transported to this site, burying the lowermost bBt2 and CRt horizons that had formed in situ. Soil exposure ages support this last conclusion, as the two bottom horizons were last exposed 20,000 years ago, while the upper 'moved' horizons were exposed much more recently, roughly 2,000 years ago (Table 1). Importantly, within the two soil brackets above, {CRt-bBt2} and {bBt-A}, the total soil P and % P remaining do not diminish with decreasing depth, indicating no net P loss. This is in contrast to the net P loss at the higher GLV and SLM profiles. The relatively larger fraction of Ca-bound P in the surface A horizon suggests that soil P distribution in the near surface environment is skewed by an external influx of unweathered material rich in primary mineral P (Figure 4).

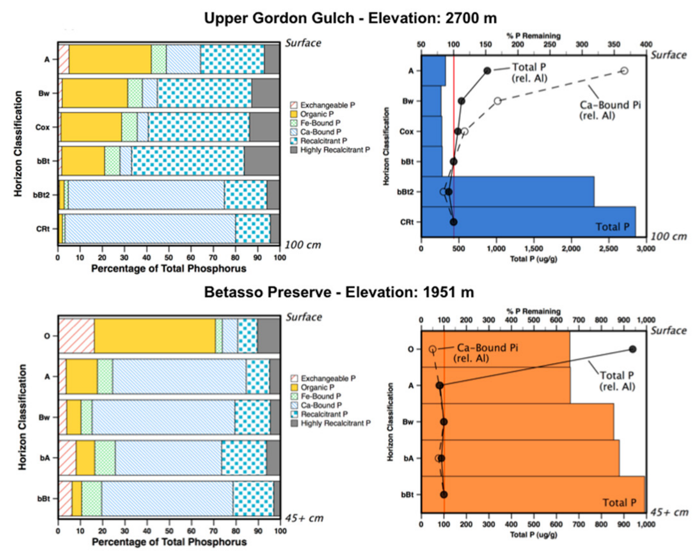

Figure 4. UGG and Betasso Soil P reservoirs, with the left-hand chart depicting the relative percentage of each P-reservoir per soil horizons, and the right-hand chart illustrating total P (bars, lower x-axis) and the % of initial total P and Ca-bound Pi remaining in each horizon, relative to Al.

The Betasso soil profile shows no similar enrichment of Ca-bound P in surface horizons, but contains a thin O horizon that is heavily enriched in organic P. This horizon is primarily composed of fresh and decaying plant litter and needles. Below the O horizon, organic

P levels do not increase greatly, total P increases only slightly, and Ca-bound P remains a dominant portion of total soil P -- suggesting that the lower A, B, bA, and bBt horizons have experienced little weathering despite their age of 5 to 12 kyr. Given the comparatively low annual levels of rainfall at this site, ~40 cm, this slow soil P development is likely due to the limited percolation of moisture to deeper horizons, which would limit both chemical weathering and soil microbial activity.

CONCLUSIONS

Soil P pools at the four sites can be explained by continued weathering and patterns of soil movement. SLM shows the most consistent trend in soil development, with surface horizons enriched in exchangeable and organic P and deeper portions of the profile enriched in Ca-bound P. GLV has a similar profile, except that the upper layer likely contains relocated primary mineral P. This addition of outside material is also evident in the A and Bw horizons of the UGG profile, suggesting that the relocation of primary mineral P by either hillslope removal or eolian deposition may be an important factor in soil P distribution and development in surface soil environments across the Front Range gradient. The Betasso site is relatively unweathered, with little accumulation of organic P in the A horizon. This may be the result of a low degree of weathering experienced by soils at this altitude. Overall, weathering appears to be more intense at the higher, wetter alpine sites of GLV and SLM, where a considerable fraction of soil P has been lost, than at UGG and Betasso, though the relocation of unweathered and weathered soil material, as seen at both SLM and UGG, serves to complicate this trend.

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