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The biogeochemistry of phosphorus across an alpine topographic/snow gradient

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Abstract

Phosphorus (P) availability has generally been assumed to be the limiting or co-limiting factor for plant growth in alpine environments. To test this assumption, the biogeochemistry of phosphorus (P) along an alpine topographic/snow gradient located on Niwot Ridge, Colorado Front Range was studied in the context of P limitation for plant growth. We measured the various P pools using a selective extraction procedure, determined sorption parameters, and quantified P availability indices. The topographic/snow gradient at Niwot Ridge is divided by the aspect and slope position in relation to the dominant westerly winds into leeward-sloping, windward-sloping and generally level sites. Our study found that the snow-melting gradient along the alpine transect greatly affected the antecedent soil moisture, which in turn, controlled the spatial pattern of the major soil attributes such as texture, OC, weathering index, bulk density, non-labile and labile P pools and P availability. The level sites exhibited the highest concentration of organically bound P (1056 ± 75 mg/kg), labile P (315 ± 32 mg/kg), and P in soil solutions corrected for soil adsorption capacity (field condition, 4.9 ± 4.1 mg/l and saturated paste, 8.0 ± 7.5 mg/l). Results of correlation analysis between the various P pools and aboveground biomass of different plant groups suggests that a high level of available P provides a growing advantage to only certain alpine plants and is not a good indicator of the spatial distribution of total aboveground biomass.

Keywords: Available P; Labile P; Alpine ecosystem; Topographic/snow gradient

1. Introduction

Most terrestrial ecosystems are considered nitrogen (N) and/or phosphorus (P) limited, which directly affect community composition and plant growth (Chapin et al., 2002; Aerts and Chapin, 2000). However, in areas that receive continuous input of anthropogenic deposition such as the Colorado Front Range (3–5 kg N/ha year) (Sievering et al., 1996), N limitation should be progressively alleviated, eventually creating a situation in which the availability of P is more

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important than that of N in regulating carbon balance and community composition.

The ratio of atmospheric N deposition to net mineralization in the alpine environs presently approaches 0.5 (Fisk et al., 1996) and is higher at the Niwot Ridge alpine tundra ecosystem than at most other ecosystems in the continental U.S. Williams et al. (1996) found that N loading in wet deposition approximated 4 kg/ha year and that NO_3^- export from streams in the Colorado Front Range has increased from below detection to ~ 10 μequiv/l, indicating that alpine and the subalpine environs of the Colorado Front Range are at the threshold of N saturation. They also found that foliar N/P ratios in bristlecone pine increase with increasing elevation, indicating that atmospheric deposition of N may be causing a change from N limitation to P limitation in the alpine environment.

Over the past 15 years, numerous studies focusing on the influence of nutrient availability on plant primary productivity, abundance, and species diversity have been conducted in the alpine tundra ecosystem at Niwot Ridge. Bowman et al. (1993) found that N availability was limiting to production in an alpine dry-meadow community, whereas N and P availability co-limited production in the wet-meadow community. In general, there was a greater production response on a relative scale to the N and N + P amendments in the dry meadow than in the wet meadow. Bowman (1994) also showed that dry-meadow plants had higher N-use efficiency in response to N fertilization than did plants in the wet-meadow community. Conversely, the wet-meadow community had a greater P-accumulation response to P fertilization and higher P-use efficiency than the dry-meadow community. Theodose and Bowman (1997) further tested the nutrient-limitation hypothesis and showed that changes in the absolute abundance of certain plant species were more pronounced in the dry-meadow community than in the wet-meadow community in response to N, and N and P additions. Seastedt and Vaccaro (2001) studied the influence of N and P limitations across a snowpack gradient in an alpine tundra ecosystem and showed that addition of either N or P enhanced plant foliage productivity ($P = 0.05$ and $P = 0.03$, respectively). Phosphorus additions had the strongest single treatment effect on plant productivity in this experiment, but neither P nor N had a significant effect on species diversity.

Despite the apparent importance of P availability in influencing alpine plant communities and ecosystem structure and function, relatively little is known of the biogeochemical processes that govern P cycling and availability in alpine soils, especially in a continuum landscape context. As part of this concept, we hypothesized that P availability in alpine soils is mainly controlled by the generation of meltwater that flows along the alpine topographic/snow gradient. This meltwater increases the soil moisture and, consequently, increases P concentrations in soil solutions and P availability in areas below the progressively retreating snowpack. If P is indeed a limiting nutrient to alpine plant growth, then the abundant soil moisture coupled with increased available P would provide better growing conditions to plants in these areas. The objective of the present work was to study the edaphic factors and processes that control the amount, nature, and spatial variations of available P in alpine soils along a topographic/snow gradient.

2. Material and methods

2.1. Field site

Field work for this study was conducted on Niwot Ridge, Colorado Front Range (Fig. 1). Niwot Ridge has been a research site for the Long-Term Ecological Research (LTER) program since 1980 and was the site of the International Biological Program (IBP) in the 1970s. Our study site is located in an area known as the Saddle, at an elevation of about 3525 m. A research grid of 17.5 ha (550 m long and 400 m wide) that encompasses seventy 50 by 50 m quadrants was established on the Saddle along a topographic/snow gradient (Walker et al., 1993).

Soil development on Niwot Ridge was studied by Burns and Tonkin (1982), who formulated a synthetic alpine slope (SAS) model to categorize microenvironments across the landscape, according to edaphic, topographic, and snow-cover relationships. The most important characteristic of these relationships was found to be the approximate number of snow-free days per year. Extremely windblown sites are characterized by more than 300 snow-free days, windblown sites by 225 to 300 days, minimal snow-cover sites by 225 to 150 days, early-melting snow sites by 100 to

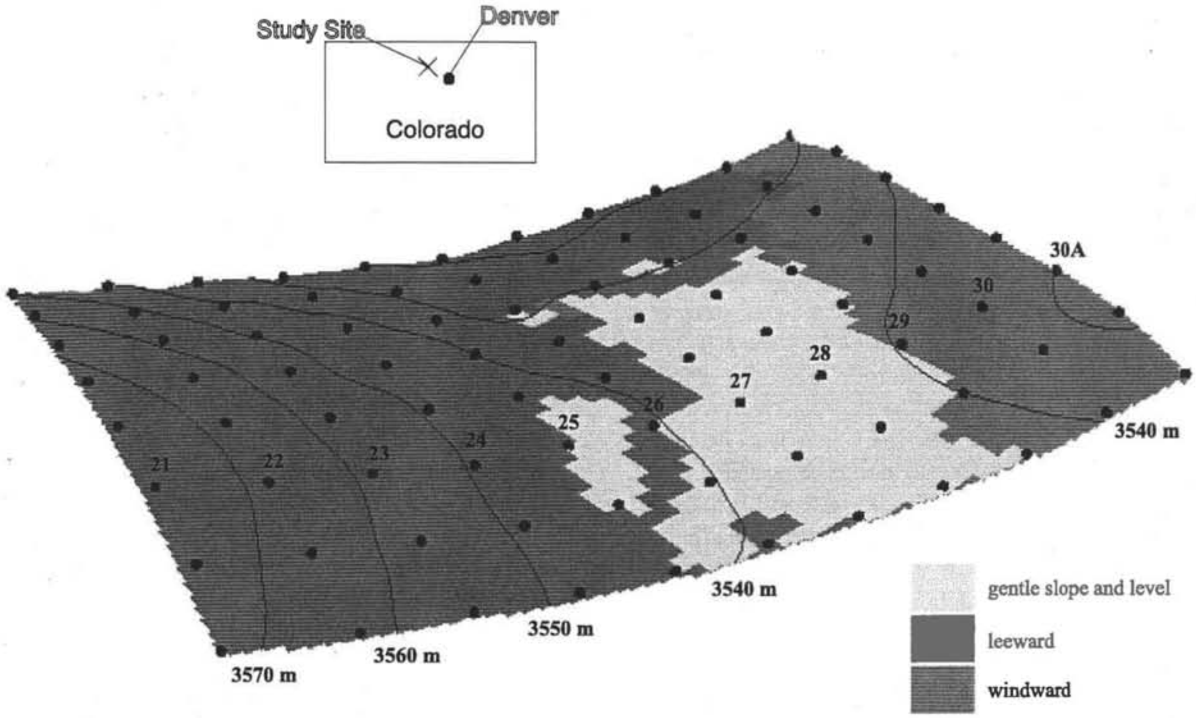

Fig. 1. General location and 3-D drape of the Saddle grid study area in Niwot Ridge, Colorado Front Range (40°03N, 105°35W). The dark gray area represents the locations of the 11 soils used in the P fractionation and sorption experiments.

150 days, late-melting snow sites by 50 to 100 days, and wet meadow sites by ∼ 100 days. Burns and Tonkin (1982) used the soil classification system outlined in the Soil Survey Staff (1975) to classify the soils along the topographic/snow transect from Dystric Cryochrept at the windblown site, Pergelic Cryumbrept at the minimal snow-cover site, Typic Cryumbrept at the early-melting site, Dystric Cryochrept at the late-melting site, and various Cryaquepts and Cryaquolls in the wet-meadow sites. Plant community distributions were found to follow the same gradient as the soil types, with patterns of species abundance and distribution, phenology, and biomass significantly correlated with the mesotopographic gradient (May and Webber, 1982; Walker et al., 1993, 1994, 1995). For the purpose of this study, the gradient was divided by the aspect and slope position in relation to the dominant westerly winds into leeward, windward and level sites (Fig. 1) similar to the landscape classification used by Isard (1986). Snowbed plant association characterizes the leeward sites; the level sites are mainly moist meadow plant community, whereas dry meadow and fellfield plant associations typify the windward sites. The dominant plant species in the study area are *Kobersia myosuroides*, *Acomastylis rossi*, *Deschampsia caespitosa*, *Trifolium* spp., *Silene acaulis*, and *Carex rupestris*.

2.2. General attributes

Composite soil samples were taken in the summer of 2001 at 11 grid points along a topographic/snow gradient (Fig. 1) from a depth of 0 to 15 cm where the bulk of the plant roots extend. This particular gradient within the Saddle grid was selected to minimize the influence of snow-fence experiment (Williams et al., 1998) and P fertilization experiments currently being conducted along other transects of the grid. All the soil samples were air-dried and sieved through a 2-mm sieve before laboratory analysis was conducted.

To assess the weathering intensity along the alpine soil transect, we measured the soil color of each soil sample with a chroma meter (CR-310, Minolta Ossaka, Japan) using ground samples. The analysis was performed by lightly pressing the glass protection tube (CR-A33a) against a 5-mm-thick layer of sample. The color was specified using the CIE-$L^*a^*b^*$ color system according to the recommendation of Melville and Atkinson (1985). The CIE-$L^*a^*b^*$ color system is defined as color coordinates where L^* measures the lightness of the sample, a^* measures redness when positive, gray when zero, and greenness when negative, and b^* values measure yellowness when positive, gray when zero, and blueness when negative. We manipulated the CIE color coordinates to get a simple multiplicative color index R_{Lab} ($R_{Lab} = a^*[a^{*2} + b^{*2}]^{0.5} \times 10^{10}/[b^*L^{*6}]$) described by Barron and Torrent (1986), which represents a relative weathering index for samples collected along the gradient.

Soil pH was determined in 1:10 soil–water suspensions using a glass electrode, organic matter content was determined by the dry combustion method (Nelson and Sommers, 1982), and bulk density was determined by the clod method. Soil moisture data were obtained by standard gravimetric analysis of soil cores taken at the peak of the growing season, as well as on soil samples under air-dried and saturated-paste conditions. Sesquioxide content was extracted from the 11 soil samples using the ammonium oxalate procedure described by Ross and Wang (1993). Elemental concentrations were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Spectro, Kleve, Germany). All elemental and general analyses were done in triplicate. Particle size distribution for the soil samples was determined using a low-angle laser diffraction particle-size analyzer (Malvern Instruments, UK).

Soil moisture was measured at 48 grid points (three probes per site) during each growing season (June to October) from 1994 to 2002, using the time-domain reflectometry (TDR) method (Topp et al., 1980). Of these 48 grid points, only 5 were located along the topographic/snow gradient selected for our study; thus, we used the entire TDR data set to ascertain the spatial and temporal variations of soil moisture in the Saddle area. The TDR probes were inserted to the top 15 cm of the soil, and soil moisture was measured as voltage waveforms using a Tektrnix 1502B cable tester. The waveforms were stored in the field on a laptop computer. The volumetric soil moisture determinations were calibrated against gravimetric measurements, and the volumetric values were converted to gravimetric values by regression analysis as described in Taylor and Seastedt (1994).

Along Niwot Ridge, the depth of the snowpack has been measured at 88 grid points within the Saddle area, from 1982 to 2000, for a total of more than 15,000 measurements. The frequency of snow-depth measurements during the winter months varied from biweekly to once a month, depending on the weather conditions. Measurements during the summer were performed biweekly until all snow disappeared or until new snow began accumulating for the next winter. Measurements of snow depth were carried out to the nearest centimeter. For the present study, we analyzed the snow-depth pattern along the selected gradient where our 11 soil samples were collected. The snow-depth data compiled for the Saddle area represented a repeated-measures design that had to be aggregated for the transect analysis of the 11 sampling points. We selected two aggregation schemes that together best represent the spatial-temporal nature of the data. First, the data were averaged for each of the 11 grid points along our sampling gradient using data from the entire monitoring period (1982 to 2000). Second, the data were aggregated at each of the 11 grid points using the data collected during the month of June each year. The rational for the aggregate scheme followed the SAS model (Burns and Tonkin, 1982), which suggests that the soil development across the alpine landscape is controlled by the number of snow-free days per year. In turn, the number of snow-free days affects soil temperature and moisture content. The entire snow-depth aggregate scheme better represents soil temperature rather than moisture because some of the snow that accumulated during the winter months was blown away or sublimated. The depth of the June snowpack provides a good measure for water equivalents because it represents the maximum snowpack in the beginning of the summer and determines the water budget during the short alpine growing season. A more detailed analysis of the spatial distribution of snow depths across the entire Saddle study area is given elsewhere (Litaor et al., 2001).

Plant biomass was determined by plant growth form (i.e., total live forbs, graminoid, herb, aboveground biomass, and several typical alpine species) during the peak biomass production (July) in 1992 and 1993 at each of the 11 sampling points. All aboveground biomass was harvested from subplots using a razor blade. The samples were sorted into growth-form classes, dried at 60 °C for 24 h, and immediately weighed to prevent reabsorption of water by the plant material.

2.3. Phosphorus fractionation

We used the modified method of Hedley et al. (1982) described by Tiessen and Moir (1993) in triplicates to extract empirically defined pools of P from 11 soils located along the topographic/snow gradient (Fig. 1). This method has been widely used to determine bioavailability of P and general pedogenesis (e.g., Tiessen et al., 1984; Sharpley et al., 1994; Cross and Schlesinger, 1995; Beck and Elsenbeer, 1999). A 0.5-g soil sample passed through a 2-mm sieve was placed in a 50-ml centrifuge tube and then sequentially extracted with anion-exchange resin, 0.5 M $NaHCO_3$ (pH 8.5), 0.1 M NaOH, 1 M HCl, and concentrated HCl. After each extraction, the samples were centrifuged at $17,000 \times g$ for 20 min at 0 °C and the supernatant was passed through a 0.45-μm filter. After the final extraction, the residual soil P left in the tubes was determined by extraction with boiling in a concentrated H_2SO_4–H_2O_2 mixture. Aliquots from the filtered $NaHCO_3$, NaOH, and HCl extracts were further digested in an autoclave at 103.5 kPa and 121 °C with ammonium persulfate to convert all the dissolved P into orthophosphate, which was then measured as total P (P_t). The inorganic P (P_i) and the total P (P_t) in all the extracts were determined colorimetrically using Murphy and Riley's (1962) method, and the organic P (P_o) was calculated as the difference ($P_t - P_i$).

2.4. Phosphorus availability

To assess the availability of P along the selected transect, we estimated the concentrations of P in soil solution at the 11 sampling sites using the paste method described by Smethurst et al. (1997). In short, the amount of P in the soil solution at sampling time can be derived from:

$$\theta_i C_{li} + \rho C_{si} = \theta_f C_{lf} + \rho C_{sf} \quad (1)$$

where θ is volumetric water content, C is P concentration and ρ is bulk density. Subscripts denote the liquid phase (l), the solid phase (s), the initial condition in the field (i) and the final condition as a saturated paste (f). The partitioning of the solute between solid and liquid phases can be described by the modified Freundlich equation (Smethurst et al., 1997):

$$C_s = AC_l^{1/B} + D \quad (2)$$

where A, B and D are fitted parameters. The derivative of Eq. (2), with respect to C_l yields:

$$dC_s/dC_l = K_d = (A/B)C_l^{[(1/B)-1]} \quad (3)$$

where K_d is the slope of the isotherm. The buffering power of the soil, which provides a nutrient replenishment appraisal of the soil solution, was computed using Eq. 7 from Van Rees et al. (1990):

$$b = \theta + \rho K_d \quad (4)$$

By assuming that A, B and D are each independent of θè, substituting Eq. (3) into Eq. (1) and rearranging, gives the following:

$$C_{lf} = \theta_2^{-1}[\theta_i C_{li} + \rho A(C_{li}^{1/B} - C_{lf}^{1/B}] \quad (5)$$

Eq. (5) was solved for the initial concentration of P in the soil solution, using the "Goal seek" tool in Microsoft Excel.

The fitted parameters of the Freundlich equation were evaluated by conducting sorption experiments on the soil samples collected for this study. The experimental sorption data were fitted to the Freundlich equation using the SigmaPlot curve-fitting routine (SPSS, 2000). The sorption experiments were carried out in triplicate at 25 °C, using a soil-to-solution ratio of 2 g to 25 ml of 0.03 M KCl (Richardson and Vaithiyanathan, 1995). The additions of P in the sorption experiment ranged from 0 to 70 (0, 0.5, 1, 2, 4, 6, 8, 10, 20, 40, and 70) mg/l, similar to the sorption-experiment conditions recommended by Nair et al. (1984). The suspensions were equilibrated for 24 h in polyethylene tubes on a reciprocal shaker, followed by centrifugation at $1500 \times g$ for 20 min. An aliquot of filtered (0.45 μm) supernatant was analyzed for P using the ammonium-molybdate colorimetric method (Murphy and Riley, 1962).

The statistical significance of the spatial distribution of the various soil parameters measured along the topographic/snow transect was tested by ANOVA and nonparametric tests using SPSS/PC version 11.

3. Results and discussion

3.1. Topographic/snow gradient

The depth of the snowpack measured along our study transect clearly indicates that the leeward east-facing slopes exhibit deep snow accumulation during the winter that lasts well into the spring and, in some years, even well into the summer (Table 1). In contrast, the windblown west-facing slopes accumulate less snow throughout the year, and the measured depth of the snowpack exhibited large standard deviations (S.D.) around the means of both aggregates. The gently sloping to level locations accumulated moderate amounts of snow, with progressively greater accumulations on the steeper, slightly east-facing slopes.

3.2. General soil characteristics

The general soils characteristics along the topographic/snow gradient are summarized in Table 2. The particle-size distribution, weathering index, gravimetric soil moisture contents, bulk density, Al- and P-oxalate concentrations and organic carbon

Table 1
Summary statistics of snow depth (cm) along the topographic/snow gradient

Site[a]	Entire data set			June snow depth		
	X	S.D.	N	X	S.D.	N
21	163	100	127	169	99	32
22	165	100	124	183	81	32
23	205	100	132	245	73	32
24	190	102	130	208	80	32
25	102	70	114	108	57	32
26	51	50	102	74	99	19
27	44	27	106	52	40	16
28	56	44	90	66	47	10
29	14	14	54	29	21	4
30	12	12	55	30	22	4
30A	16	14	50	38	20	3

[a] Sites 21 to 25 are leeward steep slopes conditions, 26 to 28 are gentle to level slopes conditions and 29 to 30A are windward position.

(OC) content varied significantly with location (Table 3). Correlation analysis showed that OC, gravimetric soil moisture, and silt content were highly positively correlated with each other; however, these three variables were strongly negatively correlated with bulk density (Table 4). These correlations support field observations that the amount of OC and soil moisture content strongly affects the structure and aggregate appearance of the top horizons (0 to 15 cm) of soils along the alpine gradient. Other significant results shown in Table 4 include weathering index, which was highly correlated with OC, silt content, soil moisture, and concentrations of P and Al oxalate. In contrast, weathering index was highly negatively correlated with sand content and moderately negatively correlated with concentrations of Fe-oxalate.

The pattern and interrelationships of soil characteristics along the study transect are best explained by the snowmelt gradient along the alpine transect. In turn, snow cover (number of snow-free days), snow depth, and snowmelt gradient are related to the aspect (windward, leeward, or level) of the location. The leeward slopes are characterized by a deep accumulation of winter and spring snow, which insulates these soils from the prevailing westerly winds, but significantly reduces the length of the growing season. Hence, the OM is poorly developed in the leeward soils and the soil texture is considerably coarser compared with soils developed on level and windward sites. The leeward soils also had the lowest weathering index and the lowest concentrations of P oxalate (Table 2). The level slopes are relatively protected from the prevailing westerly winds and receive substantial additions of snowmelt water from the progressively melting snowpack located along the steeper east-facing (leeward) slopes during most of the growing season. Hence, soils developed on the level sites exhibited the highest levels of OM and soil moisture, as well as the finest texture. Soils on the level sites also showed the highest weathering index and the highest concentrations of P oxalate, compared with soils on the leeward and windward sites. The windward slopes had the least amount of snow accumulation and once the snow on the windward sites melted, the soils dried out quickly. The soil moisture, weathering intensity, and OM and P-oxalate content for alpine soils on leeward, windward, and level sites

Table 2
The spatial pattern of major soil attributes along the alpine topographic/snow gradient

Site[a]	Elevation (m)	Slope	Aspect	Sand (%)	Silt (%)	Clay (%)	Moisture (%)	Air-dried (%)	OC (%)	R_{Lab}	BD (g/cm^3)	pH	Fe_{ox} (mg/kg)	Al_{ox} (mg/kg)	P_{ox} (mg/kg)	Ca_{ox} (mg/kg)
21	3572	3	112	74.86	17.46	7.68	29	2.4	5.1	15	0.95	4.4	5300	2170	580	118
22	3561	12	101	62.69	21.99	15.33	30	2.1	4.9	9	0.97	4.5	5000	2090	570	100
23	3550	5	170	63.60	19.22	17.18	24	2.2	4.5	11	0.91	3.5	6600	2290	510	101
24	3542	7	110	61.72	21.75	16.53	23	2.9	3.8	13	0.99	4.5	5200	1990	460	127
25	3537	5	166	58.16	24.50	17.34	40	2.8	5.2	20	0.91	4.4	5800	2790	860	106
26	3533	3	116	52.13	31.49	16.38	43	6.7	5.5	31	0.91	4.3	4360	3000	980	110
27	3529	2	60	37.00	41.50	21.51	83	6.2	14.8	44	0.53	4.3	4680	3120	1040	72
28	3530	1	295	29.62	42.95	27.42	57	6.7	10.6	43	0.69	4.5	4175	3220	1300	76
29	3532	4	297	37.01	36.59	26.41	44	5	7	28	0.84	4.8	2050	1850	600	74
30	3536	2	229	41.68	33.67	24.65	47	4.3	8	35	0.72	4.9	3560	2690	660	82
30A	3544	6	310	40.16	32.96	26.88	41	5.3	5.6	28	0.91	5.2	3490	2300	990	84

R_{Lab} is the weathering index; Fe_{ox}, Al_{ox}, P_{ox}, and Ca_{ox} are oxalated extracted elements.
[a] Sites 21 to 25 are leeward steep slopes conditions, 26 to 28 are gentle to level slopes conditions and 29 to 30A are windward position.

along our transect are in good agreement with other alpine soil and plant studies that showed the influence of the snowmelt gradient on the alpine edaphic factors (Isard, 1986; Kudo and Ito, 1992; Talbot et al., 1992; Stanton et al., 1994).

Based on the spatial distribution of soil moisture, the snowmelt generated from the progressively melting snowpack appears to be the most fundamental factor that controls many of the soil attributes along the topographic/snow gradient. However, the data set for the 11 sites along our transect represents a 'snapshot' in time; to further study these relationships we assembled a large data set of soil-moisture content measured by the TDR probes and compared the spatiotemporal variations of the soil moisture content with slope position and month of sampling (Table 5). The level of soil moisture at all study sites in the beginning of the growing season (June, while snow still covers most of the leeward sites) was significantly higher than at later dates. The level areas always exhibited higher soil moisture values than the leeward or windward slopes. The source of the moisture in the level areas during most of the growing season was snow melt from the progressively melting snowpack, which was located at the leeward slopes. After the snowpack completely melted away, the leeward sites dried quickly to level similar to the windward sites (Table 5) and plants in these leeward soils could even experience water stress.

Although there were significant differences between the years of monitoring soil moisture (due largely to variations in snowfall amounts and timing from year to year), the spatial seasonal pattern of soil moisture distribution along the topographic/snow gradient remained the same; that is, the level areas were always wetter than the leeward or windward sites during the entire growing season. These findings strongly attest to the importance of the snowmelt gradient that controls the soil moisture, which, in turn, affects the weathering rate and P availability along the alpine gradient.

3.3. Phosphorus fractionation

The P fraction in soils can be grouped by plant-available and refractory pools, or by biological and geochemical pools. For example, the plant-available P can be classified as labile P (resin P_i and $NaHCO_3$

Table 3
Nonparametric statistical analysis of the major soil attributes along the topographic/snow transect

Test statistics	R_{Lab}	Moisture	Sand	Silt	Clay	OC	BD	pH	Fe_{ox}	Al_{ox}	P_{ox}
Kruskal–Wallis test	7.76	7.73	7.0	7.0	5.9	7.42	6.31	7.66	8.35	7.73	8.12
Sig.	0.02	0.02	0.02	0.02	0.05	0.02	0.04	0.02	0.02	0.02	0.02

R_{Lab} is the weathering index, BD is the bulk density, Fe_{ox}, Al_{ox}, and P_{ox} are oxalated extracted elements.

Table 4
Correlation matrix among the major soil attributes along the alpine topographic/snow gradient

	Moisture	Air-dried	OC	P_{ox}	Fe_{ox}	Al_{ox}	BD	pH	Sand	Silt	Clay
R_{Lab}	0.90**	0.90***	0.85**	0.80**	−0.54	0.74**	−0.87**	0.33	−0.87***	0.94***	0.67*
Moisture		0.75**	0.96***	0.72**	−0.36	0.71**	−0.93***	0.18	−0.74**	0.82***	0.52
Air-dried			0.65*	0.82**	−0.58	0.65*	−0.63*	0.31	−0.83**	0.90***	0.63*
OC				0.63*	−0.28	0.65*	−0.97***	0.07	−0.70*	0.80**	0.48
P_{ox}					−0.22	0.83**	−0.58*	0.20	−0.67*	0.75**	0.50
Fe_{ox}						0.09	0.29	−0.77	0.67*	−0.66*	−0.61*
Al_{ox}							−0.67*	−0.13	−0.45	0.41	0.46
BD								−0.06	0.65*	−0.68*	−0.54
pH									−0.45	0.42	0.53
Sand										−0.97**	−0.93***
Silt											0.82***

R_{Lab} is the weathering index, BD is the bulk density, Fe_{ox}, Al_{ox}, and P_{ox} are oxalated extracted elements.
*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

extract), non-occluded P that is not plant-available but could become available through mineralization and chemical processes between the soil solution and the solid phase (NaOH and HCl extracts), and occluded P which is the most recalcitrant of the P pools and is not plant-available (residual). A somewhat different approach to P-pool interpretation, discussed by Cross and Schlesinger (1995), implies that the various inorganic forms of P (P_i) originate from a geochemical source, whereas the organic forms of P (P_o) have a biological source. We used these two interpretative schemes jointly to better understand the biogeochemical processes governing P behavior along the topographic/snow gradient. The results of the P fractionation in soils along our study transect are summarized in Table 6.

Table 5
Soil moisture content across the study area using TDR probes and the results of ANOVA using these data to test the effect of slope position, seasonality and year of sampling

Slope	Month	Soil moisture (% of dry weight)	N
Leeward	June	61 ± 9	10
	July	45 ± 25	308
	August	40 ± 15	413
	September	40 ± 11	161
Level sites	June	67 ± 10	93
	July	57 ± 16	220
	August	53 ± 19	266
	September	51 ± 18	109
Windward	June	51 ± 12	216
	July	38 ± 15	450
	August	40 ± 15	474
	September	44 ± 12	198

Source	F	Significance
Slope position—leeward, level, windward	207.1	0.001
Seasonality—June, July, August, September	22.3	0.001
Slope × season	7.6	0.001
Year—1994 to 2002	100.1	0.001

The alpine soils under study are characterized by a larger percentage of P_o (36% to 79% of total P) from biological processes than P_i (10% to 45% of total P) resulting from geochemical processes. The spatial pattern of the organically bound P (e.g., $NaHCO_3$-P_o and NaOH-P_o) followed closely the spatial distributions of OC along the alpine transect. The level sites exhibited significant higher P_o concentrations than the windward locations, and the leeward steep slopes exhibited the lowest level of P_o of all (Table 6).

The organically bound P_o fraction was dominated by the NaOH-P_o extract at all sampling locations along the topographic/snow gradient (Table 7). The spatial pattern of the total labile P fraction showed that the level locations exhibited significantly higher concentrations of available P in all plant-available categories, namely resin-P_i and $NaHCO_3$-P_i and P_o (Tables 6 and 7). These results agree well with the spatial pattern of P-oxalate concentrations, and together clearly indicate that the level location is relatively P-rich compared with the other locations along the alpine gradient.

Table 6
The results of P fractionation along the topographic/snow transect (P_i, inorganic; P_o, organically bound)

Site[a]	Resin	NaHCO$_3$			NaOH			HCl (1 M)	Residual	Total
	Pi (mg/kg)	Pi (mg/kg)	Po (mg/kg)	TP (mg/kg)	Pi (mg/kg)	Po (mg/kg)	TP (mg/kg)	Pi (mg/kg)		
21	11	10	173	184	59	351	410	379	91	1074
22	17	10	211	221	72	436	508	318	108	1171
23	5	12	107	119	120	249	369	402	85	980
24	10	11	155	165	63	281	344	391	134	1045
25	24	18	286	304	70	699	769	87	201	1386
26	33	10	294	304	54	760	814	30	150	1331
27	47	21	262	283	78	791	870	49	275	1524
28	49	22	198	219	83	970	1053	78	237	1636
29	32	36	76	112	54	487	541	108	297	1089
30	14	12	214	226	41	534	575	64	266	1145
30A	11	12	83	95	46	613	659	66	286	1117

[a] Sites 21 to 25 are leeward steep slopes conditions, 26 to 28 are gentle to level slopes conditions and 29 to 30A are windward position.

The spatial distribution of the P_i fraction extracted by HCl showed a distinct pattern of high P_i content (27% to 44%) at the leeward sites, whereas the level and windward sites exhibited significantly smaller HCl-extracted P_i (Tables 6 and 7). These results agreed well with the spatial distribution of oxalate-extractable Ca concentrations in the study area (Table 2). The HCl-extracted P_i fraction represents P that originated from a parent material enriched with Ca–P minerals, such as hydroxyapatite. Hence, the higher concentration of HCl-extracted P in the leeward soils probably represents a change in parent material enriched with Ca–P minerals, rather than the influence of meltwater on the biogeochemical processes along the alpine gradient.

We compared our findings with those of Beck and Elsenbeer (1999), who studied the biogeochemistry of P in three alpine Spodosols from the Southern Alps. They reported an average biological P of 45% versus 55% originating from geochemical sources. On Niwot Ridge, the average biological P is 60%, which is significantly higher than the geochemical P (Table 6). The dominance of organically bound P was also reported in other alpine Inceptisols of the French Pyrenees (Cassagne et al., 2000) as well as other alpine Inceptisols located in the Colorado Front Range (Parker and Sanford, 1999; Shiels and Sanford, 2001). The higher amounts of organically bound P fraction are the result of low decomposition rates that are characteristic of cold environs.

We also inferred the influence of soil moisture on total and available P from the difference in P pool sizes measured at Goliath Peak and Niwot Ridge (Shiels and Sanford, 2001). These two sites are 50 km apart within the Colorado Front Range and are characterized by similar bedrock and soil age. The concentrations of P in soils at Goliath Peak ranged between 275 and 333 mg/kg and were significantly lower than those at Niwot Ridge (988–1127 mg/kg), as measured by Parker and Sanford (1999) in an alpine site located near a tree island or in the present study (see Table 6). Shiels and Sanford (2001) explained the difference in P concentrations by the higher percentage of exposed and weathered rock at the Goliath Peak than at Niwot Ridge. On the basis of the present results, we suggest that because exposed rock has little or no water capacity, the soils on Goliath Peak are probably significantly drier than those at Niwot Ridge. Because of the relationship between soil moisture and available P, as noted

Table 7
Nonparametric statistical analysis of the P fractions distribution along the topographic/snow transect

Test statistics	Resin-Pi	NaHCO$_3$-Pi	Na-HCO$_3$-Po	NaOH-Pi	NaOH-Po	HCl-Pi	H$_2$SO$_4$-P
Kruskal–Wallis test	6.96	2.00	4.88	6.96	9.85	7.38	8.35
Sig.	0.03	0.36	0.05	0.03	0.01	0.02	0.02

in our study, soils or rock with little or no water capacity will have correspondingly low amounts of total and available P.

3.4. P concentrations in soil solution

The fitting of the Freundlich equation to our experimental results is highly significant at any level of confidence (Table 8). The spatial distribution of dissolved P at the time of sampling varied according to slope position, with the highest level of dissolved P at the level sites, followed by lesser concentrations of dissolved P at the leeward and windward sites. Similarly, the buffer power, b, which is defined as the relationship between P concentration in the solid phase and that in the soil solution (and is calculated using Eq. (4)), suggests that the lowest b values are at the level sites, followed by windblown and leeward sites. In terms of biological availability, these results suggest that the level sites provide the highest concentrations of soluble P, taking into account the sorption and buffering capacity of the soils. These results are explained by the high degree of labile P in the solid phase of the soils at the level sites along our transect (see Table 6), coupled with relatively high antecedent soil moisture that originated from snowmelt water. On the basis of these findings, it could be suggested that this locale exhibits the best conditions for plant growth along the topographic/snow gradient. Furthermore, from the pool size of labile P and the P concentrations in soil interstitial water, it could be argued that P deficiency is not a limiting factor in alpine plant growth at this local. Similar inferences were made by Parker and Sanford (1999), who found high concentrations of labile P in alpine Inceptisols adjacent to mobile tree islands and concluded that P may not be a limiting nutrient in this environ.

Table 8
P concentrations in soil solutions at time of sampling derived from the Freundlich sorption equation

Soil[a]	P concentration		Fitted parameters			r^2	K_d	b
	C_{li} (mg/l)	C_{lf} (mg/l)	A	B	D			
21	1.0	1.4	983	8	−547	0.98	97	121
22	0.7	0.9	1126	8	−684	0.98	174	199
23	0.6	0.8	1282	11	−824	0.98	179	187
24	0.8	1.0	1447	12	−988	0.95	148	169
25	1.7	2.4	930	4	−367	0.96	185	209
26	2.2	3.9	990	5	−419	0.96	68	127
27	3.6	6.5	4505	24	−3930	0.98	56	113
28	12.3	19.3	490	4	−193	0.95	23	71
29	1.0	1.2	1270	9.1	−690	0.93	168	175
30	1.7	2.9	508	5	−243	0.96	60	90
30A	0.9	1.2	518	4	−273	0.97	66	100

C_{li} and C_{lf} are P concentrations in the initial condition (i) and the final condition as a saturated paste (f), A, B and D are fitted parameters, K_d is the slope of the isotherm, and b is the buffer power.

[a] Sites 21 to 25 are leeward steep slopes conditions, 26 to 28 are gentle to level slopes conditions and 29 to 30A are windward position.

Table 9
Total aboveground biomass determination (grams of dry plant matter) according to major species groups and location along the topographic/snow gradient

Location	Forbes	Graminoid	Herbaceous	Biomass
Leeward	12.3	3.3	15.8	54.8
Level	14.5	8.8	23.4	54.2
Windward	24.2	3.4	27.7	58.7

To test the notion that P is not a limiting nutrient at the level sites along our transect, we evaluated the correlation between selected aboveground biomass measurements (Table 9) and various soil parameters (Table 10). The total biomass of the plant material did not correlate well with any of the P indices or with soil-moisture content. Nor did the total mass of forbs or herbaceous plants correlate well with any of the soil attributes. A similar lack of correlation between available P and total plant biomass in alpine soils was also reported by Michalet et al. (2002) who studied the effects of soil chemistry and water status on plant community and composition in the French Alps. They showed that available N and P were unlikely to be responsible for the increase in aboveground biomass or vegetation cover, because communities with the highest biomass were dominated by conservative species. Another possible mechanism that affects the relationship between labile P and total live biomass is the difference in P demand among individual alpine plant species (Theodose and Bowman, 1997). Although, the level sites are characterized by the highest interpolated total live biomass (180 to 200 g/m^2) compared with the leeward sites (80 to 140 g/m^2) and the windward sites (120 to 180 g/m^2) the species richness spatial distribution did not follow this pattern (Muller et al., unpublished data; Seastedt and Vaccaro,

Table 10
Correlation matrix of selected aboveground biomass determination and soil attributes

	Graminoid	Herbaceous	Biomass	Total P	P in soil solution	Labile P	Soil moisture	Occluded P
Forbs	−0.15	0.89***	0.60	−0.16	−0.30	0.25	0.19	−0.12
Graminoid		0.31	0.38	0.84***	0.71**	0.74**	0.58*	0.81**
Herbaceous			0.75*	0.12	−0.07	0.50	0.39	0.15
Biomass				0.24	−0.12	0.32	0.15	0.19
Total P					0.75**	0.89***	0.74**	0.97***
P initial						0.69*	0.50	0.73*
Pi							0.80**	0.91***
Soil moisture								0.71*

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

2001). The highest interpolated species richness was observed in the windward sites (24 to 28 species/m^2) compared with the level (18 to 24 species/m^2) and leeward sites (16 to 18 species/m^2). This difference in plant composition, richness and plant individualistic limitation to P may obscure the correlation between labile P and total live biomass. More recently, Bowman et al. (2003) reported a similar lack of correlation between foliar N/P ratio and soil N and P supply, as estimated by ion-exchange resin bags. They attributed this lack of correlation to redistribution of nutrients between foliar concentrations and belowground nutrient storage in plants. If belowground storage is an important component of P cycling in alpine soils, the lack of correlation between labile P and aboveground plant biomass is a logical outcome.

On the other hand, total graminoid biomass, the most dominant alpine species in our study transect, showed moderate to high correlations with various P availability indices, as well as with soil moisture content (Table 10). A high correlation was also observed between soil moisture and labile P_i (determined by the sequential extraction procedure), and the available P derived from our sorption experiments. These results suggest that although the total plant biomass may not be P limited in certain locations along the topographic/snow gradient, selected alpine species increase their productivity due to higher P availability. These correlation results concurred well with fertilization experiments conducted in the Saddle area by Seastedt and Vaccaro (2001). They found that N or P additions enhanced graminoid foliage productivity ($P<0.05$ and $P<0.03$, respectively) in three alpine communities: minimal snowcover, early-melting and late-melting sites, which correspond to our windblown, level, and leeward sites. Seastedt and Vaccaro (2001) explained their results as clear evidence of P limitation affecting the production of a dominant plant such as *D. caespitosa*.

4. Conclusions

Based on the correlation matrices and the spatial pattern of various soil attributes for our data set, we conclude that the spatiotemporal variations of the antecedent soil moisture content strongly affect the various labile P pools along the alpine gradient. The source of the soil moisture during most of the growing season originated from snowmelt of the progressively melting snowpack located on the leeward slopes. The combination of available soil moisture and labile P appears to provide better growing conditions at the level sites compared to other sites (leeward and windward) along the topographic/snow gradient. However, available P only provides a growing advantage to certain alpine plants and it is not a good indicator of spatial distribution of total aboveground biomass.

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