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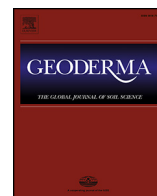Homyak, Peter M
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Pools, transformations, and sources of P in high-elevation soils: Implications for nutrient transfer to Sierra Nevada lakes

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A B S T R A C T

In high-elevation lakes of the Sierra Nevada (California), increases in P supply have been inferred from shifts in P to N limitation. To examine factors possibly leading to changes in P supply, we measured pools and transformations in soil P, and developed a long-term mass balance to estimate the contribution of parent material weathering to soil P stocks. Common Sierra Nevada soils were found to not be P-deficient and to be retentive of P due to the influence of Fe- and Al-oxides. Total P averaged 867 μg P g^{-1} in the top 10 cm of soil (O and A horizons) and 597 μg P g^{-1} in the 10–60 cm depth (B horizons), of which 70% in A horizons and 60% in B horizons was freely exchangeable or associated with Fe and Al. Weathering of parent material explained 69% of the P found in soils and lost from the catchment since deglaciation, implying that long-term atmospheric P deposition (0.02 kg ha^{-1} yr^{-1}) represented the balance of P inputs (31%) during the past 10,000 years of soil development. During spring snowmelt ~27% of the total soil P was transferred between organic and inorganic pools; average inorganic P pools decreased by 232 μg P g^{-1}, while organic P pools increased by 242 μg P g^{-1}. Microbial biomass P was highest during winter and decreased six-fold to a minimum in the fall. Interactions between hydrology and biological processes strongly influence the rate of P transfer from catchment soils to lakes.

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1. Introduction

In the Sierra Nevada of California, P supply to high-elevation lakes regulates phytoplankton productivity and biomass and may be increasing due to global change (Sickman et al., 2003b). While mineral weathering is considered the proximal source for P in most catchments, mechanisms that have been observed to control nitrogen inputs and mobility in high-elevation catchments – atmospheric deposition, changes in the timing and magnitude of snowmelt and soil redox conditions (Brooks et al., 1998; Sickman et al., 2003a) – may also influence P additions to surface waters of the Sierra Nevada. However, our understanding of P sources, pools and transformations in high-elevation soils is limited and we lack a mechanistic understanding of how and when P is transported from watersheds to lakes. In particular, information on the size and distribution of soil P pools and how these pools change in response to snowmelt is lacking. Because catchment hydrology can alter soil physicochemical conditions, P can be alternatively sequestered or mobilized from redox-sensitive pools (Miller et al., 2001), potentially controlling the rate and timing of P loading to high-elevation lakes.

Within a watershed, the mobility of P is strongly influenced by pedogenesis (Parton et al., 2005; Walker and Syers, 1976). In young

soils, P is found in stable primary calcium phosphate minerals, which are unlikely to be altered, over short timescales (seasons), by changes in soil physicochemical conditions (Walker and Syers, 1976). As soils age, geochemical weathering can release P to the soil solution where it can be allocated to plants and microbes, transferred to surface waters, sorbed to secondary soil minerals, or become occluded in soil aggregates (Smeck, 1985). Because of strong bonding with Fe- and Al-oxides, most of the P weathered from primary minerals is sorbed onto secondary soil minerals, some of which are sensitive to changes in soil redox and pH (Miller et al., 2001). Thus, changes in soil physicochemical conditions may increasingly influence P leaching and transport to surface waters as soils develop in high elevation watersheds (Kana and Kopacek, 2006).

Sierra Nevada soils in subalpine and alpine watersheds are relatively young (ca. 10,000 years old) (Fullerton, 1985), and thus may be dominated by P pools associated with primary minerals (Cross and Schlesinger, 1995). Although the lability of P in these stable pools is presumably low, atmospheric deposition of aeolian materials may subsidize the P content of soils, by adding more labile P in the form of wind-blown dusts (Chadwick et al., 1999), ash from forest fires or other biogenic materials (Vicars et al., 2010; Walker and Syers, 1976). Because high-elevation Sierran soils are acidic (pH < 5) (Lund et al., 1987), aeolian P inputs may be sequestered by Fe- and Al-oxides, increasing watershed P storage and producing Fe secondary minerals that can release P during favorable soil physicochemical and hydrologic conditions. Importantly, the Al:Fe ratio in soils and lake sediments

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affects the fate of P additions from aeolian and weathering processes. When extractable Al is higher than Fe, a larger proportion of soil or sediment P can be irreversibly adsorbed by Al during the reduction of Fe-oxyhydroxides (Kopacek et al., 2005). This Al-bound P is stable and in contrast to Fe-bound P, insensitive to changes in redox conditions. However, at pH < 4.7 the solubility of Al increases (Marion et al., 1976) and may offer a pathway whereby acidity can mobilize Al-associated P.

We designed our study to address fundamental questions regarding P cycling and mobility in high-elevation soils of the Sierra Nevada. We sought to address three questions: i) what are the sizes and distribution of soil P pools, and how does their abundance change seasonally? ii) What mechanisms control the stabilization and mobilization of P in soils and the transport of P to surface waters? and iii) What percentage of the catchment P storage and long-term export can be explained by saprolite weathering vs. atmospheric deposition? To answer these questions we employed a sequential fractionation/extraction procedure and a chloroform fumigation technique to quantify soil P pools and how they changed in response to varying soil physicochemical conditions. We used a P sorption experiment, as well as measurements of soil Ca, Fe, and Al pools, to understand the P retention capacity of the soils and determine how much of the soil P is bound in secondary minerals that are redox stable (Al vs. Fe bound). Lastly, we developed a 10,000 year watershed mass balance to estimate the contribution of mineral weathering and atmospheric deposition to soil P stocks. Since most Sierra Nevada watersheds are underlain by granitic bedrock, we hypothesized that: i) soil P concentrations would be low, ii) the dominant soil P pools would consist of unweathered primary minerals, and iii) saprolite weathering would account for the vast majority of the soil P.

2. Materials and methods

2.1. Site descriptions

Our study was conducted in the Emerald Lake (EML) watershed (UTM Zone 11, 350,054 m E, 4,051,454 m N), located along the western slope of the Sierra Nevada within Sequoia and Kings Canyon National Park. The watershed is a glacial cirque (120 ha), with an elevation ranging from 2813 to 3493 m a.s.l. The geology is dominated by fine and medium-grained porphyritic granodiorite and coarse-grained granite. The watershed is not influenced by active glaciers. Soils (Entisols, Inceptisols, and Spodosols) cover approximately 20% of the catchment, are poorly developed, acidic (pH ≈ 4.5–5.5), weakly buffered, well drained, with a bulk density of 1.0 to 1.2, with a C:N ratio of ≈17 (Huntington and Akeson, 1987), and are representative of soils throughout the Sierra Nevada (Melack et al., 1998). Important secondary soil minerals include vermiculite, kaolinite, and gibbsite (Brown et al., 1990), but smectite, chlorite, mica, and hydroxy-interlayered minerals are also present (Homyak, 2012). The climate is Mediterranean with dry summers and wet winters, with a mean annual temperature of 4.6 °C, and with an average annual precipitation of 1510 mm, of which approximately 90% falls as snow (Sickman et al., 2001). Vegetation is sparse and characterized by Lodgepole Pine (*Pinus contorta*), Western White Pine (*Pinus monticola*), Sierra willow (*Salix orestera*) and bluejoint reedgrass (*Calamagrostis canadensis*) and sedges (*Carex* spp.).

2.2. Soil sampling

In summer 2008, we sampled six dominant soils representing five soil subgroups as classified and mapped by Huntington and Akeson (1987): Typic Cryofluvents (TCF), Typic Cryorthods (TC), Lithic Cryumbrepts (LC), Rock outcrop-Lithic Cryumbrepts (RLC), Entic Cryumbrepts (EC), and Cryaquepts (CQ). TCF soils are not abundant, but are found along the shore of EML and support communities of willow and grasses. They are deep, well-drained, with a fine sandy

loam surface underlain by fine gravelly sand and subject to seasonal flooding. TC soils are well to somewhat excessively drained that form in sandy colluviums and on ridge slopes under white pine. The solum is coarse to moderately coarse. LC soils are representative of meadow areas in the EML basin (Miller et al., 2009). They are dark colored, well to somewhat excessively drained, coarse to moderately coarse textured, and formed on granitic colluvium. RLC soils are shallower than LC and found on south-facing slopes; they are grayish brown to brown and gravelly to stony. EC soils are found in exposed areas that drain directly into EML, are shallow, grayish brown to brown, well to excessively drained, gravely to stony, coarse-textured, and support mainly forbs and grasses. Lastly, CQ soils are formed in granitic alluvium–colluvium accumulated in rock basins, are poorly drained, dark colored with coarse to medium textures, strongly acidic and high in organic matter.

For each of the six dominant soils, we obtained duplicate samples from A (ca. top 10 cm) and B (ca. below 10 cm and up to a depth of 60 cm) horizons. At a few of the sites, thin O horizons (≤1 cm) were combined with A horizon samples. Soil samples were bagged, homogenized, and stored at 4 °C in the laboratory. Prior to elemental analysis, stones, gravel, roots, and other debris were removed, but the soil was not air-dried, since drying is known to affect soil P measurements (Blackwell et al., 2009). The gravimetric water content of soil (24 h at 105 °C) was used to express fresh soil elemental concentrations on an oven-dried basis.

To understand seasonal effects on soil elemental concentrations, we sampled A and B horizons in the three most common soil subgroups (EC, LC, and TCF) at approximately four-month intervals. Samples were collected during peak snow accumulation (April 2010) representative of winter conditions, spring (June 2010), summer (September 2010) and fall (October 2010). Water year 2010 (Oct 2009 through September 2010) was characterized by above average snowpack (4–5 m), which had not completely melted until July 2010. During spring, summer, and fall, we dug three pits from which A and B horizons were sampled in duplicate (n = 6 in both A and B horizons at each sampling time) and during winter, only one pit was dug at each of the three soil subgroups (n = 3 in both A and B horizons).

2.3. Elemental and chemical analyses

Fresh soil from summer 2008 and from seasonally sampled EC, LC, and TCF during water year 2010 was used for elemental and chemical analyses. Soil pH was measured in deionized water (Hendershot et al., 2008) and C and N concentrations were measured on finely ground soil samples using an elemental analyzer (Thermo Flash EA 1112). Soil P concentrations were determined using a modified version of the sequential fractionation extraction method of Tiessen and Moir (2008); a microwave digestion with HNO_3 and HCl replaced a digestion with H_2SO_4 and H_2O_2 as the final step in the procedure. Soil P fractions isolated with this method included: 1) soil extract with anion exchange membrane strips (AR204-SZRA; Ionics, Massachusetts) in water for 16 h, at 25 °C, considered freely exchangeable inorganic P fraction (Resin-P_i). After equilibration with the soil solution, resin membranes were shaken overnight with 0.5 M HCl to extract P; 2) 0.5 M $NaHCO_3$ extract (pH 8.5) for 16 h, at 25 °C, considered plant available inorganic P ($NaHCO_3$–P_i) and organic matter P ($NaHCO_3$–P_o) adsorbed on surfaces of crystalline compounds, where Po was calculated as the difference between total P (P_T; $P_T = P_i + P_o$), estimated by oxidation with ammonium persulfate, and P_i; 3) 0.1 M NaOH extract for 16 h, at 25 °C, predominantly inorganic P (NaOH–P_i) associated with amorphous and some crystalline Al oxides, but that may contain Fe-associated P, as well as organic P (NaOH–P_o) associated with humic compounds and polyphosphates considered recalcitrant (Tiessen et al., 1983); 4) 1 M HCl extract for 16 h, at 25 °C, considered Ca-associated inorganic P (1 M HCl–P_i) and not readily available in relatively short timescales; 5) concentrated HCl extract for 1 h, at 80 °C, representing inorganic (conc. HCl–P_i) and organic (conc. HCl–P_o) P bound to stable residual

pools; and 6) microwave extract with concentrated HNO_3 and HCl (3:1) representing recalcitrant P (Residual–P). For the seasonally sampled EC, LC, and TCF soils the sequential extractions did not go beyond the NaOH step, since subsequent extractions represent increasingly recalcitrant soil P pools that are not likely influenced by short-term changes in soil physicochemical conditions (Cross and Schlesinger, 1995). All extracts were analyzed for P colorimetrically (Murphy and Riley, 1962). Seasonal changes in soil C:N:P ratios were calculated using the sum (P_{sum}) of Resin–P_i, NaHCO$_3$–P_T, and NaOH–P_T, since P_T was not measured directly during seasonal measurements. We used repeated measures analysis of variance with Tukey post-hoc tests ($\alpha = 0.05$) to detect significant differences in C, N, and P_{sum} for individual soil horizons across time (seasons).

2.4. Microbial biomass P

Microbial biomass P was measured in A and B horizons in EC, LC, and TCF soils (winter, spring, summer, and fall) using a chloroform ($CHCl_3$) fumigation method (Voroney et al., 2008). Fresh soil subsamples (10 g equivalent dry weight) were fumigated for 24 h, and then extracted with 0.5 M NaHCO$_3$ at pH 8.5. Following fumigation, soil slurries were shaken at 20 °C for 30 min and filtered prior to analysis. To account for the sorption of microbially-released P onto soil colloids following fumigation, we determined the recovery efficiency of a 250 μg P spike, and used it to correct our calculations. Microbial biomass P was not corrected for extraction efficiency, and thus we report $CHCl_3$-labile P pools rather than total microbial biomass. P concentrations were determined colorimetrically (Murphy and Riley, 1962).

2.5. Ca, Al, and Fe soil pools

Soil Ca, Fe, and Al concentrations were measured in A and B horizons in EC, LC, and TCF soils (winter, spring, summer, and fall) by inductive coupled plasma, atomic emission spectroscopy (ICP-AES). Measurements were made on duplicate samples from NaHCO$_3$, NaOH, and acid microwave digestion extracts. We used these measurements to compute Al:Fe ratios and assess the likelihood of P transport during favorable soil physicochemical conditions (Kopacek et al., 2005; SanClements et al., 2009).

2.6. Soil P sorption capacities and mechanisms

We determined the P sorption capacity of A and B horizons in duplicate samples from EC, LC, and TCF soils (fall 2010 samples only) according to Sharpley et al. (2008). Phosphate solutions corresponding to 0, 50, 100, 250, 500, 750, 1000, and 1500 μg P g soil^{-1} were added to fresh soil samples (1 g; equivalent dry weight), shaken, allowed to equilibrate for 24 h, centrifuged (3000 g) for 10 min, and filtered (2.5 μm). All extracts were analyzed for P colorimetrically (Murphy and Riley, 1962).

To calculate the P adsorption maximum (P_{max}), we used the linear form of the Langmuir equilibrium-based adsorption model:

$$\frac{C}{q} = \frac{1}{kb} + \frac{C}{b} \qquad (1)$$

where C is the equilibrium or final solution concentration after equilibration with soil, q is the mass adsorbed, k is a constant related to the binding strength, and b is the maximum amount of adsorptive that can be adsorbed assuming monolayer coverage. The adsorption maximum was calculated from the slope ($1/b$) resulting from the plot between C/q vs. C.

To gain further insight on P retention mechanisms, we extracted P from experimentally P-amended soils (1500 μg P g soil^{-1}) and compared the relative size of the P pools to those obtained for unamended soils (Sharpley et al., 2008). Phosphorus concentrations in P-amended

and unamended soils were measured in duplicate on fresh samples from A and B horizons originating from EC, LC, and TCF soils collected during the fall of 2010. Differences (paired t-tests; $\alpha = 0.05$) in NaHCO$_3$–$P_{i,o}$, NaOH–$P_{i,o}$, and 1 M HCl–P_i between the P-amended and unamended soils were used to identify P pools participating in P retention.

3. Results

3.1. Soil characteristics

Soil pH, texture, cation exchange capacity (CEC), areal coverage, mean depth, bulk density and numerical results from the P sequential extraction procedure are reported in Tables 1 and 2 in the Online Supplemental Materials (OSM) section. In general, EML soils are sandy, shallow, acidic, have an approximate CEC of 11 mEq 100 g^{-1}, and an average C:N:P ratio of 100:5:1 in A horizons and 57:4:1 in B horizons (OSM Table 1). The average total P content in RLC, TCF, TC, C, LC, and EC soils was 867 μg g^{-1} in A horizons and 597 μg g^{-1} in B horizons (Fig. 1, OSM Table 2). The NaOH-extractable pool contained the highest average P concentration (534 μg g^{-1} in A horizons and 362 μg g^{-1} in B horizons) followed by the 1 M HCl pool (124 μg g^{-1} in A horizons and 119 μg g^{-1} in B horizons), NaHCO$_3$ extractable pool (115 μg g^{-1} in A horizons and 50 μg g^{-1} in B horizons), residual pool (20 μg g^{-1} in A horizons and 14 μg g^{-1} in B horizons), and freely exchangeable pool (7 μg g^{-1} in A horizons and 3 μg g^{-1} in B horizons; Fig. 1, OSM Table 2). The highest total P concentrations were found in EC soils, followed by LC, CQ, TCF, RLC, and TC soils. Although P_i and P_o concentrations in extracts varied across soil types, differences in total P concentrations among the soils sampled were attributable to differences in the NaOH–P_o-extractable pool (OSM Table 1).

On average, 14% of the total P in A horizons was labile or considered plant available (Resin–P_i + NaHCO$_3$–P_T), 62% was bound to Al and residual Fe not extracted in the NaHCO$_3$ step (NaOH–P_T), and 24% was considered refractory (1 M HCl–P_i + conc. HCl–P_T + Residual–P). For B horizons, 9% of the total P was labile, 61% was bound to Al and Fe, and 30% was refractory. Biologically controlled soil P pools, defined as the NaHCO$_3$–P_o + NaOH–P_o + conc. HCl–P_o (Cross and Schlesinger, 1995), represented 62% (540 μg g^{-1}) of the total P in A horizons and 53% (314 μg g^{-1}) in B horizons. Soil P pools previously described to be controlled by geochemical processes, Resin–P_i + NaHCO$_3$–P_i + NaOH–P_i + 1 M HCl–P_i + conc. HCl–P_i + Residual-P (Cross and Schlesinger, 1995), accounted for 38% (327 μg g^{-1}) of the total P in A horizons and 48% (283 μg g^{-1}) in B horizons. In EML soils, 66% of the total labile forms of P in A horizons and 67% in B horizons may be readily mineralized through biological processes (NaHCO$_3$–P_o/(Resin–P_i + NaHCO$_3$–P_i + NaHCO$_3$–P_o)) (Cross and Schlesinger, 1995).
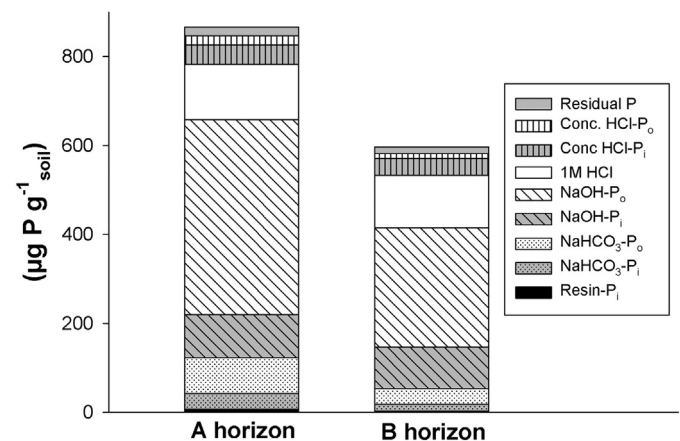

Fig. 1. Average P concentrations in A and B horizons in soils of the EML watershed obtained by sequential extraction. P_i = inorganic P and P_o = organic P.
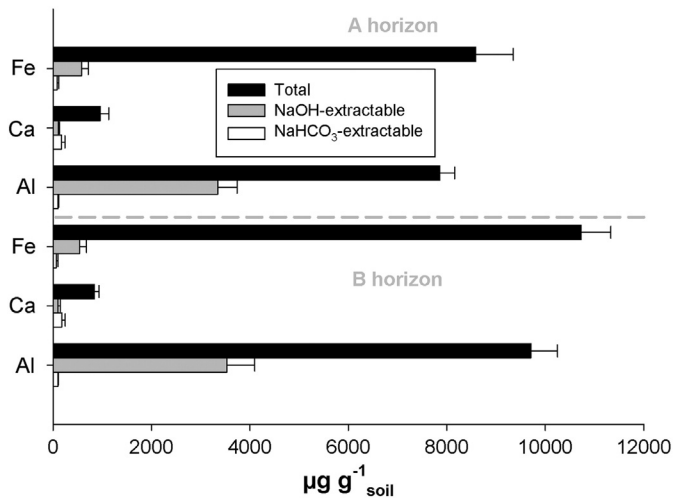
Fig. 2. Average Ca, Fe, and Al concentrations in A and B horizon for LC, EC, and TCF soils extracted with NaHCO₃ and NaOH. Error bars denote standard errors.

We estimate that the EML catchment contains approximately 78,600 kg of P in soils, of which 1% are freely exchangeable, 9% are associated with reducible metal hydroxides (plant available), 58% are sorbed mainly to Al- and Fe-oxides not extracted by NaHCO₃, 24% are associated with Ca minerals (apatite), and 8% are considered occluded in recalcitrant soil pools. Our estimates are based on P concentrations and soil characteristics reported in the OSM Tables 1 and 2, and previously published information for Typic Cryorthent (TCT) soils (Brown et al., 1990) which were not included in our study because they are found on steep, difficult to access slopes. In our calculations, we used the area covered by each soil, the mean depth, and bulk density to estimate a total soil mass. The mass of soil was then multiplied by the

P concentration in A and B horizons to yield a total P mass. For TCT soils, the distribution of P pools was approximated from comparable LC soils.

The total Fe content (average ± std error) in LC, EC and TCF soils was 8588 ± 758 μg g⁻¹ in A horizons and $10,729 \pm 602$ μg g⁻¹ in B horizons (Fig. 2). Total Al concentrations reached 7860 ± 299 μg g⁻¹ in A horizons and 9706 ± 540 μg g⁻¹ in B horizons, and total Ca was lowest, averaging 959 ± 174 μg g⁻¹ in A horizons and 841 ± 94 μg g⁻¹ in B horizons (Fig. 2). Over 92% of the total Fe was not extractable by NaHCO₃ or NaOH, suggesting that Fe was mostly found in recalcitrant soil P pools. In contrast, the sum of extractable Al (NaHCO₃ + NaOH) was five times that of Fe in A horizons and six times that of Fe in B horizons (Fig. 2).

The soil Al:Fe$_{(NaHCO3 + NaOH)}$ ratio was 5 in A horizons and 6 in B horizons and the Al$_{NaOH}$:P$_{NaHCO3}$ ratio was 33 in A horizons and 52 in B horizons (Fig. 2). Al:Fe$_{(NaHCO3 + NaOH)}$. Al:Fe ratios > 3 and Al$_{NaOH}$:P$_{NaHCO3}$ ratios > 25 are generally associated with the inactivation of P by Al (Kopacek et al., 2005), and suggest that EML watershed soils are highly retentive of P.

3.2. Seasonal changes in soil P pools and elemental ratios

Inorganic soil P concentrations (Resin–P$_i$, NaHCO₃–P$_i$, and NaOH–P$_i$) were generally highest during winter snowcover, and gradually decreased as snowmelt progressed and soils warmed during the summer (Fig. 3). For P$_o$, the effect of seasonality was generally opposite to that observed for P$_i$, and P$_o$ concentrations tended to increase as soils warmed (Fig. 3). In particular, abrupt increases in P$_o$ were noted for summer extracts. For both P$_i$ and P$_o$, the NaOH–P pool was the largest for all seasons followed by the NaHCO₃–P and resin–P pools (Fig. 3).

Soil C:N:P$_{sum}$ ratios were highest in subnivean soils (winter and spring), and gradually decreased through the summer and fall (Table 1). Consistent with this pattern, we observed higher C and N pools in A
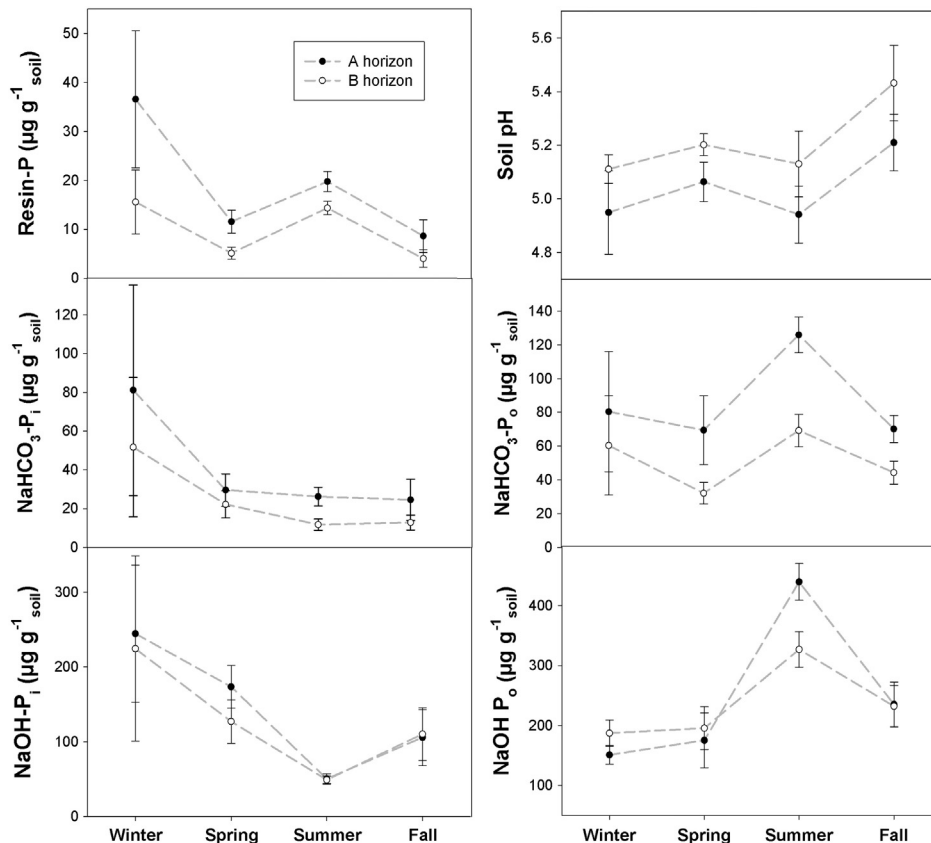

Fig. 3. Average seasonal changes in soil P concentrations and pH for LC, EC, and TCF soils. Error bars denote standard errors.

Table 1

Average soil C, N, and P_{sum} concentrations ($\pm$ standard error) for EC, LC, and TCF sampled from winter through fall 2010. $P_{sum} = Resin\text{–}P_i + NaHCO_3\text{–}P_T + NaOH\text{–}P_T$, where $Resin\text{–}P_i$ is the inorganic P fraction extracted with ion-exchange resin, $NaHCO_3\text{–}P_T$ is the total P fraction extracted with 0.5 M $NaHCO_3$, and $NaOH\text{–}P_T$ is the total P fraction extracted with 0.1 M NaOH. Significant differences ($\alpha = 0.05$) across seasons are denoted by lower case letters.

Horizon	Season	n	C (mg g^{-1})		N (mg g^{-1})		P_{sum} (µg g^{-1})		C:N:P_{sum}
A	Winter	6	99.0^a	± 22.4	6.4^a	± 1.8	594^{ab}	± 86	167:11:1
	Spring	18	73.4^a	± 12.3	5.1^a	± 0.7	459^b	± 41	160:11:1
	Summer	18	74.5^a	± 6.9	3.9^{ab}	± 0.3	662^a	± 31	112:6:1
	Fall	18	50.7^b	± 5.3	2.8^b	± 0.4	445^b	± 24	114:6:1
B	Winter	6	47.3^a	± 6.4	3.1^a	± 1.1	539^a	± 78	88:6:1
	Spring	18	26.1^b	± 2.2	2.1^a	± 0.4	382^a	± 37	68:5:1
	Summer	18	36.0^a	± 2.8	2.0^a	± 0.1	471^a	± 28	76:4:1
	Fall	18	24.4^b	± 2.1	1.6^a	± 0.1	404^a	± 34	60:4:1

horizons in winter when compared to fall ($p < 0.04$). In B horizons, we observed a significant decline in C from winter to fall ($p < 0.0001$) but not for N ($p < 0.09$). For both A and B horizons, P_{sum} generally decreased from winter to fall, but the change was not significant ($p > 0.13$). In A horizons, P_{sum} was highest in summer when compared to fall ($p < 0.0001$), winter ($p = 0.052$), and spring ($p < 0.0001$), while for B horizons differences between seasons were less pronounced ($p > 0.11$). Soil C:N:P_{sum} ratios were always higher in A horizons relative to B horizons, mostly due to differences in C and N content rather than changes in P_{sum}. The C and N content of A horizons was about 50% greater than in B horizons while P_{sum} in A horizons was only 16% greater than in B horizons (Table 1).

3.3. Soil P retention capacity

The average ($\pm$ std. error) P_{max} for EML soils was 967 ± 102 µg P g^{-1} in A horizons and 1187 ± 84 µg P g^{-1} in B horizons (Fig. 4). To understand the potential for additional P adsorption in EML soils, we compared P_{sum} to the calculated P_{max}. On average, A horizons have 368 µg P g^{-1} (61% of current P concentration) and B horizons have 586 µg P g^{-1} (98% of current concentration) of unmet adsorption capacity ($P_{max} - P_{sum}$). LC soils had the greatest P_{max} (1171 µg P g^{-1} in A and 1351 µg P g^{-1} in B horizons), followed by TCF soils (871 µg P g^{-1} in A and 1138 µg P g^{-1} in B horizons) and EC soils (857 µg P g^{-1} in A and 1072 µg P g^{-1} in B horizons).

In the P-amended soils, 19% of the added P was recovered in A horizons and 33% was recovered in B horizons. Of the recovered P, the majority was found in the NaOH–P_i pool (65% in A horizons and 66% in B horizons) and the NaHCO$_3$–P_i pool (36% in A horizons and 26% in

Fig. 5. Average P recovery of P-amended and non P-amended (control) LC, EC, and TCF soils.

B horizons). Recovery of P in the NaOH–P_i and NaHCO$_3$–P_i pools was significantly higher in the P-amended soils compared to control soils (unamended) ($p < 0.05$). The 1 M HCl–P_i pool was relatively unchanged following P additions ($p > 0.61$ for both A and B horizons; Fig. 5). For P_o, we measured lower P concentrations in P-amended soils than in control soils, but the differences were not significant ($p > 0.15$ for both A and B horizons; Fig. 5). For NaHCO$_3$–P_o, however, P concentrations were greater in P-amended soils, where we recovered 24% of the added P ($p = 0.03$ in A horizons and $p = 0.02$ in B horizons; Fig. 5).

3.4. Soil microbial biomass P

Soil microbial biomass P for EC, LC, and TCF soils (average $\pm$ std. error) was highest in winter (369 ± 90 µg P g^{-1} in A horizons and 179 ± 39 µg P g^{-1} in B horizons) and decreased as snowmelt progressed and soils warmed and reached a minimum in the fall (58 ± 17 µg P g^{-1} in A horizons and 31 ± 11 µg P g^{-1} in B horizons; Fig. 6). The greatest change in microbial biomass P occurred during the winter–spring seasonal transition, when microbial biomass P declined 58% in A horizons and 76% in B horizons (Fig. 6). During all seasons, microbial biomass P was higher in A horizons relative to B horizons (Fig. 6), and EC soils generally had the greatest microbial biomass P (up to 443 µg P g^{-1}) followed by TCF (up to 475 µg P g^{-1}) and LC soils (up to 189 µg P g^{-1}) (OSM Table 2).
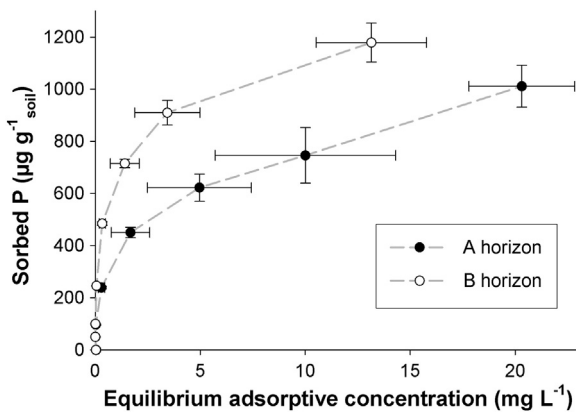

Fig. 4. Average P sorption capacity for LC, EC, and TCF soils at 0, 2, 4, 10, 20, 30, 40, and 60 mg P L^{-1} equilibrating solution concentrations. The equilibrium adsorptive concentration (x-axis) is the concentration of P in solution after equilibration with soil. Error bars denote standard errors.
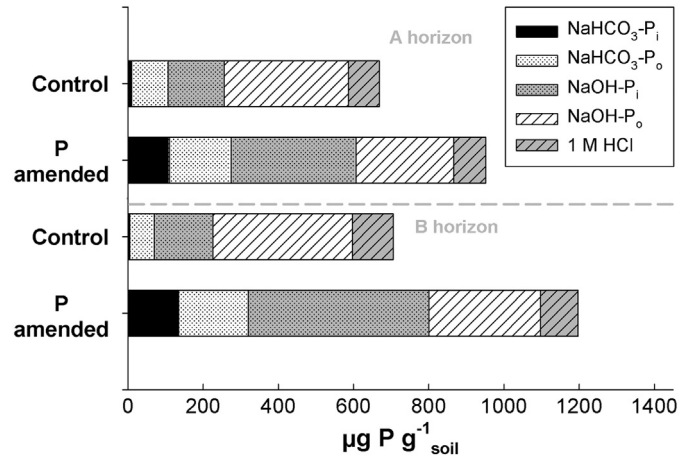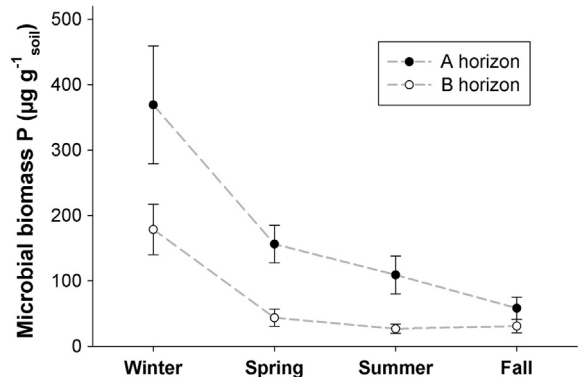

Fig. 6. Seasonal changes in microbial biomass P for LC, EC, and TCF soils. Error bars denote standard errors.

4. Discussion

We designed our study to quantify the size and distribution of P pools in high-elevation Sierran soils and to evaluate whether soil contains P pools that can be mobilized and act as a source of P to high-elevation lakes. Due to the relative young age of Sierran soils, and relatively P-deficient parent material (granite), we expected to find low soil P concentrations as well as P pools predominantly associated with stable primary minerals. However, we found that soils were not P-deficient and were rather at the high-end range of P concentrations found in most soils (50–1000 µg P g^{-1}) (Cross and Schlesinger, 1995; Harrison, 1987). Of the measured P, the freely exchangeable pool can account for 61 times the annual P export from the EML catchment (Table 2).

4.1. Phosphorus in high-elevation Sierra Nevada soils

On average, EML soils contain approximately 78,600 kg of P (Table 2), a much greater mass than the 2000 kg previously estimated (Sickman et al., 2003b). The EML soil C:N:P ratio (Table 1) was lower than the global average for soil (186:13:1) (Cleveland and Liptzin, 2007), further suggesting that Sierra Nevada soils are relatively replete in P. In general, EML soils had higher P concentrations than coniferous forest soils in Acadia National Park (334 µg P g^{-1}) (SanClements et al., 2009) and at Goliath Peak in Colorado (275–333 µg P g^{-1}) (Shiels and Sanford, 2001), but were similar to soils in other mountain regions where P concentrations ranged between 980 and 1636 µg P g^{-1} (Litaor et al., 2005) at Niwot Ridge, Colorado, 216 and 1117 µg P g^{-1} in the Pyrenees, France (Cassagne et al., 2000), and 746 and 1009 µg P g^{-1} in the Minshan Mountains of southwestern China (Zhang et al., 2011). Differences in soil P concentrations between sites may be due to differences in age and physical characteristics that affect pedogenic processes and P retention (Parton et al., 2005). For example, soils at Goliath Peak have a limited water holding capacity (Shiels and Sanford, 2001), contributing to low weathering rates, gradual soil development, and relatively low P concentrations (Litaor et al., 2005).

4.2. P mass balance

To quantify the contribution of the weathering of parent material to the P content of EML watershed soils, we developed a 10,000 year P mass balance which covers the majority of pedogenesis since deglaciation (Table 2). At least eight major Pleistocene glaciations are documented for the Sierra Nevada starting 2.7 million years ago and ending roughly 10,000 years ago (Gillespie and Zehfuss, 2004). In the mass balance, we included estimates for: i) long-term saprolite weathering rates, ii) catchment P export in streamflow, iii) P in soils, iv) P in lake water and sediments, v) vegetation, and vi) atmospheric deposition. The weathering of minerals from granite mainly occurs after the mass of the rock opens to water percolation (Graham et al., 2010), suggesting that saprolite weathering of both P-bearing minerals (apatite) and silicates occurs simultaneously. Because the range of mineral dissolution rates for silicate minerals and apatite overlaps (10^{-13}–10^{-7} mol m^{-2} s^{-1}) (Welch et al., 2002), we inferred rates of P release from bedrock weathering using observed Si weathering rates. In our approach, we first calculated modern rates of Si weathering using mean annual Si export from the EML watershed for the years 1985 through 1999 (9.4 kg Si ha^{-1} yr^{-1}; J.O. Sickman, unpublished data) and a correction for atmospheric Si inputs (0.1 kg ha^{-1} yr^{-1}) (Tegen and Kohfeld, 2006). We then increased the modern rate of Si weathering by 3.4× according to an empirical relationship derived for glaciated soils (Taylor and Blum, 1995). This correction was necessary to account for the loss of more readily weatherable minerals that can occur post-deglaciation (Norton et al., 2011). We then used the average (± std. error) Si and P content in granite and granodiorite measured in the EML watershed (n = 5, 0.5 mg P g^{-1} ± 0.08 and 308 mg Si g^{-1} ± 3.9; J.O. Sickman and A. Leydecker, unpublished data; Table 2) to estimate a P weathering rate. We assumed that for every 617 g of Si exported from the catchment, 1 g of P weathered from bedrock which yielded a total input from weathering of 61,794 kg.

Catchment P losses in streamflow were calculated yearly for 10,000 years and the cumulative sum was reported as the total catchment P export (7241 kg). In the computation of P export, we assumed that it behaved as the first order function of soil P storage (i.e., the greater the P pool, the larger the P export):

$$P_e = k \times P_s \qquad (2)$$

where P_e is the annual phosphorus exported from the catchment, P_s is the phosphorus stored in catchment soils, and k = 1.12 × 10^{-4} yr^{-1} (calculated from Eq. 2 using present-day values, P_e = 8.8 kg yr^{-1} (Sickman et al., 2003b), and P_s = 78,600 kg). Phosphorus storage in lake sediments and water, 3001 kg, and vegetation, 312 kg, was estimated from Sickman et al. (2003b) and Williams et al. (1995).

4.3. P sources to soils: mineral weathering vs. atmospheric deposition

In general, we measured lower P concentrations in 1 M HCl and concentrated HCl extracts relative to other pools. We also found that for soils in earlier stages of development (RLC), the HCl-extractable P pool accounted for a greater proportion of the total P than in more developed soils (46–50%), altogether suggesting that mineral weathering processes have contributed to soil P. Indeed, our P mass balance confirms the importance of mineral weathering processes in building soil P stocks, but that these processes may account for only 69% of the P stored in the catchment (89,154 kg of P). The positive residual in the mass balance, 27,360 kg, represents errors in the individual components (most likely uncertainties in weathering and soil P stocks) and, potentially, unmeasured inputs of P to the EML watershed. Because we corrected for the

Table 2
Comparison of annual P fluxes and pools (kg) in the Emerald Lake watershed (area = 120 ha) and 10,000-year catchment P mass balance. Mineral weathering (Section 4.2) was estimated from the average export of Si from the EML catchment from 1985–1999 (9.4 kg Si ha^{-1} yr^{-1}), corrected for Si deposition (0.1 kg Si ha^{-1} yr^{-1}; Tegen and Kohfeld (2006)) and the average (± Std. error) Si and P contents in granite from EML (n = 9; 0.7 mg P g^{-1} ± 0.096 and 297 mg Si g^{-1} ± 6.9). Lake area = 2.7 ha and soil area = 26.9 ha.

Component	Catchment flux (kg yr^{-1})	Catchment pool (kg)
Dry deposition	8.6[a]	
Deposition in snowpack	5.3[a]	
Total deposition	13.9[a]	
Modern weathering rate	1.8	
Catchment export	8.8[b]	
Lake water		0.97[b]
Lake sediment		3000[b]
Catchment soil		78,600
Freely exchangeable P$_i$		540
NaHCO$_3$–P$_i$		3300
NaHCO$_3$–P$_o$		3400

10,000 year P mass balance		
	Inputs (kg)	Outputs/storage (kg)
Mineral weathering	61,794	
Catchment export		7241
Catchment soil		78,600
Lake sediment/water		3001[b]
Vegetation		312[c]
Total	61,794	89,154
Residual	27,360	

[a] Values obtained from Vicars et al. (2010).
[b] Values obtained from Sickman et al. (2003b).
[c] Basin biomass P was estimated from biomass N (156 kg N ha^{-1}; 24 ha; Williams et al. (1995)) using an average N:P ratio of 12 (Güsewell, 2004).

loss of more readily weatherable minerals post-deglaciation, it is reasonable to assume that the positive residual is partially due to processes that supplemented catchment P accumulation during the past 10,000 years.

Atmospheric deposition of P can partially meet ecosystem P demands (Chadwick et al., 1999; Morales-Baquero et al., 2006; Vicars et al., 2010), as rock-derived elements are depleted (Smeck, 1973), helping to alleviate nutrient limitation (Chadwick et al., 1999). Present-day atmospheric P inputs for the EML watershed (13.9 kg yr^{-1}) exceed P outputs (8.8 kg yr^{-1}) (Vicars et al., 2010), and are much higher that modern day rates of P production from saprolite weathering (1.8 kg yr^{-1}). To understand the contribution of atmospheric inputs to the P content of the EML watershed, we assumed that the entire residual represented atmospheric P deposition and calculated the P deposition rate required to balance our budget in Table 2. Atmospheric subsidies of only 0.02 kg P ha^{-1} yr^{-1} would be sufficient to account for the residual in the mass balance. This deposition rate lies between historical rates for the Pacific region, 0.009 kg P ha^{-1} yr^{-1}, (Chadwick et al., 1999) and modern rates of P deposition for our study site, 0.12 kg P ha^{-1} yr^{-1} (Vicars et al., 2010), suggesting that aeolian processes could have contributed up to 31% of the P stored and exported from the catchment during the past 10,000 years. We note, however, that although we corrected for P losses during initial stages of soil development, studies suggest that rapid dissolution of apatite could have favored substantial P export from the catchment post-deglaciation (Norton et al., 2011). Therefore, our calculations may underestimate the contribution of P from aeolian sources, since additional P inputs would be required to balance P losses from apatite weathering.

4.4. Soil P retention

Soil P accumulation depends on the rate of input from weathering and atmospheric deposition and on mechanisms that retain P in soils. In the EML catchment, P retention is likely due to small-scale physicochemical and biological processes, as well as to larger-scale ecosystem processes.

The mobility of P is largely controlled by the solubility of Ca-, Fe-, and Al-phosphates, which depend on soil pH (Lindsay, 1979). Because EML soils are acidic (pH ≈ 5; Fig. 3), the solubility of P is predominantly controlled by Fe- and Al-phosphates, which become increasingly stable below pH 6.5 (Hesterberg, 2010). In the EML watershed, intense soil leaching during snowmelt, high soil hydraulic conductivity (0.1 to 0.01 mm s^{-1}) (Brown et al., 1990), and volcanic glass deposited during Pleistocene and Holocene eruptions (Wood, 1977) favor the formation of Al clay minerals (Burkins et al., 1999; Dahlgren et al., 1997), with important implications for P retention. Unlike Fe, Al-oxides are insensitive to redox, have a high affinity for P, and can therefore minimize P losses (Kana and Kopacek, 2006; SanClements et al., 2009, 2010). Supporting the important role of Al in regulating P export, was the fact that the majority of P, as well as exogenous P additions, were recovered in the NaOH-extractable P pool (Figs. 1 and 5, Table 2). We also found Al:Fe$_{(NaHCO_3 + NaOH)}$ ratios > 3 and Al$_{NaOH}$:P$_{(NaHCO_3)}$ ratios > 25, further implying strong Al control on soil P storage (Kopacek et al., 2005; SanClements et al., 2009).

Biological processes can also contribute to soil P retention (Walker and Syers, 1976), especially at EML where P$_o$ pools make up 53–62% of the total P. Similarly high proportions of P storage in organic pools have been observed in other high-elevation soils (Cassagne et al., 2000; Litaor et al., 2005; Parker and Sandford, 1999; Zhang et al., 2011) and are consistent with mechanisms of pedogenic P accumulation (Parton et al., 2005). At relatively high P concentrations, phosphatase enzyme activity can be suppressed (Quiquampoix and Mousain, 2005), minimizing P$_o$ degradation, and thereby enriching the P$_o$ pool (Bowman and Cole, 1978b; Condron and Tiessen, 2005). Phosphatase enzymes can also hydrolyze labile P$_o$ into relatively immobile PO$_4^{3-}$, where it can be taken up by plants or microbes, or stabilized in Fe and Al complexes (Turner, 2005).

Soil organic compounds can prevent the crystallization of amorphous oxides and promote further P accumulation (Celi and Barberis, 2005). In the EML catchment, amorphous Al concentrations range from 9.5 to 30 mg g^{-1} (Brown et al., 1990), which due to their greater surface area relative to crystalline forms, can significantly influence P retention (Turner, 2007). Furthermore, the cold temperatures characteristic of high-elevation environments (Conant et al., 2011; Nadelhoffer et al., 1991), relatively low weathering rates (largely restricted to a two-month period during snowmelt (Dahlgren et al., 1997)), and high sorption capacity of Fe and Al oxides (Anderson and Arlidge, 1962; Celi et al., 1999; Walker and Syers, 1976) can further limit P$_o$ decomposition while promoting P$_o$ stabilization.

In subnivean soils, we observed substantial microbial immobilization of P (Fig. 6). Although cold temperatures limit biological processes (Conant et al., 2011; Nadelhoffer et al., 1991), microbes can remain active well below 0 °C (Mikan et al., 2002; Miller et al., 2007), and can survive as long as liquid water films are present (Coxson and Parkinson, 1987); liquid water films have been observed down to −10 °C (Romanovsky and Osterkamp, 2000). In the EML catchment, winters are characterized by deep snowpacks that insulate soils to near 0 °C (Sickman et al., 2003a), allowing for the metabolism of senesced biomass deposited in the autumn and mineralization/immobilization of nutrients (Taylor and Jones, 1990). During spring, increases in soil temperature and metabolic rates can induce microbial C-limitation (Lipson et al., 2000) explaining the seasonal decline in microbial biomass P, as well as the decline in C and N pools observed at our site. We emphasize that the potential release of P held in microbial biomass to the soil solution coincides with a period during which plants begin to allocate nutrients to new growth, and may therefore represent an important mechanism whereby P is retained by ecosystem processes (Miller et al., 2009; Schmidt and Lipson, 2004). In EML, approximately 27% of the total P was transferred between P$_i$ and P$_o$ pools as soils transitioned from winter to summer. During this period, average (A + B horizons) P$_i$ pools decreased by 232 μg P g^{-1} and were balanced by an average increase in P$_o$ of 242 μg P g^{-1} (Fig. 3). These appreciable transfers between inorganic and organic pools underscore the importance of ecosystem-scale processes in sequestering P, while potentially minimizing losses during a period when snowmelt may transport P.

4.5. Potential pathways for soil P supply to high-elevation lakes

Solute transfers from terrestrial to aquatic environments depend on hydrology, and in high-elevation catchments, hydrology is predominantly controlled by snowmelt (Sickman et al., 2003a). Although we found that P is strongly held in soils, snowmelt is still the primary driver of P supply to EML. In the EML watershed, soils are well drained and have relatively high hydraulic conductivities (Brown et al., 1990), which may help mobilize exchangeable P pools in equilibrium with the soil solution. Intense hydrologic flushing may also generate conditions conducive to the reduction of Fe-oxyhydroxides and mobilization of Fe-bound P (Miller et al., 2001).

In high-elevation lakes of the Tatra Mountains, increases in P supply have been linked to increased abundance of catchment soils and to dissolved organic carbon (DOC) as a vehicle for nutrient transport (Kopacek et al., 2011). Until recently, it was thought that P$_o$ was unavailable to plants or microbes, presumably because P$_o$ forms stable complexes with Fe- and Al-oxides, and higher-order inositol phosphates are strongly sorbed in soils (Turner, 2005; Turner, 2007). However, mycorrhizal fungi can utilize inositol phosphates (Allen et al., 1981), representing a pathway by which stable forms of P$_o$ are biologically cycled. Furthermore, the adsorption of P-bearing organic acid anions on soil colloids can reverse the surface charge to negative, resulting in repulsive forces that increase particle separation and facilitate P mobilization (Celi and Barberis, 2005). Sugar phosphates and phosphate diesters are weakly bound to soils (Turner, 2005), and

can be rapidly hydrolyzed by phosphatase enzymes followed by uptake (Bowman and Cole, 1978a), or leaching to surface waters (Frossard et al., 1989). Our seasonal measurements indicate that P_o pools increase during summer, which may be mobilized via DOC transport and favorable hydrology. During the snowmelt period of 2005, as many as 14 kg day^{-1} of DOC and 40 g day^{-1} of total dissolved P flowed into EML (C.E. Nelson, unpublished data).

In addition to snowmelt, summer rainfall can mobilize P_o (Simard et al., 2000). Drying–wetting cycles can expose protected soil organic matter to microbial attack (Navarro-Garcia et al., 2012) and release P to the soil solution with potential transfers to surface waters (Butterly et al., 2011; Turner and Haygarth, 2001; Turner et al., 2003). At EML, summer rainfall transferred sufficient organic material to cause a 20–30 μM increase in DOC (Sadro et al., 2011), which likely mobilized P as well. In the summer of 2009, 15–20 cm of rain fell within a 24 h period, increasing dissolved organic P concentrations in EML by 50% and TP by 61% (Sadro and Melack, 2012). Thus, soil development and C storage (Dahlgren et al., 1997; Luckman and Kavanagh, 2000) may regulate P transfers to aquatic ecosystems via DOC (Kopacek et al., 2011).

5. Summary and conclusions

We found that high-elevation Sierran soils are not P deficient, and that bedrock weathering can explain only 69% of the P stored in the EML catchment. We hypothesize that as much as 31% of the P accumulated in soils and lost in catchment runoff since the watershed was deglaciated was contributed by atmospheric deposition, making the Sierra Nevada similar to remote islands where ecosystem productivity is influenced by atmospheric deposition of P (Chadwick et al., 1999). In high elevation soils of the Sierra Nevada, Fe- and Al-associated pools were the most important, with over half of the P found in organic pools. Although Sierra Nevada soils are highly retentive of P, we hypothesize that transfers of P from soils to lakes occur primarily during snowmelt and summer rainfall events. Because climate change models forecast reductions in snow and increases in rainfall, reductions in snow cover coupled with repeated freeze–thaw/drying–rewetting events may contribute to the destabilization of soil P pools and enhanced transport to surface waters. It is possible that through changes in climate, and development of soil organic matter, increased transport of DOC may enhance P supply to high-elevation lakes. We conclude that P cycling in Sierra Nevada soils depends on biological processes to maintain active transfers between P_i and P_o pools (Cole et al., 1978; Yanai, 1992), and that P supply to these ecosystems has been influenced by local and long-term transport of P-bearing aerosols.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2013.11.003.

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