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Journal

Aquatic Sciences, 76(4)

ISSN

1015-1621

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Publication Date

2014-10-01

DOI

10.1007/s00027-014-0350-y

Peer reviewed

Phosphorus in sediments of high-elevation lakes in the Sierra Nevada (California): implications for internal phosphorus loading

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Received: 13 December 2013 / Accepted: 27 March 2014
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Abstract In high-elevation lakes of the Sierra Nevada (California), increases in phosphorus (P) supply have been inferred from changes in phytoplankton growth during summer. To quantify rates of sediment P release to high-elevation Sierran lakes, we performed incubations of sediment cores under ambient and reducing conditions at Emerald Lake and analyzed long-term records of lake chemistry for Emerald and Pear lakes. We also measured concentrations of individual P forms in sediments from 50 Sierra Nevada lakes using a sequential fractionation procedure to examine landscape controls on P forms in sediments. On average, the sediments contained $1,445 \mu\text{g P g}^{-1}$, of which 5 % was freely exchangeable, 13 % associated with reducible metal hydroxides, 68 % associated with Al hydroxides, and the remaining 14 % stabilized in recalcitrant pools. Multiple linear regression analysis indicated that sediment P fractions were not well correlated with soluble P concentrations. In general, sediments behaved as net sinks for P even under reducing conditions. Our findings suggest that internal P loading does not explain the increase in P availability observed in high-elevation Sierran lakes. Rather, increased atmospheric P inputs and increased P supply via dissolved organic C

leaching from soils may be driving the observed changes in P biogeochemistry.

Keywords High-elevation lakes · Sequential P fractionation · Al:Fe ratios · Water chemistry

Introduction

Montane lakes are changing in response to warming climate, variations in precipitation, and altered atmospheric deposition (Jassby et al. 1990; Psenner 2003; Parker et al. 2008; Sickman et al. 2013). In high-elevation lakes of the Sierra Nevada (California), increases in phosphorus (P) supply, beginning in the early 1980s, have been inferred from shifts in P to nitrogen (N) limitation and increases in seston P (Sickman et al. 2003b). Although increased rates of atmospheric P deposition and enhanced transport of P-bearing terrestrial materials are likely contributors to the increased P supply (Kopacek et al. 1995; Morales-Baquero et al. 1999; Vicars et al. 2010), the contribution of internal P loading from lake sediments is not known.

Because P is efficiently cycled and strongly retained in most upland soils (Smeck 1985), increases in P supply to surface waters are often the result of internal loading from sediments, or recycling within the water column (Nürnberg 1985). The classic model for P supply from sediment is centered on the presence of reducing conditions at the sediment–water interface, promoting the reductive dissolution of Fe-hydroxides, and release of Fe-associated P (Mortimer 1941; Amirbahman et al. 2003). Although this process was initially considered as strictly chemical (Mortimer 1941), microbes can contain a significant proportion of soluble P (Prairie et al. 2001), and Fe-reducing bacteria are necessary to oxidize organic matter (Lovley

Electronic supplementary material The online version of this article (doi:10.1007/s00027-014-0350-y) contains supplementary material, which is available to authorized users.

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1991). Other important factors influencing P exchange between sediments and water column include temperature (Jensen and Andersen 1992; Anthony and Lewis 2012), the lysing of microbial cells induced by changes in redox (Böstrom et al. 1988; Gächter et al. 1988), and the biogeochemistry of sulfur (S) (Gächter and Muller 2003). The microbial reduction of sulfate to sulfide can form insoluble iron sulfide or iron disulfide and decrease the adsorptive control of Fe on P (Hasler and Einsele 1948; Caraco et al. 1993).

Despite the strong influence of redox processes on internal P loading, low-redox environments may not lead to P release from sediments (Schindler et al. 1973; Hupfer et al. 2004). For example, at low dissolved oxygen concentrations, nitrate can act as an alternative electron acceptor during the oxidation of organic matter, thereby limiting Fe-associated P dissolution and subsequent P release (Böstrom et al. 1988). Aluminum too can limit increases in lake water P concentrations under reducing environments, and at relatively high Al concentrations, P released from the reduction of Fe can be bound to Al-hydroxides (Kopacek et al. 2001, 2005). Because Al-hydroxides are insensitive to redox, Al-bound P is effectively inactivated and can be sequestered in sediments (Kopacek et al. 2005). In general, P is sorbed by Al when the molar ratio of sediment Al:Fe extracted in water, $\text{NaHCO}_3\text{-Na}_2\text{S}_2\text{O}_4$ (BD), and NaOH is >3 or the molar ratio of $\text{Al}_{\text{NaOH}}:\text{P}_{(\text{H}_2\text{O}+\text{BD})}$ is >25 (Kopacek et al. 2005). Because Al exerts control on the biogeochemistry of P in high-elevation Sierran soils (Homyak et al. 2014), it may also influence processes controlling P release from sediments. However, it remains unclear what factors control P release from sediments and whether sediments contribute to the P loading of high-elevation Sierran lakes.

We designed our study to improve understanding of P pools in sediments of high-elevation lakes and evaluate their contribution to internal nutrient loading. In particular, we sought to answer three questions: (1) What is the P, Fe, Al and Ca content and distribution in sediments of high-elevation Sierra Nevada lakes? (2) What is the rate of P transfer from sediments to the water column under oxic and reducing conditions? and (3) Does lake water chemistry and lake physiography influence sediment P content?

To answer these questions, we analyzed sediments from 50 high-elevation lakes distributed throughout the central Sierra Nevada and used a sequential P fractionation procedure to determine the size and distribution of sediment P, Fe, Al, and Ca pools. We conducted in situ sediment core incubations at Emerald Lake (EML) to determine rates of sediment P release under oxic and N_2 -induced reducing environments. Multiple linear regression models with stepwise selection were used to explore lake water chemistry and lake physiography effects on sediment P content.

Lastly, we evaluated long-term, limnological records for two high-elevation Sierra Nevada lakes to identify changes in lake water P concentrations during anoxic conditions. We hypothesized that P in lake sediments was stabilized in Fe- and Al-hydroxides and that little P would be transferred from sediments to the water column during oxic conditions. However, we hypothesized that reducing environments would induce P transfers from sediments to the water column.

Methods

Site description

The Sierra Nevada is a belt of plutonic rocks stretching north to south for ~ 700 km, from the Mojave Desert in California to northwestern Nevada. Its climate is characterized as Mediterranean, with precipitation occurring mainly during winter as snow. However, summer thunderstorms are not uncommon, and can influence catchment hydrology and atmospheric deposition (Sadro and Melack 2012). The Sierra Nevada is mainly composed of granitic and granodioritic bedrock polished by several glacial periods starting ~ 2.7 million years ago and lasting until about 10,000 years ago (Gillespie and Zehfuss 2004). Soils are young, poorly developed, and commonly classified as Entisols and Inceptisols (Huntington and Akeson 1987).

Here, we focus on 50 oligotrophic high-elevation lakes (denoted as the surveyed lakes) located in the central Sierra Nevada. The surveyed lakes were selected from a chemical database of 500 Sierra Nevada lakes and formed the basis for diatom-inference models of lake chemistry (Sickman et al. 2013). The average dissolved organic C (DOC) concentration was 2 mg L^{-1} , pH was 6.4, and acid neutralizing capacity (ANC) was $74 \text{ } \mu\text{Eq L}^{-1}$. The lakes range in elevation from 2,198 to 3,791 m a.s.l., have surface areas from 0.55 to 83.6 ha, watershed areas from 40 to 944 ha, and depths from 3 to 35 m.

In addition to the surveyed lakes, we measured sediment P pools and performed sediment incubation experiments in EML, a high-elevation lake located on the western slope of the Sierra Nevada within Sequoia and Kings Canyon National Parks (2,800 m a.s.l.; $36^\circ 35' 49''\text{N}$, $118^\circ 40' 29''\text{W}$). EML is a well-studied, 2.7 ha oligotrophic (total P $< 12 \text{ } \mu\text{g L}^{-1}$ and chlorophyll $< 1 \text{ } \mu\text{g L}^{-1}$) glacial cirque lake with a 120 ha watershed and representative of the water chemistry of other high-elevation Sierran lakes, including the surveyed lakes (Melack and Stoddard 1991; Sickman et al. 2013). The lake has a mean depth of 6 m (10 m max. depth), a volume of $\sim 162,000 \text{ m}^3$, the average pH is 6.1, and has weakly buffered water (ANC $10\text{--}50 \text{ } \mu\text{Eq L}^{-1}$). The geology at EML is dominated by

granitic and granodioritic bedrock with mafic intrusions, aplite dikes, and pegmatite veins (Williams et al. 1993). Vegetation is sparse, covering ~20 % of the basin and includes lodgepole Pine (*Pinus contorta*), western white pine (*Pinus monticola*), and low woody shrubs such as Sierra willow (*Salix orestera*) and grasses (e.g., *Calamagrostis canadensis*). EML is typically ice-covered from December through June (Sadro et al. 2011b).

We used the long-term limnological record of EML and Pear Lake (PRL) to assess controls on lake water P concentrations. PRL (36°36′02″N, 118°40′00″W) is an 8 ha, oligotrophic lake (2,904 m a.s.l.) located ~1 km northeast from EML. It has an average depth of 7.4 m with a maximum depth of 27 m, volume of 591,000 m³, and develops an anoxic hypolimnion when stratified during summer and winter. The PRL watershed is 142 ha with bedrock, talus, and boulders comprising 90 % of the area. The geology is dominated by coarse-grained granites containing mafic inclusions of widely variable size and texture. The vegetation is similar to that described for EML.

Lake sediment sampling

During the summer of 2007 and 2008, the top 2 cm of sediment was obtained from each of the 50 surveyed lakes by gravity coring (Aquatic Research Instruments, Hope, Idaho). Sediments were lyophilized and homogenized prior to analyses. Water samples were collected at each of the surveyed lakes and analyzed for pH, conductivity (Cond), ANC, soluble reactive P (SRP), Cl⁻, NO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, Si, Fe, particulate C (PC), particulate N (PN), particulate P (PP), total dissolved N (TDN), total dissolved P (TDP), dissolved organic N (DON), and DOC (Sickman et al. 2013).

In summer 2011, we obtained three sediment cores from the center of EML. The cores were separated into 0–2 (AD 2011–2006; denotes approximate ²¹⁰Pb dating for each core section; Landers et al. 2008), 2–5 (AD 2005–1999), 5–10 (AD 1998–1978), 10–20 (AD 1977–1926), and 20–30 (AD 1925–1885⁺) cm sections, and assayed for P, Fe, Al, and Ca. Samples were stored at 4 °C and were not freeze-dried prior to chemical analyses. Elemental concentrations were expressed on a sediment dry-weight basis by determining the water content (oven-drying 104 °C) of three 10-g samples from each depth section.

Sediment P sequential fractionation

We used a modified sequential fractionation procedure (Agemian 1997) to determine the concentration of different P fractions in the sediment samples. In our procedure, NH₄Cl was replaced with NaCl in the first step of the extraction to minimize the dissolution of Ca-bound P

(Lukkari et al. 2007). For each sediment, a 0.5 g (dry weight) sample was sequentially extracted with (1) 0.46 M NaCl under an N₂ environment for 1 h to obtain loosely bound and pore water P; (2) 0.11 M sodium dithionite (Na₂S₂O₄) in 0.11 M sodium bicarbonate (NaHCO₃) buffer (pH 7) under an N₂ environment for 1 h to obtain P bound primarily to redox-sensitive Fe-oxides (NaBD-P_i) and organic P that is easily mineralized (NaBD-P_o); (3) 0.1 M NaOH for 18 h to obtain inorganic P (NaOH-P_i) associated with amorphous and some crystalline Al oxides but that may contain Fe-associated P not extracted in the previous step, as well as organic P (NaOH-P_o) associated with humic compounds and polyphosphates; (4) 0.5 M HCl for 1 h to extract Ca-associated P found predominantly in apatite minerals (HCl-P_i); and (5) 1 M NaOH at 85 °C for 1 h to extract residual and recalcitrant forms of occluded P (85°NaOH-P). All extracts were filtered (2.5 μm pore size) prior to analysis. Inorganic P (P_i) was measured colorimetrically (Murphy and Riley 1962) using a 5 cm pathway cell and a Cary UV–vis spectrophotometer (method detection limit 0.3 μg P L⁻¹). Total P (P_t) was measured by inductive coupled plasma atomic emission spectroscopy (ICP-AES). Organic P (P_o) was estimated as the difference between P_t and P_i. NaBD extracts were sparged with He to remove dithionite prior to determining P colorimetrically, as it interferes with the development of the phosphomolybdate complex (Lukkari et al. 2007).

Sediment core incubations

During the ice-free season of 2011, we used in situ sediment core incubations to estimate ambient rates of P flux from sediments to the water column. Incubations were conducted at EML on July 12, August 15, and September 13. On July 12, eight sediment cores (ca. 30 cm length) were collected by gravity coring in 10 m deep water. Sediment cores were collected in 60 cm long, clear polycarbonate core tubes (6.8 cm ID), so that approximately half of the tube was occupied by sediment and the remaining volume by lake water (ca. 1 L). Following collection, the dissolved oxygen (DO) of the overlying water was measured (Yellow Springs Instruments O₂ meter). Next, a 250 ml water sample was collected from each core tube, filtered (Whatman GF/F; 0.7 μm), stored in polypropylene bottles, and denoted the t₀ sample; an equal volume of filtered (0.2 μm) lake water from the hypolimnion was added back to the core tube to maintain a constant water volume. Following the collection of t₀ samples, each core tube was capped, placed in a holder, and lowered back into the lake (10 m depth, ~4.2 °C). Water was collected from all sediment core tubes at: 5 h (30 mL), 22 h (250 mL), 28 h (30 mL), 45 h (250 mL), 52 h (30 mL), and 69 h (250 mL) by raising the cores back to the surface

and lowering them again after sampling. Filtered lake water was added back to the core tube following all water collection periods to maintain a constant volume. DO was measured for a second and final time at the end of the incubation.

On August 15, four sediment cores were collected as described above, incubated at 7.3 °C (lake water temperature) and processed as previously described. All sediment core tubes were sampled at time 0 h (250 mL), 15 h (30 mL), 19 h (30 mL), 25 h (250 mL), 40 h (30 mL), 44 h (30 mL), and 48 h (250 mL). Filtered lake water was added back to core tubes to maintain a constant volume. Dissolved oxygen and temperature were monitored inside a single sediment core with a D-Opto O₂ sensor (Zebra-Tech, Ltd.) at 1 min intervals. The sensors were calibrated using Winkler titrations (Sadro et al. 2011b). On September 13, eight sediment cores were incubated at 12 °C (lake water temperature), and five of the cores were initially sparged with N₂ until the O₂ concentration inside the cores fell below 0.3 mg O₂ L⁻¹. The remaining three cores were not sparged and served as controls. Temperature and O₂ concentrations inside the cores were monitored in both an N₂-sparged and reference core with D-Opto O₂ sensors. Water was collected from all sediment core tubes at time 0 h (250 mL), 15 h (30 mL), 19 h (30 mL), 25 h (250 mL), 40 h (30 mL), 44 h (30 mL), and 48 h (250 mL). Filtered water was sparged with N₂ (0.3 mg O₂ L⁻¹) and added back to the core tubes for the low redox treatments. The 250 mL water samples were analyzed for SRP, TDP, NO₃⁻, TDN, Fe, Al, SO₄²⁻, ANC, and pH, while 30 mL samples were analyzed for SRP and TDP only. All sample concentrations were corrected for the addition of filtered water.

Laboratory chemical analyses

Water samples from the surveyed lakes for PC, PN, and PP were collected on pre-combusted 47 mm Pall-Gelman A/E glass-fiber filters. Filters used to determine PC and PN were dried and analyzed for C and N on an elemental analyzer. TDN, PP, and TDP were determined by persulfate digestion (Valderrama 1981) on samples from the surveyed lakes and core incubations at EML. SRP was measured colorimetrically (Murphy and Riley 1962). NO₃⁻, Cl⁻, and SO₄²⁻ were measured by ion chromatography. DON was measured as the difference between TDN and NO₃⁻ + NH₄⁺, where TDN was measured as NO₃⁻ after persulfate oxidation (Valderrama 1981). Base cations, Fe, and Al were measured by ICP-AES. Dissolved silica was determined by the silico-molybdate method on a filtered subsample. Sediment C and N content (%) were determined on dry finely-ground samples on an elemental analyzer. A pH meter with a Ross combination electrode

was used to measure pH, and ANC was measured by Gran titration (Sickman et al. 2013).

Multiple linear regression and statistical analyses

We used ordinary least squares multiple linear regression with stepwise model selection to discern environmental variables that exerted controls on lake water SRP and TDP and sediment labile P (NaCl-P_t + NaBD-P_t) in the surveyed lakes. Models were developed as a function of water chemistry (TDP, SRP, DOC, pH, Cond, ANC, Cl⁻, NO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, Si, Fe, PC, PN, PP, PN:PP, DIN:TP, TDN, DON), physiography (elevation, lake depth, lake area, watershed area) and sediment chemistry [% C, % N, C:N, NaCl-P_t, NaBD-P_t, labile P, NaOH-P_t, Al_t, Ca_t, Fe_t, Al_{(NaCl+NaBD+NaOH)}}:Fe_{(NaCl+NaBD+NaOH)}}, Al_{(NaOH)}}:P_{(NaCl+NaBD)}}]. We used base cations to understand how catchment weathering processes and geology may influence P dynamics, and nutrient chemistry to relate trophic status to sediment and water P concentrations. Physiography was used to understand whether particular catchment characteristics would influence P biogeochemistry in sediments and lake water. Predictive models for SRP and TDP included all variables except for SRP, TDP, PP, PN:PP. Predictive models for sediment labile P were developed using two approaches. The first was based on water chemistry and physiography. The second approach incorporated all measured variables except for NaCl-P_t, NaBD-P_t, labile P, and NaOH-P_t. Model selection was based on a “significance level to enter” of $\alpha = 0.15$ and a “significance level to stay” of $\alpha = 0.05$.

We used repeated measures analysis of variance with Tukey post hoc tests ($\alpha = 0.05$) to detect significant differences between treatments and sampling times during in situ sediment core incubations. We also used simple linear regression on individual sediment core incubations to estimate rates of P sorption and desorption. Regression models were also used to understand relationships between dissolved O₂ and P concentrations in the EML and PRL limnological records.

Results

Sediment core sequential extraction

On average (\pm SD), the total sediment P concentration from the surveyed lakes was $1,445 \pm 491 \mu\text{g P g}^{-1}$. Of the total P, 5 % was considered freely exchangeable (NaCl-P_t), 13 % associated with reducible metal hydroxides (NaBD-P_t), 68 % associated with Al hydroxides (NaOH-P_t), and the remaining 14 % stabilized in recalcitrant pools (Fig. 1; Online Supplement Table S1). In EML, the largest average

Fig. 1 Average P concentrations by sequential extraction in sediments of the surveyed lakes (*top bar*) and Emerald Lake (depth increments)

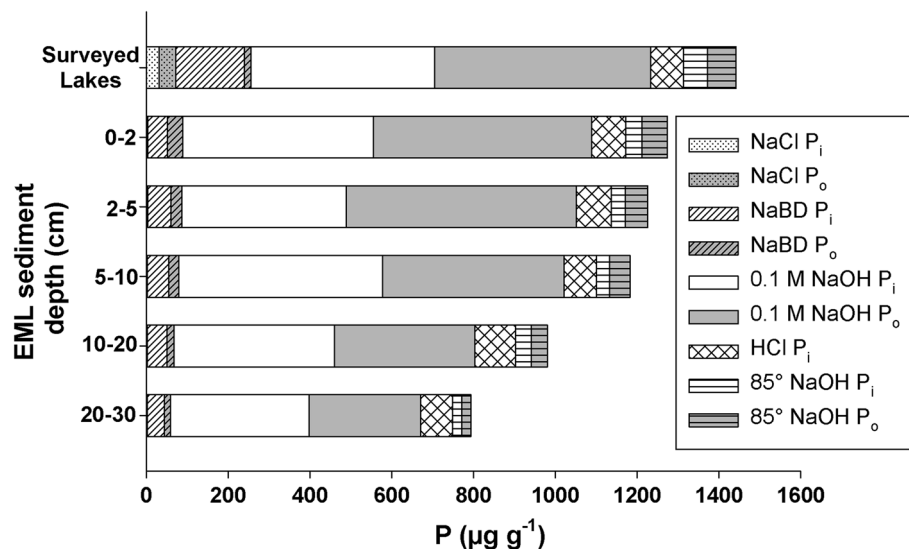
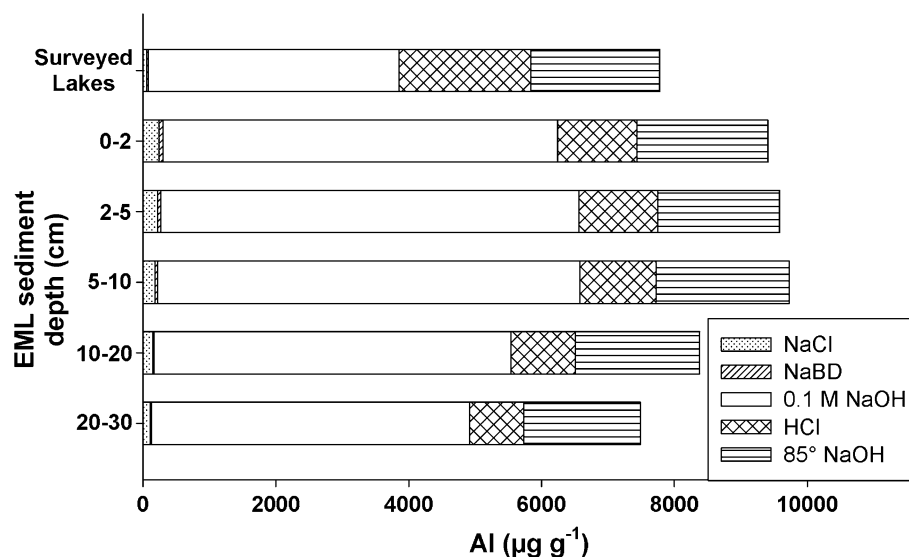


Fig. 2 Average Al concentrations by sequential extraction in sediments of the surveyed lakes (*top bar*) and Emerald Lake (depth increments)



total P concentration was found in the 0–2 cm section ($1,274 \pm 87 \mu\text{g P g}^{-1}$) with P concentrations gradually declining as a function of core depth, to a P content of $793 \pm 48 \mu\text{g P g}^{-1}$ in the 20–30 cm core section (Fig. 1; Table S1). The majority of P was found in the NaOH extractable pool (78 %), followed by P occluded in recalcitrant pools (15 %), and freely exchangeable P or associated with reducible metal hydroxides (7 %) (Fig. 1; Table S1).

Average (\pm SD) Fe and Al concentrations in sediments from the surveyed lakes were approximately equal ($7,800 \pm 2,800 \mu\text{g Al g}^{-1}$ and $7,600 \pm 7,100 \mu\text{g Fe g}^{-1}$; Figs. 2, 3), though the variation in Fe concentrations was larger. In contrast, at EML, the average total Al concentration in sediments was slightly higher than the average concentration for Fe ($8,900 \pm 1,900 \mu\text{g Al g}^{-1}$ and

$5,500 \pm 1,800 \mu\text{g Fe g}^{-1}$, Figs. 2, 3; Table S1). The highest Al concentrations were found in the 5–10 cm sections (Fig. 2; Table S1), while Fe concentrations decreased with increasing depth (Fig. 3; Table S1). Average Ca concentrations in the surveyed lakes ($2,900 \pm 1,500 \mu\text{g Ca g}^{-1}$) were more than double the concentrations found at EML ($1,200 \pm 500 \mu\text{g Ca g}^{-1}$); on average, more Ca was extracted with NaCl in the surveyed lakes than the total Ca extracted for EML (Fig. 4). Though freeze-drying could have altered Ca concentrations in the surveyed lakes, differences in Ca concentrations between 15 freeze-dried and fresh sediments from EML were $<10\%$, suggesting minor effects of freeze-drying on Ca analysis in our study (Hjorth 2004). Ca concentrations did not appreciably vary with sediment depth at EML (Fig. 4; Table S1).

Fig. 3 Average Fe concentrations by sequential extraction in sediments of the surveyed lakes (*top bar*) and Emerald Lake (depth increments)

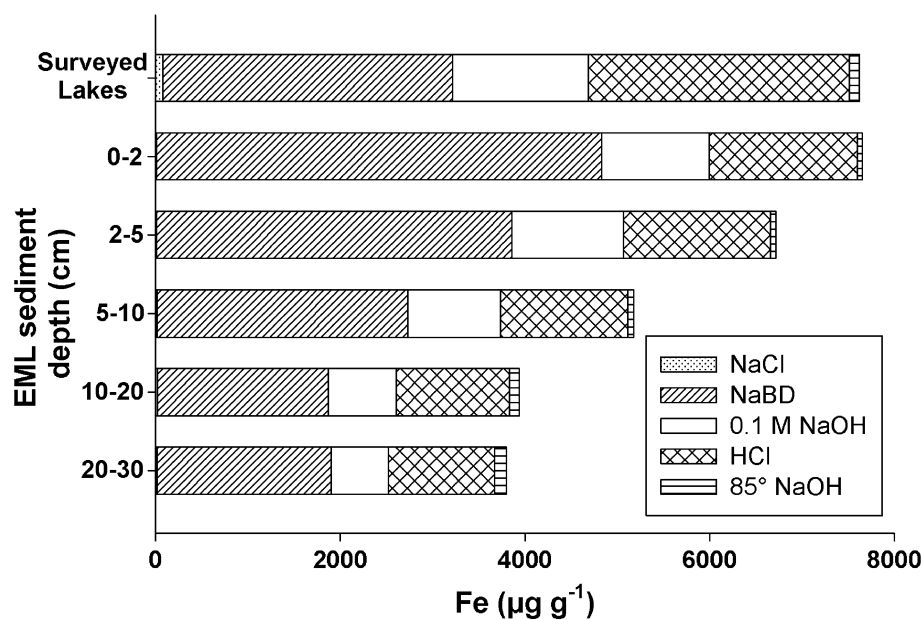
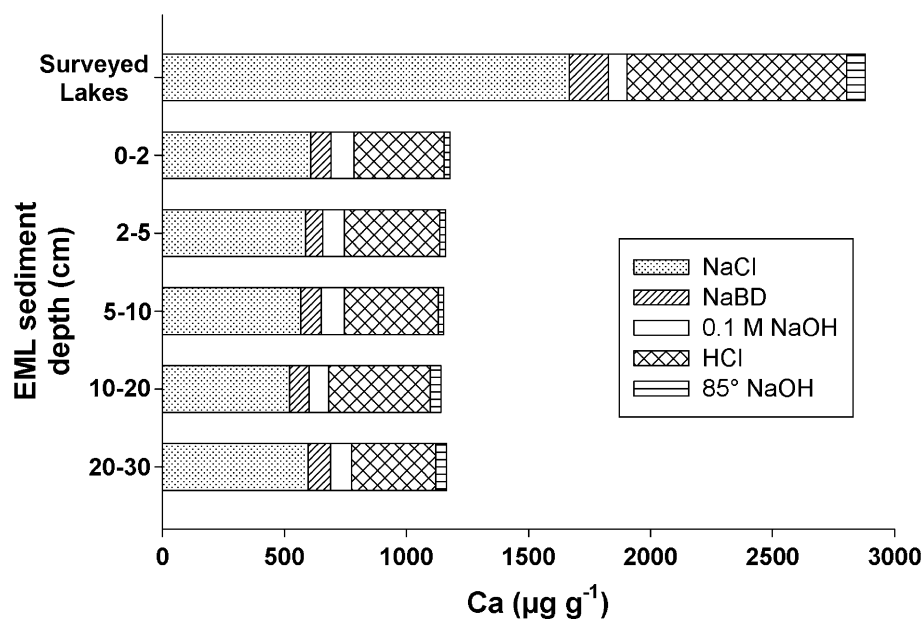


Fig. 4 Average Ca concentrations by sequential extraction in sediments of the surveyed lakes (*top bar*) and Emerald Lake (depth increments)



In-situ core water incubations

During the July and August core water incubations at EML, we generally observed decreases in both SRP and TDP concentrations with time, suggesting that lake sediments behaved as net P sinks (Fig. 5; Table 1). In September, SRP concentrations in reference cores were about an order of magnitude larger than during July and August, but a consistent increase in SRP concentrations over time was not observed ($p > 0.28$; Fig. 6). In N_2 -treated cores, a subtle, but not statistically significant ($p = 0.62$) increase in SRP was observed from t_0 to t_{25} (1.6 – $5.0 \mu\text{g P L}^{-1}$; Fig. 6), but there was no overall P-effect of treating cores

with N_2 to create low redox conditions ($p = 0.77$). From the average rate of SRP increase among reference and N_2 -treated cores during September, we estimated a P desorption rate of 0.05 – $0.1 \mu\text{g P L}^{-1} \text{h}^{-1}$ to approximate a temporary P release from sediments (Table 1). However, we emphasize that significant differences in SRP concentrations over time were not detected (Figs. 5, 6) and that the majority of slopes in Table 1 are not statistically different from zero.

In July, core water Fe concentrations decreased from $23 \mu\text{g L}^{-1}$ at t_{22} to $12 \mu\text{g L}^{-1}$ at t_{69} ($p = 0.08$) and Al from $15 \mu\text{g L}^{-1}$ at t_{22} to $7 \mu\text{g L}^{-1}$ at t_{69} ($p = 0.08$; data not shown). During August, there were no significant

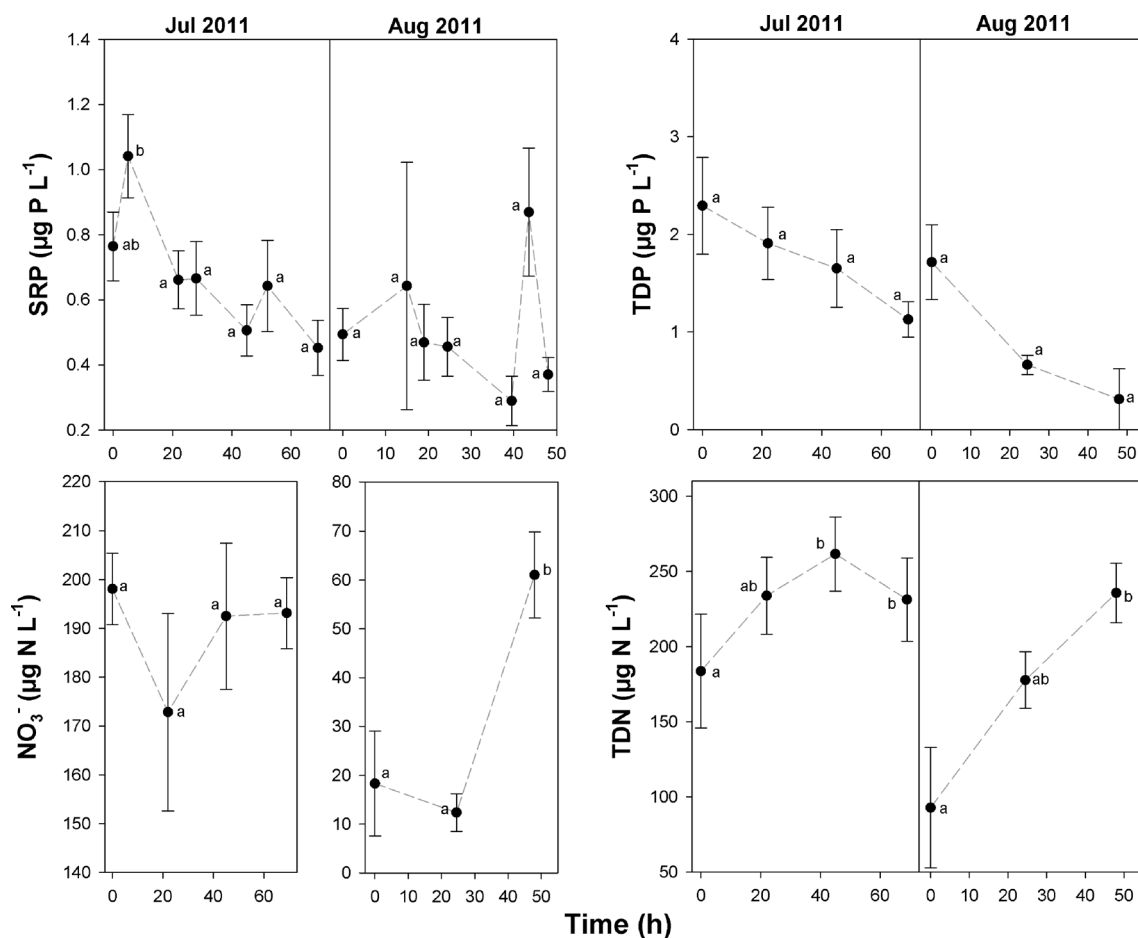


Fig. 5 Average (\pm SD) SRP, TDP, NO_3^- , and TDN concentrations in sediment cores incubated in situ at Emerald Lake during July and August, 2011. Significant differences between sampling times are denoted by *lower-case letters* ($\alpha = 0.05$)

Table 1 Rates of P transfer from lacustrine sediments to the water column. Rates of P release were estimated from linear regressions of core water P during July, August, and September incubations

Parameter	Date	Treatment	<i>n</i>	Average slope ($\mu\text{g P L}^{-1} \text{h}^{-1}$)	SD
SRP	July	–	8	–0.006	0.005
	August	–	4	–0.0003	0.01
	September	Control	3	0.1	0.07
		N_2 -treated	5	0.05	0.02
TDP	July	–	8	–0.02	0.01
	August	–	4	–0.03	0.03
	September	Control	3	–0.03	0.03
		N_2 -treated	5	–0.04	0.02

differences in concentration between sampling times for Fe and Al ($p > 0.16$). In September, average Fe concentrations trended upward ($35\text{--}51 \mu\text{g L}^{-1}$) after 25 h of incubation in N_2 -treated cores and were significantly greater than concentrations in reference cores ($26 \mu\text{g L}^{-1}$; $p = 0.01$). Al concentrations trended upward ($9\text{--}18 \mu\text{g L}^{-1}$) in reference

cores and downward ($12\text{--}7 \mu\text{g L}^{-1}$) in N_2 -treated cores. However, over the entire length of the experiment, average Fe ($35 \mu\text{g L}^{-1}$) and Al ($10 \mu\text{g L}^{-1}$) concentrations in N_2 -treated cores were indistinguishable from the controls ($p > 0.44$). We did not detect significant changes in SO_4^{2-} concentration over time (average = $0.2 \mu\text{g S L}^{-1}$; $p > 0.13$).

Core water NO_3^- concentrations remained unchanged during July ($p > 0.24$), but were about an order of magnitude larger than during August and September (Figs. 5, 6). In August, core water NO_3^- concentration increased over time ($t_0\text{--}t_{48}$; $p = 0.05$; Fig. 5), but this trend was not repeated in September ($p > 0.57$). In September, we did not observe differences in NO_3^- between reference and N_2 -treated cores ($p = 0.76$). For TDN, core water concentrations significantly increased during the incubation period in July and August ($p < 0.018$). Although we did not detect significant differences in TDN between reference and N_2 -treated cores in September ($p = 0.17$), the average TDN concentration in N_2 -treated cores increased significantly over time ($p = 0.02$; Fig. 6).

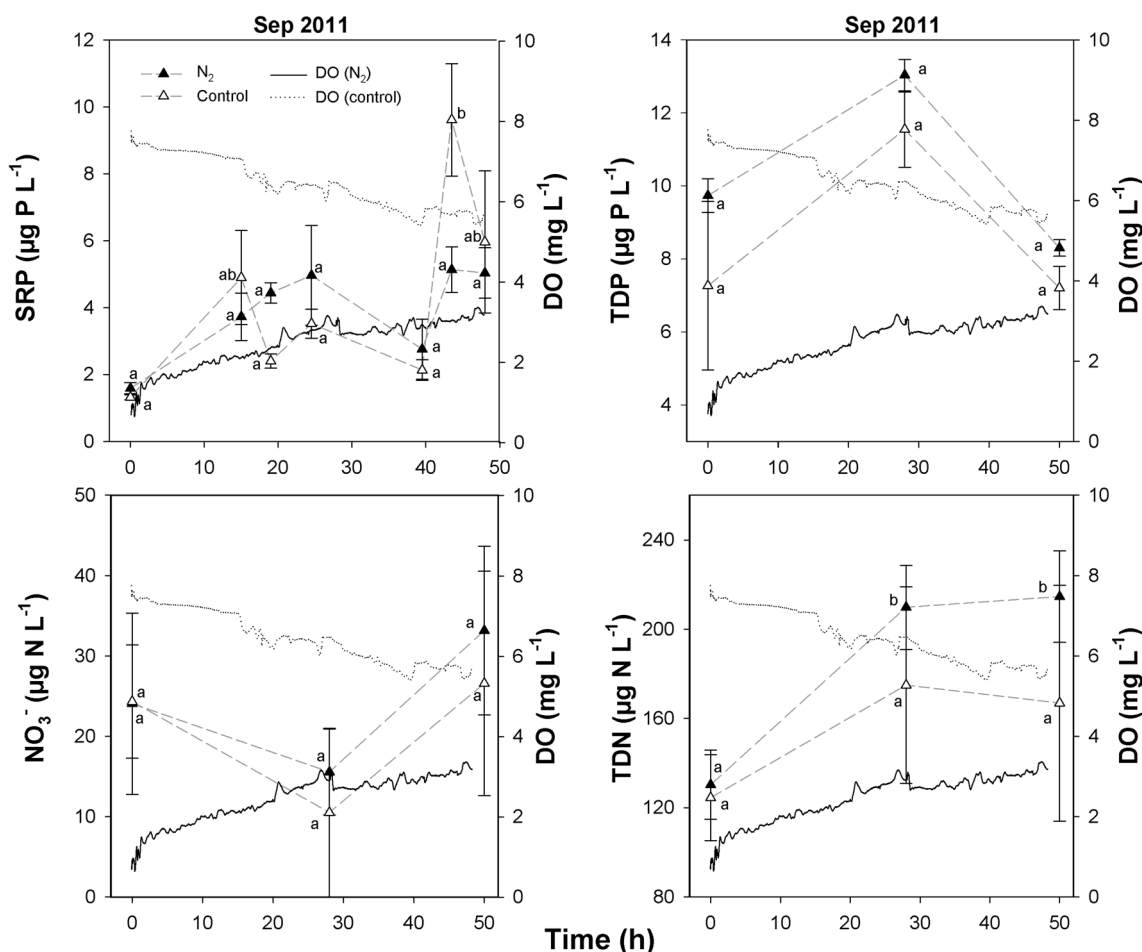


Fig. 6 Average (\pm SD) SRP, TDP, NO_3^- , and TDN concentrations in sediment cores incubated in situ at Emerald Lake during September 2011. Significant differences between sampling times are denoted by lower-case letters ($\alpha = 0.05$). Significant differences between

treatments (control and N_2) were not observed ($\alpha = 0.05$). DO concentrations are shown by the *black solid line* in N_2 -treated cores and by the *dotted line* in reference cores

Both pH and ANC remained relatively constant (pH 5.8–6.5; $\text{ANC} \approx 17\text{--}25 \mu\text{Eq L}^{-1}$) between sampling times (July, August, and September) and between treatments ($p > 0.26$) (data not shown). In July, the initial (t_0) DO concentration was $11 \text{ mg O}_2 \text{ L}^{-1}$, and presumably remained oxic until measured again at the end of the incubation ($8 \text{ mg O}_2 \text{ L}^{-1}$). In August, DO was $7.8 \text{ mg O}_2 \text{ L}^{-1}$ at t_0 and gradually rose to $8.3 \text{ mg O}_2 \text{ L}^{-1}$ at the end of the incubation. In September, DO gradually decreased in control cores and increased in N_2 -treated cores likely due to disturbances associated with sampling (Fig. 6).

Lake water chemistry

We used the long-term limnological record for both EML (1982–2008) and PRL (1986–1993) to understand how changes in DO in both epilimnion and hypolimnion affected P concentrations. We focused on years 1984–1985 for EML and 1986–1989 for PRL during which we had records for

SRP and TDP under anoxic environments (DO as low as 0.1 mg L^{-1}). In EML, DO was a poor predictor of lake water SRP ($y = -0.048x + 2$, $r^2 = 0.002$, $p = 0.76$; Fig. 7) and TDP concentrations, but for TDP, the relationship was statistically significant ($y = -0.28x + 6.2$, $r^2 = 0.22$, $p = 0.0025$; Fig. 7). In EML, the strongest relationship was observed between DO and NH_4^+ ($y = -8.6x + 74.5$, $r^2 = 0.40$, $p < 0.0001$; Fig. 7). In PRL, DO was a poor predictor of TDP concentrations, but the relationship was statistically significant ($y = -0.8x + 10.7$, $r^2 = 0.1130$, $p = 0.01$; Fig. 8). For NH_4^+ , the relationship was stronger when expressed as an exponential decay function ($y = 3,400 e^{-0.59x}$, $r^2 = 0.5$, $p < 0.0001$; Fig. 8).

Multiple linear regression models

Multiple linear regression models did not select sediment P pools as predictors of lake water P concentrations (Table 2). Of the parameters measured, sediment N content

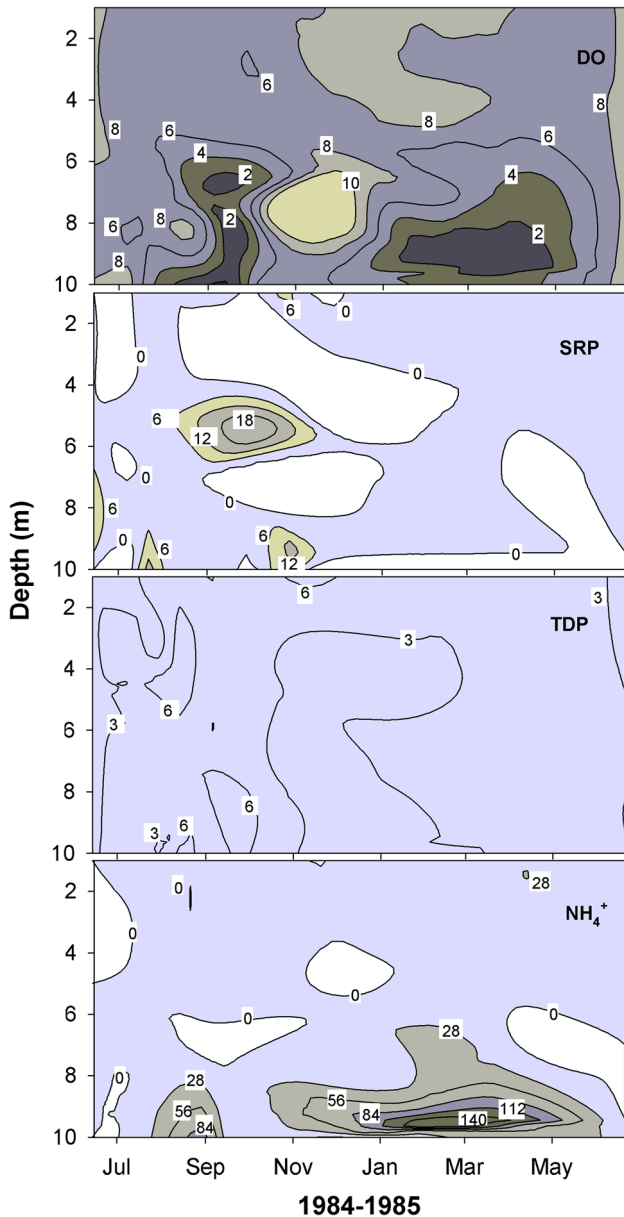


Fig. 7 Average time-depth profile for dissolved oxygen (DO), SRP, TDP, and NH_4^+ concentrations in Emerald Lake from June 1984 through July 1985 (J. Sickman, unpublished data). N and P concentrations are expressed in $\mu\text{g L}^{-1}$ and DO in mg L^{-1}

and lake water Na^+ concentrations explained $\sim 38\%$ of the variation in SRP. For TDP, 57% of the variation was explained by Si, particulate C, and DON (Table 2).

The model used to predict sediment labile P based upon lake water chemistry and physiography explained 43% of the observed variation. However, once we included lake sediment chemistry, our model explained 73% of the variation in sediment labile P as a function of lake water Na^+ and K^+ concentrations and sediment C and N content (Table 2). Although included in all our models, parameters

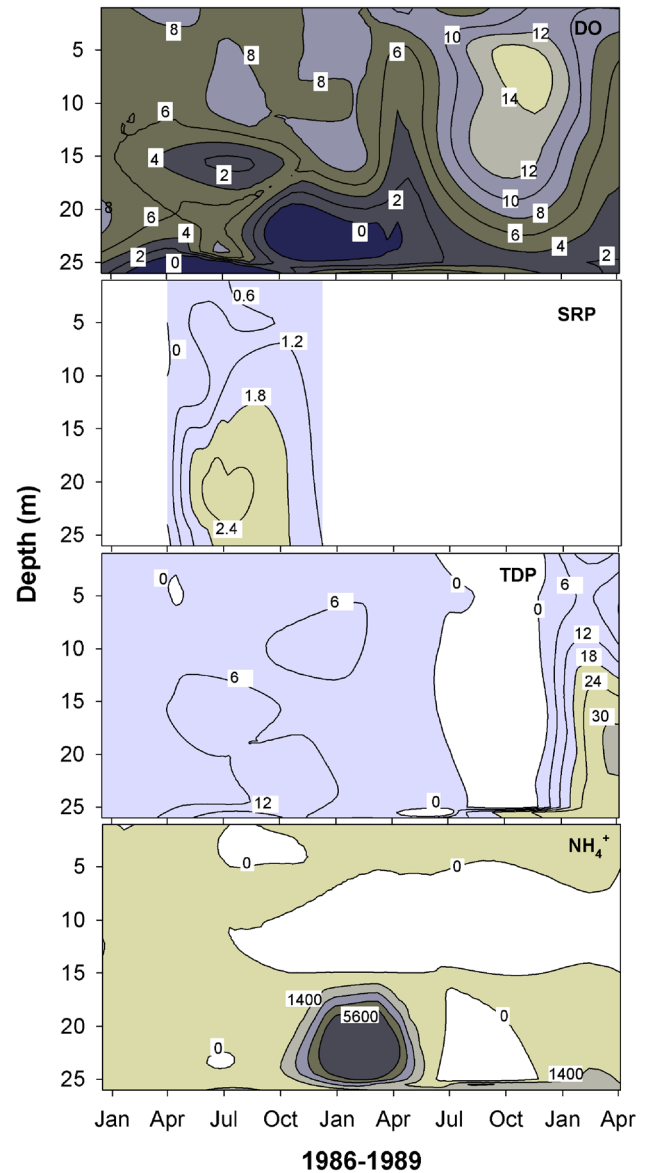


Fig. 8 Average time-depth profile for dissolved oxygen (DO), SRP, TDP, and NH_4^+ concentrations in Pear Lake from December 1986 through April 1989 (J. Sickman, unpublished data). N and P concentrations are expressed in $\mu\text{g L}^{-1}$ and DO in mg L^{-1}

for physiography were not selected as predictors for SRP, TDP, or sediment labile P (Table 2).

Discussion

We designed our study to quantify the size and distribution of the sediment P pools, and assess whether internal loading is an important P source to the water column of high-elevation Sierran lakes. We found that P concentrations in sediments were sufficiently large to potentially contribute to internal loading, but that sediments were not a

Table 2 Ordinary least squares multiple linear regression models with stepwise selection for the prediction of SRP, TDP, and sediment labile P (NaCl-P_t + NaBD-P_t)

Predicted variable	Variables included in model	Model outcome	Parameter estimate	<i>p</i> value	<i>r</i> ²	Adjusted <i>r</i> ²
SRP	Water chemistry	Intercept	0.045	<0.0001	0.38	0.35
	Lake physiography	Na ⁺	0.00053	0.003		
	Sediment chemistry	% N _{sed}	0.010	0.01		
TDP	Water chemistry	Intercept	-0.036	0.03	0.57	0.54
	Lake physiography	Si	0.00065	0.009		
	Sediment chemistry	Part. C _{seston}	0.0011	0.02		
		DON	0.0051	<0.0001		
Sediment labile P	Water chemistry	Intercept	-62	0.6	0.43	0.39
	Lake physiography	TDP	3,800	0.003		
		ANC	5.2	0.0008		
		K ⁺	-56	0.002		
	Water chemistry	Intercept	-77	0.4	0.73	0.70
	Lake physiography	Na ⁺	8.8	0.001		
	Sediment chemistry ^a	K ⁺	-30	0.01		
		% C _{sed}	-68	<0.0001		
		% N _{sed}	900	<0.0001		

Models were developed based on parameters for water chemistry (TDP, SRP, DOC, pH, Cond, ANC, Cl⁻, NO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, Si, Fe, PC, PN, PP, PN:PP, DIN:TP, TDN, DON), lake physiography (elevation, lake depth, lake area, watershed area) and sediment chemistry [% C, % N, C:N, NaCl-P_t, NaBD-P_t, Labile P, NaOH-P_t, Al_t, Ca_t, Fe_t, Al_{(NaCl+NaBD+NaOH)}}:Fe_{(NaCl+NaBD+NaOH)}}, Al_{(NaOH)}}:P_{(NaCl+NaBD)}}] TDP, PC, and DON are expressed in μM; ANC, Na⁺, K⁺, and Si are expressed in μEq L⁻¹

^a Sediment P pools were not included in sediment chemistry

source of P under most conditions. Rather, lake sediments behaved as P sinks, likely owing to well-oxygenated waters that limit reducing environments and to interactions between P and metal oxides, in particular Al. Here, we discuss the sediment P content relative to catchment soils and other lakes, evaluate evidence in support of P retention in sediments, and propose a conceptual model for P supply to high-elevation lakes.

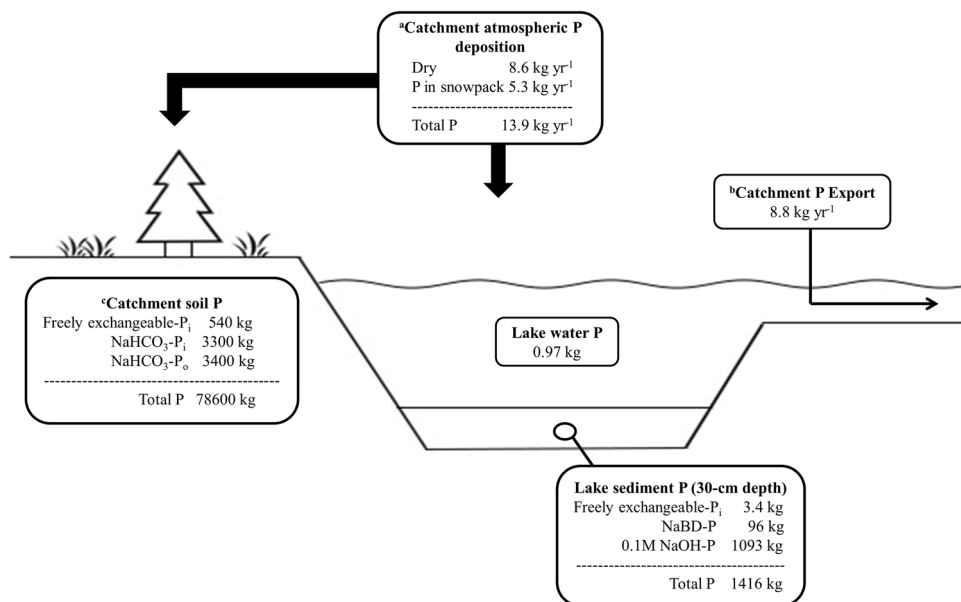
The sediment P content of Sierra Nevada high-elevation lakes

Previous studies have estimated that EML sediments contain a total P mass of 3,000 kg (area = 27,000 m², depth = 1 m, $\rho = 0.085 \text{ g cm}^{-3}$, average = 1,300 μg P g⁻¹) (Sickman et al. 2003b). However, a large fraction of this mass is permanently buried in lake sediments, and likely of little ecological significance (Carey and Rydin 2011). Assuming an active sediment depth of 30 cm (depth at which P concentrations stabilize), an area of 2.7 ha, a bulk density ranging 0.06–0.2 g cm⁻³ (Sickman 2001), and our measured P concentrations (Table S1), we estimate a potentially active P mass of 1,416 kg (Fig. 9). Of this mass, 31 % was found in freely exchangeable and reducible metal hydroxide pool (NaCl-P + NaBD-P), but we found little evidence in favor of P release from sediments.

When compared to sediments from other remote lakes, we found higher P concentrations than in the top 5 cm of oligotrophic alpine lakes in the Tatra Mountains (Slovakia and Poland) (~800 μg P g⁻¹) (Kopacek et al. 2005) or in the top 10 cm of sediments in Upper Hadlock Pond (1,041 μg P g⁻¹), an undisturbed mesotrophic lake in Acadia National Park (eastern Maine, USA) (Sanclements et al. 2009). In contrast, we found lower sediment Al and Fe concentrations (surveyed lakes = 7,800 μg Al g⁻¹, EML = 8,900 μg Al g⁻¹, Fig. 2; surveyed lakes = 7,600 μg Fe g⁻¹, EML = 5,500 μg Fe g⁻¹, Fig. 3) than in sediments from the Tatra Mountains (~18,800 μg Al g⁻¹; ~11,200 μg Fe g⁻¹) or Upper Hadlock Pond (~23,000 μg Al g⁻¹; ~10,000 μg Fe g⁻¹). In the surveyed lakes, sediment Ca concentrations were similar to those in Upper Hadlock Pond (3,500 μg Ca g⁻¹), but at EML, Ca concentrations were lower (1,200 μg Ca g⁻¹).

In comparison to EML catchment soils (Homyak et al. 2014), the upper 2 cm of EML sediments contained ~400 μg P g⁻¹ more than A horizons and 670 μg P g⁻¹ more than B horizons (Table S1). However, deeper sediments (20–30 cm) roughly equaled P concentrations in watershed soils (Table S1). Sediments had lower Fe concentrations than soils, and for Al, sediments had greater concentrations than A horizons but lower concentrations than B horizons (Table S1). EML sediments had higher Ca

Fig. 9 Comparison of annual P fluxes and pools in Emerald lake (2.7 ha) and its watershed (120 ha, soil area = 26.9 ha, lake area = 2.7 ha). ^aVicars et al. (2010). ^bSickman et al. (2003a). ^cHomyak et al. (2014)



concentrations than soils (Table S1), and concentrations remained relatively unchanged through the length of the sampled cores (Fig. 4; Table S1).

Lake sediments as P sinks

We used three different approaches to understand the contribution of sediment P release to the lakes: (1) in situ sediment core incubations, (2) long-term limnological records, and (3) multiple linear regression models; none of which indicated substantial P transfers from sediments to the water column. Sediment core incubations yielded negative P fluxes or no change in SRP and TDP concentrations, even under low DO (Table 1). Long-term limnological records for EML and PRL demonstrated weak relationships between anoxic conditions and lake water P concentrations (Figs. 7, 8). Furthermore, stepwise multiple linear regressions did not include sediment P chemistry as important parameters when modeling lake water SRP and TDP concentrations (Table 2); lakes with higher levels of P in sediments did not have higher water column concentrations of SRP or TDP.

We had expected that reducing environments would induce P release from sediments and expected a weak relationship between sediment P pools and lake water P concentrations. Because P in surficial sediments can be adsorbed onto stable metal oxide sediment pools (Pettersson 2001), sediments can be weak predictors of lake water P (Carey and Rydin 2011). However, the lack of P release under reducing environments suggests that redox levels were not low enough for the dissolution of Fe-associated P, or that reduction occurred, but other processes limited internal P loading. We suspect that some Fe reduction

occurred because: (1) Fe concentrations in N₂-treated cores were significantly greater than in reference cores ($p = 0.01$), and (2) TDN concentrations in N₂-treated cores increased significantly, presumably due to accumulating NH₄⁺ in response to anaerobic environments (Rysgaard et al. 1994), a pattern consistent with our long-term limnological records for EML and PRL (Figs. 7, 8). Thus, if Fe was reduced, other processes likely stabilized P in sediments under reducing environments that otherwise would have promoted internal P loading.

Under reducing conditions, NO₃⁻ can serve as an electron acceptor during the oxidation of organic matter, such that the reduction of Fe and associated P release is averted (Böstrom et al. 1988). However, NO₃⁻ concentrations did not significantly decrease over time (Figs. 5, 6). Alternatively, Al is known to exert control on the solubility of P (Lindsay 1979) and, unlike Fe, Al is insensitive to redox, such that Al-bound P may be permanently stored in lake sediments (Rydin et al. 2000). In sediments with a molar Al:Fe_(H₂O+BD+NaOH) >3 or a molar Al_{NaOH}:P_(H₂O+BD) >25, P release under reducing conditions ceases (Kopacek et al. 2005). In the surveyed lakes, the average (±SD) molar Al:Fe_(NaCl+NaBD+NaOH) ratio in the top 2 cm was 3.6 ± 3.5 and the molar Al_{NaOH}:P_(NaCl+NaBD) ratio was 82 ± 176. For EML sediment cores (0–30 cm), the average Al:Fe_(NaCl+NaBD+NaOH) ratio was 3.4 ± 0.9 and the Al_{NaOH}:P_(NaCl+NaBD) ratio was 87 ± 7 (both ratios increased with sediment depth). Although the molar Al:Fe_(NaCl+NaBD+NaOH) in some of the sampled lakes was <3, the high Al_{NaOH}:P_(NaCl+NaBD) molar ratios found in most Sierran lakes would have been sufficient to prevent P desorption from anoxic sediments (Kopacek et al. 2005). The control of Al on P biogeochemistry is also consistent

with decreasing trends in Al and P concentrations observed in our core water incubation experiments. Thus, similar to many European and North American lakes (Kopacek et al. 2005), Al may control P release from sediments in Sierra Nevada lakes, thereby limiting P supply from internal loading.

Evidence of allochthonous P supply to high-elevation lakes

Phosphorus can be supplied to montane lakes through direct atmospheric deposition (Vicars et al. 2010), transfer of P-bearing materials from the watershed (Kopacek et al. 2011; Homyak et al. 2014), or through internal P loading (Nürnberg 1985). We found that sediments behaved as P sinks. Hence, we conclude that allochthonous P subsidies are important in high-elevation lakes. At EML, we found evidence in favor of allochthonous P supply and control of catchment-scale processes from (1) mass balance, (2) from multiple linear regression modeling, and (3) from sediment-depth profile elemental concentrations.

We have shown that, although the total mass of P in EML sediments is sufficiently large to balance the present-day annual catchment P export, the majority of P is adsorbed onto stable Al-hydroxide pools and/or buried in lake sediments (see Carey and Rydin 2011). Of the potentially labile P, the freely exchangeable pool (NaCl-P_f) cannot balance the annual watershed P export, implying that the reducible metal hydroxide pool (NaBD- and NaOH-P_f) must supply P to surface waters if sediments are the sole source of P to the water column (Fig. 9). However, sediments acted as P sinks and reducing environments did not favor sediment P release (Figs. 6, 7, 8), altogether suggesting that autochthonous P subsidies are of minor importance in high-elevation Sierra Nevada lakes.

Our multiple linear regression models suggest that catchment denudation processes influenced allochthonous P inputs to high-elevation lakes. The positive relationships observed between lake water Na^+ concentrations with SRP and sediment labile P, and Si with TDP (Table 2), may be indicative of volcanic glass weathering (Burkins et al. 1999) and desilification of high-elevation Sierran soils (Dahlgren et al. 1997). Volcanic glass was deposited during Pleistocene and Holocene eruptions from the Mono/Inyo Craters region (Wood 1977). Weathering processes also favor the transformation in EML soils of biotite to vermiculite (Brown et al. 1990; Dahlgren et al. 1997), a clay mineral with greater cation exchange capacity than biotite (Sposito 2008), and therefore, greater affinity for P. Because formation of vermiculite releases interlayer K^+ from biotite (Farmer and Wilson 1970), this weathering process can help explain the inverse relationship we observed between K^+ and sediment labile P.

We also found support for allochthonous P inputs in sediment depth profiles. In EML, we observed that P concentrations were greater in surficial than in deeper sediments (20–30 cm depth), representing a pattern contrary to that expected for oligotrophic lakes (i.e., high burial capacity; Carey and Rydin 2011). The patterns we observed, more typical of eutrophic lake sediments, may develop as a result of limited binding sites for P (Carey and Rydin 2011), organic matter degradation (Rydin 2000), temporary sequestration of P in surface Fe-oxyhydroxides (Mortimer 1941; Rydin 2000), or simply from increased allochthonous inputs (Carey and Rydin 2011). However, EML is an oligotrophic lake ($\text{TDP} < 10 \mu\text{g L}^{-1}$), with sediments of high P retention capacity [molar $\text{Al}:\text{Fe}_{(\text{NaCl}+\text{NaBD}+\text{NaOH})} \approx 3.4$ and molar $\text{Al}_{\text{NaOH}}:\text{P}_{(\text{NaCl}+\text{NaBD})} \approx 87$] that act as P sinks (Table 1; Fig. 5). We highlight that increasing P concentrations in surficial sediments are consistent with patterns observed in oligotrophic lakes undergoing a transitional period to a more eutrophic state (Carey and Rydin 2011), and suggest increases in allochthonous P supply to EML, perhaps via atmospheric deposition (Vicars et al. 2010; Homyak et al. 2014).

Conceptual model for P supply to Sierra Nevada high-elevation lakes

We have presented evidence in favor of allochthonous P inputs as the main source of P to high-elevation Sierran lakes. However, we have not discussed mechanisms for P transport or offered explanations for the patterns in P, Fe, Al, and Ca observed in sediments. We acknowledge that large-scale catchment processes including shifts in mineral weathering rates and deposition of P-bearing aeolian materials can all influence P supply, but at EML, our findings suggest that other mechanisms may be more important. For instance, EML sediment Ca concentrations did not vary as a function of sediment depth (Fig. 4; Table S1), suggesting that accelerated mineral weathering rates are unlikely to explain increased P supply over the 20th century (i.e., Ca should mirror P, Fe, and Al, but it does not). Similarly, direct aeolian P inputs into the lake, alone, cannot balance the catchment's P export; $\sim 0.3 \text{ kg year}^{-1}$ of P fall directly into the lake (Vicars et al. 2010), but the catchment exports 8.8 kg year^{-1} (Fig. 9). If atmospheric P deposition is an important component of the P budget of EML, it must first interact with catchment soils. Thus, catchment-scale processes that integrate both soil denudation and atmospheric P deposition and that simultaneously increase the supply of Fe, Al, and P may explain P supply to these oligotrophic systems.

In the Tatra Mountains, increased supply of allochthonous materials to alpine lakes has been related to catchment soil cover and to DOC as a vehicle for nutrient

transport (Kopacek et al. 2011). Increased nutrient supply via DOC is consistent with the selection of sediment C and N content in our regression model used to predict sediment labile P, suggesting that organic materials exert control on P accumulation in sediments (Table 2); organic C can compete with P for adsorption sites on Al hydroxides (Tipping 1981). In EML, soils are characterized by relatively large organic P pools, of which the Fe- and Al-associated P_o pools represent the majority of the total P (53–62 %) (Homyak et al. 2014). Because soil P_o pools can be relatively mobile and labile (Frossard et al. 1989; Celi and Barberis 2005), favorable hydrology may enhance transfers to surface waters where photochemical reactions can release dissolved organically-bound metals (Kopacek et al. 2006). Increased transport of DOC is also consistent with numerous observations across European and North American regions, suggesting that recovery from acidification has elevated DOC concentrations across these landscapes (Monteith et al. 2007; Kopacek et al. 2013). In the Sierra Nevada, recovery from acidification has been observed in high-elevation lake reconstructions (Sickman et al. 2013), and in regional assessments of water quality (Heard 2013; Shaw et al. 2014), suggesting that increased transport of DOC, as a vehicle for nutrient transport, may be a viable hypothesis for the Sierra Nevada region.

In support of our DOC transport hypothesis, we note that during snowmelt, as many as 14 kg DOC day⁻¹ and 40 g TDP day⁻¹ have been observed to flow into EML (C.E. Nelson, unpublished data). Although hydrology in these high-elevation catchments is predominantly controlled by snowmelt (Sickman et al. 2003a), summer rainfall can also influence nutrient transport. During summer of 2009, an intense rainfall event (15–20 cm) flooded the EML catchment within a 24 h period, increasing lake water dissolved organic P by 50 % and TP by 61 % (Sadro and Melack 2012). Similarly, during precipitation events of lesser magnitude, transfers of terrestrial materials increased lake water DOC by 240–360 $\mu\text{g L}^{-1}$ (Sadro et al. 2011a), which presumably transferred P as well. We suspect that due to future climate change forecasts for the Sierra Nevada region, such as warmer temperatures, lessening of the snowpack, and increasing rainfall (Kim 2005; Knowles et al. 2006), that soil organic matter pool may be further developed (Dahlgren et al. 1997; Luckman and Kavanagh 2000) and enhance DOC and nutrient transport to high-elevation lakes.

Conclusions

High-elevation lake sediments in the Sierra Nevada have a high P content relative to Sierran soils or to lake sediments in other remote ecosystems. However, despite high P

concentrations, sediments act as P sinks even under reducing environments. Multiple linear regression models failed to include sediment P pools as significant parameters when predicting SRP and TDP in surface waters. We conclude that due to the high Al content in Sierran lake sediments, P is strongly held onto Al-oxides even under reducing environments. Rather, we hypothesize an increase in P supply from atmospheric P deposition as well as from increased terrestrial inputs through two potential mechanisms: (1) development of the soil organic matter pool and increased leaching of DOC due to a synergistic interaction between a warming climate and enhanced rates of atmospheric N and P deposition, and (2) increased transport of DOC in response to recovery from acidification similar to observations for regions across North America and Europe.

Acknowledgments We thank the National Park Service and Annie Esperanza for facilitating access to the study sites and for other logistical support. We are indebted to Thomas Martin, Ahmed Haggag, Kevin Skeen, Delores Lucero, Woody Smith, Jennifer Quach, and Amanda James for help with field sampling and laboratory analyses and to Krystal Vasquez for artwork design. We are also grateful to two anonymous reviewers for their insightful comments and suggestions on the manuscript. This research was funded by the National Science Foundation (awards 0614207 and DBI-1202894 post-doctoral research award) and support from a Graduate Mentorship award and a Chancellor's Fellowship at UC-Riverside.

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