

Lake trophic status can be determined by the depth distribution of sediment phosphorus

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Abstract

In this meta-analysis, we examine how sediment phosphorus (P) burial pattern may be related to trophic state. We present sediment P profiles from 94 lakes that demonstrate fundamental differences in P burial between oligotrophic and eutrophic systems. In sediments of eutrophic ($\geq 30 \mu\text{g}$ water column total P (TP) L^{-1}) lakes, P concentrations are elevated in the surficial sediments in comparison with deeper layers, representing a large P pool that can be recycled. This pattern directly contrasts with sediment P profiles in oligotrophic lakes ($< 10 \mu\text{g}$ water column TP L^{-1}), which exhibit increasing concentrations of permanently buried P with depth. Sediment processes regulating P burial may be important regulators of internal P recycling and consequently lake trophic status. Thus, mesotrophic lakes (10 to $30 \mu\text{g}$ water column TP L^{-1}), which exhibit consistent P concentrations with depth, are more vulnerable to external P inputs than oligotrophic lakes because they are at their maximal sediment P burial flux. Our data suggest that thresholds in sediment P pattern may correlate with thresholds in sediment P burial processes and consequently may indicate whether deposited P will be released to the water column.

Phosphorus (P) is a key limiting nutrient in freshwater systems (Schindler 1974, 1977; Schindler et al. 2008), and the major lake classification of trophic status (oligotrophic, mesotrophic, or eutrophic) is dependent on water column P concentration. P that enters the water column of a lake may eventually be deposited onto the lake sediments, of which a fraction can be recycled back into the water column by internal loading processes (Boström et al. 1982). Internal loading, or the remobilization of P from the sediments to the water column (Boström et al. 1988), has been the subject of much limnological research in the past seven decades (reviewed in Søndergaard et al. 2003; Cooke et al. 2005; Nürnberg 2009). Many studies have demonstrated that increased external loading to lakes increases the deposition and consequent decomposition of primary production, fueling anoxia in hypolimnetic sediments (Campbell and Torgersen 1980; Carignan and Flett 1981). These anoxic periods are marked by the reduction of Fe(III) to Fe(II) and the release of P previously bound to Fe(III) complexes (Einsele 1936; Mortimer 1941). The positive feedbacks between eutrophication-driven anoxia and internal P release have been well studied (Diaz 2001; Gächter and Müller 2003; Vahtera et al. 2007), because remobilized sediment P can significantly increase the water column P concentration, which in turn may cause a shift in trophic regime (Nürnberg 1991; Carpenter 2003, 2005). In several cases, the reduction of external P loading to lakes has not rendered a prompt recovery of eutrophication because of the release of sediment P to the water column (Ahlgren 1978; Cooke et al. 2005), highlighting the importance of internal P recycling processes.

Because lake trophic status can be substantially influenced by the release of P from the sediments, several past studies have examined the correspondence between total P (TP) concentrations in the surficial sediments and the water

column (Håkanson 2003; Carpenter 2005). However, no empirical relationship between sediment TP and water column TP concentration has been established (Boström 1984; Håkanson 2003; Maassen et al. 2005); perhaps because the TP concentration in the top layer of the sediment generally represents the P concentration of deposited particles from the water column (Pettersson 2001), and does not take P diagenetic processes and the fraction of inert P in the surface sediments into account (Golterman 2001). Hence, comparing surficial sediment TP with water column TP is inherently limited for two reasons: first, the surficial sediment TP does not accurately represent the concentration of P that is potentially mobile (Nürnberg et al. 1986; Golterman 2001), and second, the comparison of surficial sediment TP and water column TP will not indicate if the sediment is able to permanently bury deposited P.

To determine the share of P that will be released from lake sediments to the water column with time, it is essential to compare the sediment surface TP concentration with a reference point concentration, or the concentration of TP at which phosphorus diagenesis processes in the sediment have stabilized. This “stabilization point” is the sediment depth at which the TP concentration becomes constant, depending on the sedimentation rate, which is determined by external and internal sediment loading, resuspension, and sediment focusing (Søndergaard et al. 1993, 1996; Weyhenmeyer et al. 1997). Below the stabilization depth, mobile P has been lost to the water column, and the remaining P becomes permanently buried as part of the geosphere (Håkanson 2003), unless disturbed by major events (e.g., dredging). Thus, a more relevant and accurate measurement of ecologically significant, or “potentially mobile P,” in the sediment is a metric that incorporates TP throughout the sediment profile, as suggested by Wilson et al. (2010), from the sediment surface to the stabilization depth. In the generalized sediment P profile for a lake with

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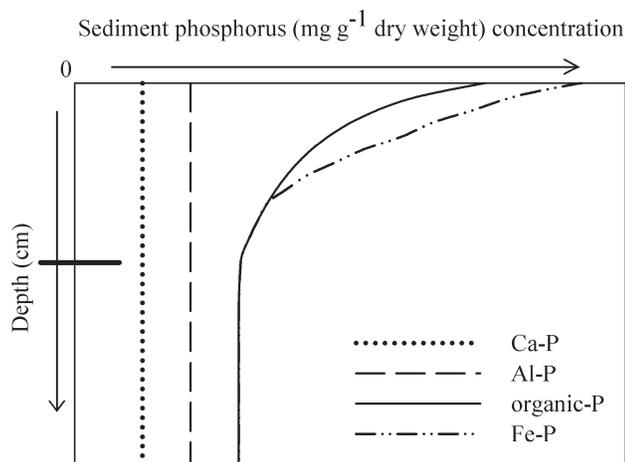


Fig. 1. Illustration of the classic hypothetical sediment phosphorus profile (modified from Boström et al. 1982), with calcium (Ca-P), aluminum (Al-P), organic (organic-P), and iron (Fe-P) fractions. The sum of these fractions at any given depth represents the sediment total phosphorus concentration. The tick line on the y-axis represents the stabilization depth, or the depth at which all phosphorus diagenesis processes have stabilized.

constant external P loading and sedimentation rate (as described by Boström et al. 1982; Fig. 1), potentially mobile P in the sediment may be represented by the difference between the surficial TP concentration and the stabilization depth TP concentration. This potentially mobile P will be released with time to the water column as dissolved P in a steady-state lake system (Boström et al. 1982; Rydin 2000) and consists primarily of iron-associated P (BD-P, bicarbonate dithionite extractable phosphorus) and organic P (NaOH-nrP, NaOH extractable nonreactive phosphorus) fractions (Rydin 2000). The size of this P pool is also an indication of the lake's sediment P burial, i.e., how well the lake sediments can bind and permanently bury deposited P. Consequently, lake sediment with a high concentration of potentially mobile P is less able to bind the P in the surficial sediments, as well as P that may be deposited on the sediments in the future.

Sediments in oligotrophic lakes release significantly less P into the water column than sediments in eutrophic lakes (Nürnberg et al. 1986), indicating that there may be smaller mobile P pools and greater P burial in oligotrophic than eutrophic systems. Mobile P may be retained permanently in oligotrophic sediments (Wilson et al. 2010), resulting in an inverse relationship between water column P concentration and the rate at which sediments permanently bury P. Thus, we hypothesized that the pattern of TP in lake sediments at depth may significantly vary between eutrophic and oligotrophic systems, which in turn may explain the maintenance of low-nutrient and high-nutrient regimes in lakes of different trophic status.

To investigate whether sediment P burial varies among lakes of different trophic status, we analyzed sediment cores from 94 lakes to test our hypothesis that lakes of different trophic status exhibit different P profiles, with greater sediment P burial in oligotrophic than eutrophic systems.

Methods

We conducted an extensive literature search to assemble a dataset of lake sediment TP profiles. We focused on sediment TP because it was by far the most commonly measured sediment P form and represents the sum of all P fractions (Fig. 1). In total, we obtained 145 sediment TP profiles for 94 lakes (Table 1). Our dataset consisted of 26 oligotrophic (water column TP < 10 $\mu\text{g L}^{-1}$), 19 mesotrophic (water column TP $\geq 10 \mu\text{g L}^{-1}$ and < 30 $\mu\text{g L}^{-1}$), and 49 eutrophic lakes (water column TP $\geq 30 \mu\text{g L}^{-1}$; Nürnberg 1996). Every profile in the dataset had a corresponding mean water column TP (hereafter, TP_{water}) concentration measured from the same year the core was extracted from the lake. Whenever possible, we averaged multiple TP_{water} concentrations sampled from the same year together to represent as reliably as possible a yearly mean TP_{water}; however, for some profiles only one TP_{water} concentration was available. We used TP_{water} as an indicator of lake trophic status because it is a continuous quantitative variable that can be compared among lakes (Carlson 1977); other metrics of trophic status (e.g., chlorophyll *a*, Secchi depth), have multiple limitations (Wetzel 2001). We also obtained a water column pH value for each lake at the time at which the cores were collected and a brief eutrophication history summary for each lake if long-term monitoring records existed (pH and summary data reported in the Web Appendix, www.aslo.org/lo/toc/vol_56/issue_6/2051a.html).

We used the digitizing software program GraphClick (Bovet 2008) to extract sediment profile TP concentrations from published figures. The mean depth of the sediment cores included in the dataset was 29.9 cm (± 1.7 cm, 1 SE, range 12–102 cm) deep with ≤ 1 -cm slicing intervals. Most of the sediment profiles were sampled for TP at a finer resolution near the surface than at depth (e.g., sediment TP was measured every 1 cm near the top of the profile, and then only once every 5 cm at depth).

Sampling design and protocol were not standardized among studies: analyses were conducted by different people using different methods, TP_{water} sampling period was variable, as was the number of samples per lake. Few studies published the exact water depth from which the cores were sampled (most studies referred to the sampling site as at or near the deepest part of the lake); however, none of the cores were sampled from the littoral zone. In addition, we could not ascertain whether the sampling locations of the water column and sediment cores matched because the studies we extracted our sediment core data from did not provide that spatial information. Nonetheless, because standardized limnological protocols often recommend collecting representative water samples from a lake's deep site (Peck 1992), we would expect that our sediment and water samples were from approximately the same spatial area. Such heterogeneity reduces the accuracy and precision of relationships between sediment TP and trophic status. However, because comparisons focus on relative magnitude and are unrelated to lake trophic status, these differences should not have affected our analysis.

Table 1. Water column total phosphorus concentration (TP_{water}), the linear slope of the function of sediment total phosphorus with depth (linear slope), best sediment total phosphorus model fit, model equation, model R^2 , and stabilization depth, if the core exhibited a best fit exponential model, for each core representing one of the 94 lakes in our analysis. The full dataset of 145 cores, as well as the model corrected Akaike's Information Criterion (AICc) values, maximum-likelihood parameter estimates, and two-unit support intervals for each core are presented in the Web Appendix. When two different lakes had the same name, an abbreviation indicating the lake's region is listed in parentheses (ME, Maine; NH, New Hampshire; WA, Washington).

Lake	Country	TP_{water} ($\mu\text{g L}^{-1}$)	Linear slope	Best model fit	Model equation	Model R^2	Stabilization depth (cm)	Reference
Paione Superiore	Italy	3	0.020	Linear	$TP=0.020(\text{depth})+0.74$	0.45	—	1
Ånn	Sweden	4	0.0074	Exponential	$TP=1.02(\text{depth})^{(0.073)}$	0.29	15.7	2
Bur	Sweden	4	0.042	Linear	$TP=0.042(\text{depth})+0.84$	0.61	—	2
Clear	Canada	4	0.017	Means	$TP=2.97$	0.00	—	3
Mjölkl	Sweden	4	0.025	Exponential	$TP=0.49(\text{depth})^{(0.30)}$	0.51	16.4	2
Thompson	USA	4	0.036	Linear	$TP=0.036(\text{depth})+1.95$	0.83	—	4
Lillesjö	Sweden	5	0.0022	Means	$TP=2.72$	0.00	—	5
Pleasant (ME)	USA	5	0.011	Exponential	$TP=1.12(\text{depth})^{(0.074)}$	0.89	19.2	4
Pleasant (NH)	USA	5	0.033	Linear	$TP=0.033(\text{depth})+1.83$	0.95	—	6
Sunapee	USA	5	0.025	Linear	$TP=0.025(\text{depth})+1.65$	0.66	—	6
Blue Chalk	Canada	6	0.030	Linear	$TP=0.030(\text{depth})+1.44$	0.65	—	3
Echo	USA	6	-0.015	Means	$TP=2.13$	0.00	—	4
Ejgdesjön	Sweden	6	0.013	Linear	$TP=0.013(\text{depth})+1.87$	0.34	—	5
Little Long	USA	6	-0.0036	Means	$TP=1.90$	0.00	—	7
Plastic	Canada	6	0.055	Linear	$TP=0.055(\text{depth})+2.05$	0.31	—	3
Red Chalk	Canada	6	0.022	Linear	$TP=0.022(\text{depth})+1.78$	0.49	—	3
Lille Öresjön	Sweden	7	0.035	Exponential	$TP=1.46(\text{depth})^{(0.16)}$	0.81	9.7	5
Long Lake (ME)	USA	7	0.011	Linear	$TP=0.011(\text{depth})+1.45$	0.80	—	4
Västrasolsjön	Sweden	7	0.0017	Means	$TP=1.54$	0.00	—	5
Harp	Canada	8	0.049	Linear	$TP=0.049(\text{depth})+1.92$	0.76	—	3
Parker	USA	8	0.015	Linear	$TP=0.015(\text{depth})+1.34$	0.97	—	4
Upper Hadlock	USA	8	-0.0075	Means	$TP=1.58$	0.00	—	7
Jerry	Canada	9	0.041	Linear	$TP=0.041(\text{depth})+1.55$	0.73	—	3
Long Pond	USA	9	-0.010	Means	$TP=1.68$	0.00	—	4
Messalonskee	USA	9	0.012	Linear	$TP=0.012(\text{depth})+1.71$	0.58	—	4
Mud	USA	9	0.021	Linear	$TP=0.021(\text{depth})+0.95$	0.26	—	7
Chub	Canada	11	0.15	Linear	$TP=0.15(\text{depth})+2.95$	0.44	—	3
Crosson	Canada	11	0.037	Linear	$TP=0.037(\text{depth})+1.78$	0.56	—	3
Dickie	Canada	11	0.000079	Means	$TP=1.61$	0.00	—	3
Middle Range	USA	11	-0.017	Means	$TP=1.77$	0.00	—	4
Svinarydsjön	Sweden	14	0.044	Linear	$TP=0.044(\text{depth})+1.73$	0.75	—	5
Heny	Canada	15	0.0036	Means	$TP=1.49$	0.00	—	8
Gyltigesjön	Sweden	16	-0.026	Linear	$TP=-0.026(\text{depth})+2.60$	0.66	—	5
Muskoka	Canada	17	-0.085	Linear	$TP=-0.085(\text{depth})+2.40$	0.80	—	9
Stechlin	Germany	18	-0.091	Linear	$TP=-0.091(\text{depth})+2.56$	0.55	—	10
Storasjö	Sweden	18	0.013	Exponential	$TP=0.91(\text{depth})^{(0.15)}$	0.24	18.6	5
Inchiquin	Ireland	20	-0.028	Exponential	$TP=4.39(\text{depth})^{(-0.12)}$	0.63	20.2	11
Vikasjön	Sweden	20	-0.015	Exponential	$TP=1.14(\text{depth})^{(-0.25)}$	0.93	19.1	12
Brunnsjön	Sweden	22	-0.017	Linear	$TP=-0.017(\text{depth})+2.42$	0.22	—	5
Cayuga	USA	22	0.0013	Linear	$TP=0.0014(\text{depth})+0.71$	0.07	—	13
Green	USA	24	-0.010	Linear	$TP=-0.010(\text{depth})+1.36$	0.92	—	14
Älgarydsjön	Sweden	25	-0.0029	Means	$TP=1.40$	0.00	—	5
Ballinger	USA	25	-0.048	Exponential	$TP=1.98(\text{depth})^{(-0.15)}$	0.47	5.8	15

Table 1. Continued.

Lake	Country	TP _{water} ($\mu\text{g L}^{-1}$)	Linear slope	Best model fit	Model equation	Model R ²	Stabilization depth (cm)	Reference
Erken	Sweden	25	-0.020	Exponential	TP=1.76(depth) ^(-0.15)	0.97	28.5	2
Kalgaard	Denmark	25	0.012	Linear	TP=0.012(depth)+1.56	0.26	—	16
Almind	Denmark	30	-0.030	Linear	TP=-0.030(depth)+2.02	0.82	—	16
Ramsen	Sweden	30	-0.027	Exponential	TP=1.89(depth) ^(-0.17)	0.81	9.7	2
Tiefer See	Germany	30	-0.021	Exponential	TP=2.07(depth) ^(-0.21)	0.79	23.9	17
Trehörningen	Sweden	30	-0.036	Exponential	TP=1.58(depth) ^(-0.19)	0.94	9.9	2
White	Ireland	31	-0.044	Linear	TP=-0.044(depth)+3.34	0.20	—	18
Balaton	Hungary	35	-0.01	Exponential	TP=0.71(depth) ^(-0.072)	0.75	10.5	19
Washington	USA	35	-0.035	Exponential	TP=2.65(depth) ^(-0.10)	0.47	13.4	20
Alserio	Italy	41	-0.0000051	Exponential	TP=0.48(depth) ^(-0.038)	0.19	26.0	21
Long Lake (WA)	USA	42	-0.048	Linear	TP=-0.048(depth)+2.05	0.82	—	22
Leven	Scotland	45	-0.075	Exponential	TP=2.15(depth) ^(-0.23)	0.77	15.3	23
Campbell	USA	49	-0.067	Linear	TP=-0.067(depth)+2.33	0.62	—	22
Malmnsjön	Sweden	50	-0.021	Linear	TP=-0.021(depth)+1.60	0.89	—	2
Longgan	China	51	-0.0083	Linear	TP=-0.0083(depth)+0.45	0.79	—	24
Limmaren	Sweden	54	-0.021	Exponential	TP=-0.021(depth)+1.71	0.86	—	12
Mullagh	Ireland	57	-0.13	Exponential	TP=5.54(depth) ^(-0.52)	0.89	20.7	11
Mann	Ireland	62	-0.063	Linear	TP=-0.063(depth)+3.03	0.52	—	18
Kasumigaura	Japan	75	-0.044	Exponential	TP=1.66(depth) ^(-0.23)	0.93	17.8	25
Monona	USA	76	-0.010	Linear	TP=-0.010(depth)+2.03	0.85	—	26
Kyrksjön	Sweden	80	-0.053	Exponential	TP=2.11(depth) ^(-0.33)	0.67	17.2	2
Mendota	USA	80	-0.012	Linear	TP=-0.012(depth)+1.83	0.77	—	27
Ballybeg	Ireland	84	-0.023	Exponential	TP=1.53(depth) ^(-0.15)	0.64	8.8	11
Crans	Ireland	89	-0.043	Linear	TP=-0.043(depth)+7.00	0.18	—	11
Central	Wales	90	-0.030	Linear	TP=-0.030(depth)+1.04	0.92	—	28
Okeechobee	USA	98	-0.035	Exponential	TP=2.03(depth) ^(-0.23)	0.82	24.9	29
Feldberger Haussee	Germany	100	-0.084	Linear	TP=-0.084(depth)+2.72	0.47	—	30
Långsjön	Sweden	100	-0.033	Linear	TP=-0.033(depth)+2.06	0.91	—	2
Væng	Denmark	100	-0.18	Linear	TP=-0.18(depth)+4.86	0.95	—	31
Erie	USA	115	-0.041	Exponential	TP=1.83(depth) ^(-0.23)	0.87	21.9	32
Taibai	China	120	-0.0087	Linear	TP=-0.0087(depth)+0.96	0.64	—	24
Kvind	Denmark	125	-0.18	Exponential	TP=4.09(depth) ^(-0.38)	0.98	14.7	31
Lugano	Italy	137	-0.083	Linear	TP=-0.083(depth)+2.43	0.90	—	33
Globsowsee	Germany	140	-0.019	Exponential	TP=2.29(depth) ^(-0.073)	0.83	3.5	34
Sillan	Ireland	141	-0.098	Linear	TP=-0.098(depth)+5.57	0.76	—	11
Lillsjön	Sweden	150	-0.039	Exponential	TP=1.82(depth) ^(-0.22)	0.99	12.1	2
Taihu	China	178	-0.0034	Exponential	TP=0.54(depth) ^(-0.14)	0.92	7.7	35
Apopka	USA	203	-0.015	Linear	TP=-0.015(depth)+1.89	0.88	—	36
Arreskov	Denmark	204	-0.030	Linear	TP=-0.030(depth)+1.27	0.92	—	37
Dianchi	China	220	-0.0051	Exponential	TP=1.48(depth) ^(-0.073)	0.46	10.8	38
San Pablo	Ecuador	220	-0.038	Exponential	TP=5.73(depth) ^(-0.095)	0.59	35.6	39
Bryrup Langsø	Denmark	300	-0.24	Linear	TP=-0.24(depth)+5.91	0.96	—	16
Tiefwareensee	Germany	300	-0.055	Linear	TP=-0.055(depth)+3.58	0.91	—	34
Vallentunasjön	Sweden	350	-0.025	Exponential	TP=1.79(depth) ^(-0.11)	0.94	15.6	40
Arresø	Denmark	430	-0.057	Linear	TP=-0.057(depth)+2.75	0.98	—	41
Esrom	Denmark	600	-0.25	Exponential	TP=9.82(depth) ^(-0.61)	1.00	4.8	16
Silver	USA	600	-0.016	Linear	TP=-0.016(depth)+0.86	0.88	—	42

Table 1. Continued.

Lake	Country	TP _{water} ($\mu\text{g L}^{-1}$)	Linear slope	Best model fit	Model equation	Model R^2	Stabilization depth (cm)	Reference
Egish	Ireland	675	-0.36	Exponential	TP=7.62(depth) ^(-0.48)	0.87	16.8	11
Søbygaard	Denmark	900	-0.049	Linear	TP=-0.049(depth)+4.91	0.14	—	43
Glumso	Denmark	1000	-0.072	Exponential	TP=3.28(depth) ^(-0.29)	0.99	17.9	16
Sønderby	Denmark	1162	-0.19	Linear	TP=-0.19(depth)+3.47	0.90	—	44

¹ Guilizzoni et al. (1996); ² E. Rydin (unpubl.); ³ Smith (1983); Nürnberg (1995); ⁴ E. Rydin and C. C. Carey (unpubl.); Pearl Database (2009); ⁵ B. Huser (unpubl.); Swedish National Monitoring Database (2008); ⁶ NHDES-VLAP Database (2009); E. Rydin and C. C. Carey (unpubl.); ⁷ Wilson et al. (2010); ⁸ Smith (1983); Langlais and Carignan (2002); ⁹ Reid and Girard (1987); G.K. Nürnberg (unpubl.); ¹⁰ Gonsiorczyk et al. (1998); Padsak et al. (2003); ¹¹ Taylor et al. (2006); ¹² Brunberg et al. (2002); ¹³ Hairston et al. (2001); N.G. Hairston, Jr. (unpubl.); ¹⁴ Dugopolski et al. (2008); ¹⁵ Rydin et al. (2000); Bell-Kinnon (2006); ¹⁶ Jacobsen (1976); ¹⁷ Selig (2001); Adler and Huebener (2007); ¹⁸ Anderson et al. (1993); ¹⁹ Herodek and Istvánovics (1986); Tatrat and Istvánovics (1986); ²⁰ Edmondson (1972, 1974); ²¹ Osservatorio dei Laghi Lombardi (2005); De Vicente et al. (2006); ²² Welch and Schriev (1994); Rydin et al. (2000); ²³ Farmer et al. (1994); Carvalho and Kirika (2003); ²⁴ Yang et al. (2006); ²⁵ Furumai and Ohgaki (1982); Havens et al. (2001); ²⁶ Bortleson and Lee (1975); Lathrop (1988); ²⁷ Bortleson and Lee (1972); Lathrop (1988); ²⁸ Rees et al. (1991); ²⁹ Aumen (1995); Brezonic and Engstrom (1998); ³⁰ Gonsiorczyk et al. (1998); ³¹ Jensen and Andersen (1992); ³² Rydin et al. (2000); Cooke et al. (2005); ³³ Ravera and Parise (1978); Barbieri and Mosello (1992); ³⁴ Gonsiorczyk et al. (1999); ³⁵ Lin et al. (2006); ³⁶ Kenney et al. (2001); ³⁷ Andersen and Jensen (1992); Jensen and Andersen (1992); ³⁸ Gao et al. (2005); ³⁹ Gunkel and Casallas (2002); Gunkel (2003); ⁴⁰ Boström (1988); ⁴¹ Søndergaard et al. (1992); ⁴² Iqbal et al. (2006); ⁴³ Jeppesen et al. (1998); Søndergaard et al. (2003); Reitzel et al. (2005).

We used maximum-likelihood estimation in the R statistical package (R Development Core Team 2008) to fit the linear slope of sediment TP with depth in each core to quantify the pattern of sediment TP, as well as determine the most appropriate model describing the relationship between sediment TP and depth for each core. We tested three possible models—mean ($y = a$), linear ($y = ax + c$), or exponential ($y = ax^c$), as commonly found in the literature describing a generalized TP profile (Boström et al. 1982; Fig. 1)—to determine whether sediment TP stabilizes with depth. We used a simulated annealing algorithm, a global parameter optimization procedure, with 10,000 iterations using a normally distributed error term to find the maximum-likelihood estimates of the parameters of each model for each core as a function of depth (Goffe et al. 1994). We used the corrected Akaike Information Criterion (AICc) to select the most parsimonious model, i.e., the best model fit for the fewest parameters (Burnham and Anderson 2002). For a few cores, AICc could not be calculated due to small sample sizes, for which we used R^2 as the criterion for model selection. For cores that exhibited an exponential best fit, we fit a segmented regression model to the TP data to estimate a breaking point, or stabilization depth, at which the TP concentration became constant. For all of our analyses, we used only the raw core data (i.e., we did not restrict the length of the core) to avoid bias in our stabilization depth determination. We divided the cores according to their model fit (i.e., exponential increase, linear increase, means, exponential decrease, or linear decrease) and then further grouped the data into three overall patterns depending on whether the model fit predicted sediment TP to increase, decrease, or remain constant with depth. The model AICc values, maximum-likelihood parameter estimates, and two-unit support intervals for all of the cores are presented in the Web Appendix.

We used regression analysis (SAS 2009) to evaluate whether the sediment TP pattern, as represented by linear slope, could predict TP_{water}. We log_e-transformed our response variable prior to analysis to normalize the data. Because our dataset included a few lakes with multiple cores sampled from the same depth, we randomly chose one core per lake to include in the analysis, rather than average sediment cores together that may have represented widely varying P profiles. Given that only 19 of the 94 lakes in our dataset had multiple cores per lake, we decided that using one representative core (as was done for the lakes that had only had one core sampled) was most consistent with the majority of lakes in our dataset. We examined the relationship between linear slope and TP_{water} using a regression model that included a quadratic term for linear slope. The full regression model was

$$Y = \beta_0 + \beta_1 X + \beta_2 X^2 \quad (1)$$

where Y represents TP_{water}, X is linear slope, X^2 is the quadratic term for linear slope, β_0 is the intercept term, and β_1 and β_2 are model parameters. We used backward elimination to arrive at a final model: if the quadratic term was significant at $\alpha = 0.05$, the lower order term remained in

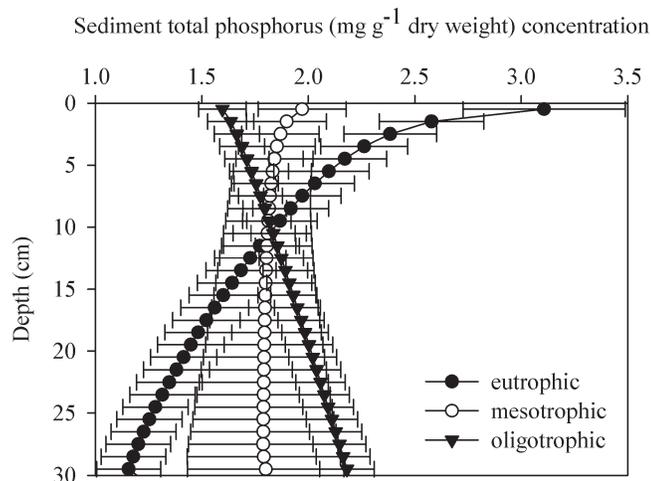


Fig. 2. Mean sediment total phosphorus concentrations, with 1 standard error, observed in sediment cores from the eutrophic (water column TP $\geq 30 \mu\text{g L}^{-1}$), mesotrophic (water column TP 10 to $30 \mu\text{g L}^{-1}$), and oligotrophic (water column TP $< 10 \mu\text{g L}^{-1}$) lakes in our dataset.

the model regardless of its significance (Kutner et al. 2005). After we evaluated this regression model with X as linear slope, a quantitative continuous variable, we analyzed the regression model with X as a categorical variable, representing sediment TP model fit and pattern (i.e., increase, decrease, constant) separately. We also divided our dataset into oligotrophic, mesotrophic, and eutrophic lakes, based on TP_{water} as described above, to test whether lakes of different trophic status exhibit different sediment TP patterns. Finally, we used a one-predictor logistic regression model to examine the relationship between linear slope (coded as 0 if the slope was positive and 1 if the slope was negative) and $\log_e \text{TP}_{\text{water}}$ concentration. We did not exclude any lakes from any of our analyses.

Results

We found that a sediment profile typically exhibited one of three sediment TP patterns that corresponded with its water column trophic status (Fig. 2; Table 1). Oligotrophic lakes generally exhibited an increase of sediment TP with depth (mean oligotrophic sediment core linear slope = 0.018 ± 0.012 , ± 1 SE); lakes with a mesotrophic water column TP exhibited constant TP with depth (mean linear slope -0.005 ± 0.014), and eutrophic lakes exhibited a decrease of TP with depth (mean linear slope -0.062 ± 0.008 ; one-way analysis of variance: $F_{2,91} = 17.80$, $p < 0.0001$). Linear contrasts demonstrate that mesotrophic lakes' linear slopes were significantly different from oligotrophic or eutrophic lakes' linear slopes (both $p < 0.02$). Lakes with sediment cores that exhibited decreasing TP with depth had significantly higher $\log_e \text{TP}_{\text{water}}$ concentrations than lakes with sediment cores with increasing TP concentrations with depth, and lakes with constant TP sediment profiles exhibited intermediate TP_{water} concentrations ($F_{2,91} = 66.17$, $p < 0.0001$). However, among lakes with the same sediment TP pattern

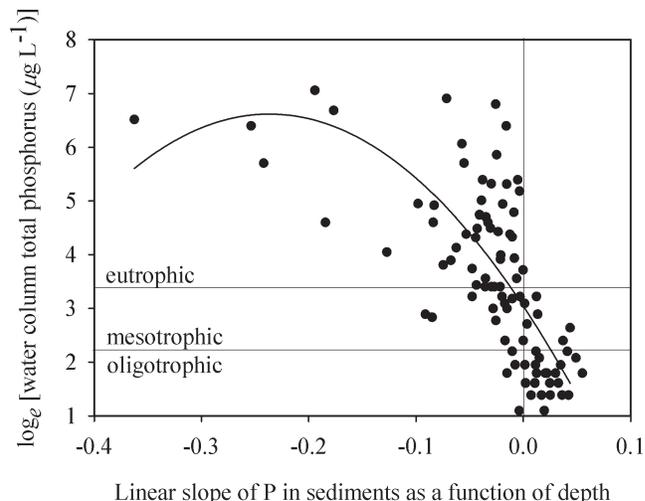


Fig. 3. The relationship between the linear slope of the function of sediment phosphorus with depth in a sediment P profile and \log_e -transformed water column total phosphorus (TP) for each of the 94 lakes in our dataset (equation provided in text). The transition between positive and negative linear slopes is denoted by the vertical line in the figure, and the threshold between eutrophic and mesotrophic water column TP concentrations ($30 \mu\text{g}$ water column TP L^{-1}) and mesotrophic and oligotrophic lakes ($10 \mu\text{g}$ water column TP L^{-1}) are denoted by the horizontal lines. Eutrophic lakes generally have negative linear slopes, oligotrophic lakes generally have positive linear slopes, and mesotrophic lakes are intermediate.

(e.g., increasing or decreasing), $\log_e \text{TP}_{\text{water}}$ did not significantly vary with model fit (i.e., exponential or linear; $p > 0.44$).

The best fitting regression model describing $\log_e \text{TP}_{\text{water}}$ as a continuous variable was $\log_e \text{TP}_{\text{water}} = 3.03(\pm 0.13) - 27.32(\pm 2.79) \times (\text{linear slope}) - 54.74(\pm 13.61) \times (\text{linear slope})^2$ (all parameters are $p < 0.0001$ and given ± 1 SE, $R^2 = 0.51$; $F_{2,91} = 46.45$, $p < 0.0001$; Fig. 3). Using the regression equation, we found that the TP_{water} concentration that was most likely observed when the linear slope = 0 (i.e., when the sediment profile exhibited a constant pattern of TP with depth) was at $20.7 (\pm 1.1) \mu\text{g TP L}^{-1}$. In our logistic regression analysis, we found a significant difference in $\log_e \text{TP}_{\text{water}}$ concentration between lakes with cores exhibiting positive and negative linear slopes (predicted logit of linear slope = $15.82(\pm 5.74) - 5.60(\pm 1.94) \times (\log_e \text{TP}_{\text{water}})$; $\chi^2 = 83.76$, $p < 0.0001$; Fig. 4). By solving the regression equation with the predicted odds ratio of the logit = 0.5, we determined that the TP_{water} concentration at which there was an equal probability that a core's linear slope would be negative or positive (i.e., the TP_{water} threshold at which cores transition between negative and positive linear slopes) occurred at $15.3 (\pm 4.1) \mu\text{g TP L}^{-1}$, similar to the $20.7 (\pm 1.1) \mu\text{g TP L}^{-1}$ threshold determined from the linear regression. Our data also exhibited a significant relationship between the concentration of TP in the surface layer of the sediment (defined as the top 1 cm of the sediment core, hereafter $\text{TP}_{\text{surface}}$) and TP_{water} ($\log_e \text{TP}_{\text{water}} = 2.63(\pm 0.25) + 0.39(\pm 0.09) \times (\text{TP}_{\text{surface}})$, $R^2 = 0.18$; $F_{1,92} = 20.23$, $p < 0.0001$).

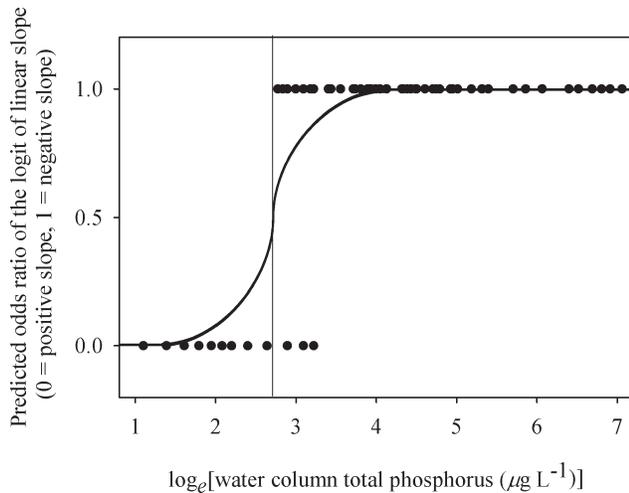


Fig. 4. The logistic relationship of the linear slope of the function of sediment total phosphorus (TP) with depth in a sediment profile (0 = positive slope, or P increasing with depth, and 1 = negative slope, or P decreasing with depth) and \log_e (water column TP); equation provided in text. In this logistic regression model, the transition between lakes with positive and negative slopes (denoted by the vertical line) occurs when the predicted odds ratio of the logit of linear slope = 0.5, at $15.3 \pm 4.1 \mu\text{g water column TP L}^{-1}$, or $2.73 \pm 1.40 \mu\text{g water column TP L}^{-1}$ on a \log_e scale.

Discussion

We found that the sediment TP pattern over the depth of a core varied significantly with lake trophic status, with more than 50% of the variation in water column TP concentration attributable to sediment TP pattern. This pattern would not be evident from examination of the surface sediment TP concentration alone, highlighting the importance of analyzing the lake sediment P profile at depth to understand sediment–water P interactions. We suggest that the weakness of the relationship between TP_{water} and TP in the surface sediments (e.g., our data; Boström et al. 1982; Håkanson 2003; Maassen et al. 2005) in comparison with the relationship between TP_{water} and sediment TP pattern results from the fact that surface sediment TP concentrations generally represent lake and watershed-specific P concentrations in deposited particles (Pettersson 2001). To determine the P available to be released to the water column with time (i.e., the potentially mobile P; Rydin 2000; Reitzel et al. 2005), it is essential to examine sediment TP concentrations over the entire length of a core. Measuring TP concentrations from the surficial sediments to the depth at which P diagenesis processes have stabilized and where the remaining P becomes permanently buried will indicate the sediment P burial, and consequently how much P could be remobilized (Fig. 1; Pilgrim et al. 2007; Rydin et al. 2011).

Sediment accumulation rates vary greatly between lakes. In three oligotrophic lakes in Maine, Wilson et al. (2010) found that a 50-cm sediment profile represented between 400 and 1500 years of accumulation. This contrasts with the moderately eutrophic Lake Erken (Sweden), where

50 cm of sediment in deposition bottom areas represented less than two centuries of sediment accumulation (Ahlgren et al. 2005). However, this variation in sediment accumulation rates, and subsequently sediment age at a given depth, did not affect the approach we used to correlate sediment TP diagenesis to water column TP. As a net result, we show that eutrophic lakes tend to release sediment P (i.e., have poor P burial), oligotrophic lakes tend to accumulate P (i.e., have good P burial), and mesotrophic lakes may still accumulate deposited P but are close to saturation. Hence, if external loading to a mesotrophic lake would increase, the sediments may not be able to bind all deposited P, which would result in P release to the water column (internal loading). Because the linear slope of the function of sediment TP with depth does not include the rates of accumulation processes, our metric for sediment TP pattern integrates TP along the entire core and is unaffected by sediment age.

We also examined the sediment TP pattern in the hypertrophic lakes, as defined by Nürnberg (1996) to be lakes with TP_{water} concentrations $> 100 \mu\text{g L}^{-1}$, which comprised approximately half of the lakes classified as eutrophic in our dataset. We found that the linear slopes of the hypertrophic lakes were not significantly different from the linear slopes of the eutrophic lakes with TP_{water} concentrations $\geq 30 \mu\text{g L}^{-1}$ and $\leq 100 \mu\text{g L}^{-1}$ (Tukey's test, $p < 0.12$). Consequently, we maintained our original classification of all lakes with $\text{TP}_{\text{water}} \geq 30 \mu\text{g L}^{-1}$ as eutrophic without a further hypertrophic grouping. This observation is supported by Fig. 3, which indicates that once the threshold between positive and negative linear slopes in sediment cores is crossed, TP_{water} concentrations will not change substantially as lakes exhibit more negative linear slopes (i.e., greater decreases of sediment TP concentrations with depth).

In about half of the eutrophic lakes in our analysis, we observe an exponential decrease of TP and then stabilization at a mean $16.0 (\pm 1.3, 1 \text{ SE})$ cm depth. The decline in sediment TP we observed in eutrophic lake sediments may, in a few cases, simply reflect a recent increase in external P loading. However, eutrophic lakes that have a constant P loading history over time (e.g., Lake Erken; Rydin 2000) also exhibit an exponential decrease of TP with depth, indicating that the decrease is not necessarily due to changes in external loading. In most eutrophic sediment cores, the exponential decrease of TP with depth reflects organic P degradation and subsequent release of P due to the limited capacity of sediment to retain mineralized organic P upon burial (Fig. 1; Rydin 2000, Rydin et al. 2011). Organic P is linked to trophic status parameters (i.e., primary production) and is to a large extent recycled between the sediments and the water column (Carignan and Flett 1981; Ahlgren et al. 2005). Additionally, in oxidized surface sediments, temporary binding (Gächter and Müller 2003) of phosphate to iron oxyhydroxides (Mortimer 1941) or polyphosphates (Huffer and Gächter 1995) might substantially increase P content, also rendering an exponential decline in P until the stabilization depth (Rydin 2000). At the stabilization depth, diagenesis processes have effectively been complet-

ed, and below this depth the sediment TP concentration remains constant.

To determine whether the typical eutrophic sediment TP pattern we observed is the result of drastically increased external P loading in recent years or, as shown for Lake Erken, whether the eutrophic TP pattern is the result of the limited capacity of the sediment to retain and bury all deposited P, we would need to analyze P budgets (created for several decades prior to each sediment core's collection), steady-state information, and sediment chemistry data for all of the eutrophic lakes in our dataset. We were unable to find this information, since these budgets and data are very time and labor intensive to collect. However, we were able to recreate qualitative external load histories for 88 of the 94 total lakes (*see* Web Appendix) from monitoring records. For example, we compiled information on which years lakes exhibited increasing TP_{water} concentrations due to increasing runoff, and if and when wastewater treatment or lake management techniques were implemented. From these data, we can infer that of the 49 eutrophic lakes in our dataset, 29 lakes had experienced constant or decreasing P loads in the decades before sediment core collection and 16 lakes had experienced increased P loading before the core was collected (we were unable to find data for four eutrophic lakes). These data, although not quantitative, support our hypothesis that for the majority of the eutrophic lakes, the eutrophic TP pattern is the result of the limited capacity of the sediment to retain and bury all deposited P and is not a result of increased external P loads.

We did not observe a stabilization point in eutrophic cores with linear fits. We hypothesize that the eutrophic lakes that exhibited a linear decrease model fit may have experienced a variable loading history of either dry matter or P. Since eutrophic lakes that have constant loading of dry matter and P exhibit exponential declines in P until a stabilization depth (Rydin 2000; Ahlgren et al. 2005), the loading rate in lakes with linear declines may not be at steady state. We found that there was no significant difference in water column TP concentration between eutrophic lakes with linear and exponential model fits. Furthermore, different cores from the same lake may have exhibited different fits (linear or exponential), which may be due to variable loading histories for different lake sites or sediment disturbance, but all cores from the same lake exhibited the same overall pattern (increasing or decreasing). Consequently, the difference between exponential or linear model fits is not as important as the general sediment TP pattern (increasing or decreasing) for predicting trophic status.

The mobile P pool in the lake, as represented by the increase of TP toward the sediment surface in the eutrophic cores in Fig. 2, causes the eutrophic condition to resist change by rapid recycling of P from sediments into the water column (Gächter and Müller 2003; Carpenter 2005; Reitzel et al. 2005) and is eventually further enhanced by the removal of available iron through the formation of insoluble iron sulfides under anoxic conditions (Caraco et al. 1989). The eutrophic TP profile is both a cause and an effect of eutrophication: high levels of external loading will

increase the deposition of P-rich primary production, which will increase TP concentrations in the surface sediments of a sediment profile. Some, but not all, of the deposited P will be permanently buried in the sediment, while the excess P will be recycled back to the water column as dissolved P, further intensifying eutrophic conditions.

In oligotrophic lakes, low P conditions might be maintained by aluminum (Al) fluxes from the watershed (Kopáček et al. 2006, 2007; Wilson et al. 2010). Mobilized Al is carried in association with dissolved organic matter to lakes where it is made soluble by ultraviolet radiation in the water column (Kopáček et al. 2005b). Once mobilized, Al precipitates as an oxyhydroxidic complex, enabling efficient P binding in the sediment (Kopáček et al. 2005b; Wilson et al. 2010). P bound to Al represents a permanent burial of P, regardless of redox status (Kopáček et al. 2005a), as reported from acidified lakes (Kopáček et al. 2000; Huser and Rydin 2005) and from eutrophic lakes after Al treatment, where a pulse of increased permanent P burial was observed (Rydin et al. 2000). The mean water column pH of the oligotrophic lakes in our dataset was 6.6 ± 0.2 (1 SE), with only 4 of the 26 oligotrophic lakes in our dataset exhibiting pH values ≤ 6.0 . These data indicate that our oligotrophic lakes were predominantly not acidic. We were unable to obtain information on the availability of Al within the watersheds of the lakes in our dataset but would expect that Al availability would be higher in oligotrophic watersheds than in eutrophic watersheds (Huser and Rydin 2005).

The cause of the pattern of increasing sediment TP with depth in oligotrophic lakes, which was present in every oligotrophic sediment core that we examined and is distinct from the classic sediment TP profile, has not heretofore been investigated. The majority (72%) of the cores we found for our dataset were from mesotrophic and eutrophic lakes, indicating that the classic sediment TP profile (as described by Boström et al. 1982) may be biased because oligotrophic sediments are understudied. We suggest three potential mechanisms that may explain the sediment TP increase with depth in oligotrophic lakes. First, diffusion of recently deposited P to deeper sediment layers could increase sediment P concentration at depth. The majority (80%) of cores from oligotrophic lakes that displayed increases of P with depth exhibited linear increases (vs. exponential increases), indicating that P concentrations would continue to increase with depth beyond the length of the core. Owing to solubility product criteria equilibrium, some phosphate will remain in sediment pore water, which potentially would be able to diffuse downward (Stumm and Morgan 1996). Al-P mineral formations in deeper sediment layers may create P forms with lower solubility product criteria, resulting in a downward P flux to older sediment layers. Second, increasing P concentrations with depth in lake sediment cores may relate to decreases in P export from the watershed since deglaciation. Since most oligotrophic lakes are situated in glaciated areas, and the weathering rate decreases as soil age increases (Engstrom et al. 2000), the increasing P concentration with depth may reflect decreased weathering rates of P minerals, such as apatite, over time.

Third, the observed TP increase with depth may be explained by increasing Al-P with depth, which in turn correlates with total Al (Kopáček et al. 2007; Wilson et al. 2008, 2010). Phosphorus fractionation of sediment cores from oligotrophic lakes exhibits an increase of Al-bound P with depth (Wilson et al. 2010). The increase of Al with sediment depth may be due to a decline in Al loading due to changes in the watershed since deglaciation (Norton et al. 2006; Kopáček et al. 2007; Norton et al. 2008) or, alternatively, increased loading of organic material. Soils of these watersheds have increased Al retention and possibly also P retention over time, which would explain a gradual decrease in Al and P concentration toward the sediment surface. Alternatively, as suggested by Engstrom et al. (2000), oligotrophic lakes might become less productive over time. The decline in lake sediment TP concentration over time might reflect this phenomenon. Losses of matter other than P (e.g., mineralization of organic matter or biogenic silica), would most likely be negligible and so would not explain the observed increase in P concentration with sediment depth. We also ruled out anthropogenically induced processes such as acidification or logging, for example, that potentially could alter loading from these typically unpopulated watersheds, since the time span represented by our data typically covered several centuries (Wilson et al. 2010).

We hypothesize that the fundamental difference in oligotrophic and eutrophic lakes may be the lack of enough P binding agents, such as Al, to bind all of the mobilized P in eutrophic lakes. Oligotrophic lake sediments typically exhibit higher Al-bound P concentrations than eutrophic lake sediments (Kopáček et al. 2005b). Since Al permanently binds P (Kopáček et al. 2000) and may be linked to increasing P concentrations at depth in oligotrophic lakes, Al may explain the difference in sediment P burial between eutrophic and oligotrophic lakes and ultimately may explain the availability of P to be released to the water column.

In several oligotrophic sediment cores analyzed in this paper (e.g., Mud Pond, Wilson et al. 2010; Long Pond and Messalonskee Lake, E. Rydin and C. C. Carey unpubl.), we observed elevated TP concentrations in the surface sediment layer: the core was similar to a eutrophic sediment profile in the surface sediments, indicating a limited capacity to retain all of the deposited TP from the water column, but also exhibited an increase of TP at depth, typical of an oligotrophic core. This kind of a hybrid profile might reflect a biologically active surface sediment layer with P incorporated in biota (Ahlgren et al. 2006). It might also be indicative of an oligotrophic lake undergoing a transition to a more eutrophic state.

Mesotrophic lakes exist within a very narrow range of P concentrations (Carlson 1977). Much research has examined the effects of external P loading at the oligotrophic–eutrophic threshold (Vollenweider and Kerekes 1980; Carpenter 2005), but our data indicate for the first time that the profiles of increasing P with depth in oligotrophic lakes may be an indicator of their relative invulnerability to eutrophication, especially in comparison with mesotrophic lakes, which have a limited capability to absorb any additional P loads. From solving the linear and logistic regression equations for the TP_{water} concentration at which a

lake sediment core exhibits constant P with depth, our data indicate that such a threshold may exist at approximately $15.3 (\pm 4.1)$ to $20.7 (\pm 1.1) \mu\text{g water column TP L}^{-1}$. At this water column TP concentration, it appears that the sediment profiles of TP fundamentally change from an increase of P with depth to a decrease of P with depth. Our data indicate that the TP_{water} concentration that identifies the transition between lakes with sediments that tend to permanently bury P (i.e., oligotrophic) and lakes with sediments that release P to the water column (i.e., eutrophic) falls exactly within the suggested water column TP range for mesotrophic conditions: $10\text{--}30 \mu\text{g water column TP L}^{-1}$ (Nürnberg 1996). Our data support many other studies that demonstrate thresholds for eutrophication (Carpenter and Lathrop 2008). Consequently, we argue that a fundamental shift in lake functioning occurs at this TP_{water} threshold, which is important for lake management.

As a lake approaches $30 \mu\text{g water column TP L}^{-1}$, its ability to tolerate increased P loads is limited and will drive the lake toward a more eutrophic state. Therefore, we hypothesize that lakes that are undergoing eutrophication will exhibit constant TP concentration sediment profiles with depth, a potential metric of determining the vulnerability of a lake to undergo a eutrophic shift. Many other factors are also important in determining a lake's vulnerability to eutrophication, such as morphometry and the external supply of P binding agents, but lake sediment TP profiles may potentially be used as an indicator of incipient eutrophication. Our work contributes to the vast internal loading literature by demonstrating that sediment P burial may be an important control of internal loading in lakes, which in turn contributes to the positive feedbacks of eutrophication. Finally, our data demonstrate the inextricably close relationship between sediment TP pattern with depth and water column TP, and indicate that sediment TP may be a more integrated metric of lake trophic state than water column P concentrations, since sediment TP pattern may determine whether deposited P is permanently absorbed or remobilized.

Acknowledgments

We thank R. Q. Thomas for his modeling assistance; B. J. Huser, A. Litt, G. K. Nürnberg, J. A. Rusak, and the Dorset Environmental Sciences Centre for sharing data; and H. A. Ewing and K. C. Weathers for sampling help. We thank N. F. Caraco, J. J. Cole, K. L. Cottingham, H. A. Ewing, N. G. Hairston, Jr., B. J. Huser, G. K. Nürnberg, L. Tranvik, K. C. Weathers, and an anonymous reviewer for their valuable suggestions on this manuscript. Financial support by the Swedish Fulbright Commission, the American–Scandinavian Foundation, and a National Science Foundation Graduate Research Fellowship to C.C.C.; the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS), and the Olsson-Borgh Foundation to E.R.; and the National Science Foundation DEB-0749022 to K. L. Cottingham, H. A. Ewing, and K. C. Weathers is gratefully acknowledged.

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Associate editor: Roland Psenner

Received: 26 January 2011

Accepted: 06 June 2011

Amended: 19 July 2011