Aluminum Control of Phosphorus Sorption by Lake Sediments

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Release of reactive (phosphate-like) phosphorus (P) from freshwater sediments represents a significant internal P source for many lakes. Hypolimnetic P release occurs under reducing conditions that cause reductive dissolution of ferric hydroxide [Fe(OH)3]. This hypolimnetic P release may be naturally low or artificially reduced by sediment with naturally high or artificially elevated concentrations of aluminum hydroxide [Al(OH)3]. We present field and laboratory data for a common extraction analysis of sediments from 43 lakes differing in trophic status, pH regime, climate, and P loading. The results indicate that a simple sequential extraction of sediment may be a useful predictor of sediment’s ability to release P. Sequential extractions of sediment P, Al, and Fe by water (H2O), bicarbonate—dithionite (BD), and NaOH (at 25 °C) showed that negligible amounts of P would be released from sediments during hypolimnetic anoxia if either (1) the molar ANaOH−25:FeBD ratio is >3 or (2) the molar ANaOH−25;P(H2O+BD) ratio is >25. These ratios can be used as operational targets for estimation of sediment P release potential and Al dosing of P-rich sediment to prevent hypolimnetic P release under anoxic conditions.

Introduction

Phosphorus sorption capacity of freshwater sediments has been related to concentrations of ferric oxyhydroxides or hydroxide [Fe(OH)3] and calcium carbonate (CaCO3) in high-pH lakes (1, 2), and aluminum hydroxide [Al(OH)3] in noncalcareous sediments of lower pH lakes (3). Release of reactive phosphorus (P) from the sediments into the water column is of great concern because it can contribute significantly to the total in-lake pool of bioavailable P (4). Lake and coastal marine sediments, whose sorption capacities are dominated by Fe(OH)3, release P during the development of hypolimnetic anoxia that results in the reductive dissolution of Fe3+ solid phases and release of Fe2+ into solution or reprecipitation as Fe0 sulfide (1, 5). Elevated concentrations of Al(OH)3 in the sediment can prevent P release during anoxia by adsorbing the P liberated from Fe(OH)3 (6, 7). The Al(OH)3 has a high sorption capacity (8) and is stable under both oxic and anoxic conditions, provided that the sediment pH is circumneutral. Such pH conditions are produced by microbial reduction that generates alkalinity by the carbonate and sulfide buffering systems. The ability of Al(OH)3 to prevent P release from sediments during anoxia suggests the following question: What are the characteristics of sediment (e.g., concentrations of P, Fe, and Al, or ratios among them) that permit or inhibit P release?

Despite numerous shortcomings of sequential P extraction schemes (e.g., their low selectivity, readsorption of liberated P, or changes of solid phases during extraction) (2, 9) they provide a rapid and inexpensive answer to the question. In this study, we use field and experimental data to show that the ratio between sediment Al and Fe hydroxide concentrations determines P release from noncalcareous sediments during reducing (low Eh) conditions.

Materials and Methods

Site Description. Data from 52 sediment samples form the basis of our hypothesis. Samples are from 43 European and North American lakes (13 alpine lakes, 8 mountain forest lakes, 6 lowland lakes, 8 mountain reservoirs, and 8 lowland reservoirs). Eighteen lakes have been acidified by atmospheric deposition and have experienced (at least episodically) elevated fluxes of Al from their watersheds (10–12). The lakes were generally studied from spring to fall turnover. The trophic status of the water bodies ranged from oligotrophic to hypereutrophic. The epilimnetic concentrations of total P ranged from 0.04 to 10 μmol L−1 and water pH from 4.5 to 8.5. The lakes covered a wide range in elevation (60–2145 m), surface area (0.2–31 500 ha), and maximum depth (1–75 m). For more detailed characteristics of the lakes, see the Supporting Information.

Sediment Sampling and Analyses. The sampling and analyses are from four studies in the 1994–2004 period. Methods and analyses varied only slightly (see Supporting Information), allowing us to reasonably compare data. The uppermost layers of 0–1 to 0–5 cm of the fresh wet sediment were used for P fractionation analyses according to Psenner and Pucsko (13). Sediment was sequentially extracted by five processes: (1) Distilled water (H2O fraction) was used to obtain loosely bound and pore-water soluble reactive P (Piso). (2) NaHCO3 (0.1 M) buffered 0.1 M sodium dithionite (Na2S2O4) at 40 °C (BD fraction) was used to release soluble reactive PBD from Fe3+ oxyhydroxides under low redox conditions. (3) NaOH (1 M) at 25 °C (NaOH–25 fraction) extracted soluble reactive PNaOH−25 from the amorphous Al(OH)3 (which dissolves due to high pH) and some Fe3+ oxyhydroxide that was not extracted in the BD step. This step also results in the extraction of some of the sediment organic P. (4) HCl (0.5 M) (HCl fraction) was used to release soluble reactive P associated with any calcite and apatite (Pcalcite). (5) NaOH (1 M) at 85 °C (NaOH–85 fraction) was used to remove refractory and other organically bound soluble reactive P (PNaOH−85). All fractions were centrifuged at ~1000 g for 15 min and filtered (glass-fiber filters, pore size 0.4 μm). In the filtrate, P concentrations were determined by the molybdate method (14) or by inductively coupled plasma atomic emission spectrometry (ICP), and Al and Fe concentrations, by ICP or colorimetrically (15). Total extractable P (PTE) is the sum of the P released in all extraction steps.
Organic carbon (OC) in the sequential extracts was determined with a TOC 5000A analyzer (Shimadzu). Sediment pH was measured directly in the wet sample. Concentrations of total phosphorus in the sediment were determined from freeze-dried subsamples after their acid digestion, either by ICP or colorimetrically (15). All chemical results reported in this paper were calculated on a dry weight sediment basis.

**Laboratory Experiments.** Samples of surface sediments (0–15 cm layer) were taken from the inlet and the deepest (pool) part of Jordán Reservoir (Czech Republic) in August 2001. Suspended sediment (10 g L⁻¹) was mixed with a suspension of poly-aluminum chloride (10 g of Al L⁻¹), with the pH adjusted to 6 with NaOH. The poly-aluminum chloride concentration was calculated so that the original concentration of total extractable Al in sediment (1.5 and 1.8 mol kg⁻¹ in the inlet and the deepest area, respectively) was increased incrementally by addition of 0, 0.5, 0.9, 1.9, and 3.7 mol of Al kg⁻¹ of dry sediment. After the Al addition, the suspension pH was adjusted to the original pH of 7.1. The samples were kept in the dark at 15 °C, underoxic conditions (stirred in the open bottles), and at constant pH (adjusted as necessary each month) for 18 months. Finally, sequential extraction (13) was performed on wet samples, and P, Al, and Fe concentrations were determined in the five fractions described above.

A second experiment was done with surface sediments (differing in Al concentration) from two mountain forest reservoirs (Saidenbach and Neunzehnhain, Germany, April 1996). Na₂HPO₄ was added at final concentrations of 46 and 38 mmol kg⁻¹ of dry sediment to the fresh sediments from Saidenbach and Neunzehnhain reservoirs, respectively, and shaken for 1 h at constant pH in the dark at 8 °C. Sequential extraction (13) was then performed on both the original and spiked samples, and P, Al, and Fe concentrations were determined as described above.

**Phosphorus Sorption Capacity of Sediments.** Sorption capacity of sediments was measured for samples taken from all lowland reservoirs, mountain forest lakes, and three alpine lakes. Methodological details are in ref. 6. In short: eight subsamples of wet sediment (containing ~15 mg of dry matter) were shaken for 24 h at ~25 °C with 25 mL of artificial lake water containing 0–1.3 mmol of KH₂PO₄ L⁻¹ at the original pH values. The equilibrium P concentrations in the water were determined as reactive P (14). The difference between P concentrations before and after the procedure was assumed to have been sorbed by the sediments. The sorption data were fitted to the linear form of the Langmuir isotherm (correlation coefficients were >0.98) and the sorption capacity (X₀) was calculated for each sample.

**Results and Discussion**

**Fractionation Results.** Total P concentrations in sediments ranged from 11 to 141 mmol kg⁻¹, with small differences among lake categories. The PTE concentrations (sum of soluble reactive P extracted by all steps) were 20–104% of total P. The average PTE concentrations were lowest in sediments of oligotrophic alpine and mountain forest lakes (Figure 1).

The P_HCl contributed <3% to the PTE for all sediments, regardless of lake category (Figure 1). The P_HCl was 1–45% of PTE. The relative importance of the BD step increased generally with the trophic status of lakes, with P_HCl being highest (on average 32% of PTE) in lowland reservoirs and lowest (on average 7% of PTE) in alpine lakes. The NaOH–25 extraction liberated 3–92% of PTE, with the lowest highest average yields of P_NaOH–25 in sediments of lowland reservoirs (39%) and mountain forest lakes (80%), respectively. The mountain forest lakes received high terrestrial Al export from naturally and atmospherically acidified soils (12), and the P_NaOH–25 was accompanied by high Al concentrations (Figure 1).
sorption characteristics. Sediment from the nonacidified lowland Rimov Reservoir (Czech Republic) had a large portion of \( P_{\text{TE}} \) associated with \( \text{Fe(OH}_3 \) liberated during the BD extraction step together with \( \text{Fe}_{\text{BD}} \) (Figure 2A). In contrast, most of the \( P_{\text{TE}} \) was liberated in the NaOH \( \sim 25 \) fraction together with \( \text{Al}_{\text{NaOH} \sim 25} \) from the acidified mountain forest Plesně Lake sediment (Figure 2B). This lake has received elevated Al inputs from the strongly acidified soils (6).

The importance of naturally high Al concentrations in the sediments on their sorption properties was also demonstrated by the experiment with sediments from mountain forest reservoirs (Table 1). Sediment from Neunzehnhain Reservoir had 5–6 times higher \( \text{Al}_{\text{NaOH} \sim 25} \) concentrations than from Saidenbach Reservoir, whereas \( \text{Fe}_{\text{BD}} \) concentrations were comparable in both reservoirs. Of the P added to the sediments, 94–96% was adsorbed, as calculated by difference. Of the adsorbed P, 96–103% was recovered as \( P_{\text{TE}} \). The \( P_{\text{BD}} \) fractionation step liberated most (49–57%) of the \( P_{\text{TE}} \) in both the original and P-spiked sediment from Saidenbach Reservoir. In contrast, the \( P_{\text{NaOH} \sim 25} \) fraction was the dominant form of \( P_{\text{TE}} \) (82% and 73% in the original and P-spiked sediments, respectively) in Al-rich sediment from Neunzehnhain Reservoir.

The importance of artificially elevated Al input to the sediments on their sorption properties was demonstrated by the experiment with sediments from inlet and deepest parts of Jordán Reservoir (Figure 3). The sediment from the inlet part had most of its P extracted by the HCl step, possibly due to the presence of CaCO₃. \( P_{\text{BD}} \) was the second most important P fraction in the sediments near the inlet. The \( P_{\text{BD}} \) fraction, however, dominated the deep water sediments in the reservoir. Concentrations of \( P_{\text{NaOH} \sim 25} \) were quantitatively insignificant in the sediments prior to the Al treatment. The Al treatment significantly affected the P sorption characteristics of both sediments. Small changes occurred in concentrations of the quantitatively insignificant \( P_{\text{H2O}} \) and \( P_{\text{NaOH} \sim 25} \) fractions. Of the Al added, 87% (on average) was found in the NaOH \( \sim 25 \) fraction (data not shown here). Even the smallest Al dose (0.46 mmol kg\(^{-1}\)) reduced the \( P_{\text{BD}} \) concentrations by up to 80% and increased the \( P_{\text{NaOH} \sim 25} \) concentrations by 300–500%. A new equilibrium between \( P_{\text{BD}} \) and \( P_{\text{NaOH} \sim 25} \) was reached at the Al dose of 0.9 mmol kg\(^{-1}\); higher Al input had no impact on the P extraction results (Figure 3).

The sediment from Jordán Reservoir is an important source of P for the water column during periods of hypolimnetic anoxia. The Al treatment increased the \( \text{Al}_{\text{NaOH} \sim 25} \) pool, and consequently, changed the sorption characteristics of Jordán sediments from those of a nonacidified lake such as Rimov Reservoir (Figure 2A) to those typical of an acidified lake such as Plesně Lake (Figure 2B) and significantly reduced the amount of P extractable under anoxic conditions. Similar results were obtained in other laboratory experiments (19, 20) and during lake restoration treatments with Al (21, 22).

The fractionation data, as well as the experience with the Al-treated lakes (7, 22), show that sediments with naturally high or elevated \( \text{Al}_{\text{NaOH} \sim 25} \) concentrations do not release P into the water column during hypolimnetic anoxia. This is the case for Plesně Lake sediment, which releases negligible

### TABLE 1. Results of Phosphorus Fractionation Analyses (‘25) of P-Spiked Sediments from the Saidenbach and Neunzehnhain Mountain Reservoirs (Germany)\(^{a}\)

|                      | Saidenbach Reservoir | Neunzehnhain Reservoir |
|----------------------|----------------------|------------------------|
|                      | original             | P-treated              | original             | P-treated              |
| \( P_{\text{ads}} \) |                      |                        |                      |                        |
| \( P_{\text{TE}} \)  | 81                   | 124                    | 23                   | 60                     |
| \( P_{\text{H2O}} \) | 48                   | 71                     | 1                    | 4                      |
| \( P_{\text{BD}} \)  | 34                   | 38                     | 19                   | 44                     |
| \( P_{\text{NaOH} \sim 25} \) | 7                   | 7                      | 3                    | 3                      |
| \( P_{\text{NaOH} \sim 25} \) | 255                  | 255                    | 1418                 | 1376                   |
| \( (\text{Al}:\text{Fe})_{\text{H2O}} + \text{BD} + \text{NaOH} \sim 25 \) | 0.3                  | 0.3                    | 2.1                  | 1.8                    |
| \( \text{Al}_{\text{NaOH} \sim 25} \) | 6                    | 3                      | 1981                 | 108                    |

\(^{a}\) Units are millimoles per kilogram (dry sediment) and molar ratios. BD, bicarbonate–dithionite; TE, total extractable.
P either through BD extraction (Figure 2B) or into the anoxic hypolimnion (6). Similarly, Amirbahman et al. (23) found, in a set of 11 oligo/mesotrophic to eutrophic lakes in Maine, that two lakes did not release P during the development of hypolimnetic anoxia, even as dissolved Fe increased substantially. The sediment of these two lakes (both oligotrophic) had relatively high proportions of AlNaOH−25 compared to FeBD (24). Minimal release of P in the BD extraction and low release of P from anoxic sediments (despite elevated Fe2+ concentrations above them) occurred also in AlNaOH−25-rich sediments from mountain reservoirs (10, 12). These data suggest that if AlNaOH−25 concentrations are high, the P (liberated either from Fe(OH)3 or by microbial processes (25)) becomes bound to Al(OH)4−, buried in the sediment, and withdrawn from in-lake cycling. In contrast, the sediment of Rîmîov Reservoir has low AlNaOH−25 Concentrations and releases considerable P both during the BD extraction (Figure 2A) and into the water column during hypolimnopic anoxia (26). The parallels between our fractionation and field studies [as well as recent research (27)] suggest that sediments with low PBD concentrations have low ability to release P into anoxic hypolimnia, and vice versa.

Even though the AlNaOH−25 concentration affects P adsorption in nontoxic sediments, it cannot, by itself, be used as a measure of sediment ability to release P during anoxia (see Figure 1 and Figure S1 in Supporting Information).

So, at what threshold in sediment composition is the P release inhibited and what should be the target for Al dose to lakes to prevent P release?

Thresholds. Figure 4 suggests that the major threshold for the PBD is the ratio between Al and Fe concentrations extracted in the first three steps of the sequential extractions. Concentrations of AlBD extracted from sediments with (Al: Fe)BD ratios >3 were low. In contrast, many sediments with AlBD ratios <3 yielded high PBD concentrations. The batch experiments with sediment from Jordán Reservoir also showed that at a (Al:Fe)BD ratio exceeding 2–3, P release under reducing conditions ceases (Figure 4). A similar threshold as for PBD was observed also for total P extracted by the H2O and BD steps (TPBD), because PBD represented the dominant (75% on average) fraction of TPBD (data not shown).

The PBD concentrations were consistently low for sediments of acidified lakes, while most of these sediments had (Al:Fe)BD ratios >3 (Figure 4). Such a result could be associated with elevated sediment concentrations of Al due to soil acidification in watersheds, as at Plešné Lake (Figure 2B). In contrast, nonacidified lakes had larger scatter in the PBD concentrations for (Al:Fe)BD ratios <3. Here, another question arises: What parameters are responsible for the variable yield of PBD if (Al:Fe)BD ratios <3? Surprisingly, no correlation (p > 0.05) occurred between PBD and FeBD even for the sediments with (Al:Fe)BD ratios <3. Only 25% of the variability in PBD concentrations was explained by the (Al:Fe)BD ratio. For most sediments in this group, most of this variability was closely associated (p < 0.001) with concentrations of OC extracted by the H2O and BD steps (OCBD) (Figure 5). Such a relationship is in concordance with models of phosphate adsorption on metal oxihydroxides in sediments and soils (28, 29). These models assume competition between OC and phosphate for available adsorption sites on Al hydroxide. The high sediment OCBD concentrations probably decrease P readsorption on Al(OH)3 during BD extraction. Concentrations of OCBD were related to concentration of total organic C (or loss on ignition) in sediments (p < 0.001), suggesting that a potential risk of P release from sediments with (Al:Fe)BD ratios <3 increases with the organic content of sediments. However, if AlNaOH−25 ratios exceeded 25 (Figure 5), only low PBD concentrations were extracted, even at high OCBD concentrations. Similarly, the experimental results showed that low PBD concentrations were extracted at high AlNaOH−25 ratios and concentrations of FeBD, while PBD dominated the P pool at the lower ratios (Table 1). We hypothesize that for AlNaOH−25 ratios >25, the Al(OH)3 adsorption capacity was high enough to prevent P release from anoxic sediments.

The (Al:Fe)BD ratio and concentrations of OCBD and AlNaOH−25 together explain 64% of the variability in the observed PBD concentrations at (Al:Fe)BD ratios <3. The remaining variability may be associated with other sediment characteristics such as particle size, degree of saturation of sorption sites, or degree of crystallinity of Fe and Al hydroxides.

Aluminum Impact on Sediment Sorption Capacity. The presence of AlNaOH−25 in the sediments affected not only their ability to release or bind P during anoxia but also their total sorption capacity. The sediment sorption capacities (Xa) averaged (±1 standard deviation) 171 ± 69, 74 ± 19, and 50 ± 40 mmol of P kg−1 for forest mountain lakes, alpine lakes, and lowland reservoirs, respectively. Concentrations of FeBD and AlNaOH−25 explained together 79% of variability in the Xa values (see Figure S3 in Supporting Information). The FeBD concentrations extracted in the first two [H2O and bicarbonate–dithionite (BD)] extraction steps (Figure 4) becomes bound to Al(OH)4−, buried in the sediment, and withdrawn from in-lake cycling. The parallels between our fractionation and field studies [as well as recent research (27)] suggest that sediments with low PBD concentrations have low ability to release P into anoxic hypolimnia, and vice versa.

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concentrations were comparable in all lake categories (with averages between 95 and 127 mmol kg\(^{-1}\)). The difference in \(X_m\) associated with high AlNaOH\(_{25}\) concentrations in mountain lakes (912 and 355 mmol kg\(^{-1}\) in forest and alpine lakes, respectively) and lower values in lowland reservoirs (108 mmol kg\(^{-1}\)). The AlNaOH\(_{25}\) concentrations alone explained 75% of the \(X_m\) variability.

The total capacity of the sediment to bind P by both sorption and chemical bonds can be estimated as the sum of \(X_m\) and \(P_{TE}\), and the original percent saturation of this total binding capacity with P can be estimated as the \(P_{TE}/(X_m + P_{TE})\) ratio (30). The \(P_{TE}/(X_m + P_{TE})\) ratio was 15% ± 7% for mountain forest lakes and 55% ± 25% for lowland reservoirs. This difference shows that sediment saturation with respect to P was lower in mountain lakes and their capacity to bind more P was substantially higher than that of lowland reservoirs, with low AlNaOH\(_{25}\) concentrations.

McLaughlin et al. (31) showed that freshly prepared Al colloids sorb 1–2 orders of magnitude more P than crystalline gibbsite. This implies that the ability of Al-rich sediments to retain P decreases with time due to Al(OH)\(_x\) aging. Studies involving Al-treated lakes (7, 22, 27), however, suggest that the increased AlNaOH\(_{25}\) concentrations can elevate P sorption in sediments and prevent its repartitioning into the BD fraction for at least several decades.

**Implication for Lakes.** The P release from Fe(OH)\(_x\) is commonly considered as a mechanism occurring in eutrophic lakes with anoxic hypolimnia (1, 4), even though P release may occur even during oxic conditions (32). Some studies (2, 33), however, show that even P-rich sediments may not release P during anoxia. Such results may be interpreted as arguments against Mortimer’s generalization of P liberation from the reduced Fe(OH)\(_x\). Our results suggest an alternative explanation for “exceptions” from Mortimer’s schema – sediments that do not release P have sufficient Al(OH)\(_x\) to provide additional sorption capacity and bind P liberated from Fe(OH)\(_x\) at low Eh conditions.

Association of P with Al(OH)\(_x\) in sediments is especially important in lakes with the following characteristics: (1) Alpine lakes with noncalcareous bedrock and high erosion rates in their watersheds. These lakes receive soil particles with Al oxyhydroxides, which have high P sorption capacity (30). (2) Lakes in atmospherically or naturally acidified watersheds that receive elevated terrestrial export of dissolved and particulate Al (10, 12, 34). If the terrestrial flux of Al is increasing as a consequence of soil acidification but that of P does not intensify, recycling of P from sediments may be reduced. The net result is oligotrophication. (3) Lakes that have undergone chemical remediation for high P concentrations by Al treatment (19, 21). The efficiency of P inactivation by addition of Al, however, depends on the extent of external P load and the resulting P sedimentation (22).

Our results suggest that under anoxic conditions small P concentrations are released from sediments with Al(OH)\(_x\): Fe(OH)\(_x\) molar ratios > 3. The Al(OH)\(_x\):Fe(OH)\(_x\) ratio can be simply estimated as the ratio between Al and Fe extracted by the first three steps of the extraction method of Psenner and Pusko (13). Alternatively, the AlNaOH\(_{25}\):FeRD ratio can be used, because the NaOH\(_{25}\)–extractable Al and BD-extractable Fe represent the dominant forms among the first three extractions (see Figure S1 in Supporting Information). At Al(OH)\(_x\):Fe(OH)\(_x\) molar ratios < 3, P release from anoxic sediments is low provided the AlNaOH\(_{25}\):FeRD (BD) ratio is > 25. These ratios may be used as simple operational predictors of sediment’s ability to release P under reducing conditions and an appropriate in-lake measure for estimation of the sediment P release potential (35). The fractionation experiments were, however, performed with 0–1 to 0–5 cm sediment layers and 1 M NaOH. The use of 0.1 M NaOH (common in other extraction schemes) may provide lower AlNaOH\(_{25}\) concentrations, which would likely increase the necessary threshold ratios somewhat. Moreover, the direct implication for natural conditions should be better based on extraction of surface sediment to better describe chemical conditions at the sediment–water interface. Surface sediments may yield slightly different results than the 0–5 cm layer, due to diagenesis and steep chemical gradients in the upper layers (10, 17, 36). An unanswered question is the effectiveness of Al(OH)\(_x\) in limiting diffusion and release of organic P compounds, concentrations of which are quantitatively important during early diagenesis (37–39).

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**Supporting Information Available**

A table listing methodological details on study sites, and figures summarizing differences in fractionation method and analytical techniques between laboratories and showing details on fractionation analyses of Fe and Al, PNaOH\(_{25}\):PTE vs lake water pH relationship, and Al impact on sediment sorption capacity. This material is available free of charge via the Internet at http://pubs.acs.org.

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