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Amount of phosphorus inactivated by alum treatments in Washington lakes

Abstract—The effectiveness of aluminum (Al) at retaining phosphate was investigated in alum-treated Washington lake sediments. Greater than background concentrations of Al and Al-bound phosphorus (Al-P) were detected in three stratified lakes (Lake Ballinger, Phantom Lake, and Medical Lake) and in three unstratified lakes (Lake Erie, Cambell Lake, and Long Lake). The ratio of added Al to P (Al : Al-P) was approximately 11 : 1 by weight in all six lakes. Added Al ranged from 6 to 83 g Al m^{-2}, and adsorbed P subsequently ranged from 0.5 to 7.3 g P m^{-2}. P bound to the added Al was apparently removed from the P cycle, as the layers of increased Al-P due to treatment were buried in the sediment at a depth corresponding to the approximate time since treatment.

Sediments provide the only significant phosphorus (P) sink in lakes and are thus an important regulator of trophic status. Part of the P deposited on the sediment surface will be recycled to the water column, and the internal cycling of P is regulated by both biotic and abiotic factors (Boström et al. 1982, 1988). The ultimate fate of P, however, in terms of permanent removal from the P cycle, is determined by the capacity of anoxic sediments to retain the buried P (Lijklema 1994). The input and accumulation of different adsorbents to the sediments is thus equally important to its P-retention capacity as the P input for the retaining capacity of the sediment (Lijklema 1994). Ferric iron (Fe) is the primary active P-retaining compound in fresh waters where the ratio between available Fe and P will determine the adsorption efficiency (Jensen et al. 1992). This adsorption capacity is drastically reduced under anoxic conditions (Mortimer 1941, 1942). The chemistry of phosphate in sediments is also closely connected to aluminum (Al) and to a lesser extent calcium (Boers et al. 1993).

For three decades Al (usually alum) has been used in North America and Europe to inactivate phosphate migrating from lake sediments regardless the redox status. Although frequently used, the longevity of treatments has ranged from <1–20 yr, averaging about 10 (Welch and Cooke 1999). This variation may be dependent on the dose of Al added and the resulting amount of formed Al-P, or the dissolution of formed Al-P with time. However, data are lacking on P-retention capacity of Al in situ (Cooke et al. 1993; Welch and Cooke 1999). Data on strong adsorbents that permanently bind P, in order to explain differences in burial rate of P, are also very limited (Boers et al. 1993). This type of information is needed to predict effectiveness/longevity of lake restoration projects where Al is added to adsorb P in the sediment. Alum treatments, where both the Al dose and the time of application are known, provide an opportunity to evaluate the P-sorption capacity in situ of Al, based on the ratio of Al to Al-P and the resistance of Al-P to early sediment diagenesis.

The objective of this work was to quantify the effects of Al on the P cycle by determining concentrations of Al and Al-P in sediment cores collected in lakes that were alum treated during the last two decades.

Materials—Sediment cores were collected from six alum-treated lakes in Washington. Three were unstratified (Cambell and Erie Lakes in Skagit county and Long Lake in Kitsap county) and three were stratified (Phantom Lake in King county, Lake Ballinger in Snohomish county, and Medical Lake in Spokane county) (Table 1). All lakes except Medical Lake, Eastern Washington, are situated in Western Washington and are low in alkalinity compared to Medical Lake.

Methods—Sediment cores were collected in April from the deeper parts of each lake (Table 1) and sliced into 1-cm layers; one core from each lake was analyzed. Sediment water content was determined after drying overnight at 105°C and organic content after ignition (two hours at 550°C). These sediment constituents are not shown as results, but were required to calculate amounts of P and Al in sediments. Sediment density was calculated, using water and organic content, according to Håkansson and Jansson (1983).

Sediment P forms were determined by following, in principle, the sequential extraction scheme on wet sediment suggested by Psenner et al. (1988): (1) Two 2-h extractions with 1 M NH_4Cl (pH 7) bringing loosely sorbed P, pore water P, and P adsorbed on calcite into solution; (2) a 1-h extraction with a buffered sodium dithionite solution (0.11 M $NaHCO_3$/0.11 M $Na_2S_2O_4$) to extract P mobilized under low redox conditions, e.g., Fe-P; (3) a 16-h extraction with 0.1 M NaOH mobilizing Al-P and ligand exchangeable P (also extracted, detected after digestion, is organic P); (4) a 16-h extraction with 0.5 M HCl to determine P forms such as Ca-P mobilized under low pH; and (5) calculation of residual P by subtracting total extracted P from sediment TP. This residual-P pool represented a relatively small fraction (10–20%) of TP, but was important to verify the detection of extracted P. The NaOH extract was the only step where a significant amount of nonreactive P was mobilized.

Total contents of P (TP) and Al (TAl) in sediments were determined following acid hydrolysis at high temperature (340°C). P was determined according to Murphy and Riley (1962) and Al by inductively coupled plasma spectrophotometry (ICP) at $\lambda = 396.152$ nm.

For a more specific measure of Al related to alum addition, Al was also determined in the stratified lakes as extracted Al (EAl), by measuring Al extracted with NaOH in the P-fractionation procedure; *see Discussion.*

Table 1. Some properties of the sampled Washington lakes. Data from Welch & Cooke (1999) and references therein. Figures of internal loading refers to pretreatment conditions.

	Unstratified lakes			Stratified lakes		
	Long Lake	Cambell Lake	Lake Erie	Lake Ballinger	Phantom Lake	Medical Lake
Area (ha)	137	150	45	40	26	62
Mena depth (m)	2	2.4	1.8	4.5	6.4	10
Sampling depth (m)	3.5	4.5	3	9	10	14
Treatment date	Sep 1980, 1991	Oct 1985	Sep 1985	Jun 1990	Sep 1990	Sep 1977
A1-dose (g m^{-2})	5.5 + 5.5	10.9	10.9	5	4.2	12.2
Internal loading (g P m^{-2} yr^{-1})	0.1	0.1	0.5	0.2	0.6	

Results—Peaks of Al, Al-P, and TP were found between 3- and 8-cm sediment depth in all six lakes (Fig. 1, Table 2). Typical results are seen in the Cambell Lake sediment core, where TAl, TP, and Al-P all increase substantially above their background concentrations (Fig. 1A). The background concentration for TAl and for Al-P was established at 17 mg g^{-1} dry weight (DW) and 0.13 mg P g^{-1} DW, respectively, by comparing concentrations above and below the peaks. The resulting peak of TAl above background is assumed to represent ‘‘added Al’’ and occurred between 1- and 10-cm sediment depth with the peak at 6–7 cm. The corresponding peaks in TP and Al-P can be explained by formed Al-P due to the added Al. The sum for added Al over all sediment layers in Cambell Lake corresponds to 12.2 g Al m^{-2}, which resulted in the complexation of 1.1 g P m^{-2} as Al-P. For these data, an Al : Al-P ratio of 11 : 1 (by weight) was calculated (Table 2, Fig. 2).

That pattern is also evident in the sediment profiles from the other two unstratified lakes, Long Lake and Lake Erie. In sediments from Long Lake, the TAl background concentration was established at 24.5 mg Al g^{-1} DW (Fig. 1C), resulting in an added amount of Al of 10.7 g m^{-2}. This Al dose resulted in the formation of 1.0 g P m^{-2}, as Al-P, using 0.16 mg Al-P g^{-1} DW as a background concentration. The ratio of added Al to formed Al-P is again 11 : 1 (by weight). Apparently, the increased concentration of TP (Fig. 1C) originated from formed Al-P. In Lake Erie (Table 2, Fig. 1B), 5.7 g of added Al m^{-2} resulted in 0.5 g P adsorbed to Al, again resulting in the same ratio of 11 : 1.

In the stratified lakes, Medical Lake (Fig. 1D) showed about a 10 times higher concentration of added Al and subsequently formed Al-P corresponding to 83 g m^{-2} and 7.3 g P m^{-2}, respectively, compared to the other five lakes. As with Lake Ballinger and Phantom Lake (Fig. 1E, F), Al in Medical Lake was determined as EAl for a more reliable estimate of the added amount of Al. The obtained added Al to formed Al-P ratio was 11 : 1 in Medical Lake and 10 : 1 in both Lake Ballinger and Phantom Lake.

Discussion—Alum treatments in lakes over the last two decades offer an opportunity to determine the long-term P-retaining properties of Al in situ. Results from these lakes show that P will be adsorbed to added Al and buried in the sediments over time (Tables 1, 2). The accumulation of Al-P apparently represents that withdrawn from the pool of mobile sediment P. The formed Al-P might consist of both P from the treated layer and of P migrating from below that layer. The corresponding peak of TP (Fig. 1) indicates that P was withdrawn from some other sources besides the treated layer.

Other P pools in the sediment profiles (not shown) were

Table 2. Amounts of aluminum (Al) and aluminum bound phosphate (Al-P) in different sediment layers and summed over all layers. The recovery is calculated on average dose applied and the mean depth of each lake, see Table 1.

	Long Lake		Cambell Lake		Lake Erie		Lake Ballinger		Phantom Lake		Medical Lake	
Layer (cm)	Added Al (g m^{-2})	Formed Al-P (g m^{-2})	Added Al (g m^{-2})	Formed Al-P (g m^{-2})	Added Al (g m^{-2})	Formed Al-P (g m^{-2})	Added Al (g m^{-2})	Formed Al-P (g m^{-2})	Added Al (g m^{-2})	Formed Al-P (g m^{-2})	Added Al (g m^{-2})	Formed Al-P (g m^{-2})
0–1					0.44	0.04						
1–2			0.30	0.01	0.55	0.07			1.91	0.18		
2–3	0.23	0.09	0.37	0.03	1.16	0.08	1.14	0.13	2.18	0.27		
3–4	1.22	0.15	1.43	0.10	1.15	0.10	5.37	0.52	5.37	0.51		
4–5	4.13	0.34	2.12	0.16	1.16	0.09					3.44	0.12
5–6	5.10	0.40	2.14	0.19	0.49	0.05					6.36	0.75
6–7			3.57	0.37	0.40	0.04					38.77	3.20
7–8			2.30	0.26	0.39	0.03					32.30	3.09
8–9											2.57	0.16
9–10												
Sum	10.68	0.97	12.23	1.13	5.74	0.50	6.51	0.65	9.46	0.96	83.45	7.32
Ratio Al : P (weight)	11.0		10.8		11.5		9.9		9.8		11.4	
Recovery (%)	49		47		29		29		35		68	

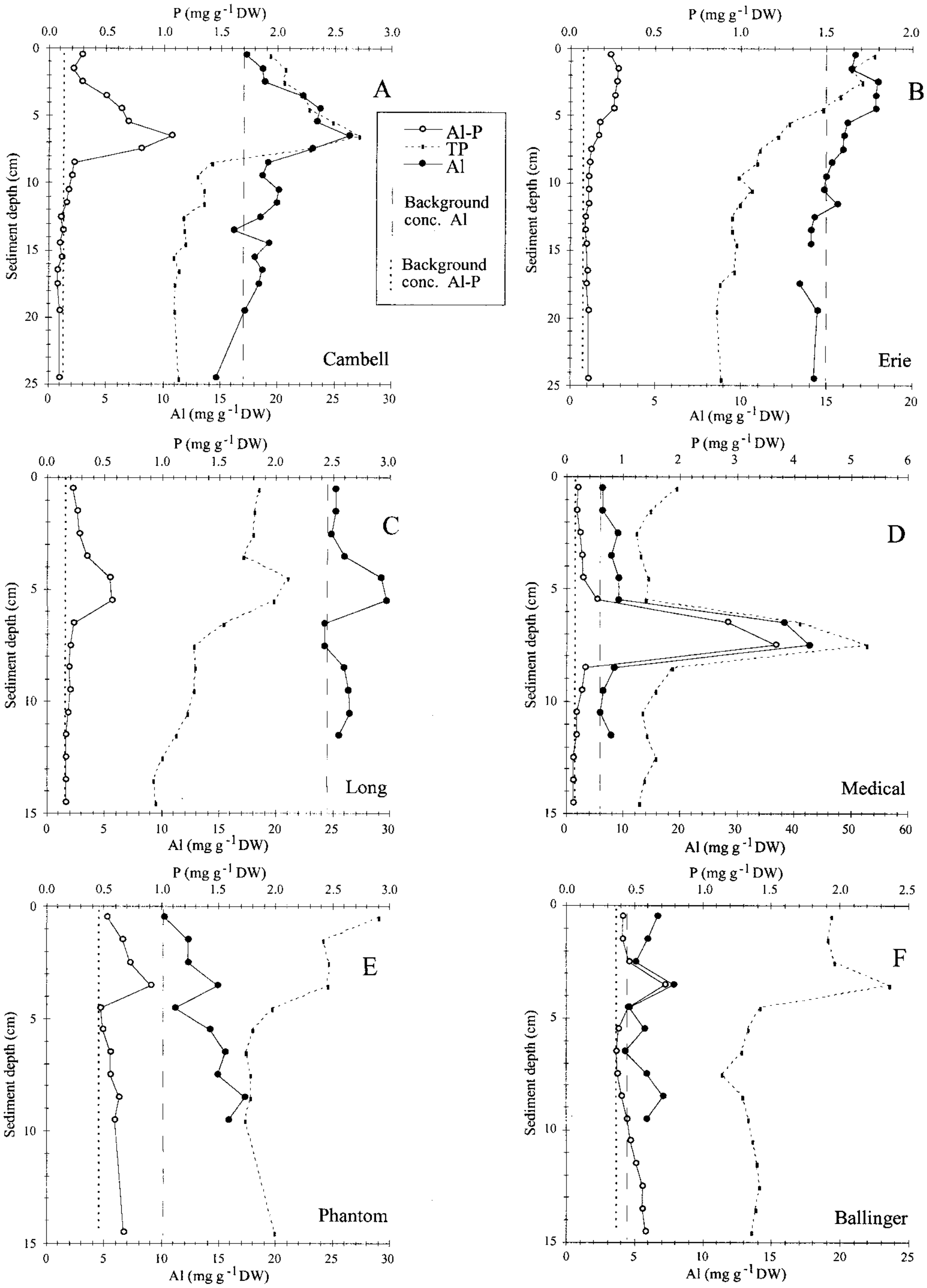

Fig. 1. Concentrations of aluminum (Al), aluminum bound phosphate (Al-P), and total phosphorus (TP) concentrations in sediment profiles from six Washington lakes. In the unstratified lakes (A, B, and C) Al is measured as the total concentration, and in the stratified lakes (D, E, and F) Al is measured as Al extracted together with Al-P; *see Methods*. The vertical dotted lines indicate assumed background concentrations of Al and Al-P.

found to be consistent throughout the entire profile, showing no effects of the Al-addition. However, newly settled Al on surface sediments can be expected to adsorb P from iron (Rydin & Welch 1998). But, with time, P migrating from deeper sediment layers may replenish free sites on iron once adsorption sites on Al are occupied, resulting in the observed lack of decreased concentration in other P pools, such as iron P, in this study.

The observed sediment Al : Al-P ratio of around 11 : 1 (by weight) in these treated lakes may seem high considering a ratio of 1 : 1 was expected in some alum treatments (Kennedy 1987; James et al. 1991) and the observed ratio of 5 : 1 in Al-

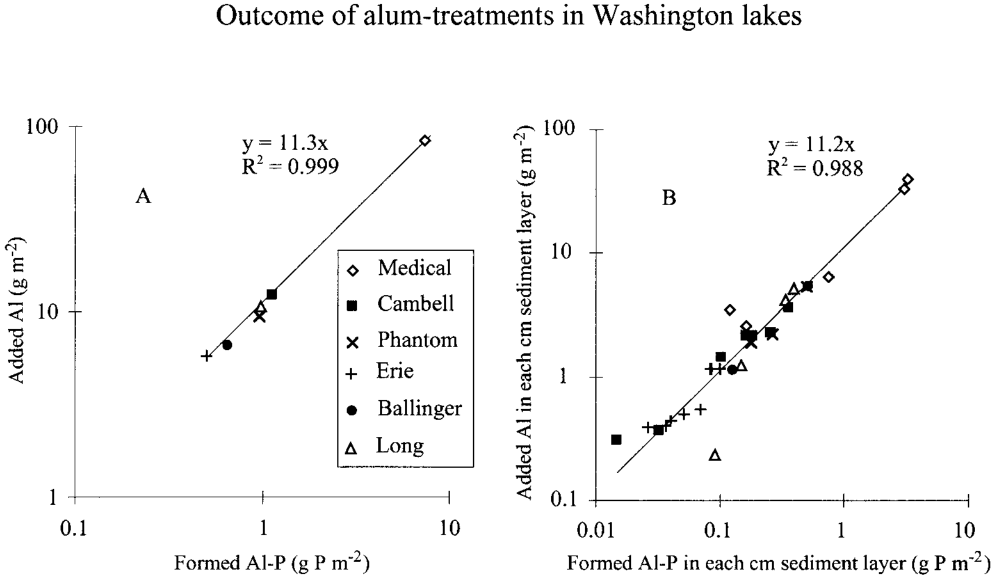

Fig. 2. Relation between added aluminum (Al) and formed aluminum bound phosphorus (Al-P) in (A) sediment profiles summing up added Al and formed Al-P. (B) Amounts of added Al and formed Al-P in each sediment layer.

treated Lake Delavan, Wisconsin (Rydin & Welch in press). According to Portielje & Lijklema (1993), the P-sorbing properties of Al exceed that for Fe. However, the observed molar ratio of the lakes in this study (14 : 1) is above that for TFe : TP 8 : 1 molar (15 : 1 by weight) suggested as the critical limit for aerobic Fe retention of phosphate in Danish lake sediments (Jensen et al. 1992). This ratio (TFe : TP) may not be a reasonable comparison, since it includes both Fe and P forms that are not available for adsorption.

The approach in this study was to find a constant TAl background concentration in the sediment profiles, with a peak in Al concentration representing Al treatment. However, TAl measurements in Lakes Ballinger, Phantom, and Medical showed fluctuating background concentrations, most likely due to their urbanized locations. It was therefore impossible to determine a specific background concentration in these sediments. For these lakes, Al was determined using the NaOH extracted Al. Using this method it was possible to determine the amount of Al added from treatment (Fig. 1). The NaOH extracted Al could be expected to represent the less stable forms, such as those formed from an Al treatment. The constant ratio obtained in all six lakes, although using different methods, seems to support the validity of the use of EAl for calculating added Al.

Mixing patterns, alkalinity, and Al dose varied among the investigated lakes. Nevertheless, a constant ratio of added Al to formed Al-P was found among all lakes. The ratio was consistent throughout the sediment profiles, suggesting that the formed Al-P in each core is the maximum possible under those conditions. The lake were treated 7–21 yr ago, and the peak concentrations of Al and Al-P were readily observed at various depths, eventually reaching a more or less stable sediment depth below 10 cm. This indicates that the formed Al-P is quite stable, and P adsorbed by Al was transformed from mobile P to permanently bound P.

The potential mobility of Al-P has been indicated by some workers. Psenner (1984) found a relationship between the concentrations of Al-P and P in the interstitial water and suggested that Al-P is capable of rapid interactions with the dissolved P pool and, thus, uptake and release of P at neutral pH. On the other hand, Housomi et al. (1981) found no release of Al-P from sediments in release experiments, where up to 90% of the Fe-P pool was released under anaerobic conditions. As expected, P is mobilized from Al at high pH (Rydin & Welch 1998). However, in most P-release experiments, Fe-P and Al-P were not separated according to the P-fractionation scheme by Hieltjes & Lijklema (1980), preventing an assessment of Al-P mobility.

Recovery of Al was 30–70% (Table 2) of the initial quantity added based on mean depth and the average dose of Al (Table 1). Therefore, the amount of Al actually reaching the sediment surface is uncertain. In addition, once the floc reaches the sediment, horizontal transport processes, such as resuspension, may affect the amount or distribution of Al.

The effect of an Al treatment in reducing internal loading can be evaluated by determining the amount of P withdrawn from the P-exchange cycle between sediment and overlying water. Assuming that the total amount of Al added remains in the sediment and that the observed ratio for Al added is valid, the P inactivated can be estimated. In the case with Lake Cambell, 39 tons of Al was added and subsequently 3.5 tons of P should be immobilized. It might be possible to divide this figure with the yearly pretreatment internal loading rate determined from mass-balance calculations (Table 1) to estimate longevity. It should be noted, however, that the internal loading figure may include numerous cyclings of the same P pool during a year. Ideally, an Al dose should be based on the total amount of mobile P in the sediment. The results from this study allow for the prediction of the effectiveness of Al from a certain dose, which until now has not been possible (Nürnberg 1998).

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Demonstration of the onshore transport of larval invertebrates by the shoreward movement of an upwelling front

Abstract—Upwelling winds off North Carolina set up upwelling fronts. As the wind forcing relaxed following such a coastal upwelling event, we observed the upwelling front move onshore. The low-density surface water moved shoreward over the upwelled water, forming a convergence zone at the front. This shoreward-moving front concentrated and transported larvae. Larval sergestid shrimp, spionid polychaete larvae, and the veligers of *Odostomia* sp. and *Bittium* sp. were concentrated on the seaward side of the moving convergence. Blue crab megalopae were concentrated at the surface immediately seaward of the front. These data demonstrate that a relaxing upwelling front can transport high concentrations of larvae shoreward over the inner shelf. This may be an important mechanism promoting the shoreward migration of larval invertebrates and fish.

Many coastal and estuarine invertebrates and fish produce planktonic larvae that over a period of weeks to months go through their development in the waters over the continental shelf. At the end of this period of development the late-stage