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Relationships between redox-sensitive phosphorus concentrations in sediment and the aluminum:phosphorus binding ratio

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Abstract


Aluminum (Al) sulfate dosage to control internal phosphorus (P) loading in lakes can be estimated by determining the mass of Al required to bind redox-sensitive P (loosely bound and iron-bound P fractions, redox-P) in sediment (Al:P binding ratio). Recent research found that the Al:P binding ratio varied negatively with redox-P, suggesting competition for binding sites between P and other constituents. We examined relationships between redox-P and the Al:P binding ratio over a broad range of redox-P to delineate general patterns that might be used to improve Al dosing calculations. Surface sediments collected from lakes in eastern Minnesota and western Wisconsin were subjected to a range of precipitated Al(OH)3 concentrations to determine the Al required to bind redox-P (Rydin and Welch 1999). Although sediments exhibited similar physical-textural characteristics, redox-P, dominated by iron-bound P, ranged widely between <0.1 and 8.8 mg/g. The Al:P binding ratio exceeded 100:1 as the redox-P concentration declined to <0.15 mg/g and approached 10:1 for redox-P concentrations exceeding 5 mg/g. These relationships were attributed to (1) competition for binding sites by other constituents at lower redox-P and (2) increased competition for binding sites by PO43− relative to other constituents at higher redox-P. Regression relationships between redox-P concentration and the Al:P binding ratio may be used with vertical sediment P profiles to estimate Al dosage required to reduce internal P loading, particularly for stratified or polymictic lakes where iron-bound P is the dominant fraction.

Key words: alum dosage, aluminum, aluminum sulfate, fractionation, internal phosphorus loading, phosphorus, redox-sensitive phosphorus, sediment

Profundal sediments often represent an important source of phosphorus (P) cycling to lakes that can delay recovery after watershed rehabilitation (Cooke et al. 1993, Søndergaard et al. 2013). An outcome of the cultural eutrophication process is the buildup of redox-sensitive P (i.e., loosely bound and iron-bound P; redox-P) in the surface sediment layer because the deposition rate of new P exceeds diagenesis and burial (Carey and Rydin 2011). Sediment P chemically adsorbed or precipitated to metal compounds (i.e., iron oxyhydroxides; Fe(OOH)~P) can diffuse into the overlying hypolimnion as a result of reduction reactions under anaerobic conditions (Mortimer 1971, Boström 1984, Nürnberg 1984). Vertically migrating phytoplankton can directly access this internal P source for assimilation and growth (James et al. 1992, Gervais et al. 2003). Additionally, if hypolimnetic Fe:P stoichiometry is relatively low (<~3.6:1 mass:mass; Gunnars et al. 2002), incomplete scavenging of P by Fe(OOH) during thermocline erosion and reoxygenation can lead to upward entrainment of P and stimulation of intense cyanobacterial blooms (Nürnberg et al. 2013a, 2013b, Orihel et al. 2015).

While tributary P loading and retention are coupled with internal sediment P recycling (Moosman et al. 2006), it may take years to flush excess sediment P out of the system after implementation of watershed best management practices (BMPs; Søndergaard et al. 2005). Aluminum sulfate (alum) application to irreversibly bind redox-P represents a viable management tool to immediately reduce and control internal P loading (Cooke et al. 2005). Recent aluminum (Al) dosage methodologies have centered on determining
the amount required to bind redox-P in the upper sediment layer to directly target reduction of internal P loading (i.e., Al:P binding ratio; Rydin and Welch 1999). James (2011) found that the Al:P ratio required to bind >90% of the redox-P varied in a negative exponential pattern as a function of increasing initial redox-P concentration and ranged between >100:1 and <20:1. This pattern was attributable to increased competition for binding sites by other constituents as the initial redox-P concentration decreased (de Vicente et al. 2008b). Huser and Pilgrim (2014) also reported that binding of redox-P by aluminum hydroxide (Al(OH)₃) was strongly dependent on the initial redox-P concentration.

Importantly, Al dosage and Al:P binding ratio determinations from laboratory sediment assays using freshly precipitated Al(OH)₃ generally target immediate binding of redox-P; however, in situ reaction and P-binding efficiency are ultimately affected by exposure to the mobile redox-P layer in the surface sediment. Binding efficiency can decline substantially with aging, polymerization, and subsequent changes in crystalline structure of Al(OH)₃, particularly when binding sites are not rapidly filled with PO₄³⁻ (Berkowitz et al. 2005, 2006, de Vicente et al. 2008a).

Our objectives were to examine variations in the Al:P binding ratio over a broad range of initial redox-P concentrations for sediment collected from a variety of lakes in the upper Midwestern USA. Sorption of redox-P decreases exponentially as a function of added Al due to changes in equilibrium conditions in relation to available binding sites (Rydin and Welch 1999, James 2011, Huser and Pilgrim 2014), making determination of 100% binding efficiency difficult to precisely quantify. Thus, >90% binding efficiency of redox-P was chosen to approximate nearly complete sediment mobile P inactivation. Expanding on the findings of James (2011), we hypothesized that the Al:P binding ratio may vary as a negative function of redox-P concentration relative to other ions that can bind to Al(OH)₃. The Al:P binding ratio was expected to be highest at relatively low redox-P concentrations due to competition for binding sites by other constituents (Cheng et al. 2004, Guan et al. 2006). Conversely, competition for binding sites by PO₄³⁻ at higher redox-P concentrations was expected to result in a lower Al:P binding ratio. We also place our findings within the context of general Al concentration (g/m²) ranges required to inactivate mobile redox-P in anaerobic profundal sediments of stratified or polymictic eutrophic lakes.

**Methods**

Intact sediment cores were collected at one to several stations (n = 48) in 16 lakes located in east-central Minnesota and west-central Wisconsin between 2009 and 2014 (Table 1). All lakes exhibited periods of stratification and summer anoxia in the bottom waters. Some lakes were strongly stratified throughout the summer while others exhibited summer polymixis. Sampling stations were usually established in the deepest basins of each lake for coring purposes; however, shallower regions were also sampled in many lakes for analysis. A gravity coring device (Freshwater Scientific Instruments, Hope, ID) equipped with an acrylic liner was used to collect samples. Sections (1–10 cm thickness) from the sediment surface layer were gently homogenized prior to analysis. Fresh sediment subsamples were dried at 105 °C to a constant weight and burned at 550 °C for moisture content, wet and dry density, and organic matter content determination (Avnimelech et al. 2001, Håkanson and Jansson 2002). Phosphorus fractionation (mg/g dry mass) was conducted according to Hiettjes and Lijekema (1980), Nürnberg (1988), and Psenner and Puckso (1988) for the determination of loosely bound P (1 M NH₄Cl extraction) and Fe-bound P (0.11 M bicarbonate-dithionite extraction). Extracted samples were centrifuged at 500 G for a minimum of 30 min before analysis of soluble reactive P (SRP; APHA 2005).

Others have shown strong correlations and relationships between these functionally defined extractions that approximate redox-P (i.e., the sum of the loosely bound and Fe-bound P fractions) and rates of P release from sediment under anaerobic conditions (Boström et al. 1982, Boström 1984, Ostrofsky 1987, Nürnberg 1988, Ostrofsky et al. 1989, Petticrew and Arcoena 2001, Pilgrim et al. 2007). Thus, redox-P represented a surrogate measure of the potentially mobile P fraction active in diffusive exchanges of phosphate between the sediment to the overlying water column under anaerobic and reducing conditions (i.e., internal P loading).

Subsamples from the same sediment sections were subjected to a range of freshly precipitated aluminum hydroxide (as Al) concentrations to determine the Al dosage required to bind redox-P (Rydin and Welch 1999). Aluminum sulfate (Al₂(SO₄)₃ · 18 H₂O) was combined with 0.1 M sodium bicarbonate (NaHCO₃) to a concentration of 0.7–1.4 g Al/L to form an Al(OH)₃ floc. Aliquots of this solution, diluted to a final volume of 10 mL with distilled water, were added to centrifuge tubes containing the equivalent of 0.025 g dry weight (DW) of fresh sediment to obtain Al concentrations ranging from 0 (i.e., control) to 150 mg Al/g DW sediment. The assay tubes were shaken for a minimum of 2 h at 20°C, centrifuged at 500 G to concentrate the sediment, and decanted for redox-P determination. The Al concentration required to bind >90% of redox-P was estimated by interpolation using exponential relationships between added Al concentration and percent reduction in redox-P concentration. The Al:P binding ratio was calculated as Al divided by redox-P removed via sequestration. Redox-P removed, rather than Al-P formed, was used to calculate ratios to
Table 1. Ranges in sediment physical-textural characteristics, redox-sensitive phosphorus (P) and Fe-bound P concentrations, and the Al:P binding ratio ranges in surface sediment (upper 5–10 cm) from various lakes in Minnesota and Wisconsin. Most lakes are either being considered for Al application (exceptions were Big Moon) or have been recently treated within the last 3 years.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Median Surface Area (ha)</th>
<th>Mean Depth (m)</th>
<th>Stratification</th>
<th>Moisture Content (%)</th>
<th>Wet Density (g/cm³)</th>
<th>Dry Density (g/cm³)</th>
<th>Organic Content (%)</th>
<th>Redox-sensitive P (mg/g)</th>
<th>Fe-bound P (%)</th>
<th>Al:P Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ardmore, MN</td>
<td>1</td>
<td>4</td>
<td>2.88</td>
<td>Dimictic</td>
<td>94</td>
<td>1.028</td>
<td>0.071</td>
<td>31</td>
<td>0.52</td>
<td>95</td>
</tr>
<tr>
<td>Bald Eagle, MN²</td>
<td>6</td>
<td>513</td>
<td>0.00</td>
<td>Dimictic</td>
<td>94–96</td>
<td>1.017–1.025</td>
<td>0.042–0.069</td>
<td>35–40</td>
<td>0.10–1.08</td>
<td>88</td>
</tr>
<tr>
<td>Big Chetac, WI</td>
<td>3</td>
<td>363</td>
<td>4.89</td>
<td>Polymictic</td>
<td>95–96</td>
<td>1.015–1.020</td>
<td>0.043–0.052</td>
<td>37–40</td>
<td>1.52–2.46</td>
<td>92</td>
</tr>
<tr>
<td>Big Moon, WI</td>
<td>2</td>
<td>77</td>
<td>0.00</td>
<td>Dimictic</td>
<td>95–96</td>
<td>1.016–1.023</td>
<td>0.039–0.058</td>
<td>29–31</td>
<td>7.77–8.84</td>
<td>97</td>
</tr>
<tr>
<td>Burandt, MN³</td>
<td>1</td>
<td>37</td>
<td>0.00</td>
<td>Dimictic</td>
<td>90</td>
<td>1.045</td>
<td>0.108</td>
<td>27</td>
<td>0.40</td>
<td>14</td>
</tr>
<tr>
<td>Cedar, WI</td>
<td>4</td>
<td>452</td>
<td>0.00</td>
<td>Polymictic</td>
<td>93–94</td>
<td>1.025–1.033</td>
<td>0.067–0.088</td>
<td>27–33</td>
<td>0.24–0.32</td>
<td>84</td>
</tr>
<tr>
<td>Desair, WI</td>
<td>3</td>
<td>32</td>
<td>0.00</td>
<td>Dimictic</td>
<td>84–86</td>
<td>1.074–1.095</td>
<td>0.199–0.260</td>
<td>15–17</td>
<td>0.52–1.77</td>
<td>92</td>
</tr>
<tr>
<td>East Alaska, WI²</td>
<td>3</td>
<td>21</td>
<td>0.00</td>
<td>Dimictic</td>
<td>93–94</td>
<td>1.026–1.034</td>
<td>0.059–0.086</td>
<td>24–28</td>
<td>0.17–0.21</td>
<td>53</td>
</tr>
<tr>
<td>Fish, MN</td>
<td>2</td>
<td>96</td>
<td>6.07</td>
<td>Dimictic</td>
<td>89–93</td>
<td>1.033–1.055</td>
<td>0.084–0.134</td>
<td>23–29</td>
<td>0.38–0.39</td>
<td>85</td>
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<tr>
<td>Golden, MN</td>
<td>3</td>
<td>23</td>
<td>0.00</td>
<td>Dimictic</td>
<td>93–96</td>
<td>1.015–1.027</td>
<td>0.040–0.072</td>
<td>34–39</td>
<td>0.83–2.61</td>
<td>97</td>
</tr>
<tr>
<td>Half Moon, MN²</td>
<td>1</td>
<td>12</td>
<td>4.08</td>
<td>Dimictic</td>
<td>96</td>
<td>1.011</td>
<td>0.041</td>
<td>54</td>
<td>0.84</td>
<td>96</td>
</tr>
<tr>
<td>Half Moon, WI²</td>
<td>7</td>
<td>62</td>
<td>0.00</td>
<td>Polymictic</td>
<td>86–92</td>
<td>1.040–1.077</td>
<td>0.104–0.201</td>
<td>15–34</td>
<td>0.15–4.96</td>
<td>98</td>
</tr>
<tr>
<td>Halsted’s Bay, MN</td>
<td>3</td>
<td>227</td>
<td>0.00</td>
<td>Dimictic</td>
<td>89–91</td>
<td>1.045–1.054</td>
<td>0.103–0.119</td>
<td>23–26</td>
<td>0.28–0.41</td>
<td>66</td>
</tr>
<tr>
<td>Long, WI</td>
<td>1</td>
<td>110</td>
<td>3.15</td>
<td>Polymictic</td>
<td>92</td>
<td>1.039</td>
<td>0.087</td>
<td>24</td>
<td>0.545</td>
<td>95</td>
</tr>
<tr>
<td>Spurzem, MN</td>
<td>2</td>
<td>26</td>
<td>3.39</td>
<td>Dimictic</td>
<td>93–95</td>
<td>1.018–1.021</td>
<td>0.056–0.072</td>
<td>44–49</td>
<td>0.30–2.23</td>
<td>93</td>
</tr>
<tr>
<td>Squaw, WI</td>
<td>5</td>
<td>52</td>
<td>0.00</td>
<td>Dimictic</td>
<td>86–97</td>
<td>1.009–1.073</td>
<td>0.030–0.146</td>
<td>18–53</td>
<td>0.13–0.60</td>
<td>83</td>
</tr>
</tbody>
</table>

¹Recently treated
avoid potential interferences caused by artificial conversion of Al-P to calcium(Ca)-P during the NaOH extraction and coprecipitation between Al and organic acids during SRP analysis (Huser and Pilgrim 2014).

Regression models were developed between the Al concentration or Al:P ratio and the initial sediment redox-P concentration after natural logarithmic transformation (SAS 1994). Because the Al concentration was based on binding of ∼90% of the redox-P in the assay experiments, we proportioned it to the initial redox-P concentration to more easily facilitate direct Al dose prediction using the initial versus 90% sediment redox-P. We assumed simple linear proportionality (Al dose to bind 90% redox-P/0.9 = Al dose to bind 100% redox-P/1.0 or Al dose/0.9) to adjust the Al dose to the initial redox-P concentration. In actuality, this adjusted Al dose probably falls somewhere between >90% and <100% of the initial redox-P concentration. The Al:P binding ratio was calculated as the adjusted Al concentration divided by the initial redox-P concentration.

**Results and discussion**

Overall, mean moisture content was high at 93% (±0.5 SE; range = 84–96%) whereas mean wet and dry density were low at 1.035 g/cm³ (±0.003 SE; range = 1.011–1.095 g/cm³) and 0.091 g/cm³ (±0.008 SE; range = 0.039–0.260 g/cm³), respectively, indicating flocculent sediment with high porosity (Table 1). Mean organic matter content was moderately high at 31% (±1.3 SE; range = 15–54%). Despite relatively uniform sediment textural characteristics over all lakes and stations, redox-P varied considerably, ranging between 0.096 and 8.837 mg/g (mean = 1.227 mg/g ± 0.265 SE). Fe-bound P was usually the overwhelmingly dominant fraction, accounting for a mean 88% (±2.0 SE) of the redox-P; however, the redox-P composition of Burandt Lake sediment deviated from this general trend. Although the concentration was moderately high at 0.40 mg/g, Fe-bound P (0.057 mg/g) accounted for only 14% of the redox-P (Table 1). Instead, loosely bound P dominated the redox-P fraction in this lake sediment. Loosely bound P also comprised a more substantial percentage of the redox-P pool in East Alaska and Halsted’s Bay sediment compared to other sediments. Fe-bound P was nevertheless the dominant fraction, accounting for >50% of the redox-P in these lake sediments.

Similar to the findings of James (2011) but over a much broader range, the Al:P binding ratio varied in a negative exponential pattern as a function of increasing redox-P concentration (Fig. 1). The ratio exceeded 100:1 as the redox-P concentration declined to <0.15 mg/g and approached 10:1 for redox-P concentrations exceeding 5 mg/g. These patterns were also consistent with those reported in Huser and Pilgrim (2014) and suggested a general conceptual model for P binding onto newly precipitated Al(OH)₃ as a function of redox-P concentration. Initial reaction between aluminum sulfate and water results in the formation of amorphous Al(OH)₃ with high surface area that can bind inorganic ions and organic acids as well as PO₄³⁻ (de Vicente et al. 2008b). Thus, higher Al:P binding ratios are required to sequester PO₄³⁻ at lower redox-P concentrations due to competition for binding sites by other constituents. Conversely, increased competition for binding sites by PO₄³⁻ relative to other constituents occurs as a function of higher redox-P concentration in the sediment (Cheng et al. 2004, Guan et al. 2006), resulting in improved binding efficiency and lower Al:P binding ratio requirements.

By contrast, relationships for Burandt Lake sediment fell well outside these general patterns; the measured Al:P binding ratio (20:1) was nearly 3 times lower than the predicted ratio (54:1). Higher binding efficiency and, thus, greater affinity for loosely bound P versus Fe-bound P by the Al(OH)₃ floc may be a possible explanation for this anomaly. The loosely bound P fraction, which accounted for most of the redox-P in Burandt Lake sediment, represented P in the porewater and adsorbed to calcite (Penn et al. 1995). These characteristics may have promoted greater exposure to and more complete reaction between loosely bound P and the Al(OH)₃ floc, resulting in a lower Al:P binding ratio compared to a similar redox-P concentration comprised primarily of Fe-bound P. More research is needed to better understand Al binding kinetics and efficiency for the loosely bound P fraction.

Vertical variations in the redox-P concentration profile of Big Chetac Lake sediments provided an example use of the Al:P binding ratio regression model to estimate the Al dosage required to control internal P loading. In this case, redox-P (primarily as Fe-bound P) exhibited a major peak in the upper 8 cm sediment layer, declining to a uniform baseline concentration below the 15 cm depth (Fig. 2). The integrated mean redox-P concentration over the upper 8 cm was 1.7 mg/g, and mean concentrations exceeded 2 mg/g in the 0–4 and 0–6 cm layers (Table 2). This vertical pattern was indicative of eutrophic sediments with redox P accumulation in excess of diagenesis and burial in the upper sediment layer. The predicted Al:P binding ratio required to sequester this redox-P varied inversely as a function of the mean concentration determined for each layer. The Al dose ranged between ~60 and >130 g/m², depending on the thickness of the redox-P sediment layer targeted for treatment. The measured Al:P binding ratio for the upper 5 cm layer of Big Chetac Lake sediment was 20:1 (Table 2). Although sinking rate and the eventual equilibration depth of the Al floc are critical determinants of Al dosage, little is currently known about its settling behavior through
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Figure 1. Relationship between the redox-sensitive P (redox-P) concentration and (1) the aluminum:phosphorus ratio needed to bind >90% of the redox-P (Al:P binding ratio; upper panels) and (2) the aluminum (Al) concentration needed to bind >90% of the redox-P. The triangle and square symbols represent Burandt and Big Chetac Lakes, respectively.

To provide further insight into general Al concentrations (g/m²) required to inactivate redox-P, Al dosages were estimated for a hypothetical flocculent (moisture content = 95%; wet density = 1.02 g/cm³; dry density = 0.05 g/cm³; organic content = 35%) profundal lake sediment over a range of mean redox-P concentrations and sediment layer thicknesses (Fig. 3). For this example, mean concentrations within the surface redox-P layer were varied between 0.25 and 5.00 mg/g, and the thickness of this sediment layer ranged between 4 and 10 cm. Overall, Al dosage varied non-linearly as a function of both mean redox-P concentration and sediment thickness, and it increased more rapidly with increasing mean redox-P concentration as sediment layer thickness increased (Fig. 3). Al dosage approached 300 g/m² to inactivate a mean redox-P concentration of 5 mg/g over a 10-cm sediment layer thickness.

Table 2. The estimated aluminum (Al) dose required to bind redox-sensitive phosphorus (redox-P) in various sediment layers. The Al:P binding ratio represents the mass of Al needed to bind >90% of the sediment redox P.

<table>
<thead>
<tr>
<th>Sediment Thickness (cm)</th>
<th>Integrated Redox P (mg/g)</th>
<th>Al:P Ratio</th>
<th>Al Dose (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–4 cm</td>
<td>2.300</td>
<td>18:1¹</td>
<td>61</td>
</tr>
<tr>
<td>0–6 cm</td>
<td>2.068</td>
<td>19:1¹</td>
<td>98</td>
</tr>
<tr>
<td>0–8 cm</td>
<td>1.711</td>
<td>21:1¹</td>
<td>131</td>
</tr>
<tr>
<td>Measured</td>
<td>1.524</td>
<td>20:1²</td>
<td>132</td>
</tr>
</tbody>
</table>

¹Predicted from regression relationship (Fig. 1)
²Measured Al:P binding ratio for the upper 5-cm layer (Fig. 1)

sediment. Thus, Al dosage may be best estimated at this point by considering inactivation of this redox-P layer rather than a specified sediment thickness. Under this assumption, a ~130 g/m² dosage would be required to inactivate the upper 8 cm redox-P layer in Big Chetac Lake sediment.
Figure 2. Vertical variations in loosely bound phosphorus (P), iron(Fe)-bound P, and redox-sensitive P (redox-P) for Big Chetac Lake, WI. The gray shaded region denotes the surface redox-P pool (i.e., P accumulation exceeds burial) that needs to be inactivated with Al. The vertical bar represents the mean Al:P binding ratio.

Figure 3. Relationships between the mean redox-sensitive phosphorus (redox-P) concentration of a hypothetical sediment (see text for explanation) and estimated aluminum sulfate dosage (as Al) for sediment layer thicknesses between 4 and 10 cm. Vertical dotted line represents the mean redox-P for the lake sediments listed in Table 1. The gray shaded area denotes the range in Al dosage over the 4–10 cm sediment layer thickness for the mean redox-P concentration ± the 95% confidence interval (CI).

The mean redox-P concentration ± the 95% confidence interval (CI), estimated from lake sediments in this study (Table 1), was used to explore possible Al dosage ranges that might be typical for eutrophic lake sediments in the upper Midwest. The predicted Al:P binding ratio was 27:1 for the mean redox-P concentration of 1.207 mg/g (Fig. 3) and ranged between 51:1 (i.e., redox-P = 0.444 mg/g, lower CI) and 20:1 (i.e., redox-P = 1.970 mg/g, upper CI). The estimated Al dosage required to inactivate redox-P within a 4–10 cm sediment layer thickness varied between 67 and 167 g/m² (Table 3). These predicted Al dosage ranges were high compared to some earlier Al applications that were not based on inactivation of sediment redox-P (Huser et al. 2011, Huser 2012). Instead, they were more comparable to some other recent applications that specifically targeted sediment redox-P with higher Al dosages ranging between ∼90 and 140 g/m² (Lewandowski et al. 2003, Dugopolski et al. 2008, Wauer et al. 2009, James 2011, Hoyman 2012).

Importantly, the redox-P–Al:P binding ratio relationships reported here were specific for reactions involving newly precipitated amorphous Al(OH)₃ to maximally bind redox-P in the short-term for internal P loading control. Research by de Vicente et al. (2008a) found that Al binding efficiency for PO₄³⁻ declined substantially with aging, polymerization, and subsequent changes in crystalline structure of Al(OH)₃ (Berkowitz et al. 2006), particularly when
Aluminum to phosphorus binding ratio

Table 3. Estimated Al dose needed to inactivate a mean redox-sensitive phosphorus (redox-P) of ∼1.2 mg/g in various sediment layers. See text for details.

<table>
<thead>
<tr>
<th>Sediment Layer Thickness (cm)</th>
<th>Integrated Redox-P (g/m2)</th>
<th>Al Dose (g/m2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–4</td>
<td>2.463</td>
<td>66</td>
</tr>
<tr>
<td>0–6</td>
<td>3.695</td>
<td>99</td>
</tr>
<tr>
<td>0–8</td>
<td>4.927</td>
<td>132</td>
</tr>
<tr>
<td>0–10</td>
<td>6.158</td>
<td>165</td>
</tr>
</tbody>
</table>

Because a desired objective of an alum treatment is to expose the Al(OH)₃ floc to the surface redox-P layer, the floc should be denser than surface sediment and sink relatively quickly for maximum binding efficiency. Recent research has suggested that Al(OH)₃ binding efficiency for P decreases substantially (i.e., >75% decrease) if it has not been exposed to and reacted with redox-P within a few months, due to changes in crystalline structure in the absence of adsorbed P (de Vicente et al. 2008a). More information is needed on Al(OH)₃ floc density and settling to better predict Al dosage. Furthermore, as binding sites on the Al(OH)₃ floc become saturated with redox-P, additional P diffusing into the alumin layer from deeper sediments over time can read-sorb to Fe(OOH) and again become an important internal P loading source years after alum treatment (Lewandowski et al. 2003). Thus, the longevity of internal P loading control may be less with a one-time versus multiple applications over time that target the mobile redox-P layer. These factors need to be considered in AI dosage methodologies and application strategies to maximize P binding effectiveness and longevity.

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References


