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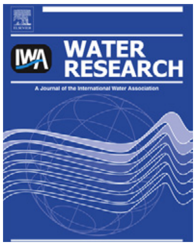

pH dependent dissolution of sediment aluminum in six Danish lakes treated with aluminum

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ABSTRACT

The possible pH dependent dissolution of aluminum hydroxides ($Al(OH)_3$) from lake sediments was studied in six lakes previously treated with Al to bind excess phosphorus (P). Surface sediment was suspended for 2 h in lake water of pH 7.5, 8.5, or 9.5 with resulting stepwise increments in dissolved Al observed in all lakes. The amount of dissolved Al increased proportional to the sediment content of $Al(OH)_3$ as quantified by a sequential extraction technique. Up to 24% of the sediment $Al(OH)_3$ could dissolve within 2 h at pH 9.5 and a portion of sediment P was dissolved concomitantly. Lowering pH to 7 caused 30–100% of the dissolved Al to precipitate again after 24 h. Re-precipitation of mobilized P varied from 50% to more than 100%. A test with untreated sediment showed the same proportionality which means that also indigenous $Al(OH)_3$ can dissolve frequently in lakes with high pH water. Release rates of dissolved Al from intact sediment cores at the same three pH values was measured in three of the lakes, and showed increased Al release rates at pH 8.5 in one of the lakes and 9.5 in two of the lakes. Our study demonstrates a risk of dissolution of sediment $Al(OH)_3$ to form aluminate in shallow lakes, where resuspension and high pH in the water occurs frequently. In the worst case dissolved Al may reach toxic levels in lakes treated by Al but also the concomitant release of P and the possible loss of dissolved Al to downstream ecosystems are negative effects that may occur already at more modest dissolution of $Al(OH)_3$ and Al-bound P.

1. Introduction

Decades of excess external phosphorus (P) input to lakes have led to accumulation of potential mobile P forms in the sediment in many lakes. When external P-loading is reduced lake water quality may still be tampered for many years due to P release from the sediments (Søndergaard et al., 2003). One of the most successful methods to combat internal P-loading has been the addition of aluminum (Al) to form $Al(OH)_3$ that binds P in the sediment independently of the redox conditions (Kennedy and Cooke, 1982; Reitzel et al., 2005; Rydin et al., 2000). Aluminum hydroxide has a high affinity for inorganic and organic P (Reitzel et al., 2009), and in addition a relatively low cost of treatment. Aluminum was originally dosed relative to the lake water alkalinity, or amount of P in the lake water (Kennedy and Cooke, 1982), but at present the Al dosing is based on targeting the mobile P (Reitzel et al., 2005; Rydin et al., 2000) pool in the whole lake system (water column and sediment), improving the chances for a long lasting P reduction in the water. Aluminum is added to the surface water as e.g. poly-aluminum chloride (Egemose et al., 2011; Reitzel et al., 2005) or alum (Cooke et al., 1993; Lewandowski et al., 2003). Between pH 5–8.5 (Gensemer and Playle, 1999), the dissolved Al undergoes hydrolysis to form solid

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amorphous $Al(OH)_3$ (a white floc) and H^+ leading to a subsequent decline in pH (Kennedy and Cooke, 1982). This solid Al floc is the dominating Al form between pH 5.5–8.5 (Gensemer and Playle, 1999). However, the mechanistic understanding of Al transformation after addition to the lake water and the factors affecting P binding to the Al floc is limited. Anderson and Berkowitz (2010) demonstrated a complex speciation of Al shortly after dosing lake water with alum, whereas Berkowitz et al. (2006) and de Vicente et al. (2008a) demonstrated that the Al floc undergoes aging in the months following addition to the lake water, resulting in an up to 70% reduction in the P binding capacity relative to the fresh Al floc. Once deposited on the surface sediment, the freshly formed Al floc is highly susceptible to resuspension events that may lead to redistribution of the Al floc in weeks or month after Al application, as demonstrated by Egemose et al. (2009, 2010). During resuspension, the Al floc might be resuspended into water with pH above the circumneutral level, resulting in dissolution of the floc and release of P (Van Hullebusch et al., 2003). In addition it has been shown that several compounds compete with P for sorption sites on the Al floc. Thus, de Vicente et al. (2008b) showed that silicate reduced the soluble reactive P (SRP) binding onto Al, at SRP concentrations below 155 $\mu g\ P\ L^{-1}$, whereas mainly humic acids competed for sorption sites at SRP concentrations above 155 $\mu g\ P\ L^{-1}$.

Several authors have tried to recover the Al quantitatively in the sediments after an Al treatment, but generally the recovery is either lower or higher than would be expected (Reitzel et al., 2005; Rydin et al., 2000). Such findings have led to speculations in export of resuspended light weight Al flocs from the lake (Lewandowski et al., 2003), or an uneven distribution of Al in the lake. However, despite the wide use of Al in lake restoration very little information exists on response of once precipitated $Al(OH)_3$ to changing pH regimes.

To gain more understanding on this issue, we performed a laboratory experiment with sediment from six Danish lakes that had been treated with Al. The Al floc in the different lakes had aged for one to nine years, allowing us to address a possible effect of aging on the pH effects. Intact Al treated sediment cores were used to demonstrate the effect of elevated pH on the passive diffusion of dissolved Al and P from the sediments, whereas experiments with suspended Al treated surface sediment were used to demonstrate the effects of pH on the Al and P release from sediment during resuspension. Finally, we followed the post treatment *in situ* concentrations of dissolved Al and pH in the six lakes during spring and summer 2010 to relate the laboratory studies to the full scale studies of the lakes.

2. Methods

2.1. Study sites

Six Danish lakes were treated with Al from 2001 to 2009 (Table 1). The lake areas are 5–55 ha, with mean depths ranging 1.3–5.0 m and the maximum depths 2–12 m. All six lakes have been treated with poly-aluminum chloride. All the lakes were treated with Al during October. The added amount of Al was 10–54 g Al m^{-2} treated lake bottom. The pool of potentially mobile P (Reitzel et al., 2005) was determined as the sum of non-reactive P (nrP) and iron (Fe) bound P in the sediment, according to the sequential extraction scheme proposed by Psenner et al. (1984) and Paludan and Jensen (1995). The aluminum hydroxide (gibbsite) active in P-binding was determined as the increase of Al (compared to the background level of Al in deeper untreated sediment layers) in the NaOH pool, as described by Reitzel (2005) and Reitzel et al. (2005).

2.2. Sampling

Sediment cores (Ø 5.2 cm) for all experiments were collected with a Kajak gravity corer at the deepest site in each lake (Table 1). Simultaneously, bottom lake water was sampled at the same site for the experiments. All lakes were sampled from May–Sep 2010. The experiments were initiated immediately after returning to the laboratory. Additionally, epilimnetic water samples from the six treated lakes were sampled 3–8 times during summer 2010 (May–Sep).

2.3. Experimental setup

Water samples were filtered on 0.45 μm cellulose acetate filters in order to separate the dissolved fraction of Al from the particulate Al fraction. Aluminum was analyzed by inductively-coupled plasma optical-emission spectrometry (ICP-OES) on a Perkin Elmer Optima 2100 DV. Soluble reactive P (SRP) was analyzed according to the standard molybdenum blue method (Koroleff, 1983). pH in the lake water was adjusted by adding 0.1 M NaOH to increase pH and 0.5 M HCl to lower the pH.

Table 1 – Characteristics of the six Danish Al treated lakes. The dose is g Al m^{-2} treated lake bottom. NaOH–Al is the recovered Al in the NaOH extract in the upper 2 cm of the sediment, determined according to Reitzel (2005).

Lake	Treatment (year)	Area (ha)	Depth (m) (mean/max)	NaOH–Al (g Al m^{-2})	Dose (g Al m^{-2})
Lake Sønderby	2001	7.9	2.9/5.8	2.8	31
Lake Kollelev	2003	5.0	1.5/2.0	7.2	54
Frederiksborg Castle lake	2005	22.3	3.5/9.0	2.0	10
Lake Glumsø	2006	25.4	1.3/2.1	2.4	30
Lake Nordborg	2006	54.6	5.0/8.5	14.7	52
Lake Vedsted	2009	7.0	5.0/12.0	9.4	44