

What role do soil and sediment play in damping or enhancing eutrophication?

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Over the years, we have given talks to LSM (and its predecessor), lake associations, the Lakes Division of the Department of Environmental Protection, and professional meetings. Some questions consistently are asked or implied by interactions with the audience: Why do we care about erosion in the watershed of a lake? Why do some lakes deteriorate in water quality, while others are quite resilient? Why must some lakes get treated with “alum” when they experience increasingly problematic algal blooms? What in the world is “alum”? What role do soil and sediment play in the answers to these questions?

The answers are not easy. To understand the mechanisms of how soil, sediment, aluminum (Al), iron (Fe), and phosphorus (P) influence eutrophication (or prevent it), we need to dig deeper. What goes on among solid inorganic matter (minerals and non-minerals), organic matter, and water in the soil, streams, lakes, and lake sediment? We use abbreviations for elements (there are more than 100). A surprising concept for some of you is that the element oxygen (O) is 93.7% by volume of Earth’s crust! We can walk on, tunnel through, drill, quarry, and move the Earth’s crust with explosions. And yet we breathe the gaseous form of oxygen, O<sub>2</sub> (two joined atoms), which only comprises 20% of our atmosphere! Dissolved O<sub>2</sub> in surface water may range from about 16 mg/L, depending on the temperature, to virtually 0 mg/L in sediment. Every element occurs in water; most occur as more than one chemical species (e.g., four for Al in Table 1). Some elements occur in different states of oxidation: Iron (Fe) occurs as ferrous [II] and ferric [III]), having different charges because of the different number of electrons in the atom; higher charge for the atom dissolved in water (Fe<sup>+3</sup>) is more oxidized. The oxidation state of Fe is designated by [brackets]. Superscript numbers are the charge of the various species dissolved in water. Subscript numbers represent the number of atoms or atom pairs in species. If we add dissolved organic carbon (DOC), the dissolved organic matter that colors lake and stream water various shades of yellow to deep brown, fluorine (F), and carbon (C), the table expands dramatically in the number of species. Elements in solutions like to associate with elements with the opposite charge! Let’s examine the behavior of Al, Fe, and P.

Aluminum (Al) is the most abundant metal in Earth’s crust (8.1% by weight). Most Al is in relatively insoluble silicate minerals, e.g., KAlSi<sub>3</sub>O<sub>8</sub> feldspar (potassium aluminum silicate) is common in granite. When Al dissolves from minerals, it occurs as one or more of the species in Table 1. The pH of the water determines which specie(s) will be present and dominant, and how much Al could dissolve. The solubility of Al(OH)<sub>3</sub> is lowest at about pH = 6-6.5 (a few µg/L), increasing dramatically below pH = 5, and less dramatically above pH = 6.5. Just below the forest floor organic-rich layer, the pH of soil water is commonly between 4 and 5, promoting the dissolving of Al. Abundant DOC produced in this layer also increases the solubility of

Al-bearing minerals, by combining with the Al as the uncharged molecule Al-DOC. As soil water moves downward, pH rises slowly from weathering (leaching), and as acidic DOC is consumed by microbes; consequently, Al is precipitated as  $\text{Al}(\text{OH})_3$  (Figure 1). That  $\text{Al}(\text{OH})_3$  adsorbs  $\text{PO}_4$ . The negative surface on the soil particle attracts  $\text{Al}^{+3}$  and  $\text{H}^{+1}$ , which then attract negative species from the soil water, thereby retaining  $\text{PO}_4$ . Al-DOC drains to streams and then to lakes. The Al-DOC remaining in surface water becomes photo-oxidized by sunlight, releasing the Al from DOC. Because the pH of many streams and most lakes in Maine is between 6 and 8, precipitation of small amounts of  $\text{Al}(\text{OH})_3$  and adsorption of P occurs, producing sediment.

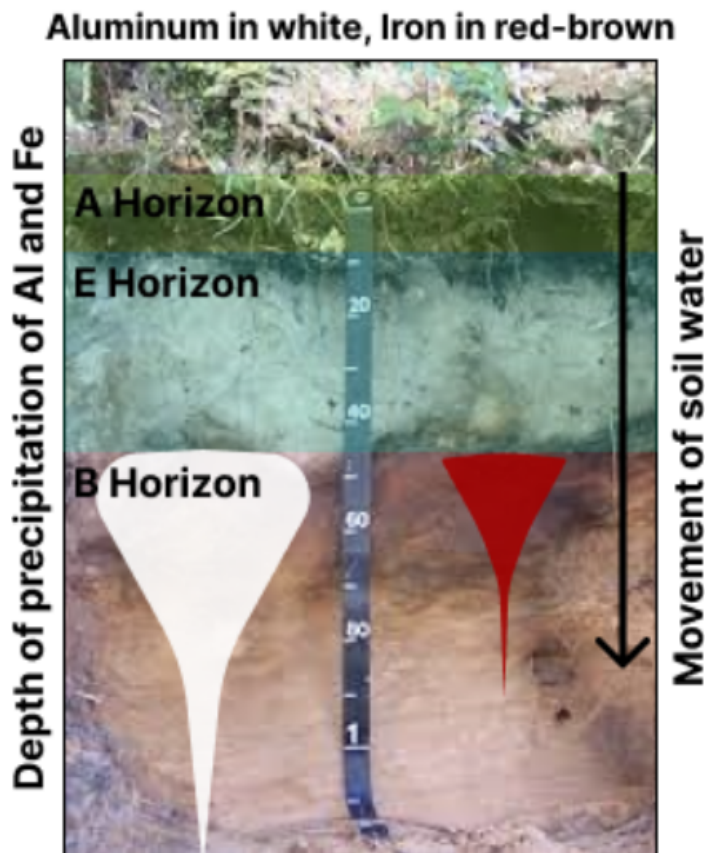


Figure 1: "A" horizon soil is a low pH layer with abundant organic matter producing abundant DOC, which slowly dissolves Al and Fe from any admixed mineral matter, transporting the Al and Fe downward in the soil profile. Al and Fe are more abundant in the less weathered B horizon. Downward weathering of the "B" soil and consumption of DOC consume oxygen and raise the pH. Fe is preferentially precipitated as  $\text{Fe}(\text{OH})_3$  in the upper B while Al is precipitated as  $\text{Al}(\text{OH})_3$  throughout "B" and into "C". The area of white and red-brown is representative of the amount of precipitated Al and Fe. Image provided by Randy Schaetzl has been modified.

Iron (Fe) is more complicated. In nature, Fe commonly occurs as either ferrous [II] iron or ferric  $\text{Fe}[\text{III}]$ , depending on the availability of oxygen when the minerals formed within Earth's crust. In normal aerated water,  $\text{Fe}^{+3}$  is virtually zero and all  $\text{Fe}^{+2}$  becomes oxidized and precipitated as light to dark brown  $\text{Fe}[\text{III}](\text{OH})_3$ . Iron-bearing minerals literally rust in place! If P species are present in the solution, they will be adsorbed on the  $\text{Fe}(\text{OH})_3$ , as for  $\text{Al}(\text{OH})_3$ . Forest soils retain their P for recycling in these two secondary products, and in organic matter. DOC also enhances

the solubility of Fe-bearing minerals, forming the neutral molecule Fe-DOC. Unlike the Al story, as soon as the water reaches the water table in forest soils it typically has been depleted of  $O_2$  because of use of  $O_2$  by microorganisms for respiration. Dissolved  $O_2$  in soil water starts out at 10 to 16 mg/L and ends up at close to 0 mg/L. Consequently, any remaining  $Fe^{+2}$  and Fe-DOC will continue moving with the groundwater; thereafter, more  $Fe^{+2}$  may be leached from the soil and bedrock. As groundwater emerges in a spring into a stream or lake, any  $Fe^{+2}$  will oxidize and precipitate. Most Fe-DOC becomes photo-oxidized by sunlight. Freshly precipitated  $Fe(OH)_3$  adsorbs small amounts of P from the water column, and the sediment gains more P-laden

Element symbols	Majors species in water	Charge on the species
Al = aluminum	$Al^{+3}$ , $Al(OH)^{+2}$ , $Al(OH)_2^{+1}$ $Al(OH)_4^{-1}$	+3, +2, +1, and -1, respectively
O = oxygen	$O_2$ , mostly $H_2O$ , $(OH)^{-1}$	$O_2$ is 0 in the atmosphere.
H = hydrogen	$H^{+1}$ , mostly $H_2O$ , $(OH)^{-1}$	H is +1 in $H_2O$ , O is -2; therefore, $H_2O$ has no overall charge.
Fe = iron	Low pH corresponds to high $H^{+1}$ mostly $Fe[II]^{+2}$ , very little $Fe[III]^{+3}$	+2 (ferrous [II]) and +3 (ferric [III]), respectively
P = phosphorus	mostly $H_2PO_4^{-1}$ and $HPO_4^{-2}$	The charge of P in the species is +5.
K = potassium	$K^{+1}$	+1

Table 1: Some chemical symbols and species used in the text. Everything is soluble, to some extent, in water and most elements in water occur as several species.

precipitate. If dissolved  $O_2$  in the lower hypolimnion during thermal stratification drops below about 2-3 mg/L (especially in the sediment), the sediment  $Fe(OH)_3$  dissolves, releasing its Fe as  $Fe^{+2}$  and the adsorbed  $PO_4$ . This recycling of P is called “the ferrous wheel”. Recycling of P is most common in shallow mesotrophic or eutrophic lakes. (This discussion explains the occurrence of the ring-around-the-collar and ring-around-the-bowl phenomenon in homes with drilled wells in Maine. Fe and manganese behave similarly so your rings can range from orange-brown to black). Dissolved Al enters a lake aided by low pH runoff (the acid rain days) and high DOC from wetlands. The Al is retained in the lake because of photo-oxidation of Al-DOC and higher pH which causes  $Al(OH)_3$  precipitation in the water column,  $PO_4$  adsorption from the water column, and accumulation as sediment. Most dissolved Fe in surface water reaches the lake in the form of Fe-DOC molecules (and some in groundwater), that are photo-oxidized to  $Fe^{+2}$ , which promptly precipitates as  $Fe(OH)_3$ , adsorbs minor  $PO_4$  from the water column, and becomes sediment. Retention of dissolved Al and Fe in streams entering Maine lakes typically exceeds 90% in the lake. *Erosion of soil transports solid  $Al(OH)_3$  and  $Fe(OH)_3$ , with substantial adsorbed  $PO_4$ , from the acidic soil environment to the higher pH environment of the lake. P is desorbed to the lake water in this transition (Figure 2). **That is why preventing erosion is important to lakes.***

The stage is set. Lakes get out of whack because of too much P. The cause can be lake susceptibility, climate change, or human activity of many kinds. The excess P causing algal blooms is from the atmosphere (which you can do almost nothing about), the watershed (which you can do something about), and from recycling from the sediment (which you can reduce with alum treatment). Years of declining Secchi disk transparency during summer stratification, and

declining pleasure and real estate values get people's attention. People prefer to swim in clear water, rather than looking at swirly pea soup. So, landowners and associations call DEP and are told that alum treatment may help. Here is what alum does in the lake.

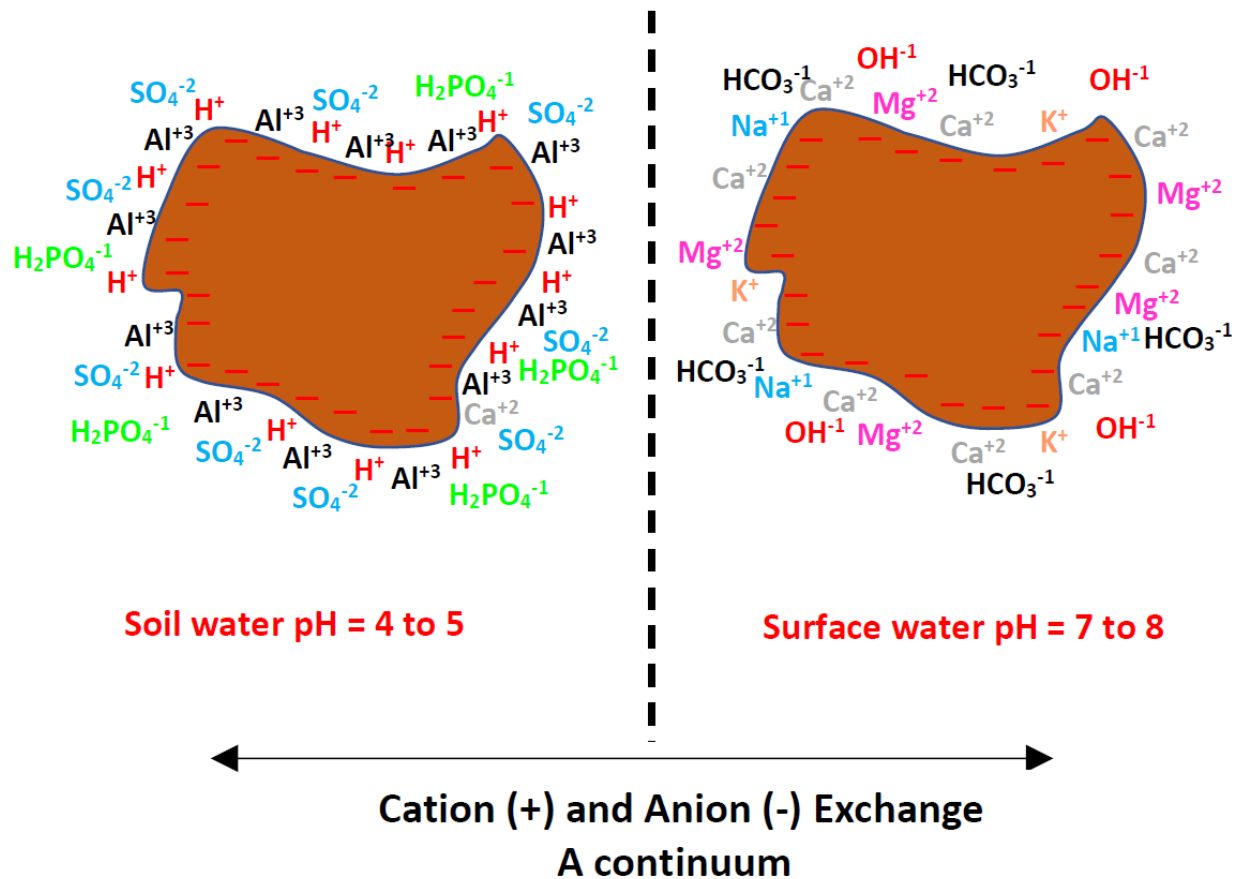


Figure 2: Schematic of the ions adsorbed on a negatively charged soil particle at low soil pH (4-5, left) versus the same particle at higher surface water pH (7-8, right). A soil particle going from low pH to higher pH, either in soil water or open water will *desorb* P ( $\text{H}_2\text{PO}_4^{-1}$  = all species of ionic P),  $\text{SO}_4^{-2}$ ,  $\text{Al}^{+3}$ , and  $\text{H}^{+1}$ , and *adsorb*  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^{+1}$ ,  $\text{K}^{+1}$ ,  $(\text{OH})^{-1}$ , and  $\text{HCO}_3^{-1}$ . This process is called ion exchange.

Alum is solid crystals of  $\text{KAl}(\text{SO}_4)_2$  (potassium aluminum sulfate), but you may read that it is also  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . It is expensive and the cost of application is even more expensive. Alum is very soluble so there is little difficulty getting it to dissolve as shown in Equation (1). The presence of water is implied by the charges of the ionic species.



$\text{Al}(\text{OH})_3$  starts to precipitate rapidly (Equation 2) because the pH of a typical lake in Maine (6.5 to 7.5) is near the minimum solubility of  $\text{Al}(\text{OH})_3$ .





Figure 3: Alum treatment on Long Pond, in Parsonsfield, ME. White aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) flocculant can be seen beneath the surface as alum is applied by the barge positioned towards the top of the image.

One solid is yielding dissolved Al while the other is precipitating Al! Reaction (2) produces acid ( $\text{H}^+$ ), lowering the pH. The release of  $\text{H}^+$  may be compensated for by adding an acid neutralizing agent which must be carefully combined with the alum. You may have seen photos or videos of an alum treatment, such as the one on Lake Auburn in Auburn, or Long Pond in Parsonsfield, ME (Figure 3). The white plume behind the boat is precipitating  $\text{Al}(\text{OH})_3$  in very tiny fluffy particles. The small particles have a high surface area to volume relationship.  $\text{Al}(\text{OH})_3$  surface area increases as the diameter of the particle decreases due to this size change for the same mass. Thus, adsorption of  $\text{PO}_4$  increases as particle size decreases. The  $\text{Al}(\text{OH})_3$  slowly sinks down through the water because it is denser than water and eventually becomes sediment. On the way to the bottom, it adsorbs substantial amounts of  $\text{PO}_4$  from the water column via adsorption.  $\text{Al}(\text{OH})_3$ 's solubility is not affected by oxidation (high dissolved  $\text{O}_2$ ) or reduction (low dissolved  $\text{O}_2$ ). So, if the upper sediment or bottom water goes anoxic (less than about 2 mg  $\text{O}_2/\text{L}$ ), only the  $\text{Fe}(\text{OH})_3$  will dissolve and yield its adsorbed  $\text{PO}_4$ . But the sediment is now “chemically capped” with a very thin layer of  $\text{Al}(\text{OH})_3$  that will adsorb any released  $\text{PO}_4$  from the dissolving  $\text{Fe}(\text{OH})_3$ . The million dollar question is how much alum should we add so that the sediment has a barrier to releasing  $\text{PO}_4$  during anoxic periods. We need to know two things.

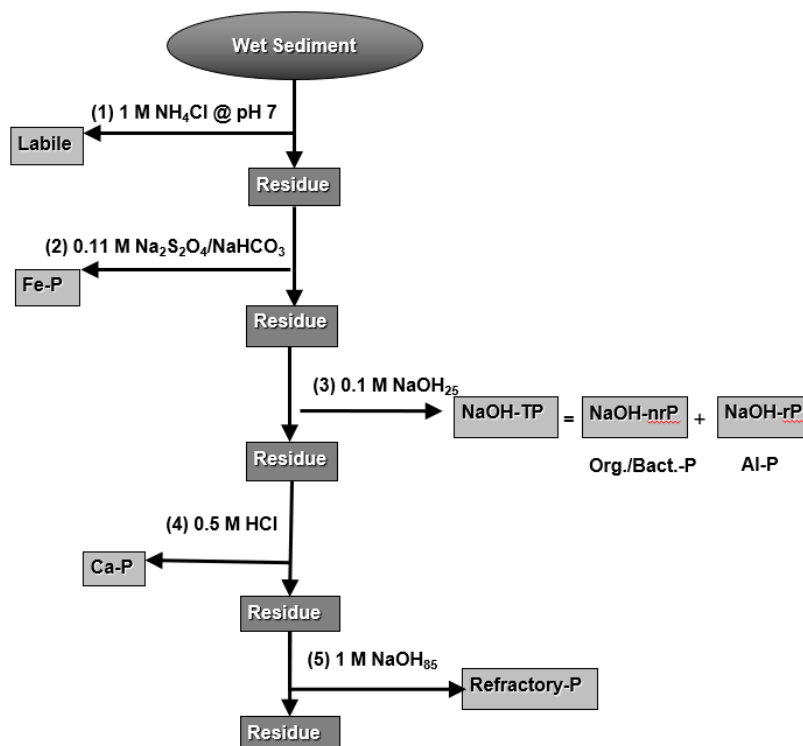


Figure 4: Wet sediment from the top of a lake sediment core is subjected to five successive extractions with the same sediment sample, using dissolved chemical reagents labeled (1)...(5). After each reagent is added to 0.500-1.000 g of sediment, with specified contact time between sediment and reagent, the solution-sample is centrifuged, solution decanted with a pipette, sample washed with the same reagent, thoroughly mixed, centrifuged, decanted, filtered, combined with the first filtered supernatant, and chemically analyzed for Al, Fe, P, and Ca. The procedure is from Psenner et al. (1988), modified by using Tessier et al. (1979) for extraction (1) and Hietjes and Lijklema (1980) for extraction (3). Most data from Maine lakes have been obtained using this procedure.

1. What are the unmodified proportions of  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ , and P in the top 3-5 cm of sediment?
2. How much  $\text{Al}(\text{OH})_3$  must be added to the sediment to prevent recycling of P during anoxic (0 to 2 mg  $\text{O}_2/\text{L}$ ) conditions.

The top 5+ cm (2+ inches) of sediment are most interactive with the lake water. Professor Jiří Kopáček (from the Czech Republic) answered the questions, in part with samples from Maine lakes. In their laboratory, uppermost sediment from cores (0-1 or 0-5 cm) was subjected to five successive increasingly rigorous chemical extractions and the resulting solutions (sol.) were analyzed for Al, Fe, P, and Ca: (sol. 1) distilled water to remove loosely bound ions; (sol. 2) a strong reducing agent (which mimics 0 mg dissolved  $\text{O}_2/\text{L}$ ) that dissolves most  $\text{Fe}(\text{OH})_3$  and any  $\text{PO}_4$  adsorbed to it; (sol. 3) a strong basic solution (NaOH) that dissolves most  $\text{Al}(\text{OH})_3$  and  $\text{PO}_4$  adsorbed to it; and sol. 4 and 5 which are irrelevant to the question (Figure 4). The conclusion of these experiment was: “negligible amounts of  $\text{PO}_4$  (are) released from lake sediments during hypolimnetic anoxia if either the molar ratio  $\text{Al}(\text{sol. 3}):\text{Fe}(\text{sol. 2})$  is  $> 3$ , or the molar ratio  $\text{Al}(\text{sol. 3}):\text{P}(\text{sol. 1}+\text{sol. 2})$  is  $> 25$ ” (Kopáček et al., 2005). These analyses have been conducted on over 150 Maine lake cores; the rules are almost universally correct! These measurements enable



us to calculate how much  $\text{Al}(\text{OH})_3$  from alum must reach the sediment to prevent release of P during anoxic periods for a calculated rate of Fe dissolution. Even as  $\text{Fe}(\text{OH})_3$  dissolves and releases its adsorbed  $\text{PO}_4$ , the  $\text{Al}(\text{OH})_3$  from alum treatment can adsorb it “immediately”. Many processes control the length of the effectiveness of the treatment, including rate of sediment accumulation and flux of P from the watershed and atmospheric inputs, but the sediments are no longer a significant source of recycled P. A treatment may last about 8-10 years or more. Shallow lakes with developed shorelines (agriculture and housing) in certain geologic settings are most vulnerable to eutrophication. Deep lakes are generally less vulnerable (Amirbahman et al., 2022; Deeds et al., 2020, 2021).

### Acknowledgments

We are very grateful to our colleagues: LSM staff, LSM’s former Executive Director Scott Williams and the 1,000+ LSM volunteers, DEP Lakes Division leader Linda Bacon who helps train the volunteers and assures reliable data is made available to the scientific community, Aria Amirbahman at Santa Clara University, CA, Jeremy Deeds of DEP, Colin Holme, Director of LEA, and Jiří Kopáček. They have been generous with assistance, data, and wisdom for 40 years.

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