Phosphorus Loading Processes in Lakes and Criteria for Assessing Zero Valent Iron as an Algal Bloom Mitigation Tool

Although zero valent iron (ZVI) has been used for over 100 years to clean up contaminated groundwater, its use in lakes has been limited. This is largely because of concerns that under anoxic conditions the iron can dissolve and release any nutrients or contaminants bound to its surfaces. Two field observations that are frequently cited as evidence that iron dissolution is a concern are low levels of dissolved oxygen (DO < 2 ppm) and elevated levels of P (particularly soluble reactive P, SRP) in the hypolimnion. Both of these are common in lakes, particularly during summer and fall, but neither is a reliable indicator of iron dissolution. The goal of this document is to review processes that regulate redox conditions and dissolved P (SRP) levels in the sediment and bottom waters of lakes, and then to propose field criteria that can be used to assess whether ZVI is likely to be an effective tool for sequestering P. The important question is not necessarily whether Fe is dissolving at depth within the sediment, but rather whether it is dissolving (or precipitating) in the vicinity of the sediment-water interface, because this is where ZVI would be applied and where it would interact with SRP.

<u>Sequestration of P by Fe and Mn Oxides.</u> In most lakes the dominant repositories for inorganic P are the surfaces of Fe and Mn oxide minerals. The most common of these are listed below along with their P adsorption capacities:

Mineral	Formula	Adsorption Capacity (mg P/gm)
Goethite	$FeO \cdot OH$	6.0 - 157
Ferrihydrite	$Fe(OH)_3 \cdot nH_2O$	257 - 617
Hematite	Fe_2O_3	0.5 – 2.0
Pyrolusite / Birnessite	MnO_2	18 - 167
Bulk sediment w/ Fe oxides	-----	71
ZVI	-----	30

In general Fe minerals are more important than Mn minerals because they are more abundant and stable under a broader range of redox conditions. Clearly some materials have a greater capacity than others to adsorb P (and other elements); this is related to their typical grain size and to the number of defects in their crystal structure. More defects (which represent sites for attachment) and smaller grain sizes (which results in greater surface area / mass) will lead to higher adsorption capacities.

<u>Where Do Algae Acquire Nutrients</u>? Algal growth requires both nutrients and sunlight, and therefore occurs most vigorously in the photic zone. Nutrients that are concentrated in the bottom waters will reach the photic zone when a lake turns over (typically in late Fall in the PNW) or where/when cyanobacteria migrate to deeper waters, which they can do on a daily cycle during blooms in late summer or fall. This gives cyanobacteria an advantage when a lake is also crowded with green algae. Some cyanobacteria can also take up nutrients directly from the sediment when they are in a dormant state. During this "luxury uptake" process the cyanobacteria take in more nutrients than needed at the time, and they can utilize this excess at a later stage.

<u>Causes of High SRP in the Hypolimnion.</u> In lakes that develop thermal stratification it is common to find elevated levels of SRP in the bottom waters. At least three processes can cause this: (1) release of P from the sediment, (2) decomposition of recently

sedimented organic matter that has accumulated on or near the bottom, and (3) pooling of SRP-rich groundwater that is colder that the lake's surface waters and has traveled from its entry points to deeper portions of the lake. It is essential to identify where the SRP-rich water is coming from before deciding on a mitigation plan.

Stability of Iron and Mn Oxides/Hydroxides. In nature Fe and Mn are highly effective at binding and sequestering P and NO_3 (and many trace metals) as long as they are in an oxidized form. Conversely, when Fe and Mn are in reduced form they will dissolve and release any bound elements. The important question for any given system is whether sufficiently oxidizing conditions are present in the water column and, if they vary seasonally (for example become more reducing in the summer), whether that change will lead to dissolution and nutrient release.

pE is an environmental parameter that describes how oxidizing or reducing an environment is. It is analogous to pH, the parameter that describes how acidic or basic an environment is. High pE values indicate oxidizing conditions; low pE values are found in reducing environments. For elements that can occur in different redox states (e.g., Fe, Mn, N, S, C), if you know the pE of the environment you can predict what forms of those elements will be present and their relative proportions (i.e., Fe^{3+} vs Fe^{2+}). We are mostly interested in Fe, but the other elements can help us determine what forms of Fe are present. Figure 1 illustrates the sequence of different redox reactions that occur in a lake (or lake sediment) as conditions become more reducing. All of these reactions basically release O, which is then used to convert organic matter (C) into CO_2. In simplified form the most important reactions are described below, listed in the order in which they would occur as pE decreases. The exact pE at which each reaction takes place will vary from case to case depending on pH (higher pH = lower pE) but the sequence will remain the same. The following steps are also illustrated in Figure 2.

(1) Dissolved O is used to make CO_2 from organic matter. This also produces NO_3 and releases P. As long as *any* DO remains the pE is buffered at ~13 and all Mn and Fe will be in their oxidized forms.

(2) *After* all DO is consumed the next step is the reduction of $Mn^{4+}O_2$ to Mn^{2+}: $CH_2O + 4MnO_2 + 12H^+ \leftrightarrow CO_2 + 4Mn^{2+} + 7H_2O$. This reaction buffers the pE at ~10. All Fe remains in oxidized form but Mn should begin to dissolve and may be measurable in water samples.

(3) *After* the Mn is reduced the next step is the conversion of NO_3 to N_2 (denitrification): $2.5C + 2NO_3^- + 2H^+ \leftrightarrow N_2 + 2.5 CO_2 + H_2O$. This reaction again buffers the pE, keeping it above ~6. All Fe remains in oxidized form; nitrate will disappear from water analyses.

(4) *After* all NO_3 is reduced the pE will decrease to ~4-2, at which point Fe^{3+} gets reduced to Fe^{2+}, which is soluble and thus Fe will begin to appear in water analyses.

(5) *After* all ferric iron is reduced the pE will drop to -2, which is the point at which sulfate (S^{6+}) is reduced to sulfide (S^{2-}): $SO_4^{2-} + 2CH_2O \leftrightarrow H_2S + 2HCO_3^-$. Once these strongly reducing conditions are reached the "rotten egg" smell of the H_2S should be noticeable in water samples. At this point all the Fe oxide minerals should have dissolved and the iron will be utilized to form pyrite (FeS_2). P does not attach to the surface of pyrite, so it would be released from the sediment.

Making Use of Water Analyses. In lakes where the bottom waters are enriched in SRP we can use the above sequence of reactions to get a better understanding of where the P is coming from and whether ZVI is likely to be an effective sequestration tool. The suggested guidelines are as follows:

(1) If the hypolimnion analyses contain measurable DO and NO_3 but not Mn, the water is not coming from the sediment.   Conditions are oxidizing and ZVI will be effective.

(2) If DO is below detection but NO_3 is present (with or without Mn) conditions are oxidizing and ZVI will be effective. It is unlikely that any SRP is coming from sediment.

(3) If the water analyses contain Fe but no H_2S there is a porewater contribution from the sediment, probably including SRP. However, it is essential to measure SRP (not just TP) in these samples because it is likely that some or all of the Fe is actually colloidal particles (i.e., not dissolved) and these particles have the ability to bind P. As a result SRP will be low. Under these conditions ZVI should be effective.

(4) If the water contains H_2S or NH_4 (ammonia) conditions are strongly reducing and inputs from the sediment are significant. Fe oxide minerals will not be stable and ZVI will not be effective.

Stability of Iron Oxide Minerals. When assessing the potential effectiveness of (or need for) ZVI the real question is whether Fe-oxide minerals are stable in the vicinity of the sediment-water interface. There is little question in most cases that strongly reducing conditions exist at depth in the sediment and that SRP levels will be elevated in pore water. However, if Fe-oxides are present at the interface at sufficient concentrations, they will intercept the SRP and prevent it from building up in the hypolimnion (Fig. 3).

For any situation of interest we can calculate whether one or more Fe oxide minerals will be stable using the USGS program PHREEQC. To do this we need a water analysis that is as complete as possible (pH, DO, temp, alkalinity, major ions). Using this input, the program will calculate the concentrations of all species in solution as well as the "degree of saturation" of any minerals that could be present. If a mineral is found to be "oversaturated" then it should be present; if it is "undersaturated" it should dissolve. Figure 4 shows some results for a hypolimnion sample from Spanaway Lake. DO is not plotted, but it would disappear at pE ~13, followed by NO3 at pE ~12. The important point to note is that the three main Fe-oxide minerals are all stable far past this point.

Fe Oxide Abundance. One final consideration is that not only must Fe oxide minerals be stable, they must be abundant enough to sequester the SRP that is present. The accepted Fe:P ratio for his is 10:1, as measured in sediment near the interface. If the ratio is above this, the lake should naturally have the capacity to sequester P emanating the sediment. If the ratio is below this and conditions indicate Fe oxides are stable, the lake is a good candidate for ZVI treatment.

Jeffrey H. Tepper
17 Nov. 2024
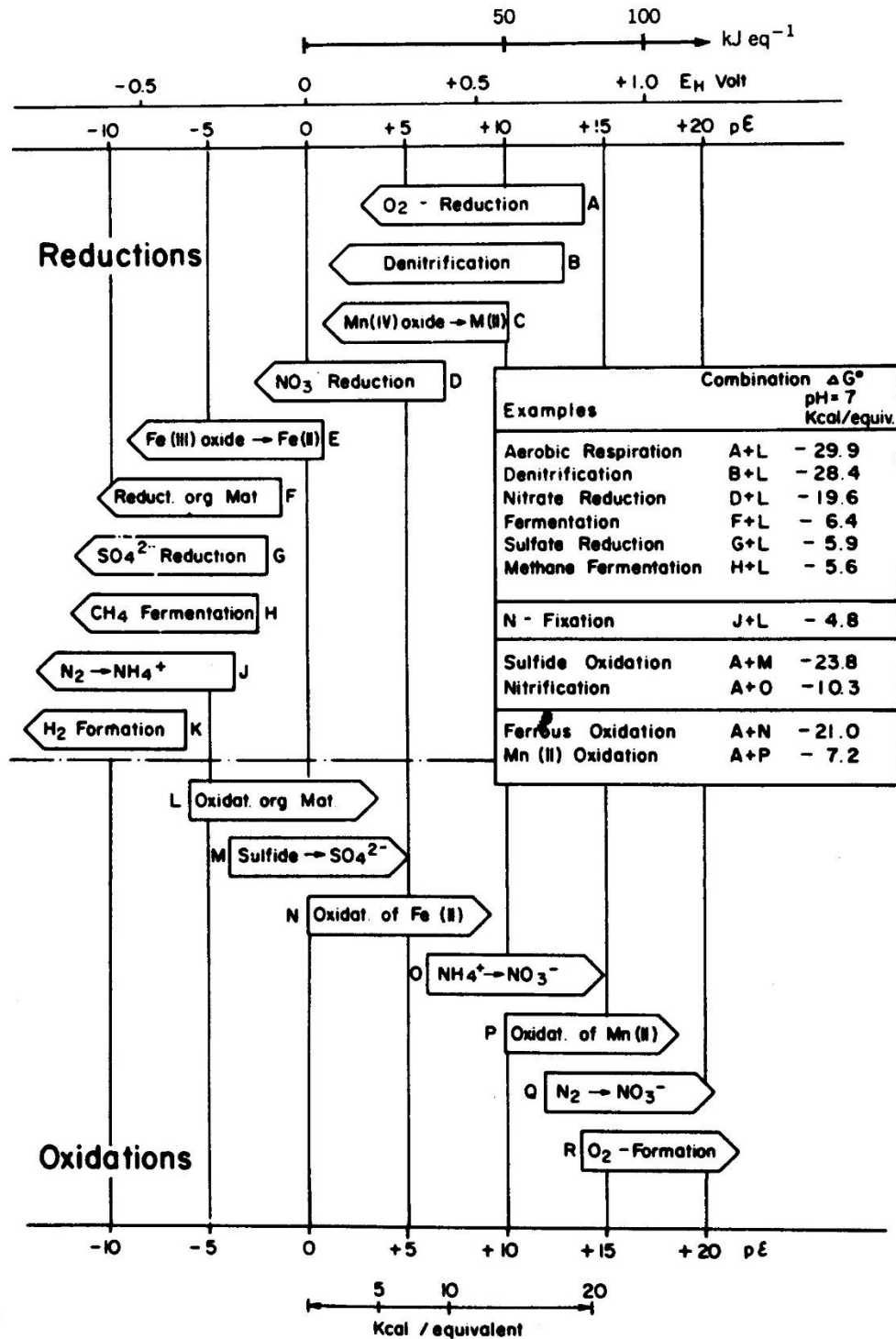
Figure 1. Sequence of redox reactions that commonly occur in lakes and lake sediments. From Stumm and Morgan (1996) Aquatic Chemistry 3rd Ed.
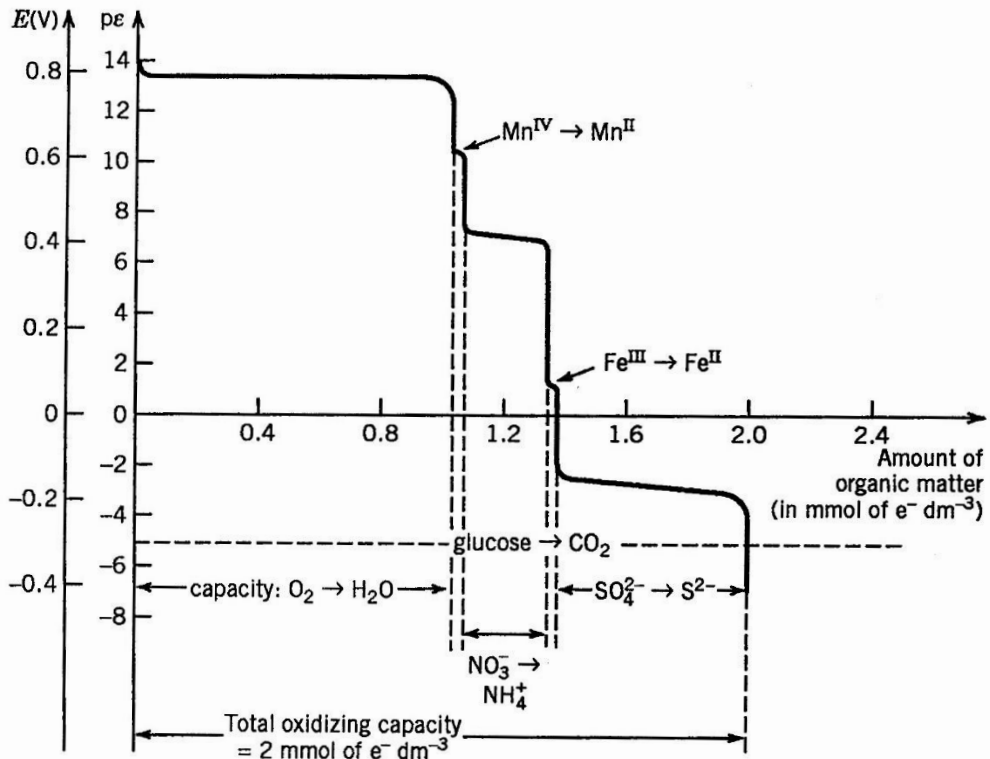
Figure 2. Simplified sequence of redox reactions occurring as organic matter in lake sediment is converted to CO_2. Note that each reaction – progressing from top to bottom - temporarily buffers the eH until its reactants are used up. Reduction of F^{3+} to Fe^{2+} cannot happen until all nitrate is gone. From Stumm and Morgan (1996) <u>Aquatic Chemistry</u> 3rd Edition.
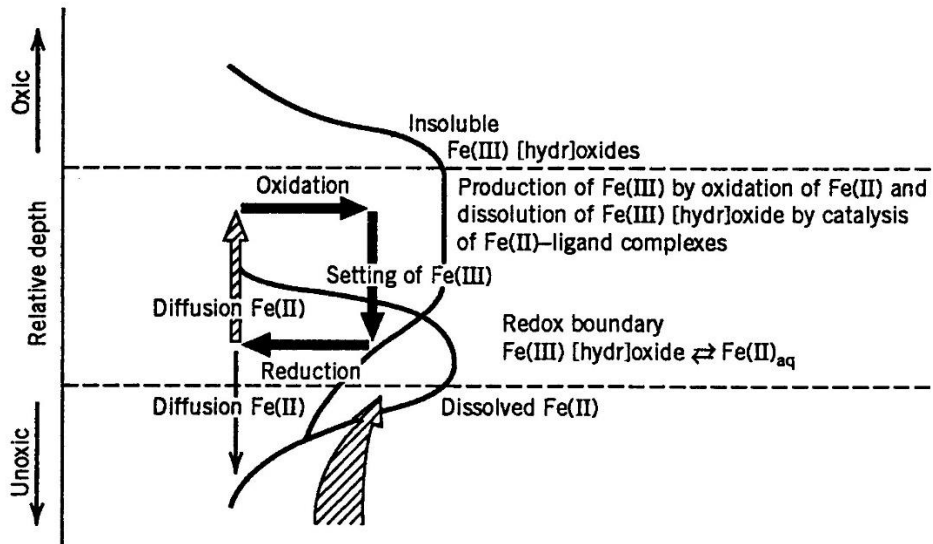
Figure 8.16. Transformation of Fe(II,III) at an oxic–anoxic boundary in the water or sediment column. (Adapted from Davison, 1985.)

Figure 3. Process of Fe^{2+} emanating from sediment, encountering oxic conditions, being converted to Fe^{3+}, precipitating, and settling to the bottom. This boundary moves upward as sediment accumulates. SRP will be sequestered by the Fe-oxides that precipitate.
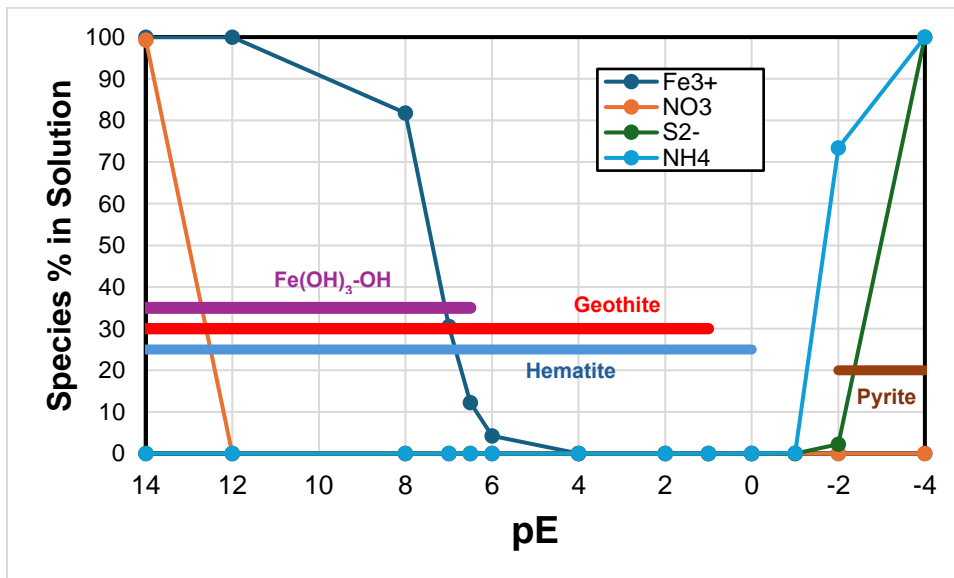
Figure 4. Stability of Fe minerals in hypolimnion water from Spanaway Lake. Calculated using PHREEQC.