Northwest Aquatic Management, LLC (Kyle Steelhammer)

The attached files were submitted by Jeff Tepper earlier in 2025. We have been working with Jeff for several years in regard to ZV Iron and its effectiveness in Lakes and agree with his findings and supported documentation.

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Kyle Steelhammer, President/Owner
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Suggestions for Revisions to APAM Guidelines for use of ZVI in Lakes

The current APAM permit guidelines for ZVI state: *Do not apply where anoxic conditions (zero percent dissolved oxygen) may occur, including anoxic conditions created by applications of herbicide and algaecide*.

I would like to suggest that the "do not apply" guideline be modified simply to state that ZVI may be less effective where conditions are [strongly] reducing. In addition, "zero percent dissolved oxygen" is not a reliable measure of whether ZVI will be effective and should be replaced with an alternative that is both easier to measure accurately and more indicative of redox conditions that are likely to exist in bottom waters. Both recommendations are explained in more detail below.

It is widely accepted that ZVI does not pose an ecological threat: the 2017 Washington State EIS states that iron is limited in solubility, inert, and non-reactive, and that there are "no toxicity concerns". Instead, the concerns are that: (1) sequestered P may be released if the Fe dissolves under reducing conditions, and (2) that Fe is also a nutrient and has the potential to enhance CAB blooms. The EIS cites Cooke and Kennedy (1981) for concerns about P release under anoxic conditions, but this report does not actually contain any data on the topic: it focuses primarily on alum and includes only two lakes where iron was applied. For both of those lakes the study reports "no data" on the effectiveness or side-effects of the treatment. The bottom line: we should be relying on more recent studies with regard to P release under "anoxic" conditions.

I have attached a separate document I wrote last year that summarizes how redox conditions control the behavior of Fe in lacustrine systems, and there are three key points. The first is that **iron does not cease to be effective for P sequestration simply because DO is low** (or even zero). As conditions become progressively more reducing the proportion of iron that remains Fe^{3+} (insoluble) will decrease, but only under strongly reducing situations will it disappear entirely. In the vast majority of cases a portion iron will remain as Fe^{3+} and continue to bind P. This is the reason for the widely accepted simple rule that Fe "is able to bind more or less permanently an amount of phosphorus equivalent to 10% or less of its own weight" (Scheffer, Ecology of Shallow Lakes, p. 54). In other words, in lakes with sediment Fe/P > 10, even after some dissolution has occurred, enough insoluble Fe^{3+} will remain to bind the P.

The second point is that **low DO is not a reliable indicator of Fe dissolution**. DO acts as a buffer – as long as any is present, even 0.01 ppm – the system will be strongly oxidizing and all Fe will be present as insoluble Fe^{3+}. Over time, DO within the sediment column or hypolimnion will be consumed as organic C is converted to CO_2. After all the DO is gone a sequence of other redox reactions will occur and this will eventually lead to Fe^{3+} being reduced to Fe^{2+} as explained in more detail in the accompanying document. It is possible to measure the redox state (ORP, or oxidation-reduction potential) directly, and this would tell us the extent to which Fe is soluble, but in my experience ORP probes are finicky and tend to equilibrate slowly, so I don't think they are widely used by consultants. Conversely, DO is easy to measure, but without tedious calibration of the probe it's

hard to obtain precise results at low (<0.5 ppm?) concentrations. To get around this problem some consultants arbitrarily define 2 ppm DO as the "anoxic" limit below which Fe will dissolve, but this is misleading and greatly exaggerates the "no ZVI zone". I suggest in the accompanying document some options for using routinely-measured water chemistry parameters to more accurately assess Fe solubility.

The third point is that **Fe dissolution and accompanying P release does not necessarily lead to increased SRP**. It is important to understand what happens to these elements <u>after</u> they are returned to the water column, and Spanaway Lake provides an excellent example. There is no question in this case that Fe and P (and Mn, etc.) are being released from the sediment into the hypolimnion: this is clearly seen in data from multiple researchers including Will Hobbs. However, all of these studies have also found that SRP is consistently very low (generally < 10 ppb). Why? Because even in the summer months the hypolimnion contains some DO, and this causes the dissolved Fe to oxidize and precipitate as minute colloidal articles that very efficiently scavenge P from the water and then settle to the bottom. One result of this is iron enrichment at the sediment-water interface, a feature of every lake sediment core I have ever analyzed and a sign this process is common. The scavenging process does appear to be more efficient at Spanaway than at other lakes in the region, and this is probably because the sediment there naturally has a very high Fe content. For full disclosure, it has alternatively been suggested that the low SRP is a result of uptake by cyanobacteria that migrate downward to "feed", but there is no evidence to support this and no explanation for why this should happen at Spanaway but not other lakes.

In the interest of getting these main ideas to you quickly I am not aiming to summarize the relevant ZVI literature in this letter, except to say that a lot has been published in the last 15 years. The work ranges from benchtop lab tests to mesocosm experiments to whole-lake manipulations, so there is much to draw from in moving beyond Cooke and Kennedy (1981). As you know, our "experiment" at Lake Steilacoom is ongoing and nothing has been formally published, but it has been successful thus far in preventing HAB and I think illustrates clearly that ZVI works in lakes where anoxia is not present. I'm not sure what kind of literature summary you would need if there are going to be revisions to the ZVI guidelines, or when you would need it, but please let me know if I can help in that regard. And I think your earlier suggestion of putting together a working group is a great idea; there is a lot of information "out there" and it comes from multiple disciplines, so having a team with mixed expertise would make it much easier to synthesize the relevant studies.

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Kyle Steelhammer, President/Owner
Northwest Aquatic Management, LLC

References Relating to the Effectiveness of ZVI Under "Anoxic" Conditions

The main concern with regard to application of ZVI to lakes is whether it remains effective in situations where the bottom waters are anoxic during at least a portion of the year. This document is a brief compilation of published studies that bear on that question. These studies document three reasons why ZVI can remain an effective P sequestrant even under anoxic conditions:

(1) a proportion of the total iron in sediment *remains ferric even after all dissolved oxygen is consumed*, and this iron will continue to bind P
(2) ferrous iron released by dissolution will combine with phosphate *in the sediment* to form vivianite, an insoluble mineral stable in the sediment column
(3) reducing conditions in sediment can cause release of SRP, but if ferrous iron is also released the two ions will combine in the water column and reprecipitate, *a geochemical cycle that prevents SRP from reaching the epilimnion*

Scheffer, M. (1998) Ecology of Shallow Lakes. Kluwer Academic Publishers, 357 pages. ISBN 1-4020-2306-5.

Scheffer reports that the concentration of P in the water of shallow lakes shows little or no correlation with the P content of the sediment, but instead "correlates well" with its Fe:P ratio. He proposes a "simple rule" that in lakes where the sediment has Fe:P > 10 (on a weight percent basis), the iron is able to bind the P "more or less permanently". Scheffer cites several field-based studies that support this idea, and I would add that it is consistent with what we know about the redox behavior of Fe. Specifically, some percentage of the total Fe in sediment will remain in the Fe^{3+} state even when conditions are anoxic and thus, where Fe/P>10, there is usually enough Fe^{3+} to sequester the P. Adding ZVI only helps in this case.

Orihel, D. M., et al. (2016) Experimental iron amendment suppresses toxic cyanobacteria in a hypereutrophic lake, Ecological Applications, v. 26, no.5, p 1517-1534.

This experiment at a hypereutrophic Canadian lake involved 12 in situ mesocosms that received varying doses of Fe (2 – 225 g/m^2). Iron amendment decreased the P content of porewaters and the flux of P from sediments, lowering P concentrations in the water column by up to 72%. Iron application also had significant dose-dependent negative effects on the biomass of phytoplankton and periphyton, reduced the dominance of cyanobacteria, and even at the lowest doses appeared to reduce the toxicity of cyanobacterial blooms, as measured by the concentrations of microcystins.

Kleeberg, A., et al., (2013) Redox sensitivity of iron in phosphorus binding does not impede lake restoration, Water Research, v. 47, no. 3, p. 1491-1502.

This study evaluated the long-term results of Fe application 19 years after the original treatment. They found that Fe had become concentrated at the sediment-water interface, creating a "dynamic P trap" with Fe:P ~7. While this was not sufficient to prevent all sediment P release, they concluded that P release was not relevant for the P supply to the epilimnion, because most SRP was co-precipitated by Fe that had accumulated concurrently in the hypolimnion. They suggest long-term control of P release can be achieved if Fe level is >200 g/m^2. I would add that this co-precipitation process is exactly what Will Hobbs' data suggest is taking place at Spanaway Lake, where hypolimnion Fe levels are above saturation, but SRP levels are very low.

Natarajan P., Gulliver, J.S., and Arnold, W.A. (2021) Iron filings application to reduce lake sediment phosphorus release, Lake and Reservoir Management, v. 27, p143–159.

This was a laboratory study in which P release was measured on lake sediment cores that had been amended with 0.01 – 1.0 g/cm^2 of powdered Fe and then monitored under both oxic and anoxic conditions. In the oxic experiments no P release was detected and that was to be expected, but the same was also true for anoxic experiments that had Fe>0.1 g/cm^2. My comment: this is experimental confirmation that ZVI is effective under anoxic conditions as long as the Fe:P ratio is high enough.

Gachter, R., and Muller, B. (2003) Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface. Limnology and Oceanography, v. 48, no. 2, p. 929–933.

This brief paper eloquently explains how under reducing conditions dissolution of ferric oxides (and accompanying P release) leads to formation of insoluble Fe-phosphate minerals such as vivianite. Only if conditions are strongly reducing and <u>sulfur is abundant</u> (leading to pyrite formation and thus no Fe to bind P) will P release occur. Otherwise the dissolution of Fe oxides does not promote internal P loading of a lake.

Rothe, M., et al. (2013) Evidence for vivianite formation and its contribution to long-term phosphorus retention in a recent lake sediment: a novel analytical approach, Biogeosciences, v. 11, p. 5169–5180.

Analysis of sediment cores from a Swiss lake that was treated with iron over 20 years earlier showed that the Fe addition had resulted in formation of the Fe-phosphate mineral vivianite, which is stable under reducing conditions and highly insoluble. As sediment accumulated, the original Fe^{3+}-oxide minerals were buried and dissolved, providing the iron needed to bind P as vivianite. My comment: this demonstrates that reduction and dissolution of ferric oxide minerals does not necessarily lead to P release. On the contrary, the added iron enhances long-term storage of P as Fe-phosphate minerals.

A separate concern noted in the 2017 Supplemental EIS, Section 4.8.2.3, and based on a study by Molot et al. (2014) is that Fe additions could fuel enhanced cyanobacteria growth. More recently, Orihel et al. (2016) note that, while this is true for marine ecosystems, there is "no evidence that Fe controls primary productivity at the ecosystem level in freshwaters." My comment: the solubility of Fe in oxic waters is *extremely* low and thus it is highly improbable that Fe is the biolimiting element is the photic zone of any local lake. Fe levels in an anoxic hypolimnion would be higher but I am not aware of any data that establish this as a cause of HAB.

Closing comment: Several studies note that Fe also has bactericidal benefits, either by killing CAB during their dormant stage in the sediment, or by reducing their production of microcystins. This is outside my area of expertise and thus not mentioned above, but there may be others who can comment on these studies.

Compiled and summarized by Jeff Tepper; 12 July 2025.