Restoring a Functional Iron Cycle

Many lakes have become more eutrophic over the past 20 years. Due to the amount of autochthonous organic material supplied by in-lake primary productivity, and allochthonous organic matter supplied by the watershed, respiratory demand often exceeds aerobic respiration capacity. A substantial proportion of the lake's total respiration is carried by alternate terminal electron acceptors (ATEAs). In most softwater ecosystems of this type the primary ATEA used is iron, with ferric iron reduction to ferrous iron. However, an "iron deficiency" can develop over many years of exhibiting a eutrophic productivity state. There are several reasons for the development of the "iron deficiency", including:

- permanent loss of iron as ferrous sulfide compounds,

- watershed drainage basins draining to the lake via other highly eutrophic ecosystems (swamps, marshes, other eutrophic waterbodies).

Iron is a particularly important metabolite in a softwater lake. It is what gives sediments an affinity for binding phosphorus. It is an important phosphorus removal mechanism after fall circulation. It is a "desirable ATEA", certainly preferable to ATEAs that operate at lower oxidation-reduction potentials. For example, after ferric iron is exhausted as an available ATEA sulfur compounds take over that role, resulting in hydrogen sulfide production. Hydrogen sulfide is very toxic to most aquatic biota, iron is not.

As one component of a holistic lake-watershed restoration program, the restoration of a "functional iron cycle" at the bottom of a lake has been accomplished. Other aspects include watershed management, biomanipulation (which is inhibited when sulfide production dominates), aeration (which works best in iron-dominated ATEA systems), area-selective macrophyte harvesting, and occasional winter drawdown. Restoring a "functional iron cycle" has been a multi-year, incremental addition of redox available ferric iron solids as a sediment amendment in deep areas of the lake. Incremental additions, each dosed to increase maximum hypolimnetic iron concentration by approximately 0.5 mg/L with extensive annual monitoring, has been the approach. Addition of ferric oxide solid (powder) either through the ice in a grid pattern, or directly into the hypolimnion during summer stratification (through a hypolimnetic aerator) are alternative application methods.

Restoring the "desirable ATEA pool" at the bottom of a eutrophic lake can be an effective part of a lake ecosystem restoration program. Although this approach has been done, and is becoming more widely understood in the lake management community, it is much less "common" than algaecide, herbicide, and other "chemical treatments".   Several publications are attached which describe the function and operation of respiration in stratified lakes, the importance of ATEAs and particularly iron, and other aspects related to the proposed restoration of a "functional iron cycle". The following information provides background and summarizes much of the literature and research regarding lake ecosystem energetics, the role of iron, natural occurrence of iron below the thermocline of eutrophic soft water lakes and water supply reservoirs, and relationships to eutrophication abatement efforts.

Internal Phosphorus Cycling Dynamics

Phosphorus plays a central role in the bioenergetics of organisms and ecosystems; a role which no other atom can duplicate. Phosphorus is of paramount importance in lake management because it most often limits the degree of phytoplanktonic autotrophy (algae growth).

The mechanisms of internal phosphorus cycling within lakes are very important to the quality of the lake. Large amounts of phosphorus are released from sediments of eutrophic lakes, especially when waters in contact with sediment become depleted of oxygen. The mechanism by which sediment phosphorus flux occurs is different between softwater lakes rich in iron, hardwater lakes with high alkalinity and conductivity, and soft- to moderately hardwater lakes which have become deficient in iron. Before examining the specific mechanisms of Internal Phosphorus Loading and Water Column Removal, a review of lake community respiration is warranted. After all, "lakes are living ecosystems" ("lakes are heterotrophic too.")
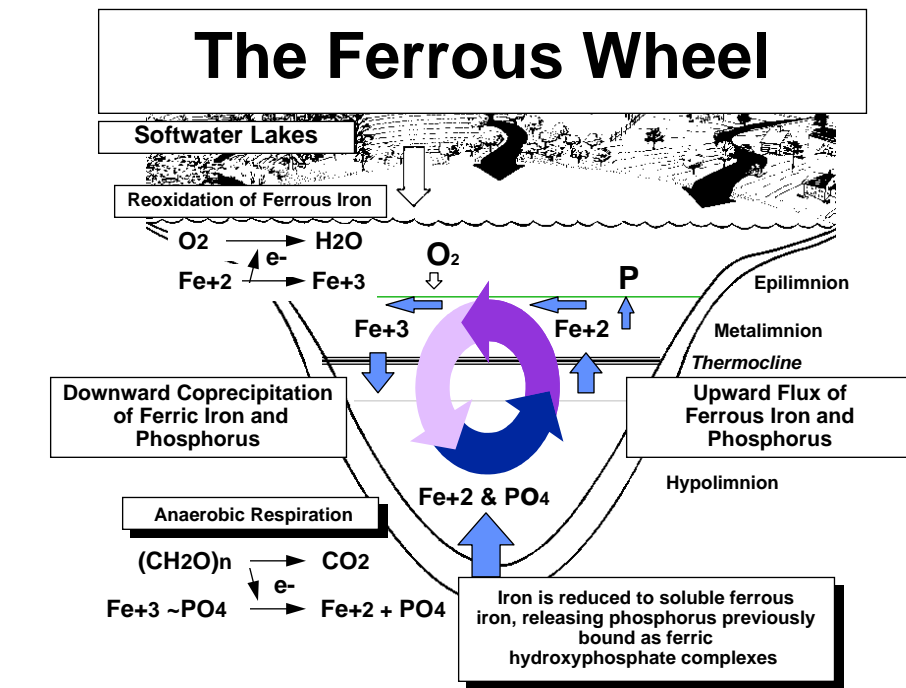
Respiration is an "oxidation-reduction" reaction where organic matter is "oxidized" to carbon dioxide and another substance (X) is "reduced." ***All*** organisms do this. The only differentiating feature is the substance (X) used to accept transferred energy ("terminal electron acceptor" [TEA]).   In aerobic respiration, organic matter is oxidized to carbon dioxide and oxygen (TEA) is reduced to water.   Anaerobic respiration is the process by which organic matter is combusted (oxidized) using an alternate (ATEA). The alternate can be a variety of substances (X) which become reduced. Some examples include dissimilatory nitrate reduction, manganese reduction, iron reduction, sulfur reduction, and fermentation. It is important to note that carbon dioxide is the common product of all lake community respiration processes; it is the product of the oxidation of organic matter regardless of what reduction reaction was coupled to it.

This is one very important reason for measuring carbon dioxide during lake diagnostic studies.
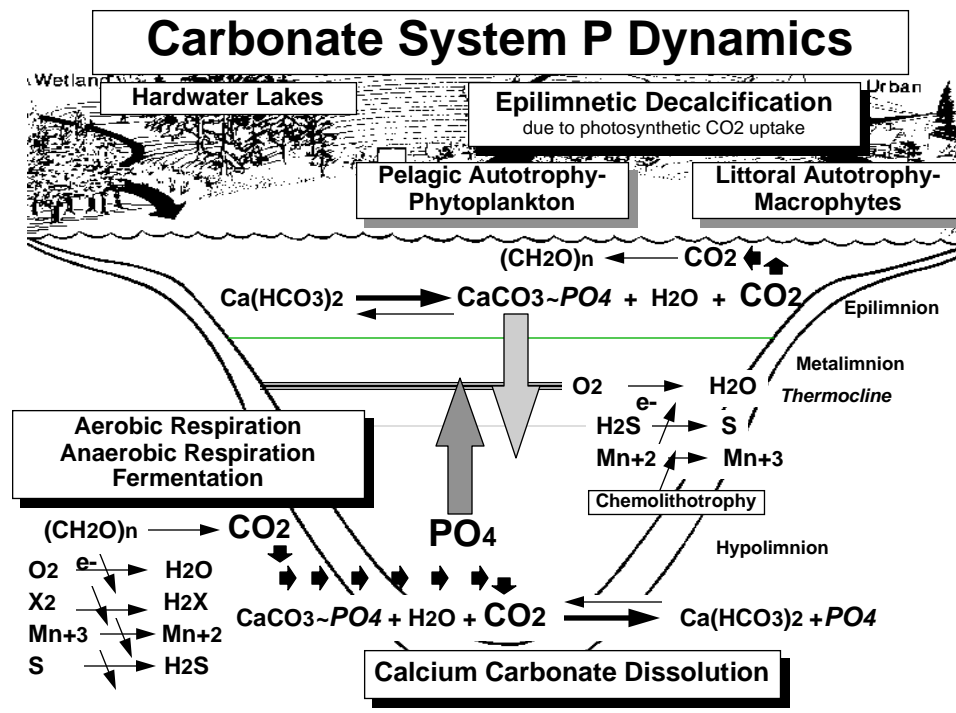
As a lake becomes more eutrophic, more organic matter needs to be "combusted" via lake community respiration. This is first observed as a higher oxygen demand and more rapid consumption of dissolved oxygen (increased aerobic respiration). Once available oxygen is consumed (as a TEA), alternate compounds are used in place of oxygen (ATEAs). *Increased lake community res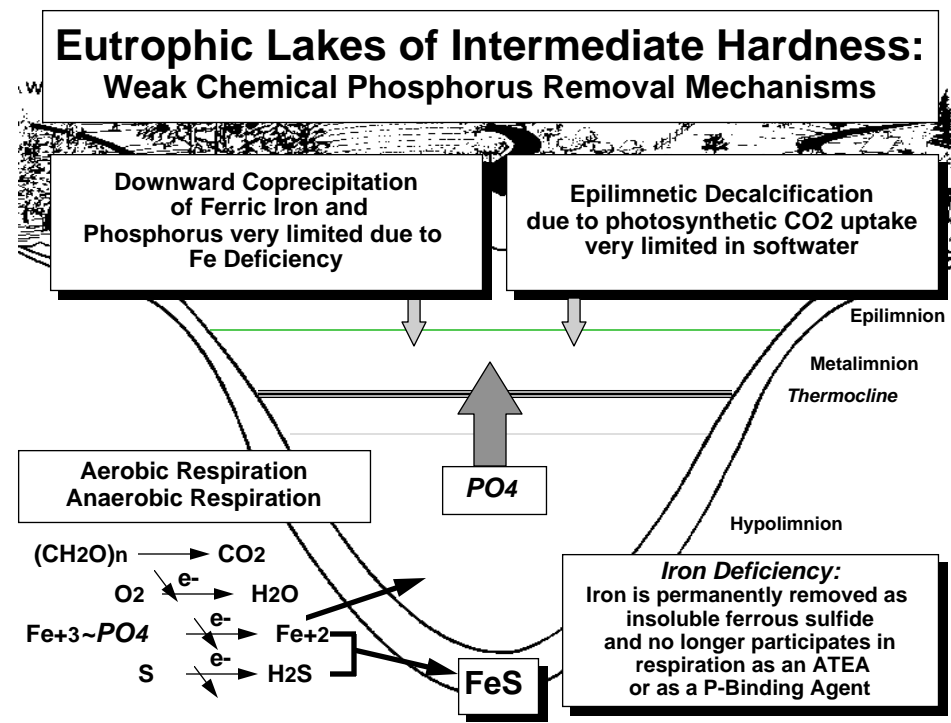piration is a consequence of eutrophication.* As demand for respiration continues to increase, more ATEAs are used in respiration. The first ATEA used is nitrate (in dissimilatory nitrate reduction). While anaerobic respiration takes place in the nitrogen cycle no dramatic increase in phosphorus release from sediments occurs. (Nitrate is beneficial at the bottom of lakes.) However, as respiratory demand increases further, ferric iron acts as an ATEA, becoming soluble ferrous iron and releasing the phosphorus it had bound while it was oxidized. Fortunately, in most iron-dominated lakes, much more ferrous iron is generated during anaerobic respiration than phosphorus is released to hypolimnetic waters. Furthermore, the accumulated iron beneath the thermocline acts as a precipitation agent for phosphorus removal from lake waters in the fall.   Further respiratory demand (in excess of what available ferric iron can carry) results in reduction of sulfur to hydrogen sulfide. Hydrogen Sulfide is extremely toxic to most biota, and readily reacts with ferrous iron, *permanently removing it as insoluble ferrous sulfide* (Doyle, 1966). Hence, iron is no longer available to participate in respiration as an ATEA, or to bind phosphorus.

The Ferrous Wheel

Softwater Lakes

Reoxidation of Ferrous Iron

$O_2 \longrightarrow H_2O$

$Fe^{+2} \xrightarrow{\ e^-\ } Fe^{+3}$

O_2

P

Epilimnion

Fe^{+3} Fe^{+2}

Metalimnion

Thermocline

Downward Coprecipitation of Ferric Iron and Phosphorus

Upward Flux of Ferrous Iron and Phosphorus

Hypolimnion

Fe^{+2} & PO_4

Anaerobic Respiration

$(CH_2O)_n \longrightarrow CO_2$

$Fe^{+3} \sim PO_4 \xrightarrow{\ e^-\ } Fe^{+2} + PO_4$

Iron is reduced to soluble ferrous iron, releasing phosphorus previously bound as ferric hydroxyphosphate complexes

In soft water lakes (generally below about 50 mg CaCO3/L alkalinity), iron tends to control internal phosphorus dynamics. Oxidized ferric iron binds with phosphorus as ferric hydroxy phosphate complexes, giving sediments a capacity to bind phosphorus. When oxygen depletion occurs in bottom strata (for example, during lake stratification), alternate compounds are used by the biota for respiration. The use of alternate terminal electron acceptors (ATEAs) occur in a sequence of decreasing oxidation-reduction potential: first nitrate, then iron and manganese, then sulfur (producing hydrogen sulfide), and finally organic compounds in fermentation and methanogenesis (see Kortmann and Rich 1994). Once iron is used as an ATEA, both ferrous iron and previously bound phosphate are released to the water as soluble forms. Iron carries much of the anaerobic respiration in many softwater lakes. When ferrous iron again encounters oxygen, it is reoxidized and precipitates out of solution; carrying large amounts of phosphorus with it as ferric hydroxy phosphate complexes (see Kortmann 1980, Kortmann and Rich 1994, Kortmann 1994). This "ferrous wheel" controls much of the deep-shallow phosphorus exchanges in soft water lakes. Fortunately the release of iron typically exceeds the release of phosphates (iron concentrations typically reach 5-10 mg/L while TP concentrations are typically less than 0.3 mg/L in anoxic hypolimnetic waters). Unfortunately, observed iron concentrations are low in many lakes of moderate hardness which have been eutrophic for an extended duration. In such lakes available ferric iron has become depleted over years of eutrophication (it has been permanently removed from "redox availability" as ferrous sulfide). The release of phosphorus from sediments and chemical precipitation from the water column are directly due to oxidation-reduction reactions (the oxidation state of iron, hence its solubility).

Carbonate System P Dynamics

Hardwater Lakes   Wetland   Urban

Epilimnetic Decalcification
due to photosynthetic CO2 uptake

**Pelagic Autotrophy-
Phytoplankton**

**Littoral Autotrophy-
Macrophytes**

$(CH_2O)_n \longleftarrow CO_2$

$Ca(HCO_3)_2 \longrightarrow CaCO_3 \sim PO_4 + H_2O + CO_2$ Epilimnion

Metalimnion

$O_2 \longrightarrow H_2O$ *Thermocline*
$H_2S \overset{e^-}{\longrightarrow} S$
$Mn^{+2} \longrightarrow Mn^{+3}$

Chemolithotrophy

**Aerobic Respiration
Anaerobic Respiration
Fermentation**

Hypolimnion

$(CH_2O)_n \longrightarrow CO_2$ **PO4**

$O_2 \overset{e^-}{\longrightarrow} H_2O$
$X_2 \longrightarrow H_2X$
$Mn^{+3} \longrightarrow Mn^{+2}$
$S \longrightarrow H_2S$

$CaCO_3 \sim PO_4 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2 + PO_4$

Calcium Carbonate Dissolution

Phosphorus cycling dynamics are different in hard water lakes. In a hard water lake, internal phosphorus cycling tends to be controlled by the carbonate buffering system. Water column removal of phosphorus (P) occurs when carbon dioxide (CO_2) is consumed by photosynthesis in surface waters. Removal of CO_2 disrupts the equilibrium between carbon dioxide and bicarbonate. Calcium carbonate precipitates from surface waters to reestablish equilibrium conditions. This process is called "epilimnetic decalcification" and results in the removal of large amounts of phosphorus associated with carbonate complexes (see Wetzel 1975). Unfortunately, this process doesn't occur in softer water lakes (pH must exceed 8.3). Sediment P release in hard water lakes also tends to be a function of "non-equilibrium" of the carbonate system. As CO_2 increases in bottom strata, pH decreases due to carbonic acid formation, and a disequilibrium occurs in the opposite direction. Calcium carbonates are dissolved in order to reestablish equilibrium. This results in significant sediment phosphorus release from its previous association with carbonates. Phosphorus release from sediments and precipitation from the water column tend to be a functions of carbonate system equillibria as effected by the accumulation of carbon dioxide by lake community respiration and photosynthetic carbon dioxide uptake, respectively. Unlike the "iron-controlled" system described above, neither sediment release nor water column removal is driven directly by oxidation-reduction reactions. Rather, these processes are driven by free carbon dioxide - carbonate equilibria as controlled the biological processes (respiration and photosynthesis).
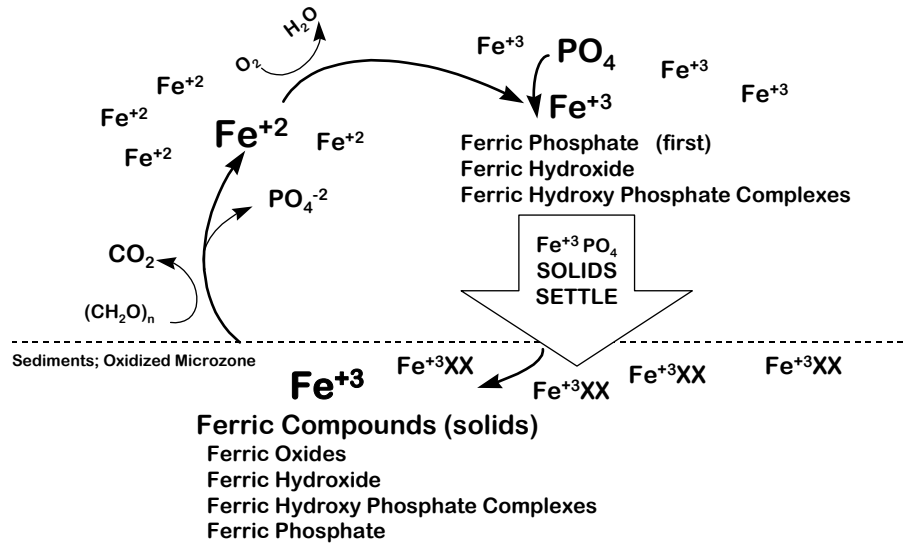
Eutrophic Lakes of Intermediate Hardness:
Weak Chemical Phosphorus Removal Mechanisms

**Downward Coprecipitation
of Ferric Iron and
Phosphorus very limited due to
Fe Deficiency**

**Epilimnetic Decalcification
due to photosynthetic CO2 uptake
very limited in softwater**

Epilimnion

Metalimnion

Thermocline

**Aerobic Respiration
Anaerobic Respiration**

PO4

Hypolimnion

$(CH_2O)_n \longrightarrow CO_2$

$O_2 \xleftarrow{e^-} H_2O$

Fe^{+3}~*PO4* $\xrightarrow{e^-}$ Fe^{+2}

$S \xrightarrow{e^-} H_2S$

FeS

Iron Deficiency:
**Iron is permanently removed as
insoluble ferrous sulfide
and no longer participates in
respiration as an ATEA
or as a P-Binding Agent**

In soft water lakes which have experienced a "eutrophic productivity level" for many years, the chemical mechanisms for phosphorus removal from the water column are weak. Such lakes are not hard enough for epilimnetic decalcification to remove significant amounts of phosphorus, yet sediment release is high due to CO_2 production and pH decreases from respiration. An iron deficiency appears to be common in eutrophic lakes of low-to-moderate hardness because sulfur dominates as an ATEA, producing hydrogen sulfide which is very toxic to most biota, and which permanently removes iron as ferrous sulfide precipitate. High sediment P release rates, and low water column P removal rates contribute to the high observed phosphorus concentrations in such lakes.

A Closer Look:

Changes in Respiration Systems (Fe and S) in response to Eutrophication

• *Ferrous Iron is typically in excess compared to phosphorus.*
• *Iron is precipitated as phosphate before hydroxide is formed.*

H_2O

O_2

Fe^{+3} PO_4 Fe^{+3} Fe^{+3}

Fe^{+2}

Fe^{+2}

Fe^{+2} Fe^{+2} Fe^{+2} Fe^{+3}

Fe^{+2}

PO_4^{-2}

Ferric Phosphate (first)
Ferric Hydroxide
Ferric Hydroxy Phosphate Complexes

CO_2

$(CH_2O)_n$

$Fe^{+3} PO_4$
SOLIDS
SETTLE

Sediments; Oxidized Microzone

Fe^{+3} $Fe^{+3}XX$ $Fe^{+3}XX$ $Fe^{+3}XX$ $Fe^{+3}XX$
$Fe^{+3}XX$

Ferric Compounds (solids)
  Ferric Oxides
  Ferric Hydroxide
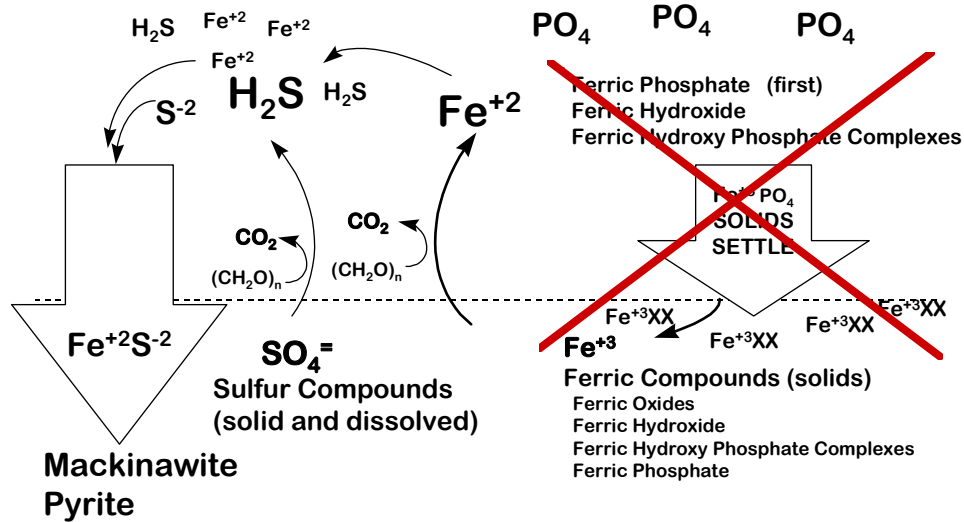 **Ferric Hydroxy Phosphate Complexes**
  Ferric Phosphate

• *Ferric Iron gives sediments a "Phosphorus Binding Capacity".*

Einsele (1936,1938)
Hutchinson (1941)

 In soft water lakes which exhibit enough respiration demand to exceed aerobic capacity, but which have not been highly eutrophic for many years, iron tends to be the dominant ATEA in anaerobic respiration. Much more iron than phosphorus is released to the hypolimnion due to anaerobic respiration. When reduced ferrous iron is again oxidized to insoluble ferric iron it settles out of the water column, removing phosphorus from lake water. This is a very important nutrient removal mechanism.

 As respiration demand continues to increase due to increasing amounts of organic matter which must be respired (due to eutrophication) eventually the amount of iron available as an ATEA is exceeded. The next available ATEA is sulfur, which is reduced to hydrogen sulfide. Among the impacts of this is the permanent loss of iron from the ATEA pool. Hydrogen sulfide reacts with reduced ferrous iron to form insoluble ferrous sulfide (see Roger Doyle, 1968). Note that the iron so deposited remains in a reduced oxidation state (ferrous). It is no longer available to participate as an ATEA in lake respiration, nor is it available to oxidation to ferric iron with the subsequent benefit of phosphorus removal from lake water.
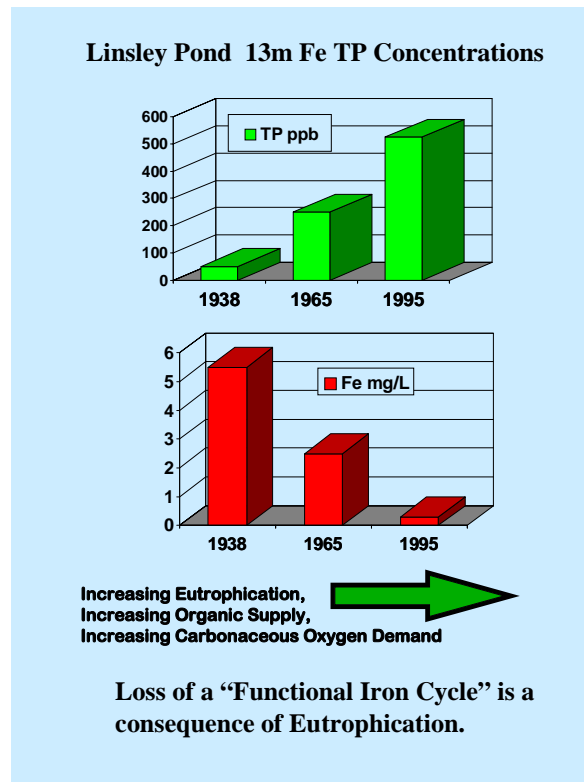
- *Iron no longer participates in anaerobic respiration (it is permanently deposited as ferrous sulfide).*
- *Iron no longer cycles between the sediments and the water column.*
- *Iron no longer removes phosphorus from the water column, (phosphorus is left behind in the water).*
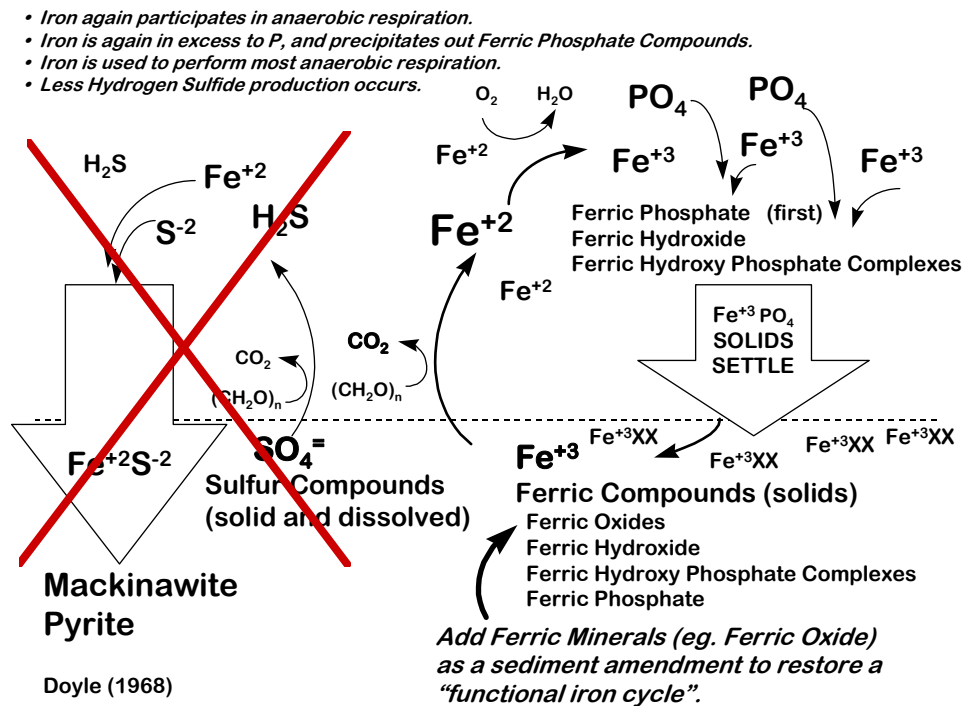- *More Hydrogen Sulfide production occurs to replace the respiration role previously filled by iron.*

H_2S Fe^{+2} Fe^{+2}

Fe^{+2}

PO_4 PO_4 PO_4

S^{-2} H_2S H_2S Fe^{+2}

Ferric Phosphate (first)
Ferric Hydroxide
Ferric Hydroxy Phosphate Complexes

CO_2 CO_2

$(CH_2O)_n$ $(CH_2O)_n$

Ferric PO_4
SOLIDS
SETTLE

$Fe^{+3}XX$ $Fe^{+3}XX$ $Fe^{+3}XX$

$Fe^{+2}S^{-2}$

$SO_4^=$
**Sulfur Compounds
(solid and dissolved)**

Fe^{+3} $Fe^{+3}XX$

Ferric Compounds (solids)
Ferric Oxides
Ferric Hydroxide
Ferric Hydroxy Phosphate Complexes
Ferric Phosphate

**Mackinawite
Pyrite**

Doyle (1968)

- *The Phosphorus Binding Capacity of sediments is lost.*
- *AlSO$_4$ = ALUM, Might the sulfate load have an adverse impact?*

The research performed by Roger Doyle at Linsley Pond in Connecticut was (and is) very prominent in the limnological literature.   Research over 60 years at Linsley Pond has identified some of the relationships between eutrophication, iron-sulfur systems, and phosphorus cycling.

Linsley Pond 13m Fe TP Concentrations

TP ppb

600
500
400
300
200
100
0

1938   1965   1995

6
5
4
3
2
1
0

Fe mg/L

1938   1965   1995

**Increasing Eutrophication,
Increasing Organic Supply,
Increasing Carbonaceous Oxygen Demand**

**Loss of a "Functional Iron Cycle" is a
consequence of Eutrophication.**

As Linsley Pond experienced eutrophication (it was oligomesotrophic in 1939, highly eutrophic in 1995) internal phosphorus loading increased while hypolimnetic iron accumulation decreased. Iron had become depleted as an ATEA, lost permanently to the sediments as ferrous sulfide. Linsley Pond is now a hydrogen sulfide producing lake, because available iron has been depleted. This is probably what occurred in Culver Lake over many years of eutrophication. Fortunately, restoration of iron availability at the bottom of a lake to return an iron-dominated ATEA pool rather than hydrogen sulfide production is not difficult or expensive. Unfortunately the technique has not become commonplace, few lake diagnostic studies even study respiration rates, anaerobic respiration products, or even carbon dioxide production.

- *Iron again participates in anaerobic respiration.*
- *Iron is again in excess to P, and precipitates out Ferric Phosphate Compounds.*
- *Iron is used to perform most anaerobic respiration.*
- *Less Hydrogen Sulfide production occurs.*

Doyle (1968)

Add Ferric Minerals (eg. Ferric Oxide) as a sediment amendment to restore a "functional iron cycle".

The iron-ATEA pool can be restored by adding mineral ferric iron compounds as a sediment amendment. Iron would again be available as an ATEA and for phosphorus removal from the water column annually following stratification. Hydrogen sulfide production would be inhibited. Other iron compounds (such as ferric chloride) could also be used, as they now are being used in more water treatment plants. However, mineral iron supplement has been proposed because it is more "natural", only the iron used for respiration would be mobilized and there would be no "chloride impact".

Alum treatments have become quite popular in lake restoration. *For a variety of reasons it is believed that alum is more appropriate for use in hard water systems where sulfur is the dominant ATEA. Alum treatment may be less desirable in soft water lakes and for management of respiration systems.*

Why Iron Replenishment rather than Alum?

- **Alum Treatments add 1.3 lb of Sulfur for every 1.0lb of Aluminum.**
  This could further shift the respiration system toward Hydrogen Sulfide Production.

- **Ferric Iron Sediment Ammendments restore a "Functional Iron Cycle"**
  - **Although some P is released upon the reduction of iron to ferrous, if excess Fe^{+2} is released it will continue to remove P from the water column, this can have a longer term P control effect. P is only released from the reduction of P-containing ferric iron compounds.**
  - **Iron will supress Hydrogen Sulfide production, with much lower toxicity (H_2S is very toxic, iron is not).**

- **Al Floc is not redox active, no post-treatment water P removal.**
  Although the non-redox nature of the Al Floc is good for sediment inactivation, there is no subsequent water column P removal as with iron.

- **It is better for the bottom of a lake to operate in the iron cycle (or nitrogen cycle) than in the sulfur cycle.**

Natural Concentrations of Iron in the Hypolimnia of Lakes and Water Supply Reservoirs - Water Quality Standards

Understandably, the initial reaction to a suggestion to add iron to a lake ecosystem could be that it is adding a "pollutant". After all, iron content in discharges to receiving surface waters is regulated to low levels.   The difficulty here is that our regulatory programs are designed to protect surface waters from "pollution", but don't consider that under some environmental conditions what we consider to be "pollutants" are actually very natural and beneficial substances. Our permit programs don't account for what is "good" in hypolimnetic waters, below a strong thermocline, that are totally devoid of oxygen for 4 months. The water quality standards we regulate to often do not consider certain natural environments, especially those which operate anaerobically.

One of the most interesting examples is Lake Waramaug, CT. In the late 1970's and early 1980's Lake Waramaug was eutrophic and experienced intense blooms of Cyanobacteria (esp. *Anabaena sp.*). A hypolimnetic treatment system was designed and built through the Clean Lakes Program (Section 314 of the US Clean Water Act). The system withdraws deep hypolimnetic water from the lake, puts it through a series of holding basins, and returns it to the top of the hypolimnion immediately below the thermocline. Subsequent monitoring and a Phase III Clean Lakes Research study determined that very significant reductions in lake phosphorus concentrations occurred. The lake reverted to a

more mesotrophic condition, largely due to the use of iron generated by lake anaerobic respiration as a precipitation agent for phosphorus. The high hypolimnetic iron content was viewed as a healthy feature and was used to restore the lake.   Indeed, it is likely that soft water lakes that have been eutrophic for many years have become deficient in available iron. Restoration and management of respiration systems in lakes may become very common in the future.