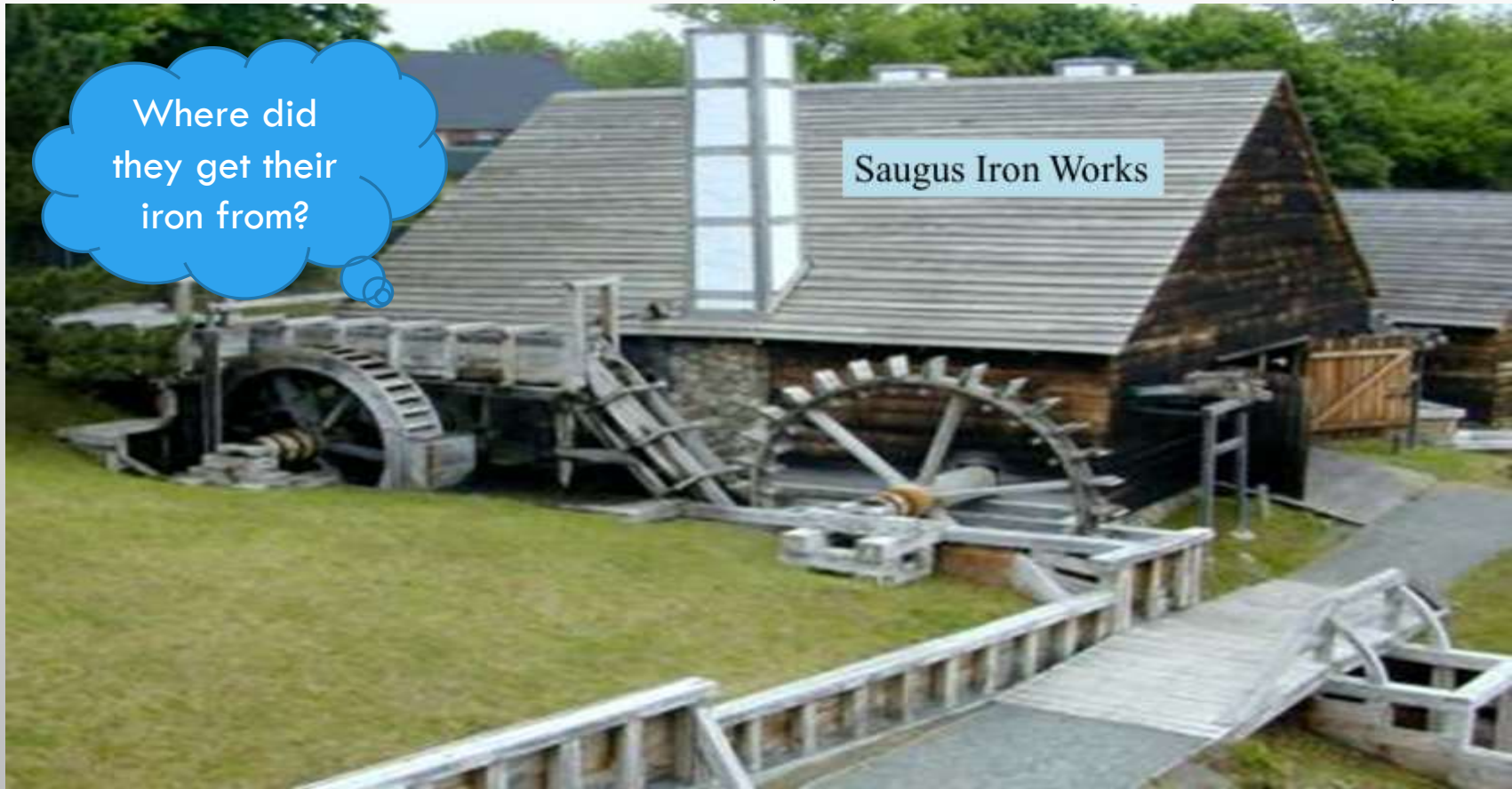


LAKE IRON NODULES AN “INDEX MINERAL” TO ASSESS THE IMPACT OF SULFATE/SULFIDE ON SURFACE WATER AND SEDIMENT QUALITY OVER TIME IN NEW ENGLAND LAKES, PONDS AND RIVERS (PRE-1800S TO TODAY)



Reference: Saugus Iron Works National Park, website photographs

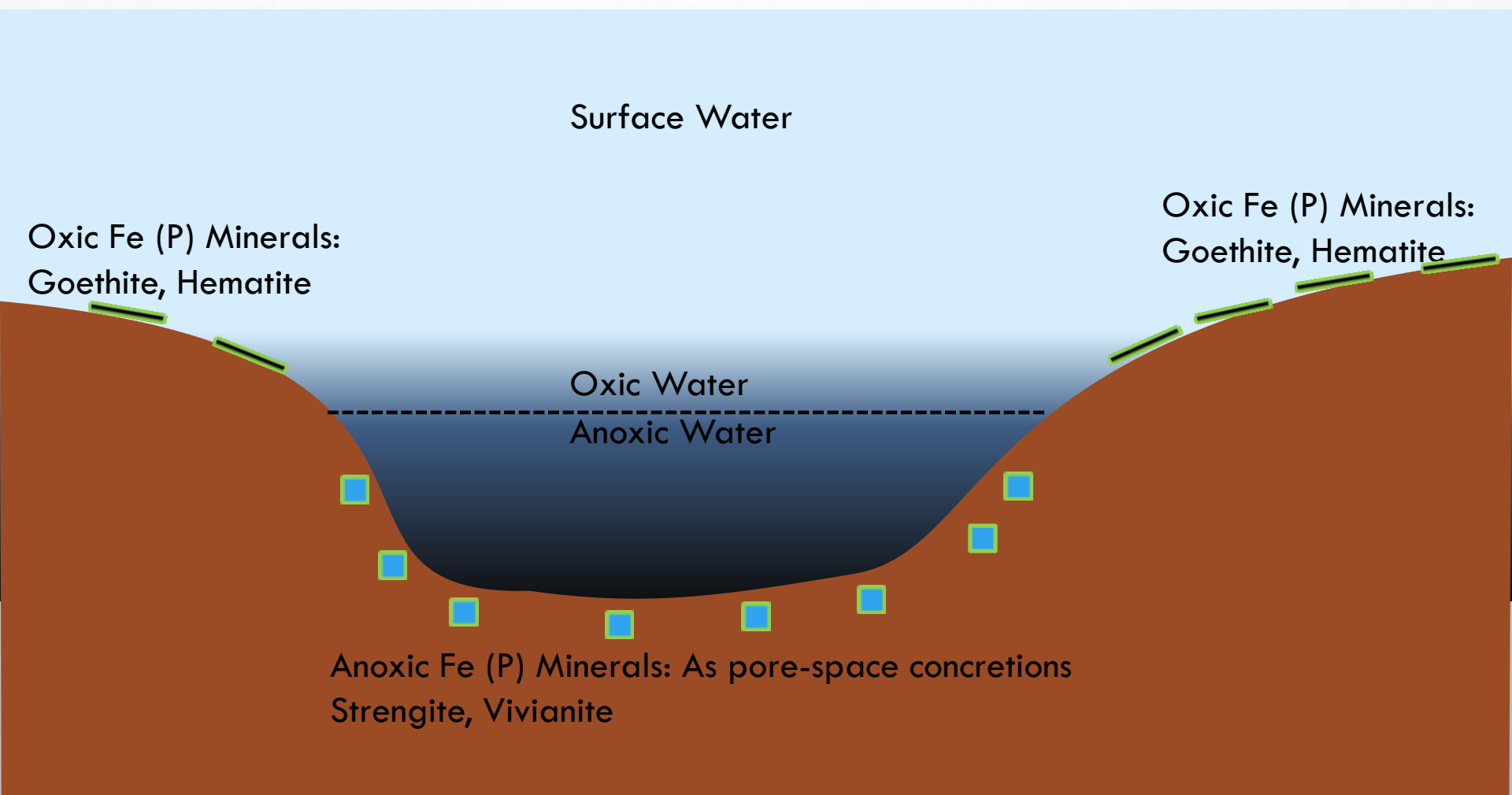
- JONATHAN B. HIGGINS, CPG, LSP
- PRINCIPAL EARTH SCIENTIST, HIGGINS ENVIRONMENTAL ASSOCIATES, INC. MARCH 1, 2020

WHAT ARE LAKE IRON NODULES?

- AN IRON-ENRICHED CONCRETION, OFTEN CONTAINING MORE THAN 30 PERCENT IRON BY WEIGHT. THERE ARE BOTH OXIC AND ANOXIC FORMS. OXIC IRON NODULES FORM AT THE SEDIMENT/WATER INTERFACE (SWI). THEY ARE COMMONLY COMPOSED OF THE MINERALS GOETHITE AND HEMATITE. ANOXIC IRON NODULES FORM IN ANOXIC SEDIMENT PORE-SPACE. THESE ARE COMMONLY EITHER SIDERITE OR THE FERROUS PHOSPHATE HYDRATED MINERALS: VIVIANITE AND STRENGITE.
- IRON NODULES ARE A NATURAL SINK FOR PHOSPHORUS (CAN TAKE UP TO 4 % BY WEIGHT) IN LAKES, PONDS AND RIVERS.
- PICTURED HERE ARE OXIC LAKE IRON NODULES COLLECTED BY THE PRESENTER IN NOVA SCOTIA.



WHERE ARE LAKE IRON NODULES FOUND IN LAKES?



Simplified Figure for Illustrative Purposes Only

© Higgins Environmental Associates, Inc., Amesbury, Massachusetts, 978 834-9000. All Rights Reserved.

OXIC LAKE IRON NODULE = INDEX MINERAL?

- **INDEX MINERALS LIKE FOSSILS SHOULD BE DISTINCTIVE, WIDELY DISTRIBUTED, AND ABUNDANT OR ABSENT UNDER CERTAIN GEOLOGIC CONDITIONS.**

OXIC LAKE IRON NODULES ARE:

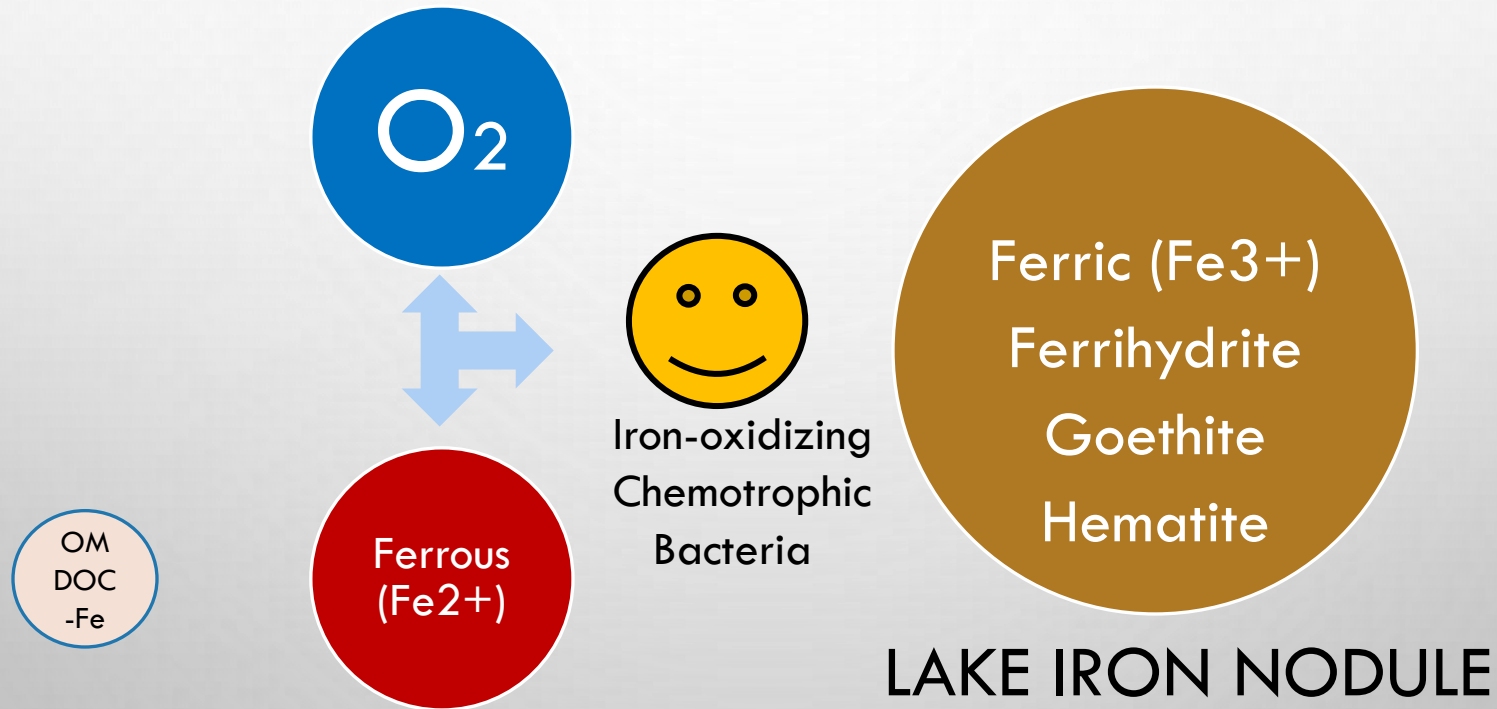
- PLANAR AND CAN GROW TO LARGER THAN THE PALM OF YOUR HAND.
- DISPLAY CONCENTRIC GROWTH RINGS LIKE A TREE'S CROSS-SECTION.
- WHEN PRESENT, CAN BE FOUND IN "BEDS" WITH NUMEROUS OTHER NODULES NORTH OF LATITUDE 40^{ISH}.
- FORM JUST OFF THE SEDIMENT SURFACE AND CAN BE SAMPLED WITH A BASKET RAKE OR SIMILAR.
- CONTAIN GREATER THAN 20 PERCENT (200,000 MG/KG IRON).
- ABSENT IN ANOXIC AREAS OF LAKES.
- ABSENT WHEN IRON:SULFUR RATIO LESS THAN 1 IN SEDIMENT OR WHEN SULFATE EXCEEDS 200 UM IN OVERLYING WATERS**

** THE OCCURRENCE OF OXIC OR ANOXIC LAKE IRON NODULES DEPENDS ON THE IRON TO INORGANIC SULFUR RATIO. IN ANOXIC SEDIMENTS, THE RATIO NEEDS TO BE GREATER THAN 1. IN OXIC SEDIMENTS, THE RATIO NEEDS TO BE MUCH HIGHER (E.G., MUCH LESS SULFUR) THAN 1 DUE TO THE "CRYPTIC SULFUR CYCLE"; IN OXIC WATERS, SULFATE CONCENTRATIONS OF GREATER THAN 200 MICROMOLS HAS BEEN SHOWN TO LEAD TO REDUCTION OF OTHERWISE GEOCHEMICALLY- STABLE GOETHITE AND HEMATITE IRON OXIDE (LAKE IRON NODULE) MINERALS. INORGANIC SULFUR NEEDS TO BE REMOVED FROM OXIC SEDIMENTS AND LIMITED TO THE EXTENT POSSIBLE IN SURFACE WATERS.

P.S. ANOXIC IRON NODULES (VIVIANITE) TURN A DEEP BLUE COLOR UPON EXPOSURE TO OXYGEN AND SUNLIGHT.

OXIC LAKE IRON NODULES FORM BY BIOGEOCHEMICAL PROCESSES IN WATER INVOLVING IRON, OXYGEN AND IRON OXIDIZING CHEMOTROPHIC BACTERIA.

THEY GROW ABOUT 1 TO 20 MILLIMETERS PER YEAR OVER A RANGE IN pH FROM 4 TO 10 UNITS



Simplified and Illustrative Process

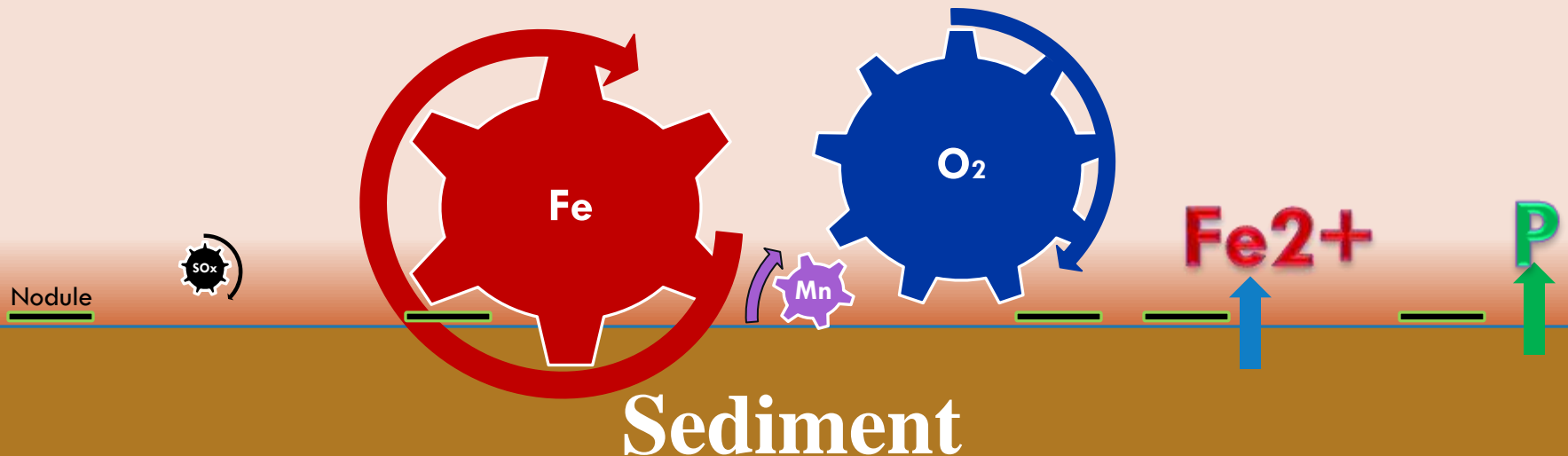
WHERE ARE THEY FORMED? – CURRENTLY AND PRE-1800s ON A NUCLEATION SITE 1 TO 2 CENTIMETERS ABOVE THE SEDIMENT SURFACE

Oxic Lake Iron Nodule Biogeochemical Setting (today and by analogy, pre-1800s in New England)

Limited Sulfate Concentrations in Surface Water (<200uM) or Sediments (Fe/S >>1)

DOC/Fe-rich water, reduced water clarity (more of a tea-colored water). Lake iron nodules can incorporate up to 4% (40,000 mg/kg) phosphorus by weight. Sulfates/Sulfides and anoxia are documented limiting factors.

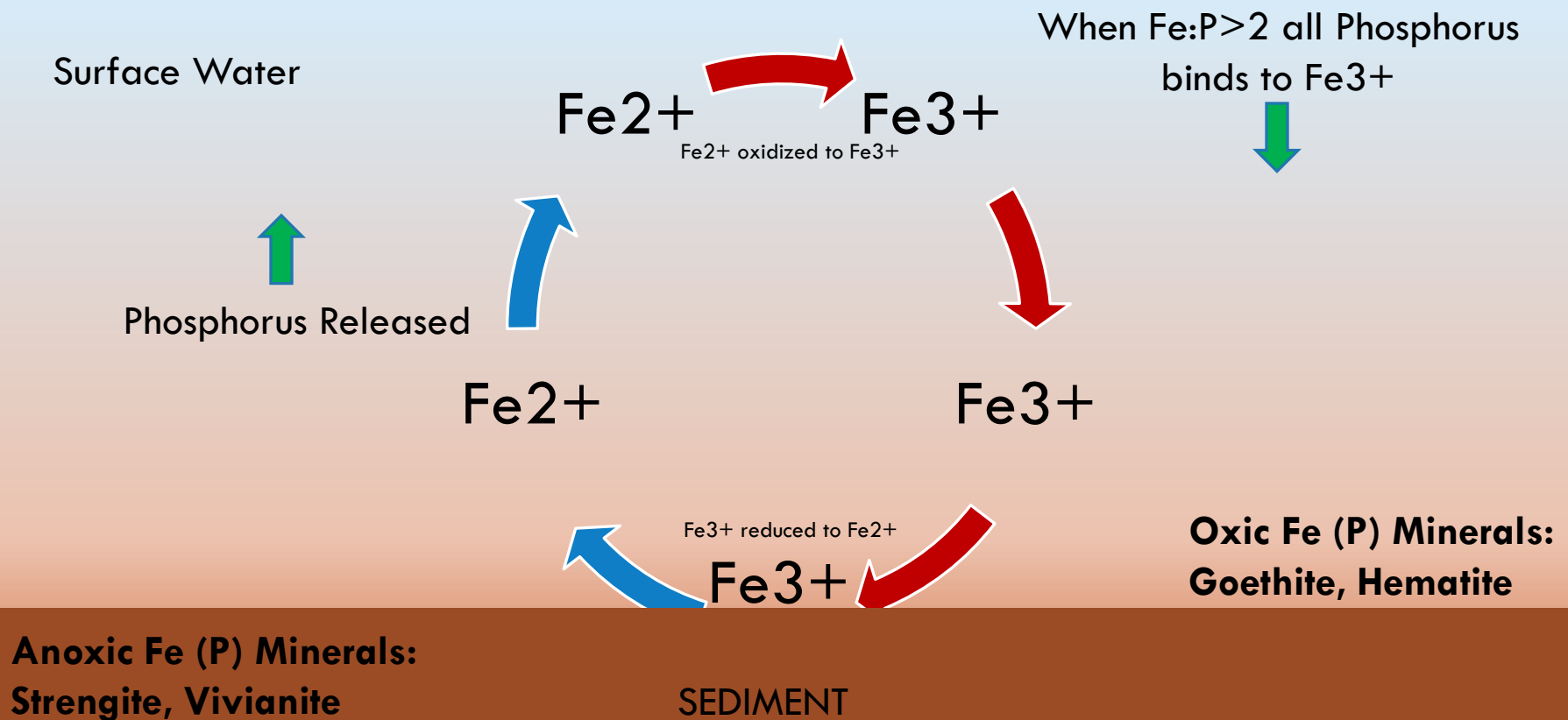
Oxygenated Surface Water



Simplified Figure for Illustrative Purposes Only

© Higgins Environmental Associates, Inc., Amesbury, Massachusetts, 978 834-9000. All Rights Reserved.

IRON CYCLE (WITHOUT SULFATES/SULFIDE)- DRIVEN BY BIOTIC AND ABIOTIC PROCESSES



PAST RECORDS –

- 1614: CAPT. JOHN SMITH DOCUMENTED THE PRESENCE OF IRON NODULES IN WATERS OF THE MASSACHUSETTS BAY COLONY (NEAR PROVINCETOWN).
- EARLY 1600s: EXPLORATION JOURNALS BY MINERAL MEN HIRED BY VENTURE CAPITALISTS FROM ENGLAND TO ASSESS THE MINERAL RESOURCES OF EARLY NEW ENGLAND. THESE RECORDS INCLUDE DOCUMENTATION OF LOCAL BOG AND LAKE IRON NODULES RESOURCES. 1654+ SAUGUS IRON WORKS FOLLOWED BY OTHER IRON WORKS WERE STARTED IN MASSACHUSETTS.
- 1770: EXPORT OF IRON PRODUCTS BY THE COLONIES TO BRITAIN TRAILED ONLY TOBACCO IN VALUE AND EXCEEDED TWICE THE EXPORT VALUE OF GRAIN AND WOOD.
- 1793: DR. FORBES OF MASSACHUSETTS NOTICED THAT THE RAYNHAM FORGE HAD BEEN HARVESTING ORE FROM AN ADJACENT POND FOR EIGHTY YEARS WITH LITTLE EVIDENCE OF A DECREASED SUPPLY. DR. FORBES STATED “THERE MAY COME A TIME WHEN ITS AS EASY TO RAISE A BED OF BOG ORE AS A BED OF CARROTS”.
- BY THE 1840S, COMPETITION FROM LOWER PRICED IRON SMELTED WITH MINERAL COAL IN PENNSYLVANIA PUT MANY NEW ENGLAND IRON WORKS OUT OF BUSINESS.

SOURCES: *AMERICAN IRON 1607-1900*, R.B. GORDON, 1996; SMITHSONIAN INSTITUTE RECORDS; BUSINESS RECORDS BY IRONWORKS IN AMESBURY, BRAINTREE, CONCORD, RAYNHAM/TAUNTON (120 YEARS), ROWLEY, AND SAUGUS (20 YEARS).

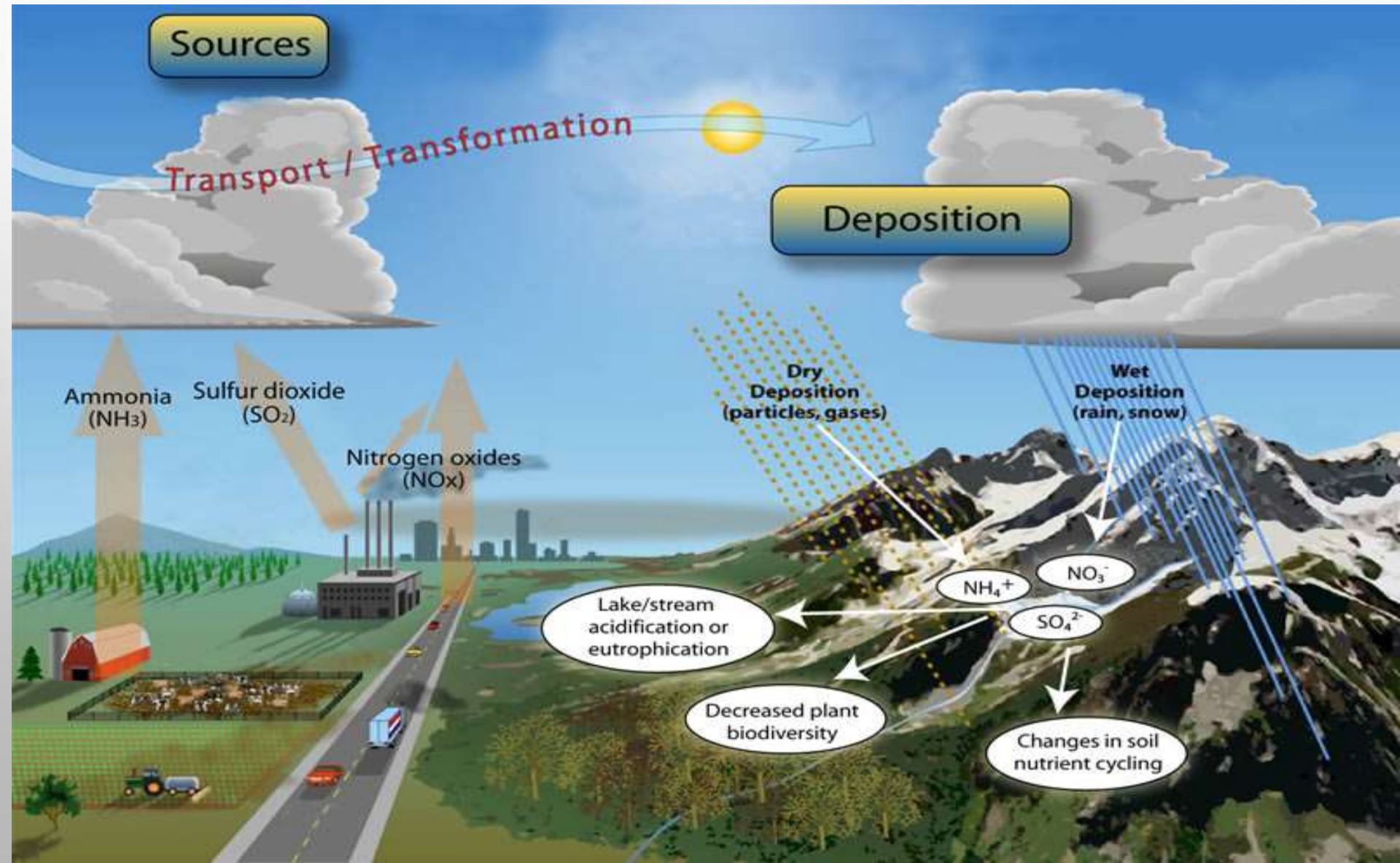
BY YEAR 2010 -

TO MY KNOWLEDGE, THERE
ARE CURRENTLY NO LAKE OR BOG
IRON NODULES SOUTH OF LAKE
WINNIPESAUKEE

RED LINE MARKS
TENTATIVE KNOWN LIMITS
OF IRON NODULES.

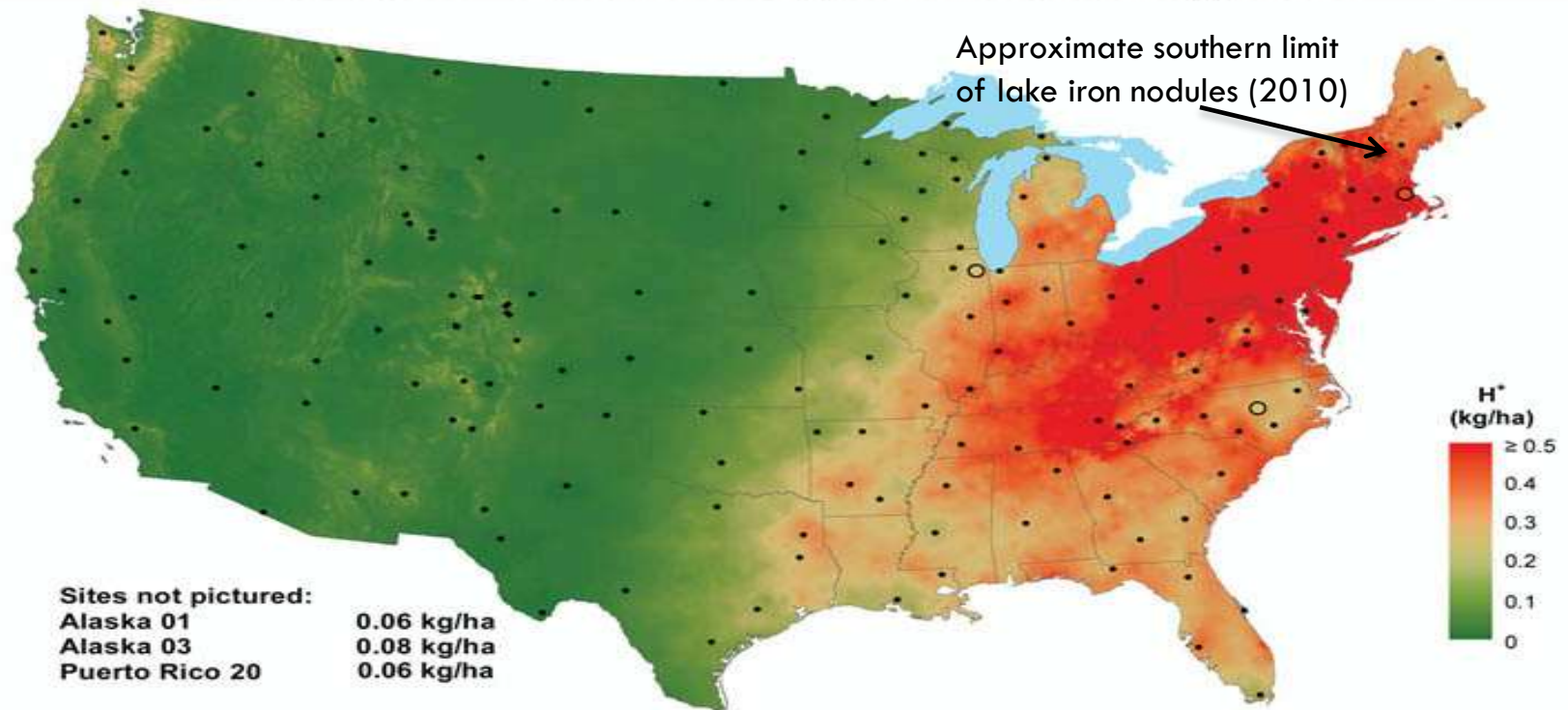


WHAT HAPPENED TO THE IRON NODULES?

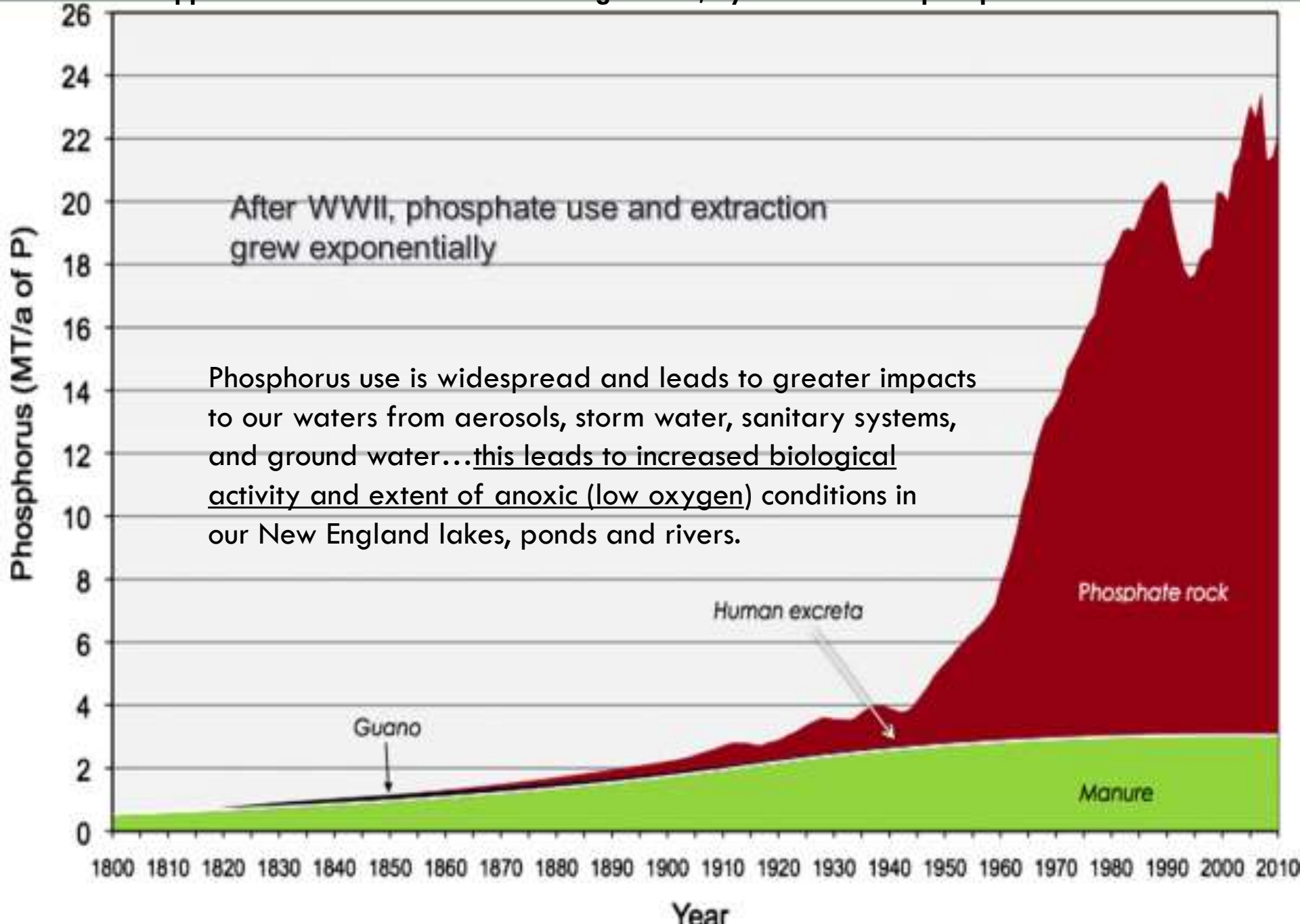


NITRATE AND SULFATE IMPACTS TO SURFACE WATER, SOIL AND SEDIMENT

Hydrogen ion wet deposition from measurements made at the Central Analytical Laboratory, 1994



Its not just acid rain deposition. Use of Phosphorus has significantly increased since 1945 and would tend to support more anoxic events – favoring anoxic, hydrated ferrous phosphate minerals

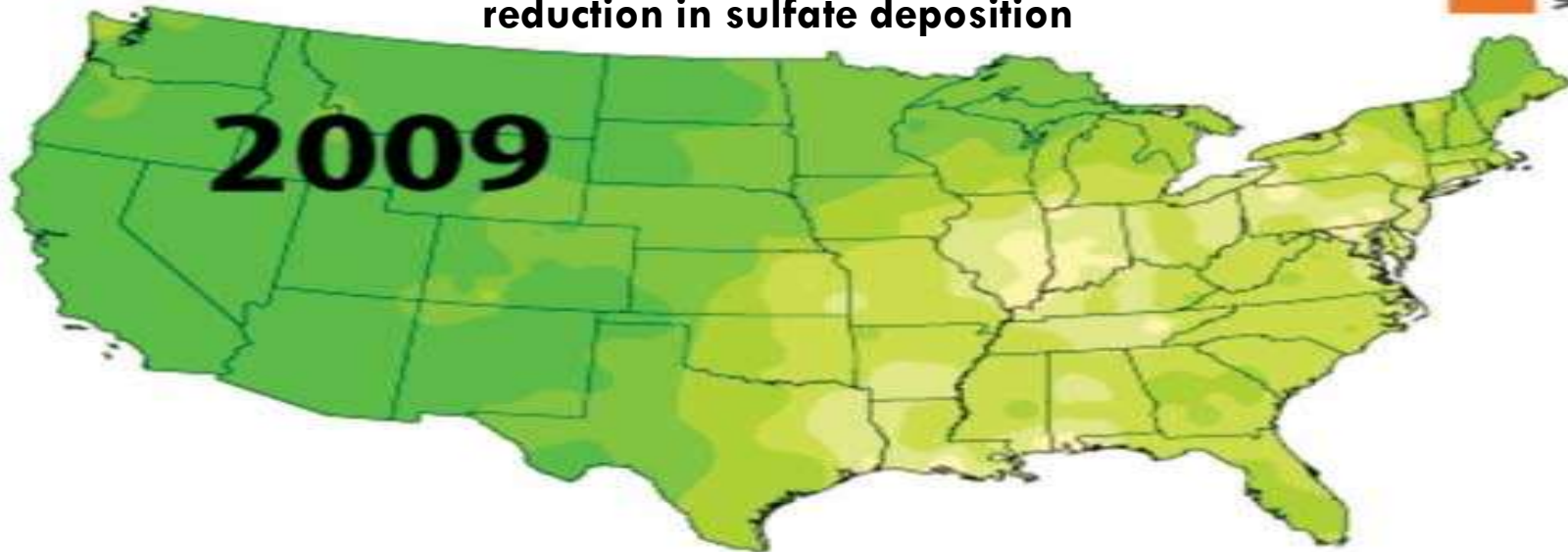


CHANGES IN GEOCHEMISTRY - SULFATE DEPOSITION REDUCED

Approximate southern limit
of lake iron nodules (2010)

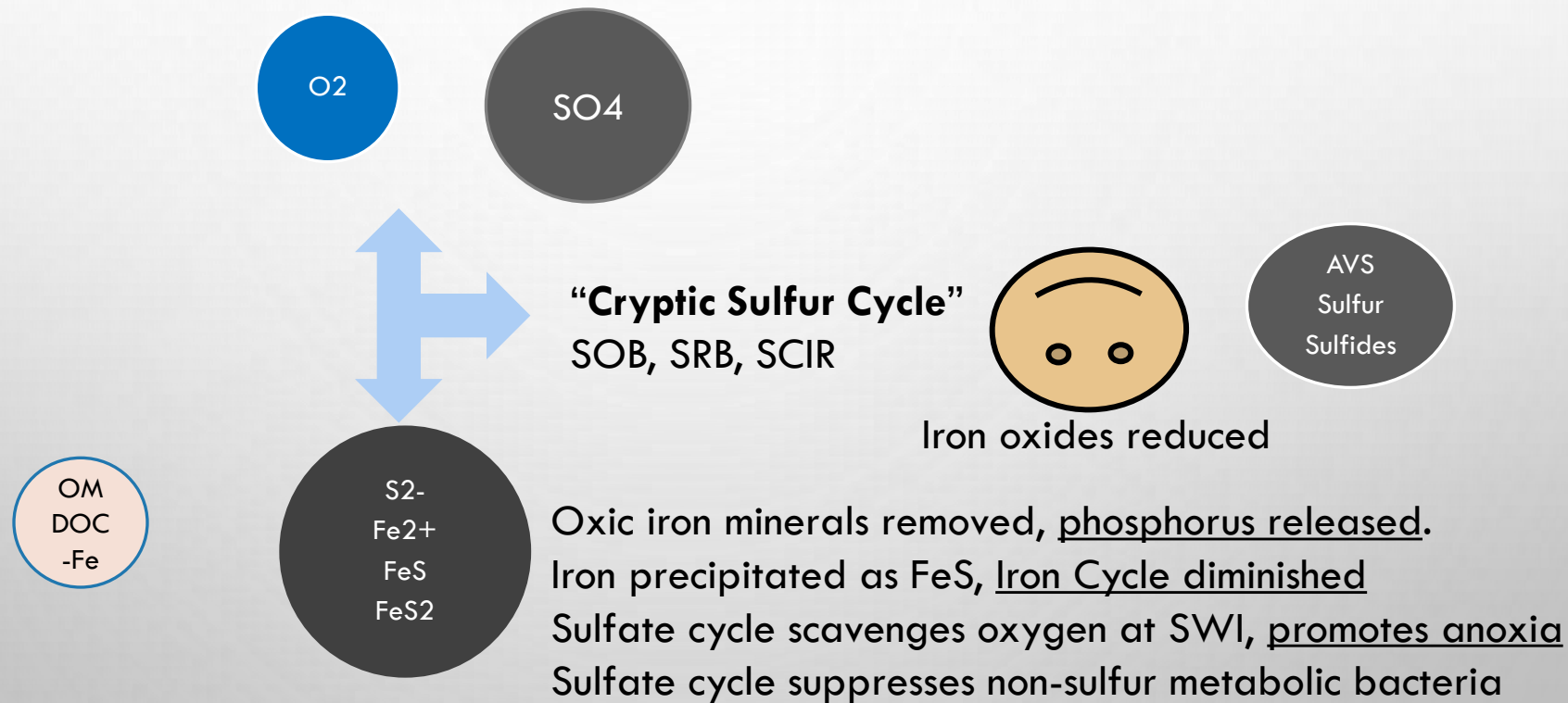


**1990 Clean Air Act Amendments – significant
reduction in sulfate deposition**



HOWEVER, SULFATE/SULFIDE IMPACTS TO SEDIMENT REMAIN (30+ YEARS AND COUNTING SINCE THE 1990 CAA)

FE³⁺, FERRIHYDRITE, GOETHITE AND HEMATITE ARE REMOVED BY BIOGEOCHEMICAL PROCESSES INVOLVING SULFATE/SULFIDE, BACTERIA AND ANOXIC CONDITIONS.



Simplified and Illustrative Process

“DIMINISHED AQUATIC IRON CYCLE” - SULFIDE REDUCES IRON OXIDE MINERALS AND SHUNTS IRON INTO SEDIMENT AS IRON SULFIDE

Sulfide removes Fe binding capacity for Phosphorus; P released.
Fe removed as iron sulfide minerals. Fe cycle diminishes.

Sulfide reduces oxygen content of sediment, porewater and of water near the sediment water interface.

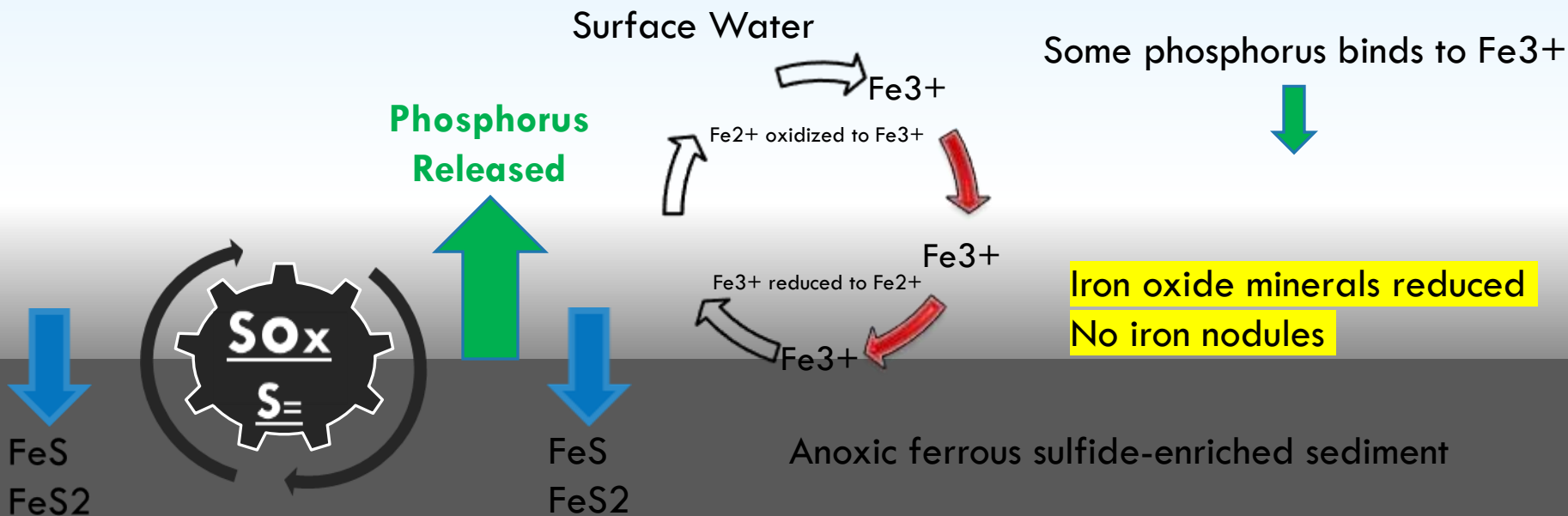
Phosphorus taken up by Algae and Plants

↓ Detritus/settling

Some phosphorus binds to Fe³⁺



Iron oxide minerals reduced
No iron nodules



Simplified Figure for Illustrative Purposes Only

© Higgins Environmental Associates, Inc., Amesbury, Massachusetts, 978 834-9000. All Rights Reserved.

CIRCA 1970 – 2010 BIOGEOCHEMICAL SETTING

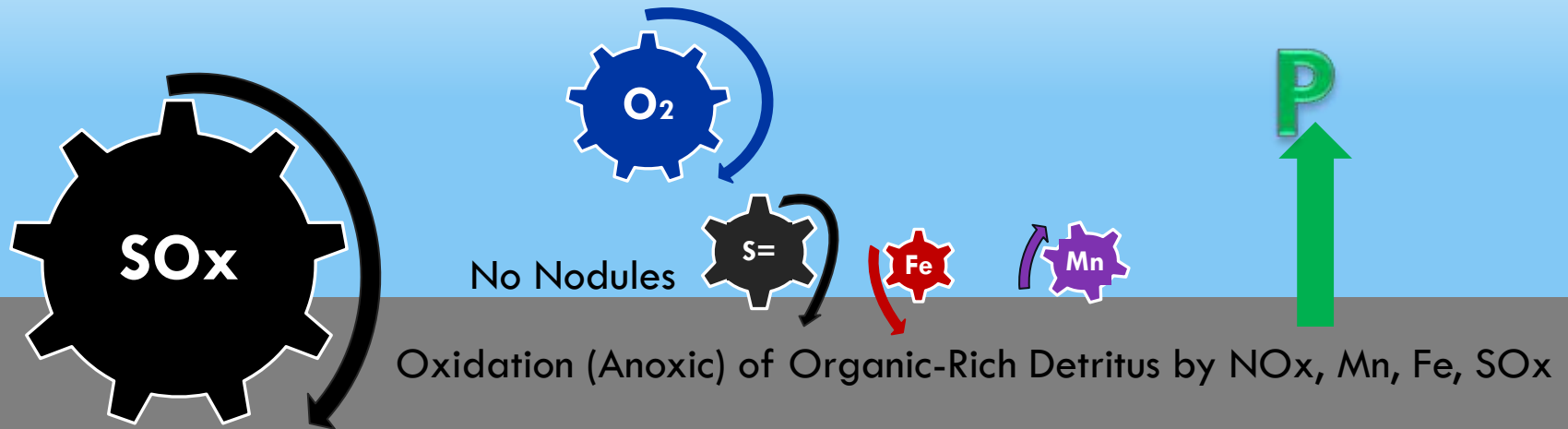
PALEOLIMNOLOGICAL STUDIES HAVE DOCUMENTED FOUR TIMES AS MUCH SULFUR IN SEDIMENT IN SOUTHERN NEW ENGLAND SINCE THE 1940s AS COMPARED TO PRE-1900s

Sulfate- and Phosphorus- Enriched Surface Water and Sediment

DOC/Fe-depleted, increased water clarity, increased phototrophs (algae and rooted plants)

Increased production and sedimentation of organic-rich detritus containing nutrients.

Decreased oxygen with depth. Increased release of phosphorus from sediment.



No Iron Nodules – Replaced by Iron Sulfide Minerals (FeS , greigite Fe_3S_4 , and pyrite FeS_2). Iron Cycle Diminished Significantly.



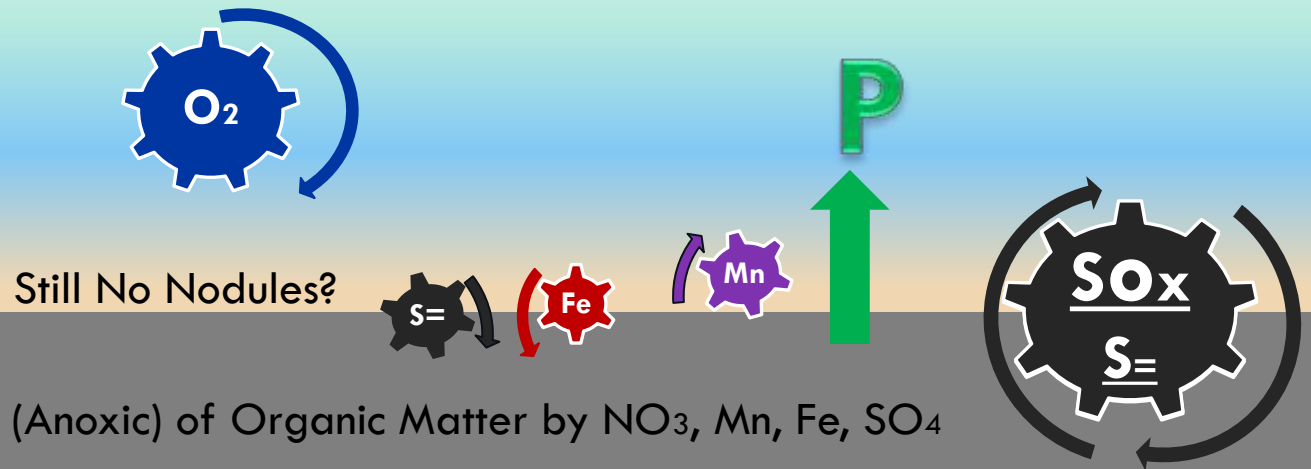
Anoxic, sulfide-enriched Sediment and Pore Water

CIRCA 2020 – MY INTERPRETATION AN IMPROVEMENT SINCE 2010

Phosphorus-Enriched, Sulfate-Low to Moderate in Surface Water but Sulfate/Sulfide still Moderate to High in some Sediments – particularly in Southern New England.

DOC/Fe increasing and water clarity decreasing (more tea-colored) from North-South in New England.

Seasonal low oxygen still common in deeper parts of lakes and ponds.



No Iron Nodules – Replaced by Iron Sulfide Minerals



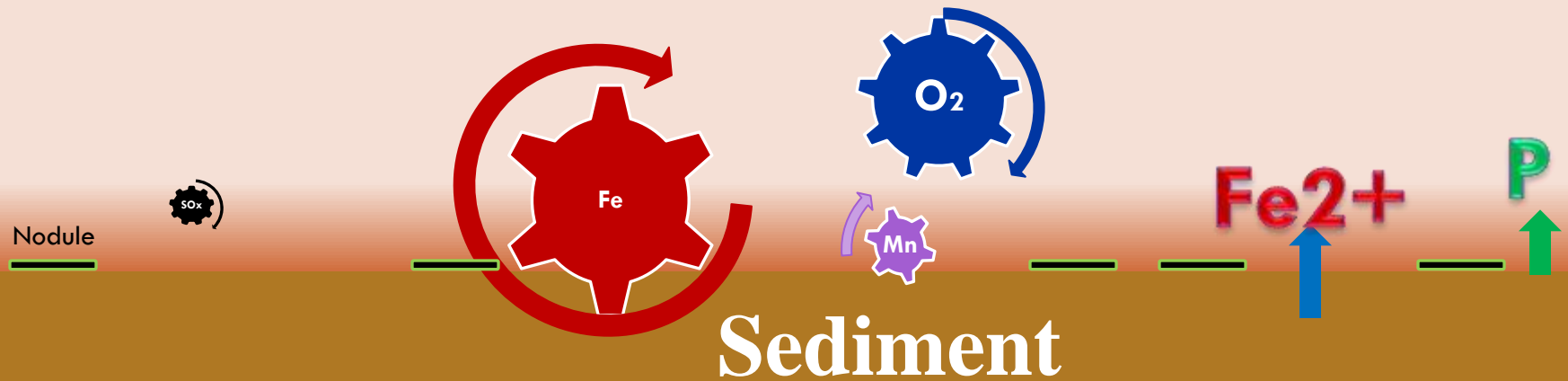
Anoxic, sulfide-enriched Sediment and Pore Water

GO BACK TO THE FUTURE? (BY REMOVING SULFATES AND EXCESS PHOSPHORUS)

Limited Phosphorus and Sulfate Concentrations in Surface Water

DOC/Fe-rich water, reduced water clarity (more of a tea-colored water), infrequent algae blooms. By removing excess sulfates and phosphorus in our sediment/waters, the natural aquatic iron cycle is restored. This promotes development of native microbial, plant and animal species and minimizes conditions favoring algae blooms and invasive species (clear water, sulfates and excess phosphorus). Oxic and anoxic lake iron nodules can be restored and serve as natural sinks for phosphorus.

Oxygenated Surface Water



TAKE AWAYS

- AS AN INDEX MINERAL, LAKE IRON NODULES (OXIC AND ANOXIC FORMS) HELP TO EVALUATE THE LONG TERM AND WIDESPREAD IMPACT OF SULFATE/SULFIDES ON OUR FRESHWATER RESOURCES .
- GIVEN THEIR HISTORICAL USE AND DOCUMENTED OCCURRENCE AS A PRE-1800s STRATEGIC MINERAL, THEY CAN ALSO BE CONSIDERED A “GATEWAY” MINERAL - ALLOWING US TO TRAVEL BACK IN TIME (PRE-1800S) AND TO INTERPRET THE QUALITY OF OUR FRESHWATER SEDIMENT AND WATER RESOURCES BEFORE WIDESPREAD SULFATE/SULFIDE POLLUTANT IMPACTS.
- WATER QUALITY RESTORATION GOALS NEED TO TAKE INTO ACCOUNT ONGOING BIOGEOCHEMICAL-IMPACTS BY SULFATES/SULFIDES TO OUR FRESHWATERS.
- NEGATIVE IMPACTS TO OUR FRESHWATER RESOURCES BY SULFATES/SULFIDES LAST FOR DECADES...AND COUNTING.

RECOMMENDATIONS

- INCLUDE IRON AND SULFUR/SULFATE/SULFIDE ANALYSIS IN OXIC AND ANOXIC SEDIMENT AND SURFACE WATER SAMPLING ASSESSMENTS
- ACCOUNT FOR SPATIAL AND TEMPORAL VARIATIONS IN IRON, SULFUR/NITROGEN AND PHOSPHORUS IN SURFACE WATER AND SEDIMENT SAMPLING PROGRAMS.
- PLEASE LET ME KNOW WHEN AND WHERE “NEW” LAKE IRON NODULES ARE FOUND.

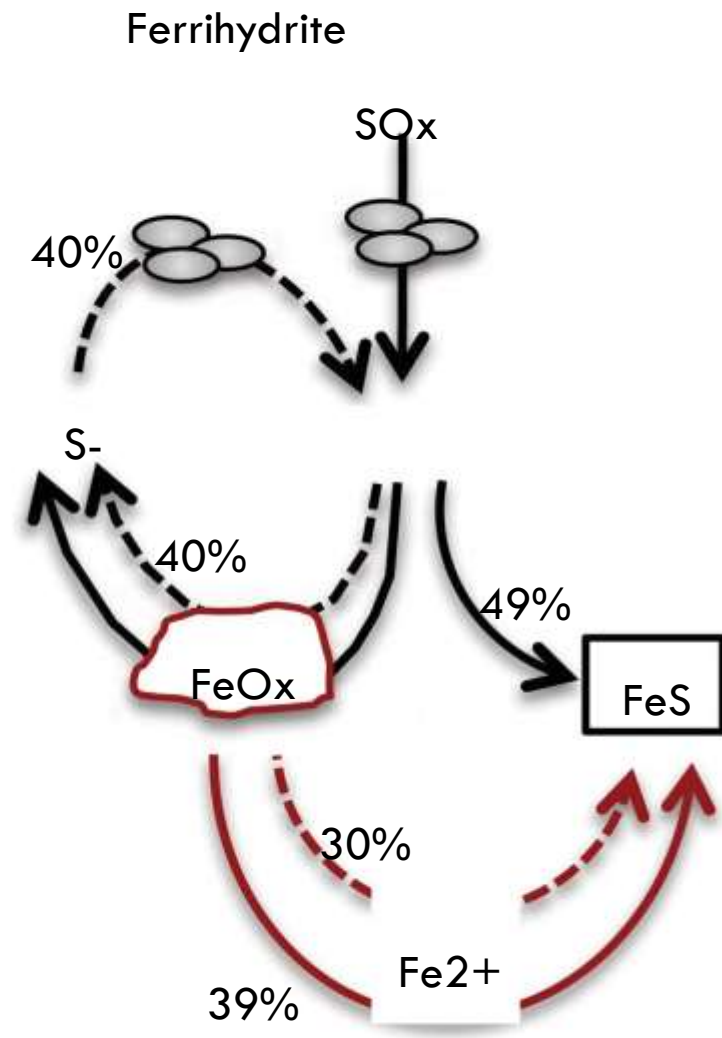
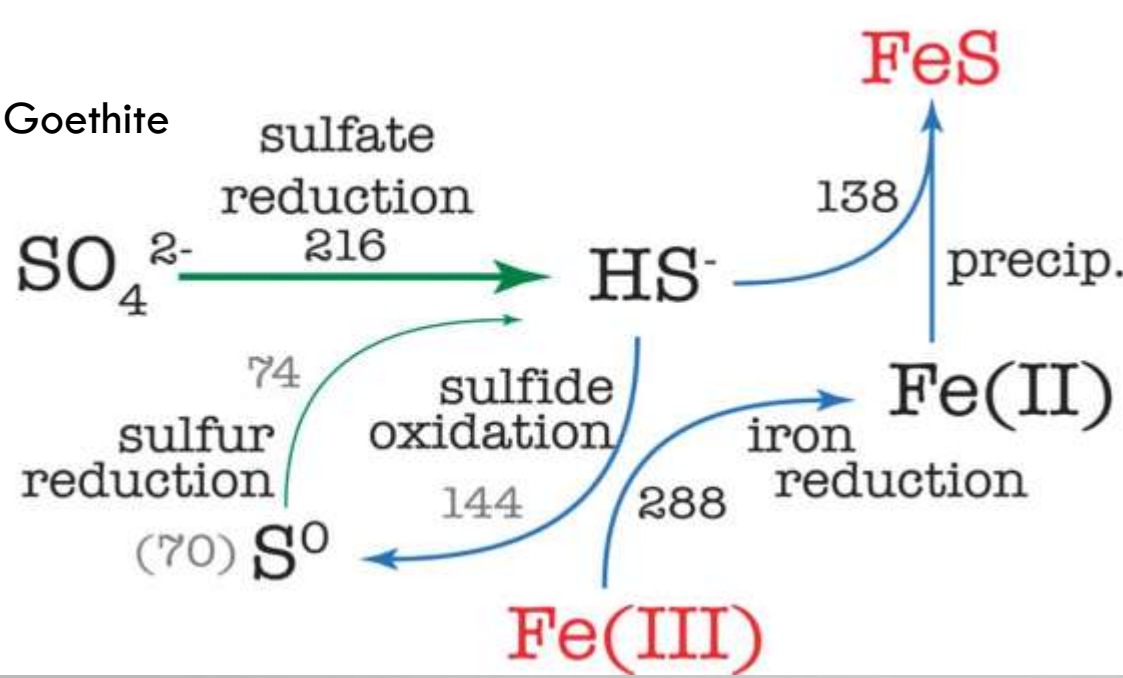
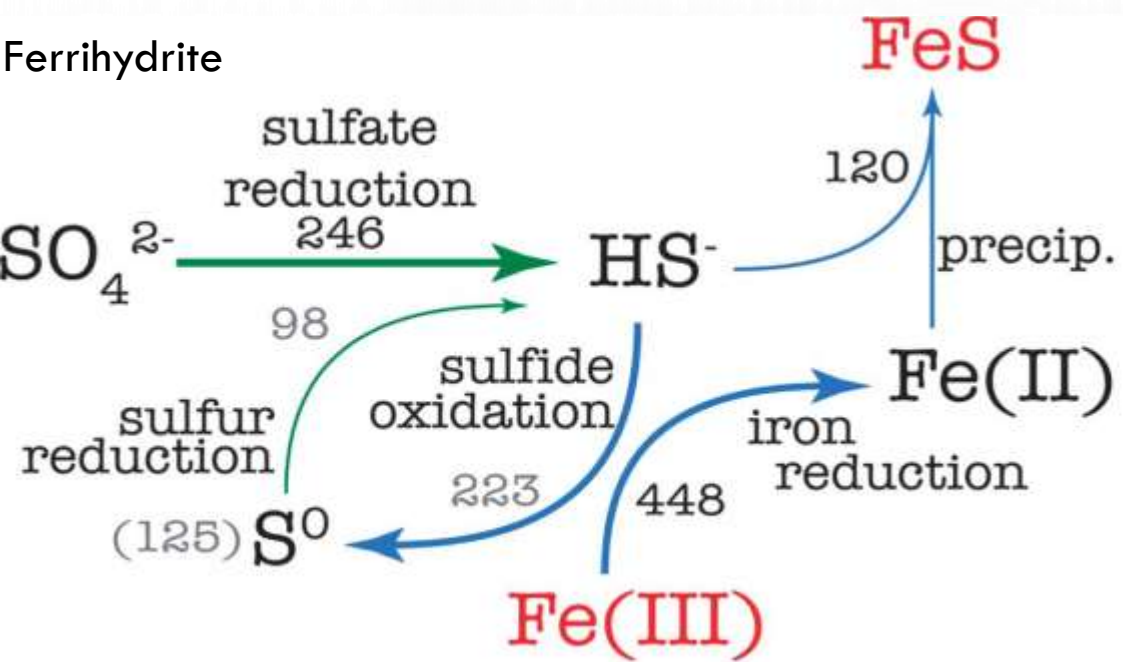
QUESTIONS?

CONTACT INFORMATION

Jonathan Higgins, CPG, LSP
Principal Earth Scientist
Higgins Environmental Associates, Inc.
19 Elizabeth Street, Amesbury, MA 01913
Ph: (978) 834-9000
Email: higginsenv@comcast.net
Web: www.higginsenv.com
Web: www.ppodtech.com

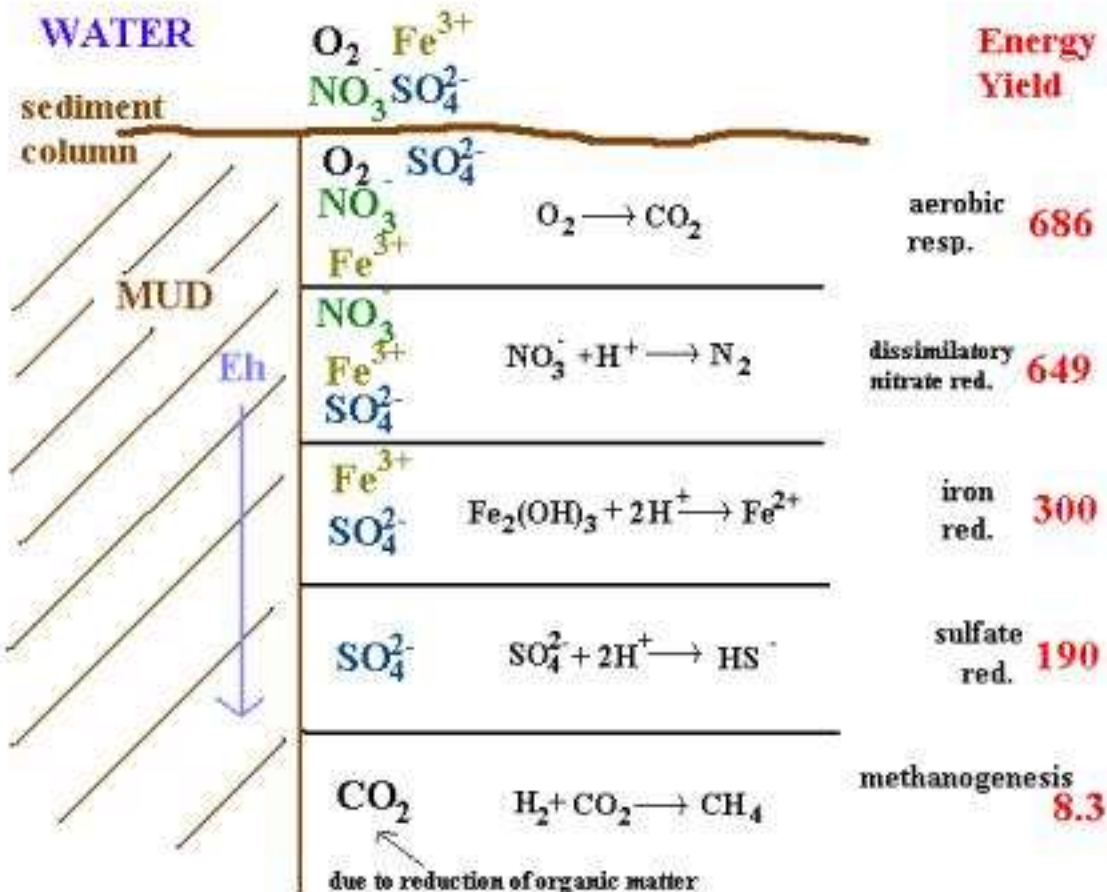
REFERENCES AND MORE INFORMATION

- I HAVE ATTACHED SOME SUPPORTING REFERENCE MATERIAL.
- THIS PRESENTATION WILL BE AMENDED AND IMPROVED OVER TIME AS ADDITIONAL INFORMATION BECOMES AVAILABLE.
- IF ANOTHER GROUP WOULD LIKE TO SEE THIS PRESENTATION, PLEASE CONTACT ME DIRECTLY.



Source: Fig.4.; Dominance of sulfur-fueled iron oxide reduction in low-sulfate freshwater sediments; Hansel C.M., Lentini C.J., Tang Y., Johnston D.T., Wankel S.D., Jardine P.M.; The ISME Journal (2015), 9, 2400-2412

Oxidation of organic matter



This sequence also occurs in stratified lakes with anoxic hypolimnia

Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems

N. F. Caraco, J. J. Cole & G. E. Likens

Institute of Ecosystem Studies, The New York Botanical Garden, Millbrook, New York 12545, USA

SEDIMENTS of aquatic systems play a critical part in controlling phosphorus loading to the water column¹. Because P loading is an important determinant of productivity in aquatic systems, there has been keen interest in variables that influence P release from sediments. In disagreement with present theories^{1,2} our data from 23 different aquatic systems indicate that sulphate concentration of waters is an extremely important variable controlling P release from sediments. The increased P release from sediments at higher sulphate concentrations may help to explain why primary production in freshwater systems (with relatively low sulphate concentrations) tends to be P limited³, whereas in many saline systems (with high sulphate concentrations) production is often P sufficient⁴. Further, our results indicate that anthropogenically induced changes from atmospheric S inputs could, over time, alter the P cycle of aquatic systems.

ORIGINAL ARTICLE

Dominance of sulfur-fueled iron oxide reduction in low-sulfate freshwater sediments

Colleen M Hansel¹, Chris J Lentini², Yuanzhi Tang³, David T Johnston⁴, Scott D Wankel¹ and Philip M Jardine^{*}

¹Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA; ²School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA; ³School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA and ⁴Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA

A central tenant in microbial biogeochemistry is that microbial metabolisms follow a predictable sequence of terminal electron acceptors based on the energetic yield for the reaction. It is thereby oftentimes assumed that microbial respiration of ferric iron outcompetes sulfate in all but high-sulfate systems, and thus sulfide has little influence on freshwater or terrestrial iron cycling. Observations of sulfate reduction in low-sulfate environments have been attributed to the presumed presence of highly crystalline iron oxides allowing sulfate reduction to be more energetically favored. Here we identified the iron-reducing processes under low-sulfate conditions within columns containing freshwater sediments amended with structurally diverse iron oxides and fermentation products that fuel anaerobic respiration. We show that despite low sulfate concentrations and regardless of iron oxide substrate (ferrihydrite, Al-ferrihydrite, goethite, hematite), sulfidization was a dominant pathway in iron reduction. This process was mediated by (re)cycling of sulfur upon reaction of sulfide and iron oxides to support continued sulfur-based respiration—a cryptic sulfur cycle involving generation and consumption of sulfur intermediates. Although canonical iron respiration was not observed in the sediments amended with the more crystalline iron oxides, iron respiration did become dominant in the presence of ferrihydrite once sulfate was consumed. Thus, despite more favorable energetics, ferrihydrite reduction did not precede sulfate reduction and instead an inverse redox zonation was observed. These findings indicate that sulfur (re)cycling is a dominant force in iron cycling even in low-sulfate systems and in a manner difficult to predict using the classical thermodynamic ladder.

The ISME Journal (2015) 9, 2400–2412; doi:10.1038/ismej.2015.50; published online 14 April 2015

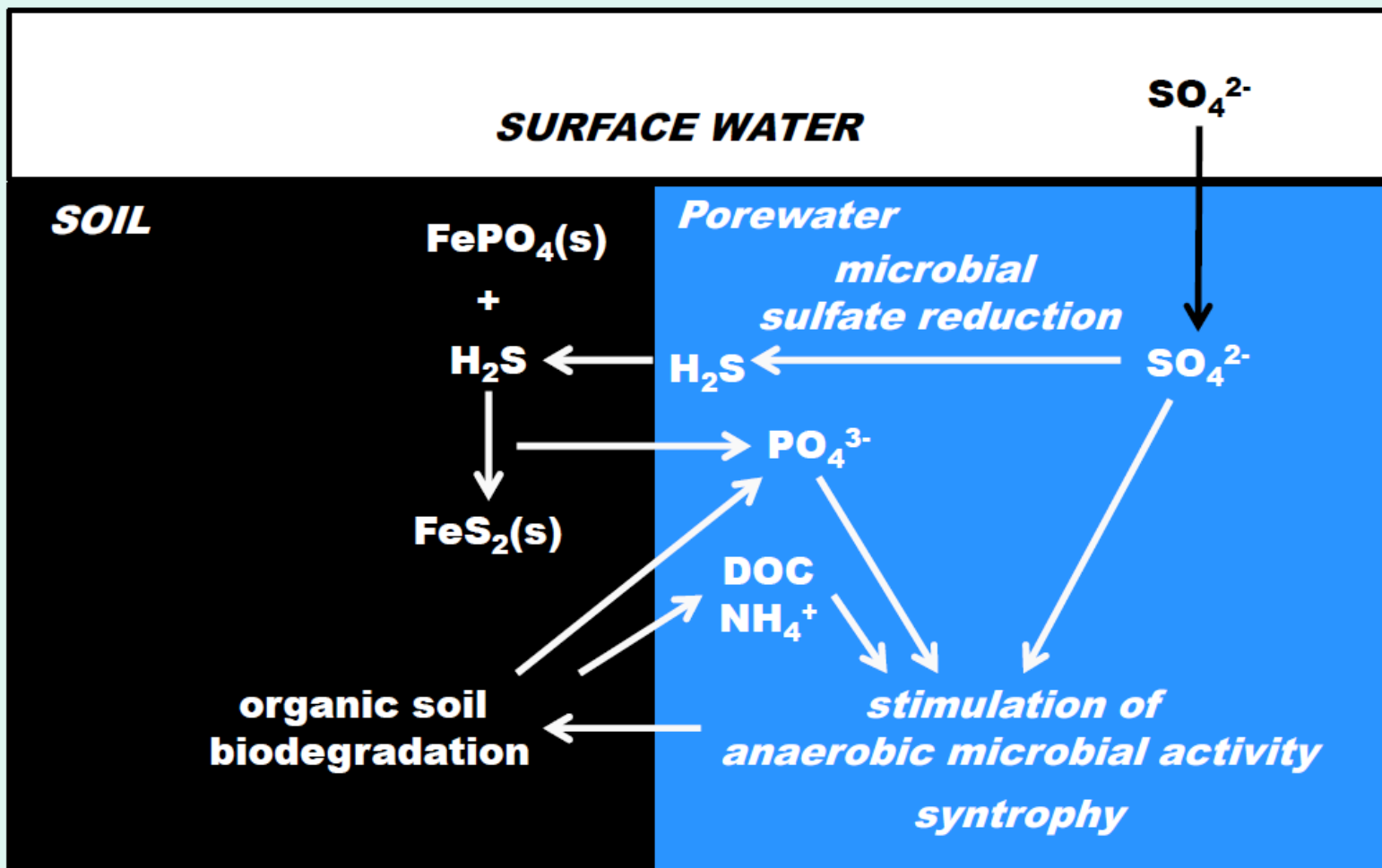
Sulfate as a Contaminant in Freshwater Ecosystems: Sources, Impacts and Mitigation

Sulfur Impacts on Freshwater Wetlands

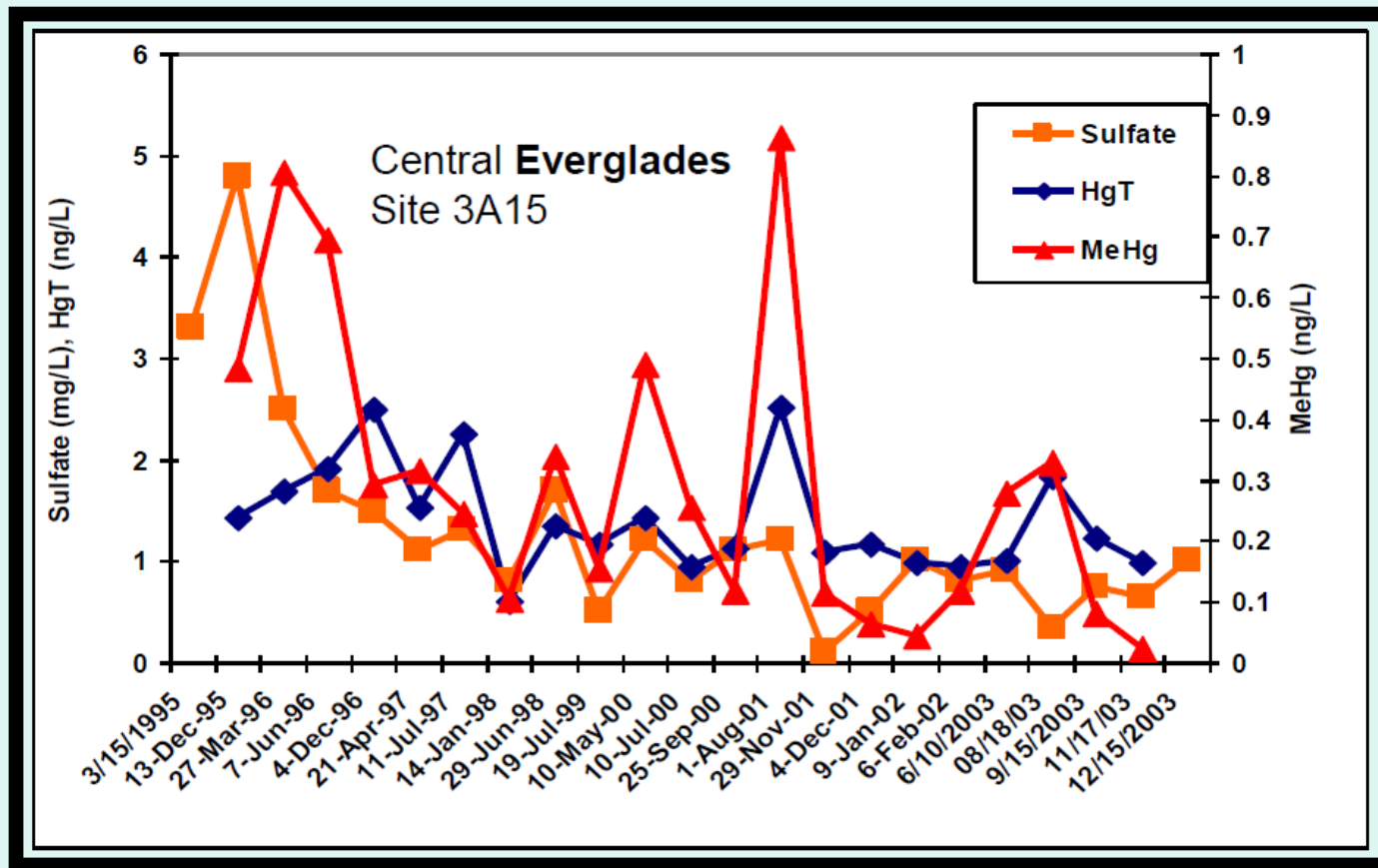
- Sulfate promotes methylation of mercury to its most toxic and bioaccumulative form: methylmercury
- Sulfide is toxic to plants and animals
- Sulfate promotes release of nutrients from sediments (internal eutrophication)
- Sulfide binds metal ions and sequesters them in soils as metal sulfides
- Sulfate enhances biodegradation of organic soils



Internal Eutrophication from Sulfate Contamination of Freshwater Wetlands



Response of Wetlands to Reduction in Sulfate Loading can be Rapid



Decreasing sulfate loading in central Everglades resulted in rapid decline in methylmercury production and levels of methylmercury in fish in <3 years



Estimating historical in-lake alkalinity generation from sulfate reduction and its relationship to lake chemistry as inferred from algal microfossils

Peter A. Siver^{1,*}, Richard Ricard¹, Richard Goodwin¹ and Anne E. Giblin²

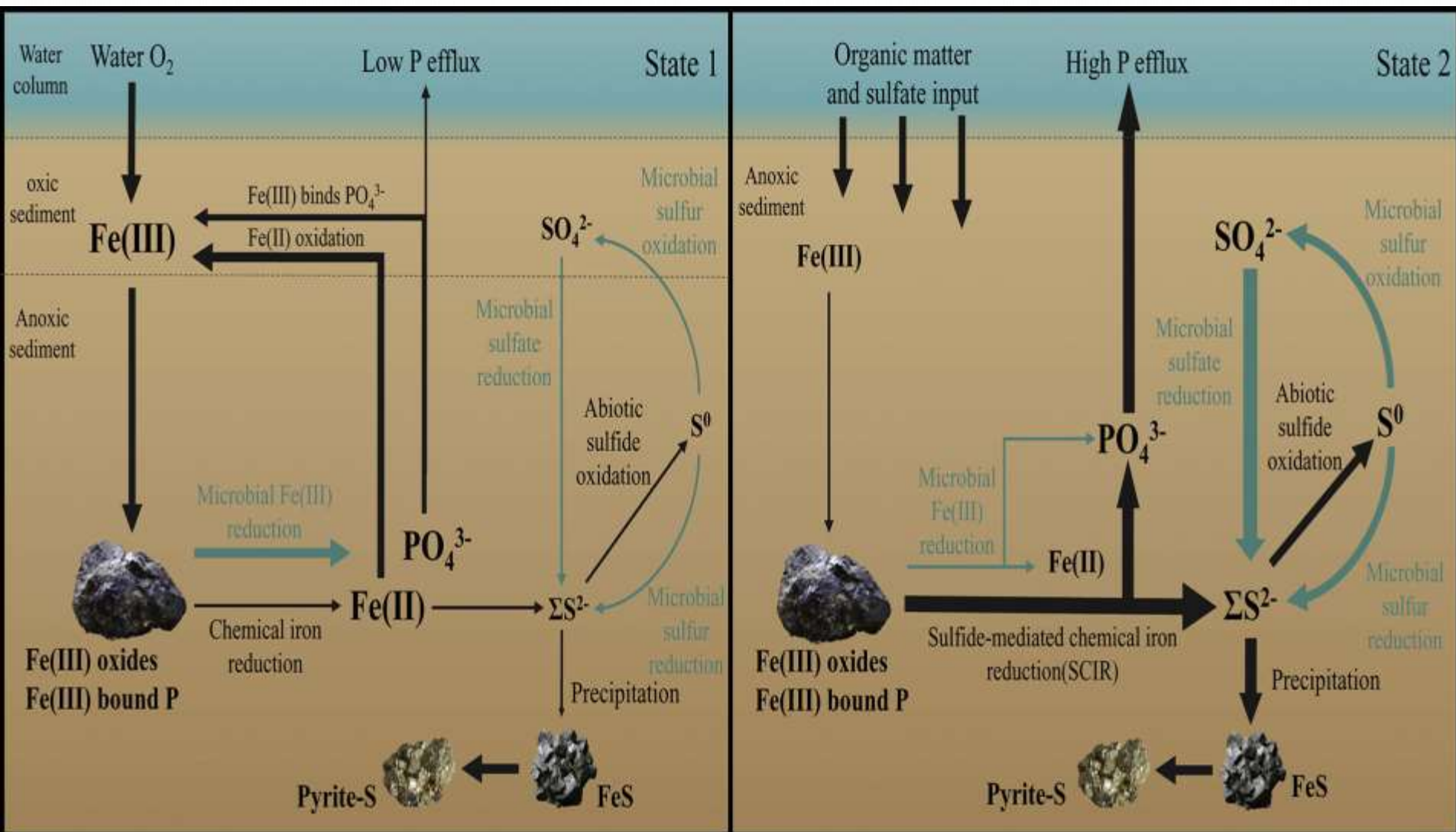
¹Botany Department, Connecticut College, New London, CT 06320, USA; ²Marine Biological Laboratory, The Ecosystem Center, Woods Hole, MA 02543, USA; *Author for correspondence (e-mail: pasiv@conncoll.edu)

Received 1 September 2001; accepted in revised form 2 September 2002

Key words: Acid deposition, Alkalinity generation, Connecticut, Diatoms, Scaled chrysophytes, Southern New England, Sulfate reduction

Abstract

Sediment cores were used to estimate in-lake alkalinity generation resulting from sulfate reduction relative to inferred changes in lakewater pH and trophic status over the last century in three Connecticut lakes. Despite being situated in geological settings with crystalline bedrock and thin, poorly buffered soils, and being impacted with high rates of acidic precipitation, none of the study lakes have declined in inferred pH based on scaled chrysophyte and diatom remains. In fact, the pH of one of the lakes, Coventry Lake, has significantly increased over the last century. Over the last ~44 to 69 years the amount of sulfur stored in the sediments from each lake increased from ~two to three times resulting in mean rates of alkalinity generation ranging from 78 to 145 meq m⁻² yr⁻¹, significantly higher than the 45 to 48 meq m⁻² yr⁻¹ of hydrogen ions falling directly on the lake surfaces. In-lake alkalinity generation resulting from sulfate reduction has been sufficient to neutralize all of the acid falling directly onto the lake surfaces, as well as between 9% and 25% of the acid deposited onto the surrounding watersheds. Despite the increased importance of in-lake alkalinity generation, our findings support the hypothesis that significant amounts of alkalinity are also being generated in the catchments of the study lakes. The bulk of the increases in stored sulfur in all three lakes were as Fe sulfides and not in the form of organic sulfur, suggesting that the increases were the result of dissimilatory bacterial reduction of sulfate. As a result of the large increases in storage of Fe sulfides the ratio of total iron to chromium reducible sulfur (Fe:CRS) has declined in all cores over time. Despite the overall decline in Fe:CRS in recent sediments, values are still largely above 3 in more recent sediments of two of the lakes. However, values of Fe:CRS have dropped below 1 in surface sediments of Uncas Lake, suggesting that in-lake loading of phosphorus may be responsible for a recent shift in the algal flora towards a slightly more eutrophic condition.



Source: Sulfur Cycling in freshwater sediments: A cryptic driving force of iron deposition and phosphorus mobilization; Wu S., Zhao Y., Chen Y., Dong X., Wang M., Wang G.; *Science of the Total Environment* (2019), **657**, pp. 1294-1303