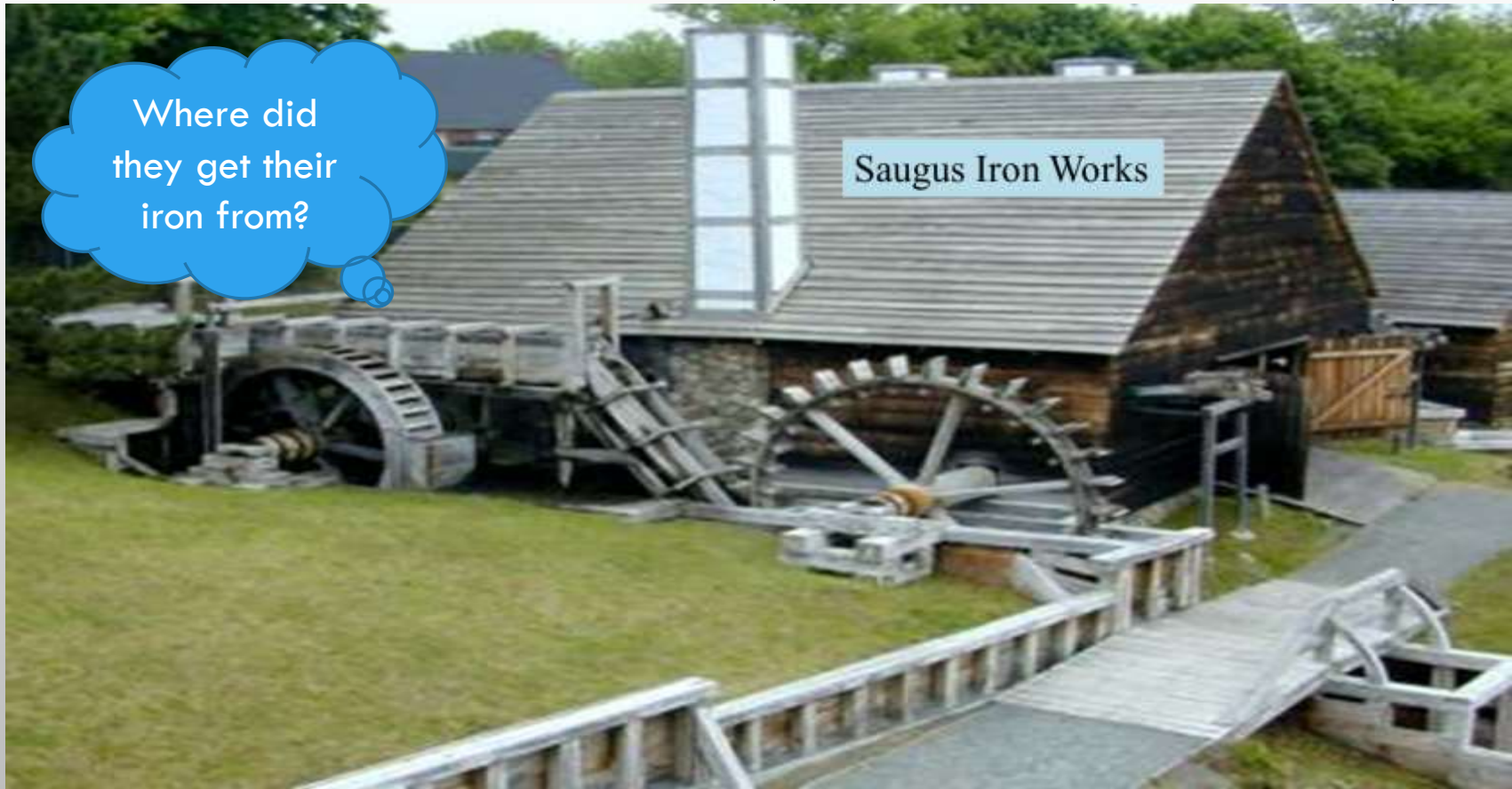


LAKE IRON NODULES AN “INDEX MINERAL” TO ASSESS THE IMPACT OF SULFATE/SULFIDE ON SURFACE WATER AND SEDIMENT QUALITY OVER TIME IN NEW ENGLAND LAKES, PONDS AND RIVERS (PRE-1800S TO TODAY)



Reference: Saugus Iron Works National Park, website photographs

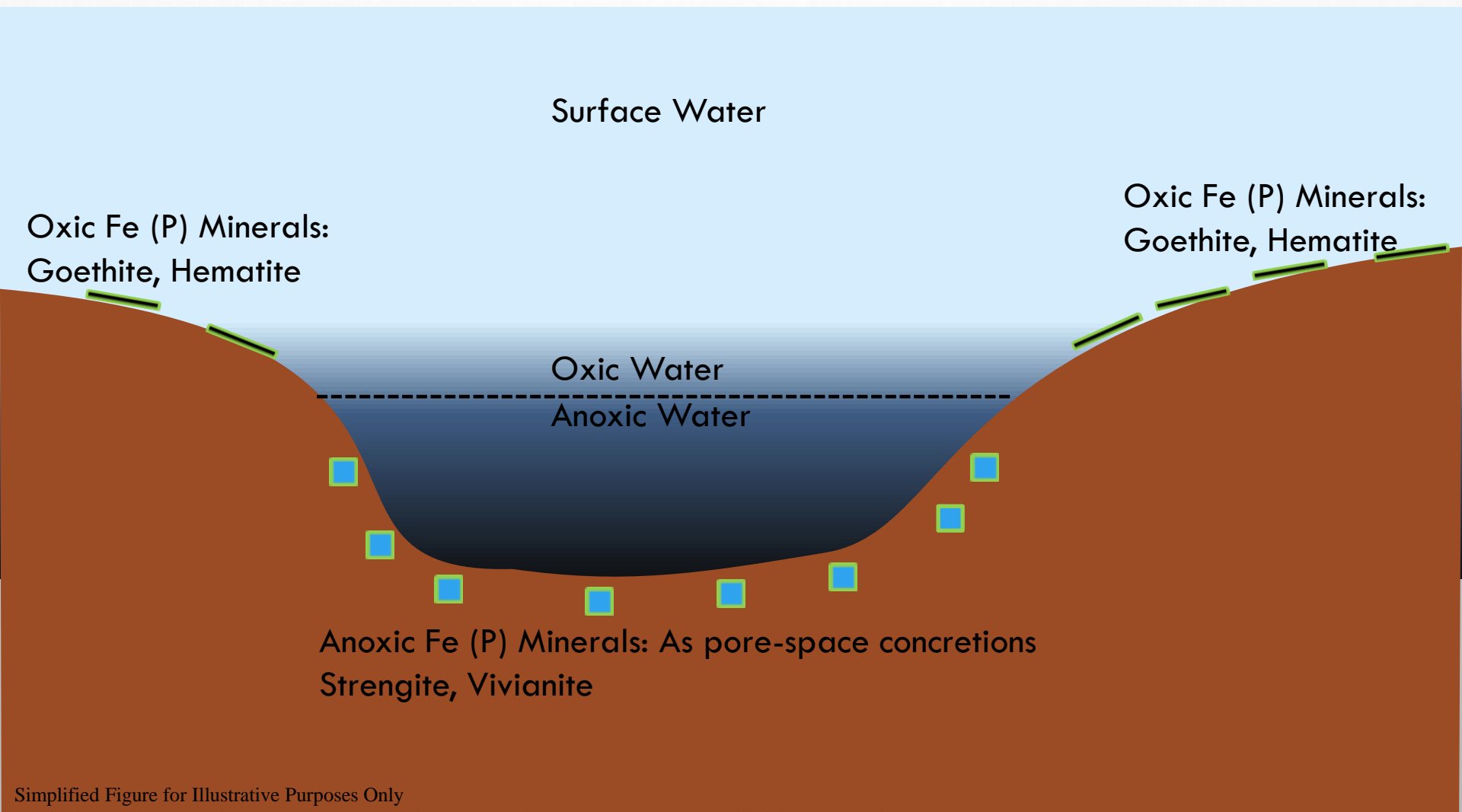
- JONATHAN B. HIGGINS, CPG, LSP
- PRINCIPAL EARTH SCIENTIST, HIGGINS ENVIRONMENTAL ASSOCIATES, INC. FEBRUARY 4, 2020

WHAT ARE LAKE IRON NODULES?

- AN IRON-ENRICHED CONCRETION, OFTEN CONTAINING MORE THAN 30 PERCENT IRON BY WEIGHT AND FORMED AT THE SEDIMENT/WATER INTERFACE (SWI) IN OXIC SURFACE WATERS . THEY ARE PREDOMINANTLY COMPOSED OF THE MINERALS GOETHITE AND HEMATITE. THERE ARE OTHER FORMS OF AQUATIC IRON NODULES AND CONCRETIONS, IMPORTANTLY THE ANOXIC, FERROUS PHOSPHATE HYDRATED MINERALS: VIVIANITE AND STRENGITE; OR IN CARBONATE RICH SYSTEMS, SIDERITE (Fe_2+CO_3).
- IMPORTANTLY, IRON NODULES ARE A NATURAL SINK FOR PHOSPHORUS IN LAKES, PONDS AND RIVERS.
- PICTURED HERE ARE LAKE IRON NODULES FROM 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.**

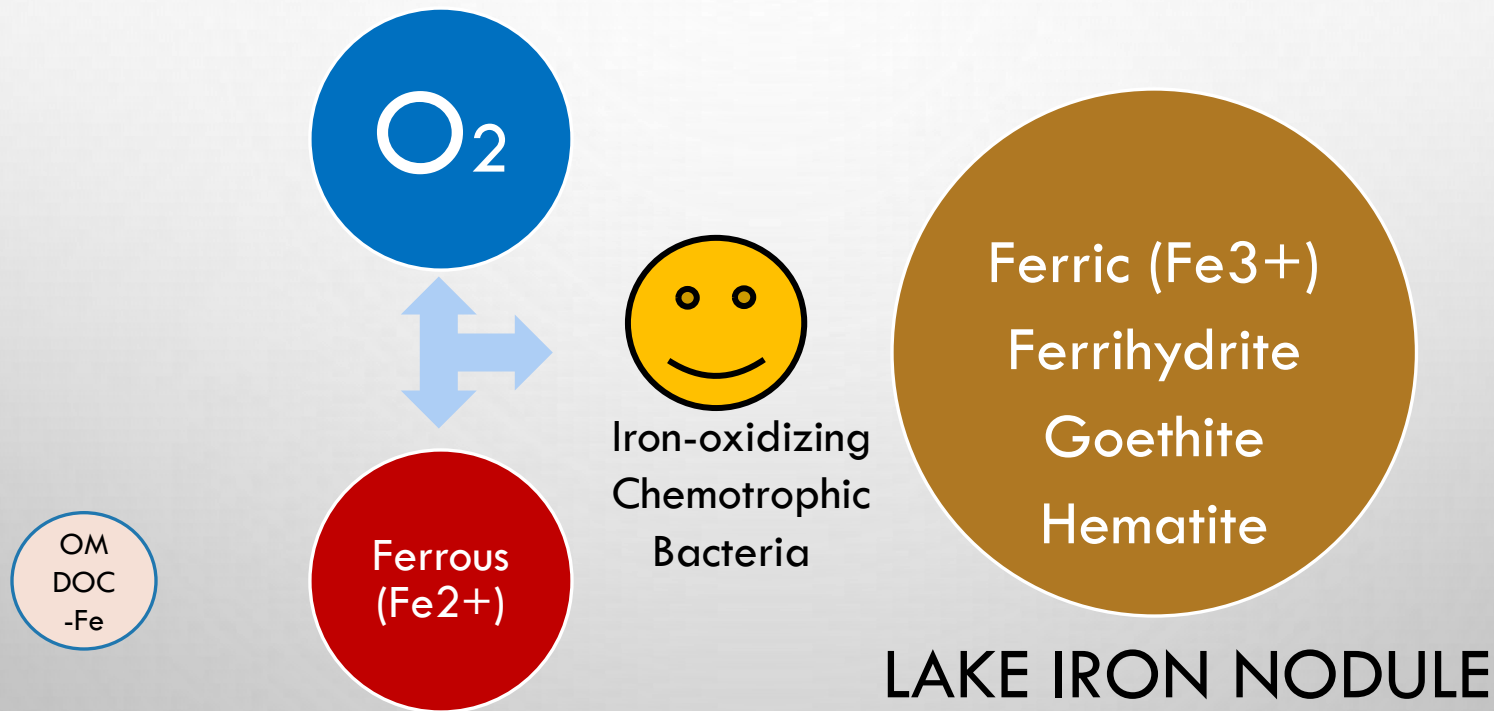
OXIC LAKE IRON NODULES ARE:

- 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
- 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 THAN 1 DUE TO THE "CRYPTIC SULFUR CYCLE"; IN OXIC WATERS, SULFATE CONCENTRATIONS OF GREATER THAN 200 MICROMOLES HAS BEEN SHOWN TO LEAD TO REDUCTION OF OTHERWISE GEOCHEMICALLY-STABLE GEOTHITE AND HEMATITE MINERALS.

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

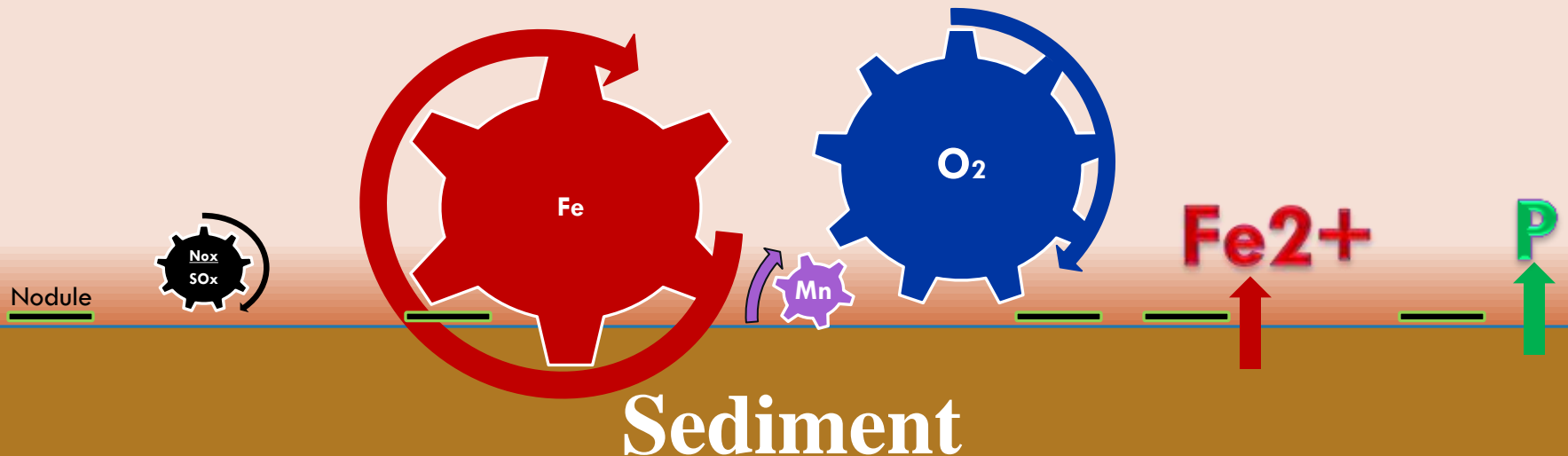
WHERE ARE THEY FORMED? – CURRENTLY AND PRE-1800s ON A NUCLEATION SITE 1 TO 2 CENTIMETERS ABOVE THE SEDIMENT SURFACE

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

Limited Nitrate and Sulfate Concentrations in Surface Water or Sediments

DOC/Fe-rich water, reduced water clarity (more of a tea-colored water). Lake iron nodules can be found in areas with elevated phosphorus. Sulfates/Sulfides and anoxia are documented limiting factors.

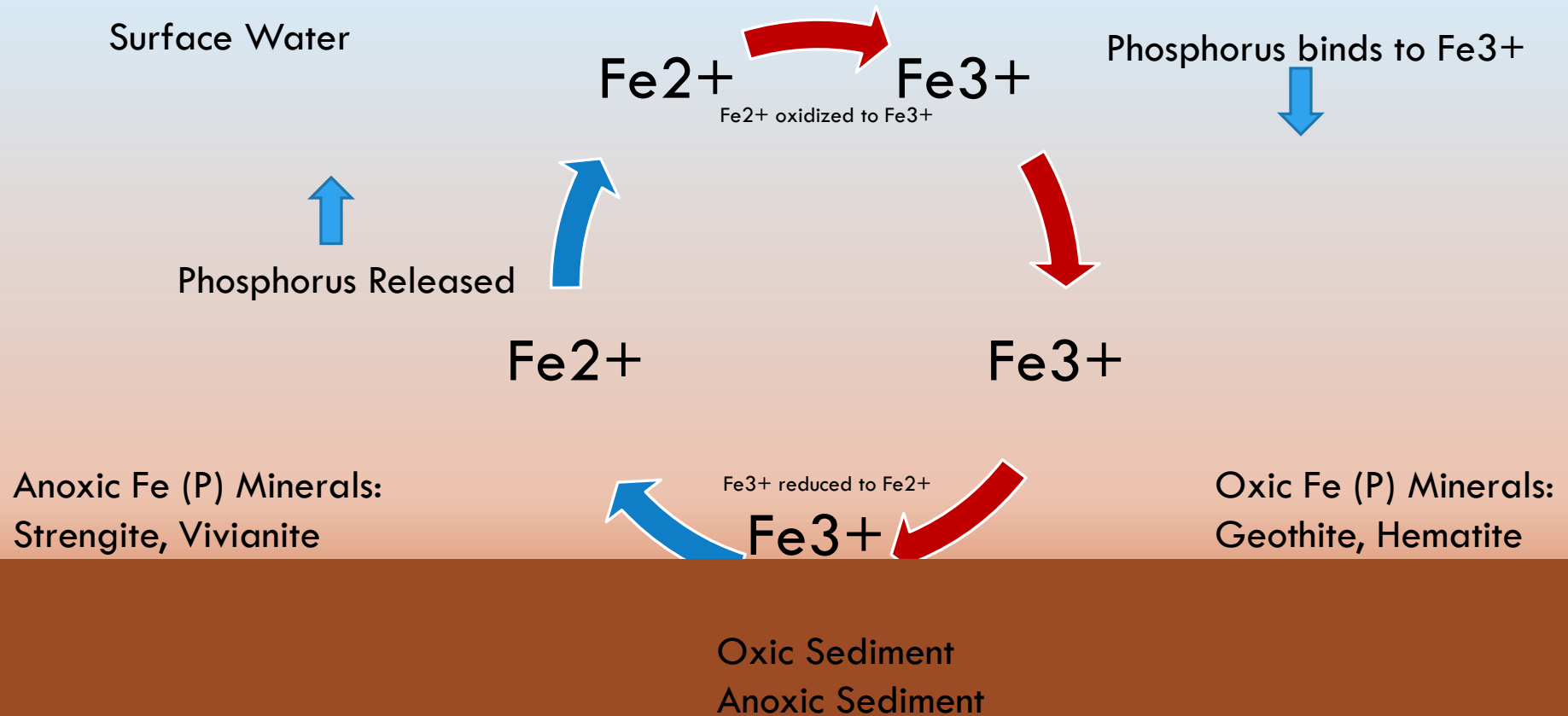
Oxygenated Surface Water



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



Simplified Figure for Illustrative Purposes Only

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

PAST RECORDS –

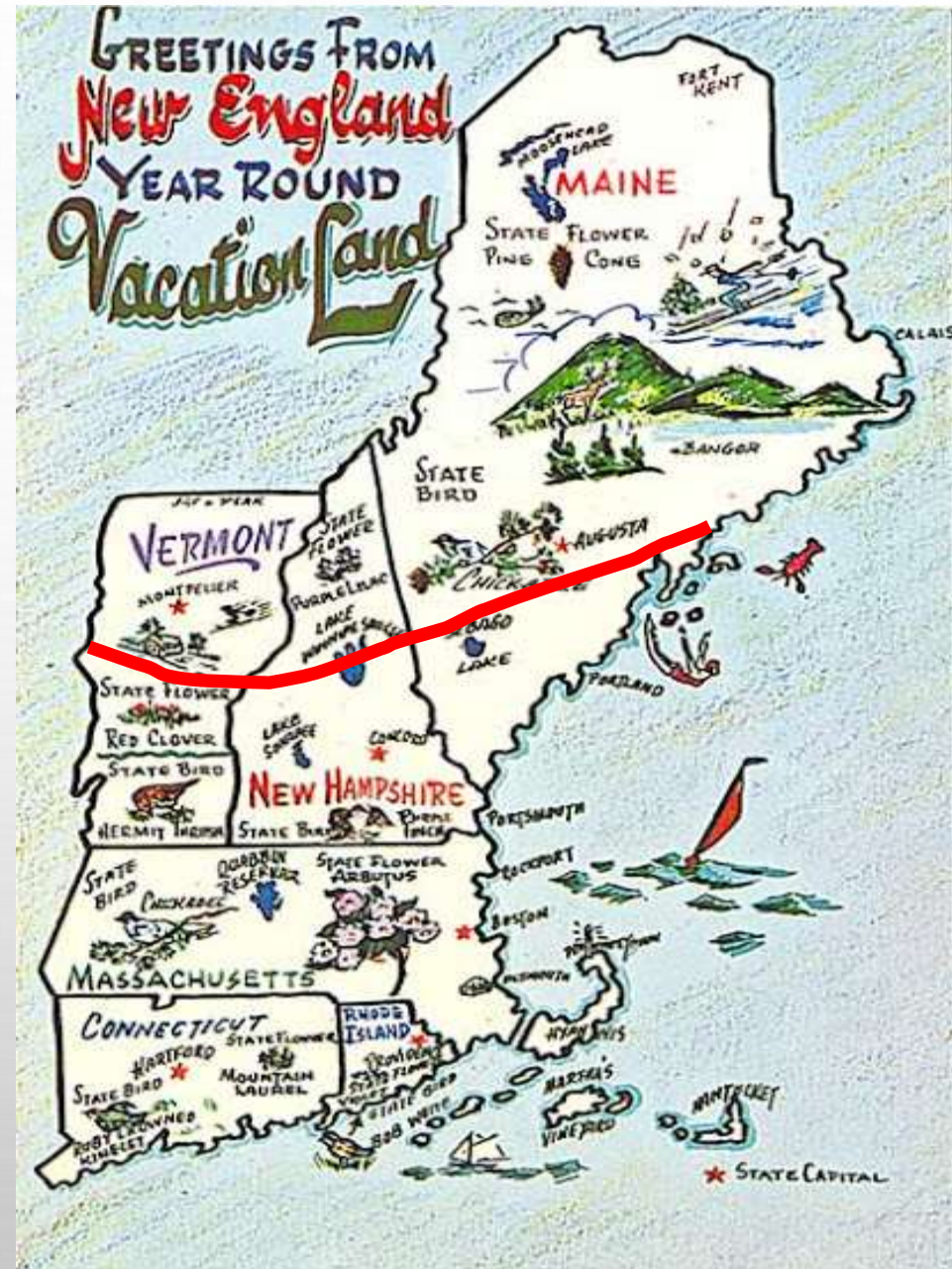
- 1614: CAPT. JOHN SMITH DOCUMENTED THE PRESENCE OF IRON NODULES IN WATERS OF THE MASSACHUSETTS BAY COLONY.
- EARLY 1600s: EXPLORATION JOURNALS BY MINERAL MEN HIRED BY VENTURE CAPITALISTS FROM ENGLAND TO ASSESS THE MINERAL RESOURCES OF EARLY NEW ENGLAND. THESE RECORDS INCLUDE DOCUMENTATION OF LOCAL BOG 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).

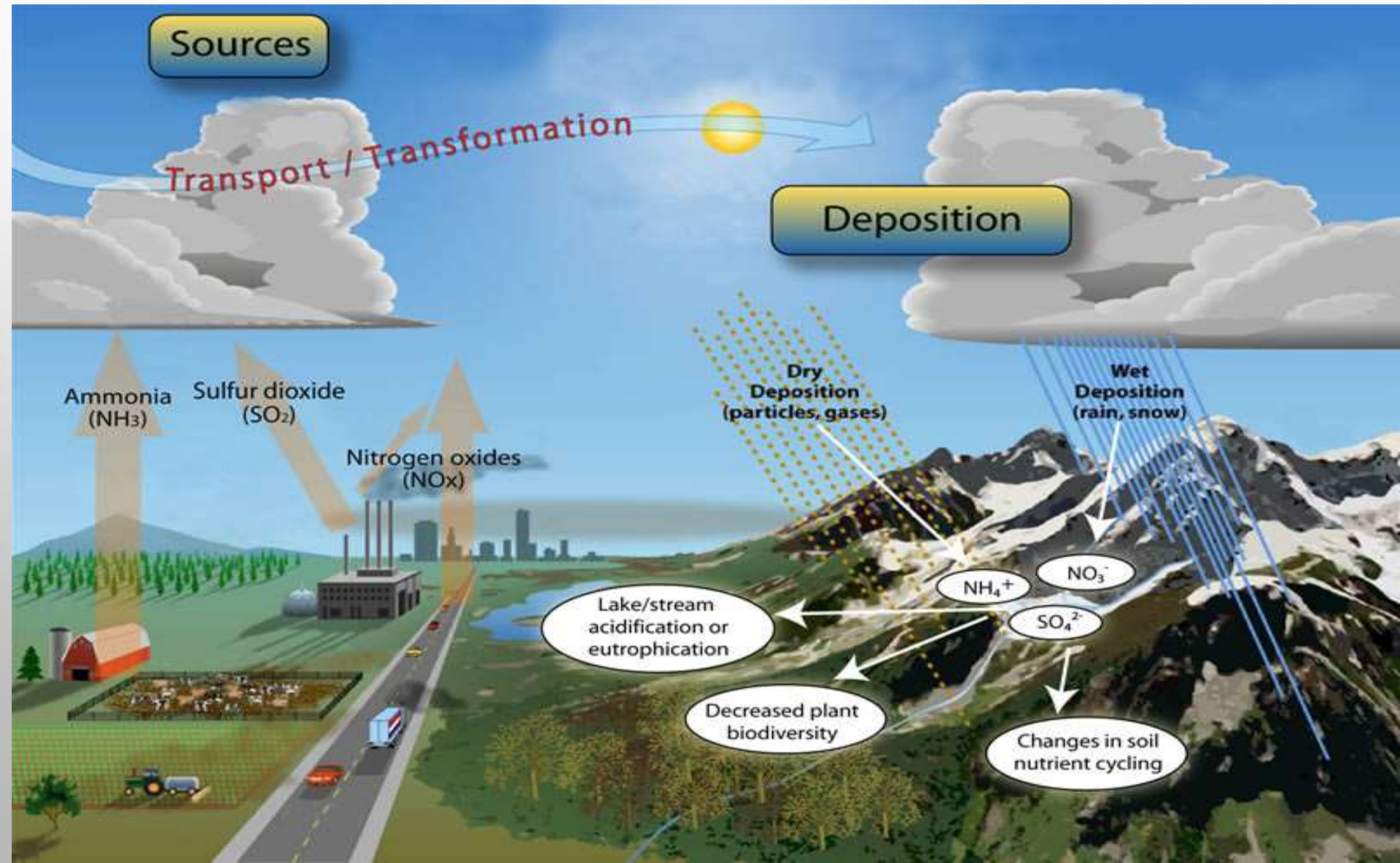
BY YEAR 2010 -

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

RED LINE MARKS CURRENT AND
TENTATIVE KNOWN LIMITS
OF IRON NODULES.

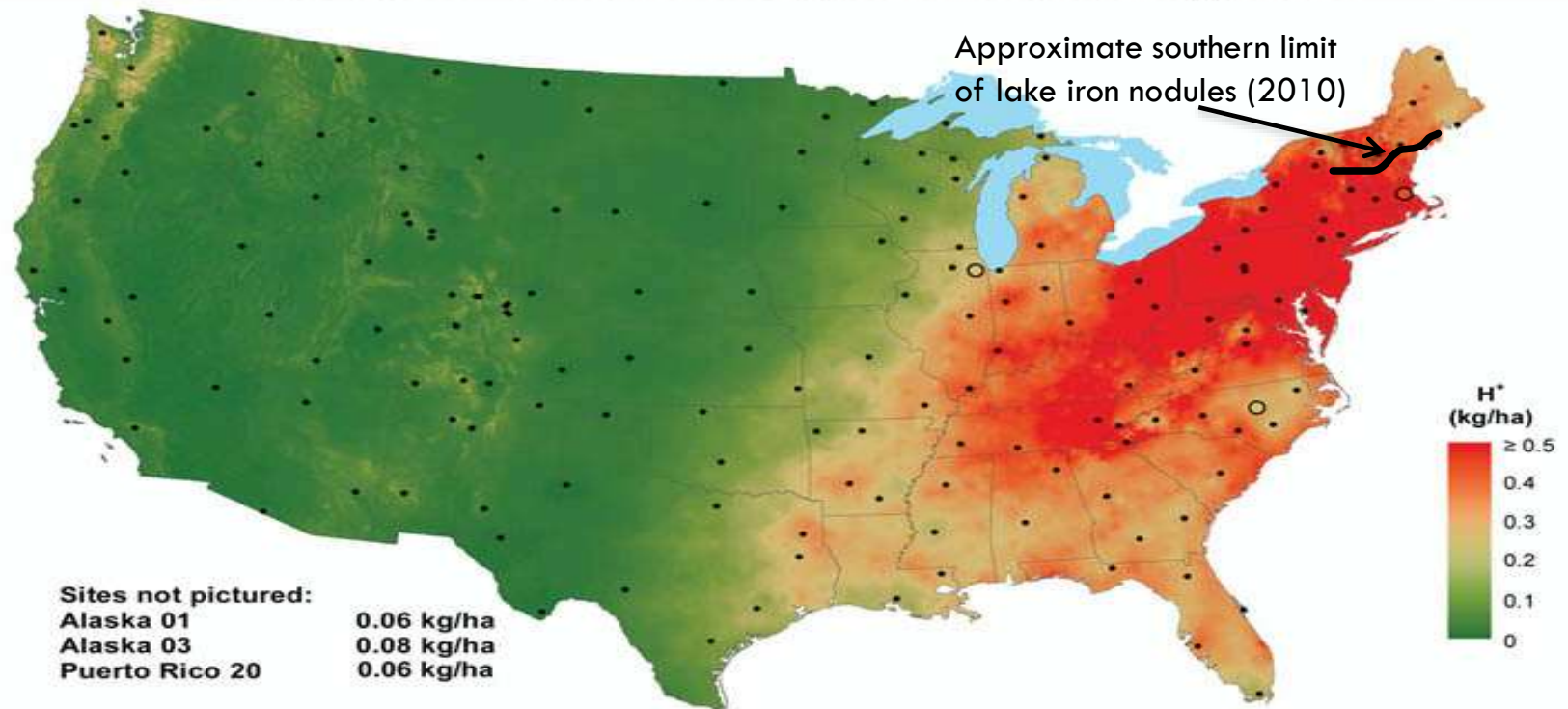


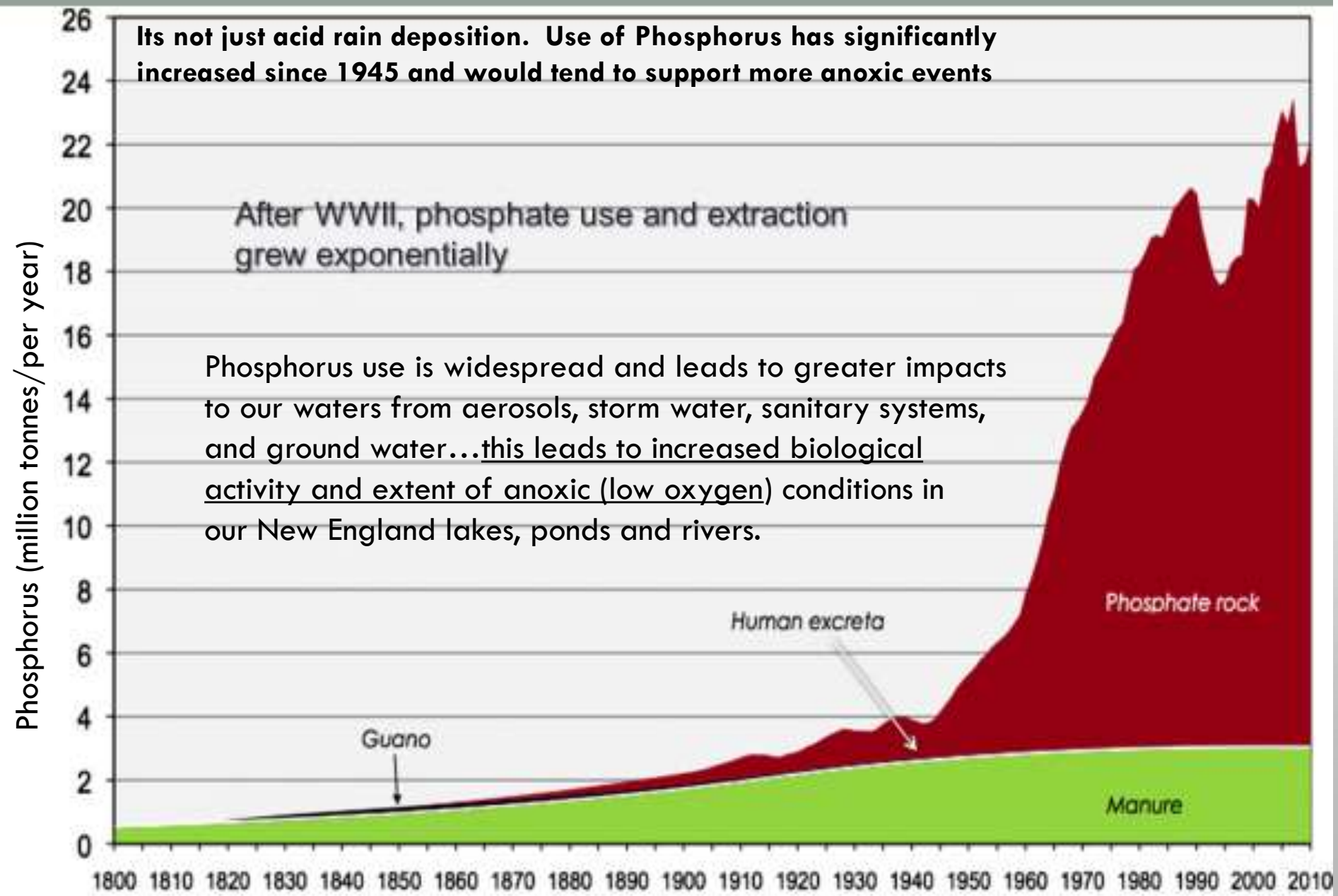
WHAT HAPPENED TO THE IRON NODULES?



NITRATE AND SULFATE IMPACTS TO SURFACE WATER, SOIL AND SEDIMENT

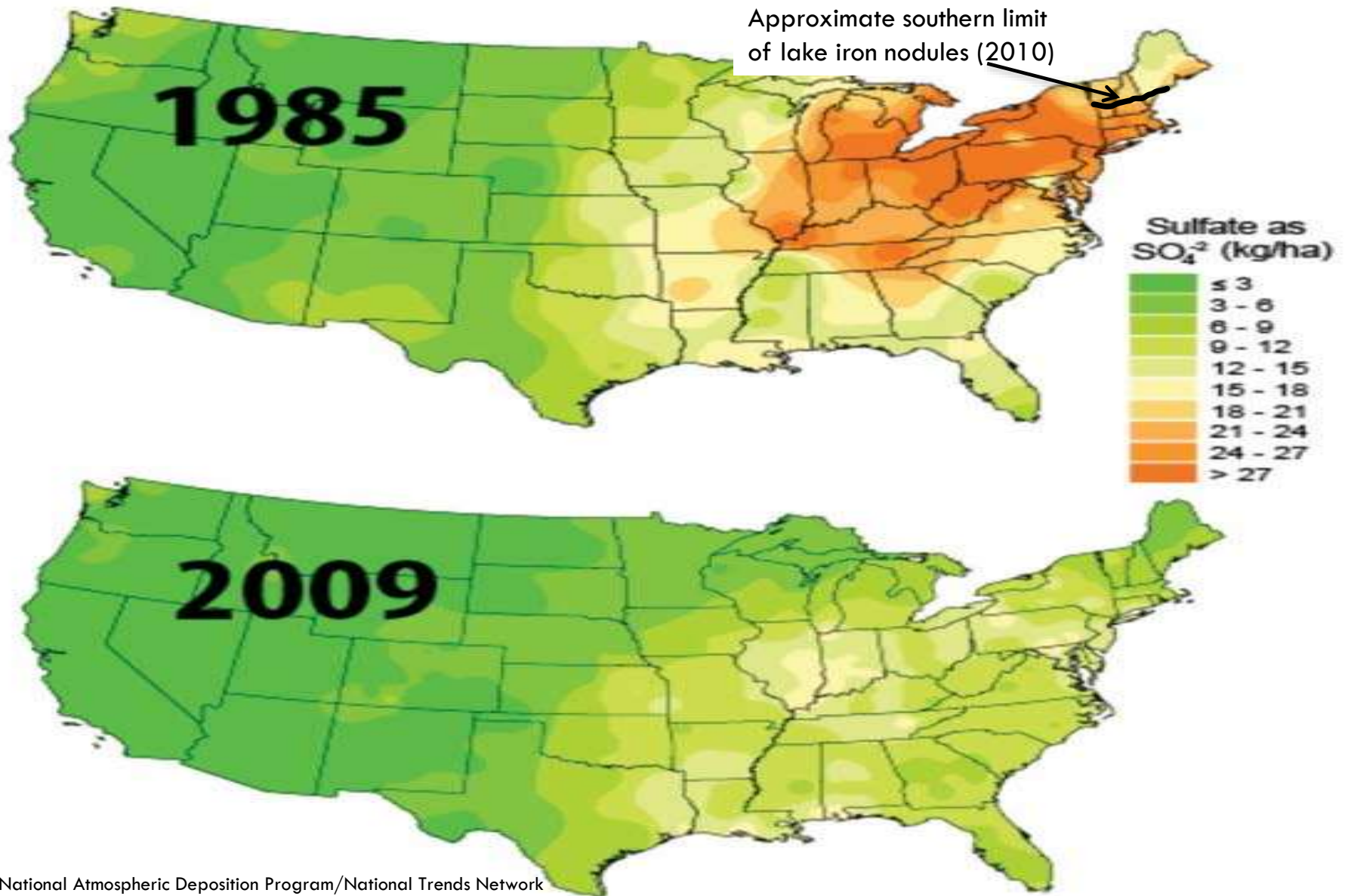
Hydrogen ion wet deposition from measurements made at the Central Analytical Laboratory, 1994





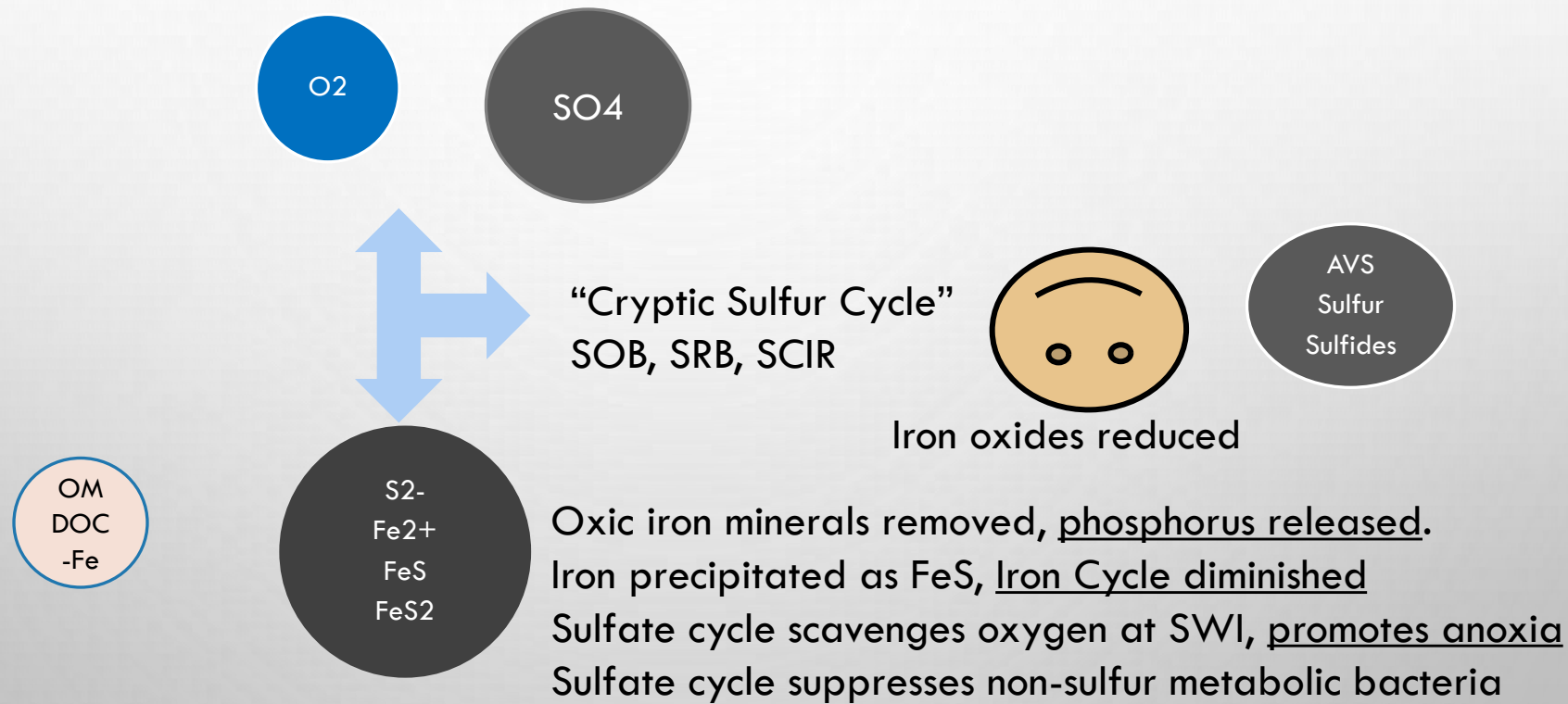
Source: Cordell et al., 2009

CHANGES IN GEOCHEMISTRY - SULFATE DEPOSITION REDUCED



HOWEVER, SULFATE/SULFIDE IMPACTS TO SEDIMENT REMAIN

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



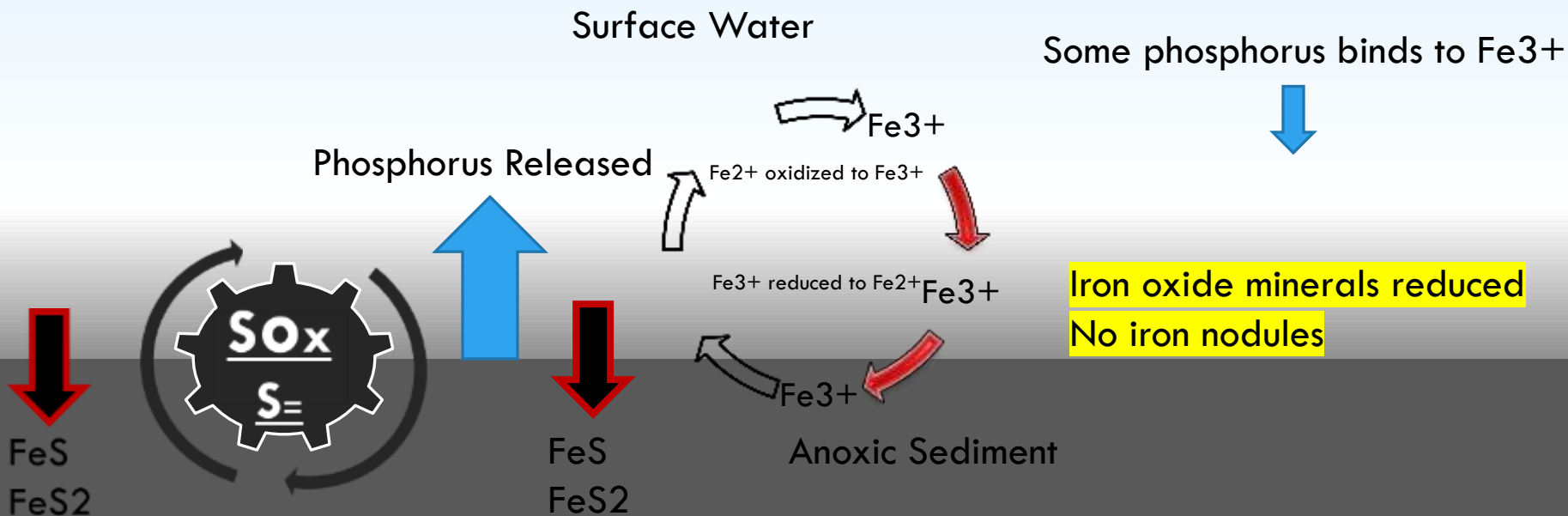
Simplified and Illustrative Process

“DIMINISHED FERROUS 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



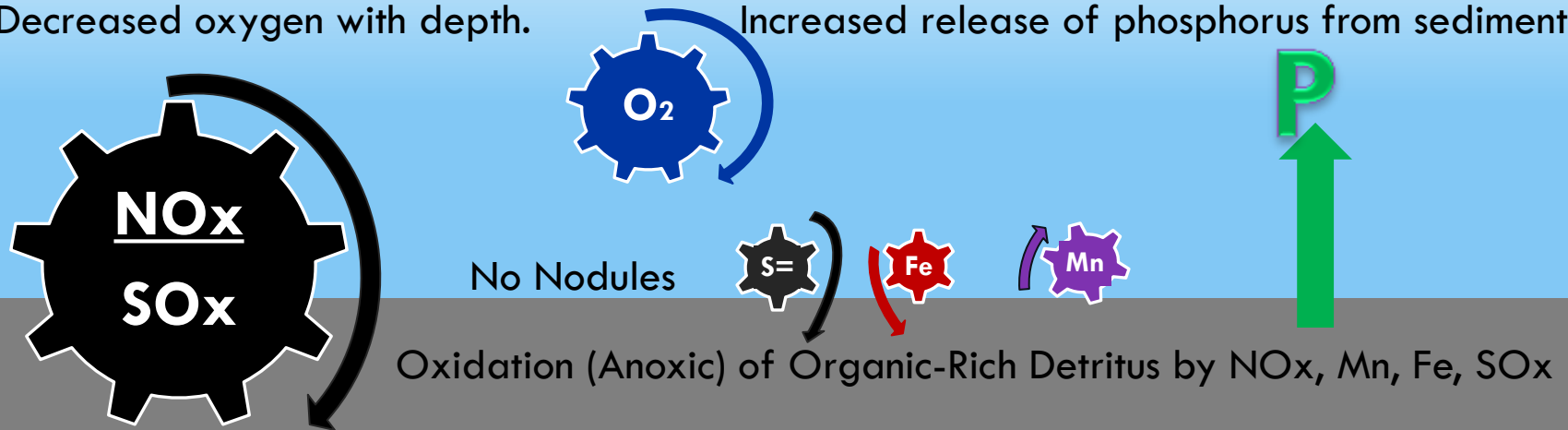
Simplified Figure for Illustrative Purposes Only

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

CIRCA 1970 – 2010 BIOGEOCHEMICAL SETTING – MY INTERPRETATION

NO_x
SO_x ↘
↙ Phosphorus (P)
Nitrate- and 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 phosphorus
Decreased oxygen with depth. Increased release of phosphorus from sediment.



No Iron Nodules – Replaced by Iron Sulfide Minerals (FeS, greigite Fe₃S₄, and pyrite FeS₂). Iron Cycle Diminished Significantly.



Reduced (Anoxic) Sediment and Pore Water

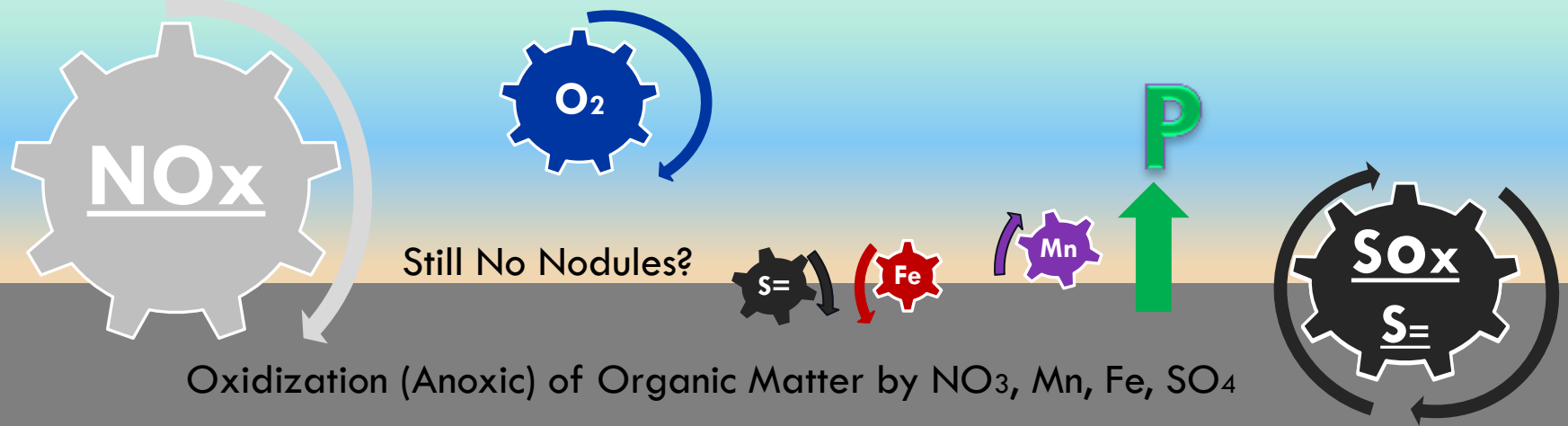
CIRCA 2019 – MY INTERPRETATION AN IMPROVEMENT SINCE 2010

NO_x
 SO_x ↗ ↘

Phosphorus (P)
↗ ↘

Nitrate- and Phosphorus- Enriched, Sulfate-Low to Moderate in Surface Water but Sulfate/Sulfide still Moderate to High in some Sediments.

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.



Still No Nodules?

No Iron Nodules – Replaced by Iron Sulfide Minerals

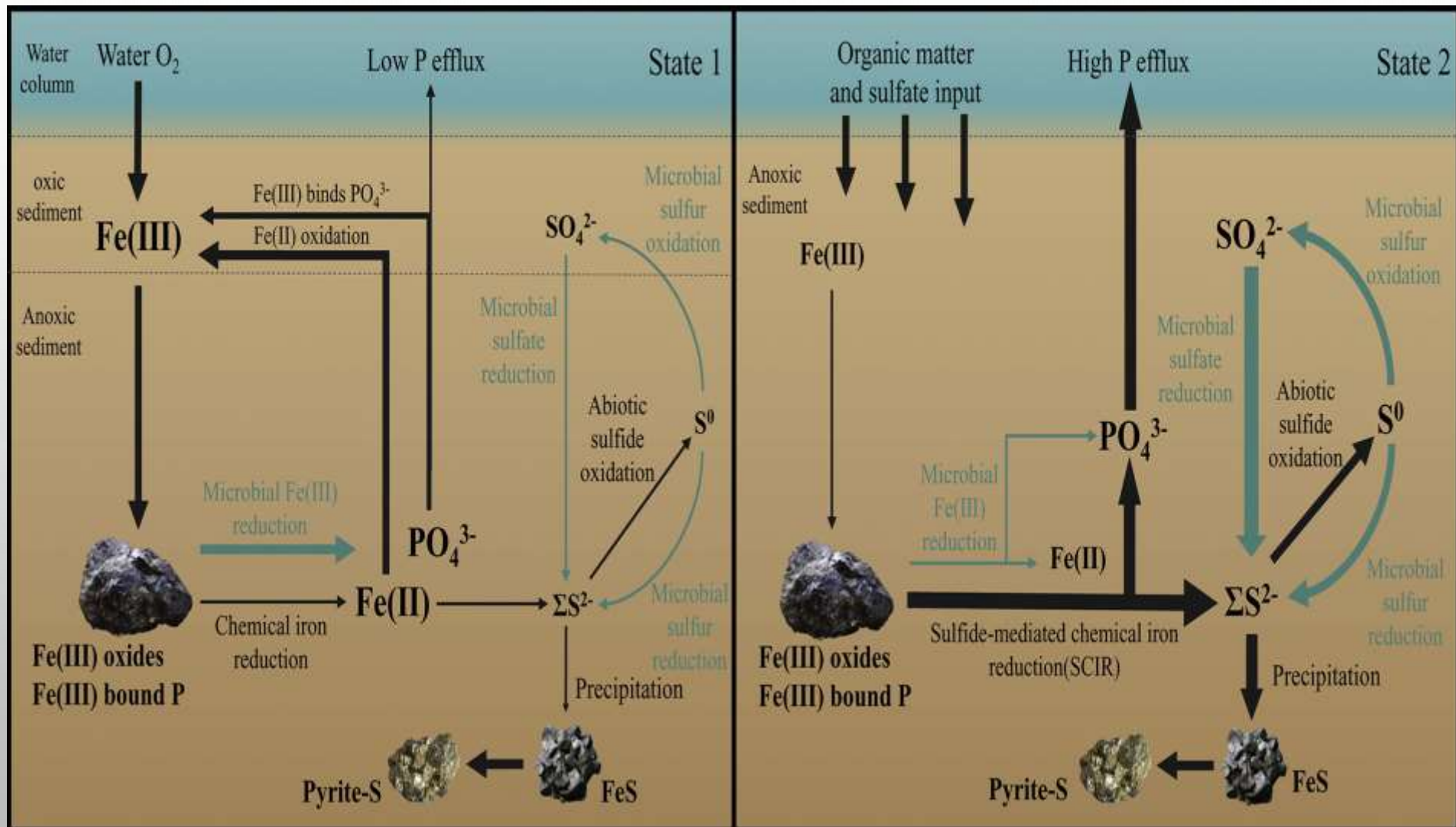


Reduced (Anoxic) Sediment and Pore Water

PUBLISHED ILLUSTRATION OF THIS PROCESS

State 1: Low Sulfur

State 2: Increased Sulfur



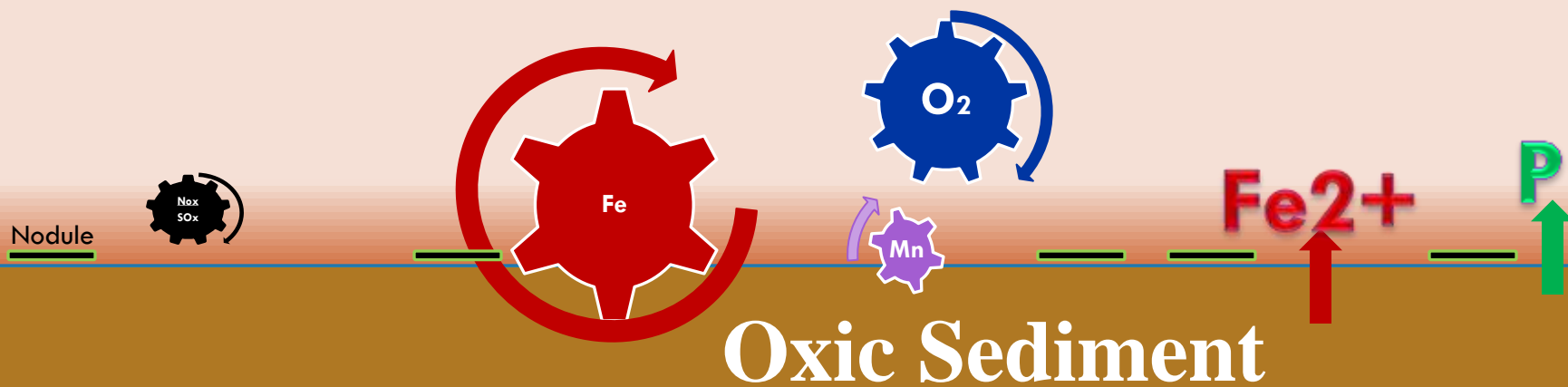
Source: Sulfur Cycling in freshwater sediments: A cryptic driving force of iron deposition and phosphorus mobilization; Wu S., Zhao Y., Chen Y., Dong X., Wang M., Wang G.; Science of the Total Environment (2019), **657**, pp. 1294-1303

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 ferrous (iron) cycle is restored. This promotes development of native plant and animal species and minimizes conditions favoring algae blooms and invasive species (clear water, sulfates and excess phosphorus). Lake iron nodules can be restored and serve as natural sinks for phosphorus.

Oxygenated Surface Water



TAKE AWAYS

- PRIOR TO THE 1800S, IRON NODULES WERE WIDESPREAD IN NEW ENGLAND. THEIR CURRENT LIMITED OCCURRENCE IN NEW ENGLAND IS CONSISTENT WITH AREAS OUTSIDE OF HISTORICAL IMPACTS BY SULFATE DEPOSITION.
- IRON NODULES CONCENTRATE AND BIND IRON AND TRACE ELEMENTS LIKE PHOSPHORUS. THEY ARE NATURAL “SINKS” FOR PHOSPHORUS. THEY “GREW” AND HISTORICALLY RECOVERED IF REMOVED.
- TESTING OF NODULES SHOWS THEY CAN CONTAIN UPWARDS OF 4 PERCENT PHOSPHORUS BY WEIGHT (40,000 MG/KG).
- PHOSPHORUS AND SULFATE IMPACTS TO SURFACE WATER/SEDIMENT QUALITY CAN ALTER THE NATURAL IRON CYCLE AND CHANGE BIOGEOCHEMICAL CONDITIONS REQUIRED FOR GROWTH OF IRON NODULES. PHOSPHORUS PROMOTES INCREASED BIOLOGICAL PRODUCTIVITY AND ANOXIA. SULFIDE REDUCES AND BINDS WITH IRON, AND SULFATE ENHANCES ANAEROBIC DEGRADATION OF ORGANIC MATTER, EACH RESULTING IN INCREASED AND SUSTAINED RELEASE OF PHOSPHORUS.
- SULFATE/SULFIDE MINERALIZATION PROMOTES ANOXIC CONDITIONS AND EUTROPHICATION BY SCAVENGING DISSOLVED OXYGEN AT DEPTH AND WITHIN SEDIMENTS, REDUCING IRON OXIDES AND RELEASING PHOSPHORUS.
- SOURCES OF SULFATE IMPACTS INCLUDE HISTORIC ACID RAIN DEPOSITION, WATER TREATMENT CHEMICALS (ALUMINUM SULFATE AND COPPER SULFATE), PESTICIDE SURFACTANTS AND ADJUVANTS, DETERGENTS/SOAPS (PRIMARILY AS SODIUM LAURYL SULFATE), FERTILIZERS, ORGANIC DETRITUS, SOIL AND MINERAL WEATHERING.
- REMOVING EXCESS SULFATE AND PHOSPHORUS IMPACTS WOULD HELP TO RESTORE THE NATURAL IRON CYCLE AND ITS LONG TERM BINDING CAPACITY FOR PHOSPHORUS IN OUR LAKES, PONDS AND RIVERS OF NEW ENGLAND.
- REGIONAL TRENDS IN INCREASED COLORED DISSOLVED ORGANIC CARBON (DOC) AND IRON, AS APPARENT BY “TEA-COLORED” SURFACE WATER IMPACTS WOULD FAVOR OUR NATIVE PLANT AND ANIMAL SPECIES OVER HARMFUL ALGAE BLOOMS, INVASIVES AND NUISANCE GROWTH CONDITIONS.
- SULFATE IMPACTS SINCE THE 1800S HAVE SIGNIFICANTLY ALTERED THE IRON CYCLE AND WATER CLARITY IN NEW ENGLAND FRESHWATER RESOURCES.

RECOMMENDATIONS

- INCLUDE CARBON, IRON AND SULFUR/SULFATE/SULFIDE WITH TOTAL PHOSPHORUS ANALYSIS IN SEDIMENT. SAMPLE THE TOP, MIDDLE AND BOTTOM OF VERTICAL CORE SEDIMENT INTERVALS AND SHALLOW (TOP 2 INCH) GRAB SAMPLES TO SHOW CHANGES OVER TIME.
- ACCOUNT FOR AND INCORPORATE SPATIAL AND TEMPORAL VARIATIONS FOR THE NUTRIENTS: CARBON, IRON, NITROGEN, PHOSPHORUS AND SULFUR IN SURFACE WATER, ALGAE/CYANOHABS 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.

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.

Phosphorus release from anoxic sediments: Lakes that break the rules

Nina F. Caraco, Jonathan J. Cole and Gene E. Likens

Introduction

Phosphorus plays an important role in the control of primary production in aquatic systems (SCHINDLER 1971, VOLLENWEIDER 1968). Thus, there has been an extensive amount of research on P cycling in both marine and freshwaters (BOSTROM et al. 1982, FROELICH et al. 1982). This research on P cycling has revealed that a major loss of P from the surface waters of most aquatic systems is by sinking of particles to sediments (CARACO et al. 1988, CARACO 1986, LEVINE et al. 1986, MOELLER 1985, ULEN 1978, BLOESCH et al. 1977). The extent to which sediments recycle P to overlying waters is critical in maintaining system productivity (BOSTROM et al. 1982, CALLENDER 1982, ZEITZSCHELL 1980, NIXON 1980) and controlling eutrophication of freshwater lakes (HENRIKSON-SELLERS & MARKLAND 1989).

Early research in freshwaters revealed that an important variable determining P release from sediments was oxygen content of waters overlying sediments (MORTIMER 1941, EINSELE 1936). When water overlying sediments is oxic, an FeOOH micro-layer at the surface of sediments can trap P, preventing its release into overlying waters. Under anoxic conditions this micro-layer can be reduced chemically and the previously sorbed P is released into solution. This "oxygen control model" of P release is still widely accepted (BURGIS & MORRIS 1987, BOSTROM et al. 1982, WETZEL 1982, FENCHEL & BLACKBURN 1977). Data from the Experimental Lakes Area of Canada suggest, however, that some lakes continue to have extremely low P release from sediments even after the overlying water become anoxic (anoxic P release) (LEVINE et al. 1986, SCHINDLER et al. 1987, ARMSTRONG & SCHINDLER 1971). These aberrant lakes, which are generally believed to be oddities (BOSTROM et al. 1982), contrast sharply with the expectations of the oxygen control model. In this paper we demonstrate that such lakes are widespread and need further investigation.

Methods and approach

Relative phosphorus release (RPR) - The phosphorus which is recycled from a lake's sediment to the overlying water comes ultimately from the decomposition of organic matter. Thus, a low rate of P release may be caused by two very different cases. Case 1: the total rate of decomposition is very low; Case 2: the P, which is liberated from organic matter during decomposition,

does not escape from the sediments. Because decomposition both consumes oxygen and liberates P, P in bottom waters (from sediment P release) would be expected to be greater when oxygen had been depleted than when oxygen was still abundant whether or not the binding of P to sediments decreased under anoxia (RICHARDS et al. 1965). Although this point is simple it has led to much confusion and tautological reasoning in the literature (e.g., BOSTROM et al. 1982, LARSEN et al. 1981, MORTIMER 1971, TAFT & TAYLOR 1976).

To examine Case 2, both the P release and the total rate of decomposition (oxic plus anoxic) must be known. The difference between the ratio of liberated P to liberated inorganic C from the sediments and the P:C ratio of the organic material supplied to those sediments is a quantitative measure of the extent to which P is sorbed by the sediments. We term this measure relative P release (RPR) and use it to distinguish between Cases 1 and 2.

Values of RPR are analysed in the following context. The material delivered, by sinking, to the sediments of lakes ranges generally in P:C ratios between 4 and 10 mmol P · mol⁻¹ C (UEHLINGER & BLOESCH 1987, CARACO 1986, MOELLER 1985, ULEN 1978). If there were no sorption of P in sediments after the decomposition of this material, the expected range for RPR would, therefore, be between 4 and 10 mmol P · mol⁻¹ C. Values of anoxic RPR above 10 mmol P · mol⁻¹ C indicate the re-release of P which had been sorbed previously when the sediments were oxic (SEN GUPTA 1973, BURNS & ROSS 1972). These high values of RPR are in agreement with the expectation of the oxygen control model. Values of anoxic RPR less than 4 mmol P · mol⁻¹ C indicate that sediment uptake continues after bottom waters become anoxic, and are not in agreement with the oxygen control model.

To obtain values of RPR for various lakes, we made measurements, over time, of the accumulation of total dissolved phosphorus and of total decomposition in the hypolimnia of lakes during stratification. Total decomposition was measured as both the net accumulation of dissolved inorganic carbon (DIC) over time and as the sum of all electron acceptors used. Because this approach used concentrations of P and DIC in the lake itself it does not suffer from any of the potential pitfalls of sediment core incubations. The details of this method are provided elsewhere (CARACO et al. 1989, CARACO et al. 1991). In addition to our own measurements we

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



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.