

# LAKE IRON NODULES IN NEW ENGLAND LAKES AND PONDS – GEOLOGIC INDICATORS OF SURFACE WATER QUALITY CHANGES OVER TIME



Saugus Iron Works

Reference: Saugus Iron Works National Park, website photographs

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- APRIL 12, 2019

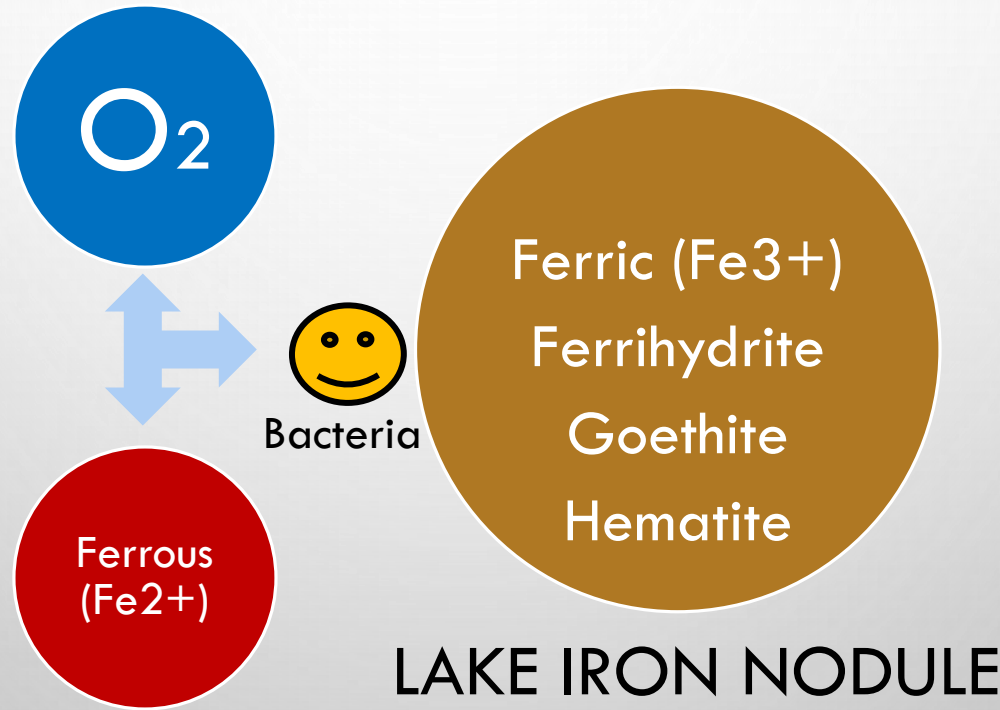
# WHAT IS A LAKE IRON NODULE?

- AN IRON-ENRICHED CONCRETION, OFTEN CONTAINING MORE THAN 30 PERCENT IRON BY WEIGHT AND FORMED IN WATER AT STANDARD TEMPERATURE AND PRESSURE ON THE EARTH'S SURFACE. THEY ARE PREDOMINANTLY COMPOSED OF THE MINERALS GOETHITE AND HEMATITE.
- IMPORTANTLY, IRON NODULES ARE A NATURAL SINK FOR PHOSPHORUS IN LAKES AND PONDS



THEY FORM BY BIOGEOCHEMICAL PROCESSES IN  
WATER INVOLVING IRON, OXYGEN AND BACTERIA.

THEY GROW ABOUT 1 TO 20 MILLIMETERS PER YEAR



Simplified and Illustrative Process

# PRE-1800s

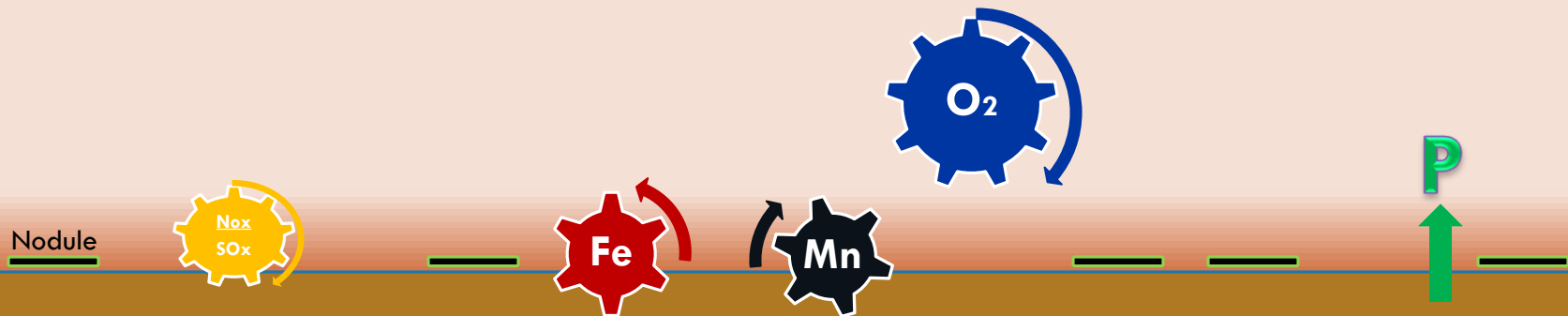
WHERE ARE THEY FORMED? - ON A NUCLEATION SITE  
1 TO 2 CENTIMETERS ABOVE THE SEDIMENT SURFACE

## Pre-1800s Biogeochemical Setting

Limited Nitrate and Sulfate Concentrations in Surface Water

DOC-rich water, reduced water clarity (more of a tea-colored water), infrequent algae blooms

## Oxygenated Surface Water



## Oxygenated (oxic) Sediment

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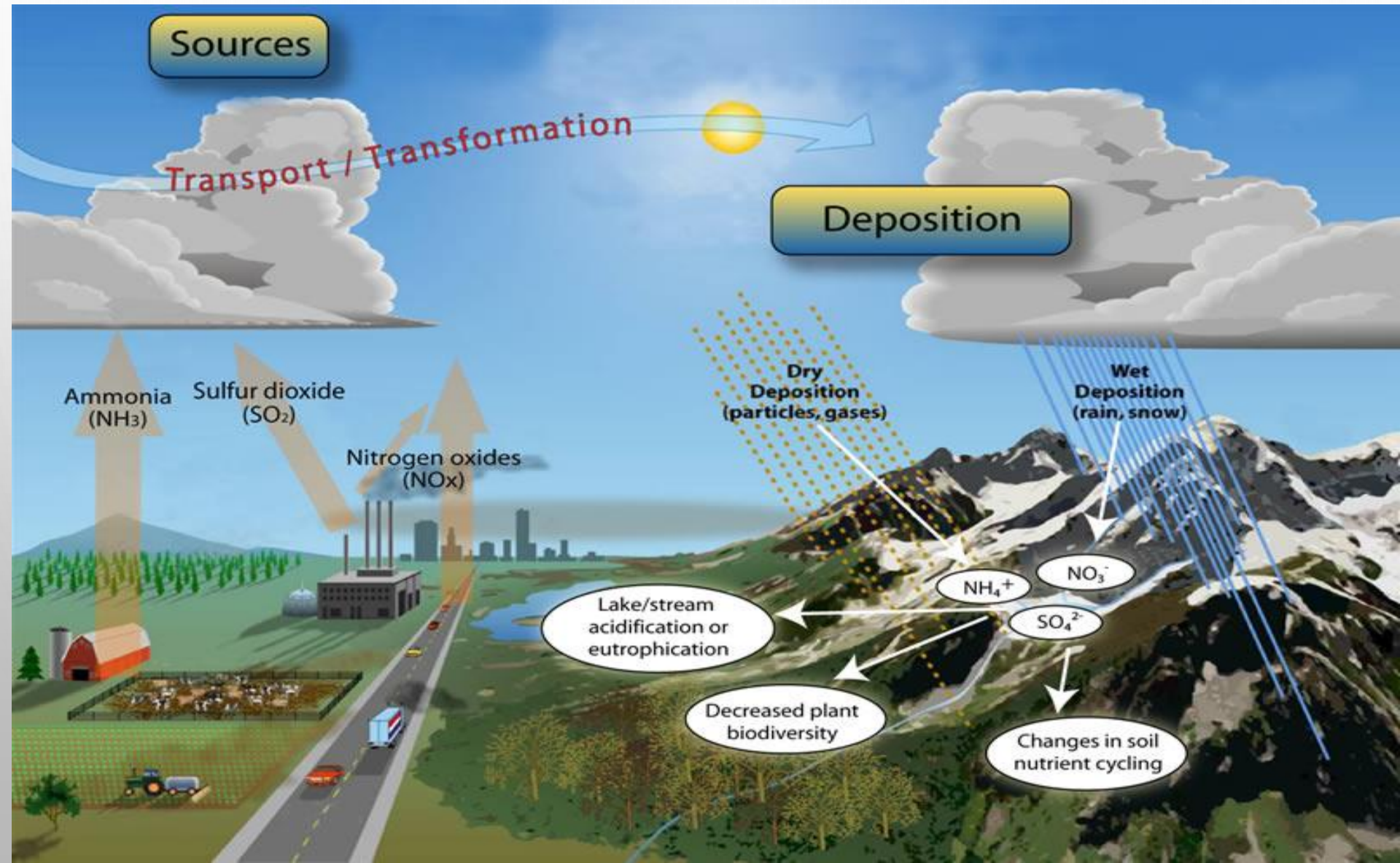
# PAST RECORDS –

- 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.
- 1640: THERE WERE APPROXIMATELY 15,000 PEOPLE (EUROPEAN DESCENT) IN THE MASSACHUSETTS BAY COLONY. BY 1770, THIS HAD INCREASED TO APPROXIMATELY 1,000,000 PEOPLE.
- 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 IRONWORKS 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).

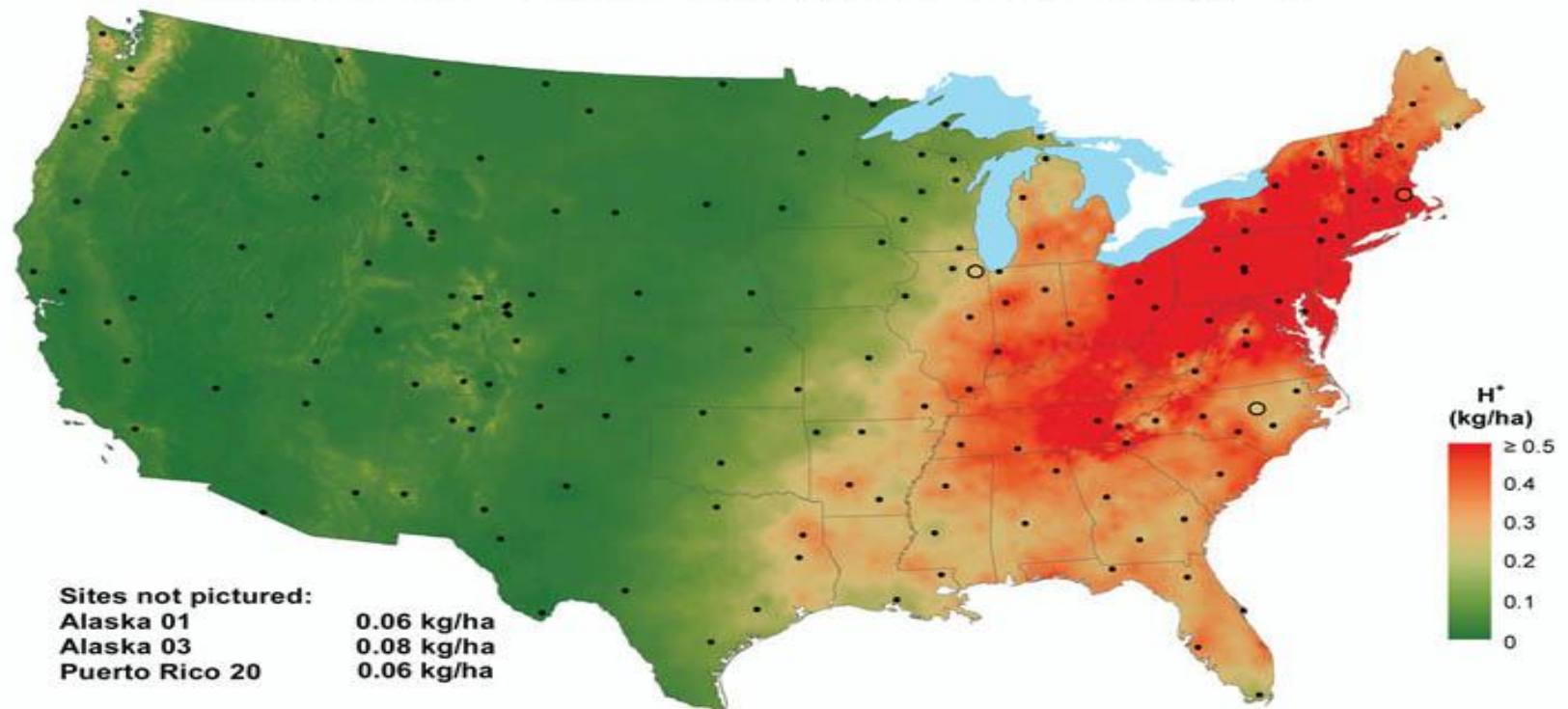


# SO WHY/WHERE DID THE NODULES GO?

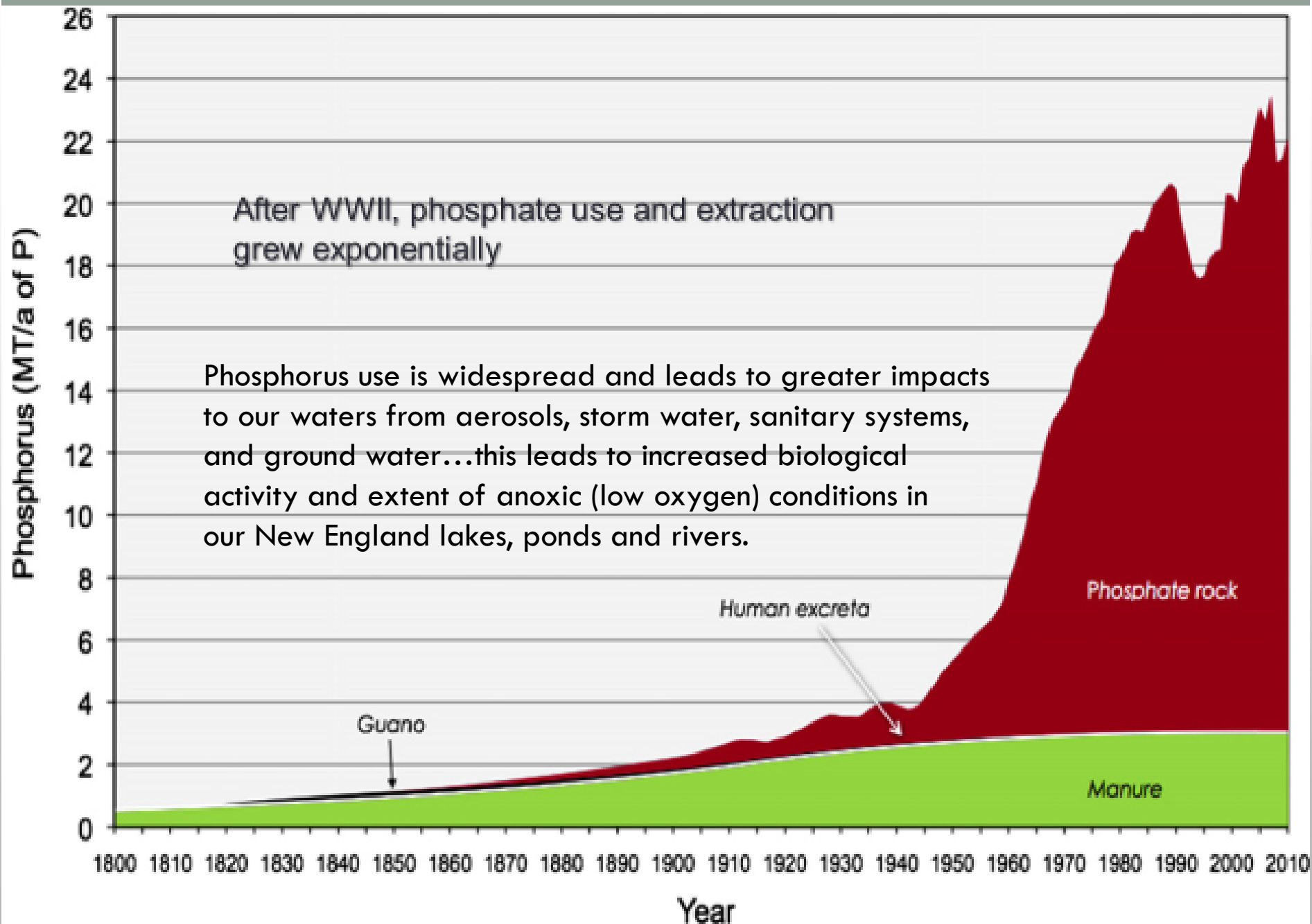


# 1994 ACID RAIN DEPOSITION INCREASES NITRATE AND SULFATE IMPACTS TO OUR WATERS

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

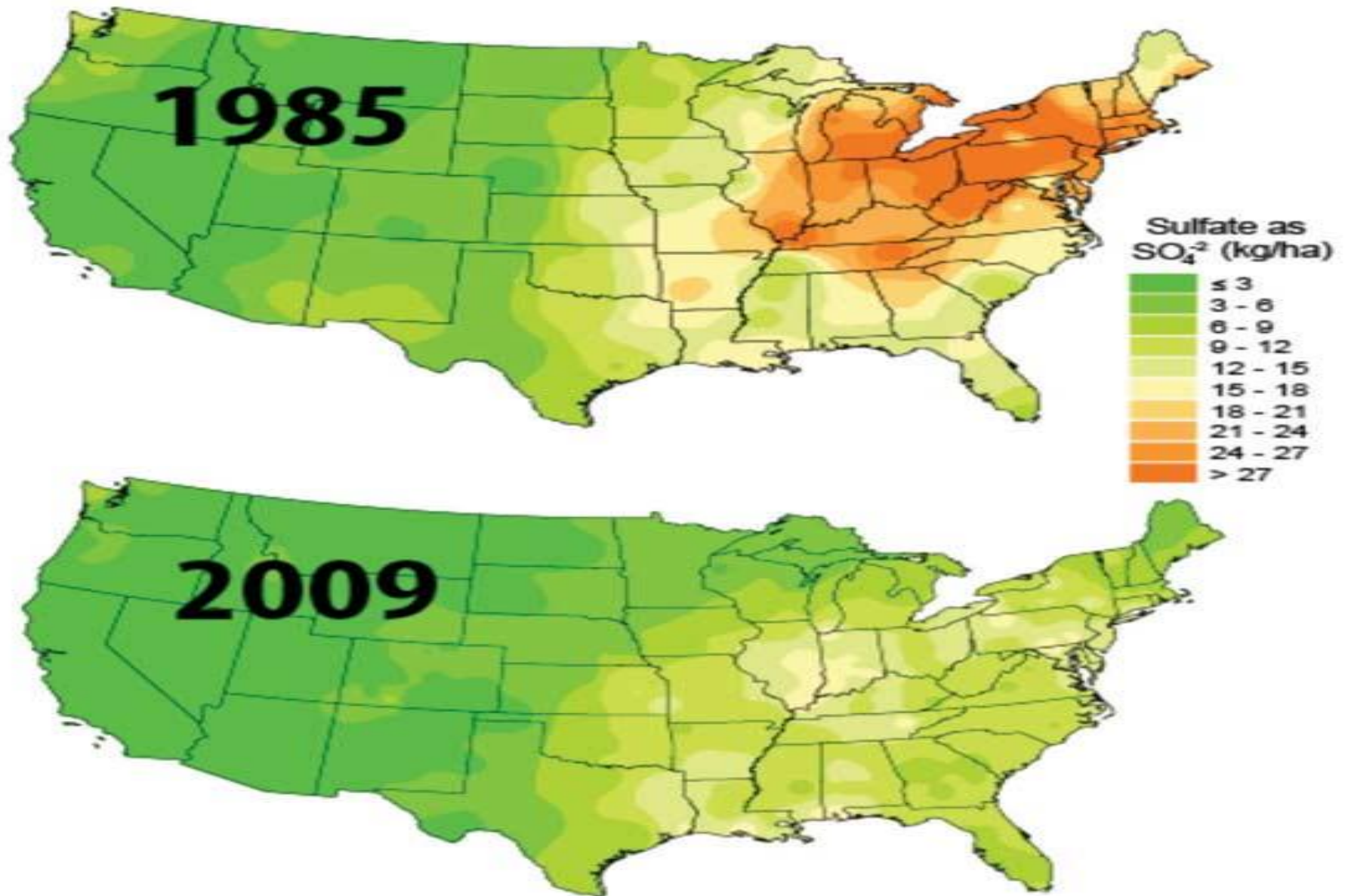


## Its not just acid rain deposition. Use of Phosphorus has significantly increased since 1945





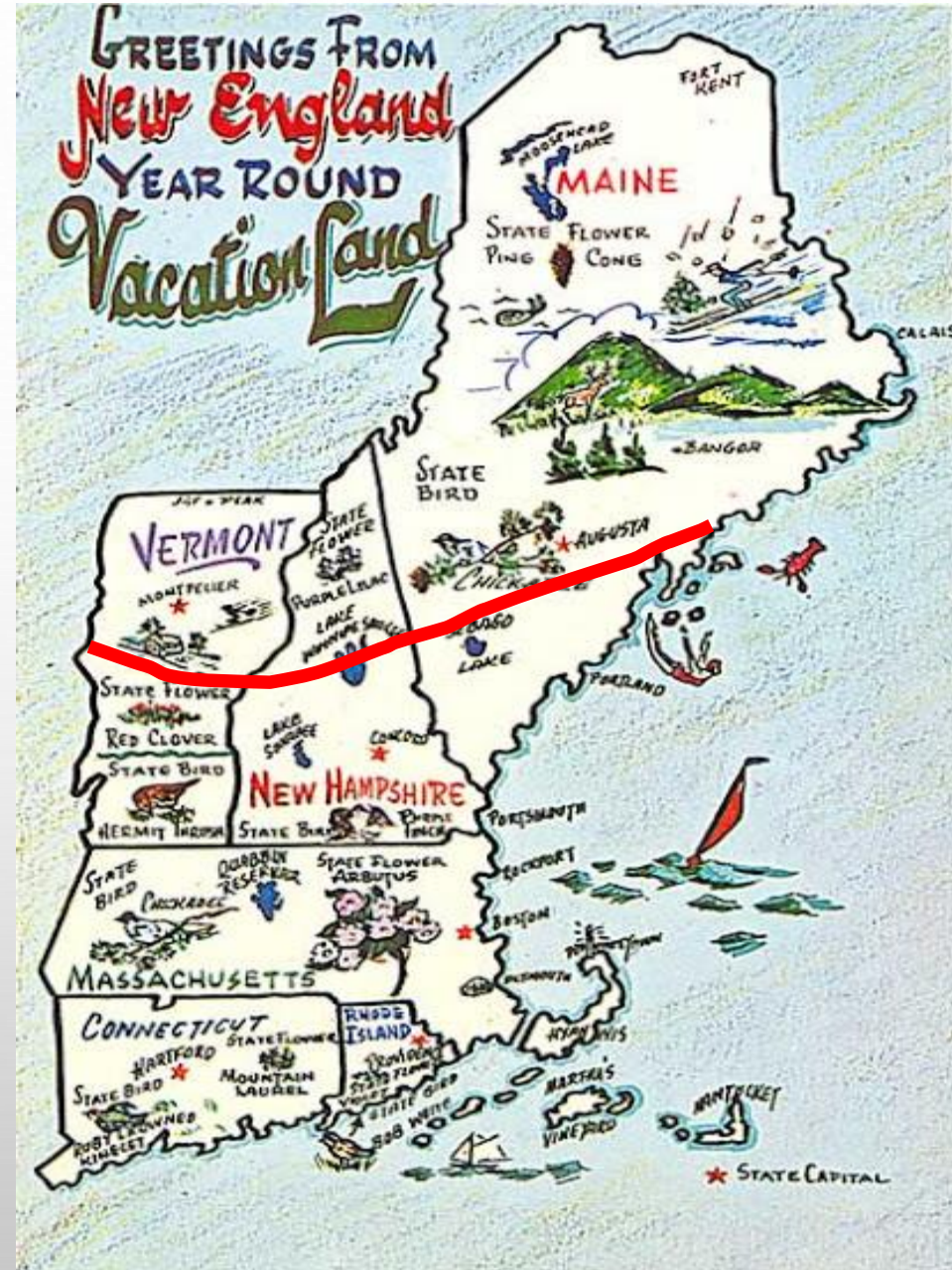
# CHANGES IN GEOCHEMISTRY - SULFATE DEPOSITION REDUCED



BY YEAR 2010 -

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

RED LINE MARKS  
TENTATIVE KNOWN LIMITS  
OF IRON NODULES.



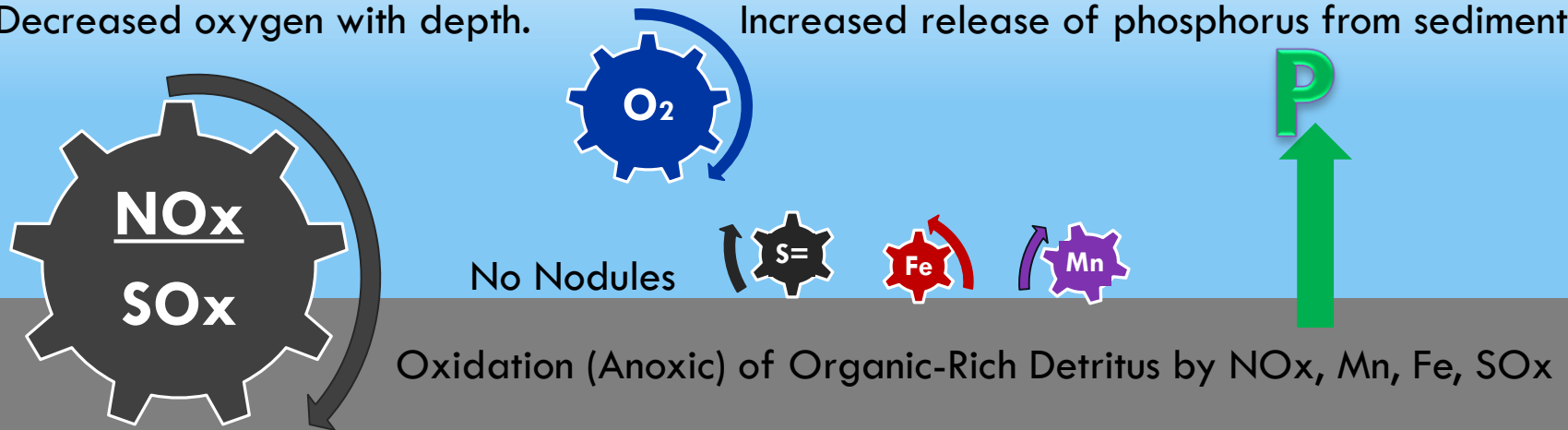
# CIRCA 1970 – 2010 BIOGEOCHEMICAL SETTING – MY INTERPRETATION

NO<sub>x</sub>  
SO<sub>x</sub> ↘  
↗ Phosphorus (P)

Nitrate- and Sulfate- and Phosphorus- Enriched Surface Water

DOC-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.



Oxidation (Anoxic) of Organic-Rich Detritus by NO<sub>x</sub>, Mn, Fe, SO<sub>x</sub>

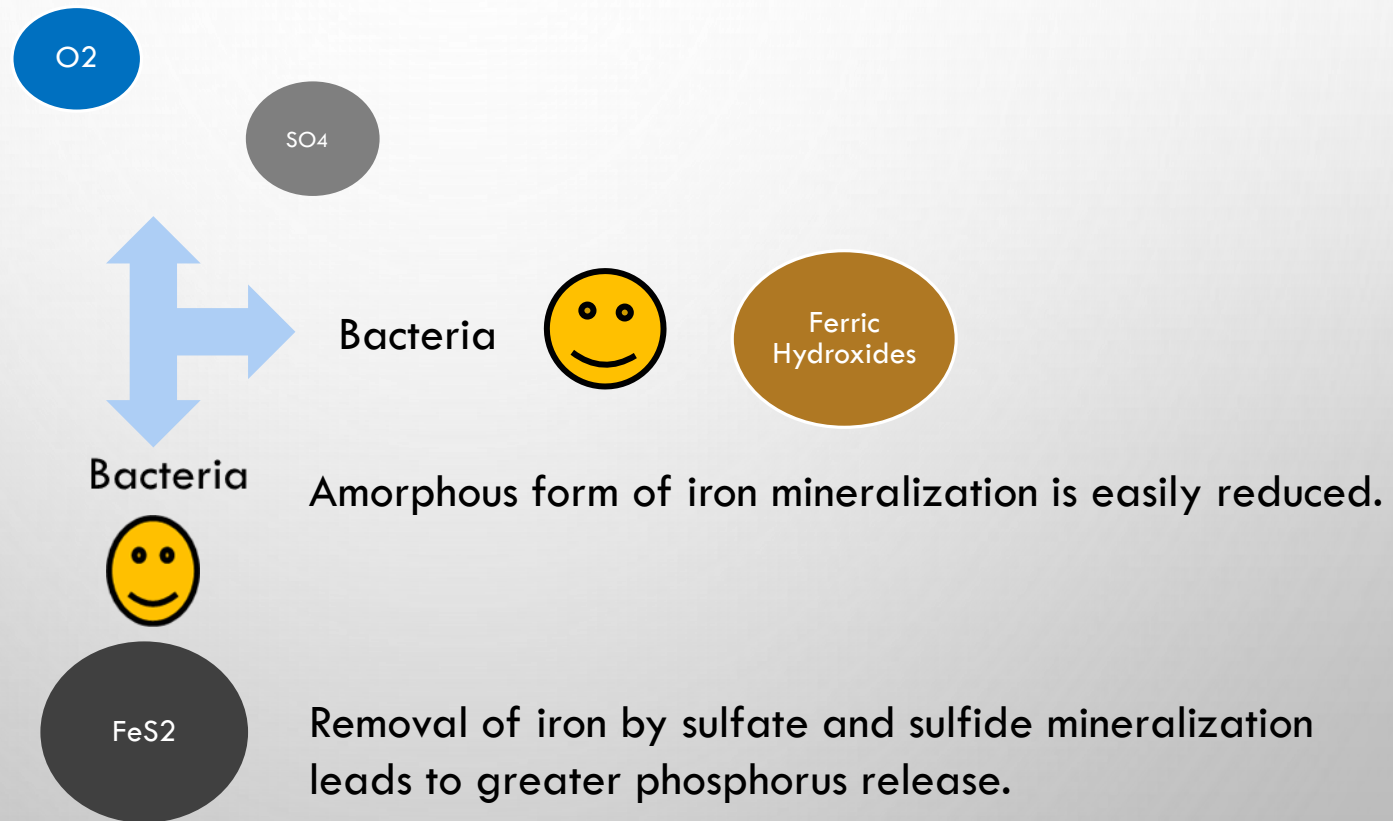
No Iron Nodules – Replaced by Iron Sulfide Minerals (greigite Fe<sub>3</sub>S<sub>4</sub>, and pyrite FeS<sub>2</sub>)



**Reduced (Anoxic) Sediment and Pore Water**



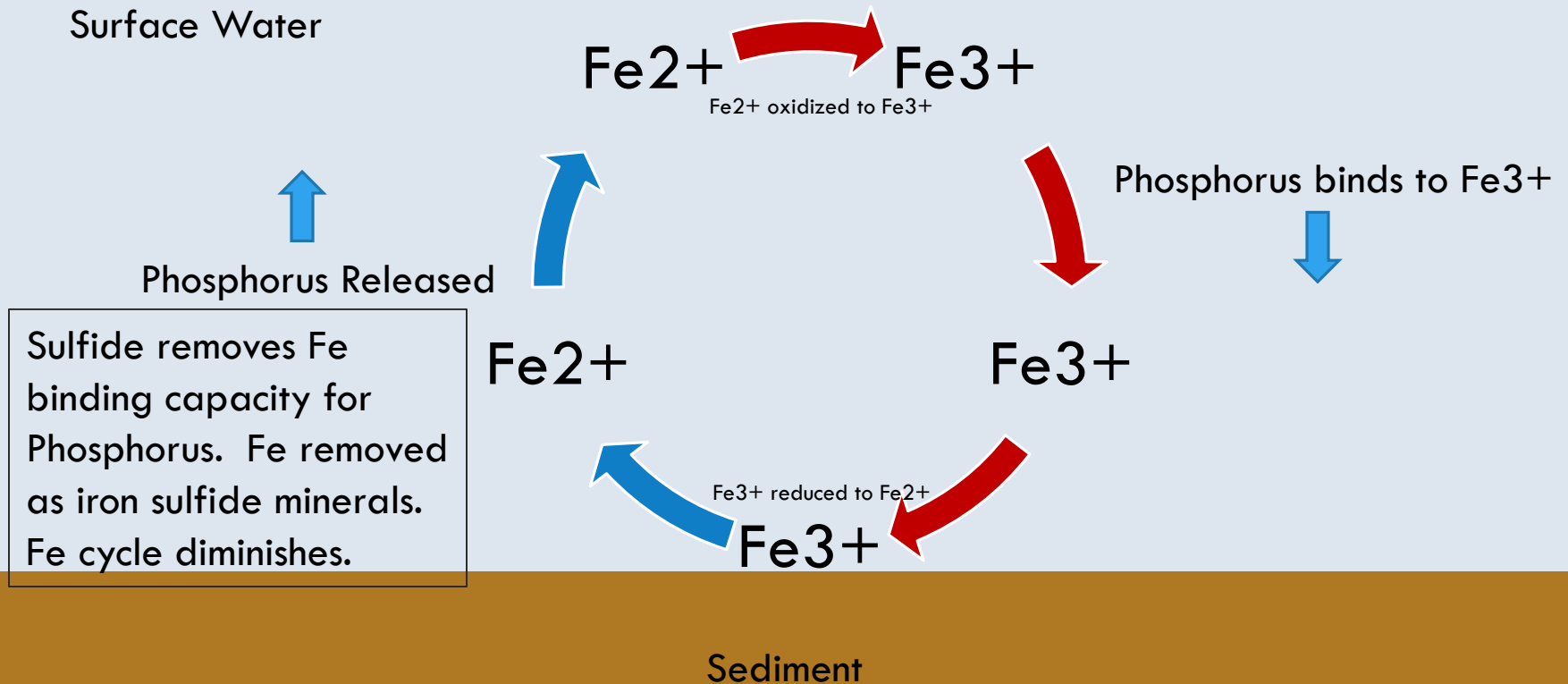
# NODULES AND MORE MINERALIZED FORMS OF IRON (GOETHITE AND HEMATITE) ARE REMOVED BY BIOGEOCHEMICAL PROCESSES IN WATER INVOLVING ANOXIC CONDITIONS, SULFATE AND BACTERIA.



Simplified and Illustrative Process

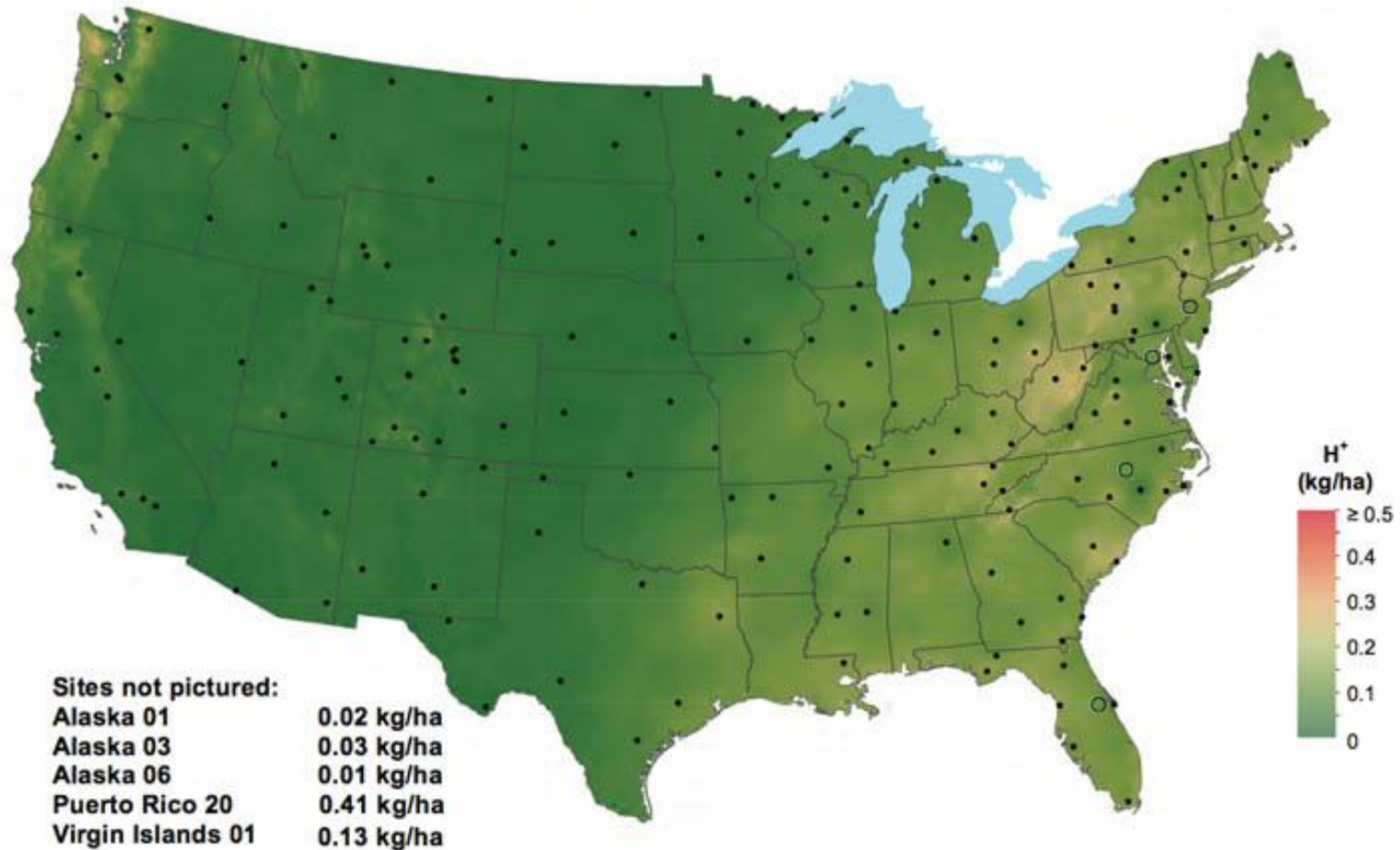


# FERROUS CYCLE



# 2010 ACID RAIN DEPOSITION

Hydrogen ion wet deposition from measurements made at the Central Analytical Laboratory, 2010

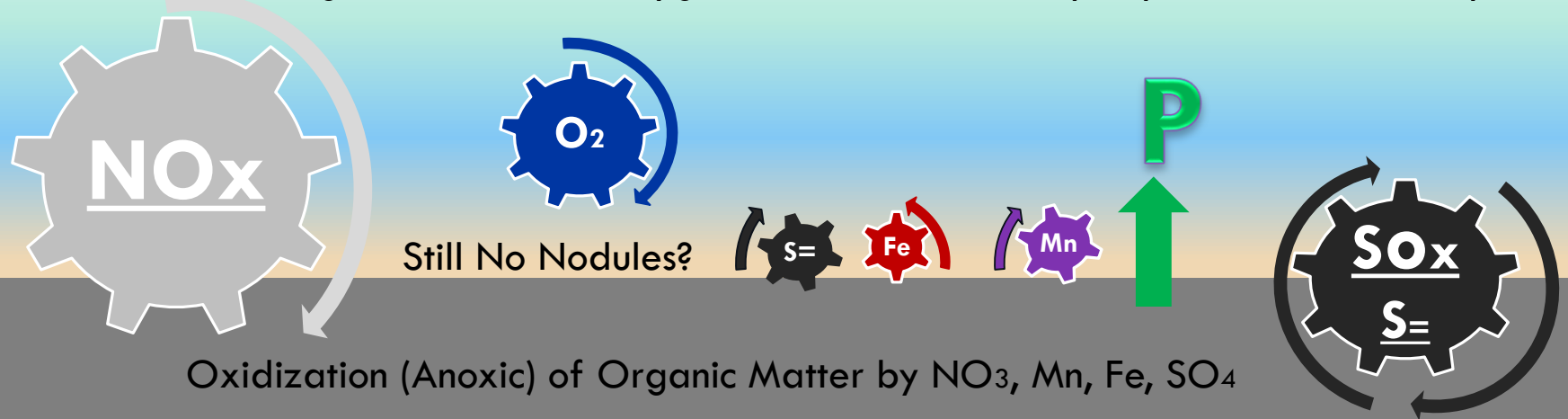


# CIRCA 2019 – MY INTERPRETATION

## AN IMPROVEMENT SINCE 2010

NO<sub>x</sub> SO<sub>x</sub> ↗  
Phosphorus (P) ↗  
Nitrate- and Phosphorus- Enriched, Sulfate-Low to Moderate in Surface Water

DOC increasing from North to South in New England, water clarity decreasing (more tea-coloration), algae blooms moderating. Seasonal low oxygen still common in deeper parts of lakes and ponds.



### No Iron Nodules – Replaced by Iron Sulfide Minerals



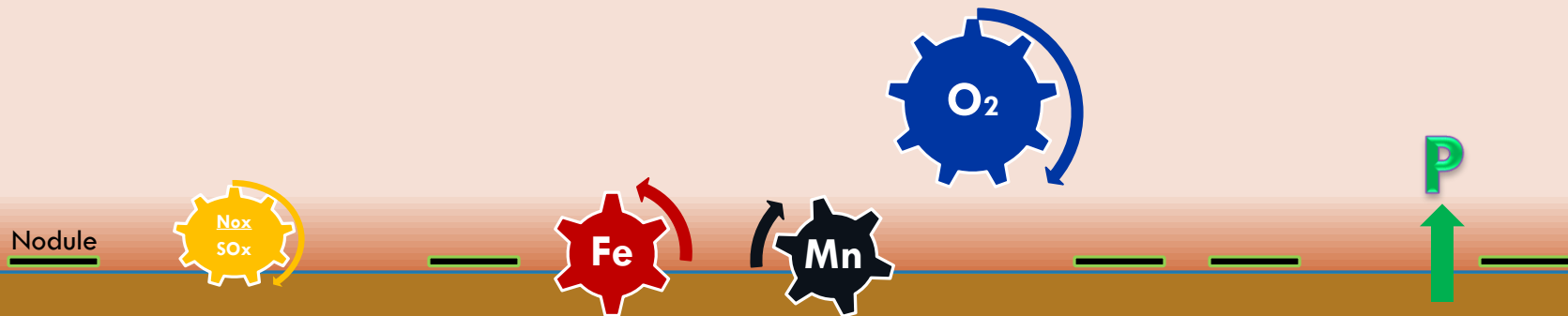
**Reduced (Anoxic) Sediment and Pore Water**

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

Limited Nitrate, Phosphorus and Sulfate Concentrations in surface Water

DOC-rich water, reduced water clarity (more of a tea-colored water), infrequent algae blooms. By removing excess sulfates and phosphorus in our waters, the natural ferrous (iron) cycle is restored. This promotes development of native plant and animal species and minimizes conditions favorable for invasive species (clear water, sulfates and excess phosphorus). Lake iron nodules can be restored.

## Oxygenated Surface Water



## Oxygenated (oxic) Sediment

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# FINDINGS

- PRIOR TO THE 1800S, IRON NODULES WERE WIDESPREAD IN NEW ENGLAND.
- 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 QUALITY CAN ALTER THE NATURAL IRON CYCLE AND CHANGE BIOGEOCHEMICAL CONDITIONS REQUIRED FOR GROWTH OF IRON NODULES. PHOSPHORUS PROMOTES INCREASED BIOLOGICAL PRODUCTIVITY AND ANOXIA. SULFATE AND SULFIDES BIND WITH IRON AND ENHANCE BIODEGRADATION AND RELEASE OF PHOSPHORUS FROM SEDIMENTS.
- SULFATE MINERALIZATION PROMOTES ANOXIC CONDITIONS AND EUTROPHICATION BY SCAVENGING DISSOLVED OXYGEN AT DEPTH AND WITHIN SEDIMENTS.
- REMOVING EXCESS SULFATE AND PHOSPHORUS IMPACTS HELPS TO RESTORE THE NATURAL IRON CYCLE AND ITS LONG TERM BINDING CAPACITY FOR PHOSPHORUS IN OUR LAKES AND PONDS OF NEW ENGLAND.
- INCREASED DISSOLVED ORGANIC CARBON (DOC), AS APPARENT BY “TEA-COLORED” WATER WOULD FAVOR OUR NATIVE PLANT AND ANIMAL SPECIES OVER HARMFUL ALGAE BLOOMS, INVASIVES AND NUISANCE GROWTH CONDITIONS.

# QUESTIONS?

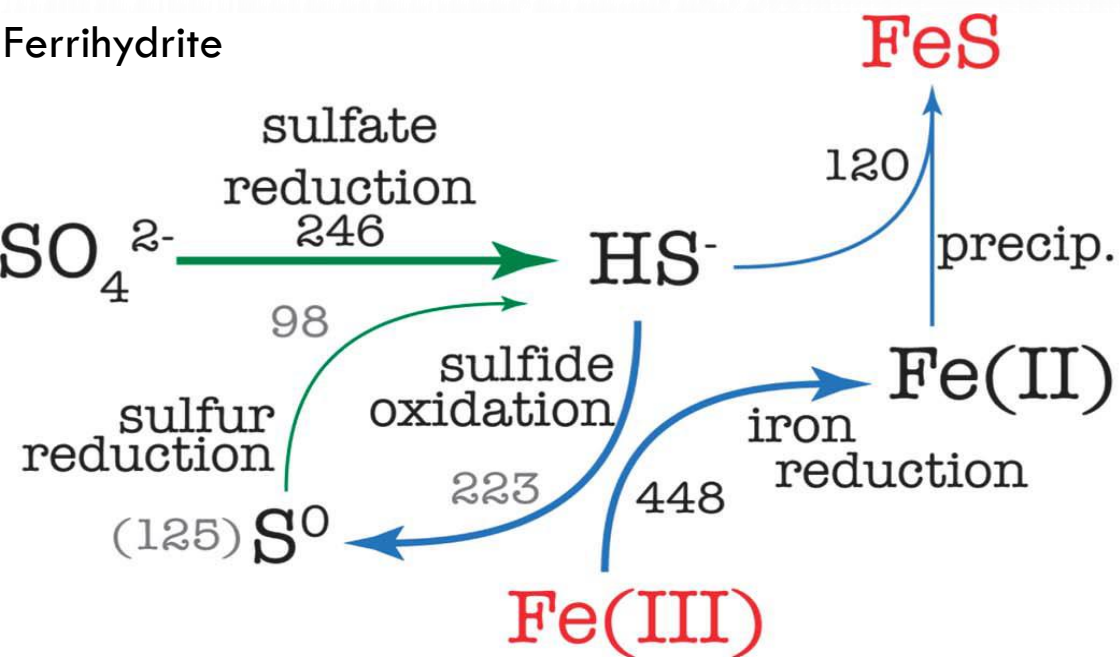
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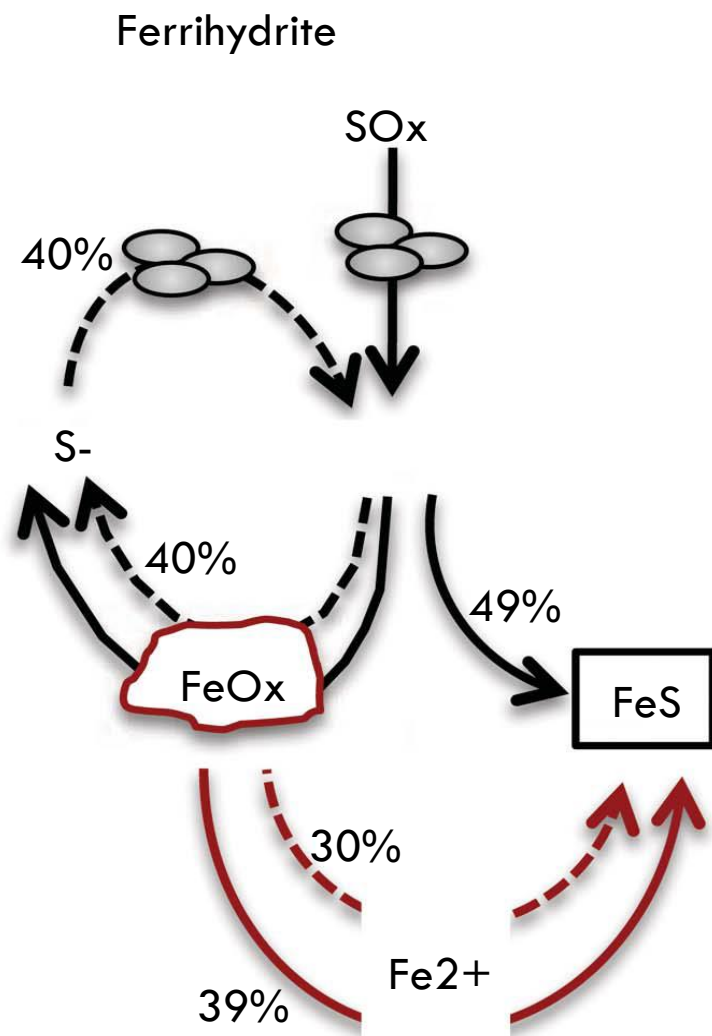
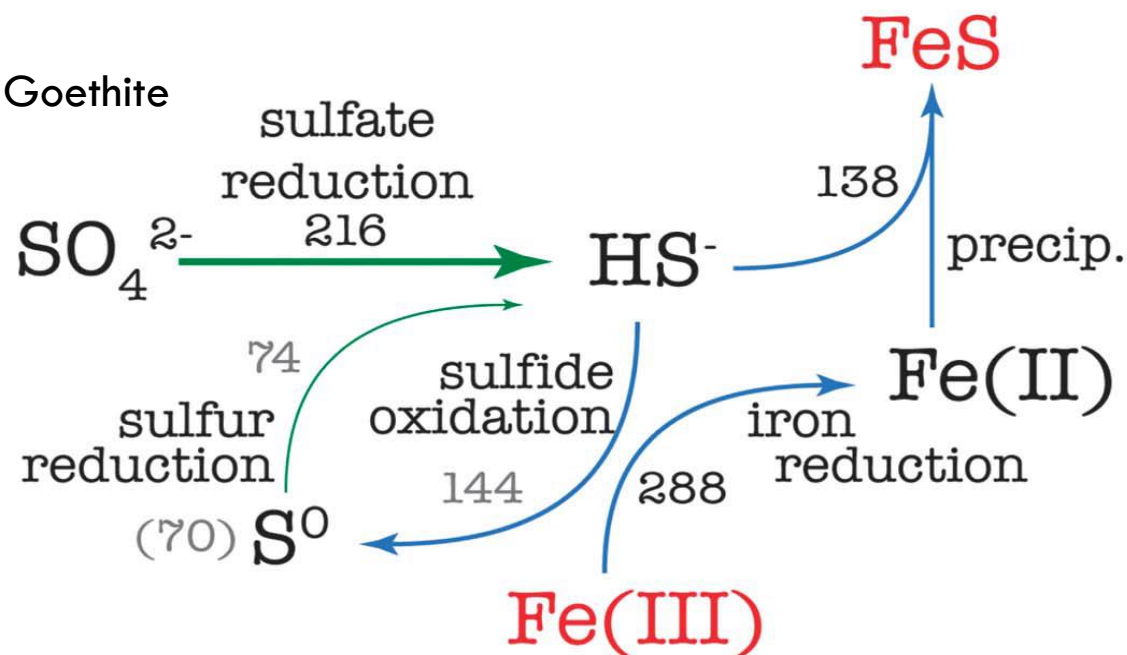
## REFERENCES AND MORE INFORMATION

- 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.

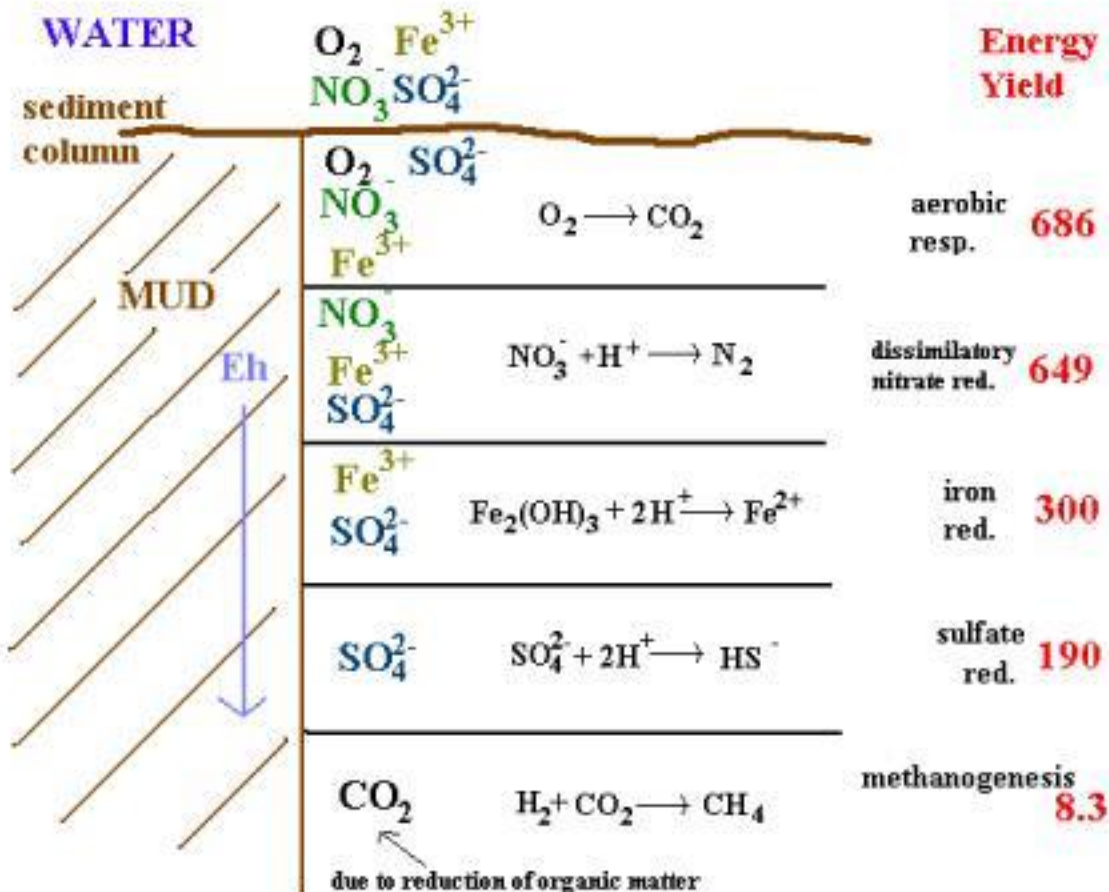
# Ferrihydrite



# Goethite



# 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

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**SEDIMENTS** of aquatic systems play a critical part in controlling phosphorus loading to the water column<sup>1</sup>. 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<sup>1,2</sup> 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 limited<sup>3</sup>, whereas in many saline systems (with high sulphate concentrations) production is often P sufficient<sup>4</sup>. 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 Hansel<sup>1</sup>, Chris J Lentini<sup>2</sup>, Yuanzhi Tang<sup>3</sup>, David T Johnston<sup>4</sup>, Scott D Wankel<sup>1</sup> and Philip M Jardine\*

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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



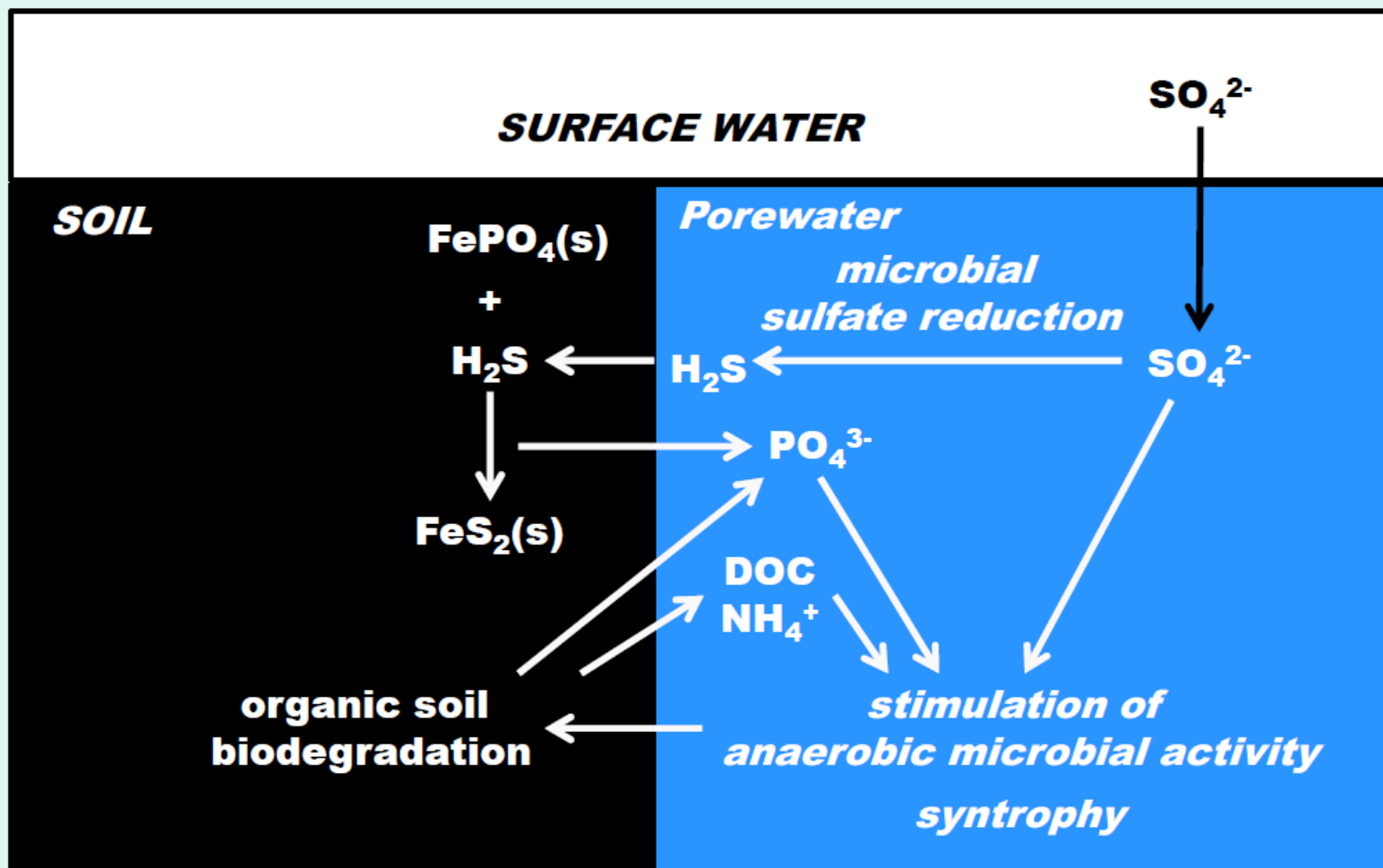
# Sulfate as a Contaminant in Freshwater Ecosystems: Sources, Impacts and Mitigation

## 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

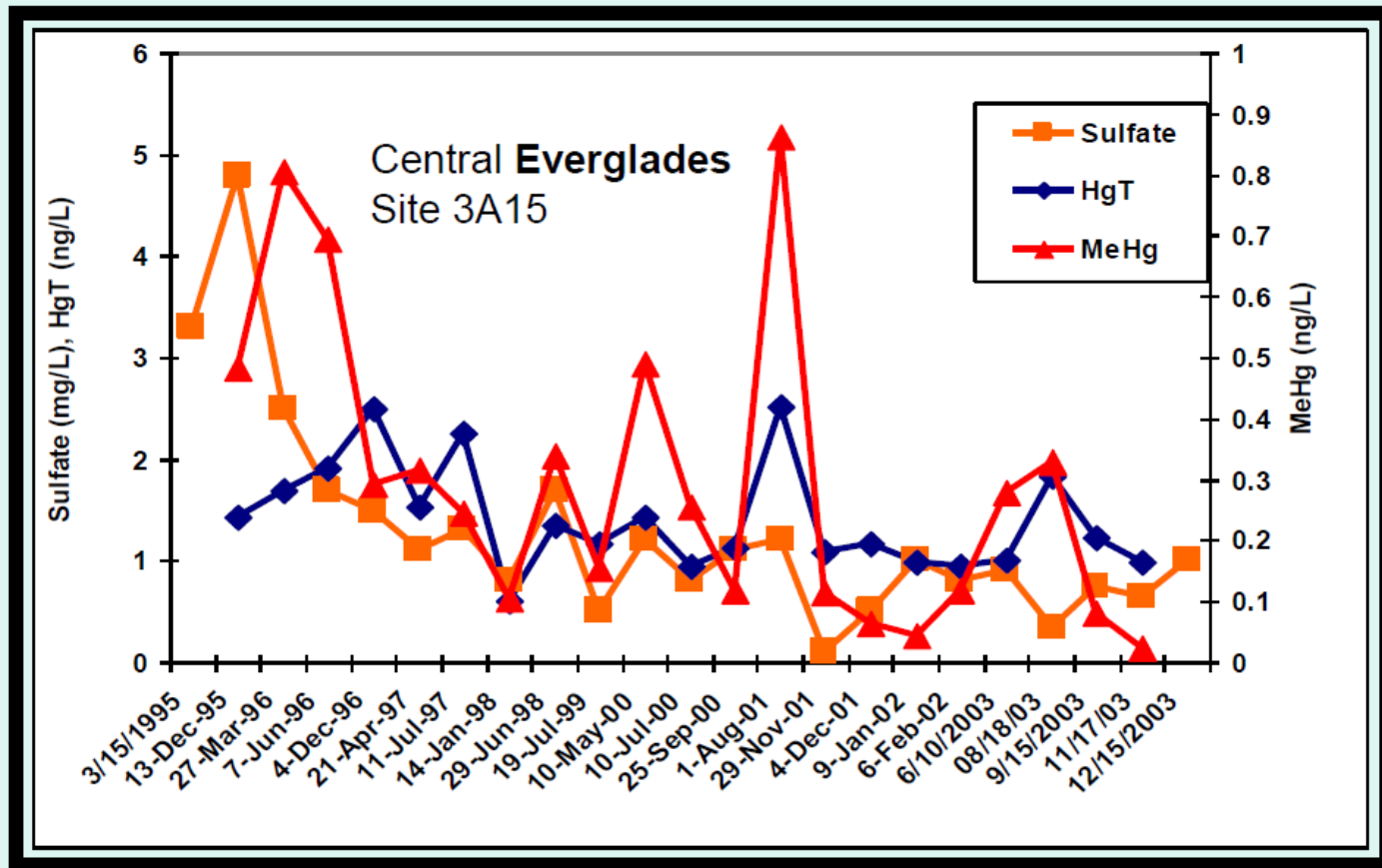


# Internal Eutrophication from Sulfate Contamination of Freshwater Wetlands





## 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

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

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**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<sup>-2</sup> yr<sup>-1</sup>, significantly higher than the 45 to 48 meq m<sup>-2</sup> yr<sup>-1</sup> 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.