The Phosphorus Cycle beyond the 'Ferrous Wheel'

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P studies in:

- Calcasieu River LA (auxiliary to Cr study)
- Florida Everglades
- Chesapeake Bay watershed
  - Riverine
    - Pocomoke River Potomac River
  - Reservoirs
    - Conowingo
    - Lee Hall – Harwood Mills
  - Streams of Eastern Shore
    - Delmarva Peninsula
- Snake River watershed
- Upper Klamath Lake

These studies focused on the fractionation but not speciation of phosphorus.

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Included in fractionation schemes *

*Requires minimal equipment

$MgCl_2$ (pH=8) extractable –
Bioavailable

Dithionite-citrate-bicarbonate extracts
poorly-crystalline Fe and associated P
Bioavailable with reducing conditions

1M HCl extracts carbonates and P-containing
minerals Not Bioavailable

Residual P includes organic P and refractory P
Limited bioavailability

LEAG:

J Are iron oxides a major control on phosphorus in lower Mississippi sediments?
Iron oxides not expected to be important where there is sulfide formation

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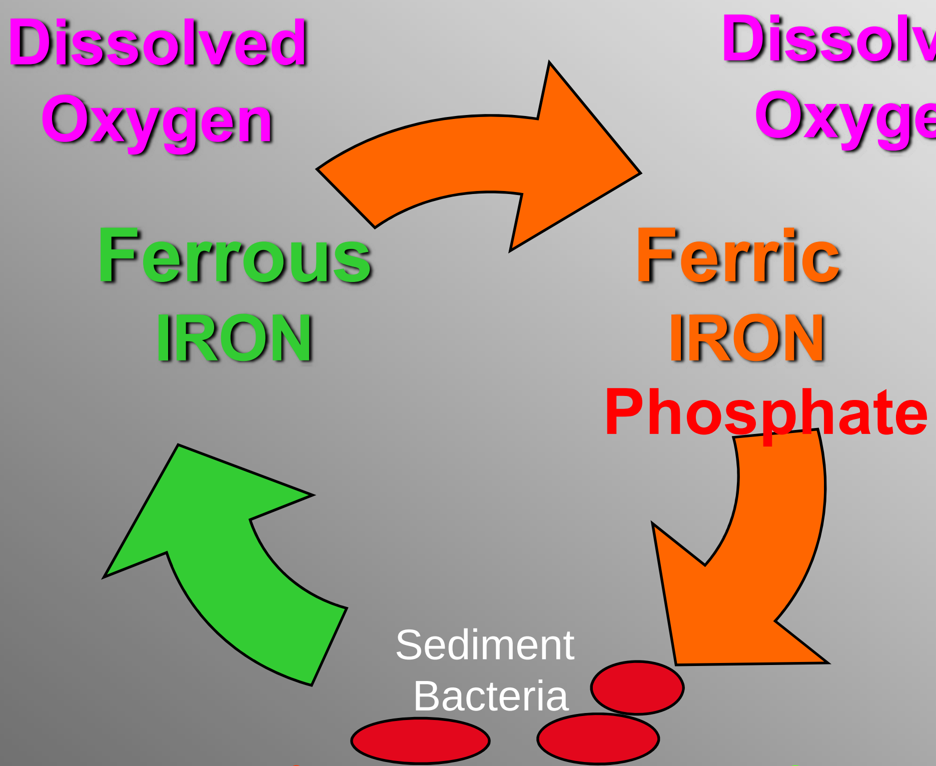
Reduction of ferric iron to more soluble ferrous iron releases sorbed phosphate. (Mortimer 1941)

Still useful to identify sediments vulnerable to release of phosphate. An valuable tool used in our P studies in lakes, reservoirs, rivers and estuaries



ZPC = 8.5

Bacteria: (Fe^{3+})(Phosphate) $\longrightarrow$ Fe^{2+} + Phosphate

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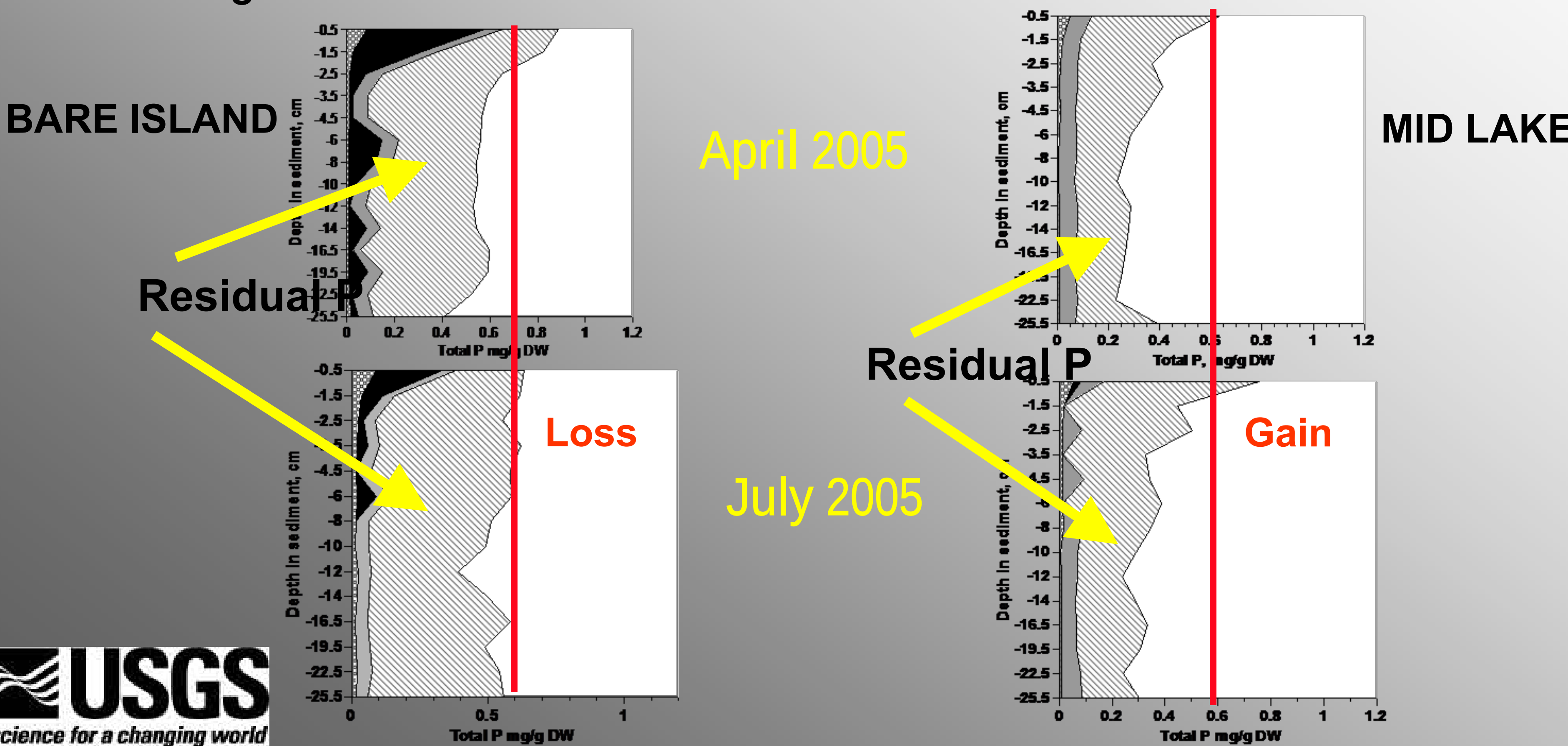
Statistically significant gain OR loss of total P from surficial sediment during 2005 AFA bloom.

Between April and July, 2005, there was a significant loss of total P and poorly-crystalline Fe oxides associated P from Bare Island surface sediment and a significant gain of total P and P associated with organic matter in Mid Lake surface sediment.



Geochemists have used, and are using, fractionation schemes to evaluate:

(a) the bioavailability of P in water and sediment and

(b) the probability of P flux (loss) from sediment to overlying water column.

With tools like ^{31}P NMR, we are now identifying and semi-quantifying forms (species) of P in water and solid (sediment, algae) samples.

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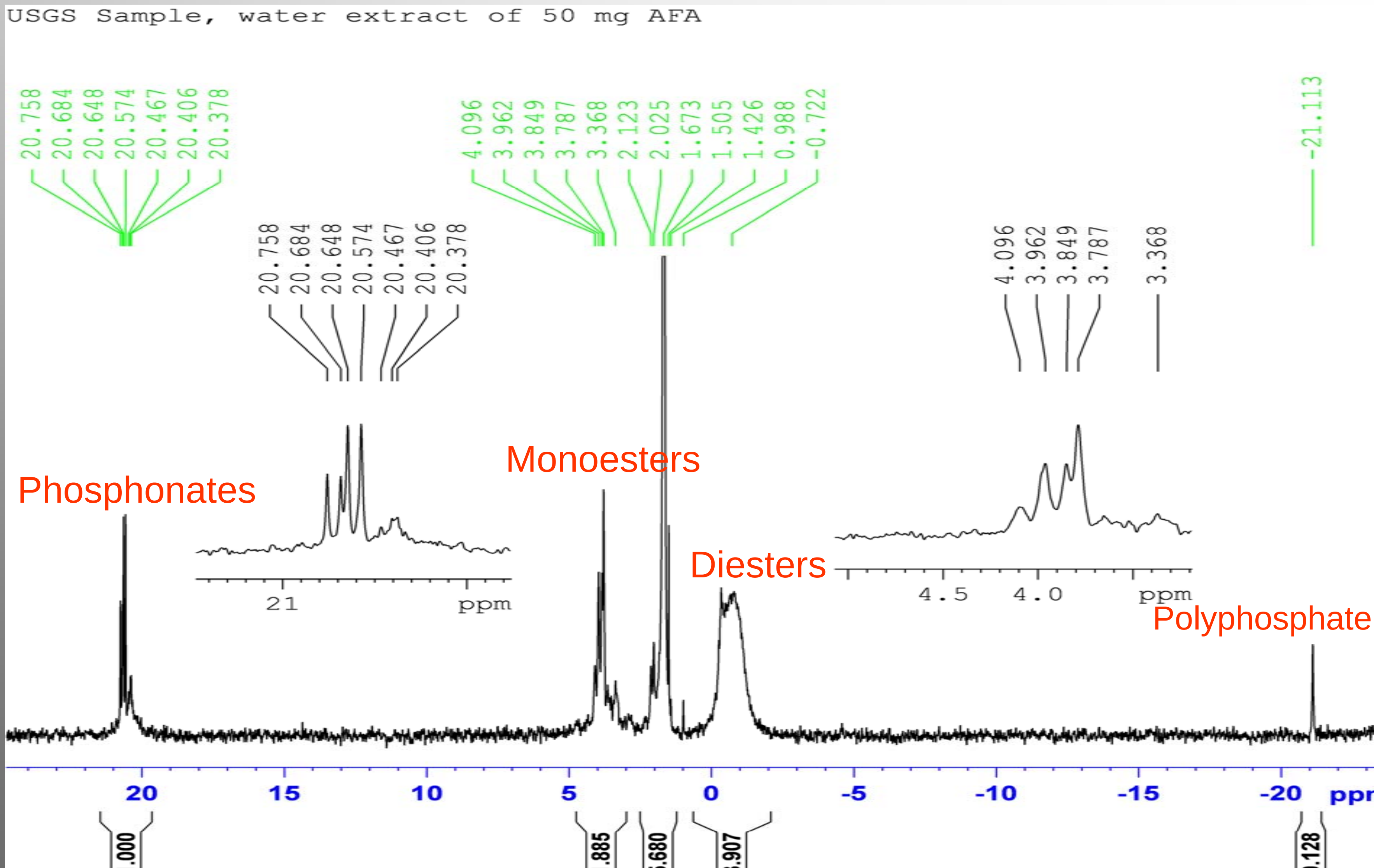

Hot water extract of *Aphanizomenon* collected from Upper Klamath Lake, September 2007 Extraction time=1/2 hr.

Polyphosphates play a role in bacterial metabolism when:

IN WATER

N P C	Growth not limited; Can store polyphosphates.
N P C	If polyphosphate available Growth not limited.
N P C	Grow can be rapid because abundant P for RNA (protein synthesis) allows rapid utilization of C.

Feed back mechanism:

Algae - require N, P release organic C ⟷ Bacteria – Require N,P require organic C

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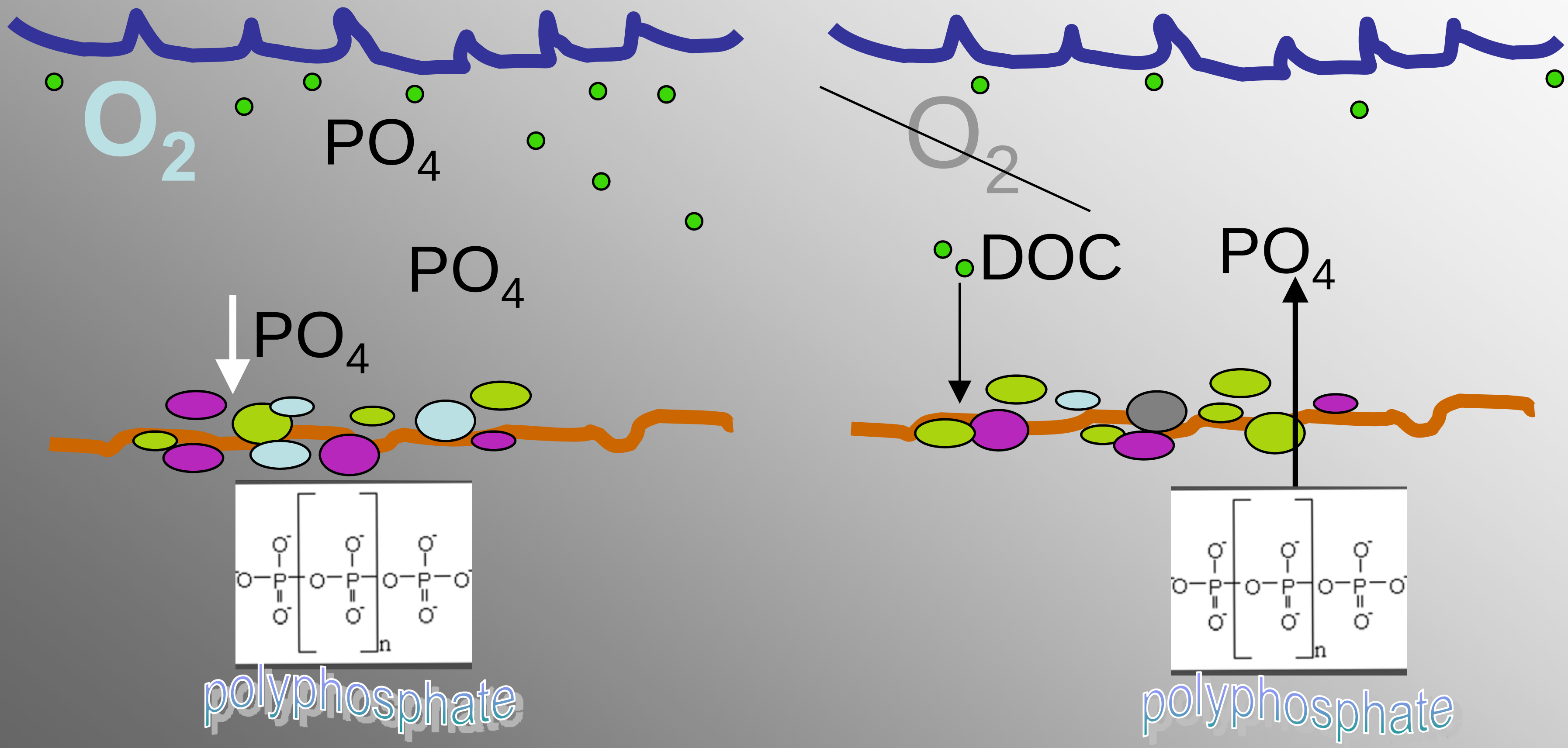
Mechanism for removal of P from STP water for use as fertilizer is thought to occur in natural freshwater sediments.



Determination of DRP concentrations in water samples:

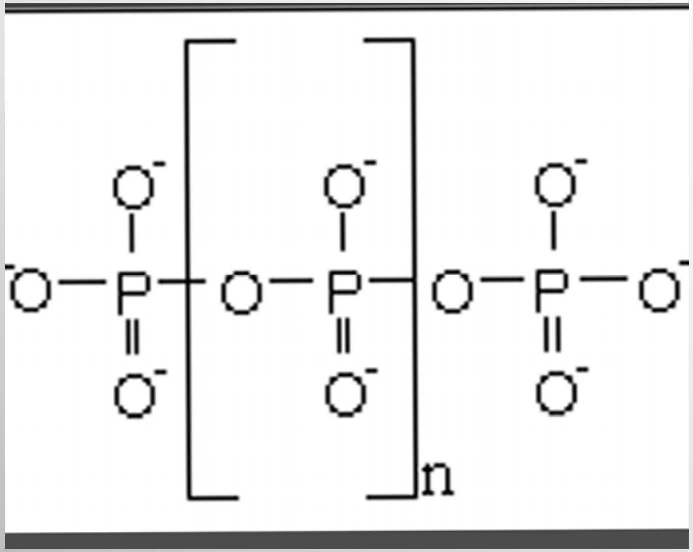
Phosphate that is not detected using the colorimetric method for dissolved (soluble) reactive phosphate. (DRP or SRP).

$$
\begin{array}{ccccccccc}
 & & O^- & & & & O^- & & \\
 & & | & & & & | & & \\
{}^-O & - & P & - & O & - & P & - & O^- \\
 & & \| & & & & \| & & \\
 & & O & & & & O & &
\end{array}
$$

Pyrophosphate

Presence in wetlands related to human impact (Sundareshwar, 2001)

Fertilizer /STP/ Industry



Polyphosphate: An inorganic anion both natural and anthropogenic sources.

LEAG:

J Insure total dissolved P concentrations by including enzymatic pretreatment of water samples.

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Climate change

Marine diatoms store P as polyphosphate (intracellular pellets)

Ian McNulty – Argonne National Laboratory

Pellets of polyphosphate sink to bottom and form apatite. **Sequestration of phosphorus**

If P is sequestered, it is not available to algae (or bacteria) and fixation of carbon by algae is hampered. **Reduced sequestration of carbon**

LEAG:

- **What is the dominant phytoplankton in the Gulf of Mexico?**
- **Is phosphorus from the Mississippi River converted by diatoms in the Gulf of Mexico to intracellular polyphosphate?**
- **When diatoms are the dominant phytoplankton , are polyphosphates sequestered in the sediment limiting the P available to algae?**

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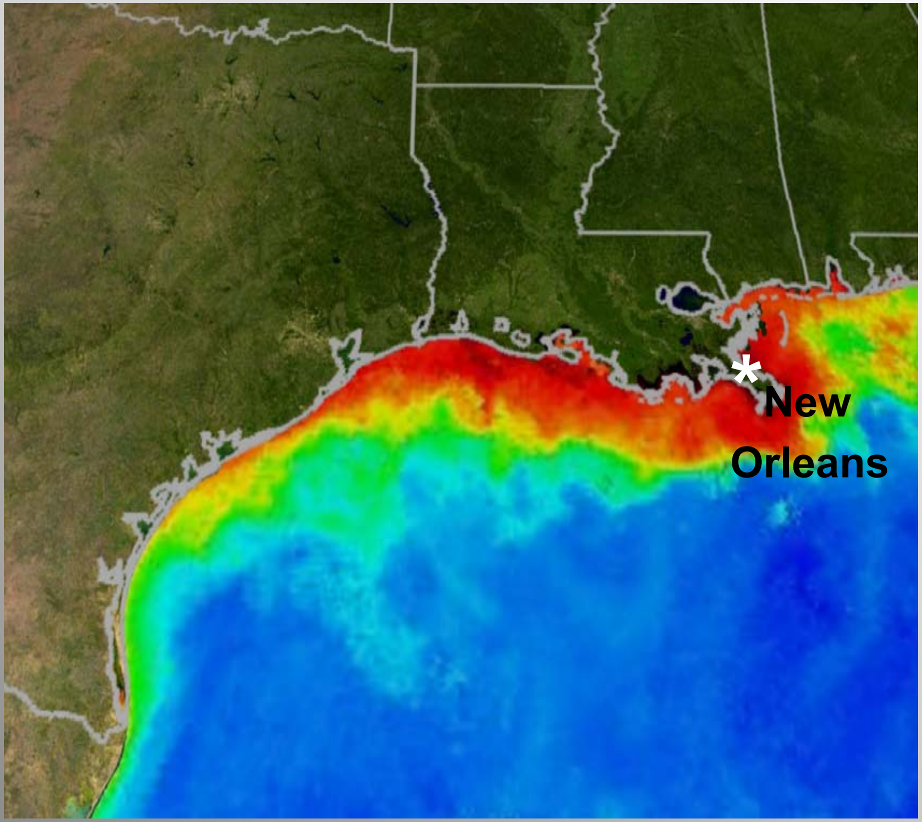
Dead zones



Extent of dead zone in Gulf of Mexico.

From
Kenyon College - Microbial life educational resources web site.

Dead zones

(A) Nitrogen fixation by Trichodesmium limited by P concentration in algal cells

Saňudo-Wilhelmy Nature 2001

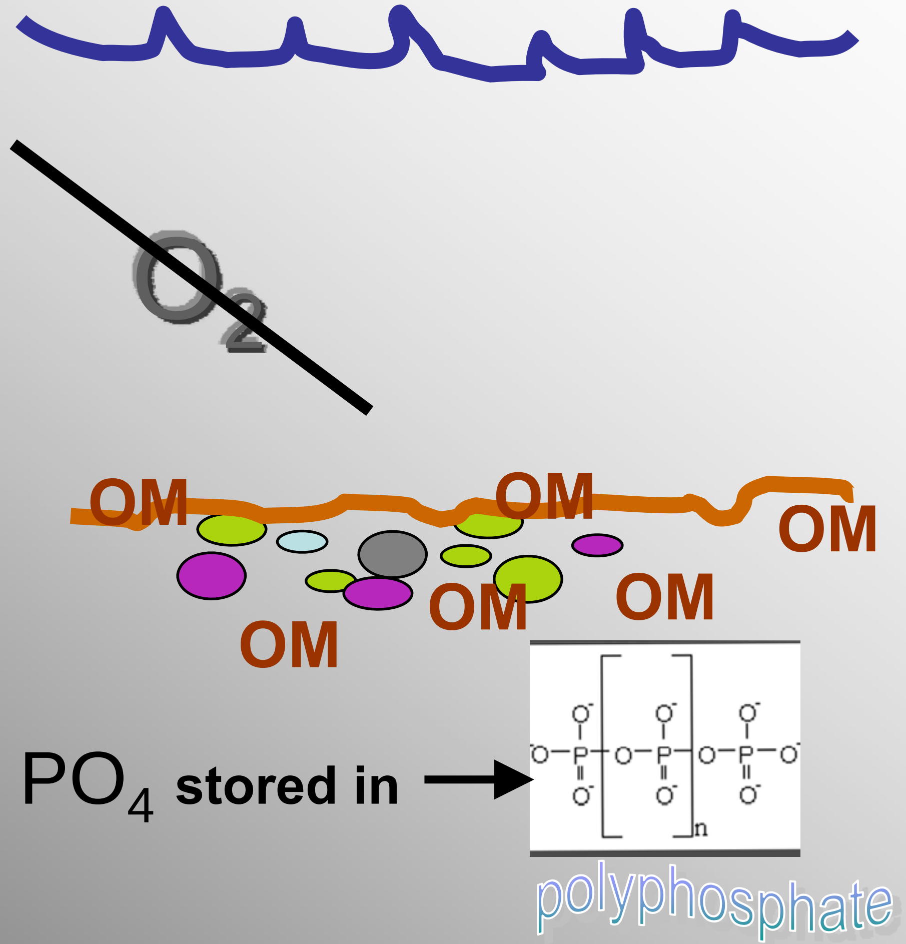
Fe not a factor

LEAG:

J How are N and P cycles linked; in particular, what is the connection between N and P in areas of dead zone?

Dead zones

(B) **Polyphosphates stored in bacteria are energy currency (hydrolysis of phosphate bonds) for rapid growth of bacteria (use of phosphate for RNA and production of proteins) when labile organic C is abundant. Degradation of organic matter provides required N.**



LEAG:

Preliminary study of sediments
In area of yearly dead zone.
J Are polyphosphates present?

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Instrumentation:

My project:

- J Fourier Transform Infrared Spectrometer
- J **Microwave digestion**
- J Freeze drier

Supercritical Fluid Extraction

Calorimeter

Liquid Chromatography with EC detection

Polarograph

Access to:

- J **ICP-OES** Inductively coupled plasma – optical emission spectrometer
- J **^{31}P NMR**
- J **CHN analyzer**

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Thank you ……..
for your invitation

and

looking forward to
working with LEAG.

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