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
- 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.
Included in fractionation schemes *

*Requires minimal equipment

MgCl₂ (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
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.

\[
\text{Bacteria: } (\text{Fe}^{3+})(\text{Phosphate}) \rightarrow \text{Fe}^{2+} + \text{Phosphate}
\]

\[\text{ZPC} = 8.5\]
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.

Statistically significant gain OR loss of total P from surficial sediment during 2005 AFA bloom.
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.
Hot water extract of *Aphanizomenon* collected from Upper Klamath Lake, September 2007 Extraction time=1/2 hr.

Phosphonates

Monoesters

Diesters

Polyphosphate
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
Mechanism for removal of P from STP water for use as fertilizer is thought to occur in natural freshwater sediments.
Polyphosphate: An inorganic anion both natural and anthropogenic sources.

O - O-
 l          l
O         O
Pyrophosphate
Presence in wetlands related to human impact (Sundareshwar, 2001)
Fertilizer /STP/ Industry

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

Determination of DRP concentrations in water samples:
Phosphate that is not detected using the colorimetric method for dissolved (soluble) reactive phosphate. (DRP or SRP).

Pyrophosphate

Polyphosphate: An inorganic anion both natural and anthropogenic sources.
Climate change

Marine diatoms store P as polyphosphate (intracellular pellets)

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:

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

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. Are polyphosphates present?
Instrumentation:

My project:

- Fourier Transform Infrared Spectrometer
- Microwave digestion
- Freeze drier
- Supercritical Fluid Extraction
- Calorimeter
- Liquid Chromatography with EC detection
- Polarograph

Access to:

- ICP-OES Inductively coupled plasma – optical emission spectrometer
- \(^{31}\)P NMR
- CHN analyzer
Thank you ……..

for your invitation

and

looking forward to

working with LEAG.