Biogeochemistry of Wetlands
Science and Applications

Phosphorus Cycling Processes

Wetland Biogeochemistry Laboratory
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Phosphorus Cycling Processes

Water column

City of Orlando - Orlando Eastern Wetlands

6/22/2008
WBL
Phosphorus Cycling Processes

**Topic Outline**
- Introduction
- Forms of phosphorus
- Inorganic Phosphorus retention mechanisms
- Organic phosphorus dynamics
- Phosphorus exchange between soil and overlying water column
- Regulators of phosphorus reactivity and mobility
- Phosphorus memory in wetlands

**Learning Objectives**
- Identify sources, and inorganic and organic forms of phosphorus
- Inorganic phosphorus retention mechanisms in soil
- Describe the influence of soil type on inorganic phosphorus retention
- Role of enzymes and microorganisms in organic phosphorus mineralization
- Biotic regulation phosphorus retention
- Phosphorus exchange between soil and overlying water column
- Draw the phosphorus cycle and identify, storages, abiotic and biotic processes, and fluxes in soil and water column
Terminology

- Total Phosphorus (TP)
- Dissolved total P (DTP)
  - Total P in solutions filtered through 0.45 um membrane filter
- Dissolved reactive P (DRP) or Soluble Reactive P (SRP)
  - Water samples filtered through 0.45 um membrane filter and analyzed for ortho-P.
- Dissolved Organic P (DOP)
  - DTP – DRP = DOP
- Particulate inorganic P (PIP)
  - Particulate matter or soil extracted with acid
- Particulate organic P (POP)
  - TP-PIP = POP

Phosphorus Cycle

- Runoff, Atmospheric Deposition
- Plant biomass P
- Litterfall
- Outflow

AEROBIC
- Peat accretion
- Periphyton P
- Adsorbed IP
- [Fe, Al or Ca-bound P] PIP

ANAEROBIC
- DIP
- DOP
- POP

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Phosphorus Imports from Various Sources: Florida

- Fertilizers: 69%
- Animal Manures: 8%
- Composts (?): 0%
- Natural weathering of minerals (?): 0%
- Wastewater: 5%
- Biosolids: 8%

Total = 61,300 mt P per year

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Phosphorus Loads from Uplands

- Uplands have been a steady source of P to wetlands and aquatic systems, where substantial amounts of P has accumulated in soils and sediments.
- Best management practices and other remedial measures can significantly reduce P loads from uplands to wetlands and aquatic systems.
- How will wetlands and aquatic systems respond to P load reduction?
- How long P memory lasts in wetlands and aquatic systems before they reach stable condition?
Phosphorus Memory in a Watershed

- Capacity for storing phosphorus in various ecosystem components (uplands, wetlands, and aquatic systems)
  - Transient pools
  - Stable pools
- Capacity for showing effects as the result of past practices
- Length of time over which phosphorus release extends before returning to a stable condition

Phosphorus Transfer
[Lake Okeechobee Basin]

- Uplands (82%)
- Wetlands & Streams (8%)
- Lake Okeechobee

Phosphorus Budget [tons/year]

- [415] (10%)
- [4157]
- [754]
Phosphorus Gradient in Wetlands

Gradient in nutrient enrichment in soil and water column
[Distance from inflow]

Water column TP - WCA-2A transect

Total P (µg/L) vs Distance from Inflow (km)
Phosphorus accretion rates in Everglades WCA-2A

Total P concentration in WCA-2A soil (0-10 cm)
Everglades – Soil phosphorus

Soil Phosphorus
Blue Cypress Marsh-1992

Depth (cm)

0-4
8-12
16-20
24-28
32-36
36-44

Total P (mg/kg)

0 1,000 2,000

0-4
4-8
8-12
12-16
16-20
20-24
24-28
32-36
40-44

Unimpacted
Impacted
Phosphorus Memory

Water Column Phosphorus

External Load Reduction

Internal Memory

Background Level

Lag time for Recovery

Time - Years

Ecological Significance – Phosphorus Loading

PLANTS

WATER

SOIL

Microbial Biomass

Lable DETRitus

NC P

Microbial Biomass

NC P

P N
Phosphorus Cycle

- Runoff, Atmospheric Deposition
- Litterfall
- Peat accretion
- DOP, DIP, POP
- Adsorbed P
- Metal oxides and clay mineral surfaces
- Organic phosphorus
- Uptake by algae and plants
- Soil porewater phosphorus [dissolved]

Phosphorus in Wetlands
Soil Phosphorus Forms

- **Inorganic P**
  - KCl-Pi - Bioavailable P
  - NaOH-Pi - Fe-/Al- P [slowly available]
  - HCl-Pi - Ca-/Mg- P [slowly available]

- **Organic P**
  - Microbial Biomass P - Bioavailable P
  - NaOH-Po - Fulvic Acid -P [slowly available]
  - NaOH-Po - Humic Acid -P [very slowly available]
  - Residual P - Highly resistant [unavailable]

Phosphate ions and pH

- $\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$  $\text{pK} = 2.15$
- $\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$  $\text{pK} = 7.20$
- $\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$  $\text{pK} = 12.35$

<table>
<thead>
<tr>
<th>Oxidation number for P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{PO}_4$  [+5]</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_4^-$  [+5]</td>
</tr>
<tr>
<td>$\text{HPO}_4^{2-}$  [+5]</td>
</tr>
<tr>
<td>$\text{PO}_4^{3-}$  [+5]</td>
</tr>
<tr>
<td>$\text{PH}_3$  [-3]</td>
</tr>
</tbody>
</table>

Oxidation number for P

6/22/2008 WBL 23
6/22/2008 WBL 24
Inorganic Phosphorus - Organic Soils - WCA-2A

\[ Y = 0.01X^{1.54} \]
\[ R^2 = 0.897; n=390 \]

Stream Sediments – Okeechobee Drainage Basin

Total P = 877 mg P/kg

DL-Stream

Total P + 93 mg P/kg

Rucks-Stream
Organic Wetland Soils – Drainage Effects

Peat Depth < 10 cm
Total P = 836 mg P/kg

Peat Depth > 30 cm
Total P = 411 mg P/kg

Inorganic Phosphorus

- Pore water P
- Exchangeable
- Fe-/Al- bound P
- Ca-/Mg-bound P
- Residual P

Bioavailability
High
Low
Inorganic Phosphorus

- **Acid soils**
  - AlPO$_4$ · 2H$_2$O [Variscite]
  - FePO$_4$ · 2H$_2$O [Strengite]
- **Alkaline soils**
  - Ca (H$_2$PO$_4$)$_2$ [Monocalcium phosphate]
  - Ca HPO$_4$ · 2H$_2$O [Dicalcium phosphate]
  - Ca$_8$ (H$_2$ PO$_4$)$_6$ · H$_2$O [Octacalcium phosphate]
  - Ca$_3$ (PO$_4$)$_2$ [Tricalcium phosphate]
  - Ca$_5$ (PO$_4$)$_3$ OH [Hydroxyapatite]
  - Ca$_5$ (PO$_4$)$_3$ F [Fluorapatite]

Phosphate Minerals

Apatite

Vivianite

W. G. Harris, 2002
Phosphate Availability

- Readily available phosphates
  - Soil porewater.

- Slowly available phosphates
  - Fe, Al, and Mn phosphates (acid soils) and Ca and Mg phosphates (alkaline soils) that have been freshly precipitated or are held mostly on the surface of fine particles in the soil. Labile organic compounds.

- Very slowly available phosphates
  - Precipitates of Fe, Al, Mn, Ca, and Mg phosphates that have aged and are well crystallized. Phosphates that were held on particle surfaces have penetrated the particles, little remaining on the surface. Stable organic compounds.

Phosphorus

- Is P one of the redox elements?
  - $\text{HPO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- = \text{PH}_3 + 4\text{H}_2\text{O}$

- Is P solubility affected by changes in redox potential?
  - $\text{FePO}_4 + \text{H}^+ + \text{e}^- = \text{Fe}^{2+} + \text{HPO}_4^{2-}$
**Phosphorus Retention by Soils**

- Adsorption – Desorption
- Precipitation – Dissolution
- Immobilization - mineralization

Retention = Adsorption + Precipitation + Immobilization

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**Sorption of Phosphate**

- **Intensity factor**: Concentration of phosphate in soil porewater.
- **Capacity factor**: Ability of solid phases to replenish phosphate as it is depleted from solution.
Inorganic Phosphate Reactions

- Precipitation by Al, Fe, Mn, Ca, and Mg ions
  - \( \text{Al}^{3+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} = 2\text{H}^+ + \text{Al(OH)}_2\text{H}_2\text{PO}_4 \text{(insoluble)} \) (Variscite)

- Anion exchange

- Reaction with hydrous oxides

- Fixation by silicate clays
  - \( \text{Al}_2\text{SiO}_5(\text{OH})_4 + 2\text{H}_2\text{PO}_4^- = 2\text{Al(OH)}_2\text{H}_2\text{PO}_4 + \text{Si}_2\text{O}_5^{2-} \)

pH-Dependent Charge on Solid Phase

Charge vs. pH graph showing:
- Negative charge (loss of H\(^+\))
- Positive charge (gains H\(^+\))
- ZPC (zero point charge)

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Variable Charge on Solid Phase

<table>
<thead>
<tr>
<th>No charge</th>
<th>Soil Solution</th>
<th>Negative charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid phase</td>
<td>Solution</td>
<td>Solid phase</td>
</tr>
</tbody>
</table>

\[ \text{Al} - \text{OH} + \text{OH}^- = \text{Al}^-- + \text{H}_2\text{O} \]
\[ - \text{COOH} + \text{OH}^- = - \text{COO}^- + \text{H}_2\text{O} \]

\[ \text{AlOH} + \text{H}^+ = \text{AlOH}_2^+ \]

Inorganic Phosphate Reactions

Alkaline pH conditions:

\[ \text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^- = \text{Ca} (\text{H}_2\text{PO}_4)_2 \]
\[ \text{Ca} (\text{H}_2\text{PO}_4)_2 + \text{Ca}^{2+} + 2\text{OH}^- = 2\text{CaHPO}_4 + 2\text{H}_2\text{O} \]
\[ 2\text{CaHPO}_4 + \text{Ca}^{2+} + 2\text{OH}^- = 2\text{Ca}_3 (\text{PO}_4)_2 + 2\text{H}_2\text{O} \]
Sorption of Phosphate

I: Initial equilibrium condition

II: Increase in solution P concentration ---
Rapid adsorption to solid surface
[Time = seconds to minutes]

III: Diffusion into solid phase
[Time = hours to days]

Phosphorus Sorption Isotherm

Smax

EPCo

slope = KD

P desorption under ambient conditions

Phosphorus in Soil Porewater
Phosphorus Sorption Isotherm

Influence of Phosphorus Loading on $EPC_0$

[Nair et al. 1997]

<table>
<thead>
<tr>
<th>Land use</th>
<th>Total P (mg/kg)</th>
<th>$EPC_0$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensive</td>
<td>2,330</td>
<td>5.0</td>
</tr>
<tr>
<td>Holding</td>
<td>181</td>
<td>1.4</td>
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<tr>
<td>Pasture</td>
<td>31</td>
<td>0.1</td>
</tr>
<tr>
<td>Beef</td>
<td>31</td>
<td>0.1</td>
</tr>
<tr>
<td>Forage</td>
<td>23</td>
<td>0.2</td>
</tr>
<tr>
<td>Native</td>
<td>18</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Influence of Phosphorus Loading on EPC₀
[Everglades – WCA-2a]

Phosphorus Sorption
[Richardson, 1985]
P Sorption by WCA-2A soils

![Graph showing P sorption by WCA-2A soils with two sites: Site 1 and Site 8. The x-axis represents solution P concentration (mg P/L), and the y-axis represents sorbed P (mg P/kg).](image)

Phosphorus Sorption Isotherm

- **Linear Equation**
  - \[ S = K_L \cdot C \]
  - where: \( S \) = mass of P sorbed per mass of solid phase; \( C \) = P concentration in solution; \( K_L \) = adsorption coefficient related to binding strength

- **Freundlich Equation**
  - \[ S = K_F \cdot C^N \]
    \[ \log S = N \log C + \log K_F \]
  - where: \( S \) = mass of P sorbed per mass of solid phase; \( C \) = P concentration in solution; \( K_F \) = adsorption coefficient related to binding strength; \( N \) = empirical constant
**Phosphorus Sorption Isotherm**

- **Langmuir Equation**
  - $S = \frac{k C S_{\text{max}}}{1 + k C}$
  - $\frac{C}{S} = \frac{1}{S_{\text{max}}} C + \frac{1}{k S_{\text{max}}}$
  - where: $S = \text{mass of P sorbed per mass of solid phase}; \ C = \text{P concentration in solution}; \ k = \text{constant related to binding strength}; \ S_{\text{max}} = \text{maximum amount of P sorbed per mass of solid phase}$

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**Phosphorus Sorption Isotherm**

- **Adsorption**
- **Sorption**
- **Precipitation**
- **Smax**
- **EPCo**
- **slope = KD**
- **P desorption under ambient conditions**
- **So**

**Slope = 1/S_{\text{max}}**
**Saturation Index (SI)**

\[ C_\text{a}A_b = aC + bA \]

\[ K = \frac{[C]^a [A]^b}{[C_\text{a}A_b]} \]

Ion Activity Product (IAP) = \([C]^a [A]^b\]

**Saturation Index (SI) = IAP/K**

- SI < 1 = Solution is “undersaturated”
- SI > 1 = Solution is “supersaturated”
- SI = 1 = Solution saturated (near equilibrium)

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**Precipitation of Phosphate**

- P in solution; t = 0
- Supersaturation with respect to B
- Supersaturation with respect to C
Co-precipitation of Phosphorus

Coating of hydrated ferric oxide (Fe₂O₃ · nH₂O) co-precipitated with ferric phosphate, aluminum phosphate, and calcium phosphate.

Silt or Clay Particle

Phosphorus Retention Isotherm

P release under ambient conditions

P release under EPCₜ

Pmax

slope = A

Phosphorus in Water Column
Phosphorus Retention Isotherm

$P$ added to water column – range of concentrations

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Phosphorus Retention by Wetlands Soils and Stream Sediments

[Okeechobee Basin, Florida]

- **Wetlands**
  - $P_r = 118$ [SRP] - 54.2
  - $r^2 = 0.71$  $n = 11$
  - $EPC_w = 0.47$ mg P/L

- **Stream sediments**
  - $P_r = 128$ [SRP] - 12.4
  - $r^2 = 0.95$  $n = 175$
  - $EPC_w = 0.1$ mg P/L
Phosphorus Retention by Mud Sediments – Lake Okeechobee

![Graph showing DRP retention/release vs. Water Column DRP ug/L]

Phosphorus Adsorption Coefficient [Organic Soils]

![Graph showing K vs. Ash content]

- $r^2 = 0.89$
- $n = 36$
**Phosphorus Retention Capacity**

**Mineral Wetland Soils - Okeechobee Basin**

\[ S_{\text{max}} = 1.74 + 0.172 \, [\text{Fe + Al}] \]

\[ r^2 = 0.78 \quad n = 285 \]

**Phosphorus Retention – Peat/Mineral Wetland Soils**

\[ Y = 1.21 + 0.015(x) \]

\[ R^2 = 0.87 \]

Richardson, 1985
Phosphorus solubility as a function of pH and Eh

Iron solubility as a function of pH and Eh
Dissolved P in Sediments

Redox potential (mV) vs. Dissolved P (μM P)

Lake Apopka

Lake Okeechobee

y = 13e -0.0003x
r² = 0.98

Phosphorus Solubility under Anaerobic Soil Conditions

SO₄²⁻ + H₂S + FePO₄ → Fe₂⁺ + PO₄³⁻ + Fe(OH)₂⁺PO₄
                          [Strengite]          [Strengite]

FeS + FePO₄ → FePO₄ + Fe₃(PO₄)₂
                     [Vivianite]               [Strengite]

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Mechanisms of Phosphorus Release in Wetlands

- Reduction of insoluble ferric phosphate to more soluble ferrous phosphate
- Release occluded phosphate by reduction of hydrated ferric oxide coating
- Higher solubility of ferric and aluminum phosphates due to increased soil pH
- Displacement of phosphate from ferric and aluminum phosphate by organic anions
- Increased phosphate availability during sulfate reduction
- Increased solubility of calcium phosphate in alkaline soils as result of pH decrease under flooded conditions
Regulators of Inorganic Phosphorus Retention

- pH and Eh
- Phosphate concentration
- Clay content
- Iron and aluminum oxides
- Organic matter content
- Calcium carbonate content
- Time of reaction/aging
- Temperature

Phosphorus Cycle

Runoff, Atmospheric Deposition

Plant biomass P

Litterfall

DIP

DOP

POP

Peat accretion

Periphyton P

Adsorbed IP

[Fe, Al or Ca-bound P]

PIP

Outflow

AEROBIC

ANAEROBIC
Organic Phosphorus

- Plant Litter Attached to plant
- Detritus deposited on soil surface
- Decomposed detritus from previous years
- Well decomposed detritus accreted into soil

Leaching of POP leads to:
- DOP
- EA
- Epiphytic periphyton

POP Leaching DOP EA Epiphytic periphyton

- Microbial biomass
- POP DOP EA DIP Benthic periphyton

Inorganic solids

- Microbial biomass
- POP DOP EA DIP Inorganic solids

Inorganic solids

Detrital Matter
- Phytin
- Phospholipids
- Nucleic acids
- Sugar phosphates

Plants Animals Microbes

Humus

Inorganic Phosphate

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Organic P fractions (% of total organic P) in growing organisms and soils*

<table>
<thead>
<tr>
<th></th>
<th>E. coli</th>
<th>Fungi</th>
<th>Spirodella</th>
<th>Nicotiana</th>
<th>Soils</th>
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<tbody>
<tr>
<td>Nucleic Acids</td>
<td>65</td>
<td>58</td>
<td>60</td>
<td>52</td>
<td>2</td>
</tr>
<tr>
<td>Phospholipids</td>
<td>15</td>
<td>20</td>
<td>30</td>
<td>23</td>
<td>5</td>
</tr>
<tr>
<td>Monoesters</td>
<td>20</td>
<td>22</td>
<td>10</td>
<td>25</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>


Soil Phosphorus
Blue Cypress Marsh

TPo = -49 + 0.89 TP
Organic Phosphorus

- Microbial biomass P
- Labile organic P
- Fulvic acid - P
- Humic acid - P
- Residual organic P

Solution $^{31}$P NMR spectrum of an alkaline extract of a Swedish tundra soil

Soil phosphorus composition

- Inorganic orthophosphate
- Phosphonates
- Orthophosphate monoesters
- Phospholipids
- DNA
- Polyphosphate end-groups
- Pyrophosphate
- Mid-chain polyphosphates

Chemical shift (ppm)
Organic Matter Decomposition and Nutrient Release

Periphyton/Macrophytes → Extracellular Enzymatic Activity → Organic/Complex Organic Compounds → Simple Organic Compounds → Hydrolysis → Acid Fermentation → Short-chain Fatty Acids Hydrogen → CO₂ → Bioavailable Nutrients

Oxygen Reduction → Nitrate Reduction → Manganese Reduction → Iron Reduction → Sulfate Reduction → CO₂ Reduction → Bioavailable Nutrients

Phosphorus Availability

Detrital Matter
- Phytin
- Phospholipids
- Nucleic acids
- Sugar phosphates

Organic P + Enzymes Phosphatases → Organic + P
Enzyme – Catalyzed Reaction

\[ S + E \rightarrow ES \rightarrow E + P \]

S = Substrate    E = Enzyme    P = Product

\[ R - O-PO_3^{2-} + H_2O \rightarrow R-OH + HO-PO_3^{2-} \]

Alkaline phosphatase

Phosphatase Activity

Periphyton APA along the WCA 2a Nutrient Gradient

July 1996 [Newman, S]
Phosphatase-Cyanobacterial Cells
Alkaline Phosphatase Activity
Everglades - WCA-2A

May 1996

Distance from inflow (km)

p-nitrophenol (mg g⁻¹ hr⁻¹)

Litter

0-10 cm

10-30 cm

Soil Phosphatase Activity
Blue Cypress Marsh

APA, mg MUF/g hour

Mar, June, July, Sept, Dec, Jan

2001, 2002

NE

NW [R]

SW
Phosphatase Activity
[Sunnyhill Farm Wetland]

- Acid Phosphatase
- Alkaline Phosphatase
- Total Phosphatase

μg p-nitrophenol g⁻¹ h⁻¹

<table>
<thead>
<tr>
<th>Oxygen</th>
<th>Nitrate</th>
<th>Sulfate</th>
<th>Bicarbonate</th>
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<tbody>
<tr>
<td>Eh (mV)</td>
<td>pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>616</td>
<td>4.7</td>
<td>228</td>
<td>-162</td>
</tr>
<tr>
<td>228</td>
<td>7.5</td>
<td>-162</td>
<td>-217</td>
</tr>
<tr>
<td>-162</td>
<td>7.7</td>
<td>-217</td>
<td></td>
</tr>
<tr>
<td>-217</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

y = 0.36x - 0.32
R² = 0.72
Microbial Biomass P
[Sunnyhill Farm Wetland]

Microbial P, (% of total P)

<table>
<thead>
<tr>
<th></th>
<th>Oxygen</th>
<th>Nitrate</th>
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<th>carbonate</th>
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</table>

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Microbial Biomass Phosphorus
[Water Conservation Area-2A]

Distance from inflow (km)

0-10 cm Soil Depth

Feb '96  Aug.'96  Mar. '97

0  5  10  15  20  25

Microbial biomass P (as % total P)
Lake Apopka Marsh

Soluble P, mg L⁻¹

Dissolved Fe, mg L⁻¹

Depth, cm

Water

Soil
**Periphyton-Phosphorus-Interactions**

- BP = Benthic Periphyton
- FP = Floating Periphyton
- EP = Epiphytic Periphyton

**Calcareous Periphyton Mats**

- Soil
- Water
- Soluble P
- Ca-P
- Ca
- Soil

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Calcareous Periphyton Mats

With CaCO₃

Without CaCO₃

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Distribution of $^{32}$P between Water and Benthic Periphyton

Water DRP = 5 ug L$^{-1}$  Light = 10 W m$^{-2}$

Water DRP $= 5$ ug L$^{-1}$  Light $= 10$ W m$^{-2}$
Periphyton-Phosphorus-CaCO₃ Interactions

Solution P → Periphyton → CaCO₃

Plant Tissue Phosphorus-WCA-2A

Total P (mg kg⁻¹)

- Live-above ground
- Detritus-above ground
- Below ground

F-1 Typha
F-3 Typha
F-3 Cladium
F-5 Cladium

Impacted
Transition
Unimpacted
Everglades-WCA 2A

![Graph showing the relationship between Phosphorus Accumulation (g/m² year) and Calcium Accumulation (g/m² year). The graph includes a data point at (20, 0.8) with an R² value of 0.969.]

Soil/Sediment-Water Interactions

![Diagram illustrating Soil/Sediment-Water Interactions. The diagram shows processes such as Diffusion, Resuspension, and Sedimentation, with exchanges between DIP, DOP, PIP, and POP.]

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Total Phosphorus in WCA-2A soils (0-10 cm)

Phosphorus Memory

External Load Reduction

Internal Memory

Background Level

Lag time for Recovery

Water Column Phosphorus

Time - Years

6/22/2008

WBL 1998
Internal Phosphorus Load

Nutrient Impacts in Wetlands
Soluble Phosphorus Flux from Sediments

Lower St. Johns River - SRP Profiles

[Malecki et al. 2003]
### Internal vs. External Loads

**Lower St. Johns River Estuary**

- **Total Non-point**
  - TN: 32%
  - TP: 25%

- **Total Point Source**
  - TN: 24%
  - TP: 33%

- **Total Internal Load**
  - TN: 44%
  - TP: 42%

- **Total = 7,969 mt year⁻¹**

### Phosphorus Flux from Soil to Water Column

<table>
<thead>
<tr>
<th>Station</th>
<th>Porewater equilibrators</th>
<th>Benthic chambers</th>
<th>Incubated Soil cores</th>
</tr>
</thead>
<tbody>
<tr>
<td>[km]</td>
<td>[mg P/m² day]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>0.3</td>
<td>10.0</td>
<td>6.5</td>
</tr>
<tr>
<td>3.3</td>
<td>0.8</td>
<td>9.1</td>
<td>1.5</td>
</tr>
<tr>
<td>10.1</td>
<td>-0.001</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

6/22/2008 WBL
### Flooded Agricultural Land
Lake Griffin Flow-way, Florida

<table>
<thead>
<tr>
<th>Station</th>
<th>P – Flux mg P m⁻² day⁻¹</th>
<th>EPCw mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DRP</td>
<td>TP</td>
</tr>
<tr>
<td>1D</td>
<td>0.40</td>
<td>0.74</td>
</tr>
<tr>
<td>2E</td>
<td>0.94</td>
<td>1.54</td>
</tr>
<tr>
<td>3D</td>
<td>1.62</td>
<td>2.38</td>
</tr>
<tr>
<td>5C</td>
<td>0.25</td>
<td>0.34</td>
</tr>
</tbody>
</table>

P memory = 30 – 140 years

### Internal Phosphorus Load
Everglades -WCA-2A

![Graph showing P flux vs. Distance from inflow](image_url)

P flux (mg P/m² day) vs. Distance from inflow (km)

6/22/2008  WBL  Reddy et al., 1997
Phosphorus Flux from Flooded Agricultural Land

\[ y = 5.31 e^{-0.051x} \]

\[ R^2 = 0.95 \]

Soluble Phosphorus Flux from Wetlands

- Lake Apopka Marsh: 2 - 5.5 mg/m² day
- Disney World: 0.3 - 1.1 mg/m² day
- Orange County: 0.02 – 0.16 mg/m² day
- STA-1W: 0.3 - 1.6 mg/m² day
### Soluble Phosphorus Flux from Sediments [mg P/m² day]

<table>
<thead>
<tr>
<th>Location</th>
<th>DRP (mg P/m² day)</th>
<th>PP (mg P/m² day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Apopka</td>
<td>1 - 5.3</td>
<td></td>
</tr>
<tr>
<td>Lake Okeechobee</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mud Zone</td>
<td>0.1 - 1.9</td>
<td></td>
</tr>
<tr>
<td>Peat Zone</td>
<td>0.2 - 2.2</td>
<td></td>
</tr>
<tr>
<td>Sand Zone</td>
<td>0.1 - 0.5</td>
<td></td>
</tr>
<tr>
<td>Littoral Zone</td>
<td>0.6 - 1.5</td>
<td></td>
</tr>
<tr>
<td>Lower St. Johns River</td>
<td>1.3 - 7.4</td>
<td></td>
</tr>
<tr>
<td>Lake Barco</td>
<td>0.02 - 0.05</td>
<td></td>
</tr>
<tr>
<td>Indian River Lagoon</td>
<td>0.6 - 1.7</td>
<td></td>
</tr>
<tr>
<td>Otter Creek</td>
<td>-0.8 - 3.3</td>
<td></td>
</tr>
<tr>
<td>Tampa Bay</td>
<td>1.9 - 6.3</td>
<td></td>
</tr>
</tbody>
</table>

### Soluble Phosphorus Flux from Sediments

![Diagram of DRP and PP in water column and sediment](image)
Lake Apopka Marsh Soils
[Effect of Chemical Amendments on Phosphorus Release]

- **CaCO₃**: 8.6 t/ha
- **Ca(OH)₂**: 6.3 t/ha
- **Dolomite**: 8.2 t/ha
- **CaCO₃ + Ca(OH)₂**: 4.3 + 3.2 t/ha

Lake Apopka Marsh Soils
[Effect of Chemical Amendments on Phosphorus Release]

- **Alum**: 4.0 t/ha
- **Alum + CaCO₃**: 2.1 + 4.3 t/ha
- **FeCl₃**: 1.0 t/ha
- **FeCl₃ + CaCO₃**: 0.5 + 2.5 t/ha
Processes Controlling Phosphorus

**Water Column**

- $O_2$ → $PO_4^{3-}$ → Periphyton/Detritus

**Aerobic**

- $FePO_4$ → $Fe^{3+} + PO_4^{3-}$ → Organic P
- $Fe^{2+} + PO_4^{3-}$ → $3Fe^{2+} + 2PO_4^{3-}$ → $Fe_3(PO_4)_2$ (vivianite)
- $Fe^{2+} + CO_3^{2-}$ → $3Ca^{2+} + 2PO_4^{3-}$ → $B-Ca_3(PO_4)_2$ (beta tricalcium phosphate)

**Anaerobic**

- $Fe^{2+} + CO_3^{2-}$ → $Ca^{2+} + CO_3^{2-}$ → $CaCO_3$ (calcite)

**Soil/Sediment**

- $Fe^{2+} + CO_3^{2-}$ → $FeCO_3$ (siderite)

Phosphorus Cycle

- Runoff, Atmospheric Deposition → Litterfall → Peat accretion → DIP → POP → DIP → PIP
- DOP → Periphyton P → Adsorbed IP → [Fe, Al or Ca-bound P] PIP
Phosphorus Cycling Processes

Summary

- Common inorganic phosphorus pools include: loosely bound; fractions associated with Al, Fe, and Mn oxides and hydroxides; Ca and Mg bound fraction; minerals
- Phosphate is not commonly used as an oxidant, but is affected by redox dynamics. Oxidized forms of iron can react with phosphorus and form insoluble compounds
- Soil's capacity to adsorb phosphorus is regulated by the EPCO, at which point adsorption equals desorption
- Inorganic phosphorus retention is regulated by pH, Eh, phosphate concentration (there is a limited amount of substrate for adsorption), concentrations of Fe, Al, and calcium carbonate, and temperature

Summary

- Much of the organic phosphorus is present as monoesters and diesters. Monoesters include sugar phosphates, phosphoproteins, mononucleotides, and inositol phosphates. Diesters include nucleic acids, phospholipids, and aromatic compounds. Compared to monoesters, diesters are more accessible to microbial attack.
- Organic phosphorus availability from monoesters requires enzymatic cleavage of the ester linkage. This occurs primarily through several extracellular enzymes such as phosphatases through hydrolysis of phosphate esters.
- The “phosphorus memory” can extend the time required for a wetland or an aquatic system to reach an alternate stable condition to meet environmental regulation such as TMDLs (total daily maximum daily load)