Response of Water from Wind Lake, Wisconsin, to Runoff Contaminants

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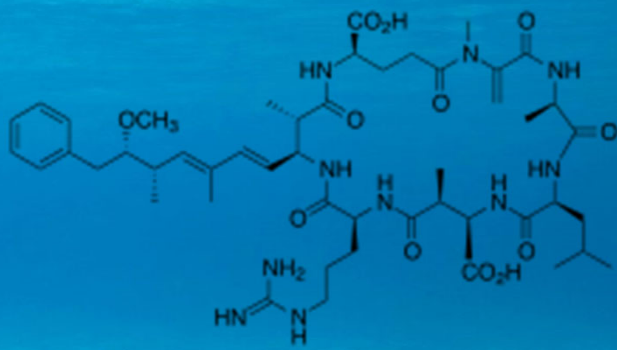
Outline

- Topic Discussion
  - Nitrogen
  - Phosphorous
- Objectives of PHREEQC analyses
- Details of PHREEQC Analyses
- Conclusions

Algae Blooms

<u>Causes:</u>
- Internal loading of Phosphorous from sediments
- Additions of unnatural nitrogen into the system
- Drainage and runoff from nearby bodies of water

<u>Effects:</u>
- Algal blooms – release a toxin called **Microcystin**
- Block sunlight from underwater plants
- Shortage of drinking water due to poor water quality
- Biological interactions
- Chemical changes



Epilimnion

Photosynthesis

$6CO_2 + 6H_20 \rightarrow C_6H_{12}O_6 + 6O_2$

Results in larger concentrations of dissolved oxygen

Separation of Layers

Metalimnion

- Two major separate zones the Hypolimnion and Epilimnion
- Each layer is stratified and distinctive from the other
- Formed as a result of wind action and differential temperature

Respiration

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + ATP$

Dissolved oxygen is a reactant, drastically lowering DO values

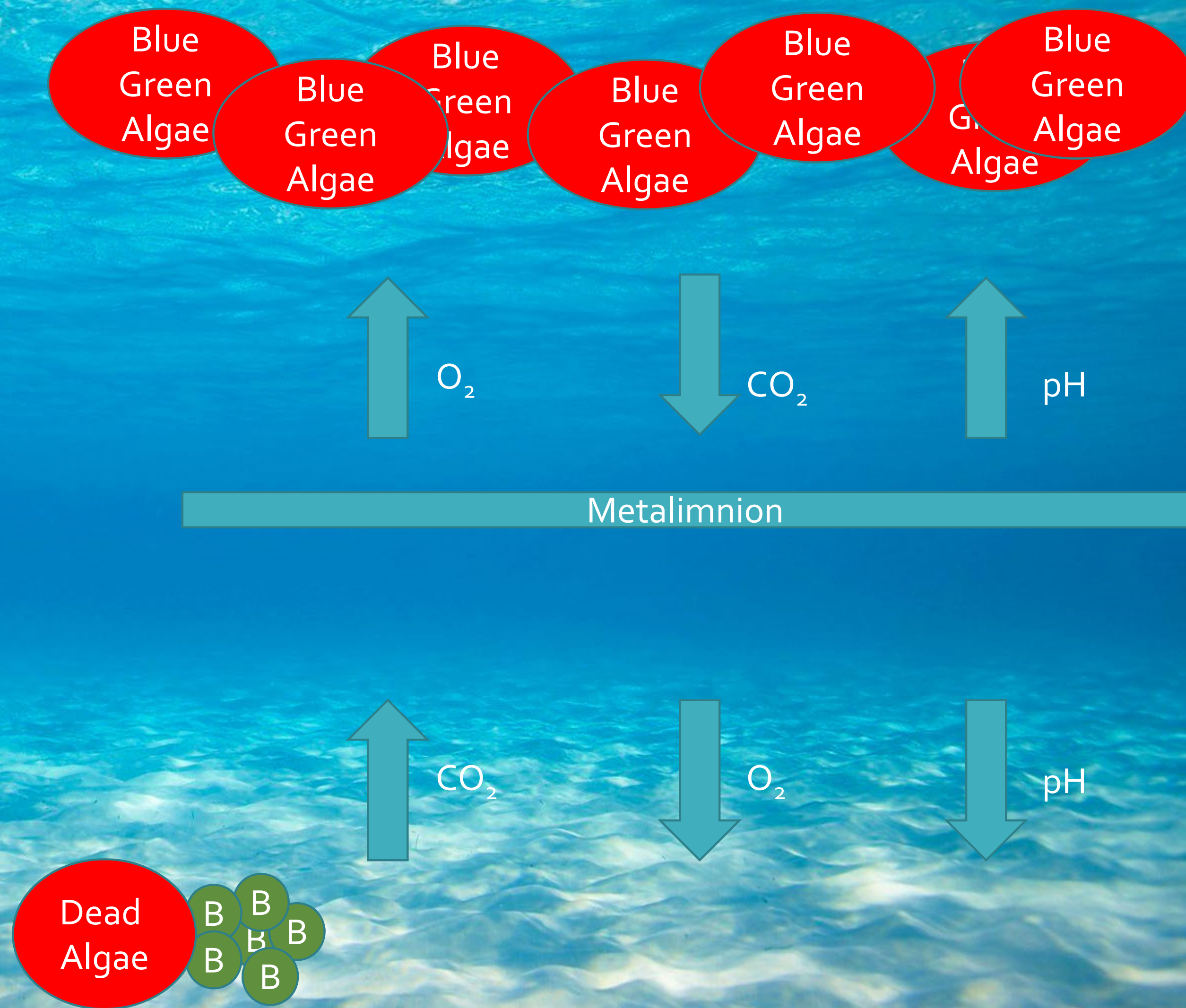
Depth of sample (feet)	3	51
Lake stage (feet)	8.19	
Specific conductance	529	533
pH	8.6	8.5
Water temperature (degrees Celsius)	6.5	5.5

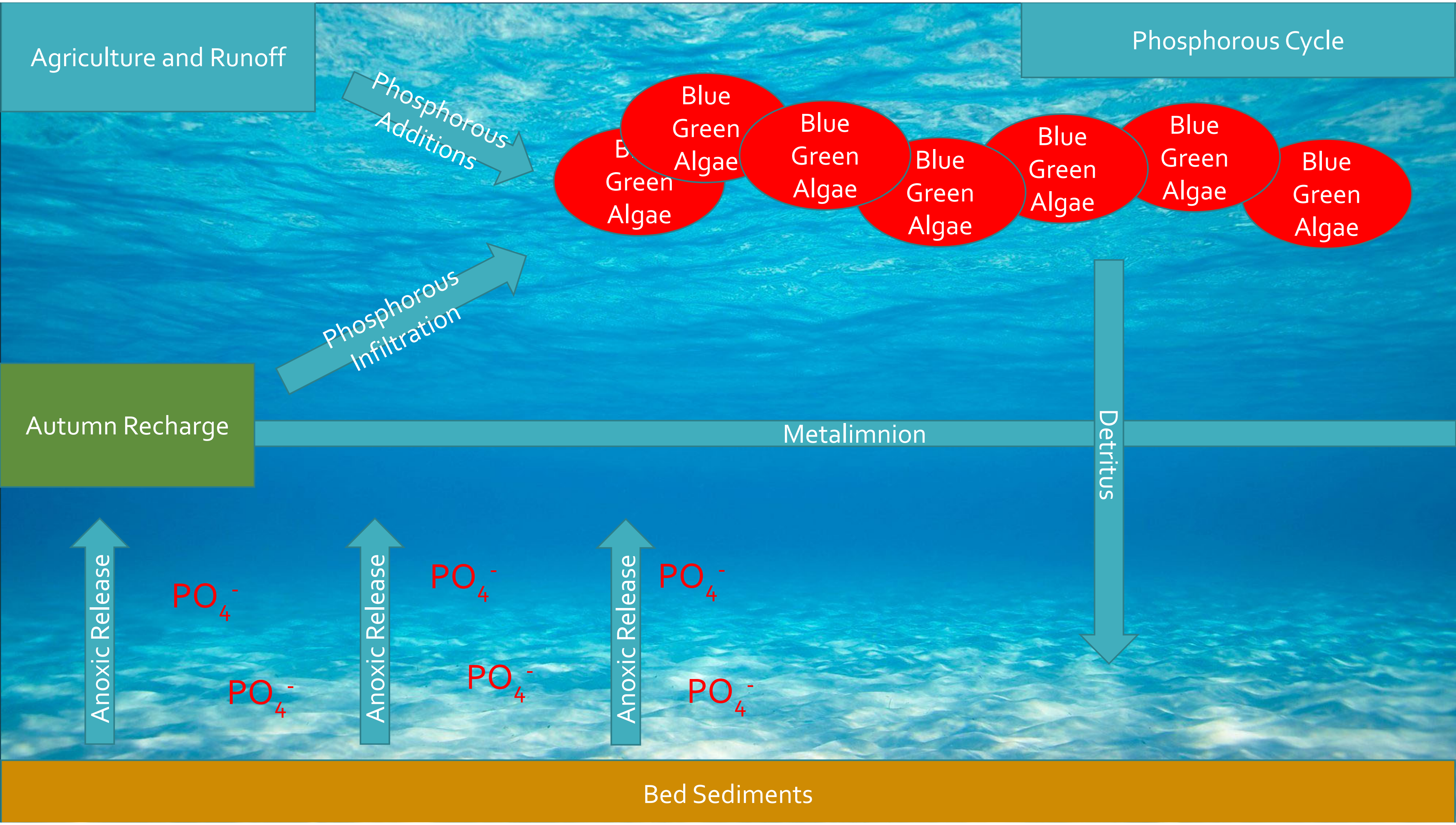
Field, 1991

Hypolimnion

Additions

- Water Eutrophication results from an overabundance of nitrogen and phosphorous added into the system from storm runoff
- Wind lake has a nitrogen ratio of greater than 15:1 so it is much more numerous in the system (Stephen, 1991)





Agriculture and Runoff
Phosphorous Cycle
Phosphorous Additions
Blue Green Algae
Blue Green Algae
Blue Green Algae
Blue Green Algae
Blue Green Algae
Blue Green Algae
Blue Green Algae
Phosphorous Infiltration
Autumn Recharge
Metalimnion
Detritus
Anoxic Release
Anoxic Release
Anoxic Release
PO_4^-
PO_4^-
PO_4^-
PO_4^-
PO_4^-
PO_4^-
Bed Sediments

Phytoplankton

Algae blooms are classified when there are 500,000 algae cells per liter of water

Chlorophyll a is another key indicator

- Present in all autotrophs
- Wind Lake has Chlorophyll a values of 1.8 to 58

Productivity/Trophic Status	What does the water look like?	Maximum chlorophyll concentration (µg/L)
Oligotrophic	Clear	Less than 8
Oligo-mesotrophic	Usually clear	Occasionally over 8
Mesotrophic	Sometimes green	8 to 25
Eutrophic	Green most of summer	26 to 75
Hyper-eutrophic	Frequent dense algal blooms	Over 75

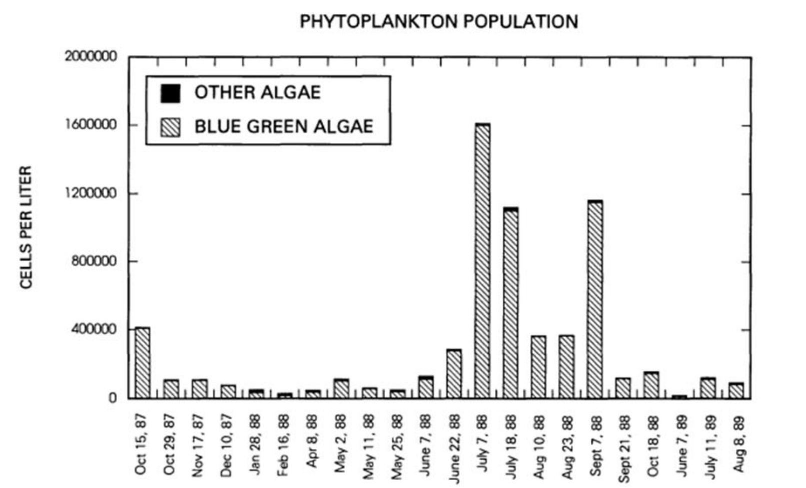
Table adapted from: Atlas of Alberta Lakes, http://sunsite.ualberta.ca/Projects/Alberta-Lakes

Field, 1991

Table 10. Types and densities of phytoplankton in Wind Lake, water years 1988-89

[a, population, in cells per milliliter; b, percentage of total population; <, less than; --, none present]

Date	Total population (cells per milliliter)	Diatoms a	Diatoms b	Green algae a	Green algae b	Golden-brown algae a	Golden-brown algae b	Blue-green algae a	Blue-green algae b
10-15-87	413,000	596	<1	3,890	1	28	0	408,000	99
10-29-87	110,000	596	<1	4,740	4	0	0	104,000	95
11-17-87	110,000	223	<1	3,260	3	113	<1	106,000	96
12-10-87	77,700	340	<1	2,365	3	788	1	73,900	95
1-28-88	51,400	451	<1	2,140	4	11,900	23	36,000	70
2-16-88	28,200	80	<1	993	4	11,200	40	15,900	56
4-08-88	47,700	5,890	12	4,450	9	744	2	36,400	76
5-02-88	115,000	179	<1	9,780	8	263	<1	104,000	91
5-11-88	60,400	65	<1	3,960	7	--	--	56,400	93
5-25-88	49,500	19	<1	9,180	19	--	--	40,300	81
6-07-88	130,000	17	<1	16,100	12	--	--	114,000	88
6-22-88	284,000	105	<1	7,140	2	--	--	277,000	98
7-07-88	1,610,000	--	--	6,660	<1	657	<1	1,600,000	99
7-18-88	1,120,000	--	--	18,100	2	612	<1	1,100,000	98
8-10-88	365,000	40	<1	3,440	1	--	--	361,000	99
8-23-88	367,000	263	<1	1,810	1	--	--	365,000	99
9-07-88	1,160,000	--	--	11,700	1	309	<1	1,150,000	99
9-21-88	121,000	389	<1	2,900	2	--	--	117,000	97
10-18-88	156,000	3,250	2	7,330	4	--	--	146,000	94
6-07-89	16,200	108	<1	981	6	1,850	11	12,100	74
7-11-89	123,000	544	<1	4,080	3	4,080	3	112,000	91
8-08-89	92,500	1,090	1	4,080	4	2,720	3	82,100	89



Anoxic Conditions

- Wind Lake is strongly thermally stratified throughout the summer
- Stratification prevents mixing
- Once stratification has occurred the hypolimnion will be more devoid of DO
- Anoxic conditions increase phosphorous percentage
- As the lake surface cools, the water increases in density, sinks and mixes. This occurs during the autumn and spring and recharges the system

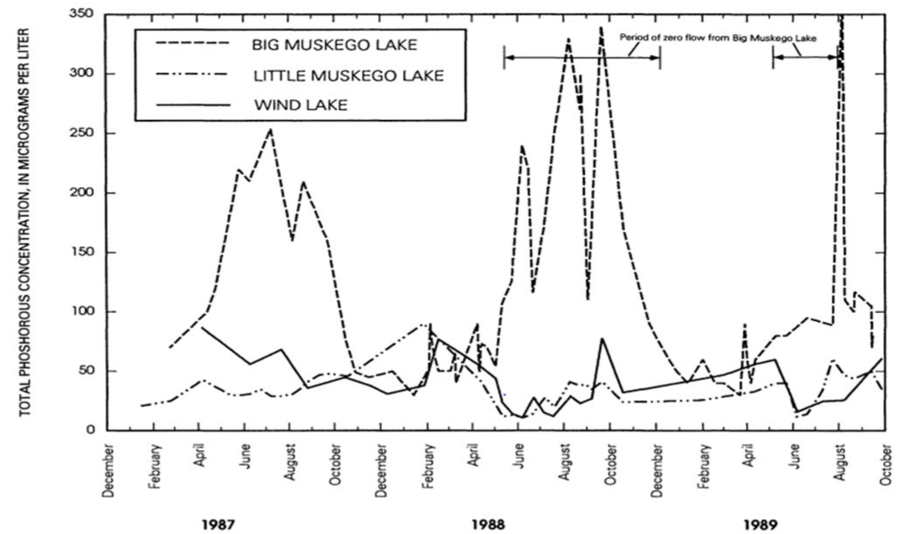
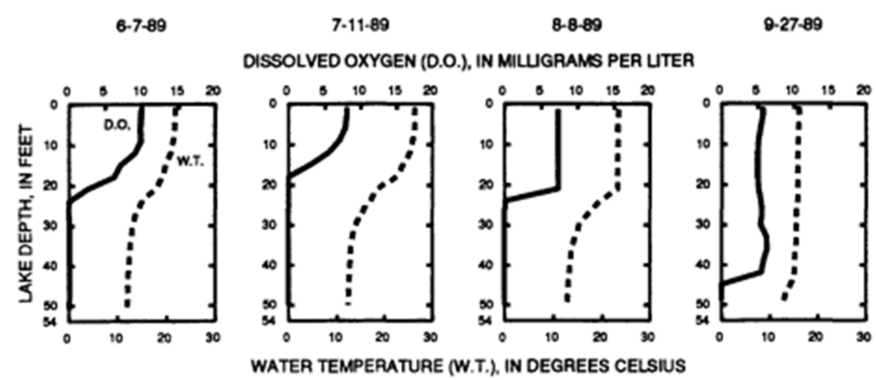


Figure 9. Total phosphorus concentrations 1.5 feet below lake surface at Wind, Big Muskego, and Little Muskego Lakes, 1987-89.

Field, 1991



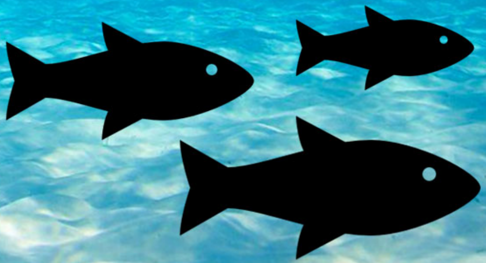
Phosphorous Additions

https://www.chesapeakebay.net/issues/stormwater_runoff

- Nitrogen is in overabundance, phosphorous is the limiting nutrient for more algae growth (Stephen, 1991)
- Phosphorous is supplied to the system from Lake Muskego via Carp
- Orthophosphate was taken up by algae and incorporated into its cello structure
- Orthophosphate released from the bottom of lakes depleted in dissolved oxygen

Dead algae sinks to the bottom, incorporating P into sediments

Carp are bethnic bottom feeders that act as phosphorous transporters

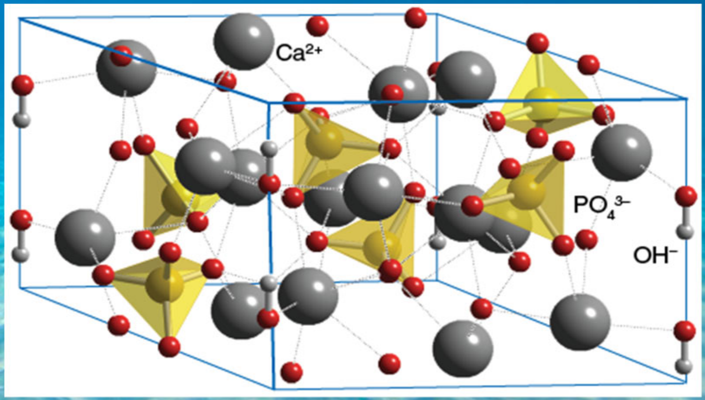


Anoxic Conditions release P from sediments

Possible Solutions Using PHREEQ

- Plants, prominently cattails, absorbing P
- Co-precipitation with $CaCO_3$ by adding Ca
- Aluminum Sulphate additions
- Iron additions

http://www.mtpr.org/post/cattail-plant-thousand-uses



http://www.chemtube3d.com/solidstate/SShydroxyapatite.htm

Calcium Carbonate in relation to Hydroxyapatite

- Adding calcium into the system to form more calcite
- Calcium carbonate will combine with hydrogen phosphate
- This produces Hydroxyapatite, effectively taking phospherous out of the system for algae growth

Phase	SI**	log IAP	log K(279 K, 1 atm)	
Anhydrite	0.12	-3.97	-4.09	CaSO4
Fe(OH)3(a)	6.92	11.81	4.89	Fe(OH)3
Fluorite	1.54	-9.31	-10.85	CaF2
Goethite	12.11	11.81	-0.30	FeOOH
Gypsum	0.64	-3.97	-4.61	CaSO4:2H2O
H2(g)	-25.22	-28.26	-3.04	H2
H2O(g)	-2.01	-0.00	2.01	H2O
Halite	-4.74	-3.18	1.55	NaCl
Hausmannite	0.91	66.82	65.91	Mn3O4
Hematite	26.14	23.63	-2.51	Fe2O3
Hydroxyapatite	9.80	8.13	-1.67	Ca5(PO4)3OH
Jarosite-K	10.57	2.88	-7.69	KFe3(SO4)2(OH)6
Manganite	1.13	26.47	25.34	MnOOH
Melanterite	-4.03	-6.49	-2.46	FeSO4:7H2O
O2(g)	-39.49	-42.22	-2.73	O2
Oxg(g)	0.89	-1.84	-2.73	Oxg
Pyrochroite	-1.33	13.87	15.20	Mn(OH)2
Pyrolusite	-5.47	39.07	44.54	MnO2:H2O
Sylvite	-5.04	-4.24	0.80	KCl
Vivianite	3.77	-32.23	-36.00	Fe3(PO4)2:8H2O

Formula for Hydroxyapatite formation

$$10CaCO_3 + 6HPO_4^- + 2H_2O + 2H^+ \text{-->} Ca_{10}(PO_4)_6(OH)_2 + 10HCO_3^-$$

PHREEQ Values For Liming

Table 1: HPO_4^- concentration 29%

Table 2: HPO_4^- concentration 18%

Table 3: HPO_4^- concentration 14%

Ca at 46 ppm (Normal Values from epilipmnion)

Hydroxyapatite	9.80	8.13	-1.67	Ca5(PO4)3OH

P	3.700e-05					
CaHPO4	1.343e-05	1.396e-05	-4.872	-4.855	0.017	(0)
CaPO4-	1.189e-05	9.065e-06	-4.925	-5.043	-0.118	(0)
HPO4-2	1.081e-05	3.526e-06	-4.966	-5.453	-0.487	8.22
FeHPO4	4.324e-07	4.494e-07	-6.364	-6.347	0.017	(0)
H2PO4-	2.090e-07	1.593e-07	-6.680	-6.798	-0.118	34.02
NaHPO4-	1.644e-07	1.254e-07	-6.784	-6.902	-0.118	42.90
CaH2PO4+	3.818e-08	2.911e-08	-7.418	-7.536	-0.118	(0)
KHPO4-	1.446e-08	1.102e-08	-7.840	-7.958	-0.118	40.24
PO4-3	6.607e-09	4.267e-10	-8.180	-9.370	-1.190	-19.26

Ca at 92 ppm

Hydroxyapatite	10.65	8.98	-1.67	Ca5(PO4)3OH

P	3.700e-05					
CaHPO4	1.548e-05	1.633e-05	-4.810	-4.787	0.023	(0)
CaPO4-	1.428e-05	1.061e-05	-4.845	-4.974	-0.129	(0)
HPO4-2	6.728e-06	1.964e-06	-5.172	-5.707	-0.535	8.45
FeHPO4	2.392e-07	2.523e-07	-6.621	-6.598	0.023	(0)
H2PO4-	1.195e-07	8.875e-08	-6.923	-7.052	-0.129	34.14
NaHPO4-	9.331e-08	6.931e-08	-7.030	-7.159	-0.129	46.29
CaH2PO4+	4.584e-08	3.405e-08	-7.339	-7.468	-0.129	(0)
KHPO4-	8.106e-09	6.021e-09	-8.091	-8.220	-0.129	40.35
PO4-3	4.955e-09	2.377e-10	-8.305	-9.624	-1.319	-18.79

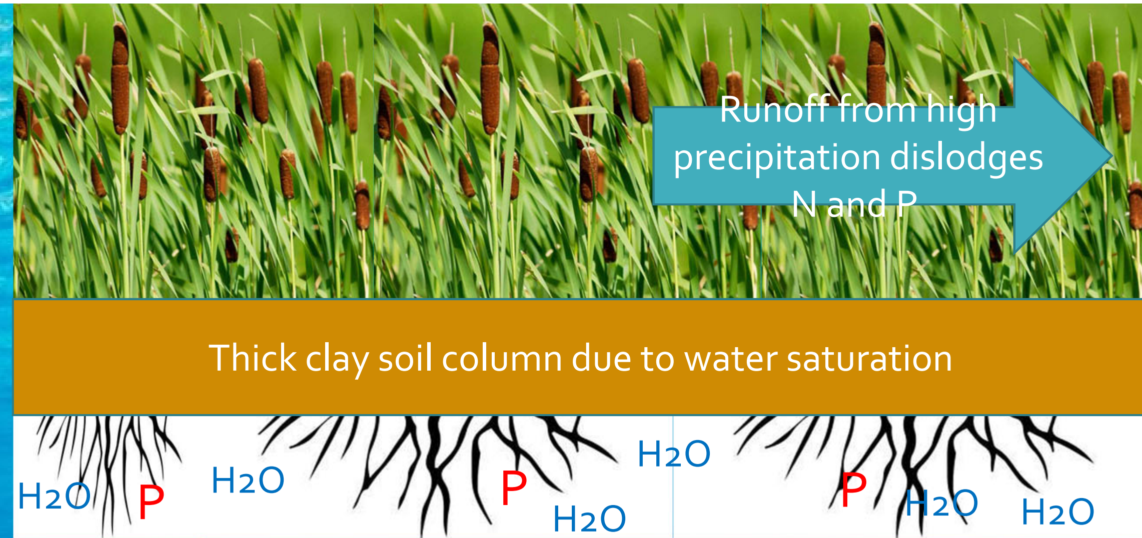
Ca at 138 ppm

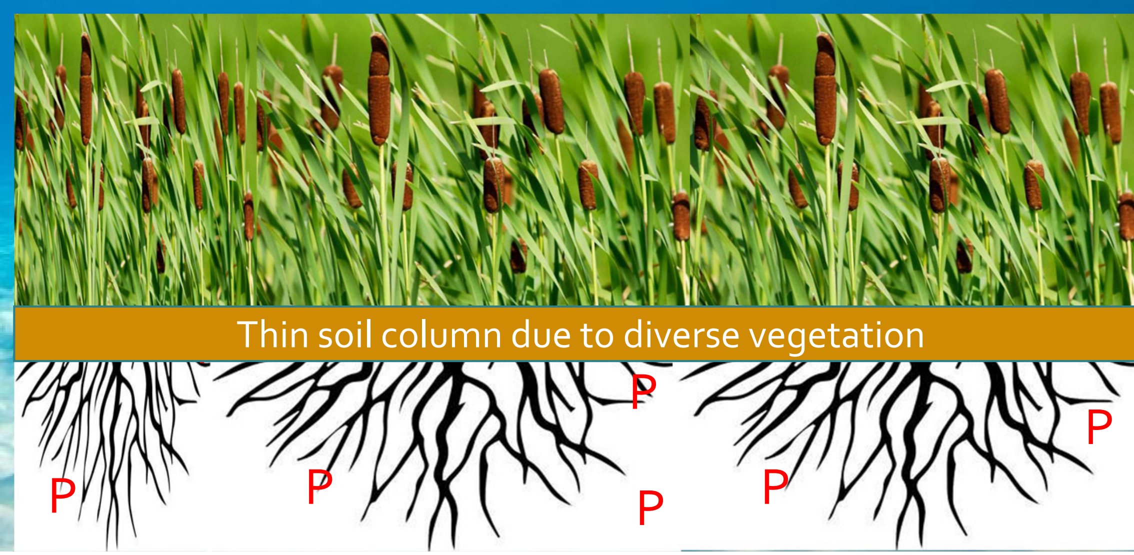
Hydroxyapatite	11.07	9.40	-1.67	Ca5(PO4)3OH

P	3.700e-05					
CaHPO4	1.601e-05	1.720e-05	-4.796	-4.764	0.031	(0)
CaPO4-	1.540e-05	1.117e-05	-4.813	-4.952	-0.139	(0)
HPO4-2	5.210e-06	1.374e-06	-5.283	-5.862	-0.579	8.69
FeHPO4	1.661e-07	1.784e-07	-6.780	-6.749	0.031	(0)
H2PO4-	8.561e-08	6.210e-08	-7.067	-7.207	-0.139	34.26
NaHPO4-	6.627e-08	4.808e-08	-7.179	-7.318	-0.139	50.40
CaH2PO4+	4.944e-08	3.587e-08	-7.306	-7.445	-0.139	(0)
KHPO4-	5.671e-09	4.114e-09	-8.246	-8.386	-0.139	40.47
PO4-3	4.571e-09	1.663e-10	-8.340	-9.779	-1.439	-18.30

Plant Biota Controlling Phosphorous Levels

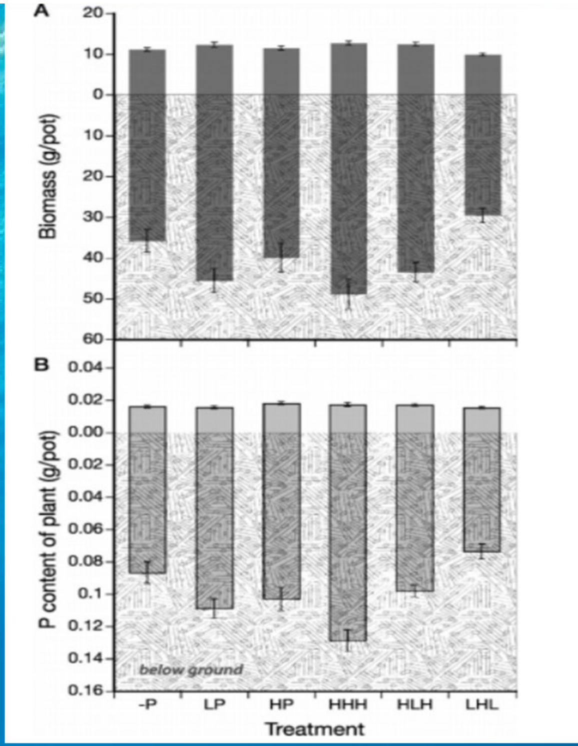
- Nature has its own system of regulators, cattails take in P through sorption
- Graphic 2 trapped more total dissolved solids and nitrogen, and it exported less P from runoff
- More light penetration allowed for moss to grow
- Thinner soil column resulted in less clay which increased P removal
- Nutrients were leached in graphic 1
- Resulted in a net export of phosphorous



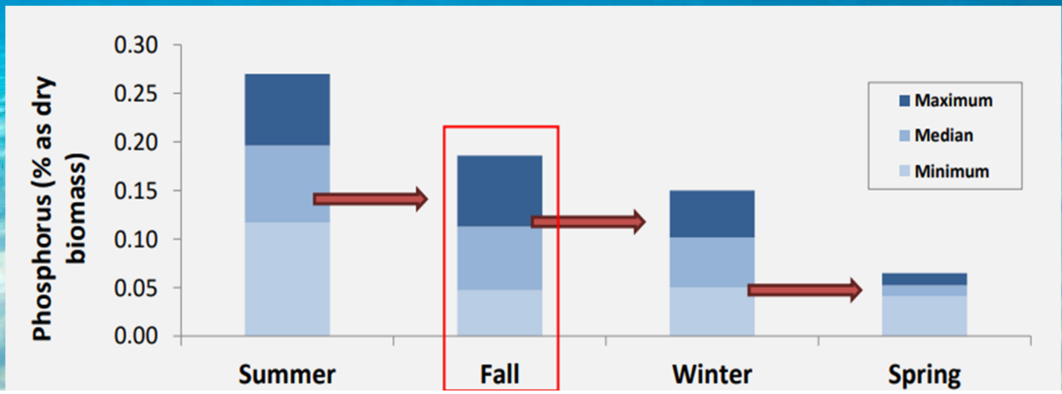


Organic Control

- A natural solution that doesn't harm the environment
- Cattails remove phosphorous from the system without causing pollution
- The limiting factor for cattail growth is phosphorus, as they take in P their biomass is drastically increased
- Once biomass is increased the plant requires more to sustain itself



Field, 1991



Grosshans, 2016

Phosphorous Removal Through Aluminum Sulphate $Al_2(SO_4)_3$

- When Aluminum Sulphate reacts with water it forms Alum
- Alum is a coagulant commonly used in water treatment plants to clarify drinking water
- Alum disrupts the nitrogen cycle and internal loading of phosphorous from sediments
- Upon contact with water Alum will form Aluminum Hydroxide, commonly called "floc"

$Al_2(SO_4)_3$*$14H_2O$ (Alum) + $2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2SO_4 + 18H_2O$

This then dissociates to form trivalent Al^{3+} ions and becomes hydrated with water

$Al^{3+} + 6H_2o \rightarrow Al(H_2O)6^{3+}$

The species then undergoes a series of rapid hydrolytic reactions to form $Al(OH)_3$ precipitate

$Al^{3+} + H_2O \rightarrow$ Intermediate Reactions $\rightarrow Al(OH)_3$

This material loses a hydroxide and has a high capacity to adsorb phosphates

$Al(OH)_2^{+} + HPO_4^{3-} \rightarrow Al(OH)_2HPO_4^{-}$

Boisvert, et al. 2013

$Al(OH)_2HPO_4^-$ was not found in any of the PHREEQ databases. To use this compound more info is needed.

Table 1: HPO_4^{-2} concentration 31.5%

Table 2: HPO_4^{-2} concentration 31.7%

Table 3: HPO_4^{-2} concentration 32%

Table 4: HPO_4^{-2} concentration 32.4%

10 ppm of Aluminum

Al(OH)3(a)		2.06	14.22	12.16	Al(OH)3	

P	3.700e-05					
CaHPO4	1.399e-05	1.456e-05	-4.854	-4.837	0.017	(0)
HPO4-2	1.164e-05	3.758e-06	-4.934	-5.425	-0.491	8.22
CaPO4-	9.666e-06	7.350e-06	-5.015	-5.134	-0.119	(0)
FeHPO4	1.162e-06	1.209e-06	-5.935	-5.917	0.017	(0)
H2PO4-	2.829e-07	2.151e-07	-6.548	-6.667	-0.119	34.05

20 ppm of Aluminum

Al(OH)3(a)		2.36	14.52	12.16	Al(OH)3	

P	3.700e-05					
CaHPO4	1.390e-05	1.449e-05	-4.857	-4.839	0.018	(0)
HPO4-2	1.175e-05	3.752e-06	-4.930	-5.426	-0.496	8.25
CaPO4-	9.644e-06	7.315e-06	-5.016	-5.136	-0.120	(0)
FeHPO4	1.160e-06	1.209e-06	-5.936	-5.918	0.018	(0)

30 ppm of Aluminum

Al(OH)3(a)		2.54	14.70	12.16	Al(OH)3	

P	3.700e-05					
CaHPO4	1.382e-05	1.442e-05	-4.860	-4.841	0.018	(0)
HPO4-2	1.186e-05	3.746e-06	-4.926	-5.426	-0.500	8.27
CaPO4-	9.622e-06	7.280e-06	-5.017	-5.138	-0.121	(0)
FeHPO4	1.158e-06	1.208e-06	-5.936	-5.918	0.018	(0)
H2PO4-	2.835e-07	2.145e-07	-6.547	-6.669	-0.121	34.07

40 ppm of Aluminum

Al(OH)3(a)		2.66	14.82	12.16	Al(OH)3	

P	3.700e-05					
CaHPO4	1.374e-05	1.435e-05	-4.862	-4.843	0.019	(0)
HPO4-2	1.196e-05	3.741e-06	-4.922	-5.427	-0.505	8.29
CaPO4-	9.601e-06	7.247e-06	-5.018	-5.140	-0.122	(0)
FeHPO4	1.156e-06	1.207e-06	-5.937	-5.918	0.019	(0)
H2PO4-	2.837e-07	2.142e-07	-6.547	-6.669	-0.122	34.08

Ferric Iron: $Fe_2(SO_4)*9H_2O + 2PO_4^{-3} \rightarrow 2FePO_4 + 3SO_4^{-2} + 9H_2O$

Phosphorous Removal Through Iron

Vivianite

http://www.minclassics.com/VivBol508.php

- There are two types of iron sulphate used to remove phosphorous, ferric iron and ferrous iron
- Both compounds react with dissolved phosphate to form unique mineral precipitates
- Iron Chloride is similarly used for phosphorous removal creating ferric phosphate

Ferrous Iron: $3FeSO_4*7H_2O + 2PO_4^{-3} \rightarrow Fe_3(PO_4)_2 + 3SO_4^{-2} + 7H_2O$

Strengite

https://www.minfind.com/mineral-581259.html

Iron chloride: $FeCl_3 + H_3PO_4 \rightarrow FePO_4 + 3HCl_3$

Aluminum salts usually outperform iron salts at anaerobic condition because part of ferric is reduced to ferrous which is less effective in coagulation

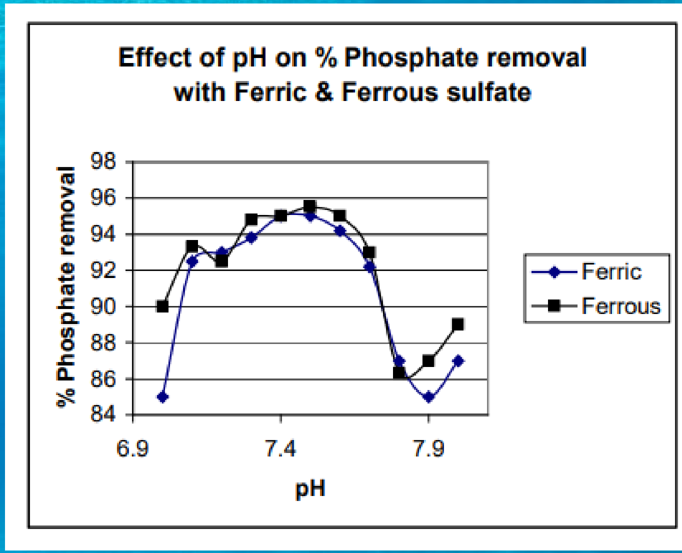
Phosphorous Removal from Iron

1) Treatment with either ferrous or ferric sulfate
2) Precipitation of ferrous or ferric phosphate
3) Settling of the precipitate

The product must settle out or the water will become turbid and useless

Is most optimal in a pH range from 7.3-7.6

Removes up to 95% phosphate



Neethling, 2013

At pH of 8.5

Table 1: HPO_4^{-2} concentration 31%

Table 2: HPO_4^{-2} concentration 29.9%

Table 3: HPO_4^{-2} concentration 34.5%

Ideal: HPO_4^{-2} concentration 11.5%

% efficiency	Fe^{+3} dose (ppm)	Fe/TP
95	7.5	4.2
95.6	12.0	6.6
98	22.4	12.4

Neethling, 2013

14ppm of Iron (value from article)

Vivianite	4.81	-31.19	-36.00	Fe3(PO4)2:8H2O

P	3.700e-05					
CaHPO4	1.408e-05	1.463e-05	-4.852	-4.835	0.017	(0)
HPO4-2	1.153e-05	3.764e-06	-4.938	-5.424	-0.486	8.20
CaPO4-	9.688e-06	7.387e-06	-5.014	-5.132	-0.118	(0)
FeHPO4	1.164e-06	1.210e-06	-5.934	-5.917	0.017	(0)
H2PO4-	2.826e-07	2.155e-07	-6.549	-6.667	-0.118	34.04

34ppm of Iron

Vivianite	5.92	-30.08	-36.00	Fe3(PO4)2:8H2O

P	3.700e-05					
CaHPO4	1.343e-05	1.397e-05	-4.872	-4.855	0.017	(0)
HPO4-2	1.108e-05	3.595e-06	-4.956	-5.444	-0.489	8.21
CaPO4-	9.260e-06	7.051e-06	-5.033	-5.152	-0.118	(0)
FeHPO4	2.703e-06	2.811e-06	-5.568	-5.551	0.017	(0)
H2PO4-	2.703e-07	2.058e-07	-6.568	-6.687	-0.118	34.04

44ppm of Iron

Vivianite	5.34	-30.66	-36.00	Fe3(PO4)2:8H2O

P	3.700e-05					
HPO4-2	1.280e-05	3.861e-06	-4.893	-5.413	-0.521	8.37
CaHPO4	1.164e-05	1.222e-05	-4.934	-4.913	0.021	(0)
CaPO4-	1.060e-05	7.934e-06	-4.975	-5.100	-0.126	(0)
FeHPO4	1.480e-06	1.553e-06	-5.830	-5.809	0.021	(0)
H2PO4-	2.331e-07	1.745e-07	-6.632	-6.758	-0.126	34.10

Ideal Ferric Iron ratio at 22.4ppm

Vivianite	7.23	-28.77	-36.00	Fe3(PO4)2:8H2O

P	3.700e-05					
FeHPO4	2.418e-05	2.534e-05	-4.617	-4.596	0.020	(0)
CaHPO4	4.592e-06	4.813e-06	-5.338	-5.318	0.020	(0)
HPO4-2	4.248e-06	1.298e-06	-5.372	-5.887	-0.515	8.33
FeH2PO4+	2.433e-06	1.826e-06	-5.614	-5.738	-0.124	(0)
H2PO4-	9.899e-07	7.432e-07	-6.004	-6.129	-0.124	34.10

Results

Treatments for Lake Wind

Recommendations:

- Cattail Swales
- Liming Which Increases pH and Precipitates Hydroxyapatite
- Ferrous Iron Sulfate Treatment Would Not Be Viable
- Nets to Prevent Carp Migration from Lake Muskego

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