

Utilization of wastewater as phosphorus fertilizer & modeling sorption to soil as mediation of P loss

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Geochemistry (Spring 2025)

Phosphorous

- Plant essential nutrient
- PO_4^{3-} is plant available
 - Comes mostly from mineral sources in inorganic forms
 - Availability influenced by mineral solubility
 - Can leave soil through leaching or erosion
- Usually supplemented by fertilizer
 - Rock phosphate ($\text{Ca}_{10}(\text{PO}_4)_6(\text{X})_2$)
 - Fluorapatite

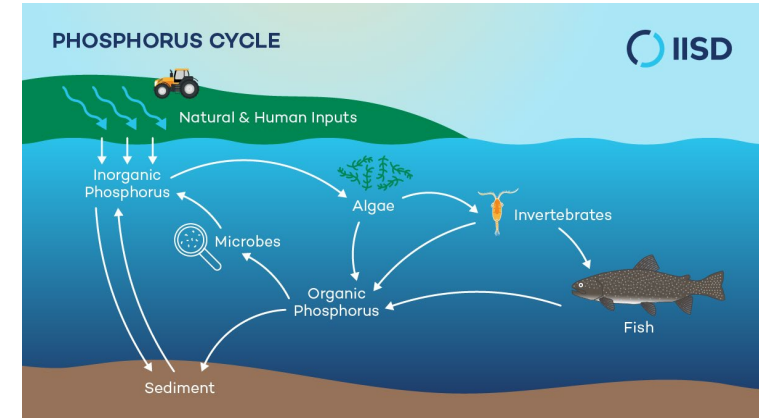


Photo courtesy of IISD



Photo courtesy of MinDat

Factors impacting P availability

- **pH**
 - More soluble around neutral pH
 - Binds with Ca at high pH
 - Binds with Al and Fe
- **Organic matter content**
 - C promotes P mineralization
- **Aeration**
 - Aeration promotes adsorption
- **Eh**
 - More available when oxidized
 - Reduced form is prone to leaching



Photo courtesy of UMN

Why use wastewater?

- Byproduct that is reported to supply >70% of P for plant growth (Davand et al.)
 - Through precipitation of struvite (Omidire, 2022)
- Sustainable alternative to rock phosphate
- Environmental concerns and application limits
 - Depends on the industry

Can we modify wastewater for use as a source of P fertilizer?



Photo courtesy of Davand, et al, 2022

Wastewater composition

- Water was collected in West Azerbaijan, Iran
 - 70% domestic & 30% Industrial
- We are not interested in EC or BOD
 - Do not impact the ions within water
 - Tells you about those ions at a specific condition
- TOC → acetate
- IC → carbon

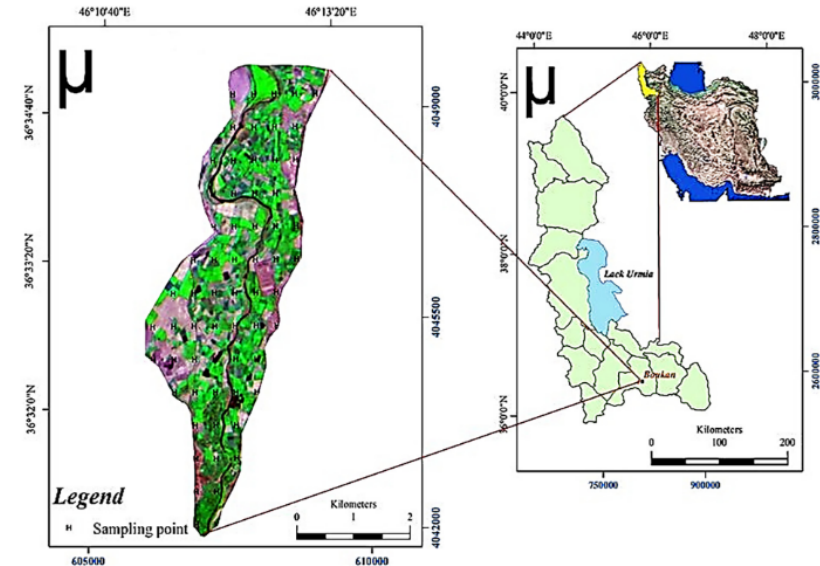


Fig. 1. Location map of the soil sampling area, Boukan province, West Azerbaijan, Iran.

	pH	EC (dS m ⁻¹)	BOD ₅ (mg L ⁻¹)	COD	TOC	IC	PO ₄	Cd (μg L ⁻¹)	Cu	Co	Ni	Pb	Zn
Treated wastewater	7.82	6.04	20	40	33.8	135	7.5	1.20	8.52	0.027	12.12	45.31	325

Original output

-----Description of solution-----

pH = 7.820
pe = 4.000
Density (g/cm3) = 0.99710
Volume (L) = 1.00297
Viscosity (mPa s) = 0.89002
Activity of water = 1.000
Ionic strength (mol/kgw) = 7.162e-04
Mass of water (kg) = 1.000e+00
Total alkalinity (eq/kg) = 7.740e-04
Total CO2 (mol/kg) = 2.250e-06
Temperature (oC) = 25.00
Electrical balance (eq) = -1.006e-03
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -98.08
Iterations = 10
Total H = 1.110140e+02
Total O = 5.550781e+01

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm3/mol
P	2.422e-04					
HPO4-2	1.988e-04	1.762e-04	-3.702	-3.754	-0.052	(0)
H2PO4-	4.336e-05	4.208e-05	-4.363	-4.376	-0.013	(0)
PO4-3	6.453e-09	4.910e-09	-8.190	-8.309	-0.119	(0)
H3PO4	8.955e-11	8.955e-11	-10.048	-10.048	0.000	(0)
CoHPO4	6.503e-11	6.503e-11	-10.187	-10.187	0.000	(0)

PO₄⁻ & pH

- What if we change pH?
 - Optimal pH of wastewater is between 6.5 to 8.5 (J mark)

-----Description of solution-----

pH	=	6.500
pe	=	4.000
Density (g/cm3)	=	0.99710
Volume (L)	=	1.00297
Viscosity (mPa s)	=	0.89002
Activity of water	=	1.000
Ionic strength (mol/kgw)	=	4.776e-04
Mass of water (kg)	=	1.000e+00
Total alkalinity (eq/kg)	=	6.062e-04
Total CO2 (mol/kg)	=	2.250e-06
Temperature (oC)	=	25.00
Electrical balance (eq)	=	-8.380e-04
Percent error, 100*(Cat- An)/(Cat+ An)	=	-97.54
Iterations	=	12
Total H	=	1.110141e+02
Total O	=	5.550781e+01

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm3/mol
P	2.422e-04					
H2PO4-	1.991e-04	1.943e-04	-3.701	-3.712	-0.011	(0)
HPO4-2	4.300e-05	3.894e-05	-4.367	-4.410	-0.043	(0)
H3PO4	8.638e-09	8.638e-09	-8.064	-8.064	0.000	(0)
PO4-3	6.500e-11	5.193e-11	-10.187	-10.285	-0.098	(0)
CoHPO4	1.671e-11	1.671e-11	-10.777	-10.777	0.000	(0)

-----Description of solution-----

pH	=	8.500
pe	=	4.000
Density (g/cm3)	=	0.99710
Volume (L)	=	1.00297
Viscosity (mPa s)	=	0.89002
Activity of water	=	1.000
Ionic strength (mol/kgw)	=	7.651e-04
Mass of water (kg)	=	1.000e+00
Total alkalinity (eq/kg)	=	8.118e-04
Total CO2 (mol/kg)	=	2.250e-06
Temperature (oC)	=	25.00
Electrical balance (eq)	=	-1.044e-03
Percent error, 100*(Cat- An)/(Cat+ An)	=	-98.46
Iterations	=	10
Total H	=	1.110139e+02
Total O	=	5.550781e+01

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm3/mol
P	2.422e-04					
HPO4-2	2.316e-04	2.045e-04	-3.635	-3.689	-0.054	(0)
H2PO4-	1.052e-05	1.020e-05	-4.978	-4.991	-0.013	(0)
PO4-3	3.616e-08	2.727e-08	-7.442	-7.564	-0.122	(0)
CoHPO4	7.011e-11	7.011e-11	-10.154	-10.154	0.000	(0)
H3PO4	4.537e-12	4.537e-12	-11.343	-11.343	0.000	(0)

Changing Fe and Al activities

- More Fe and Al are available to bind with PO₄
 - Less available solution P
- Legal limits: (*LIQTECH*)
Al < 0.2 ppm

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm3/mol
Al						
Al	7.413e-06					
Al(OH)4-	7.321e-06	7.103e-06	-5.135	-5.149	-0.013	(0)
Al(OH)3	8.481e-08	8.481e-08	-7.072	-7.072	0.000	(0)
Al(OH)2+	6.584e-09	6.389e-09	-8.181	-8.195	-0.013	(0)
AlOH+2	1.364e-11	1.209e-11	-10.865	-10.918	-0.052	(0)
Al+3	2.390e-14	1.817e-14	-13.622	-13.741	-0.119	(0)
P						
P	2.422e-04					
HPO4-2	1.988e-04	1.762e-04	-3.702	-3.754	-0.052	(0)
H2PO4-	4.335e-05	4.207e-05	-4.363	-4.376	-0.013	(0)
PO4-3	6.455e-09	4.909e-09	-8.190	-8.309	-0.119	(0)
H3PO4	8.953e-11	8.953e-11	-10.048	-10.048	0.000	(0)
CoHPO4	6.499e-11	6.499e-11	-10.187	-10.187	0.000	(0)

Fe < 7 ppm

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm3/mol
Fe (2)						
Fe (2)	1.274e-06					
Fe+2	7.630e-07	6.707e-07	-6.117	-6.173	-0.056	(0)
FeHPO4	4.684e-07	4.684e-07	-6.329	-6.329	0.000	(0)
FeOH+	1.832e-08	1.776e-08	-7.737	-7.750	-0.013	(0)
FeH2PO4+	1.452e-08	1.408e-08	-7.838	-7.851	-0.013	(0)
Fe (3)						
Fe (3)	1.241e-04					
Fe(OH)2+	7.143e-05	6.926e-05	-4.146	-4.160	-0.013	(0)
Fe(OH)3	4.949e-05	4.949e-05	-4.306	-4.306	0.000	(0)
Fe(OH)4-	3.161e-06	3.065e-06	-5.500	-5.514	-0.013	(0)
FeHPO4+	9.310e-10	9.028e-10	-9.031	-9.044	-0.013	(0)
FeOH+2	3.028e-10	2.676e-10	-9.519	-9.572	-0.054	(0)
Fe (Acetate) 2+	7.386e-15	7.151e-15	-14.132	-14.146	-0.014	(0)
Fe (Acetate) +2	4.147e-15	3.645e-15	-14.382	-14.438	-0.056	(0)
Fe+3	8.245e-16	6.230e-16	-15.084	-15.205	-0.122	(0)
FeH2PO4+2	5.604e-16	4.955e-16	-15.251	-15.305	-0.053	(0)
P						
P	2.422e-04					
HPO4-2	1.985e-04	1.754e-04	-3.702	-3.756	-0.054	(0)
H2PO4-	4.319e-05	4.189e-05	-4.365	-4.378	-0.013	(0)
FeHPO4	4.684e-07	4.684e-07	-6.329	-6.329	0.000	(0)
FeH2PO4+	1.452e-08	1.408e-08	-7.838	-7.851	-0.013	(0)
PO4-3	6.468e-09	4.887e-09	-8.189	-8.311	-0.122	(0)
FeHPO4+	9.310e-10	9.028e-10	-9.031	-9.044	-0.013	(0)
H3PO4	8.914e-11	8.914e-11	-10.050	-10.050	0.000	(0)
CoHPO4	6.459e-11	6.459e-11	-10.190	-10.190	0.000	(0)
FeH2PO4+2	5.604e-16	4.955e-16	-15.251	-15.305	-0.053	(0)

PO_4^- & organic carbon

- Increasing carbon results in P mineralization
 - Double the amount of SOC

```
-----Description of solution-----
pH = 7.820
pe = 4.000
Density (g/cm3) = 0.99727
Volume (L) = 1.00297
Viscosity (mPa s) = 0.89003
Activity of water = 1.000
Ionic strength (mol/kgw) = 2.068e-03
Mass of water (kg) = 1.000e+00
Total alkalinity (eq/kg) = 3.466e-03
Total CO2 (mol/kg) = 2.250e-03
Temperature (oC) = 25.00
Electrical balance (eq) = -3.698e-03
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -99.64
Iterations = 10
Total H = 1.110162e+02
Total O = 5.551448e+01
```

P	2.422e-04					
HPO4-2	2.009e-04	1.647e-04	-3.697	-3.783	-0.086	(0)
H2PO4-	4.131e-05	3.932e-05	-4.384	-4.405	-0.021	(0)
PO4-3	7.218e-09	4.588e-09	-8.142	-8.338	-0.197	(0)
H3PO4	8.368e-11	8.368e-11	-10.077	-10.077	0.000	(0)
CoHPO4	4.761e-11	4.761e-11	-10.322	-10.322	0.000	(0)

Takeaways

For this particular wastewater:

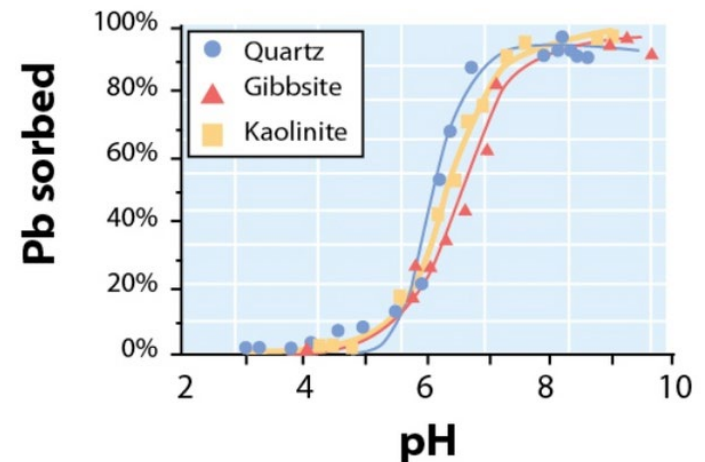
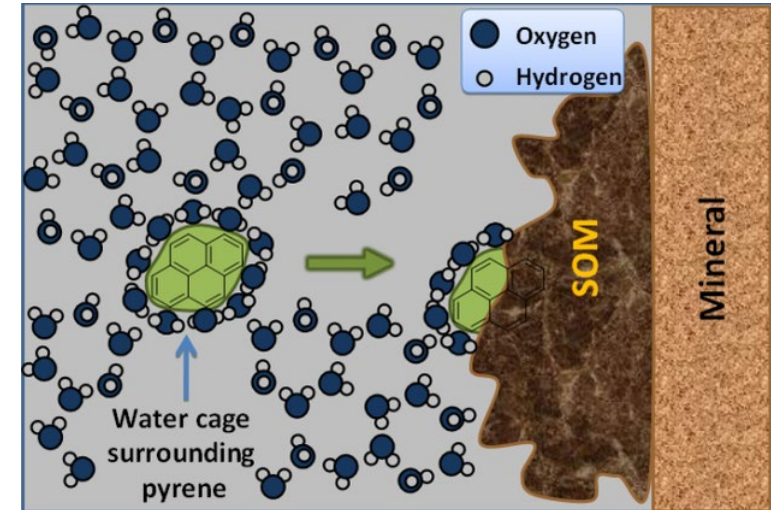
- PO_4^{3-} is higher at higher pH
- Fe and Al don't really impact available P
- Increasing SOC doesn't impact available P

We can modify wastewater to serve as a viable source of P

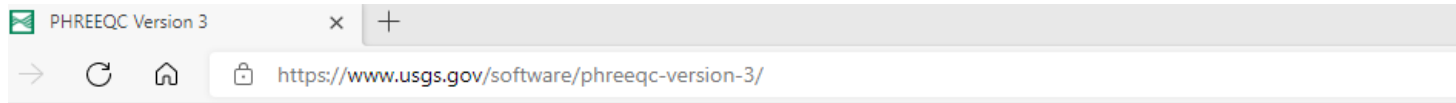
- May not be economically feasible
- Within legal application limits

Modeling P sorption in PHREEQ

- Sorption is how sticky something is to a surface
- Phosphate is an anion
 - Cannot be modeled in PHREEQc
 - Davand, et. al, models in a different software
- Utilize PHREEQ-N-Titration-PO₄-Adsorption Model
 - coding program developed in 2021 by USGS & Pennsylvania Water Science Center
 - Single or mixed solutions
 - Stagnant or flowing
 - Can be modeled on a mass or mol basis



Photos courtesy of Nature Education



Graphical User Interfaces

- Windows 32-bit: [phreeqci-3.7.1-15876.msi \[13M\]](#) - Executable, database files, examples, PDF documentation
- Windows 32-bit: [Notepad ++ interface](#) - Appelo's Notepad ++ interface to PHREEQC version 3

Batch Versions of PHREEQC

- Windows 64-bit: [phreeqc-3.7.1-15876-x64.msi \[16M\]](#) - Executable, database files, examples, PDF documentation
- MacOS (OS 10.7 - 10.12) 64bit: [phreeqc-3.5.0-14000.dmg \[12M\]](#) - Executable, database files, examples, and PDF documentation
- Windows (any processor): [phreeqc-3.7.1-15876.zip \[12M\]](#) - Source, CMake, database files, examples, PDF documentation
- Linux (any processor): [phreeqc-3.7.1-15876.tar.gz \[12M\]](#) - Source, configure, database files, examples, PDF documentation

PhreeqcRM Reaction Module for Transport Models

- Windows (any processor): [phreeqcrm-3.7.1-15876.zip \[7M\]](#) - Source, CMake, database files, examples, HTML documentation
- Any Platform (any processor): [phreeqcrm-3.7.1-15876.tar.gz \[7M\]](#) - Source, configure, database files, examples, HTML documentation

IPhreeqc Modules

- Windows (any processor): [iphreeqc-3.7.1-15876.zip \[13M\]](#) - Source with CMake, database files, examples, and documentation
- Linux (any processor): [iphreeqc-3.7.1-15876.tar.gz \[13M\]](#) - Source with configure, database files, examples, and documentation
- Windows COM 32-bit: [IPhreeqcCOM-3.7.1-15876-win32.msi \[4M\]](#) - COM server, CHM documentation
- Windows COM 64-bit: [IPhreeqcCOM-3.7.1-15876-x64.msi \[4M\]](#) - COM server, CHM documentation (Both 32-bit and 64-bit COM versions should be installed on 64-bit versions of Windows)

IPhreeqc runs in the background of the PO_4^{3-} sorption GUI

File

Select Workspace: C:\Users\cravotta\Documents\AMD Titration PO4mg_wateq\BradleyRun\Sep022014 - 210825

	Soln#A	Soln#B	Soln#C	HMeO.mg	Fe%	Mn%	Al%	SPECIFIED CONSTANT SORBENT (EXISTING)
Design flow (gpm)	0	0	0	50	2.0	0.2	97.8	A=UP, B=MWW, C=AMD; HMeO fractions
Mix fraction	0.289	0.187	0.524		0.0049	0.157		<-Site density (strong or x), mol/mol, computed
Temp (C)	20	20	20		0.1957	0.0883	0.0684	<-Site density (weak or y), mol/mol, computed
SC (uS/cm)	0	0	0		1.925	1.91	8	<-Site density, sites/nm2
DO (mg/L)	0.01	0.01	0.01		600	746	68	<-Surface area, m2/g
pH	2	2	2					
Acidity (mg/L)	0	0	0					
<input type="checkbox"/> Estimate NetAcidity	0	0	0					
Alk (mg/L)	0	0	0					
TIC (mg/L as C)	18	2	9					
<input type="checkbox"/> Estimate TIC	2.4	2.4	2.4					
Fe (mg/L)	0.02	0.02	0.34					
Fe2 (mg/L)	0.02	0.02	0.34					
<input type="checkbox"/> Estimate Fe2	0	0	0					
Al (mg/L)	0.03	0.03	4.35					
Mn (mg/L)	1E-08	0.03	0.47					
SO4 (mg/L)	41.13	29.63	205.70					
Cl (mg/L)	40.58	70.29	59.03					
Ca (mg/L)	0	0	0					
Mg (mg/L)	0	0	0					
Na (mg/L)	0	0	0					
K (mg/L)	0	0	0					
Si (mg/L)	0	0	0					
NO3N (mg/L)	0	0	0					
PO4P (mg/L)	0	2.55	0					
TDS (mg/L)	0	0	0					
DOC (mg/L as C)	0	0	0					
Humate (mg/L as C)	0	0	0					

Specified Saturation Index Value at Which Precipitation Will Occur--ADDED TO SORBENT

SI_Fe(OH)3	0.0	SI_Al(OH)3	-1.345	SI_MnOOH	99
SI_Schwertmannite	99	SI_Basaluminite	99	SI_Mn(OH)2	0.0
SI_Fe(OH)2	0.0	SI_CaCO3	0.3	SI_FeCO3,MnCO3	2.5

Specified Saturation Index Value at Which Precipitation of PO4 Will Occur--COMPETES WITH SORPTION

SI_Fe(PO4)	99	SI_Al(PO4)	0.0	SI_Ca(PO4)	99
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Equilibrium Constants for PO4, SO4, and Ca Adsorption by HFO, HAO, and HMO

	HFO	HAO	HMO
LK1_H2PO4	31.29	26.89	LK1_xPO4-2 27.5
LK2_HPO4-	25.39	19.37	LK2_yPO4-2 19.5
LK3_PO4-2	17.72	13.57	LK3_yOH2HPO4- 22.8
LK2_SO4-	7.78	-0.45	LK4_yOH2H2PO4 25.2
LK3_OHSO4-2	0.79	1.19	LK3_yOH2HSO4 5.7
LK1_OHCa+2	4.97		LK_xOCa+ -1.5
LK2_OCa+	-5.85	-10.49	

Select titrant: ☒ NaOH ☐ CaCO3 ☐ Ca(OH)2 ☐ CaO ☐ Na2CO3

Maximum pH (<=11): 11

Generate Output File + Selected Graphs

☒ Gr1 Conc.aq ☒ Gr2 Sat.Index ☒ Gr3 HMeO.ppt ☒ Print PHREEQC Output Report

☒ Gr4 PO4.sor% ☒ Gr6 SO4.sor% ☐ Gr8 Ca.sor% ☒ Gr10 Fe.sor% ☒ Gr12 Al.sor% ☒ Gr14 Mn.sor%

☒ Gr5 PO4.spec ☐ Gr7 SO4.spec ☐ Gr9 Ca.sp ☐ Gr11 Fe.spec ☐ Gr13 Al.spec ☐ Gr15 Mn.spec

CausticTitration_PO4mg.exe created by C.A. Cravotta III, U.S. Geological Survey. Version Beta 1.5, August 2021

The Bradley Run Case

- Spellman et al., 2021
 - This example is programmed into the downloaded zip file
- Simulates the interaction of stream water, municipal wastewater and mine drainage
- Shows that P sorption is impacted by available quantity of previously accumulated HMeO sorbent
- PO_4^{3-} is able to precipitate and thus sorb by reducing (Al)
 - Adjusts the of gibbsite and $\text{Al}(\text{OH})_3$

File

Select Workspace

C:\PHREEQC\phreeq-n-titration-po4-adsorption-v1.0.0

	Soln#A	Soln#B	Soln#C
Design flow (gpm)	0	0	0
Mix fraction	0.289	0.187	0.524
Temp (C)	20	20	20
SC (uS/cm)	0	0	0
DO (mg/L)	0.01	0.01	0.01
pH	2	2	2
Acidity (mg/L)	0	0	0
<input type="checkbox"/> Estimate NetAcidity	0	0	0
Alk (mg/L)	0	0	0
TIC (mg/L as C)	18	2	9
<input type="checkbox"/> Estimate TIC	2.4	2.4	2.4
Fe (mg/L)	0.02	0.02	0.34
Fe2 (mg/L)	0.02	0.02	0.34
<input type="checkbox"/> Estimate Fe2	0	0	0
Al (mg/L)	0.03	0.03	4.35
Mn (mg/L)	1E-08	0.03	0.47
SO4 (mg/L)	41.13	29.63	205.70
Cl (mg/L)	40.58	70.29	59.03
Ca (mg/L)	0	0	0
Mg (mg/L)	0	0	0
Na (mg/L)	0	0	0
K (mg/L)	0	0	0
Si (mg/L)	0	0	0
NO3N (mg/L)	0	0	0
PO4P (mg/L)	0	2.55	0
TDS (mg/L)	0	0	0

HMeO.mg	Fe%	Mn%	Al%	SPECIFIED CONSTANT SORBENT (EXISTING)
0	2.0	0.2	97.8	A=UP, B=MWW, C=AMD; HMeO fractions
	0.0049	0.157		<--Site density (strong or x), mol/mol, computed
	0.1957	0.0883	0.0684	<--Site density (weak or y), mol/mol, computed
	1.925	1.91	8	<--Site density, sites/nm2
	600	746	68	<--Surface area, m2/g 62736.6 77324.4 5147.3 Surface area, m2/mol, comp.

Specified Saturation Index Value at Which Precipitation Will Occur--ADDED TO SORBENT

SI_Fe(OH)3	0.0	SI_Al(OH)3	-1.345	SI_MnOOH	99
SI_Schwertmannite	99	SI_Basaluminite	99	SI_Mn(OH)2	0.0
SI_Fe(OH)2	0.0	SI_CaCO3	0.3	SI_FeCO3,MnCO3	2.5

Specified Saturation Index Value at Which Precipitation of PO4 Will Occur--COMPETES WITH SORPTION

SI_Fe(PO4)	99	SI_Al(PO4)	0.0	SI_Ca(PO4)	99
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Equilibrium Constants for PO4, SO4, and Ca Adsorption by HFO, HAO, and HMO

	HFO	HAO	HMO
LK1_H2PO4	31.29	26.89	LK1_xPO4-2 27.5
LK2_HPO4-	25.39	19.37	LK2_yPO4-2 19.5
LK3_PO4-2	17.72	13.57	LK3_yOH2HPO4- 22.8
LK2_SO4-	7.78	-0.45	LK4_yOH2H2PO4 25.2
LK3_OHSO4-2	0.79	1.19	LK3_yOH2HSO4 5.7
LK1_OHCa+2	4.97		LK_xOCa+ -1.5
LK2_OCa+	-5.85	-10.49	

Select titrant:

☒ NaOH
 ☐ CaCO3
 ☐ Ca(OH)2
 ☐ CaO
 ☐ Na2CO3

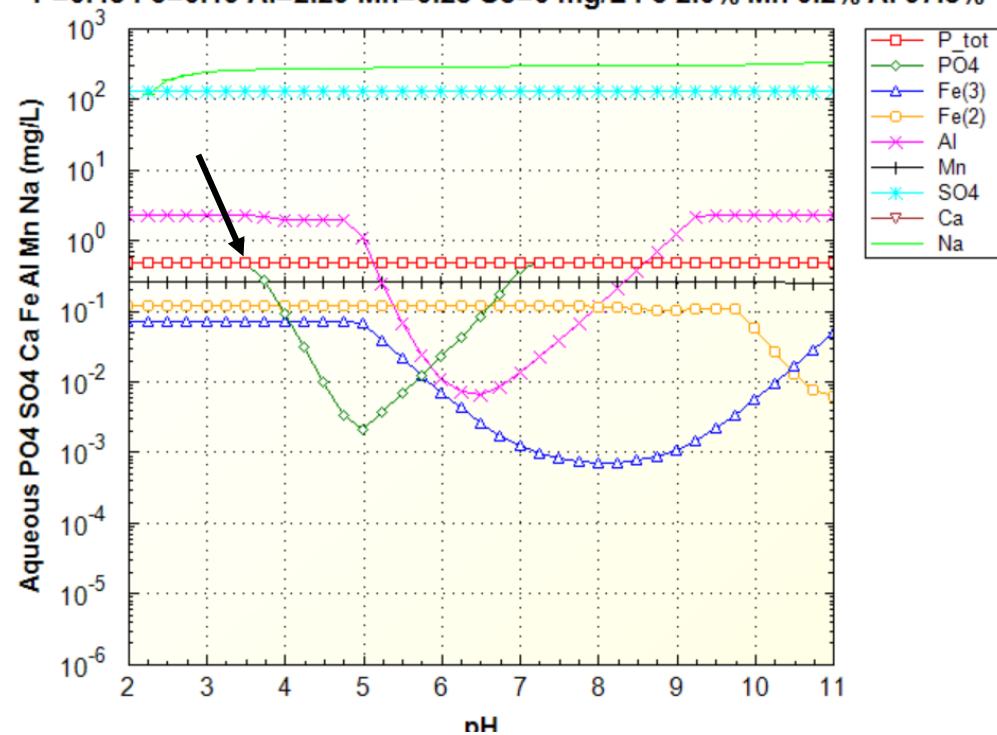
Maximum pH (<=11):

11

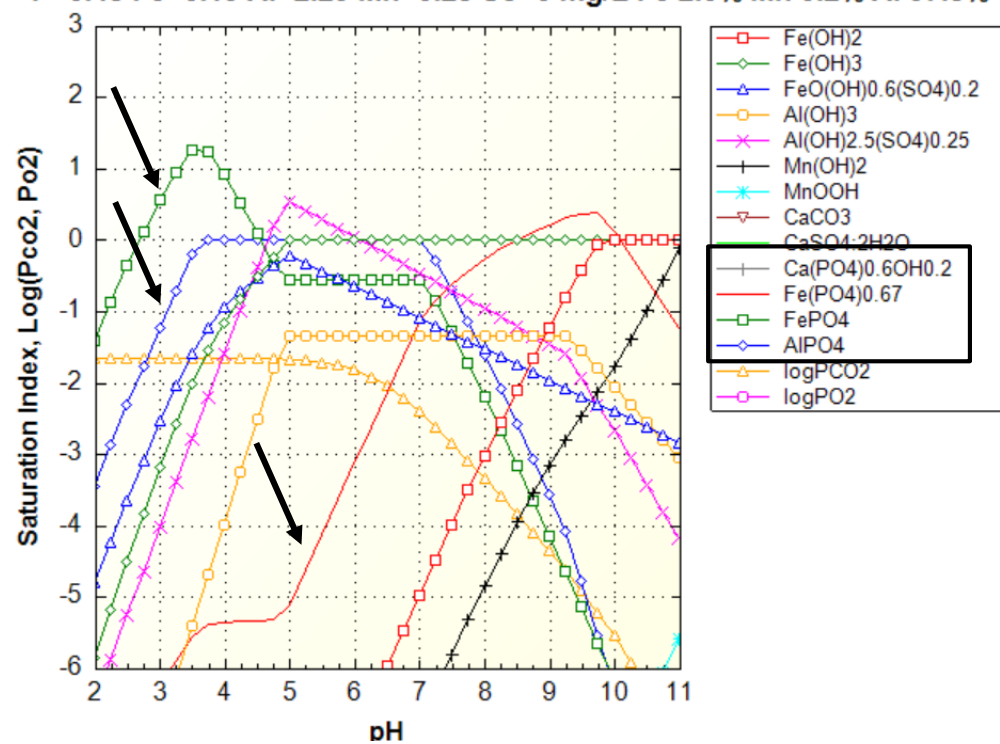
Generate Output File + Selected Graphs

<input checked="" type="checkbox"/> Gr1 Conc.aq	<input checked="" type="checkbox"/> Gr2 Sat.Index	<input type="checkbox"/> Gr3 HMeO.ppt	<input type="checkbox"/> Print PHREEQC Output Report
<input checked="" type="checkbox"/> Gr4 PO4.sor%	<input type="checkbox"/> Gr6 SO4.sor%	<input type="checkbox"/> Gr8 Ca.sor%	<input type="checkbox"/> Gr10 Fe.sor%
		<input type="checkbox"/> Gr12 Al.sor%	<input type="checkbox"/> Gr14 Mn.sor%

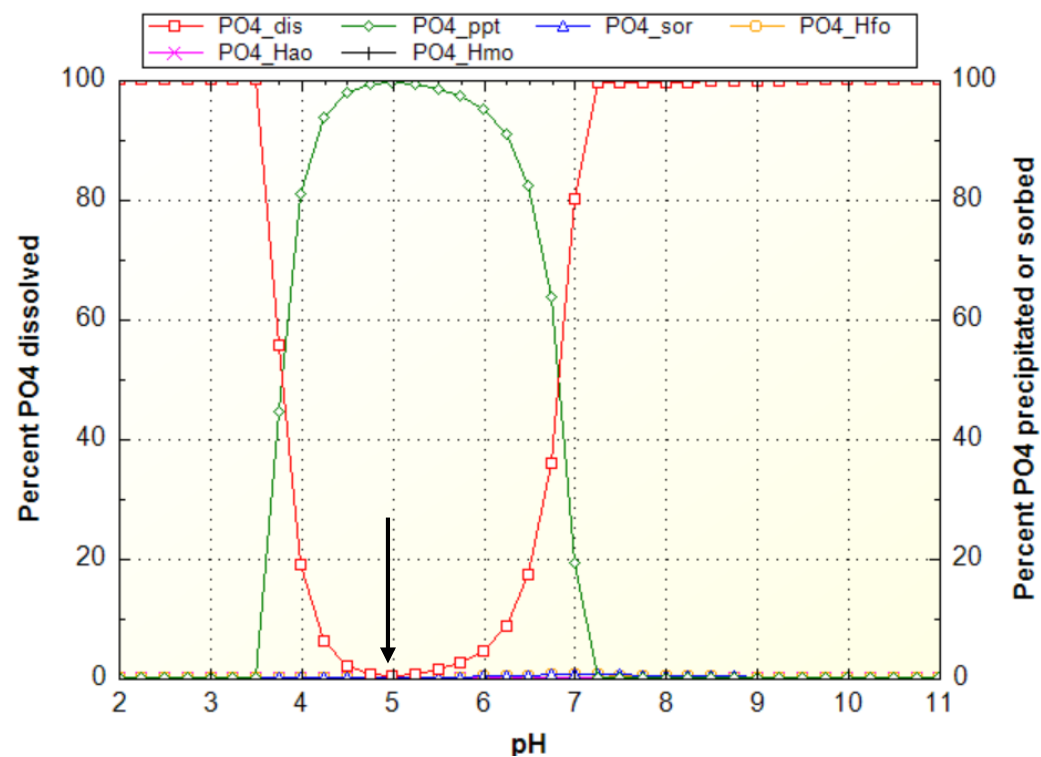
P=0.48 Fe=0.19 Al=2.29 Mn=0.25 So=0 mg/L Fe 2.0% Mn 0.2% Al 97.8%



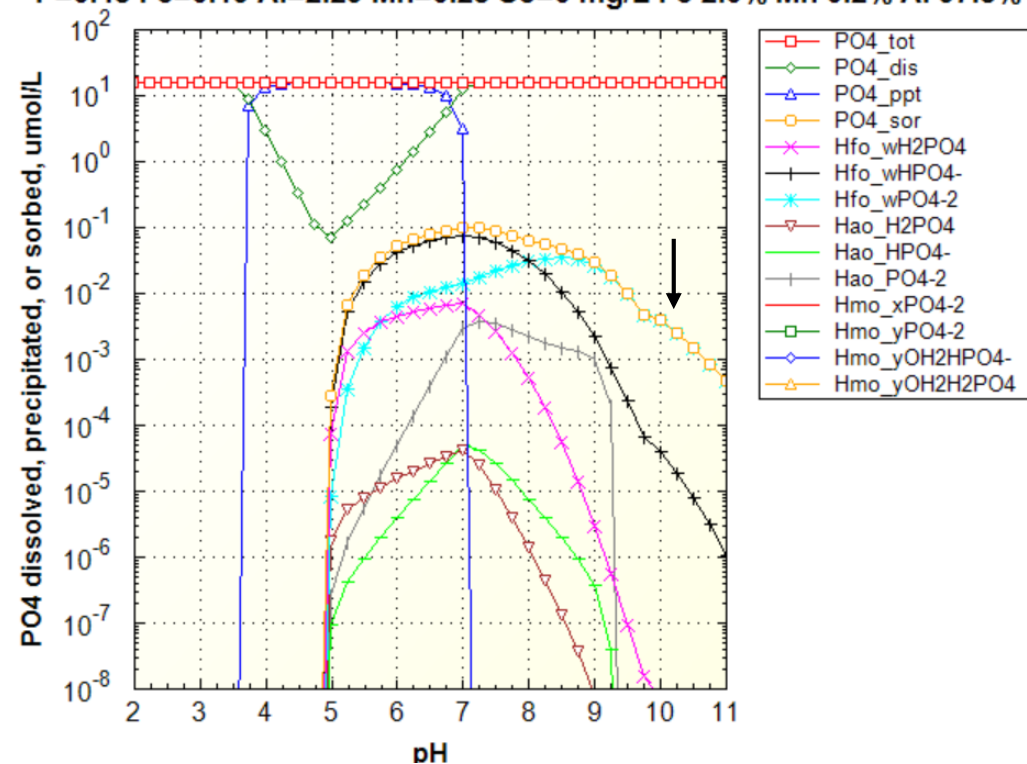
P=0.48 Fe=0.19 Al=2.29 Mn=0.25 So=0 mg/L Fe 2.0% Mn 0.2% Al 97.8%



P=0.48 Fe=0.19 Al=2.29 Mn=0.25 So=0 mg/L Fe 2.0% Mn 0.2% Al 97.8%



P=0.48 Fe=0.19 Al=2.29 Mn=0.25 So=0 mg/L Fe 2.0% Mn 0.2% Al 97.8%



Conclusions

- We can now model sorption of both anions and cations!
 - Informs management practices to avoid P loss
 - Can be used for a wide variety of scenarios
- Lots more to be done and learn
 - In order to model this particular water, we would need to add ions to the database
- For more information this software download can be found on the summary sheet

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Pictures

- <https://www.iisd.org/ela/blog/back-to-basics-how-and-why-phosphorus-cycles-through-a-lake/>
- <https://www.mindat.org/photo-409848.html>
- <https://blog-crop-news.extension.umn.edu/2020/03/how-to-prevent-fallow-syndrome-in-corn.html>
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