Change in plant available phosphorus species in a water-logged calcareous soil as a function of Eh

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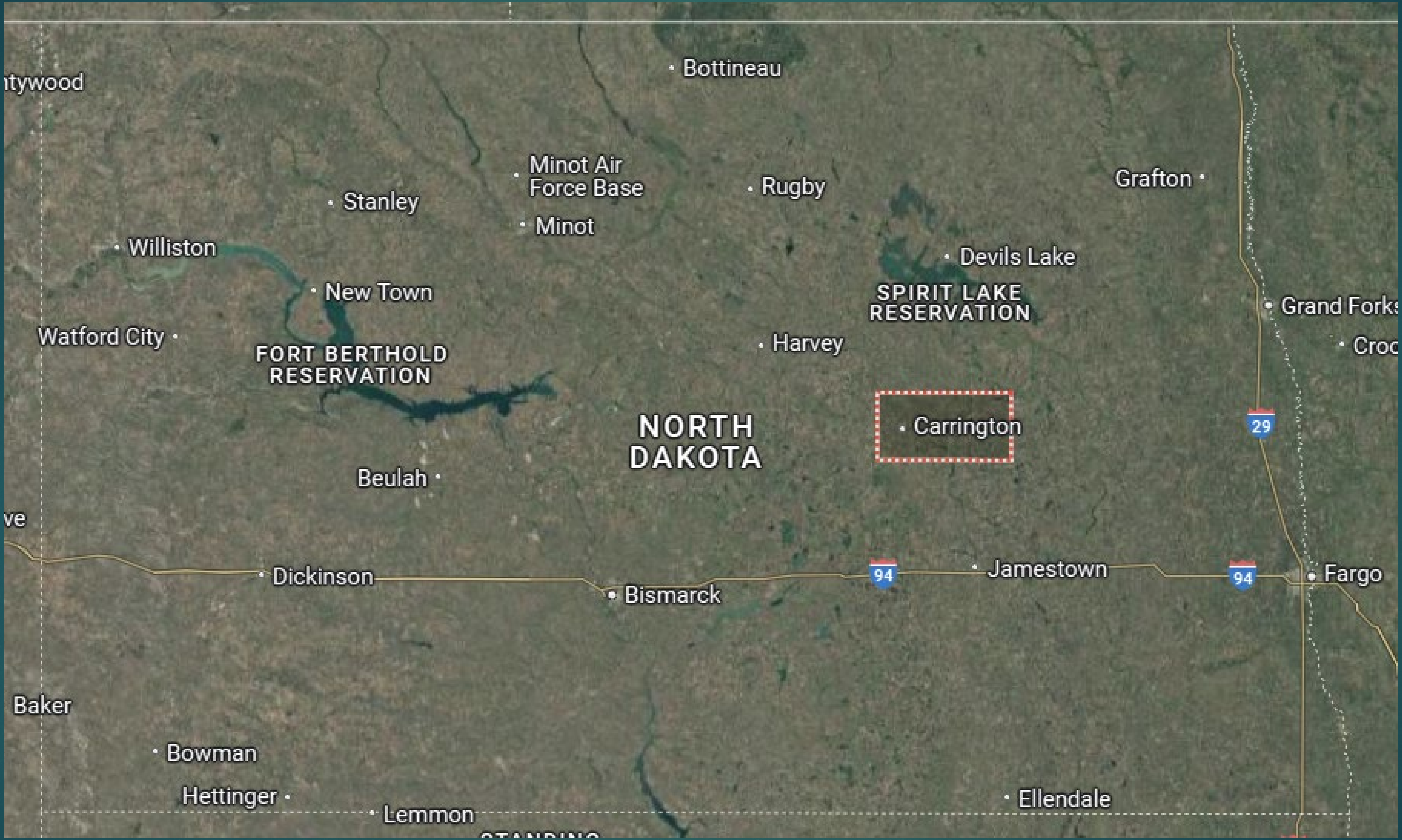
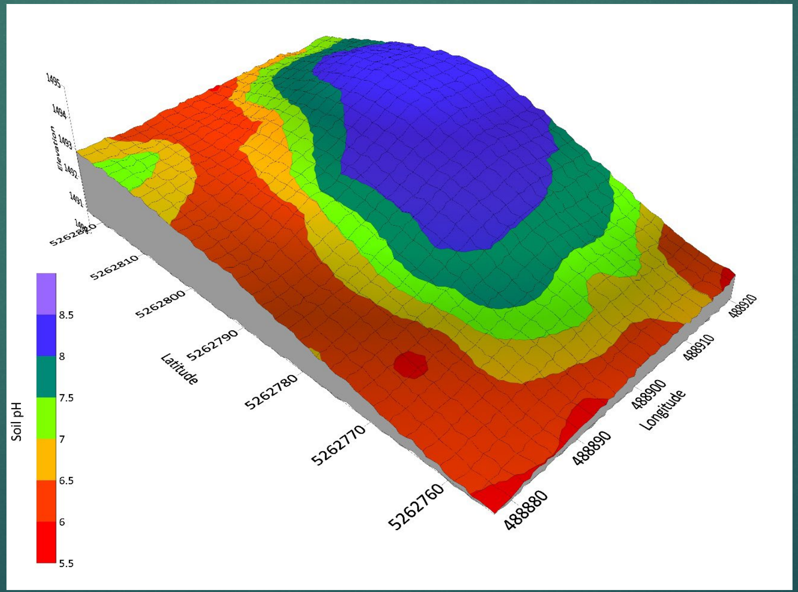
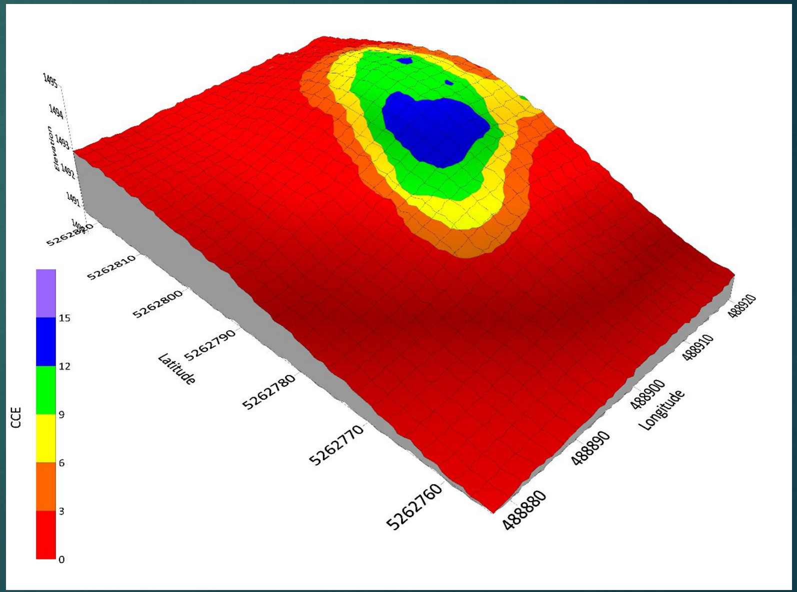


ntywood
Bottineau
Minot Air
Force Base
Stanley
Rugby
Grafton
Minot
Williston
Devils Lake
New Town
SPIRIT LAKE
RESERVATION
Grand Forks
Watford City
Harvey
Croo
FORT BERTHOLD
RESERVATION
NORTH
DAKOTA
Carrington
29
Beulah
ve
94
Jamestown
94
Fargo
Dickinson
Bismarck
Baker
Bowman
Hettinger
Lemmon
Ellendale

Heimdal-Emrick loam: Well drained soils formed on calcareous glacial till



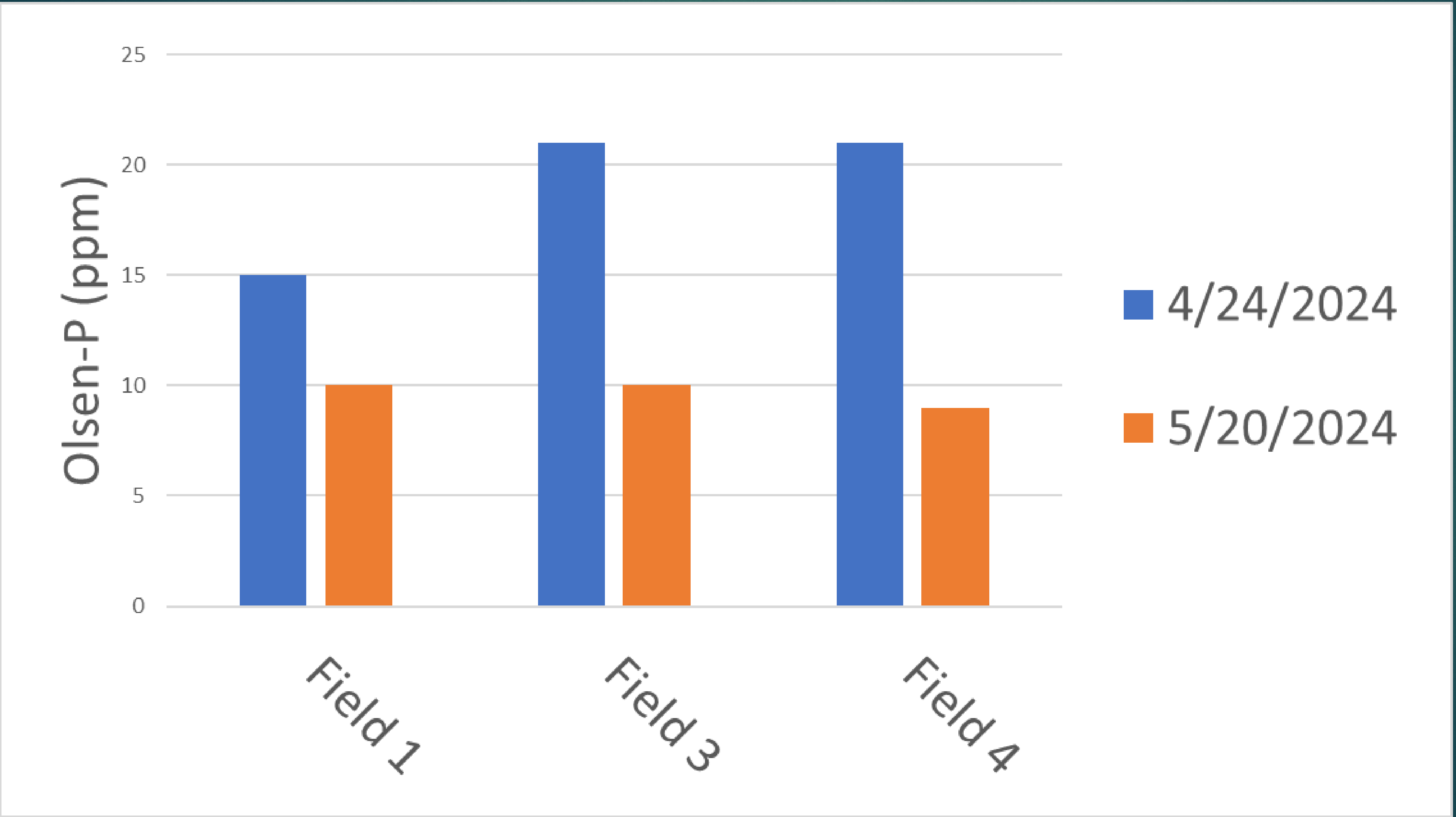
pH



CCE

- Microbial activity reduces ferric iron (+3) to ferrous iron (+2) which releases P from ferrihydrite, strengite
- Organic matter decomposition, anaerobic respiration
- Ferric to ferrous +0.77 V
- O2 to H2O +0.82 V
- Olsen P test shows high P levels after waterlogging

Seasonal change in Olsen-P levels on a farmer's fields



Solubility of soil phosphorus in extended waterlogged conditions: An incubation study

Rupngam, Messiga, Karam 2023

Conditions: field capacity, water saturation, water logging

Effects of Waterlogging:

- Eh decreased (-155 mV)
- water extractable P increased (1.47 to 2.58 mg/kg)
- ferric iron reduction to ferrous iron (1190 mg/kg)
- Increase in pH (+0.8)

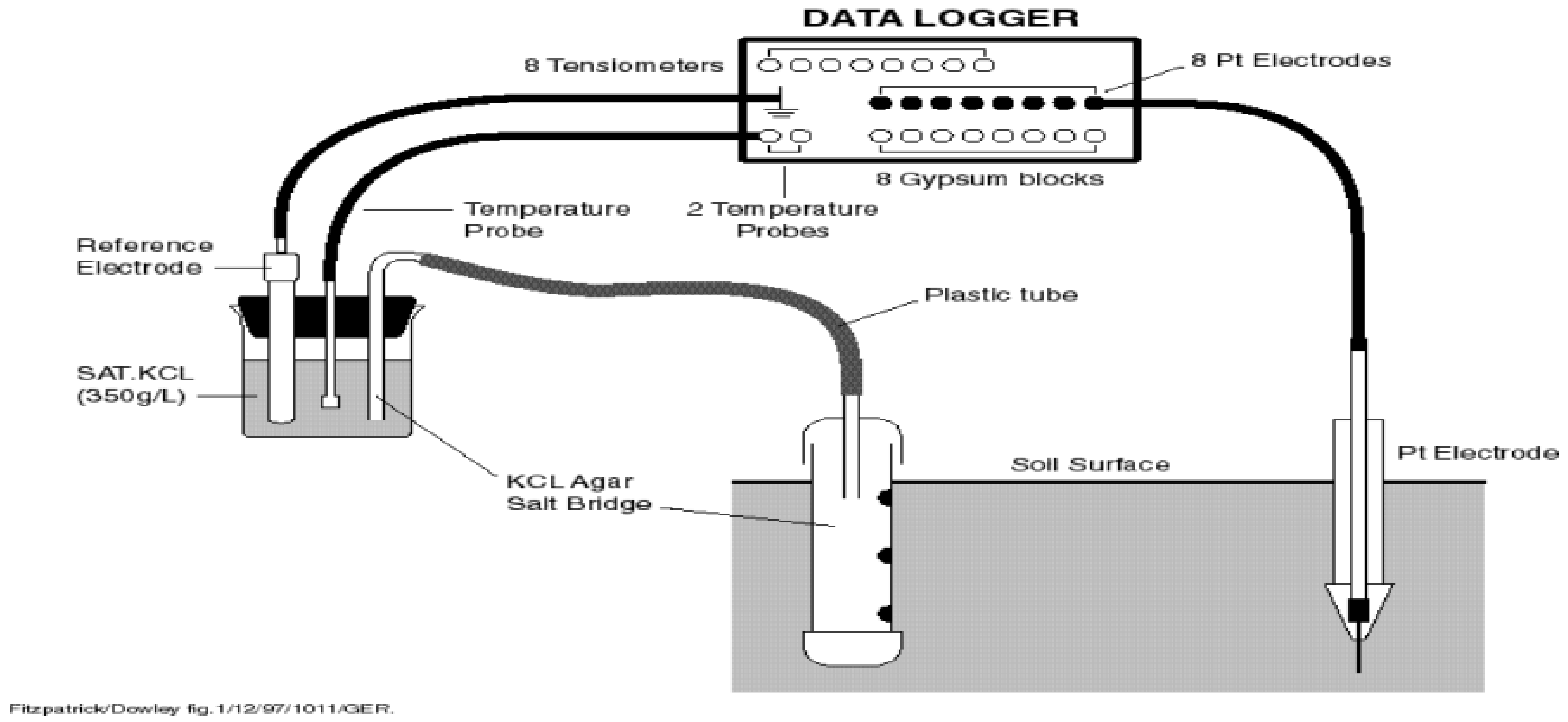


Figure.1: Schematic diagram of the automated redox monitoring assembly.

DOWLEY, A., FITZPATRICK, R., CASS, A., & BESZ, W. (1998). Measurement of Redox Potential (Eh) in Periodically Waterlogged Viticultural Soils In *16th World Congress of Soil Science* (Vol. 35).

Phreeqc Inputs

- Hydroxyapatite as a proxy for phosphorus containing minerals
- Calcite for the source of carbonates
- Irrigation water sample from the center pivot

pH	7.9	
K	8.3	ppm
Na	61	ppm
Ca	126	ppm
Mg	38	ppm
Sulfate	43	ppm
Nitrate	0	ppm
Cl	7	ppm
Carbonates	0	meq/L
Bicarbonates	8.04	meq/L

Field 4 pivot water sample, CREC, 2014, analyzed by Agvise

1st approach: change the Eh, fix the pH

```
TITLE Untitled
SOLUTION 1
      pH 8.432
      pe 9.656
      temp 25
      units mol/L
C                1.446e-04
Ca               3.158e-03
Cl               1.975e-04
K                2.123e-04
Mg               1.563e-03
Na               2.654e-03
P                5.549e-08
S                4.477e-04
EQUILIBRIUM_PHASES 1
      hydroxyapatite
      calcite
END
```

Eh = 0.575 V

	Molality
P	5.60E-08
HPO4-2	1.77E-08
CaHPO4	1.27E-08
CaPO4-	9.83E-09
MgHPO4	8.47E-09
MgPO4-	6.53E-09
H2PO4-	7.03E-10
NaHPO4-	5.93E-11
CaH2PO4+	3.63E-11
MgH2PO4+	2.28E-11
KHPO4-	4.73E-12
PO4-3	4.10E-12
H3PO4	3.17E-16

Eh = -0.23 V

	Molality
P	5.60E-08
HPO4-2	1.77E-08
CaHPO4	1.27E-08
CaPO4-	9.83E-09
MgHPO4	8.47E-09
MgPO4-	6.53E-09
H2PO4-	7.03E-10
NaHPO4-	5.93E-11
CaH2PO4+	3.63E-11
MgH2PO4-	2.28E-11
KHPO4-	4.73E-12
PO4-3	4.10E-12
H3PO4	3.17E-16

Eh = -0.23 V, no phases

	Molality
P	5.55E-08
HPO4-2	1.79E-08
CaHPO4	1.29E-08
CaPO4-	9.18E-09
MgHPO4	8.58E-09
MgPO4-	6.10E-09
H2PO4-	7.72E-10
NaHPO4-	6.01E-11
CaH2PO4+	3.99E-11
MgH2PO4-	2.50E-11
KHPO4-	4.79E-12
PO4-3	3.83E-12
H3PO4	3.77E-16

2nd approach: change Eh, float the pH

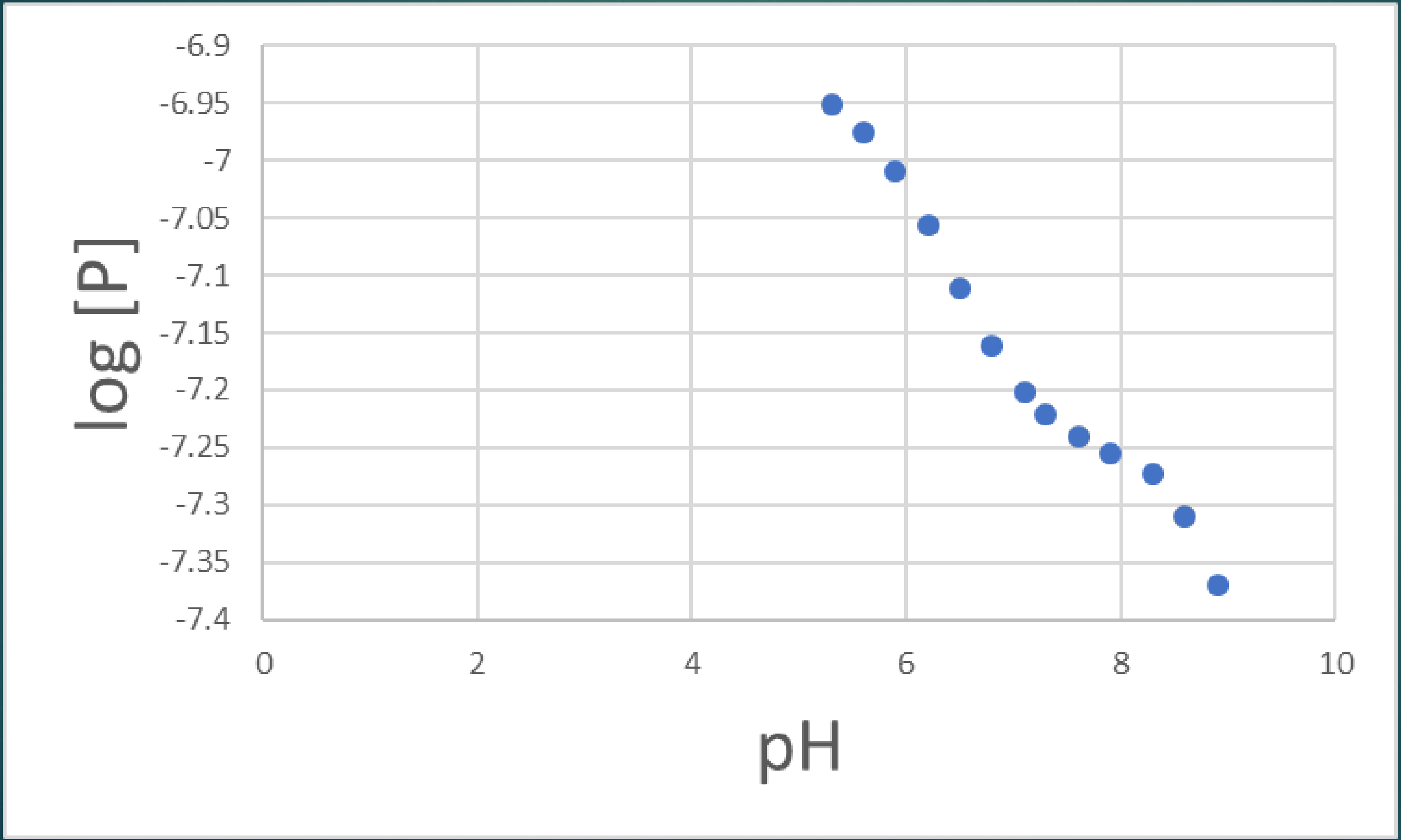
Eh = 0.575 V

	Molality
P	5.60E-08
HPO4-2	1.77E-08
CaHPO4	1.27E-08
CaPO4-	9.83E-09
MgHPO4	8.47E-09
MgPO4-	6.53E-09
H2PO4-	7.03E-10
NaHPO4-	5.93E-11
CaH2PO4+	3.63E-11
MgH2PO4+	2.28E-11
KHPO4-	4.73E-12
PO4-3	4.10E-12
H3PO4	3.17E-16

Eh = -0.23 V, pH=11.9

	Molality
P	9.82E-10
CaPO4-	7.86E-10
MgPO4-	1.94E-10
HPO4-2	6.05E-13
PO4-3	4.25E-13
CaHPO4	3.51E-13
MgHPO4	8.70E-14
NaHPO4-	1.95E-15
KHPO4-	1.56E-16
H2PO4-	8.17E-18
CaH2PO4+	3.54E-19
MgH2PO4-	8.26E-20
H3PO4	1.27E-27

Phosphorus concentration by pH



New input: organic matter and iron

```
      TITLE Untitled
PHASES
Organic_matter
    CH2O + O2 = CO2 + H2O
    log_k 83.14 # Approx log_k for aerobic respiration

      SOLUTION 1
            pH 8.432
            pe -3.9
            temp 25
            units mol/L
      Ca                  3.158e-03
      Cl                  1.975e-04
      K                   2.123e-04
      Mg                  1.563e-03
      Na                  2.654e-03
      P                   5.549e-08
      S                   4.477e-04
      Fe(3)  0.1 # Fe(OH)3 as Fe3+
      C(4)  0.1 # Organic carbon as CH2O
      O(0)  0.2
      EQUILIBRIUM_PHASES 1
            hydroxyapatite
            calcite
            Organic_matter

      END
```

Eh = 0.575 V

	Molality
P	7.53E-02
FeH2PO4+	3.80E-02
H2PO4-	3.15E-02
CaH2PO4+	3.23E-03
FeHPO4	1.39E-03
HPO4-2	5.32E-04
CaHPO4	3.18E-04
MgH2PO4+	2.36E-04
H3PO4	3.09E-05
MgHPO4	2.47E-05
NaHPO4-	7.30E-07
CaPO4-	1.13E-07
KHPO4-	5.77E-08
MgPO4-	8.75E-09
PO4-3	1.58E-10
FeH2PO4+2	5.23E-14
FeHPO4+	1.40E-16

Eh = -0.23 V

	Molality
P	7.53E-02
FeH2PO4+	3.80E-02
H2PO4-	3.15E-02
CaH2PO4+	3.23E-03
FeHPO4	1.39E-03
HPO4-2	5.32E-04
CaHPO4	3.18E-04
MgH2PO4-	2.36E-04
H3PO4	3.09E-05
MgHPO4	2.47E-05
NaHPO4-	7.30E-07
CaPO4-	1.13E-07
KHPO4-	5.77E-08
MgPO4-	8.75E-09
PO4-3	1.58E-10
FeH2PO4+	5.23E-14
FeHPO4+	1.40E-16

Conclusions

- Changing the Eh while fixing the pH did not result in an increase in dissolved phosphorus.
- Changing the Eh while allowing for pH change created a large increase in pH which would not occur in soil
- pH has a strong effect on phosphorus release but the model did not adequately account for the change in soil composition that accompanies different soil pH levels
- Organic matter decomposition by microbial activity needs to be modeled because it is the main driver of phosphorus release under anaerobic conditions
- The input of organic carbon and iron did not model phosphorus release due to microbial activity.
- A better, more nuanced model is needed.

References

- DOWLEY, A., FITZPATRICK, R., CASS, A., & BESZ, W. (1998). Measurement of Redox Potential (Eh) in Periodically Waterlogged Viticultural Soils Suivi du portentiel rédox (Eh) dans des sols viticoles à engorgement temporaire. In *16th World Congress of Soil Science* (Vol. 35).
- Rupngam, T., Messiga, A. J., & Karam, A. (2023). Solubility of soil phosphorus in extended waterlogged conditions: An incubation study. *Heliyon*, *9*(2).