Mineral deposition in ombrogenic bogs; Jura Mtns

Kevin Young
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North Dakota State University

Overview

- Study Background and Summary
  - *"Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two Sphagnum peat bogs, Jura Mountains, Switzerland"* [1]
- Water Chemistry
- PHREEQC Model
- Discussion

Study Objectives

- (1) Evaluate the composition of vertical porewater profiles at two different bog locations
- (2) Evaluate the redox state of the porewaters with respect to S and Fe

Study Background - Bogs

- Ombrogenic
  - Hydrologically isolated from local ground and surface waters
  - Inorganic solids are supplied by atmospheric deposition
- Minerogenic
  - Hydrologically connected to local waters
  - Receive inorganic solids from percolating groundwater
- Bog surface waters are acidic (pH 4)
- Below surface, bog waters are anoxic

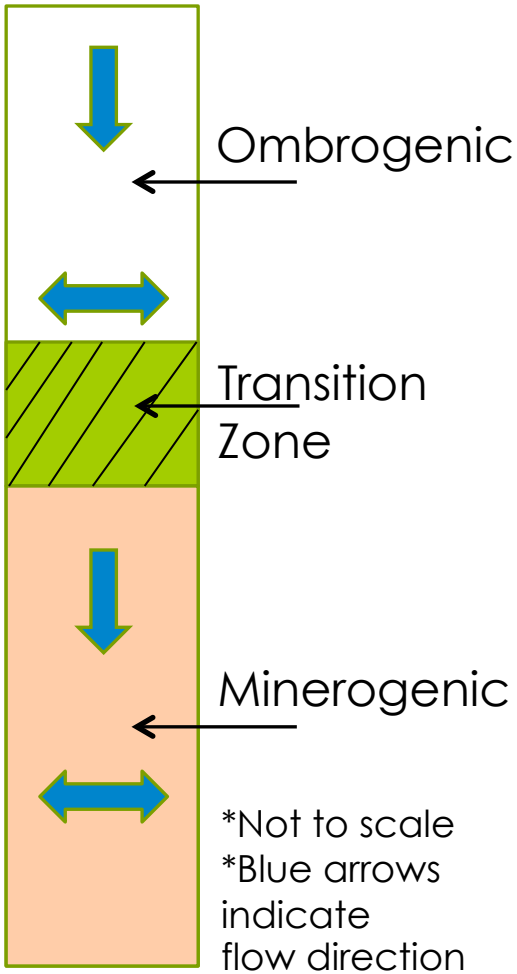
Study Background

- Location: Franches Montagnes region, Jura Mountains, NW Swizterland
- Average annual temperature = 5.5°C
- Annual Precipitation exceeds 1300 mm (~51 in)/yr.

[2]

Study Background

- La Tourbière des Genevez (TGe)
  - Area: 7.2 ha (590 m_{E-W} x 170 m_{N-S})
  - Pronounced domed structure: 2.5 m rise to center from N-S edges
  - Maximum peat depth: 140 cm
- Etang de la Gruère (EGr)
  - Area: 22.5 ha
  - Sampling location 4 m higher than edge
  - Maximum peat depth: 650 cm



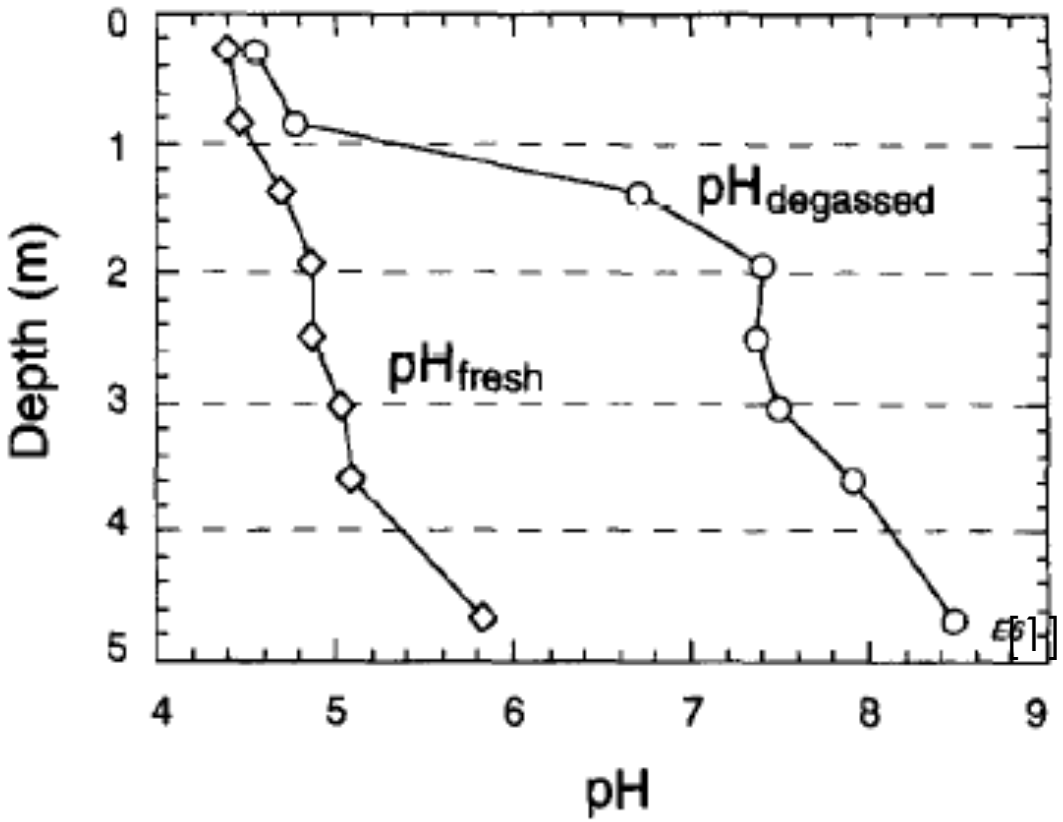
Study Background

Google earth miles 1 km 2 [3]

Study Results

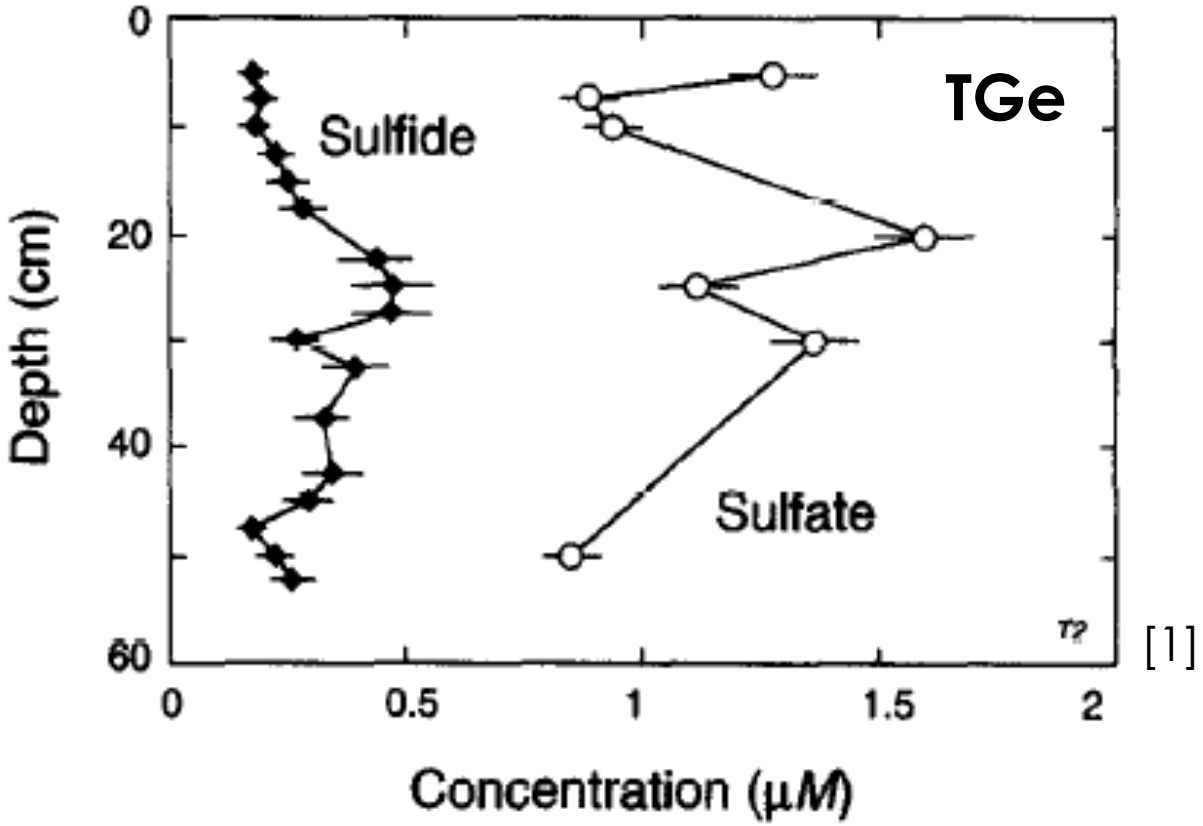
- Peepers
  - Plexiglas housing made of individual 30 mL chambers
    - Filled with deionized, deaerated water
    - Covered with 0.2 μm membrane filter
  - Inserted into bogs and left for 4-6 weeks to equilibrate
- Peeper samples were compared with water from squeezed peat slices for quality assurance

Study Results



- Results for TGe are similar
- Profiles confirm dissolved CO_2 is very important to the pH of bog waters

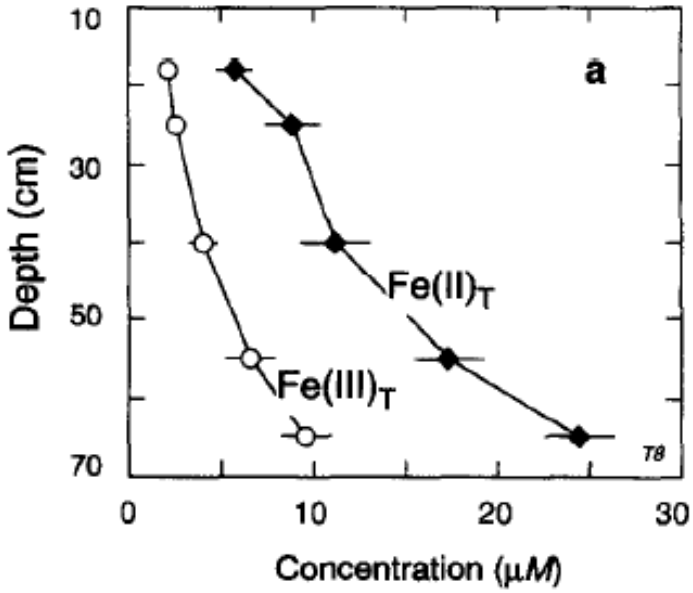
Study Results



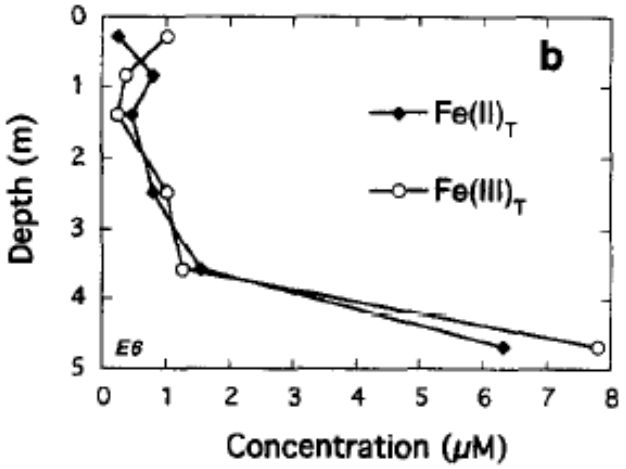
[1]

Sulfate is the dominant S species

Study Results



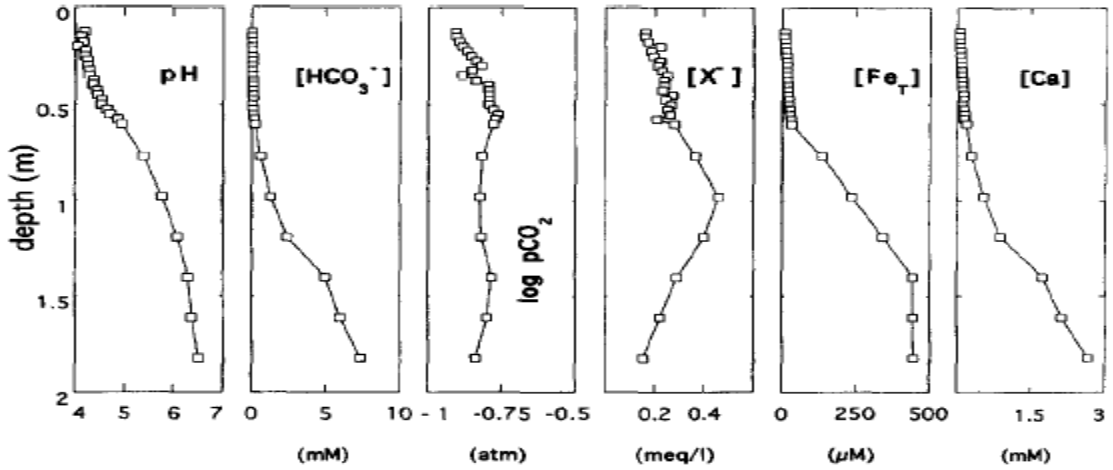
TGe



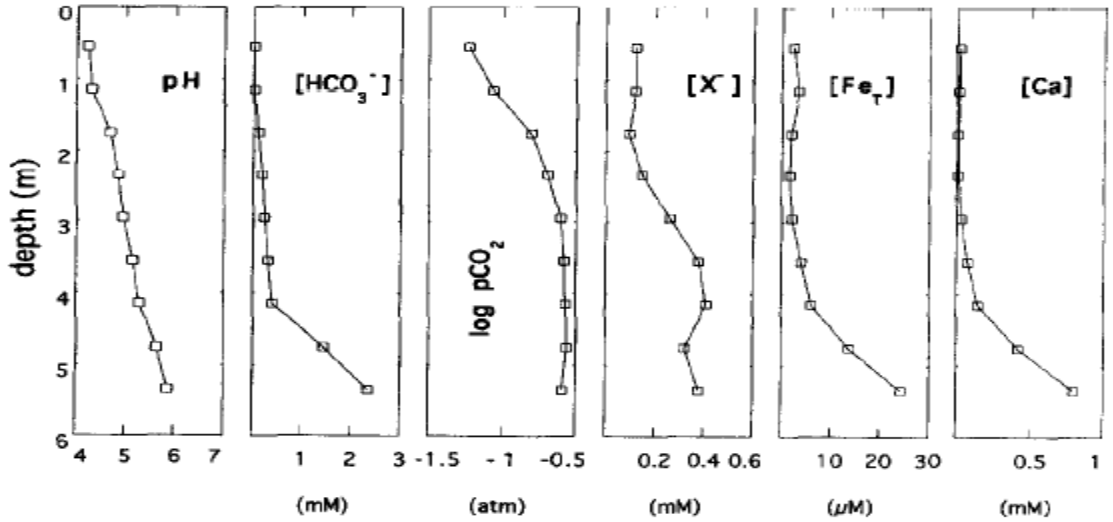
EGr

[1]

Study Results



TGe



EGr

[1]

Water Chemistry

	1	2	3	4
species	rainwater	evaporated rainwater	sink/source of H^+	porewater EGr 50 cm
	µM	**µM**	**µeq/l**	**µM**
Cl^-	8.7	12.5	0.0 [a]	12.5
SO_4^{2-}	22.4	32.1	-63.8 [b]	0.2
NO_3^-	28.5	41.0	-41.0 [c]	0.0
$H_2PO_4^-$	0.0	0.0	3.6 [d]	3.6
Ac^-	0.0	0.0	16.9 [e]	16.9
HCO_3^-	0.4	0.3	19.7 [f]	20.0
X^-	0.0	0.0	95.0 [g]	95.0
H^+	11.0	15.5	-43.4 [h]	58.9
Na^+	6.1	8.7	-10.0 [i]	18.7
NH_4^+	41.8	60.1	23.2 [j]	36.8
K^+	2.3	3.3	-0.5 [i]	3.8
Mg^{2+}	1.6	2.4	-1.0 [i]	2.9
Ca^{2+}	9.0	12.9	5.8 [l]	10.0
$Fe^{2+/3+}$	0.0	0.0	-4.5 [k]	1.8
balance	*0.0*	*0.0*	*0.0*	*0.0*

[1]

PHREEQC Model - Objectives

- (1) Determine types of minerals deposited by atmosphere in ombrogenic bog at EGr
  - Mixture of rainwater and bog water which then evaporates
- (2) Successfully run mixing and evaporation functions of PHREEQC
- (3) Evaluate model results and determine discrepancies between the model and real world conditions

PHREEQC Model – Mixing Inputs

- Minteq.v4 database

```
SOLUTION 1 Rainwater
    temp      5.5
    pH        4.75
    pe        4
    redox     pe
    units     umol/kgw
    density   1
    Cl        8.7 as Cl-
    S(6)      22.4
    N(5)      28.5
    P         0 as H2PO4-
    Acetate   0
    C         0.4 as HCO3-
    Na        6.1
    N(-3)     41.8
    K         2.3
    Mg        1.6
    Ca        9
    Fe        0
    water     1 # kg
```

```
SOLUTION 2 Porewater EGr 50cm
    temp      5.5
    pH        4.23
    pe        4
    redox     pe
    units     umol/kgw
    density   1
    Cl        12.5
    S(6)      0.2
    N(5)      0
    P         3.6 as H2PO4-
    Acetate   16.9
    C         0 as HCO3-
    Na        18.7
    N(-3)     36.8
    K         3.8
    Mg        2.9
    Ca        10
    Fe        1.8
    water     1 # kg
```

```
MIX 1
    1     0.7
    2     0.3
END
```

*Rainwater pH [4]

PHREEQC Model – Mixing Solution

```
Mixture 1.

       7.000e-001 Solution 1  Rainwater
       3.000e-001 Solution 2  Porewater EGr 50cm

-----------------------------Solution composition------------------------------

      Elements           Molality       Moles

      Acetate          5.070e-006  5.070e-006
      C                2.800e-007  2.800e-007
      Ca               9.300e-006  9.300e-006
      Cl               9.840e-006  9.840e-006
      Fe               5.400e-007  5.400e-007
      K                2.750e-006  2.750e-006
      Mg               1.990e-006  1.990e-006
      N                6.025e-005  6.025e-005
      Na               9.880e-006  9.880e-006
      P                1.080e-006  1.080e-006
      S                1.574e-005  1.574e-005

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

                                    pH  =   4.369      Charge balance
                                    pe  =  10.459      Adjusted to redox equilibrium
                       Activity of water  =   1.000
                          Ionic strength  =  1.185e-004
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  = -4.180e-005
                       Total CO2 (mol/kg)  =  2.800e-007
                      Temperature (deg C)  =   5.500
                   Electrical balance (eq)  =  4.353e-005
Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  23.78
                                Iterations  =  15
                                   Total H  = 1.110139e+002
                                   Total O  = 5.550696e+001
```

PHREEQC Model – Mixing (Step 1)

```
-----------------------------Distribution of species-----------------------------

                                                  Log         Log         Log
   Species                 Molality    Activity  Molality    Activity    Gamma

   H+                   4.326e-005  4.274e-005    -4.364      -4.369    -0.005
   OH-                  4.935e-011  4.875e-011   -10.307     -10.312    -0.005
   H2O                  5.551e+001  1.000e+000     1.744      -0.000     0.000
Acetate          5.070e-006
   H(Acetate)           3.572e-006  3.572e-006    -5.447      -5.447     0.000
   Acetate-             1.498e-006  1.480e-006    -5.825      -5.830    -0.005
C(4)             2.800e-007
   H2CO3                2.777e-007  2.777e-007    -6.556      -6.556     0.000   (Carbonic acid)
Ca               9.300e-006
   Ca+2                 9.275e-006  8.832e-006    -5.033      -5.054    -0.021   (Calcium)
Cl               9.840e-006
   Cl-                  9.840e-006  9.720e-006    -5.007      -5.012    -0.005   (Chloride)
Fe(2)            4.586e-008
   Fe+2                 4.572e-008  4.351e-008    -7.340      -7.361    -0.022   (Ferrous iron)
Fe(3)            4.941e-007
   Fe(OH)2+             4.917e-007  4.858e-007    -6.308      -6.314    -0.005   (Ferric hydroxide)
K                2.750e-006
   K+                   2.750e-006  2.716e-006    -5.561      -5.566    -0.005   (Potassium)
Mg               1.990e-006
   Mg+2                 1.986e-006  1.891e-006    -5.702      -5.723    -0.021   (Magnesium)
N(-3)            3.429e-005
   NH4+                 3.429e-005  3.387e-005    -4.465      -4.470    -0.005   (Ammonium)
N(3)             2.427e-005
   NO2-                 2.427e-005  2.397e-005    -4.615      -4.620    -0.005   (Nitrite)
N(5)             1.685e-006
   NO3-                 1.685e-006  1.665e-006    -5.773      -5.779    -0.005   (Nitrate)
Na               9.880e-006
   Na+                  9.879e-006  9.759e-006    -5.005      -5.011    -0.005   (Sodium)
P                1.080e-006
   H2PO4-               1.072e-006  1.060e-006    -5.970      -5.975    -0.005   (Dihydrogen phosphate ion)
S(-2)            0.000e+000
   H2S                  0.000e+000  0.000e+000   -90.503     -90.503     0.000   (Hydrogen sulfide)
S(6)             1.574e-005
   SO4-2                1.567e-005  1.492e-005    -4.805      -4.826    -0.021   (Sulfate)

-------------------------------Saturation indices--------------------------------

        Phase               SI log IAP  log KT
        Fe(OH)2.7Cl.3     2.88   -0.16   -3.04  Fe(OH)2.7Cl.3
        Goethite          1.42    2.65    1.23  FeOOH
        Hematite          5.14    5.30    0.16  Fe2O3
        Lepidocrocite     1.28    2.65    1.37  FeOOH
        Magnetite         0.72    6.68    5.96  Fe3O4
        O2(g)           -30.79   59.31   90.10  O2              (Anoxic water)
```

PHREEQC Model – Mixing (Step 2)

```
----------------------------Distribution of species----------------------------

                                                  Log        Log        Log
   Species                Molality    Activity  Molality   Activity     Gamma

   H+                   4.328e-005  4.276e-005    -4.364     -4.369    -0.005
   OH-                  4.933e-011  4.873e-011   -10.307    -10.312    -0.005
   H2O                  5.551e+001  1.000e+000     1.744     -0.000     0.000
Acetate          5.070e-006
   H(Acetate)           3.572e-006  3.572e-006    -5.447     -5.447     0.000
   Acetate-             1.497e-006  1.479e-006    -5.825     -5.830    -0.005
C(4)             2.800e-007
   H2CO3                2.777e-007  2.777e-007    -6.556     -6.556     0.000   (Carbonic acid)
Ca               9.300e-006
   Ca+2                 9.275e-006  8.831e-006    -5.033     -5.054    -0.021   (Calcium)
Cl               9.840e-006
   Cl-                  9.840e-006  9.720e-006    -5.007     -5.012    -0.005   (Chloride)
Fe(2)            5.400e-007
   Fe+2                 5.383e-007  5.122e-007    -6.269     -6.291    -0.022   (Ferrous iron)
Fe(3)            2.020e-012
   Fe(OH)2+             2.010e-012  1.986e-012   -11.697    -11.702    -0.005   (Ferric hydroxide)
K                2.750e-006
   K+                   2.750e-006  2.716e-006    -5.561     -5.566    -0.005   (Potassium)
Mg               1.990e-006
   Mg+2                 1.986e-006  1.891e-006    -5.702     -5.723    -0.021   (Magnesium)
N(-3)            6.025e-005
   NH4+                 6.024e-005  5.950e-005    -4.220     -4.225    -0.005   (Ammonium)
N(3)             0.000e+000
   NO2-                 0.000e+000  0.000e+000   -43.125    -43.131    -0.005   (Nitrite)
N(5)             0.000e+000
   NO3-                 0.000e+000  0.000e+000   -57.202    -57.207    -0.005   (Nitrate)
Na               9.880e-006
   Na+                  9.879e-006  9.759e-006    -5.005     -5.011    -0.005   (Sodium)
O(0)             0.000e+000
   O2                   0.000e+000  0.000e+000   -58.414    -58.414     0.000
P                1.080e-006
   H2PO4-               1.073e-006  1.060e-006    -5.969     -5.975    -0.005   (Dihydrogen phosphate ion)
S(-2)            1.481e-039
   H2S                  1.481e-039  1.481e-039   -38.829    -38.829     0.000   (Hydrogen sulfide)
S(6)             1.574e-005
   SO4-2                1.566e-005  1.492e-005    -4.805     -4.826    -0.021   (Sulfate)

-----------------------------Saturation indices-------------------------------
        Phase               SI log IAP   log KT
        Fe(OH)2.7Cl.3    -2.51   -5.55    -3.04  Fe(OH)2.7Cl.3
        Goethite         -3.97   -2.74     1.23  FeOOH
        Hematite         -5.64   -5.48     0.16  Fe2O3
        Lepidocrocite    -4.11   -2.74     1.37  FeOOH
        Magnetite        -8.99   -3.03     5.96  Fe3O4
        O2(g)           -56.62   33.48    90.10  O2              (Anoxic)
```

PHREEQC Model – Evaporation

```
SOLUTION 3 Mix 1
    temp      5.5
    pH        4.369
    pe        4
    redox     pe
    units     umol/kgw
    density   1
    Acetate   5.07
    C         0.28
    Ca        9.3
    Cl        9.84
    Fe        0.54
    K         2.75
    Mg        1.99
    N         60.25
    Na        9.88
    P         1.08
    S         15.74
    -water    1 # kg
```

```
REACTION 1
        H2O    -1.0
```

PHREEQC Model – Evaporation

```
----------------------------Distribution of species----------------------------

                                                  Log         Log         Log
   Species                Molality    Activity  Molality    Activity     Gamma

   H+                  1.989e-004  1.957e-004    -3.701      -3.708    -0.007
   OH-                 9.702e-012  9.543e-012   -11.013     -11.020    -0.007
   H2O                 5.551e+001  8.963e-001     1.744      -0.048     0.000
Acetate          6.184e-006
   H(Acetate)          5.663e-006  5.663e-006    -5.247      -5.247     0.000
   Acetate-            5.208e-007  5.123e-007    -6.283      -6.290    -0.007
C(4)             3.415e-007
   H2CO3               3.409e-007  3.409e-007    -6.467      -6.467     0.000   (Carbonic acid)
Ca               1.134e-005
   Ca+2                1.131e-005  1.059e-005    -4.947      -4.975    -0.029   (Calcium)
Cl               1.200e-005
   Cl-                 1.200e-005  1.181e-005    -4.921      -4.928    -0.007   (Chloride)
Fe(2)            1.490e-015
   Fe+2                1.485e-015  1.388e-015   -14.828     -14.858    -0.029   (Ferrous Iron)
Fe(3)            6.587e-007
   Fe(OH)2+            6.399e-007  6.295e-007    -6.194      -6.201    -0.007   (Ferric hydroxide)
K                3.354e-006
   K+                  3.354e-006  3.299e-006    -5.474      -5.482    -0.007   (Potassium)
Mg               2.427e-006
   Mg+2                2.421e-006  2.267e-006    -5.616      -5.645    -0.029   (Magnesium)
N(-3)            0.000e+000
   NH4+                0.000e+000  0.000e+000   -68.277     -68.284    -0.007   (Ammonium)
N(3)             2.204e-020
   NO2-                2.204e-020  2.168e-020   -19.657     -19.664    -0.007   (Nitrite)
N(5)             7.349e-005
   NO3-                7.349e-005  7.229e-005    -4.134      -4.141    -0.007   (Nitrate)
Na               1.205e-005
   Na+                 1.205e-005  1.185e-005    -4.919      -4.926    -0.007   (Sodium)
O(0)             1.220e+001
   O2                  6.099e+000  6.099e+000     0.785       0.785     0.000
P                1.317e-006
   H2PO4-              1.283e-006  1.262e-006    -5.892      -5.899    -0.007   (Dihydrogen phosphate ion)
S(-2)            0.000e+000
   H2S                 0.000e+000  0.000e+000  -155.831    -155.831     0.000   (Hydrogen sulfide)
   HS-                 0.000e+000  0.000e+000  -159.405    -159.413    -0.007
S(6)             1.920e-005
   SO4-2               1.897e-005  1.776e-005    -4.722      -4.750    -0.029   (Sulfate)

-------------------------------Saturation indices-------------------------------
        Phase               SI log IAP  log KT
        Fe(OH)2.7Cl.3     2.52   -0.52   -3.04  Fe(OH)2.7Cl.3
        Goethite          0.87    2.10    1.23  FeOOH
        Hematite          4.09    4.25    0.16  Fe2O3
        Lepidocrocite     0.73    2.10    1.37  FeOOH
        Magnetite        -9.20   -3.24    5.96  Fe3O4
        O2(g)             2.58   92.68   90.10  O2              (Aerobic)
```

Discussion

- Supersaturated minerals are mainly composed of Fe
- N, P, and S present would be taken up by plants very quickly
- There are significant changes in the amount of $Fe^{2+/3+}$ and $N^{-3/+3/+5}$ present
- Minimal changes in amount of $S^{-2/+6}$ present

- Errors
  - Possibly caused by not being familiar with PHREEQC
  - Uncertainty of mixing fractions
  - N, S, P uptake by plants is not accounted for

References

[1] Steinmann, P., & Shotyk, W. (1997). Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two Sphagnum peat bogs, Jura Mountains, Switzerland. *Geochimica et Cosmochimica Acta, 61*(6), 1143-1163.

[2] http://wikitravel.org/en/Switzerland

[3]Google Earth

[4] Burch, H., Waldner, P., & Fritschi, B. (1996). Variation of pH and concentration of nutrients and minerals during rain-events. Strasbourg.