Definitions

Types of Soil Organic Matter

Detritus : un-modified residues from dead plants & animals

Humus : Microbial Modified Residues

Types of soil Bacteria

Aerobes: require oxygen for respiration

True Anaerobes: don't function in the presence of oxygen, but can function in the absence of it

Facultative Anaerobes: when oxygen isn't available, they can use alternate electron acceptors for respiration

Heterotrophic: require pre-formed organic matter as a source of carbon for growth & Energy source

Photo-autotrophic: get their energy from sunlight

Chemo-autotrophic: get their energy from the oxidation of inorganic compounds, & not organic compounds

Types of Wetlands

Bog: a peat-accumulating wetland with no significant inflows or outflows, & supports acidophilic mosses (esp. sphagnum)

Bottomland: lowlands along streams & rivers, usually on forested alluvial floodplains (aka. Bottomland hardwood forests)

Marsh: a frequently or continually inundated wetland with emergent herbaceous vegetation adapted to flooding

Peatland: a generic term for any wetland with accumulated partially decayed plant matter

Pothole: shallow marsh-like ponds, thought to be left behind by retreating glaciers (often found in the Dakotas)

Riparian Ecosystem: have high water tables because they're close to water bodies, usually a stream or rivers (aka. Bottomland hardwood forests, bosques, riparian buffers, & streamside vegetation strips)

Slough: a swamp or shallow lake system (in the NE & mid-west U.S.); or a slowly flowing shallow swamp or marsh (SE U.S.)

Swamp: a wetland dominated by trees & shrubs (U.S.), or reed grass areas dominated by wetlands; a forested fen (Europe)

Thermally Stratified Layers

Epilimnion: top-most layer of water in a thermally-stratified lake (above thermocline), warmer, higher pH, D.O. present

Hypolimnion: bottom layer of water in a thermally-stratified lake (below thermocline), colder, dense, lower pH, no D.O.

2 Master Biological Reactions

Photosynthesis: uses energy from the sun to convert CO_2 & H_2O into carbohydrates (ie. organic matter) → plants store this light energy as chemical energy → organisms can release this energy during respiration

Respiration: biological release of energy by oxidation of this carbohydrate back into its original constituent components, it is actually a 2-part reaction: (1) oxidation of glucose, (2) the reduction of oxygen

Glucose ($C_6H_{12}O_6$): a carbohydrate (ie. simple sugar, or organic matter) that is produced by plants during photosynthesis, often used as a model organic compound for comparing energy yields in respiration reactions

Photosynthesis

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

Respiration

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

Glucose Oxidation: $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$

+

Oxygen Reduction: $6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$

$= C_6H_{12}O_6 + 6H_2O + 6O_2 + 24H^+ + 24e^- \rightarrow 6CO_2 + 12H_2O + 24H^+ + 24e^-$

$= C_6H_{12}O_6 + \cancel{6H_2O} + 6O_2 + \cancel{24H^+} + \cancel{24e^-} \rightarrow 6CO_2 + \cancel{12}H_2O + \cancel{24H^+} + \cancel{24e^-}$

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

Definitions

Having to do with Oxidation & Reduction Processes

Oxidation : describes the **loss** of **electrons** (H^+) or gain of oxygen (OH^-)

Oxidized compounds : insoluble, non-mobile, , names usually end in "**-ic**"

Oxidizing conditions : drained, oxygenated (Dissolved Oxygen present), Aerobic,

Reduction : describes the **gain** of **electrons** (H^+) or loss of oxygen (OH^-)

Reduced compounds : soluble, mobile, dissolvable, threats to water quality, names usually end in "**-ous**"

Reducing conditions : flooded, anoxic (No dissolved oxygen present), Anaerobic,

Redox : shorthand for **Reduction-Oxidation Reaction**

Diffusion : the movement of a substance in response to a chemical activity (concentration) gradient

Concentration Gradient (**$\Delta C/\Delta X$**): (change in **concentration**)/(**distance** over which diffusion is occurring)

Reductant : a substance that **reacts with oxygen** (either chemically or through microbial processes)

ex: **Ferrous** (**Fe^{2+}**) → **Ferric** (**Fe^{3+}**), **Manganous** (**Mn^{2+}**) → **Manganic** (**Mn^{4+}**), **Hydrogen Sulfide**(**H_2S**) → **Sulfate** (**SO_4^{2-}**), & **Ammonium** (**NH_4**) → **Nitrate** (**NO_3^-**)

Non-mobile Reductant : solid-state reductants, these are insoluble & thus can't diffuse in water & are immobile
(ex. precipitated forms of Ferrous Fe, Manganous Mn, Sulfide, etc.)

Mobile Reductant : dissolved reductants that can diffuse in water due to their concentration gradient
(ex. soluble forms of Ferrous Fe, Manganous Mn, Sulfide, etc.)

Electrical Conductivity (**EC**): a solution's ability or capacity to transfer an electric current (which is held by the ions)
→ EC ↑as the amount of dissolved ions ↑ (ie. system becomes more reducing)

Free Energy : Total Energy derived from the microbial oxidation of one mole of glucose

Measuring Redox Potentials

Electrochemical Cell : an electrode system that must contain 2 half cells in order to be complete

Half Cell : either the **working electrode** or the **reference electrode**

Junction Potential : the voltage contributed to a reference electrode half cell at the point of contact between the solution in the electrode & the solution (or soil) outside the electrode; this should ideally = 0

Poise : has to do with the ability of a solution to resist changes in measured redox potentials
the **higher the poise** of a system the **more quickly the redox potential** readings **will stabilize** on a value, whereas, the **less poised** a system (ie. **oxidizing** soils) cause **drift** in the redox readings

Redox Potential (Eh) : a measure of electron availability or potential (voltage)

Nernst Equation : used to estimate the redox potential

Physical, Chemical, & Biological Properties of Soil & Sediments

- Soils consist of 3 things: 1) **Solid Matter** (Mineral or Organic Material) 2) **Water** 3) **Pore space**
  - predominantly mineral (Upland) soils & sediments ~1/2 their volume is pore space
  - predominantly organic (wetland) soils & sediments >1/2 of their volume is pore space

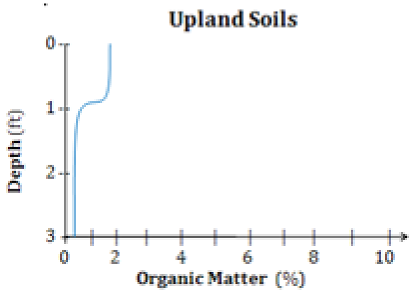
- Soil & Sediment **Density** as a **Function** of the **Pore Space** of Mineral vs. Organic Material:
  - The **density of water** is near **1.0 gm/cm^3** (varies a bit depending on temperature)
  - The **mineral** particles of soils (this <u>excludes pore space</u>) tend to have a density of **~2.6 gm/cm^3**
  - The **organic** matter tends to have a density somewhat near **1 gm/cm^3** if you compressed all of the pore space out of soil organic matter, which does not happen in natural systems
  - Typical upland, **predominantly mineral** soils will have a bulk density of **1.4** (near optimum) to 1.8 (somewhat compacted) when you consider the entire soil volume (solids plus pore space) where the pore space is filled with air
  - The density of **mainly organic wetland** soils & **peats** is usually **~ 0.2 to 0.3 gm/cm^3 or less**.

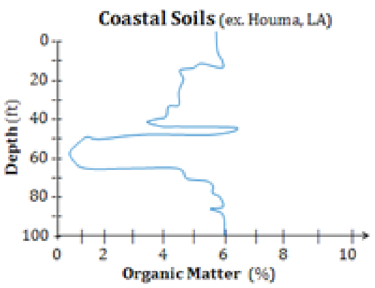
- **Total Organic Matter** in Soils & Sediments consists of: 1) Detritus 2) Humus 3) living organisms

- **Fulvic** Acid: **soluble** mixture of organic matter that has been modified by microorganisms, turns water **brown to yellow**

- **Humic** Acid: Makes up a large % of the total soil organic matter, serves as an energy source for microbes, **insoluble** & gives soils their **dark color** (ex. **lignin** = form of Humic Acid that's very resistant to degradation)

- The Amount of **Organic Matter** in **Upland** vs. **Wetland** Soils & Sediments





- Factors that affect the **Amount of Soil Organic Matter** : 1) **Production** 2) **Loss**
  - Amount of plant biomass produced (warmer climates tend to favor maximum plant biomass production).
  - temperature (warmer temperatures also favor more microbial decomposition of organic matter).
  - Much of the world's <u>total soil organic</u> matter is in **colder regions** where you may have **good plant growth during short growing seasons**, & then **long periods of cold weather** when d**egradation is much slower**.
  - In the **tropics**, vegetation **production can be very high**, but in the <u>upland soils</u>, high temperatures favoring **High microbial decomposition** → low organic matter
  - oxygen limitations for microbial respiration because of very wet or flooded conditions

- Factors that **affect microbial numbers**, activity, etc:

  1) optimum temperature
  2) moisture content
  3) pH
  4) the energy source available
  5) whether oxygen is present or not
  6) nutrients present
  7) are there toxic substances present
  8) other factors

- **Histols**: one of the 10 Soil Orders, (Order = highest classification level), very high organic matter, low bulk density(< 0.25), constantly saturated with water, most wetlands are Histols

“Wetlands”

Definitions:

Major legal definition**:** The term "**wetlands**" means those areas that are **inundated** or **saturated by surface or ground water** at a **frequency** & **duration** sufficient to **support**, & that under normal circumstances do support, a **prevalence of vegetation** typically adapted for life in saturated [water saturated] soil conditions. Wetlands generally include **swamps**, **marshes**, **bogs**, etc

Broad Scientific definition: “A wetland is a **biologically active soil** or **sediment** in which the **content of water** in or on the sediment is **great enough** to **inhibit diffusion of oxygen** into the soil or sediment & **stimulate anaerobic** (oxygen-free) **microbial processes**. Also, a larger part of the earth's surface consists of these 2 water-dominated systems than exists as upland land areas”

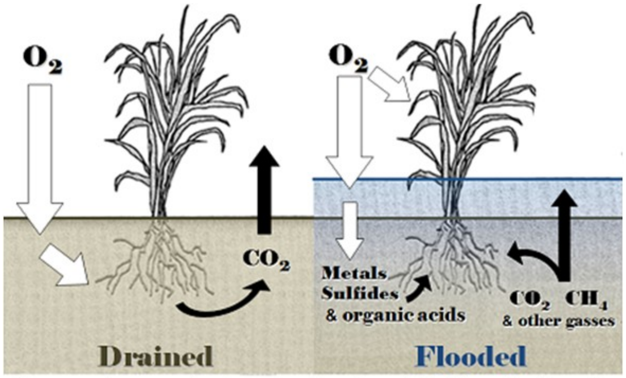
Note: this definition doesn’t necessarily contain any reference to plants, but, a **biologically active** soil or sediment is necessary, which means the presence of an **energy source**, **organic matter** is the most common energy source & organic matter comes from 1) plants, 2) **waste droppings of aquatic organisms**, or 3) settling of dead algae, bacteria, & aquatic animals in lakes & oceans

* **lack of availabile oxygen** & of **oxygen-free microbial processes** is a key characteristic of wetland soils

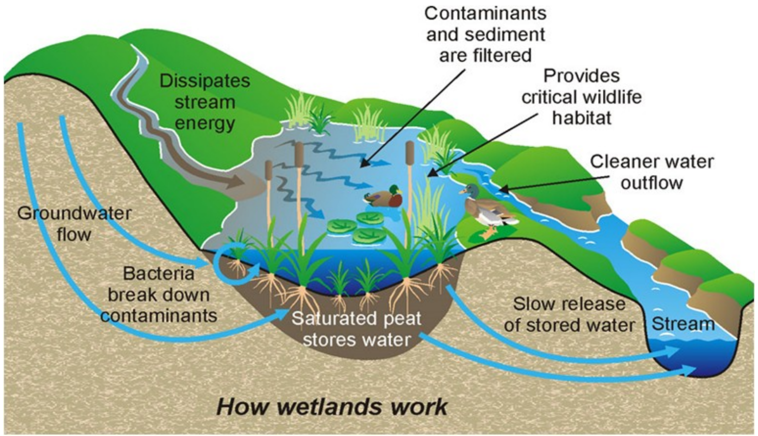
Narrow Scientific Definition: (& the most commonly accepted one) limits wetlands to areas in which there are **emergent plants**. This type of wetland usually is **much higher in organic matter** than the wetland without emergent plants. The reason for this is the high production of plant biomass & the restricted decomposition because of the limitation of oxygen in the wet soil where decomposition takes place

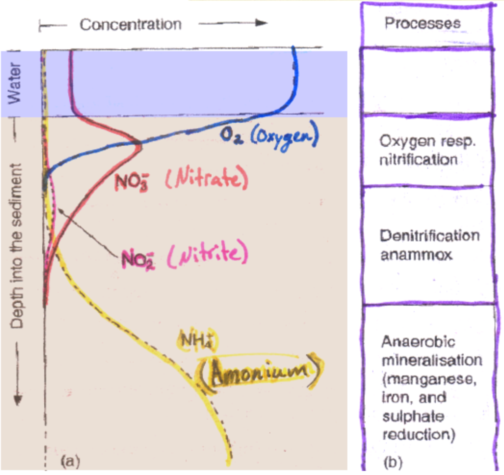
In summary, three important considerations for **identifying wetlands i**nclude:

1) **Soil types** & **properties**
2) **plant species present**
3) **hydrology** (flooding frequency & duration)

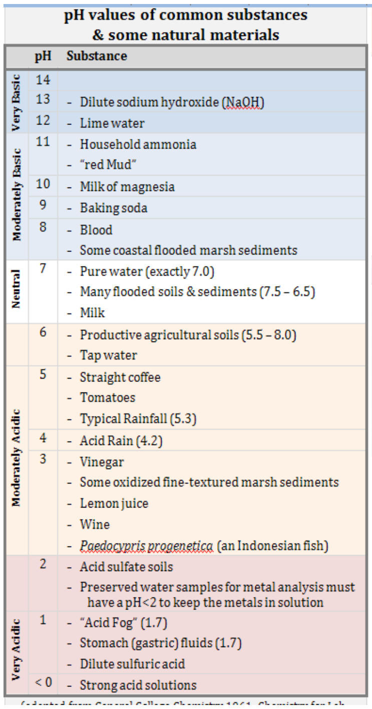


Gas exchange between Drained & Flooded soils
(Adapted from, Reddy & DeLaune 2008, Fig. 6.1, pg. 186)





pH



pH values of common substances & some natural materials

	pH	Substance
Very Basic	14	
	13	- Dilute sodium hydroxide (NaOH)
	12	- Lime water
Moderately Basic	11	- Household ammonia - "red Mud"
	10	- Milk of magnesia
	9	- Baking soda
	8	- Blood - Some coastal flooded marsh sediments
Neutral	7	- Pure water (exactly 7.0) - Many flooded soils & sediments (7.5 – 6.5) - Milk
	6	- Productive agricultural soils (5.5 – 8.0) - Tap water
Moderately Acidic	5	- Straight coffee - Tomatoes - Typical Rainfall (5.3)
	4	- Acid Rain (4.2)
	3	- Vinegar - Some oxidized fine-textured marsh sediments - Lemon juice - Wine - *Paedocypris progenetica* (an Indonesian fish)
	2	- Acid sulfate soils - Preserved water samples for metal analysis must have a pH<2 to keep the metals in solution
Very Acidic	1	- "Acid Fog" (1.7) - Stomach (gastric) fluids (1.7) - Dilute sulfuric acid
	< 0	- Strong acid solutions

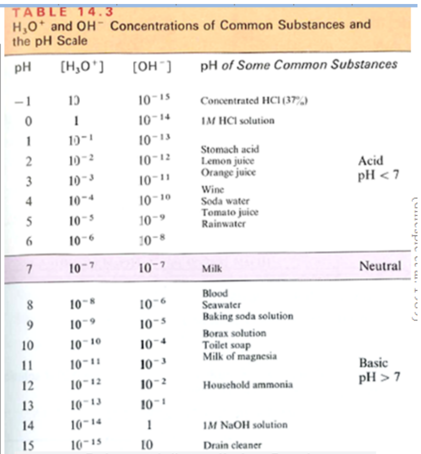


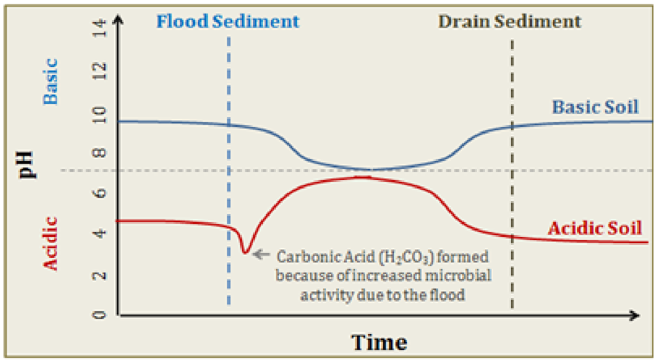
TABLE 14.3
H_3O^+ and OH^- Concentrations of Common Substances and the pH Scale

pH	$[H_3O^+]$	$[OH^-]$	pH *of Some Common Substances*	
−1	10	10^{-15}	Concentrated HCl (37%)	
0	1	10^{-14}	1*M* HCl solution	
1	10^{-1}	10^{-13}		
2	10^{-2}	10^{-12}	Stomach acid Lemon juice	Acid pH < 7
3	10^{-3}	10^{-11}	Orange juice	
4	10^{-4}	10^{-10}	Wine Soda water	
5	10^{-5}	10^{-9}	Tomato juice Rainwater	
6	10^{-6}	10^{-8}		
7	10^{-7}	10^{-7}	Milk	Neutral
8	10^{-8}	10^{-6}	Blood Seawater	
9	10^{-9}	10^{-5}	Baking soda solution	
10	10^{-10}	10^{-4}	Borax solution Toilet soap	
11	10^{-11}	10^{-3}	Milk of magnesia	Basic pH > 7
12	10^{-12}	10^{-2}	Household ammonia	
13	10^{-13}	10^{-1}		
14	10^{-14}	1	1*M* NaOH solution	
15	10^{-15}	10	Drain cleaner	

Environmental effects	pH value	Examples
	pH = 0	Battery acid
	pH = 1	Sulfuric acid
	pH = 2	Lemon juice, vinegar
	pH = 3	Orange juice, soda
All fish die (4.2 and below)	pH = 4	Acid rain (4.2–4.2) Acidic lake (4.5)
Salmon eggs (5.5 and below)	pH = 5	Bananas (5.0–5.3) Clean rain (5.6)
	pH = 6	Healthy lake (6.5) Milk (6.5–6.8)
	pH = 7	Pure water
Calcifying marine organisms begin to dissolve (8.0 and below)	pH = 8	Healthy ocean (8.2)
	pH = 9	Baking soda
	pH = 10	Milk of magnesia
	pH = 11	Ammonia
	pH = 12	Soapy water

(Chamberlin & Dickey 2008)

➢ pH changes in Flooded vs. Drained Soils & Sediments



An initial decrease in pH of both acid & alkaline soils may be due to a burst of microbial activity & the production of CO_2, as a result of microbial respiration (equation shown previously for reason for the pH of standing pure water or rain water being less than 7.0 due to carbonic acid formation)

Acid Buffering reaction:

$CO_2 + H_2O \leftrightarrow H_2CO_3$ (carbonic acid)

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

- **pH change in Acid Soils as a result of Flooding**
  - An important reaction affecting pH in acid soils is the oxidation & reduction of iron:

$$\underset{\text{Oxidized iron}}{3Fe(OH)_3 + 3H^+ + e^-} \leftrightarrow \underset{\text{Reduced iron}}{3Fe(OH)_2 + 3H_2O}$$

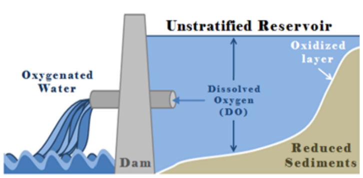
  - Thus upon flooding & soil reduction, H^+ is consumed, increasing pH.
  - Oxidation is the opposite of this, so, if a sediment containing reduced ferrous iron is oxidized, the reaction goes to the left which increases acidity, decreasing pH.
  - If iron oxidation & reduction is the primary processes affecting pH as a soil or sediment material goes from reduced to oxidized, the pH changes are only moderate

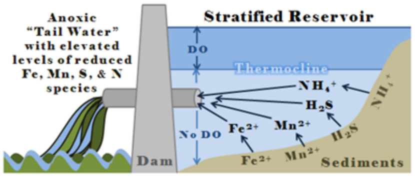
➢ Extreme Acidity (low pH)

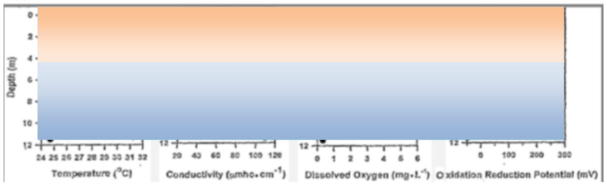
Mine waters of negative pH in this situation are the result of 4 processes:

1) Acid generation by pyrite oxidation
2) Concentration of H+ & other ions by evaporation
3) Consumption of H+ during the oxidation of Fe2+ to Fe3+ (they are reporting this for a pH of < 2 whereas, we have discussed a different reaction with opposite results in wetlands with less extreme pH levels).
4) acid production or consumption during efflorescent mineral formation

Oxidation & Reduction Processes







Depth		Zone	Redox	Oxidized Forms	Reduced Forms	Bacteria	Energy Available	Reduction Strength	Redox Potential Eh (available electrons)	Conductivity (# ions in solution)	Temp.	pH
	1	**Oxygen** (O_2)	**Oxygen** reduced to **Water** ($O_2 + e^- \rightarrow H_2O$)	O_2	H_2O	Aerobes	More	Oxidizing	800 mv (more e^-)	**Less** conductive (fewer ions)	**Warmer**	More **Basic**
	2	**Nitrate** (NO_3^-)	**Nitrate** reduced to **Nitrogen Gas** or **Nitrous Oxide** ($NO^{3-} + e^- \rightarrow N_2$)	NO^{3-}, NO^{2-}, N_2O	NH_4, N_2O, N_2	Facultative Anaerobes		Weakly Reducing	300 mv			
	3	**Manganic** Mn (Mn^{4+})	**Manganic** Mn reduced to **Manganous** Mn ($MnO_2 + e^- \rightarrow Mn^{2+}$)	MnO_2 (Mn^{4+})	Mn^{2+}				200 mv			
	4	**Ferric** Fe (Fe^{3+})	**Ferric Iron** compounds reduced to **Ferrous Fe** ($Fe_2O_3 + e^- \rightarrow Fe^{2+}$)	Fe_2O_3 or $Fe(OH)_3$ (Fe^{3+})	Fe^{2+}			Moderately Reducing	100 mv			
	5	**Sulfate** (SO_4^{2-})	**Sulfate** reduced to **Sulfide** ($SO_4^{2-} + e^- \rightarrow S^{2-}$)	SO_4^{2-}	S^{2-}, HS^-, H_2S	Anaerobes		Strongly Reducing	0 -100 mv			
	6	**Carbon Dioxide** (CO_2)	**Carbon dioxide** reduced to **Methane** ($CO_2 + e^- \rightarrow CH_4$)	CO_2, CO_3^{2-}, HCO_3	CH_4		Less		-200 mv (less e^-)	**More** conductive (More ions)	**Colder**	more **Acidic**

For **all** of the proposed layers associated with the various alternate electron acceptors to exist in a profile, at least 2 conditions must be met:

1) **reducing conditions must be intense enough to produce methane at some depth in the profile**

2) **there must be enough O_2 coming from the atmosphere to penetrate the surface of the saturated sediment**

These conditions will insure that the most oxidized layer (oxygen consumption) & the most reduced layer (carbon dioxide reduction to methane) will occur in the same profile, &, this is likely usually the case

Terminal electron Acceptor Reduction ½ Reactions

$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$

$SO_4^{2-} + 8H^+ + 8e^- \rightarrow S^{2-} + 4H_2O$

Iron & Manganese Redox Chemistry

Oxidation

$Mn^{2+} + O_2 \rightarrow MnO_2$ $Fe^{2+} + O_2 \rightarrow Fe_2O_3$

Mn^{2+} is being **oxidized** to Mn^{4+} & Fe^{2+} is being **oxidized** to Fe^{3+}

Reduction

$MnO_2 + 2e^- + 4H^+ \rightarrow Mn^{2+} + 2H_20$ $FeOOH + e^- + 3H^+ \rightarrow Fe^{2+} + 2H_20$

Mn^{4+} is being **reduced** to Mn^{2+} & Fe^{3+} is being **reduced** to Fe^{2+}

Oxidized Forms: **Ferric** Iron (**Fe^{3+}**) & **Manganic** Manganese (**Mn^{4+}**)

Reduced Forms: **Ferrous** Iron (**Fe^{2+}**) & **Manganous** Manganese (**Mn^{2+}**)

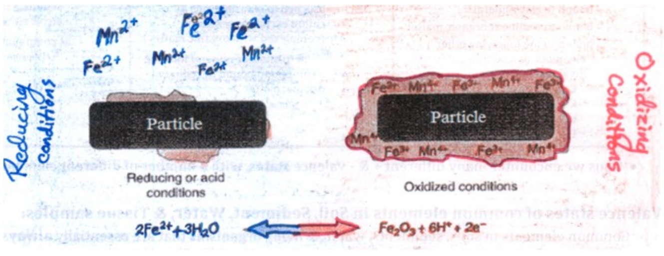
Oxidation: $Fe^{2+} - e^- \rightarrow Fe^{3+} + e^-$ = **Ferrous Iron** (reduced Fe) **losses 1 e-** → **more positively charged Ferric Iron**

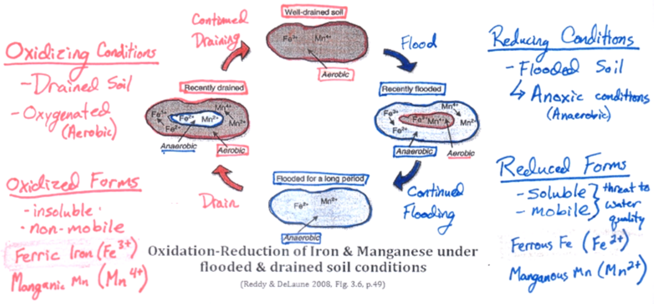
Reduction: $Fe^{3+} + e^- \rightarrow Fe^{2+} - e^-$ = **Ferric Iron** (oxidized Fe) → **gains 1 e-** to become the **reduced Ferrous** Iron

Iron is more abundant at strongly reducing & Low pH conditions, &almost completely precipitates out in strongly oxidizing conditions

Manganese is also more prevalent at low pHs, but its more consistent across the redox conditions

Remember the wetland soil will likely have mostly reduced iron & reduced forms of sulfur present, & oxidation will cause H^+ (acid) to form as reduced iron & sulfur compounds oxidize.





Oxidation-Reduction of Iron & Manganese under flooded & drained soil conditions

(Reddy & DeLaune 2008, Fig. 3.6, p.49)

Reduction Sequence

Depth		Zone	Redox	Oxidized Forms	Reduced Forms	Bacteria	Energy Available	Reduction Strength	Redox Potential Eh (available electrons)	Conductivity (# ions in solution)	Temp.	pH
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	3	**Manganic** Mn (Mn^{4+})	**Manganic** Mn reduced to **Manganous** Mn ($MnO_2 + e^- \rightarrow Mn^{2+}$)	MnO_2 (Mn^{4+})	Mn^{2+}				200 mv			
	4	**Ferric** Fe (Fe^{3+})	**Ferric Iron** compounds reduced to **Ferrous Fe** ($Fe_2O_3 + e^- \rightarrow Fe^{2+}$)	Fe_2O_3 or $Fe(OH)_3$ (Fe^{3+})	Fe^{2+}			Moderately Reducing	100 mv			
	5	**Sulfate** (SO_4^{2-})	**Sulfate** reduced to **Sulfide** ($SO_4^{2-} + e^- \rightarrow S^{2-}$)	SO_4^{2-}	S^{2-}, HS^-, H_2S	Anaerobes		Strongly Reducing	0 -100 mv			
	6	**Carbon Dioxide** (CO_2)	**Carbon dioxide** reduced to **Methane** ($CO_2 + e^- \rightarrow CH_4$)	CO_2, CO_3^{2-}, HCO_3	CH_4		Less		-200 mv (less e^-)	**More** conductive (More ions)	**Colder**	more **Acidic**