# *Wetland Hydrogeochemisry*


EARTH 444

*BIOLOGY 462*

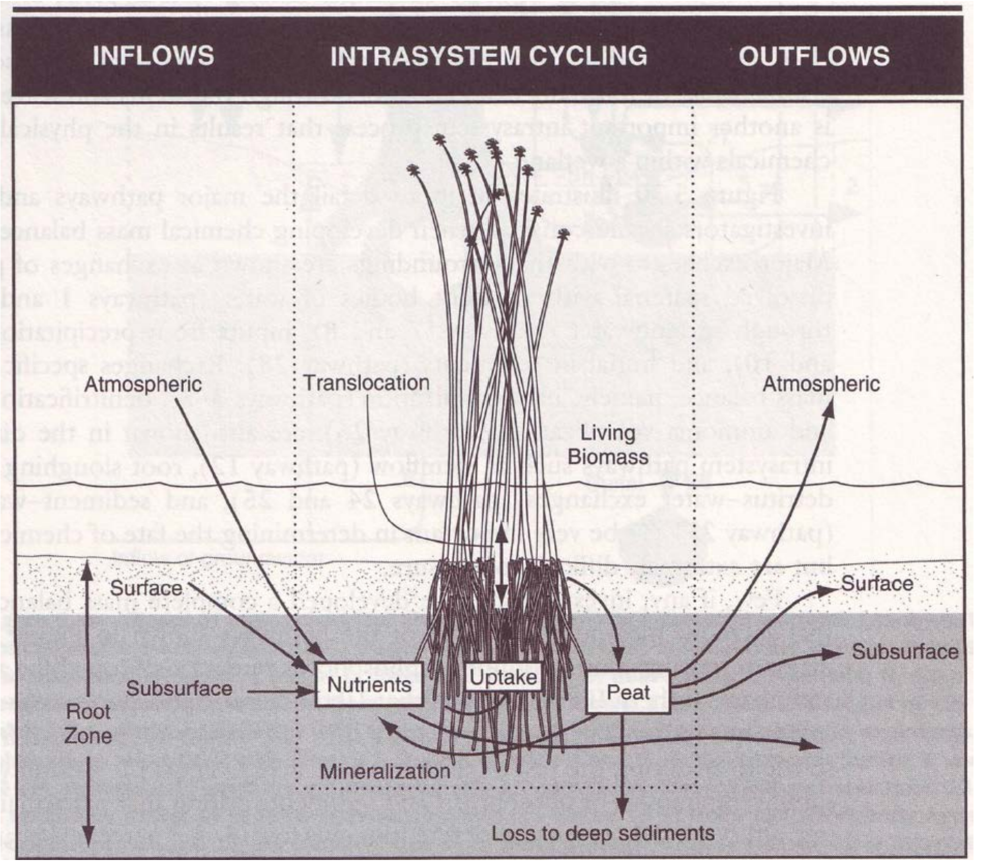
*B.G. Warner*

# Geochemistry

- anaerobic or oxygenless conditions prevail; biochemical transformations unique to reduced conditions
- transport and transformation of chemicals in wetland ecosystems: solid, dissolved and gaseous states
- involves internal cycling through various transformations; **closed systems**
- involves external exchange of chemicals between wetlands and surroundings; **open systems**

# Biogeochemical Cycling

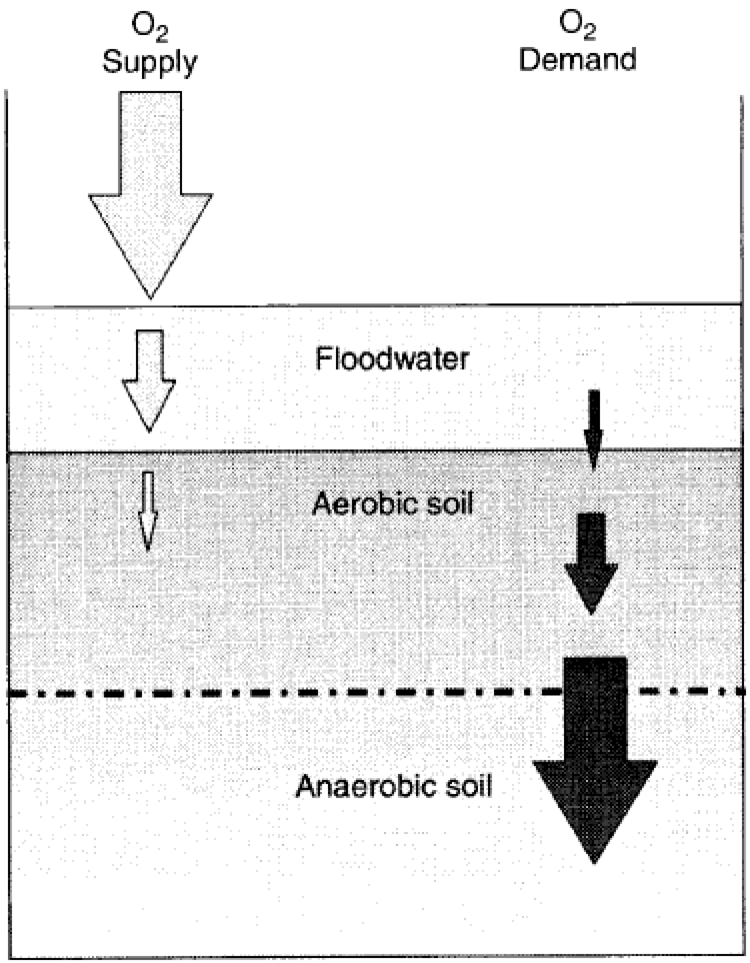
- Quantifying chemical inputs & outputs & internal cycling of materials = ecosystem mass balance
- If P, N, or C = nutrient budget
- **Inputs & outputs** by hydrologic pathways; long-term burial is output
- **Intrasystem cycling**: chemicals inside; biomass production, translocation
- Mass balances good to define ecosystem function and wetlands as sources, sinks and transformers

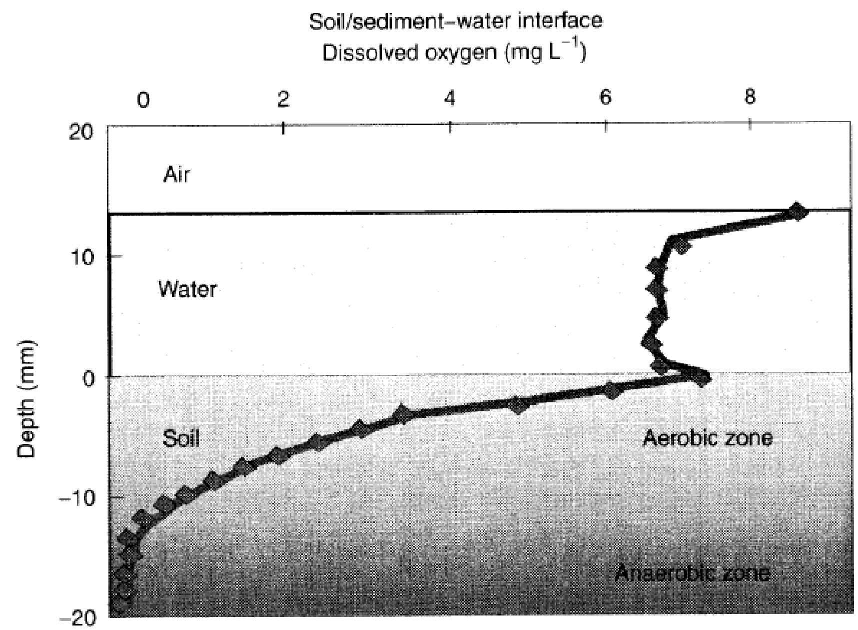



General Mass Balance

(From Mitsch & Gosselink 2007)

# Oxygen




Aerobic-anaerobic interfaces

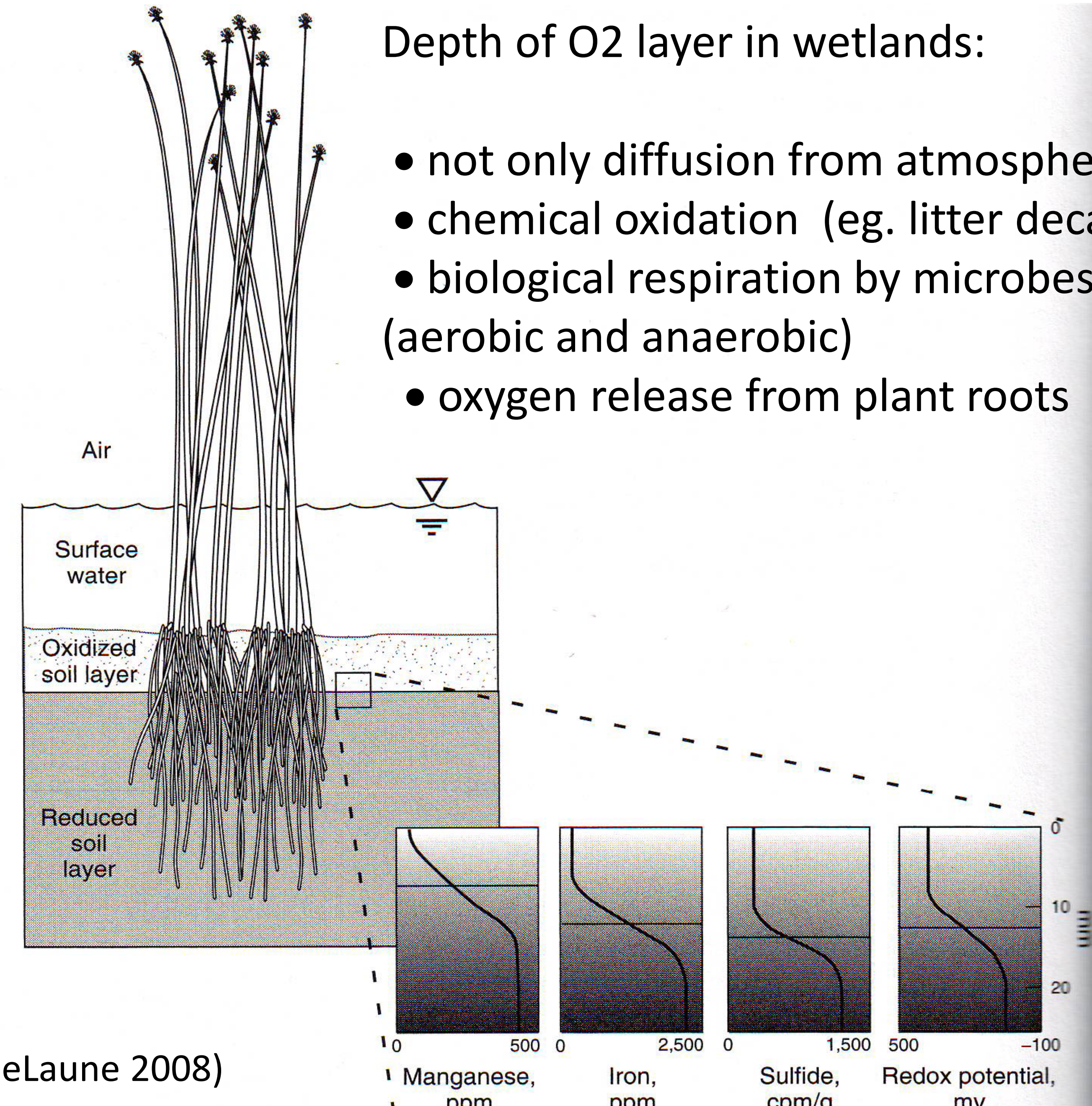
(From Reddy & DeLaune 2008)

# Oxygen: A 2-layered “cake”

- Wetlands are not always lacking in oxygen
- Oxygen content depends on:
  - the rate of oxygen transport across the atmosphere-surface water interface
  - a small population of oxygen-consuming organisms
  - photosynthetic oxygen production by algae within the water column
  - surface mixing by convection currents and wind

Depth of O2 layer in wetlands:

- not only diffusion from atmosphere…
- chemical oxidation  (eg. litter decay)
- biological respiration by microbes (aerobic and anaerobic)
- oxygen release from plant roots




(From Reddy & DeLaune 2008)

# Important geochemical characteristics of saturated soils

- pH
- ionic strength
- reduction-oxidation potential (Eh or redox potential)
- Horizontal and vertical gradients

# 1. pH

- Mostly towards neutral (6.5-7.0)
- Mineral soils - alkaline conditions (as high as pH 9)
- Higher pHs in day due to photosynthesis and warming by loss of dissolved $CO_2$
- Organic soils - acidic conditions (as low as pH 4)
- pH varies between pools, interstitial water and intercellular water; pH can be affected
- Buffered by reduction reactions;  i.e. Fe  in acidic and Mn in alkaline conditions

# 2. Ionic Strength (conductivity)

- Flooding $\rightarrow$ increase in ions in solution
- Measured as conductivity ($\mu$S/cm); be careful of using conductivity meters for total dissolved solids and salinity
- Pure water=0.06, distilled water=0.5, tap water=500-800, sea water 56,000 $\mu$S/cm
- acid conditions, mostly by reduction of insoluble Fe, and possible Mn
- neutral to slightly alkaline soils, mostly by $Ca^{2+}$, and $Mg^{2+}$

# Two broad categories of wetlands

- Saline wetlands – high conductivities
  - Oceans: mostly sodium and chloride
  - Saltwater lakes: more potassium, calcium
- Freshwater wetlands – lower conductivities

# Classifications based on Geochemistry - SALINE

- inland salt water
- sea water
- salt spray
- estuarine

In vegetation ecology and ecological land classification, more specific terms are used. This is an example from British Columbia.

**Fresh:** <0.5 parts per thousand (ppt) salts

**Oligosaline:** Weakly brackish; 0.5–5 ppt salts

**Mesosaline:** Moderately brackish; 5–18 ppt salts

**Polysaline:** Strongly brackish 18–30 ppt salts

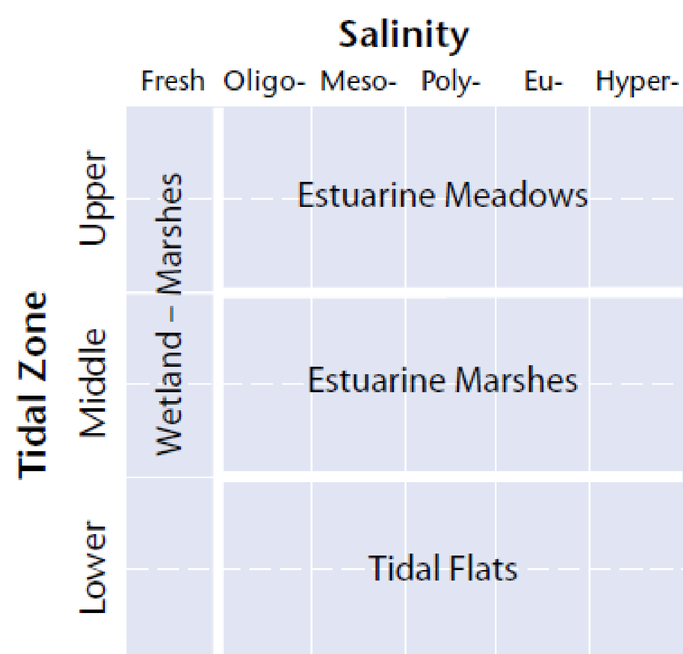



FIGURE 5.0.4 *Distribution of Site Classes relative to intertidal zone and salinity.*

**Eusaline:** Normal seawater; 30–40 ppt salts

**Hypersaline:** >40 ppt salts

Elevation above chart datum is a corollary for duration of flooding but is dependent on the magnitude of tides in a particular area. The definitions below are from Howes et al. (1999).

The **Upper Intertidal** describes the upper third of the elevation range between the highest high tide and zero tide for a particular area

# Classifications based on Geochemistry - FRESHWATER

- minerotrophic wetlands: water high in dissolved minerals, high pH, neutral and alkaline; usually only freshwater wetlands, not marine and estuarine
    - Rich calcareous fen:  7.1-7.7
    - Rich fen: 5.8-7.5
    - Poor fen: 4.0-5.5

(from: Mullen et al. 2000, Can. J. Bot. 78:718-727)

# Classifications based on Geochemistry - FRESHWATER

- oligotrophic wetlands: water low in dissolved minerals, low pH
- ombrotrophic wetlands: extreme oligotrophy; peatlands with sole source of water from precipitation, very low pH
  - Bog: 3.6-4.5

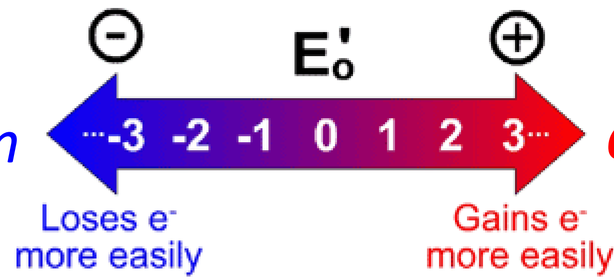
# 3. Reduction-oxidation potential (Redox potential)

- =oxidation-reduction potential: measure of a tendancy of a soil to oxidize or reduce substances
- Oxidation = uptake of oxygen and loosing of hydrogen
- Reduction = giving up of oxygen and gaining hydrogen
- a higher (more positive) redox (reduction) potential will have a tendency to lose electrons (i.e. to be reduced by oxidizing the new species): oxidation (+Eh)
- a lower (more negative) redox (reduction) potential will have a tendency to gain electrons (i.e. to be oxidized by reducing the new species): reduction (-Eh)

# How to measure redox potential?

- <u>Measure of strength of wanting to gain H electrons, or wanting to be reduced</u>
- Measured as $E_h$

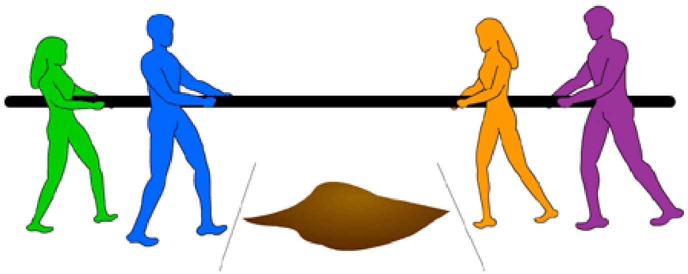
*no oxygen*




*oxygen*

- The oxidation-reduction "tug of war"

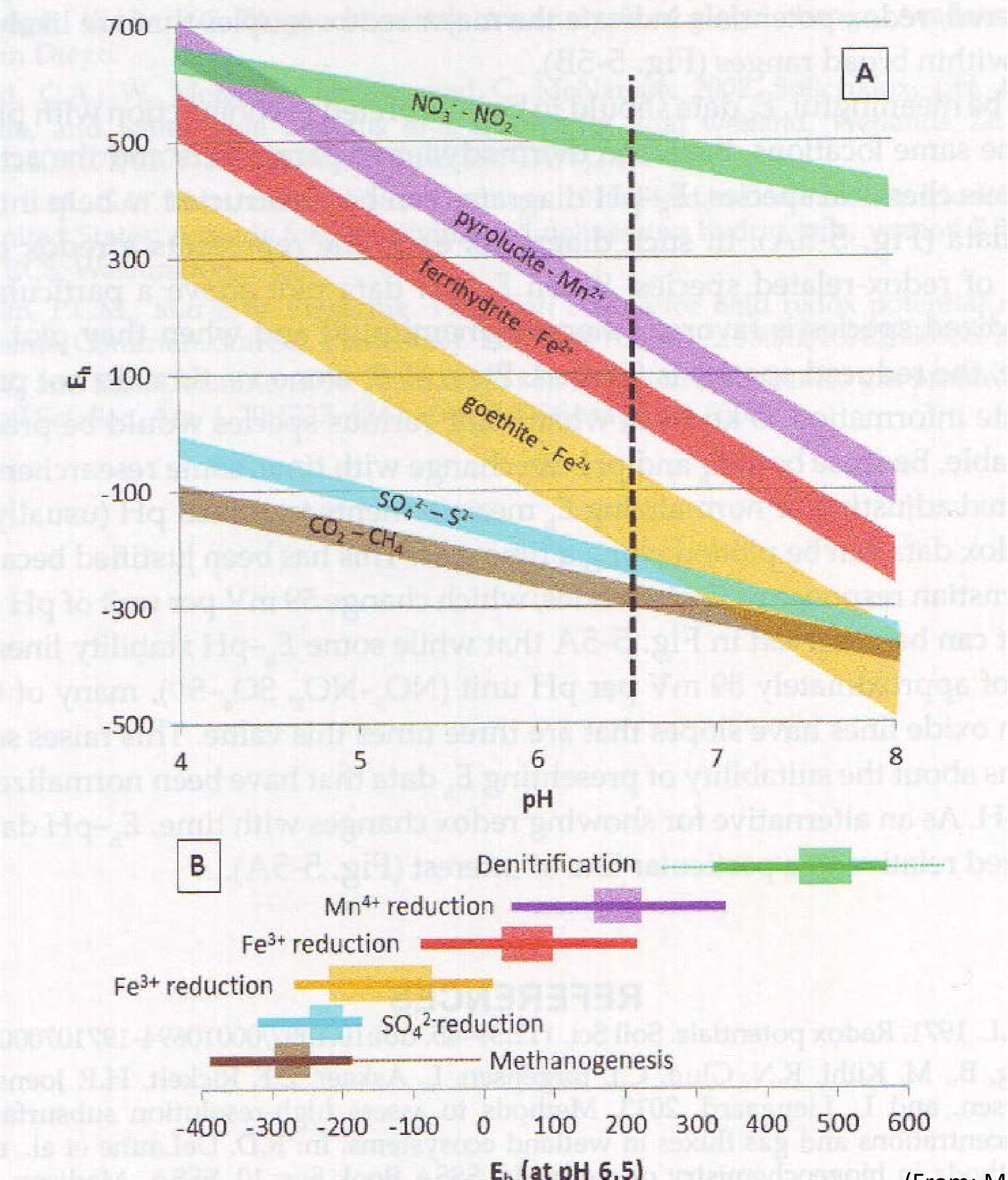
(Figs. taken from www.wiley.com)



- Wants to oxidize too; can be interpreted from Eh
- Higher or more + Eh values = more oxygen, lower or more – Eh values = less oxygen present

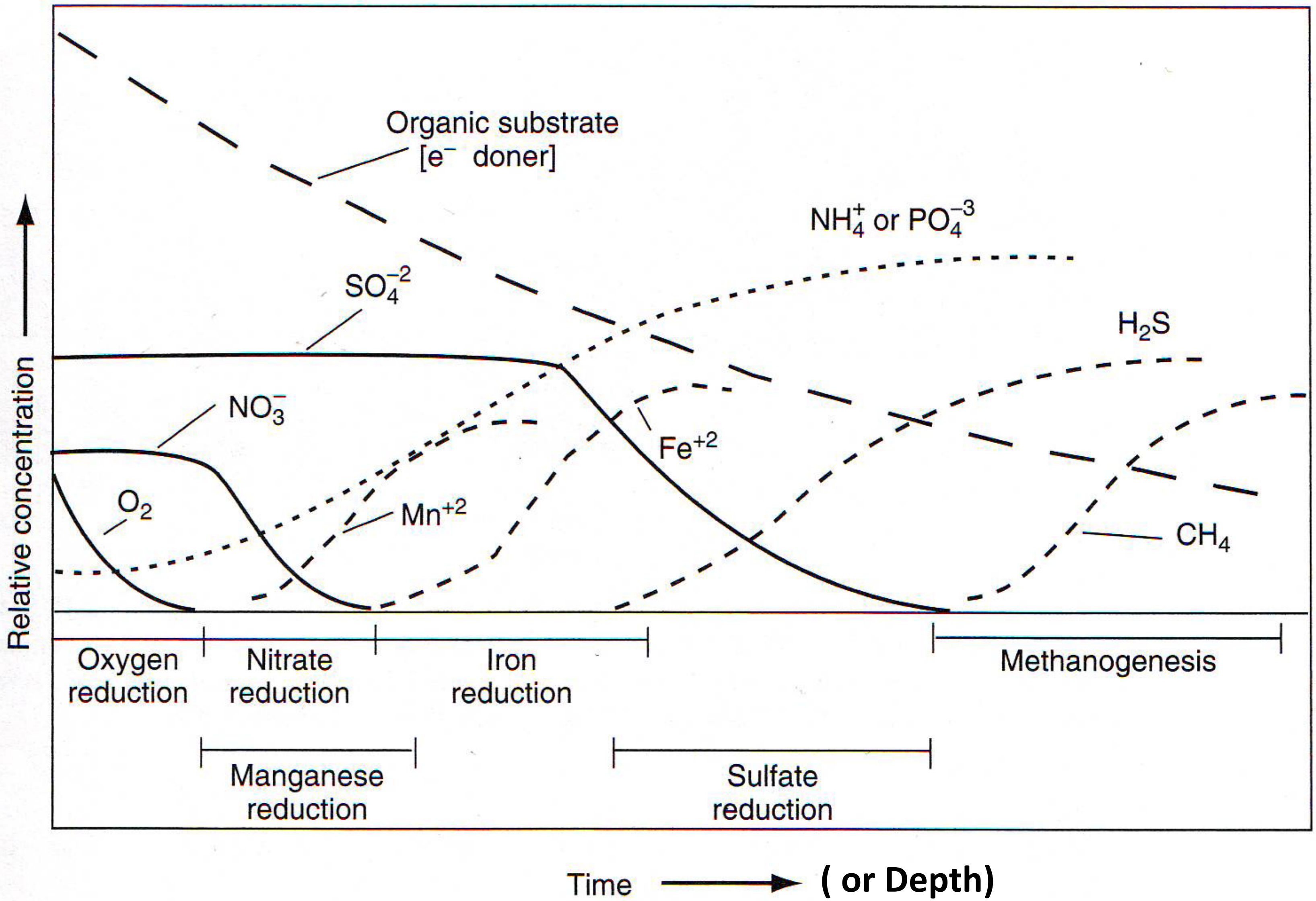
# Time sequence for reduction of inorganic substances

- Follows a time sequence: thermodynamic sequence for reduction
- After flooding, oxygen decline begins immediately; O depletion may take a few hours or a few days




(From: Megonigal & Rabenhorst 2013)

Sequence in time of transformations in wetland soil after flooding beginning with oxygen depletion, then nitrate and then sulfate reduction. Then..get increases in reduced manganese, reduced iron, hydrogen sulfide and methane. (taken from Mitch and Gosselink 2007).




**( or Depth)**

# 1. Disappearance of $O_2$

$$O_2 + 4H^+ + 4e \Leftrightarrow 2\ H_2O$$

oxygen + hydrogen $\Leftrightarrow$ water

REDOX POTENTIAL = 0.8 Eh

# 2. Disappearance of nitrate = DENITRIFICATION

$$NO_3^- + 2H^+ \; 2e \Leftrightarrow NO_2^- + H_2O$$

nitrate + hydrogen $\Leftrightarrow$ nitrogen (ammonia, nitrite)

REDOX POTENTIAL = 0.42 Eh

# 3. Formation of Manganous

$$MnO_2 + 4H^+ = 2e \Leftrightarrow Mn^{2+} + 2H_2O$$

manganic + hydrogen $\Leftrightarrow$ manganous

REDOX POTENTIAL = 0.39 Eh

# 4. Iron Reduction

$$Fe(OH)_3 + 3H^+ + e^- \Leftrightarrow Fe^{2+} + 3H_2O$$

ferric iron + hydrogen $\Leftrightarrow$ ferrous iron

REDOX POTENTIAL = -0.18 Eh

# 5. Formation of hydrogen sulfide
# SULFATE REDUCTION

$$SO_4^{2-} = 10H^+ + 8e^- \Leftrightarrow H_2S + 4H_2O$$

sulfate + hydrogen $\Leftrightarrow$ hydrogen sulfide

REDOX POTENTIAL = -0.22 Eh

# 6. Formation of Methane METHANOGENISIS

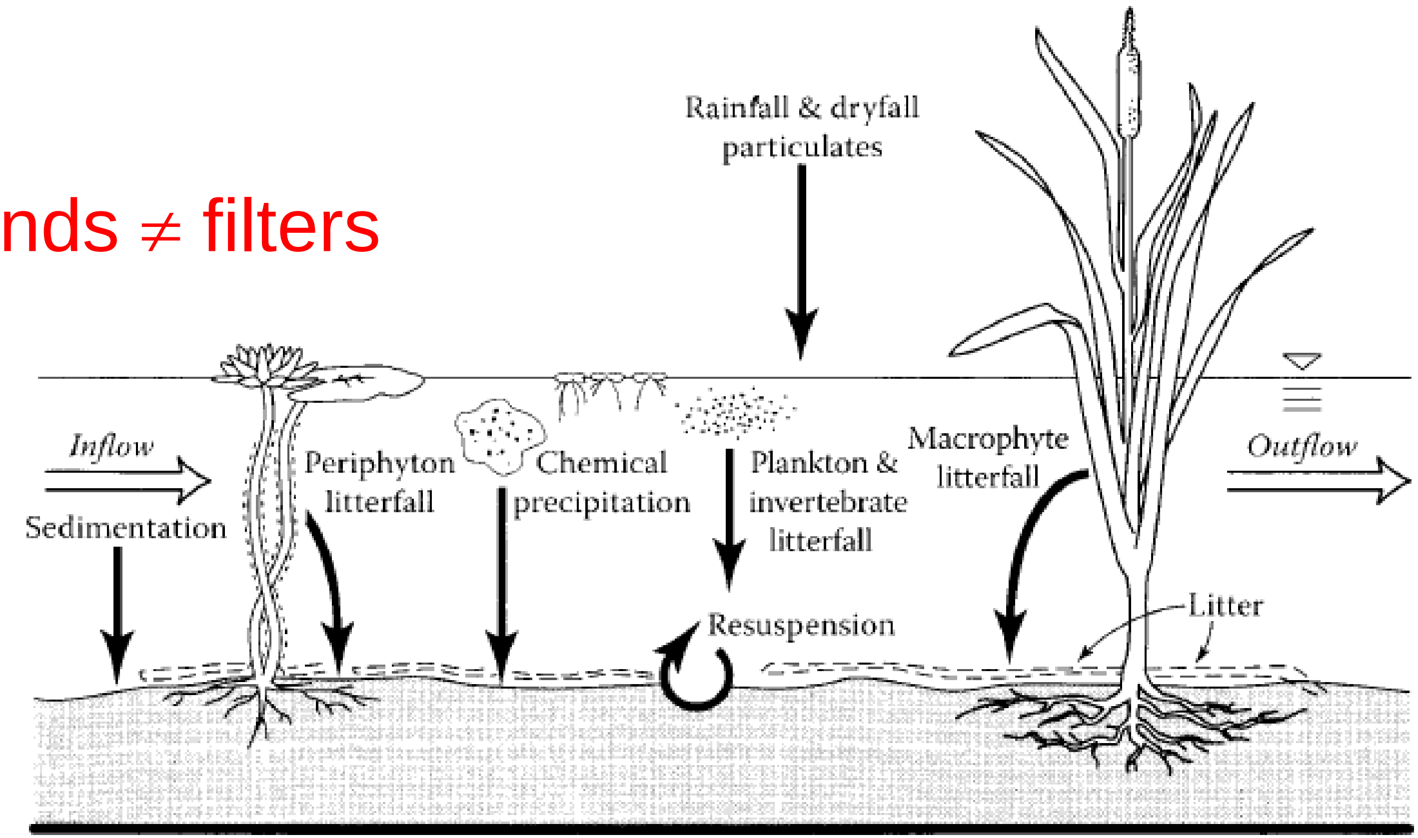
$$CO_2 + 8H^+ + 8e^- \Leftrightarrow CH_4 + 2H_2O$$

carbon dioxide + hydrogen $\Leftrightarrow$ methane

REDOX POTENTIAL = -0.24 Eh

# 4. Other parameters: Suspended solids

wetlands ≠ filters




Source is from sediment input and from vegetation within wetland

(Taken from Kadlec & Wallace 2008)

# 4. Other parameters: Total suspended solids (TSS)

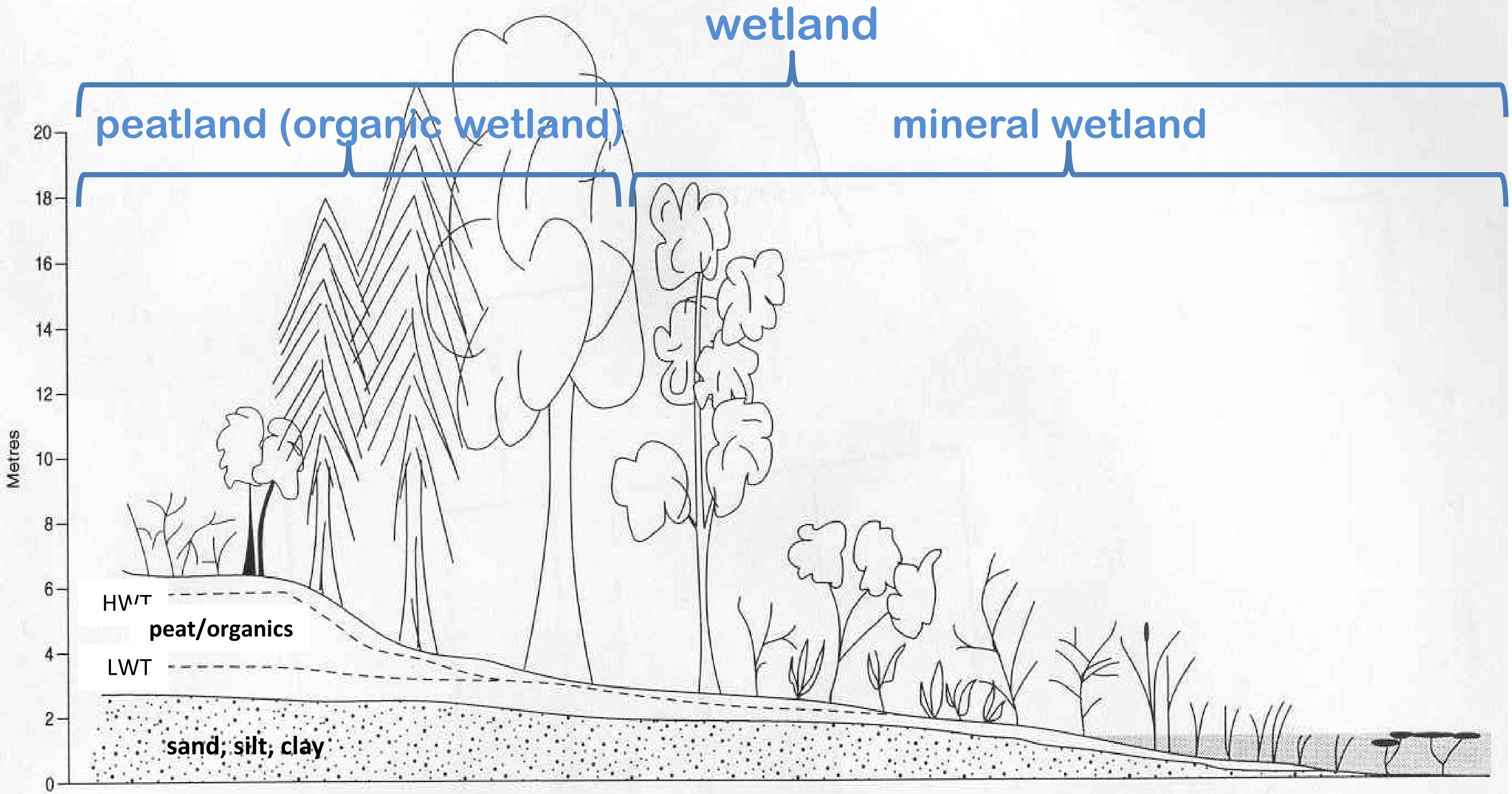
- Easy to measure: collect known water volume, filter, dry filter and weigh
- Less easy to collect in field because of shallow water column; do not measure in peatlands
- Less easy to interpret because can be both organic and inorganic; fragmentation of detritus and litter, algal cells, and bioturbation by benthic invertebrates

# Solids measurements

- TSS (mg/L) are measured after filtration and drying; volatile suspended solids (VSS) as % wt loss on ignition
- Problem because different aliquot size used; wide variation at low TSS concentrations; biased low compared to TSS
- suspended sediment concentration (SSC) is better as per Standard Methods

# 4. Other paramaters: Turbidity


- Turbidity = suspended matter and coloured organics measured with turbidometer
- Turbidometer measures light scattering = nephelometer + light source + photodetector
- Difficult to interpret data from wetlands
- Different method for peatlands (decomposition of peat=humification)

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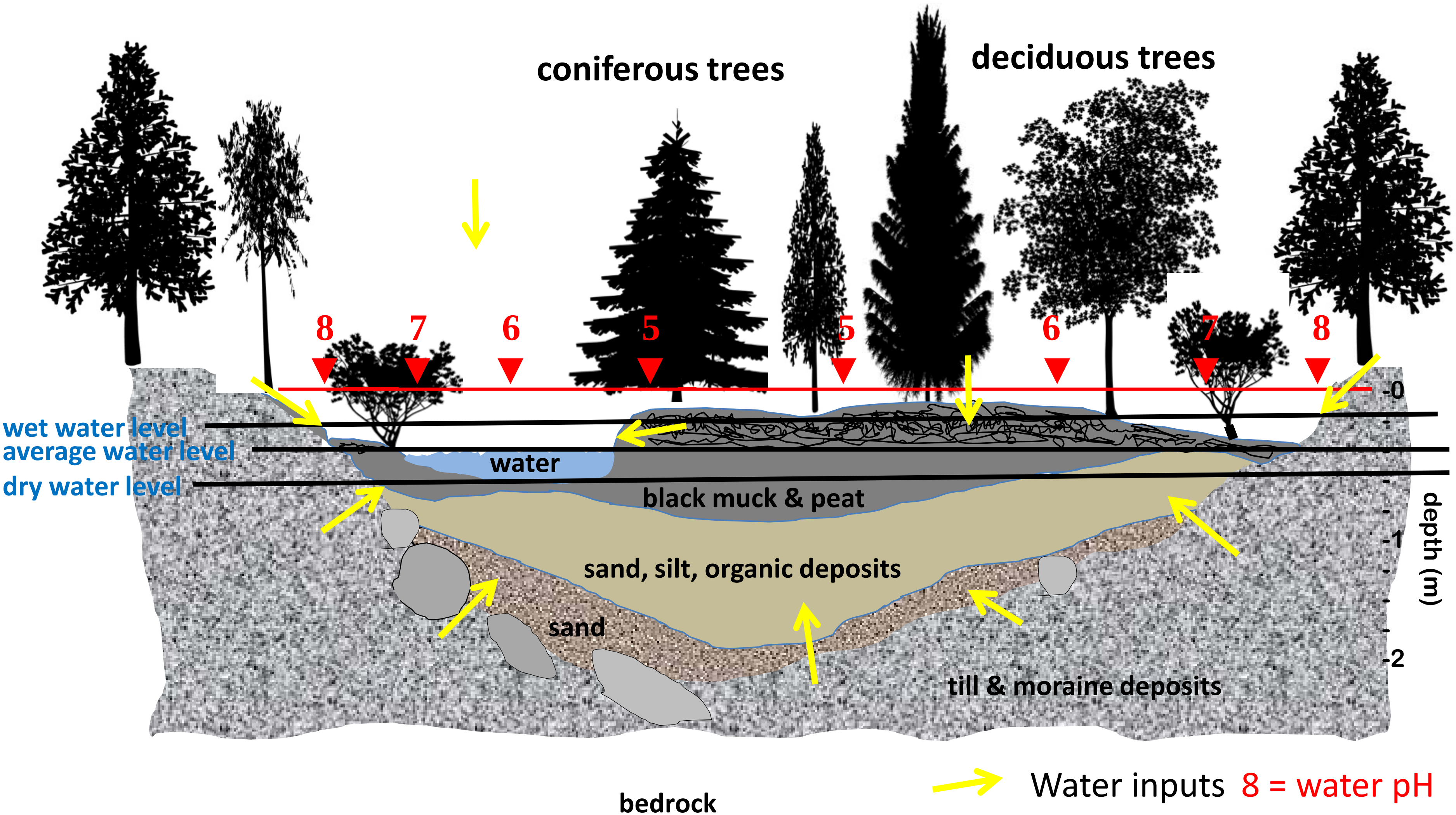
|---|---|---|---|---|---|
| **Wetland Class** | BOG | Treed SWAMP Shrub | | MARSH | OPEN WATER |
| **Water pH** | 4.8 5.0 | 6.0 | 7.0 | 7.5 | 8.0 9.0 |
| **Vegetation & Soil Water** | Ombrotrophic<br>Oligrotrophic | Minerotrophic | | | |

no dissolved minerals ⟷ high dissolved minerals




# Typical Swamp in S. Ontario