WETLAND SOILS

1) Soil environment generally
2) Wetland soils and their characteristics
3) Redox
4) Nitrogen transformation
5) Mn, Fe, SO4 transformation
6) CH4 production
7) Phosphorus

Soil consists of:
- mineral particles of various sizes, shapes, and chemical characteristics,
- plant roots,
- living soil microbial and fungal population,
- organic matter component in different stages of decomposition,
- gases, soil water, and dissolved minerals

Soil formation is traditionally described as a function of soil forming factors:
- parent material
- climate
- relief
- biota
- time

Soil sequences:
- litho
- clima
- topo
- bio
- chrono

SOIL DEVELOPMENT:
- Additions (precipitation, dust, organic materials)
- Transformations (decomposition, changes in primary minerals)
- Transport (both up – capillary rise, and down – leaching)
- Losses
Ecosystem differences in additions, transformations, transfers and losses result in distinct soils and soil profiles.

- **O** – organic material accumulated above mineral soil
- **A** – zone of most active plant and microbial processes
- **B** – zone of maximum accumulation of aluminum and iron oxides and clays
- **C** – significant proportion of unweathered parent material

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**Hydric (hydromorphic) soils** - soils flooded long enough to develop anaerobic conditions

(Book: Field Indicators of hydric soils in the US (USDA 1998))

1. **MINERAL (GLEYS)**
   - <12-20% org. C or < 20-35% OM
   - **A**luvial (deposited by streams) materials
   - soil profile well or poorly developed
   - characterized by a pale grey or olive-grey (low chroma) gleyed horizon, due to the conversion of Fe3+ to Fe2+, mottles
   - redoximorphic feature
   - drained soils show hydromorphic conditions centuries after draining
   - newly created wetlands no hydromorphic features (2 years to form)
   - no glaying or mottling where no iron

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**GLEYED HORIZON**

**MOTTLES**

**SOIL PITS**

**SEDIMENT CORES**
1) **MINERAL (GLEYS)** - cont.
calicitic muds and marls - short hydroperiod, oxidation of detritus, no peat accumulation - when flooded, dense algal production, CaCO3 precipitation
with silt - calcitic mud
with clay (sand) - marl
(K = 0.02m/d poorly conductive)

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**ORGANIC (HISTOSOLS, PEAT SOILS)**
contain more than 12-20% of organic C or 20-35% OM

**Bulk density** (dry W/unit of volume)
- mineral 1-2 g/cm3
- organic soils: high x mineral soils: low

**Water holding capacity**
- OS high x MS low

**Hydraulic conductivity**
- OS depends x MS high except for clay

**Cation exchange capacity**
- the sum of exchangeable cations that a soil can hold
- Mineral soils - CEC dominated by Ca, Mg, K, Na,
- Organic soils - high exchangeable hydrogen

Litter (detritus) layer not part of a soil horizon

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**Important characteristics of organic soils**
1) botanical composition of peat
   (mosses – peat moss, herbaceous material, wood and leaf litter; mangroves)
2) state of decomposition:
   - Fibric
   - Hemic
   - Sapric
**Production of organic material (OM) and its preservation**
- Important for hydric soil processes
- OM accumulates when photosynthetic production > decomposition (mineralization)
- Energy bound in OM has to be released in order to be available to other organisms
- How do organisms obtain energy?
  - *Photoautotrophs* -- from sun radiation
  - *Heterotrophs* -- from organic materials
  - *Chemoautotrophs* -- by oxidation of inorganic sources

<table>
<thead>
<tr>
<th>Peat:</th>
<th>Porosity (%)</th>
<th>K (m/d)</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FIBRIST</strong> (peat)</td>
<td>&gt;90</td>
<td>&gt;10</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td><strong>HEMIST</strong> (mucky p.)</td>
<td>84-90</td>
<td>0.01-1.3</td>
<td>0.09-0.2</td>
</tr>
<tr>
<td><strong>SAPRIST</strong> (muck)</td>
<td>&lt;84</td>
<td>&lt;0.01</td>
<td>&gt;0.2</td>
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</tbody>
</table>

Energy is released in respiration -- a chain of oxidation-reduction reactions during which electrons are moved along electron transport chains to oxygen as a final electron acceptor.

Everyone needs this energy: microorganisms, fungi, roots of plants

Most organisms obtain their energy in *aerobic* environments.

The reason for oxygen to be the final electron acceptor is that it most strongly attracts electrons.

What happens when soil is flooded?
The rate of diffusion of O₂ through the water-filled pores is about **10,000x slower**

<table>
<thead>
<tr>
<th></th>
<th>O₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drained</td>
<td>20%</td>
<td>0.1-1%</td>
</tr>
<tr>
<td>Flooded</td>
<td>~0%</td>
<td>up to 10%</td>
</tr>
</tbody>
</table>
O2 removed - no final electron acceptor available for oxidation reactions that provide energy
NO₃⁻, Fe³⁺, Mn⁴⁺, SO₄²⁻ and CO₂ can act as electron acceptors in anaerobic microbial processes such as denitrification, sulfate reduction, methanogenesis.
The secondary electron acceptors are yielding less energy and can also be toxic to organisms.

**Concept of redox potential:**

All these transformations in wetland soils include transfer of electrons and are called oxidation reduction reactions or **REDOX**

- **e donors (reducing agents)**
- **e acceptors (oxidizing agents)**

In a redox reaction, the e transfer changes original oxidizing agent into a reducing agent (and vice versa)

**The major e donor in flooded soils is OM**

Processes in soil driven by presence of OM and various types of bacteria.

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**Redox potential** - measure of e availability

Absolute values of redox potentials are unknown. Only the difference from a standard or reference state is measurable.

Redox measured using a system of Pt electrode - inert, does not react with anything in the soil but electrically conductive, and calomel reference electrode - has a constant potential independent on soil conditions (244 mV)
**IDEALIZED (!!) sequence of reductions**

<table>
<thead>
<tr>
<th>Eh, mV</th>
<th>O₂</th>
<th>NO₃</th>
<th>Mn</th>
<th>Fe</th>
<th>SO₄</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Few e</td>
<td>+400</td>
<td></td>
<td></td>
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<tr>
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<td>-200</td>
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<td>-150</td>
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<tr>
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<td>-150</td>
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<tr>
<td></td>
<td>-250</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Many e</td>
<td></td>
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</table>

**pH**

Following flooding, pH of soils changes as well, stabilizes around 6.7-7.2

- When acid soil is flooded, its pH usually increases
- When alkaline soil is flooded, its pH usually decreases

The increase in pH of acid soils is due mainly to reduction of Fe³⁺ to Fe²⁺ with corresponding consumptions of H⁺ which explains increase in pH.

If not enough Fe in soil - pH would not increase

In flooded alkaline soils, the Na₂CO₃-H₂O-CO₂ and CaCO₃-H₂O-CO₂ systems operate to control pH at about neutrality (buildup of CO₂ and resulting carbonic acid).

**NITROGEN TRANSFORMATIONS** (from +5 (NO₃⁻) to -3 (NH₄⁺))

Nitrogen is an essential plant macronutrient absorbed in either nitrate (NO₃⁻) or ammonium (NH₄⁺) form.

Biologically important forms of nitrogen include:

- organic nitrogen in living organisms and detritus (e.g., proteins, nucleic acids)
- inorganic compounds.

**TRANSFORMATIONS:**

- Mineralization (ammonification)
- Plant uptake (immobilization)
- Denitrification
- Nitrification
- Volatilization
- Nitrogen fixation
IRON AND MANGANESE TRANSFORMATION

Reduction of Mn and Fe follows the reduction of nitrate (120-220 mV).
Mn$^4$ (Manganic) $\rightarrow$ Mn$^2$ (Manganous)
Fe$^3$ (Ferric) $\rightarrow$ Fe$^2$ (Ferrous)

5-50% of iron can be reduced within few weeks of flooding
Bacteria responsible for iron reduction are e.g., from Clostridium group.
Both Mn and Fe are more soluble and more available to plants in reduced form -- high concentrations in wetland plants

Plants from waterlogged soils have an increased resistance to high Mn and Fe concentrations (partly by precipitation oxides on the root surface)
Ferric compounds that form the reddish plaque around roots -- this may result in immobilization of available P and cause a barrier to nutrient uptake. (Metal binding)

SULPHUR TRANSFORMATIONS (*6 in SO$_4^{2-}$ to 2 in H$_2$S*)

Sulphur occurs in wetland soils in both inorganic and organic compounds
Reduction of sulfates into sulfides at $E_h = -75$ to $-150$ mV
Obligate anaerobic bacteria of the genera Desulfovibrio desulphuricans reduce $SO_4^-$ to:
$H_2S$,
DMS ($CH_3$)$_2S$, dimethylsulfide
DMDS ($CH_3$)$_2S$, dimethyldisulfide

Analogous reaction is reduction of $SeO_4^{2-}$ (selenate) to $Se$ (Selenite)

volatilization by cyanobacteria
Sulfides toxic to both microorganisms and higher plants;
>0.1 ppm toxic
Sulfur is only seldom a limiting nutrient not as much attention as nitrogen
Sulfides can combine with Fe and form insoluble ferrous sulfide (FeS$_2$)
**CARBON TRANSFORMATIONS**

Organic carbon can be degraded by several anaerobic processes. **Fermentation** results in low m.w. acids and alcohols and CO$_2$; these are then used in:

**Methanogenesis** - production of CH$_4$ (Eh -250 to -350 mV)

Methanogenic bacteria (archaeobacteria) strictly anaerobic

CH$_4$ produced by two pathways:
1) cleaving acetate to CO$_2$ and CH$_4$, $\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$
   (delta $^{13}$C - 50 to -65%)
2) reduction of carbon dioxide to methane with H$_2$, $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
   (delta $^{13}$C - 60 to -100%)

**Methanogenic bacteria** inhibited by sulfates (= low methane emissions from salt marshes and mangroves)

- competition of sulfate reducing and methanogenic bacteria for organic substrate (acetate)
- inhibition of methanogens by sulfate reduction products
- if too much SO$_4$, redox does not drop enough

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**FACTORS AFFECTING METHANE EMISSIONS**

- temperature, wind
- topography / water table / soil moisture
- salinity / presence of sulfates
- vegetation type
- composition of organic material incl. plant exudates

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How does methane get from the sediments to the air??

- Through plants
- Ebulition
- Diffusion

**Methanotrophs!!!**

- methane oxidizing bacteria

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**Role of plants:**
- Provide OM (litter, root exudates)
- Serve as a conduit - up to 90%

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**Fig. 2** The relationship between mean seasonal soil temperatures and the overall range of CH$_4$ fluxes from the different sites and years represented in the study (Ohtaki et al. in prep.)
METHANE - GREENHOUSE GAS

~18,000 years ago atmospheric concentrations ~ 350 ppb (0.35 ppm)
~200 years ago ~ 650 ppb
present ~ 1,800 ppb (1.8 ppm)

Methane is chemically as well as radiatively active
25x stronger effect than CO₂
10 y residence time in the troposphere (lower atmosphere)
OH radicals - atmospheric sink for methane

Pre-industrial times - wetlands were the dominant source with small contributions from wild fires, animals and oceans.
Natural methane sources totaled about ~180-380 Tg (10¹² g) methane per year

Uncertainties in methane emission estimates
Monitoring of global atmospheric concentrations (NOAA, CMDL)
Global estimates of methane sources and sinks; top-down x bottom-up
Use of remote sensing (scaling!!)
Natural wetlands contribute 25-40% of the global methane source (145-232 Tg/y)

Lack of data on methane emissions from large wetland regions both in boreal and tropical zones (Siberia, Pantanal, Okavango)
Largest emissions from tropical wetlands
Tropical wetlands - seasonal cycle dominated by water tables
High latitude wetlands - seasonal cycle controlled by soil temperature

From Walter et al. 2001

http://icp.giss.nasa.gov/research/methane/gmc.html

From Walter et al. 2001
Examples of projects studying methane emission:

A) "Biospheric controls on trace gas fluxes in northern wetlands (CONGAS)"

**Methods:** chamber technique, stable isotopes, tower gas measurements; specific focus on the direct influence of vascular plants.

**Sites:** Greenland, Iceland, northern Scandinavia, Siberia.

**Conclusions:** The strongest control – soil temperature. Implication for global warming. The relationship between vascular plants and methane emissions is complex and may vary substantially between and even within ecosystems.

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Examples of projects studying methane emission:

B) "Regional methane emissions from the Amazon Basin" (John Melack et al.)

**Methods:** remotely sensed estimates of seasonally flooded wetland vegetation; measurement of methane emissions from wetland habitats (flooded forests, floating macrophytes, open water); evaluation of methane emission for the whole basin.

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Digital videography for validation

Chamber measurements – air samples collected from the chambers into air-tight syringes in consecutive time increments to be later analyzed using GC.

For the whole Central Amazon Basin (1.77 million sq. km) **7.6 (+/- 2.3) Tg/y**

Central Amazon Basin (1.77 million sq. km total) **7.6 (+/- 2) Tg/y**

Lowland Amazon Basin (5.19 million sq. km total) **25.0 (+/- 8) Tg/y**

Other SA wetlands (115,000 sq. km flooded) **8.3 Tg/y**

Research needs: ecological studies and methane emission measurements in other regions both low and high latitudes; models.
TRANSFORMATION OF PHOSPHORUS

P is not directly involved in redox reactions occurring in waterlogged soils, but is associated with number of elements subject to redox reactions.

Occurs in +5 valence state $\text{PO}_4^{3-}$

P has only liquid/solid storage forms; no gaseous form except for a very minor phosphine gas ($\text{PH}_3$)

Cannot be lost as N (in denitrification)

Phosphorus (like nitrogen) is one of the most important plant nutrients, often limiting.

Retention of P in wetlands is primarily through the geochemical processes

(C & N added biologically x released through biological mineralization
P added from parent soil material x released through external enzymes)

Forms of P in sediments:

1. **Soluble** (orthophosphate) extractable w. water
2. **Labile** (in equilibrium with P in soil solution; anion resin exchangeable)
3. **Primary P minerals** (apatites; acid extractable); P released through weathering
4. **Secondary P minerals** (minerals with P chemisorbed to their surfaces: Fe and Al oxides and carbonates
5. **Organic P** (e.g., inositol, ester-bond; NA, phospholipids – readily hydrolyzed)
6. **Ocluded P** (P physically encapsulated by minerals (in iron oxides)

In wetland soils P occurs in soluble and unsoluble complexes in both inorganic and organic forms

Precipitation of insoluble phosphates with ferric iron and aluminum under aerobic conditions; under anaerobic conditions, ferric iron is reduced to more solubleferrous compounds and phosphate is released into solution

Nutrient addition experiments to confirm nutrient limitation

Model of P transformations (Johnson et al 2003; according to Tiessen et al 1984)

Shaded portions represent the soil pools considered to be available to plants over the course of a growing season
RESPONSE TO NUTRIENT ADDITION:

C, N

P, N&P