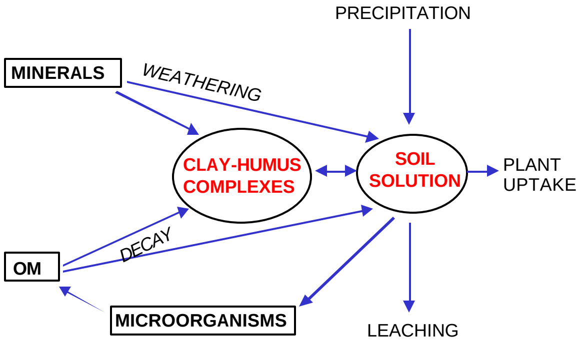
WETLAND SOILS

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



PRECIPITATION

MINERALS

WEATHERING

CLAY-HUMUS COMPLEXES

SOIL SOLUTION

PLANT UPTAKE

OM

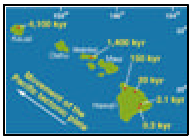
DECAY

MICROORGANISMS

LEACHING

Soil formation is traditionally described as a function of

soil forming factors	soil sequences:
- parent material	- litho
- climate	- clima
- relief	- topo
- biota	- bio
- time	- chrono



(Jeny 1941 Factors of Soil Formation)

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 addditions, 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

SOIL PITS

SEDIMENT CORES

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

alluvial (deposited by streams) materials

soil profile well or poorly developed

characterized by a pale grey or olive-grey (low chroma)

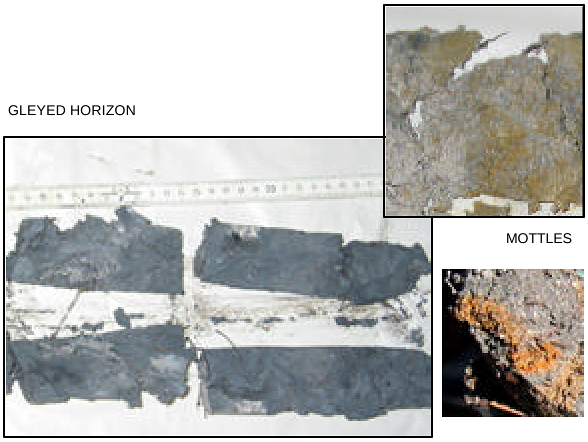
gleyed horizon, due to the conversion of Fe3+ to Fe2+., mottles

redoximorphic feature

drained soils show hydromorphic conditions centuries after draining

x newly created wetlands no hydromorphic features (2 years to form)

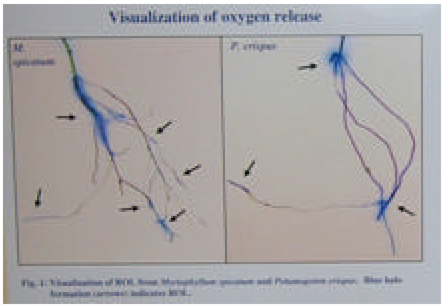
no glaying or mottling where no iron



GLEYED HORIZON

MOTTLES

Methylenblue-agar-method	Visualization of ROL and spatial patterns	Leukomethylenblue (colorless) oxidizes to methylenblue (blue)



Visualization of oxygen release

Fig. 1: Visualization of ROL from Myriophyllum spicatum and Potamogeton crispus. Blue halo formation (arrows) indicates ROL.

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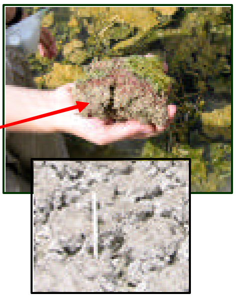
1) MINERAL (GLEYS) – cont.

calcitic 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)



ORGANIC (HISTOSOLS, PEAT SOILS)

contain more than 12-20% of organic C or 20-35% OM

Bulk density (dry W/unit of volume)		0.2 g/cm3 or less
	mineral	1-2 g/cm3

Porosity: 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 exchangable cations that a soil can hold - Mineral soilos - CEC dominated by Ca, Mg, K, Na,

- Organic soils - high exchangable hydrogen

Litter (detritus) layer not part of a soil horizon

Important characteristics of organic soils:

1) botanical composition of peat

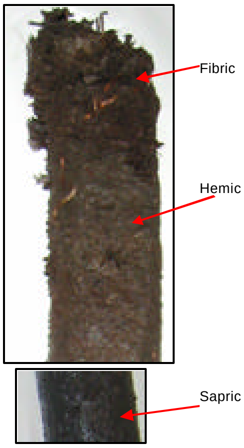
(mosses – peat moss, herbaceous material, wood and leaf litter; mangroves)

2) state of decomposition:

Fibric

Hemic

Sapric



Peat:	Porosity (%)	K (m/d)	Bulk density (g/cm3)
FIBRIST Fibric (peat) >2/3 identifiable	> 90	>10	<0.09
HEMIST Hemic (mucky p.)	84-90	0.01-1.3	0.09-0.2
SAPRIST Sapric (muck) >2/3 decomposed	<84	<0.01	>0.2

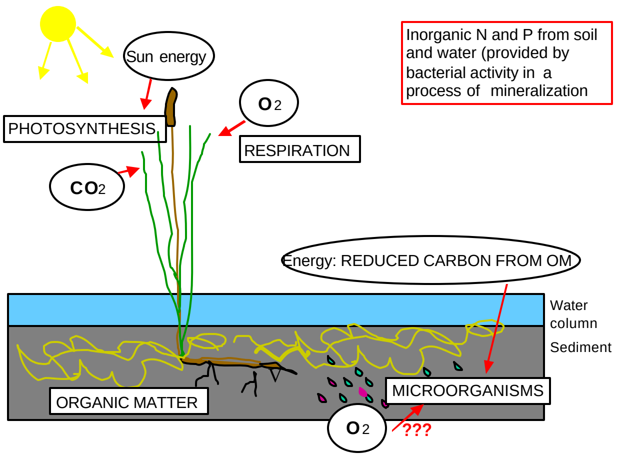
Production of organic material (OM) and its preservation

- 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)



Inorganic N and P from soil and water (provided by bacterial activity in a process of mineralization

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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 elector acceptor.

Everyone needs this energy: micrororganisms, 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

	O2	CO2
drained soil	20%	0.1-1%
flooded soil	~0%	up to 10%

O2 removed - no final electron acceptor available for oxidation reactions that provide energy

NO^{3-}, Fe^{3+}, Mn^{4+}, SO_4^{2-} and CO_2 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**

Important: e donors (reducing agents)

e acceptors (oxidazing 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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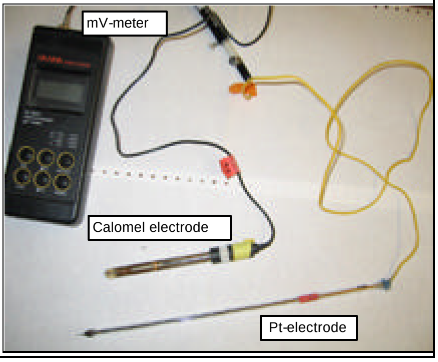
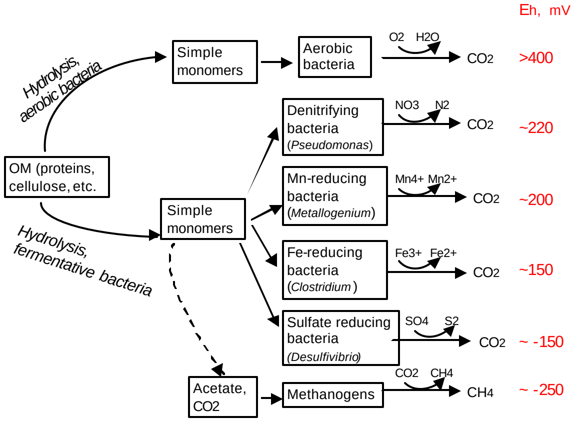
Redox potential – measure of e availability

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)





Eh, mV

OM (proteins, cellulose, etc.)

Hydrolysis, aerobic bacteria

Simple monomers → Aerobic bacteria → CO2 (O2 → H2O) >400

Hydrolysis, fermentative bacteria

Simple monomers

Denitrifying bacteria (*Pseudomonas*) → CO2 (NO3 → N2) ~220

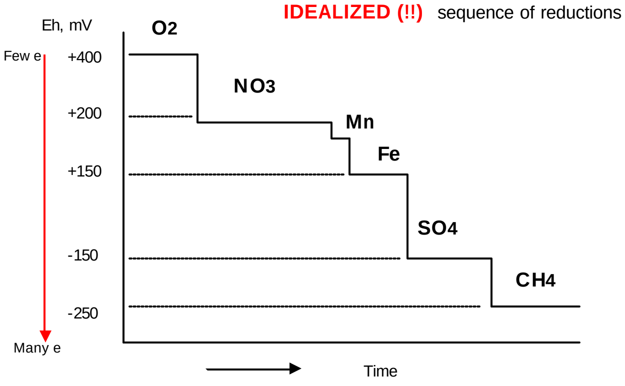
Mn-reducing bacteria (*Metallogenium*) → CO2 (Mn4+ → Mn2+) ~200

Fe-reducing bacteria (*Clostridium*) → CO2 (Fe3+ → Fe2+) ~150

Sulfate reducing bacteria (*Desulfivibrio*) → CO2 (SO4 → S2) ~ -150

Acetate, CO2 → Methanogens → CH4 (CO2 → CH4) ~ -250

IDEALIZED (!!) sequence of reductions



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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 Na_2CO_3-H_2O-CO_2 and $CaCO_3$-H_2O-CO_2

systems operate to control pH at about neutrality (buildup of CO2 and resulting carbonic acid)

Vertical gradients of redox

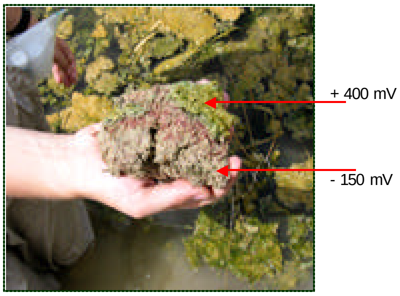
water

oxidized sediment layer

anoxic sediment layer

Gradients along roots

Diurnal changes



NITROGEN TRANSFORMATIONS (from +5 (NO^3) to -3 (NH_4^+))

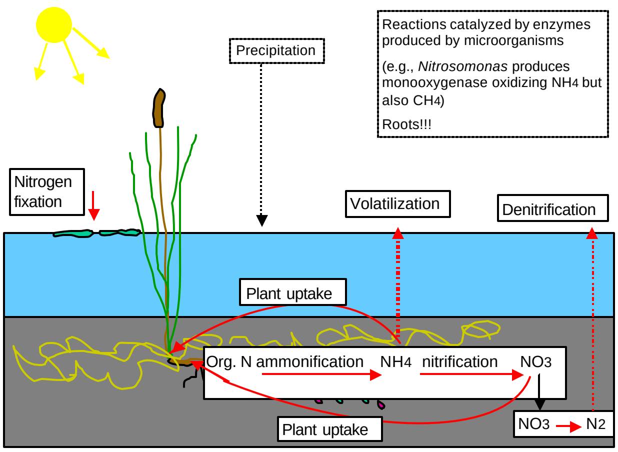
Nitrogen is an essential plant macronutrient absorbed in either nitrate (NO^{3-},) or ammonium (NH_4^+) form.

Biologically important forms of nitrogen include:

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

TRANSFORMATIONS:

- Mineralization (ammonification)
- Plant uptake (immobilization)
- Denitrification
- Nitrification
- Volatilization
- Nitrogen fixation



Reactions catalyzed by enzymes produced by microorganisms

(e.g., *Nitrosomonas* produces monooxygenase oxidizing NH4 but also CH4)

Roots!!!

Precipitation

Nitrogen fixation

Volatilization

Denitrification

Plant uptake

Org. N ammonification NH4 nitrification NO3

Plant uptake

NO3 → N2

N-fixation

cyanobacteria, free-living Azotobacter (Spartina), symbiotic Rhizobia;

Acetylene reduction technique

(enzyme nitrogenase reduces acetylene into ethylene

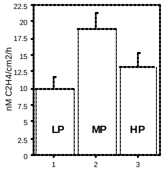
C2H2 → C2H4

measured on GC as ethylene concentration)

Sensitivity to oxygen

Special cells (heterocytes)

Limitation by phosphorus



IRON AND MANGANESE TRANSFORMATION

Reduction of Mn and Fe follows the reduction of nitrate (120-220 mV).

Mn+4 (Manganic) → Mn+2 (Manganous)

Fe+3 (Ferric) → 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_2S)

Sulphur occurs in wetland soils in both inorganic and organic compounds

Reduction of sulfates into sulfides at Eh = -75 to -150 mV

Obligate anaerobic bacteria of the genera *Desulfovibrio desulphuricans* reduce SO4 to:

H_2S,

DMS $(CH_3)_2S$, dimethylsulfate

DMDS $(CH_3)_2S_2$ dimethyldisulfate

Analogous reaction is reduction of **SeO_4 (selenate) to Se (Selenite)**

volatilization by cyanobacteria

Sulfides toxic to both microorganisms and higher plants;

> 0.1 ppm toxic

Sulphur is only seldom a limiting nutrient not as much attention as nitrogen

Sulfides can combine with Fe and form insoluble ferrous sulfide (FeS).

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)

terminal anaerobic mineralization process

methanogenic bacteria (archaeobacteria) strictly anaerobic

CH_4 produced by two pathways:

1) cleaving acetate to CO_2 and CH_4 $CH_3COOH \rightarrow CO_2 + CH_4$

(delta ^{13}C –50 to –65%)

2) reduction of carbon dioxide to methane with H_2

$CO_2 + 4H_2 \rightarrow CH_4 + H_2O$

(delta ^{13}C –60 to –100%)

Methanogenic bacteria inhibited by sulfates

(= low methane emissions from salt marshes and mangroves)

a) competition of sulfate reducing and methanogenic bacteria for organic substrate, acetate)

b) inhibition of methanogens by sulfate reduction products

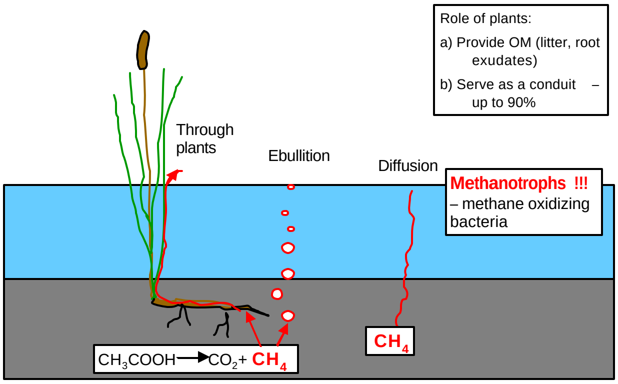
c) if too much SO_4, redox does not drop enough

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

Role of plants:

a) Provide OM (litter, root exudates)

b) Serve as a conduit – up to 90%



Methanotrophs !!! – methane oxidizing bacteria

FACTORS AFFECTING METHANE EMISSIONS

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

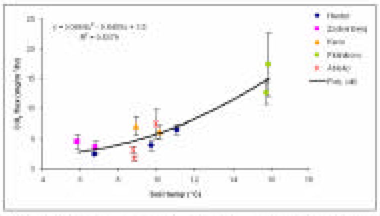


Fig. 2. The relationship between mean seasonal soil temperatures and the overall mean of CH_4 fluxes from the different sites and years represented in this study (Christensen et al. in prep.).

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 CO_2

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 (10^{12} g) methane per year

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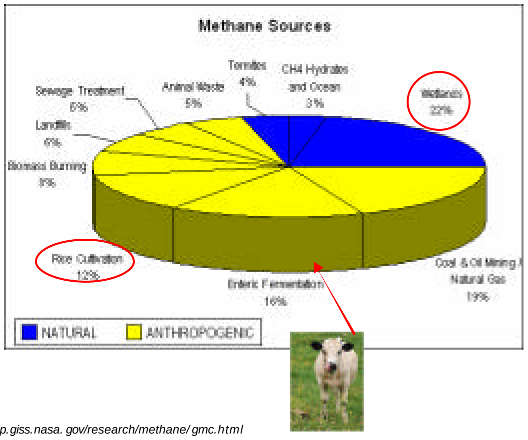


http://icp.giss.nasa. gov/research/methane/ gmc.html

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)

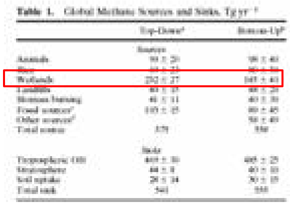


Table 1. Global Methane Sources and Sinks, Tg yr⁻¹

	Top-Down	Bottom-Up
Sources		
Animals	[illegible]	[illegible]
Rice	[illegible]	[illegible]
Wetlands	232 ± 27	145 ± 40
Landfills	[illegible]	[illegible]
Biomass burning	[illegible]	[illegible]
Fossil sources	[illegible]	[illegible]
Other sources		[illegible]
Total source	[illegible]	[illegible]
Sinks		
Tropospheric OH	[illegible]	[illegible]
Stratosphere	[illegible]	[illegible]
Soil uptake	[illegible]	[illegible]
Total sink	[illegible]	[illegible]

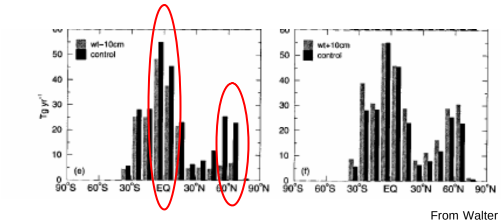
From Walter et al. 2001

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

Examples of projects studying methane emission:

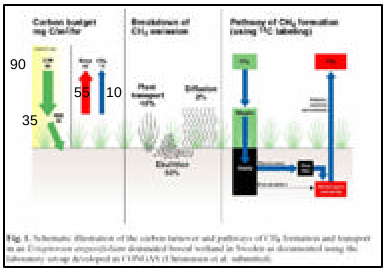
A) "Biospheric controls on trace gas fluxes in northern wetlands (CONGAS)"

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.

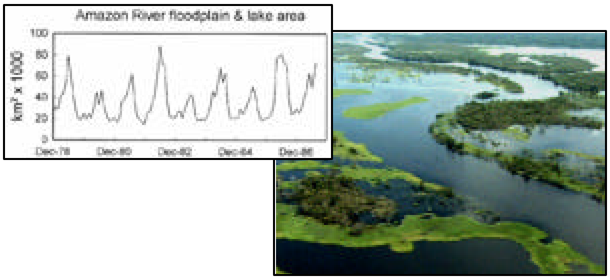


The relationship between vascular plants and methane emissions is complex and may vary substantially between and even within ecosystems.

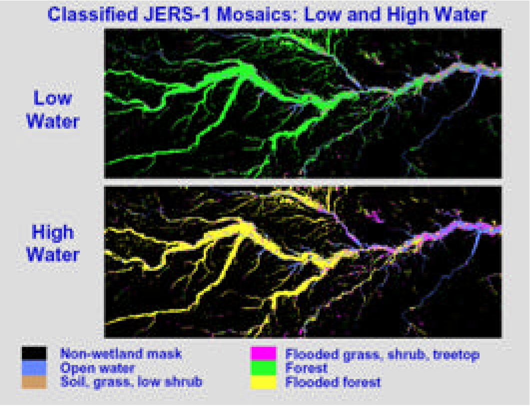
Examples of projects studying methane emission:

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

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

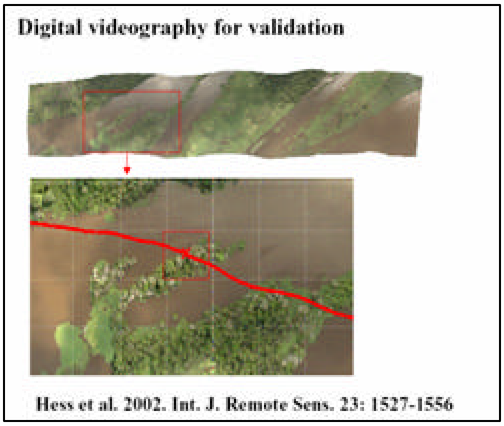


Classified JERS-1 Mosaics: Low and High Water

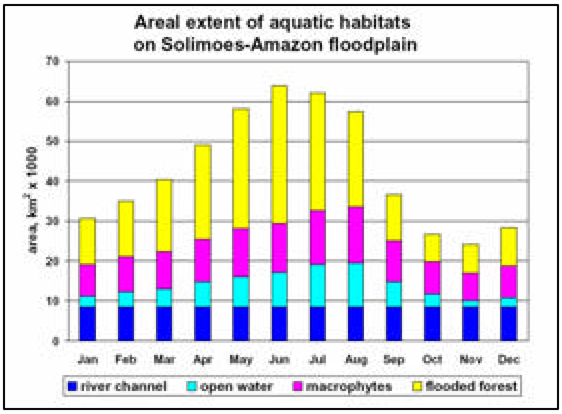


■ Non-wetland mask	■ Flooded grass, shrub, treetop
■ Open water	■ Forest
■ Soil, grass, low shrub	■ Flooded forest

Digital videography for validation

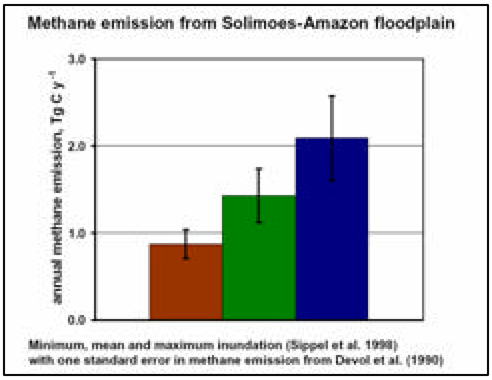


Hess et al. 2002. Int. J. Remote Sens. 23: 1527-1556



Areal extent of aquatic habitats on Solimoes-Amazon floodplain

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

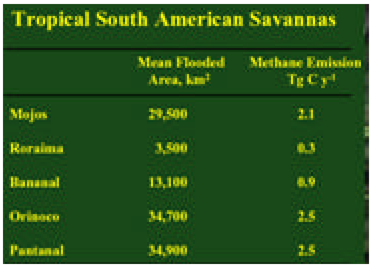


Methane emission from Solimoes-Amazon floodplain

Minimum, mean and maximum inundation (Sippel et al. 1998) with one standard error in methane emission from Devol et al. (1990)

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**



Tropical South American Savannas

	Mean Flooded Area, km^2	Methane Emission Tg C y^{-1}
Mojos	29,500	2.1
Roraima	3,500	0.3
Bananal	13,100	0.9
Orinoco	34,700	2.5
Pantanal	34,900	2.5

Research needs: <u>ecological studies and methane emission measurements</u> in other regions both low and high latitudes; <u>models</u>

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 PO_4^{3-}

P has only liquid/solid storage forms; no gaseous form except for a very minor phosphine gas (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 biologicaly 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 soluble ferrous compounds and phosphate is released into solution

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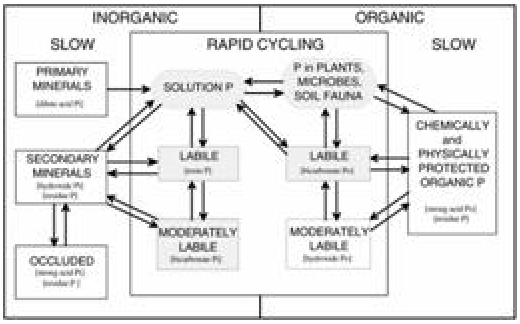

Model of P transformations (Johnson et al 2003; according to Tiessen et al 1984)
Shaded portions represent the soil pools considered to be available to plants over the course of a growing season

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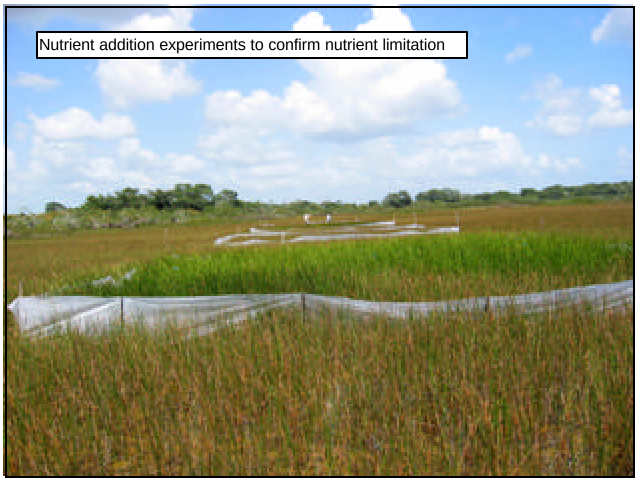
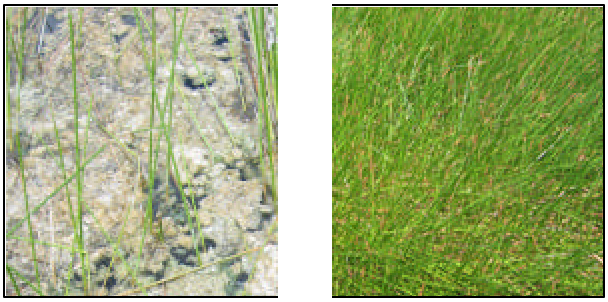


Nutrient addition experiments to confirm nutrient limitation

RESPONSE TO NUTRIENT ADDITION:



C, N

P, N&P