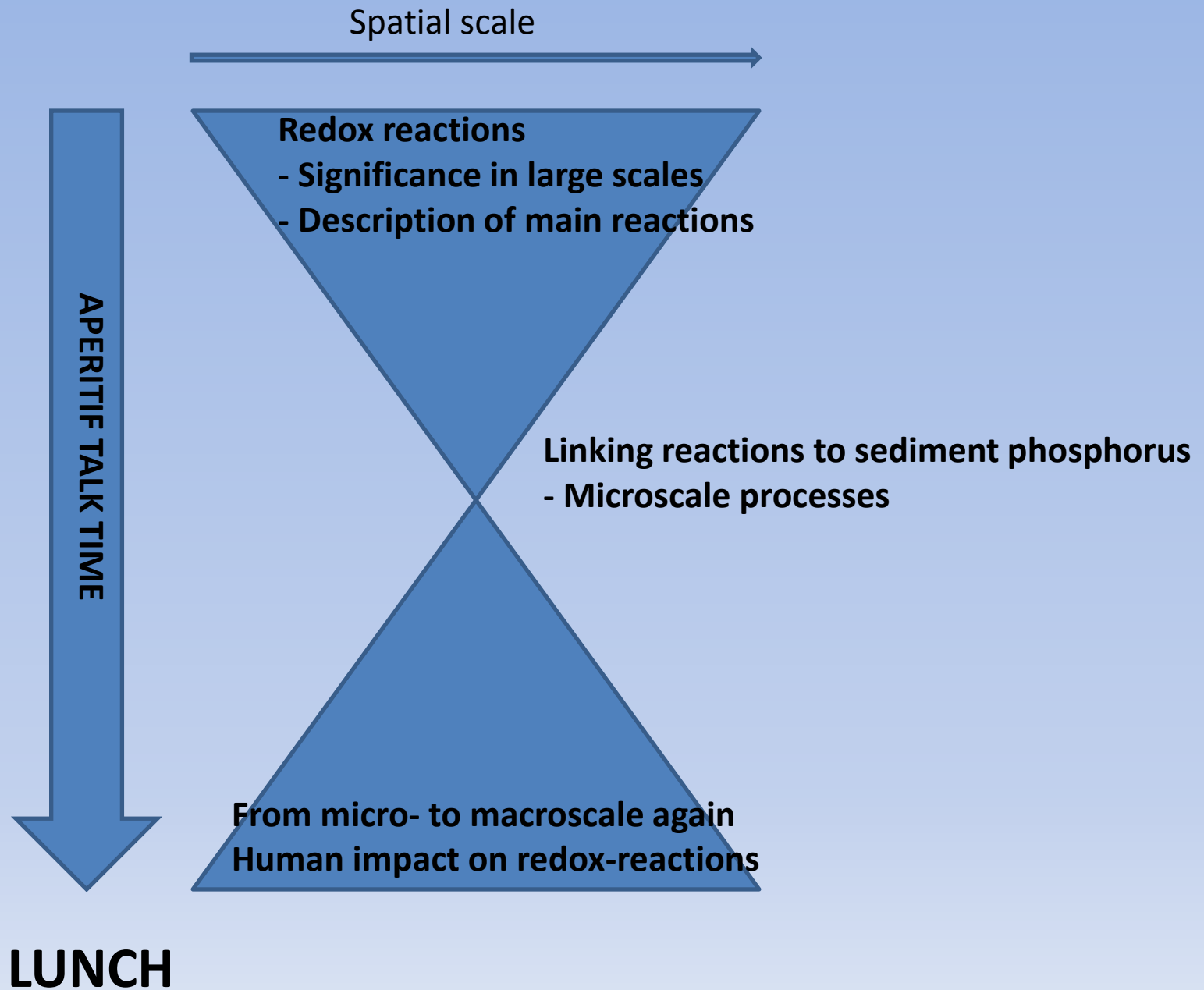


# **If you have an extra electron where do you put it?**

Jouni Lehtoranta  
Finnish Environment Institute  
Marine Research Center





Sun

$e^-$

Producers

Consumers

Life is based on electron transfer i.e. redox - reactions

Inorganic  
nutrient  
pool

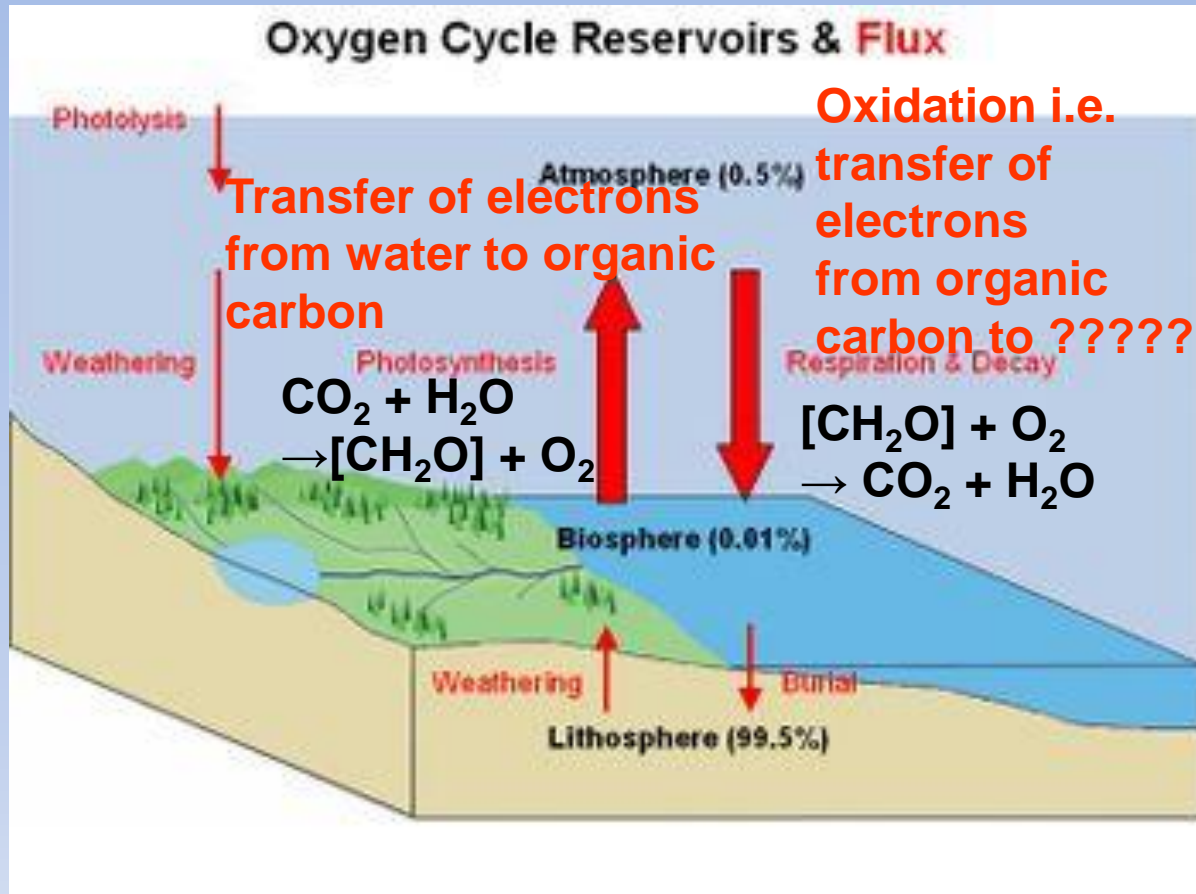
Decomposers

Energy goes  
through  
the system  
(open system)

Nutrients cycle  
in the system  
(closed system)

Life on Earth just slows down  
the flow of solar energy

# Transfer of electrons



# Pathways of organic matter oxidation

i.e. transfer of electrons

	Reduction process	Chemical reaction	Depth in sediment
oxic	Aerobic respiration	$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$	mm
anoxic	Denitrification	$2\text{N}_2 + 7\text{H}_2\text{O}$	mm
anoxic	Manganese reduction	$\text{Mn}^{2+} + 3\text{H}_2\text{O}$	cm
anoxic	Iron reduction	$+ 4\text{Fe}^{2+} + 7\text{H}_2\text{O}$	cm
anoxic	Sulfate reduction	$\text{H}_2\text{S} + 2\text{H}_2\text{O}$	m
anoxic	Methanogenesis	$\text{CH}_4 + 2\text{H}_2\text{O}$	m



Anaerobic respiration  
(reoxidation)

→  $\text{O}_2$  is the

→ In long run oxygen production = oxygen consumption (1:1)

high  $\text{O}_2$  consumption

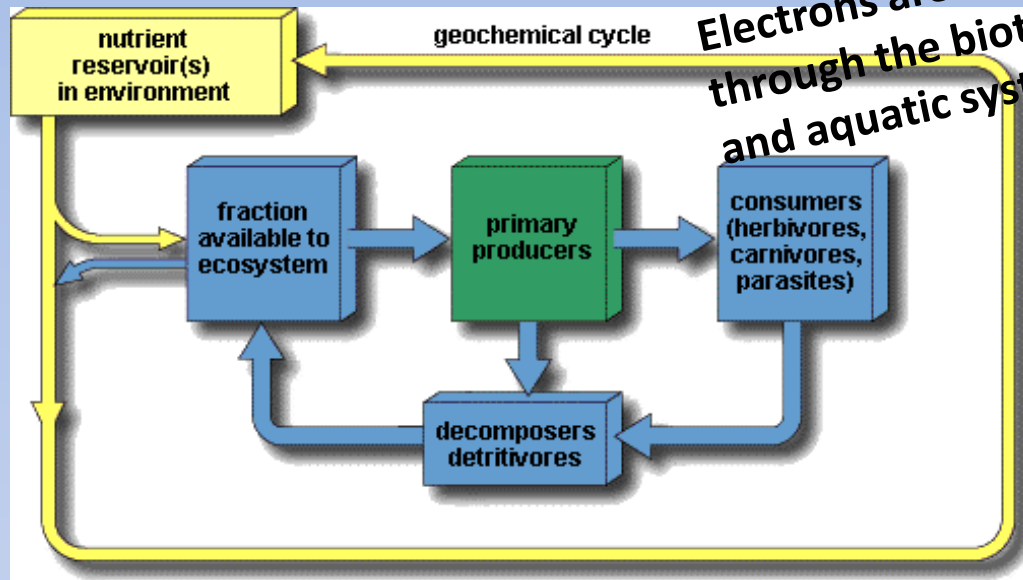
(4)

released during mineralization

Not true in geological timescales: Long term burial of organic carbon and formation of  $\text{FeS}_2$  (iron oxidizes sulphur) we have free  $\text{O}_2$  in atmosphere



# Biogeochemical cycles (closed system)



Electrons are carried by organic carbon through the biotic compartments in terrestrial and aquatic systems

*Reservoir*

chemical is held for long periods of time in one place (coal and apatite deposits)

*Exchange pool*

chemical is held for only short period of time.

Generally reservoirs are abiotic factors and exchange pools are biotic

*Residence*

the amount of time that a chemical is held in one place

## Abiotic compartments

Water = hydrosphere

Land = lithosphere

Air = atmosphere

However, there exists also abiotic electron carriers

# Terrestrial and aquatic systems

## Differences in reservoirs and exchange pools

	Terrestrial	Lake
<b>Nutrient pools</b>		
a) Reactive sites	Minerals, org. horizons, rhizosphere	Particles, sedim.-water
b) Sites of nutrient storage	Soils, vegetation	Sediment, fish
<b>Biota</b>		
a) Lifespan of primary producers	Long	Short
b) C:N, C:P of primary producers	High	Low
c) N-fixers	Symbiotic with long-lived organisms	Free living
d) Ratio consumers:producers	Lower	Higher
<b>Prevalence of anoxia</b>	Rare, microsites only	Sediments, hypolimnion

# P-pools in marine and terrestrial living organisms

- P-pool ( $50$  to  $70 \times 10^{12}$  g) in marine plankton is only 2 % of that in terrestrial living biomass
- However, the marine primary production incorporates  $1200 \times 10^{12}$  g P yr<sup>-1</sup>
  - is 3 to 4 times higher than the terrestrial incorporation rate



# Turnover times ('residence')

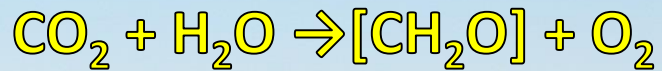
- The turnover time of living oceanic biomass is short:
  - few days for prokaryotes
  - week for phytoplankton
  - few months for zooplankton
- In terrestrial systems the P is mainly bound to long-lived forests
  - average turnover time for terrestrial living biomass is at least 10 years

Resting cells

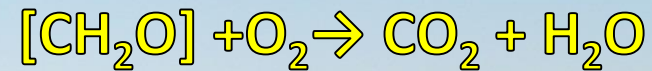
# What does this mean?

- Phosphorus cycles much faster in aquatic than terrestrial systems
- With a same amount of phosphorus we get more organic carbon (i.e. electron packages) into aquatic than terrestrial system

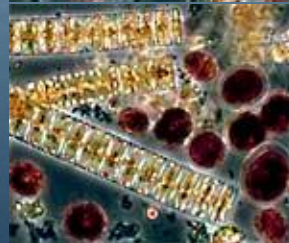
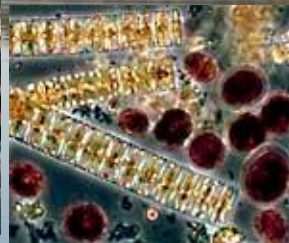
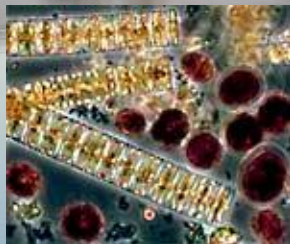
## Primary production



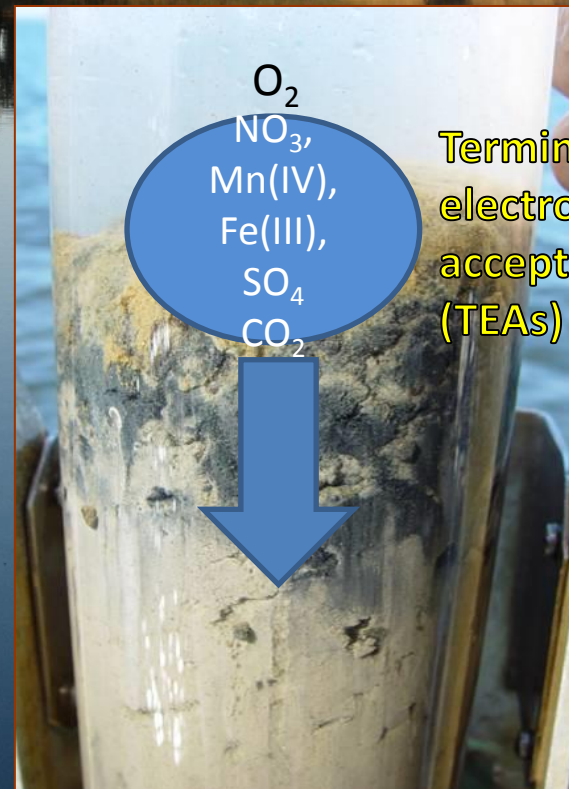
## Mineralization



**Problem:**  
Nutrient  
loading  
increases  
primary  
production



Seija  
Hällfors

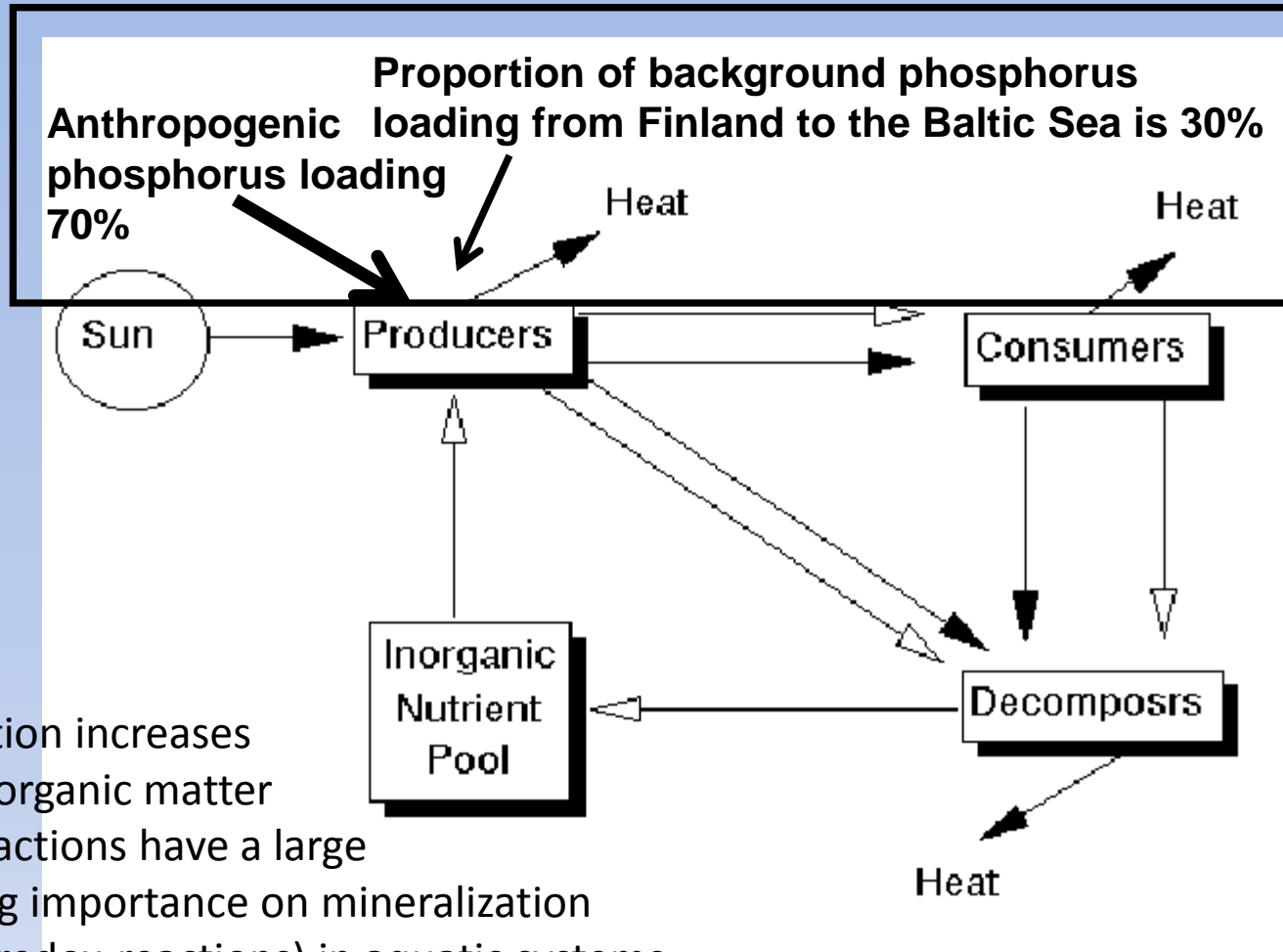


Terminal  
electron  
acceptors  
(TEAs)

nkoo

# Energy flow

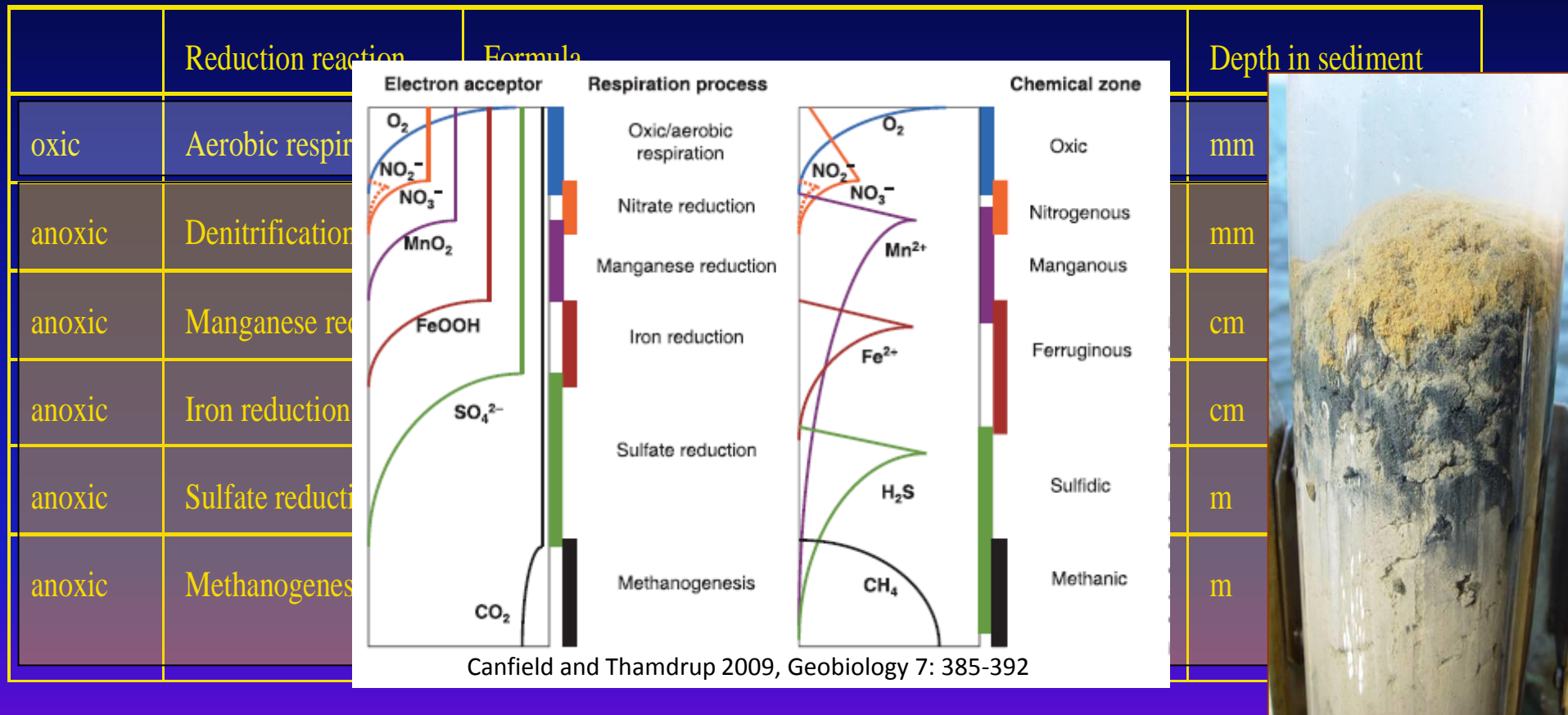
goes through the system (open system)



Eutrophication increases amount of organic matter

- Human actions have a large and growing importance on mineralization processes (redox-reactions) in aquatic systems

# Pathways of organic matter oxidation



One element is missing **Phosphorus**

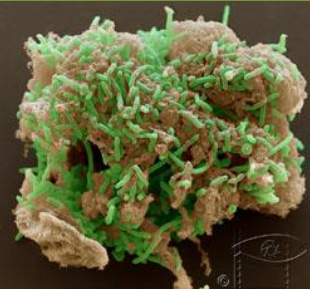

J. Lehtoranta

# **Phosphorus: What kind of sediment we would like to have considering mineralization pathways?**

If you have an extra electron (organic matter) where do you put it (which electron acceptor you prefer)



# Pathways of organic matter oxidation

	Reduction reaction	Formula	Depth in sediment
	Geobacter metallireducens		
	anoxic	Iron reduction	cm
	anoxic	Sulfate reduction	m
			

**Fe(III) is sensitive towards mineralization processes**



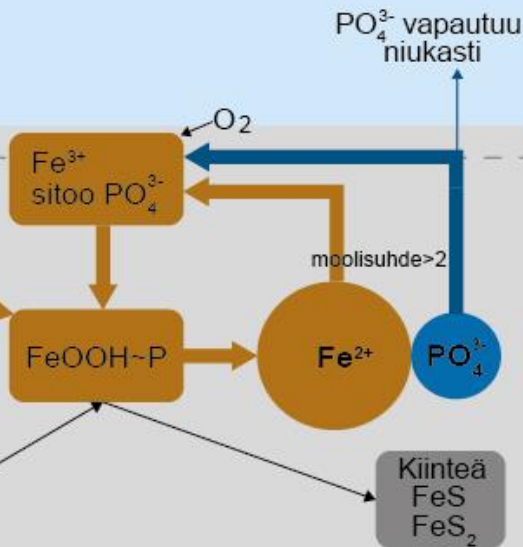
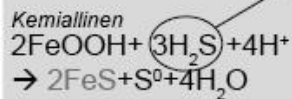
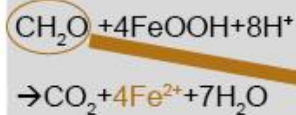
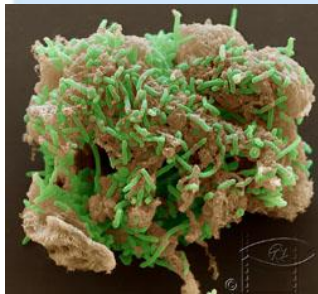
**Phosphorus starts react on redox-reactions**

# Significance of sulphate

Transfer of electrons from org.C to Fe or SO<sub>4</sub>

A

Niukasti sulfaattia

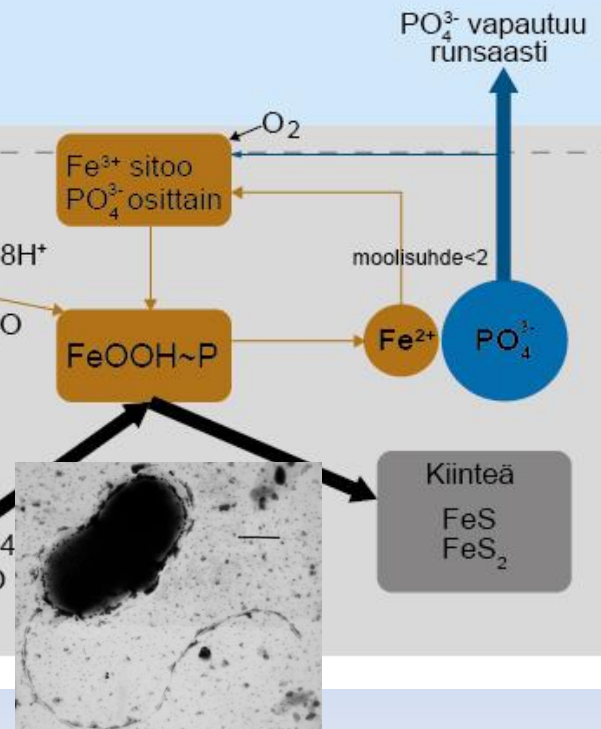
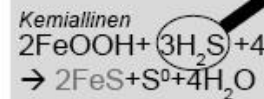
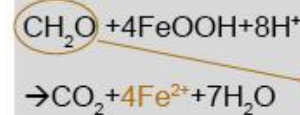


B

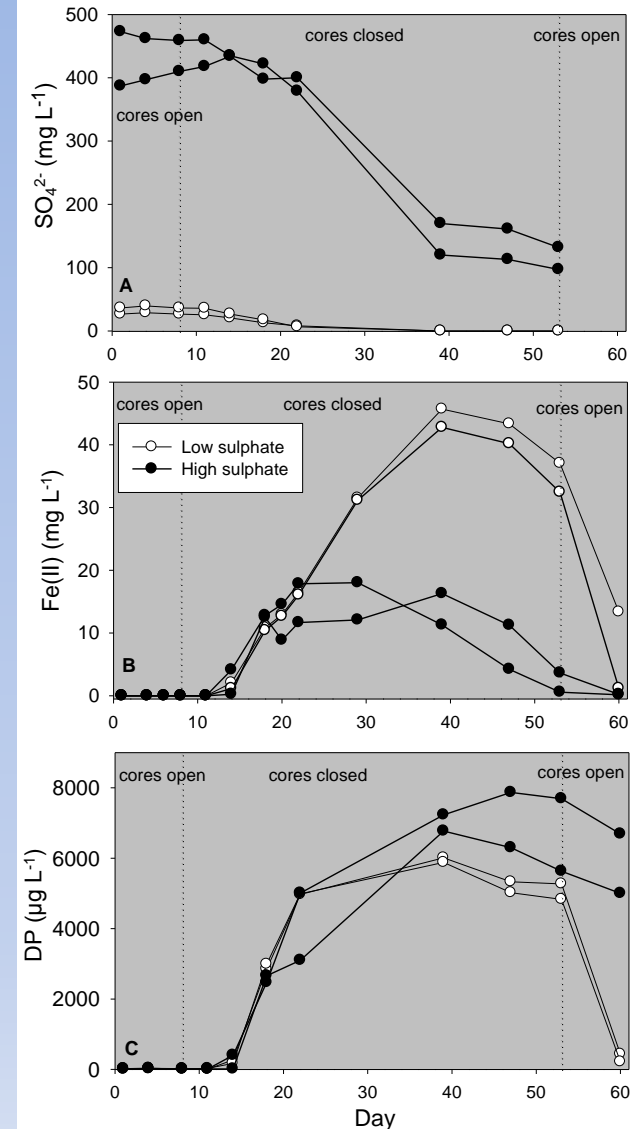
Runsaasti sulfaattia

Vesi

O<sub>2</sub>  
Hapeton sedimentti  
Mikrobiologinen



# Sulphate removed i.e. change in electron acceptor



Ekholm et al. 2011. The effect of gypsum on phosphorus losses at the catchment scale.  
**THE FINNISH ENVIRONMENT 33 | 2011**

# Addition of organic carbon (i.e. change in electron donor)

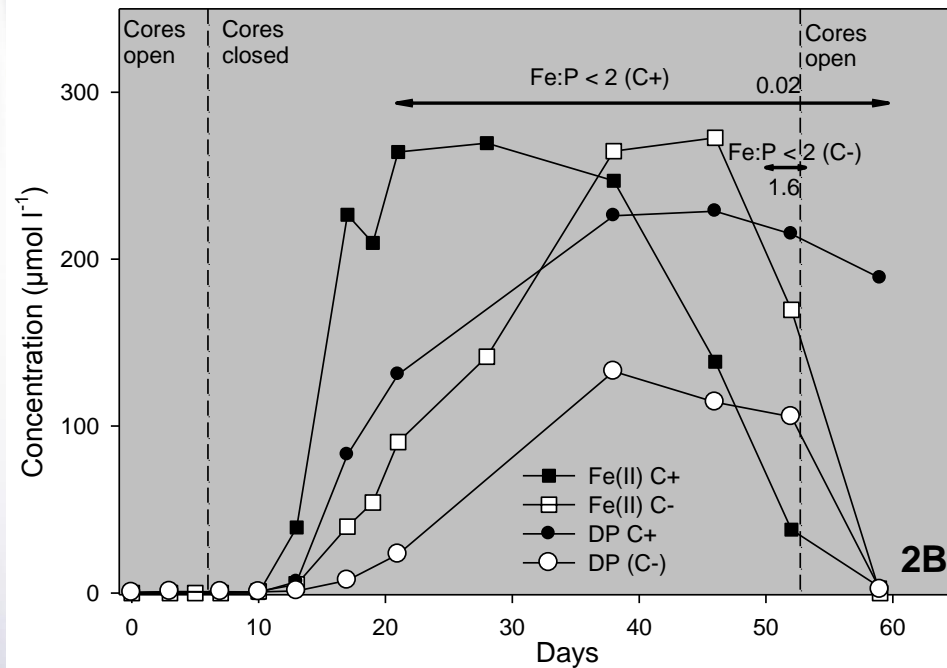
How microbial iron and sulphate reduction  
can be noticed after organic matter addition?

Fresh sample

Anoxia,

Anoxia,

dition





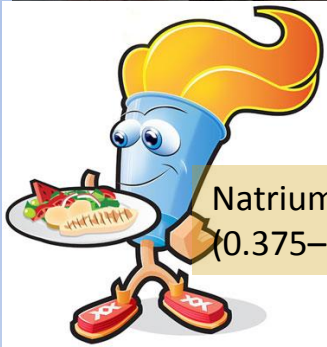
**Up-stream thinking:** Soil erosion and  
anerobic microbial processes in brackish  
sediment

- Incubation:
- At dark
  - (a) +10 °C, (b) +8 °C
  - (a) 308 d, (b) 745 d

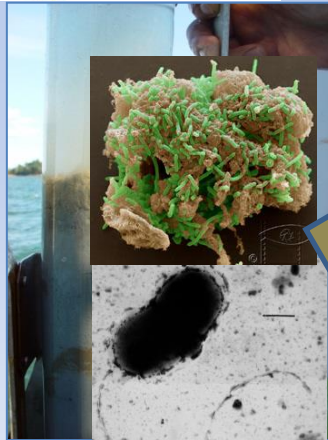
Standard field soil  
Sandy clay  
(60–1000 mg )



80 ml filtered  
Gulf of Finland water



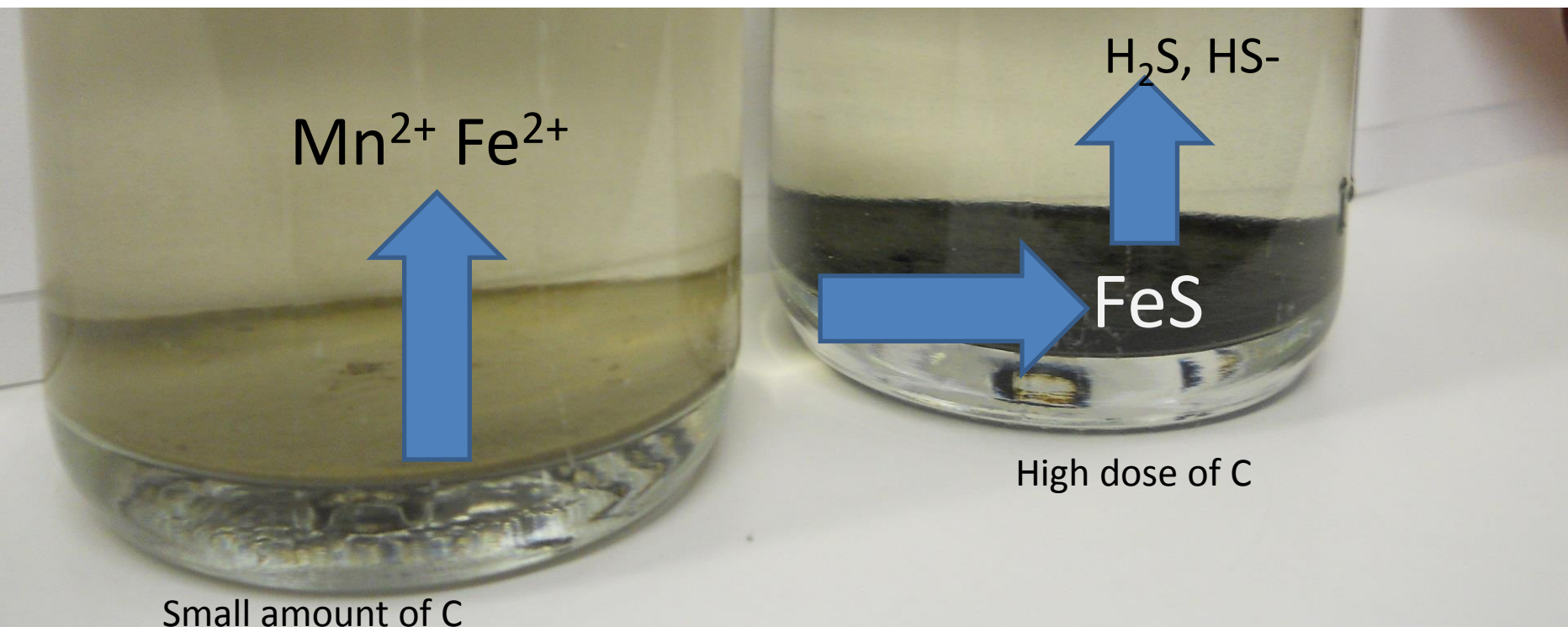
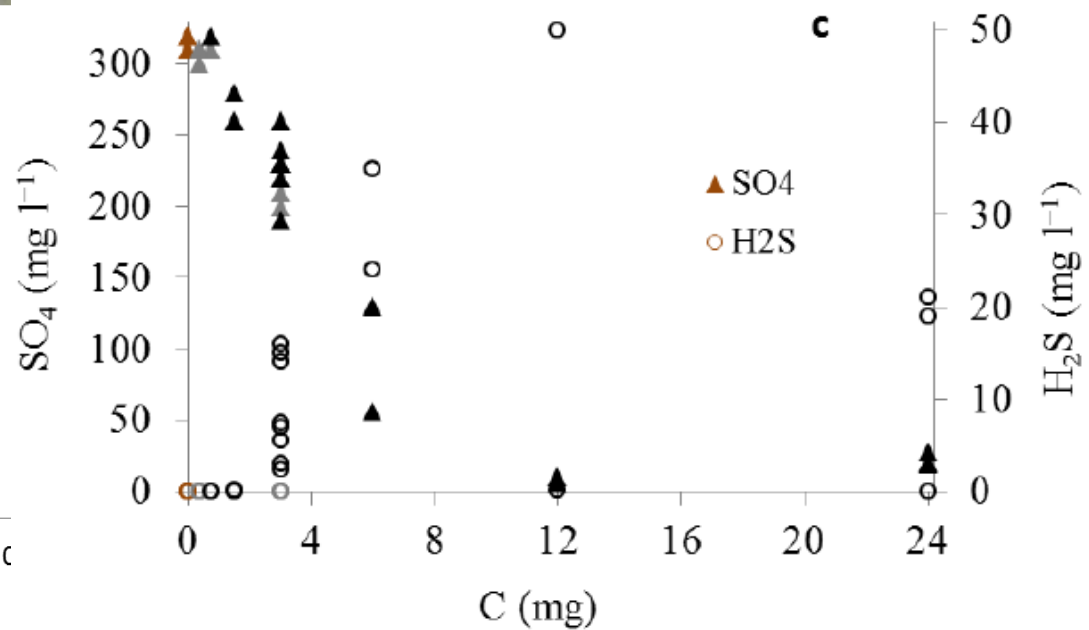
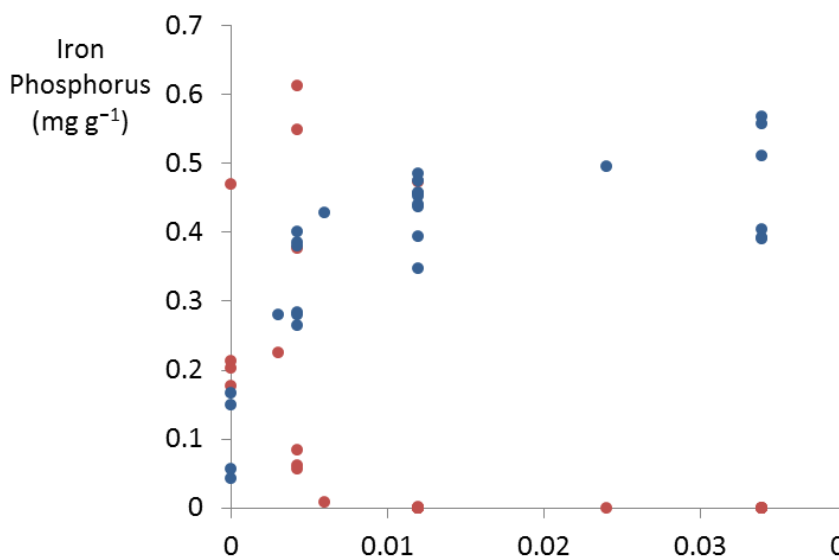
Natrium acetate  
(0.375–24 mg C)



10 µl sediment



**Lehtoranta, J., Ekholm, P.,  
Wahlström, S. Tallberg, P. and Uusitalo, R.**  
**Under revision**





# Constructed wetland of Ojainen in Jokioinen



Black  
sediment  
indicating  
presence of  
Fe sulphides



**Laakso Johanna, Kahma Tuomas, Ekholm Petri,  
Lehtoranta Jouni, Uusitalo Risto, Yli-Halla Markku**

# Consequences of eutrophication linked to electron transfer in sediments

# Eutrophication associated hypoxic areas

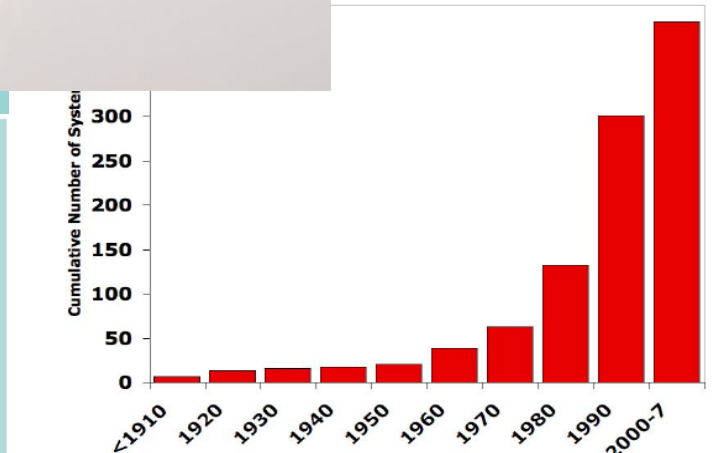
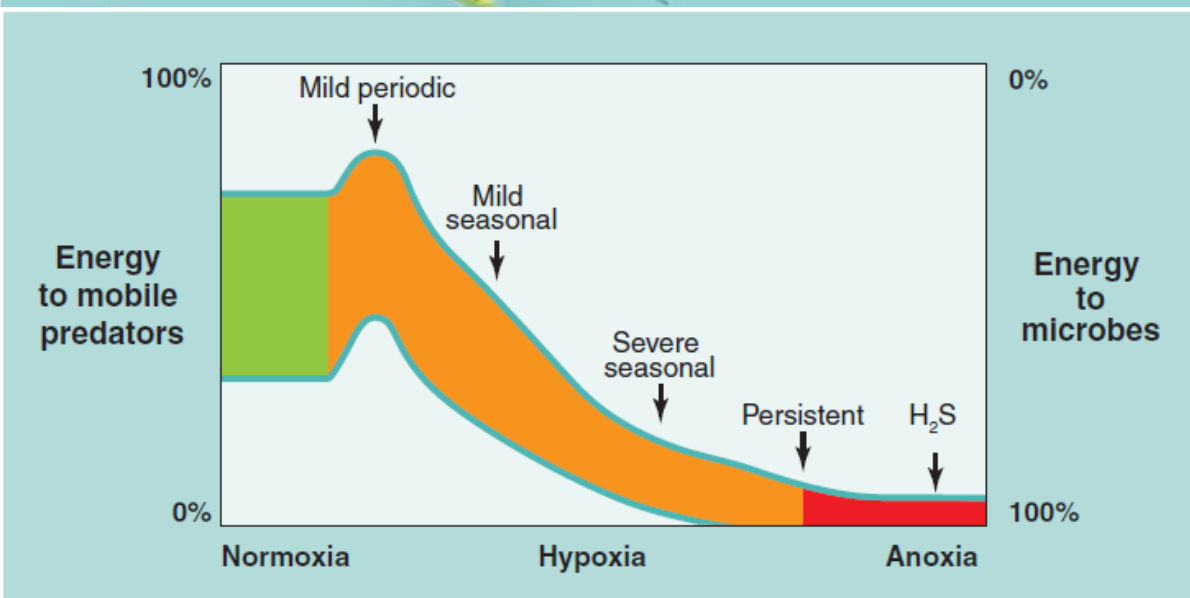
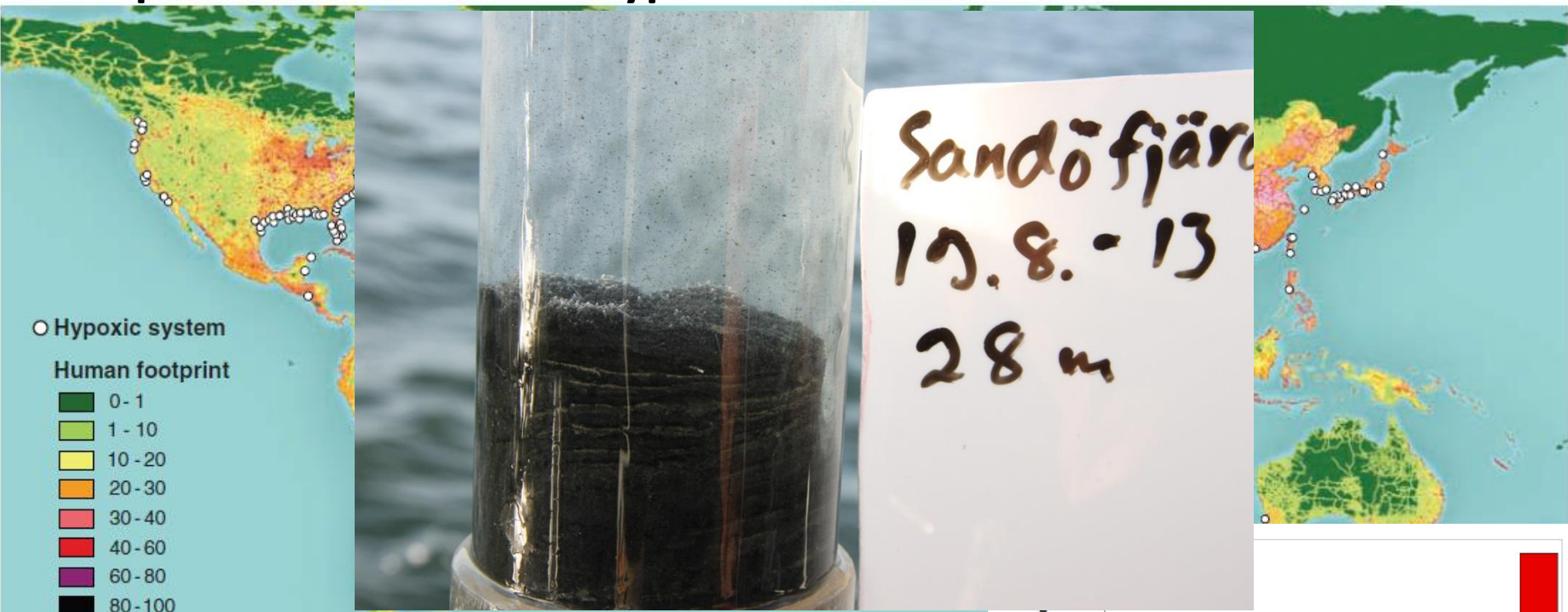


Figure S1. Cumulative increase in dead zones through time reported in the scientific literature. Systems are grouped by decade of first documented account (Table S1). The number of dead zones started to approximately double every ten years starting in the 1960s.

**Spreading Dead Zones and Consequences for Marine Ecosystems**  
Robert J. Diaz, *et al.*  
*Science* **321**, 926 (2008);



# Shift in microbial processes in the Baltic Sea?

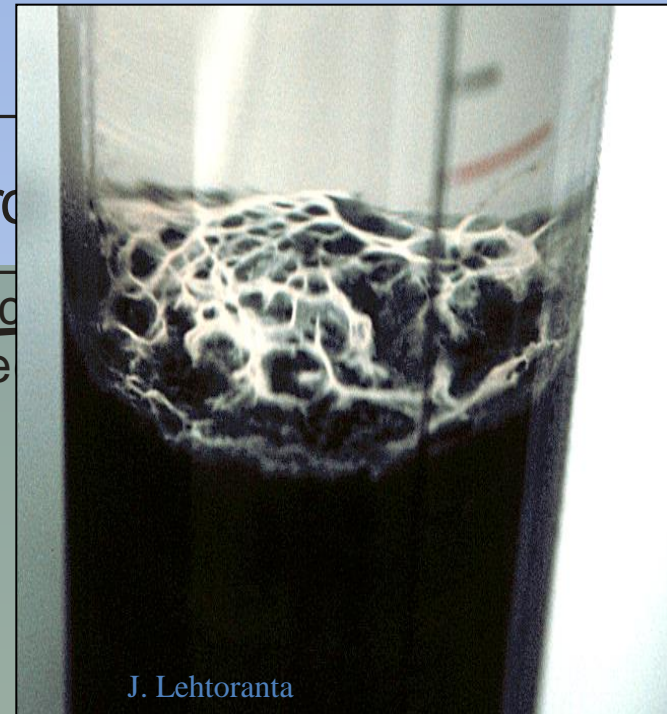


S. Knuuttila

Shift in microbial processes



Anoxic  
 $\text{SO}_4$  re



J. Lehtoranta

Sat

1

Oxic sediment surface  
Microbial Fe reduction  
dominates

Threshold

Driver  
Flux of labile organic C

Could change in microscale processes driven by  
micro-organisms cause macroscale consequences?

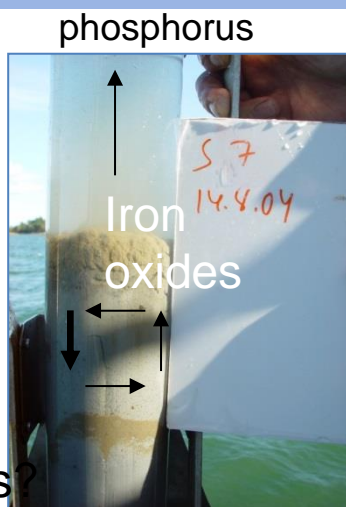


Winter surface concentration of phosphate in 2003 ( $\mu\text{g l}^{-1}$ )

Microbial iron reduction dominates?

Microscale redox-processes driven by micro-organisms cause macroscale consequences

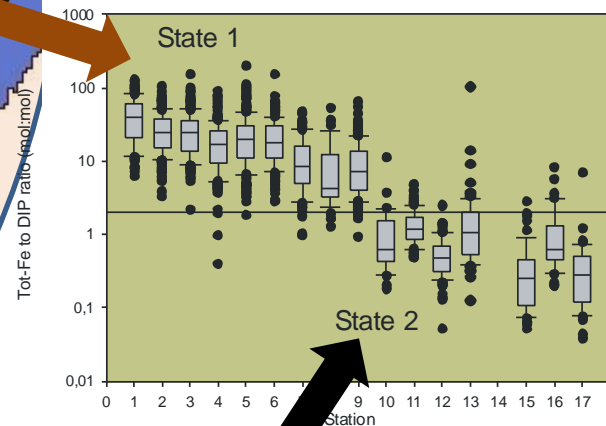
Microbial sulphate reduction dominates?



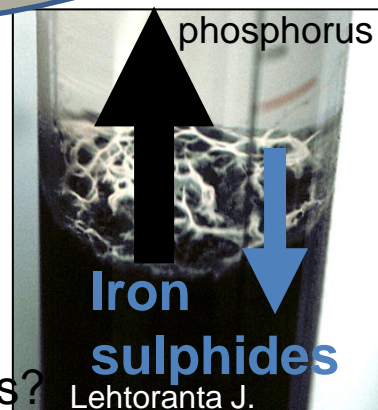
Eutrophication gradient

Oligotrophy

Mesotrophy



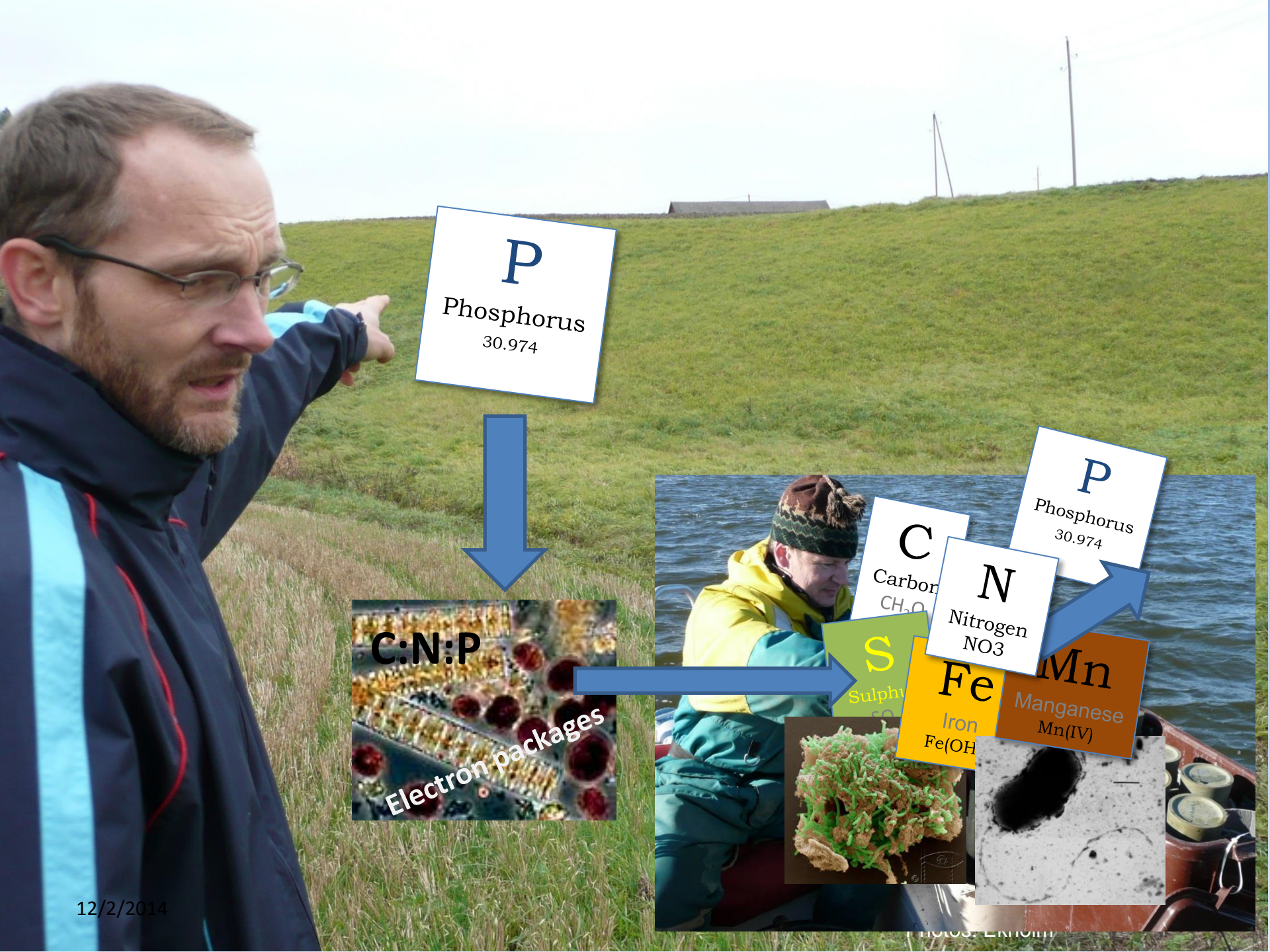
Eutrophy



Lehtoranta, Ekholm & Pitkänen 2008.  
(J. Mar. Syst. 74:495-504)

Data: PAPA Partners  
Figure: Mikko Kiirikki/SYKE





**P**  
Phosphorus  
30.974



**C:N:P**  
Electron packages



**C**  
Carbon  
 $\text{CH}_2\text{O}$

**N**  
Nitrogen  
 $\text{NO}_3$

**P**  
Phosphorus  
30.974

**S**  
Sulphur  
 $\text{SO}_4$

**Fe**  
Iron  
 $\text{Fe}(\text{OH})_3$

**Mn**  
Manganese  
 $\text{Mn(IV)}$

PHOTOSYNTHESIS



# Summary

- Eutrophication increases mineralization
- All terminal electron acceptors used produce  $\text{CO}_2$
- Reduced substances formed in the mineralization participate to further redox-reactions ( $\text{Mn(II)}$ ,  $\text{Fe(II)}$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ )
- They have different consequences on the element cycles in the system
- So "if you have an extra electron where do you put it", depends what you are trying to get

# Thank you

