Does agri-environmental erosion control abate coastal eutrophication?

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(SYKE)

COST869 Mitigation options for nutrient reduction in surface waters and groundwaters
Working group 2: Influence of nutrients on ecological processes in surface waters

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Geobacter metallireducens, http://www.geobacter.org/

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Photo: Pasi Valkama

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Pilayella
Photo: Seppo Knuuttila/SYKE

Fe reduction

SO_4 reduction

Photos: Seppo Knuuttila, Jouni Lehtoranta, SYKE

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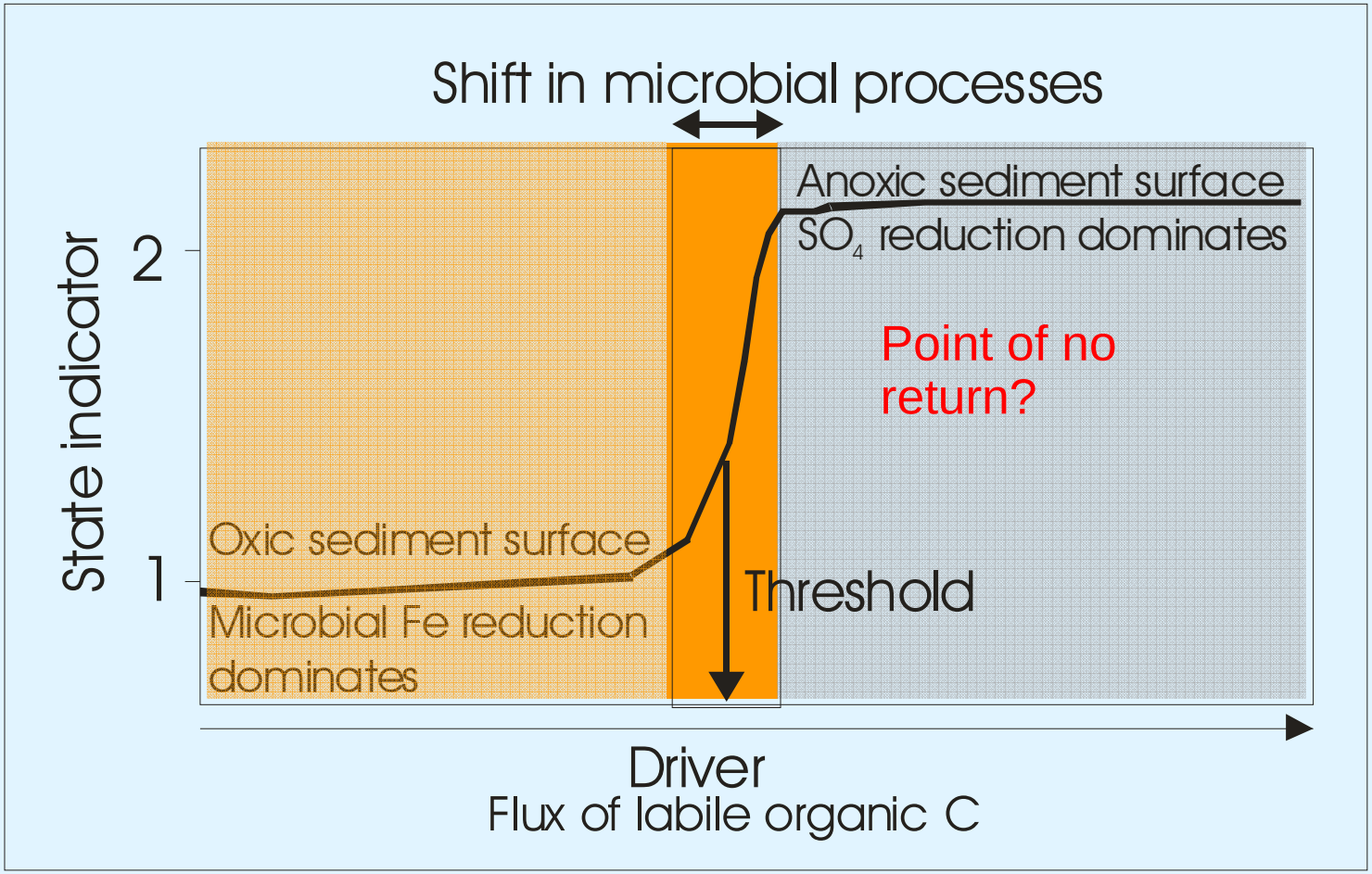
Regime shift



Lehtoranta, Ekholm & Pitkänen (Ambio, in press)

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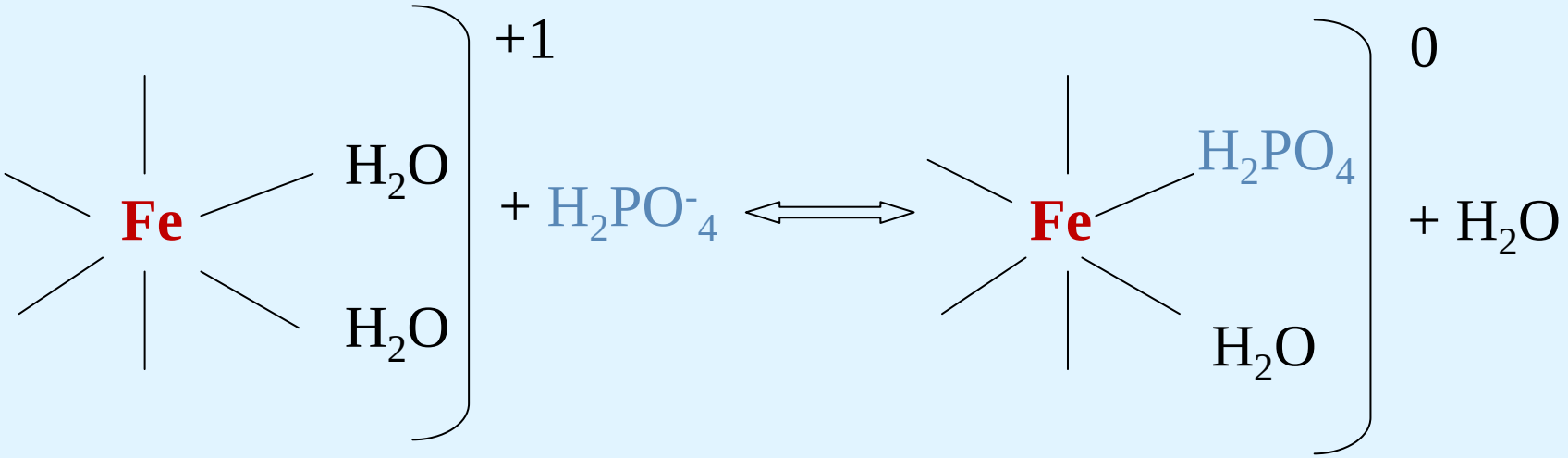
Soil erosion and eutrophication

Current paradigm: Fe(III) oxides as P binding agents

- Based on soil chemistry
  - "Specific ligand exchange theory"
- Eroded soil transported from fields rich in labile P
  - P added to soil is (at least partly) reversibly (ad)sorbed to soil particles, and
  - ... can be desorbed in P deficient surface waters
  - P-release may be strongly increased on reduction of Fe oxides in anaerobic sediments



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Practical implication

- To control P losses, farmers worldwide have e.g.
  - adopted reduced tillage, no-till, contour cropping and cover crops
  - established buffer strips and riparian zones
  - constructed settling ponds and wetlands

- **Not a single study has shown that controlling erosion abates eutrophication**

Soil erosion and eutrophication

An alternative view: Fe(III) oxides as electron acceptors

- Based on recent developments in sediment microbiology and element cycling
- Iron oxides (and clay) in eroded soil may **counteract** the eutrophying effect of P ...
  - ... in sulphidic eutrophic systems, such as coastal waters characterized by strong benthic release of P
- If so, erosion control as an agri-environmental measure should be re-evaluated
- **This hypothesis is not confirmed either**

Benthic P-release and sediment mineralization processes

- In marine anaerobic sediments, the major oxidative pathways are
  - (1) dissimilatory Fe reduction, where solid Fe(III) oxides are reduced by microbes to dissolved ferrous iron (Fe^{2+})
  - (2) dissimilatory sulfate reduction, where SO_4^{2-} is reduced by microbes to HS^- or hydrogen sulfide (H_2S)
- Benthic P-release strongly accelerated with the onset of sulphate reduction in surface sediment layer
- Fe reduction may dominate when there are
  - Microbially available Fe(III) oxides
  - An oxic sediment surface enabling re-oxidation of reduced Fe(II)
  - Bottom animals causing bioturbation
- SO_4 reduction may dominate when
  - Fe(III) oxides are consumed
  - There is plenty of labile organic matter in sediments
  - Sediment surface is anoxic (no renewal of Fe(III) oxides)

Roden and Edmonds (1997)

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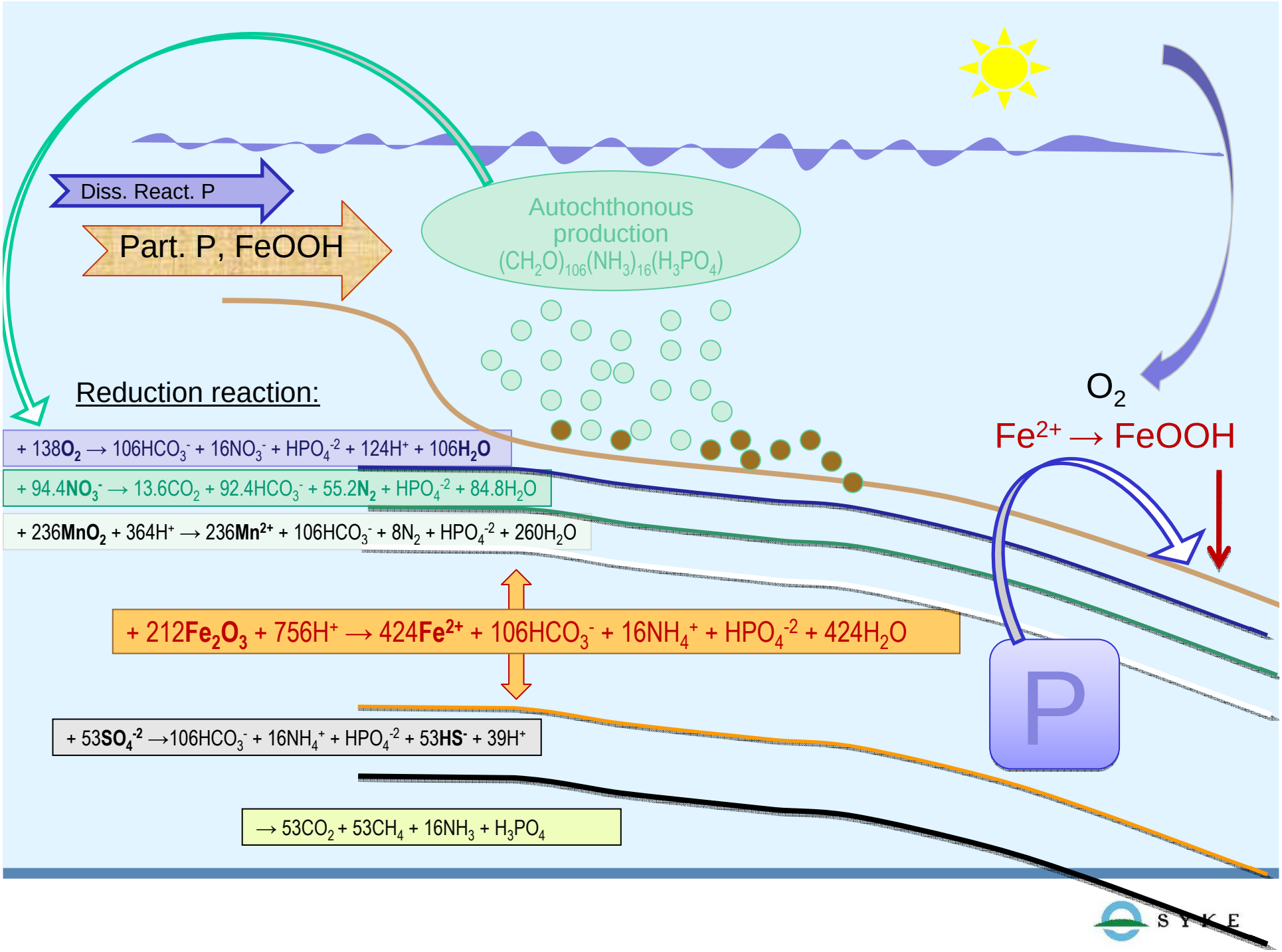
Origin of Fe(III) oxides

- Fe enters the coastal waters from the catchment
- Concentrations of total Fe in riverine suspended solids:
  - 6.1–6.5% (Finnish agricultural rivers, Mäkiaho 2007)
  - 2.7–7.3% (USA, Canfield 1997)
  - 4.8% (Worlds major rivers, Martin & Meybeck 1979)
  - Fe is present in soil e.g.
  - In silicates (largely inert)
  - As poorly crystallized oxides (microbially reactive)
  - As crystalline oxides (sulphide reactive)
  - Practically all of the global riverine flux of sulphide-reactive Fe is in a particulate form (Canfield, 1989).
  - EROSION!


Diss. React. P
Part. P, FeOOH
Autochthonous production
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$
Reduction reaction:
$+ 138\mathbf{O_2} \rightarrow 106HCO_3^- + 16NO_3^- + HPO_4^{-2} + 124H^+ + 106\mathbf{H_2O}$
$+ 94.4\mathbf{NO_3^-} \rightarrow 13.6CO_2 + 92.4HCO_3^- + 55.2\mathbf{N_2} + HPO_4^{-2} + 84.8H_2O$
$+ 236\mathbf{MnO_2} + 364H^+ \rightarrow 236\mathbf{Mn^{2+}} + 106HCO_3^- + 8N_2 + HPO_4^{-2} + 260H_2O$
$+ 212\mathbf{Fe_2O_3} + 756H^+ \rightarrow 424\mathbf{Fe^{2+}} + 106HCO_3^- + 16NH_4^+ + HPO_4^{-2} + 424H_2O$
$+ 53\mathbf{SO_4^{-2}} \rightarrow 106HCO_3^- + 16NH_4^+ + HPO_4^{-2} + 53\mathbf{HS^-} + 39H^+$
$\rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$
O_2
$Fe^{2+} \rightarrow FeOOH$
P
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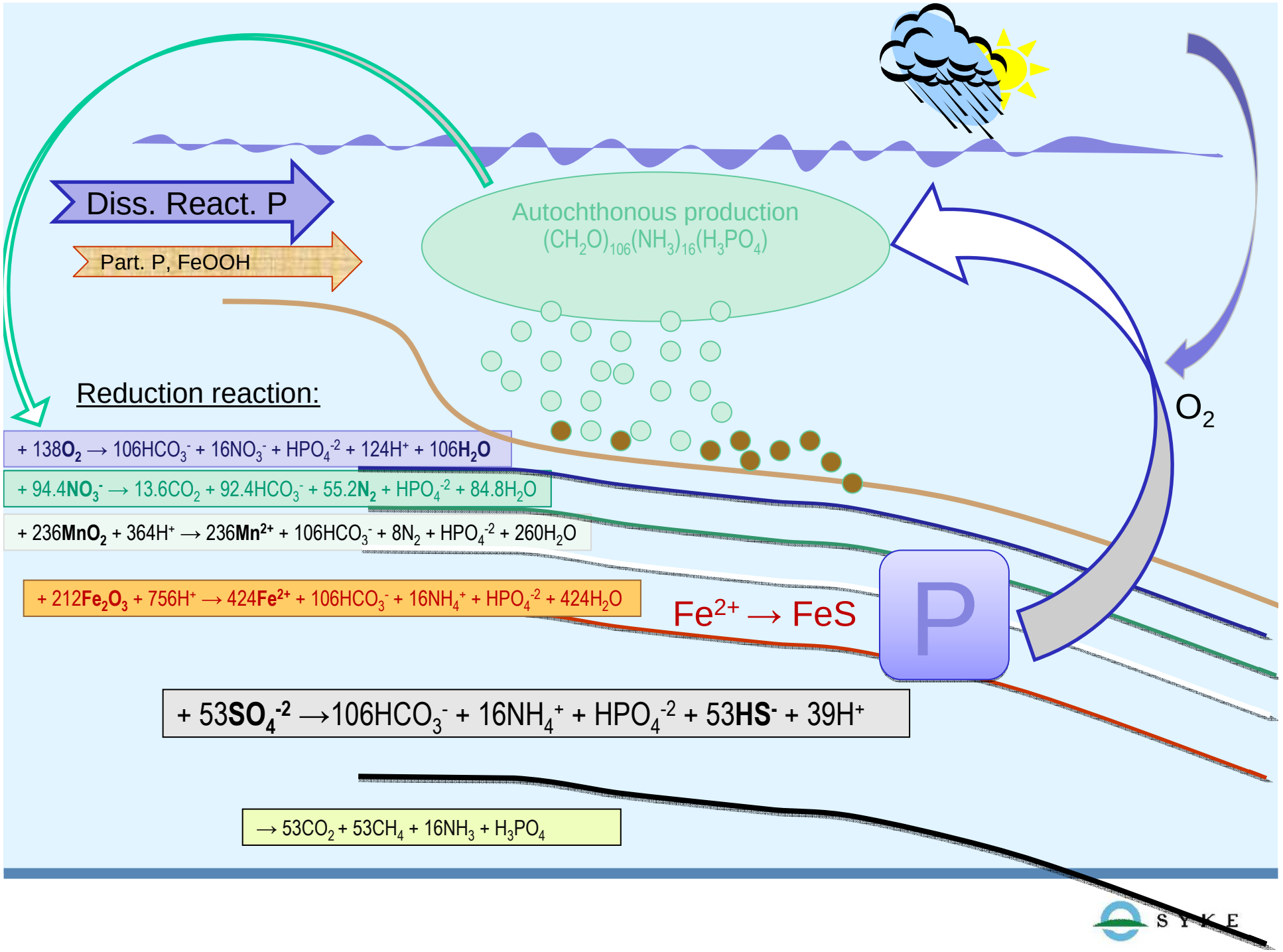
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$Fe^{2+} \rightarrow FeS$
P
$+ 53\mathbf{SO_4^{-2}} \rightarrow 106HCO_3^- + 16NH_4^+ + HPO_4^{-2} + 53\mathbf{HS^-} + 39H^+$
$\rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$
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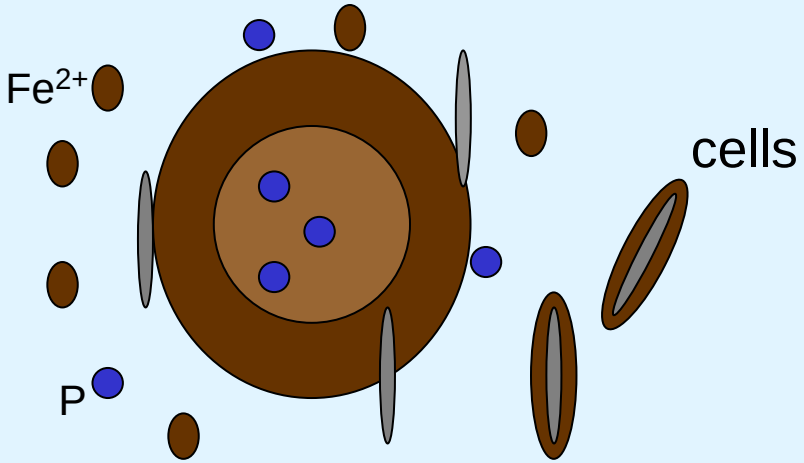
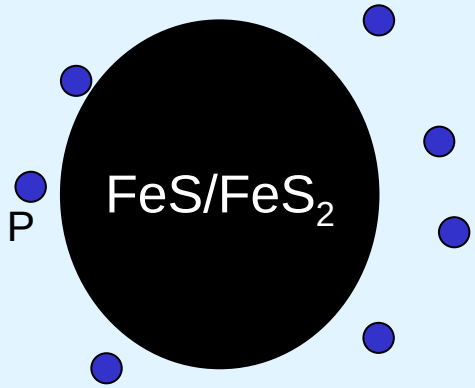
Difference between microbial and chemical reduction



Microbial Fe(III) oxide reduction



Chemical Fe(III) oxide reduction

$2FeOOH + 3H_2S + 4H^+ \rightarrow 2FeS + S^0 + 4H_2O$,
with possibly a further reaction to pyrite:

$FeS + S^0 \longrightarrow FeS_2$

Roden EE, Urrutia MM, 2002

Berner RA, 1974

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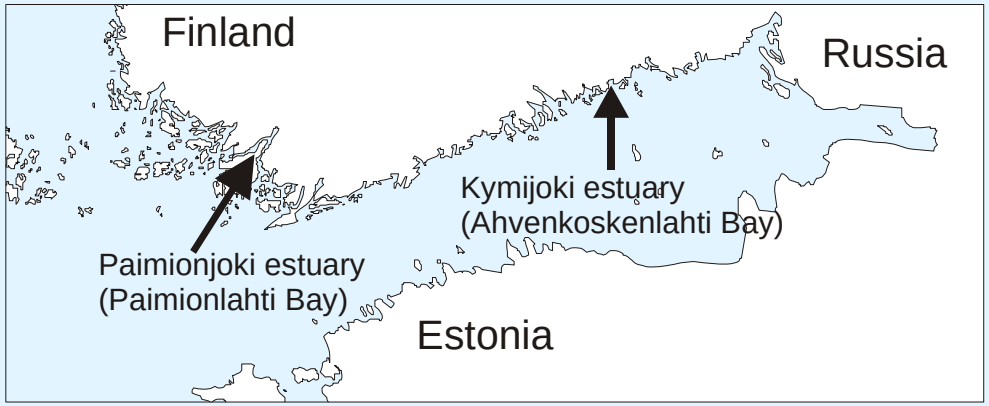

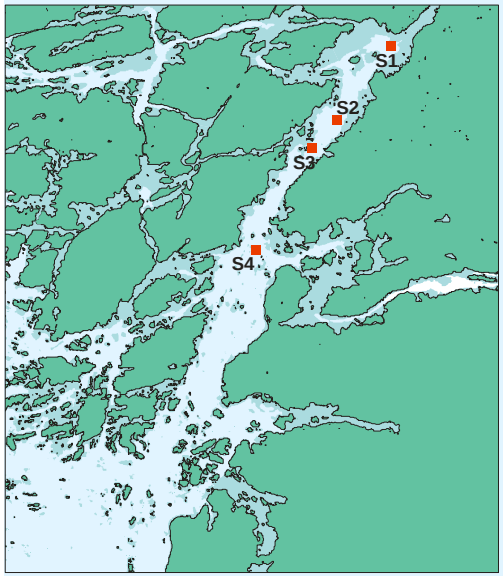

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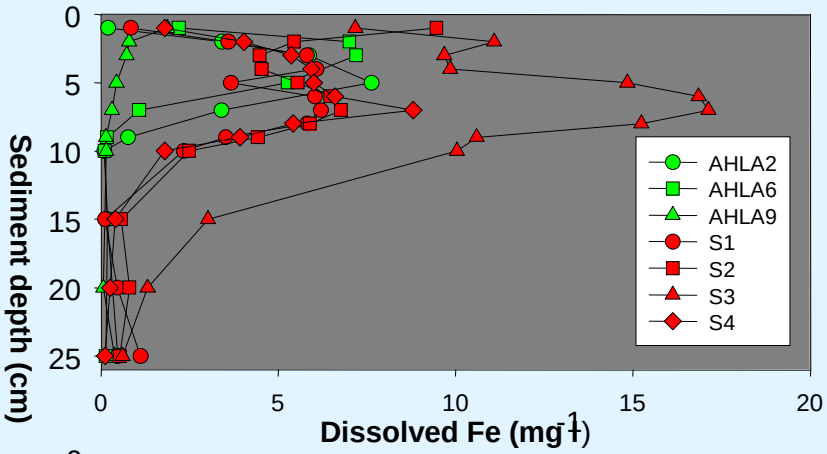

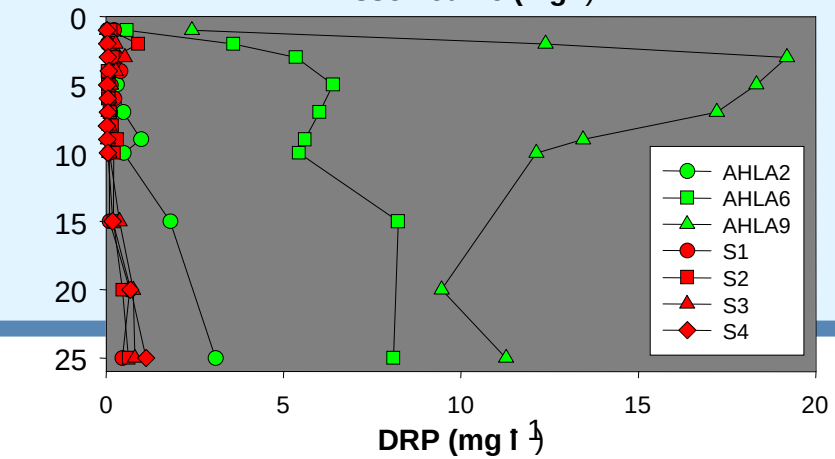

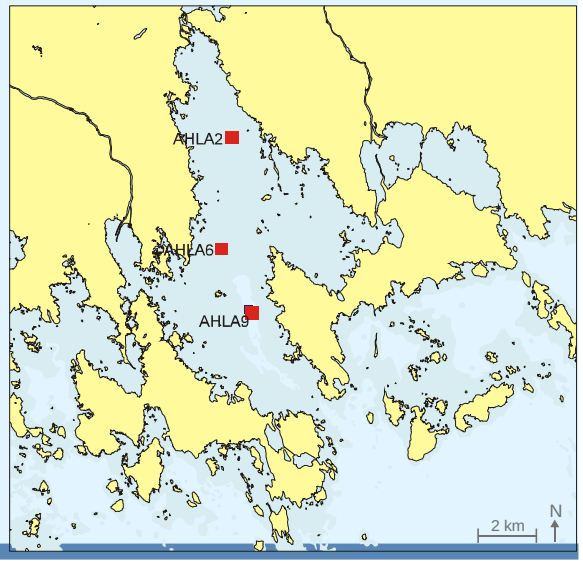

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Day 16: Clay + acetate and lactate + sulphate

Day 23: Clay + acetate and lactate + sulphate

Conclusions

- Fe(III) oxides in eroded soil may promote favourable and suppress adverse sediment mineralization pathways
- Their role in respiration should be elucidated in different types of waters
  - Sulphate concentration (coastal waters, lakes)
  - Hydromorphology (salinity stratification)
  - Trophic status
- Crucial variable: the ratio of algal-available P to microbially available Fe?
- Apart from eutrophication Fe oxides may play an important role in other environmental problems