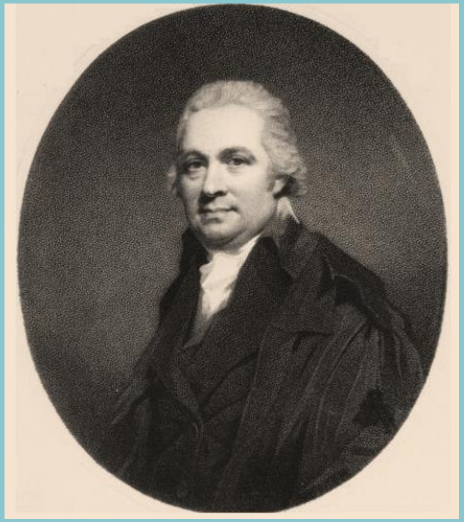
2. Nutrients and their processes

'The Discovery of Phosphorus' by Joseph Wright (1734–1797)

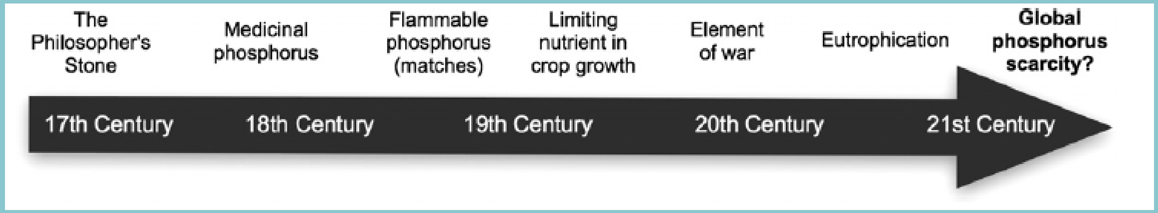
Alchemist Hennig Brand 1699



Nitrogen discovered by Daniel Rutherford in 1772

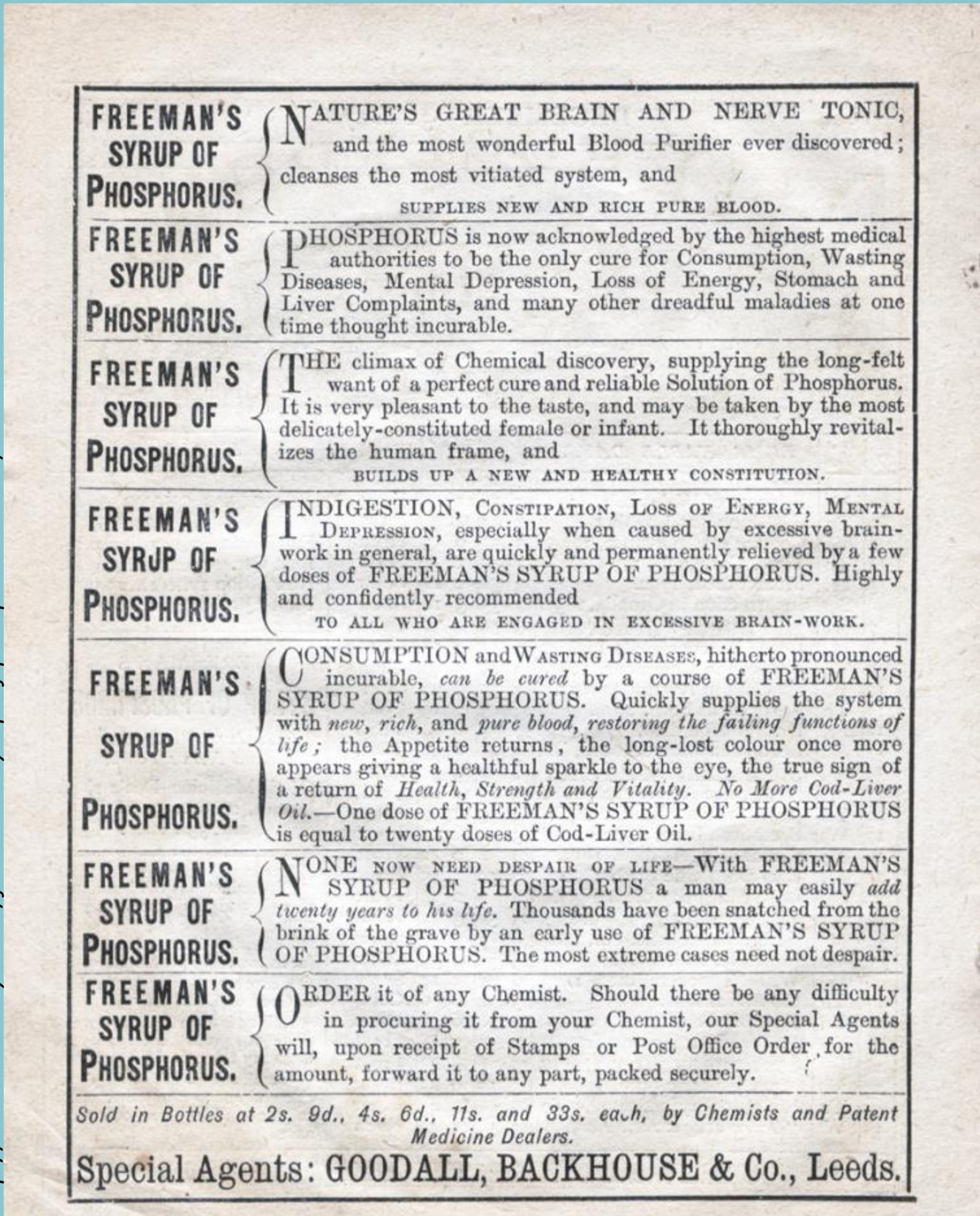
Phosphorus (P)

- *Phos* = light, *phorus* = bearer (Greek)
- Apatite
  - 79% of mined P used for fertilizers
  - Other industry 11%
  - Food and feed 5%
  - Detergents 3%
  - Other 2%
- Concentration in Earth's crust 0.1%
- Plants 0.3–0.4% DW
- Humans 1.1% (about 700 g ind^{-1})



http://phosphorusfutures.net/the-phosphorus-challenge/the-story-of-phosphorus-8-reasons-why-we-need-to-rethink-the-management-of-phosphorus-resources-in-the-global-food-system/

Do we get too much P in diet?



FREEMAN'S SYRUP OF PHOSPHORUS.

NATURE'S GREAT BRAIN AND NERVE TONIC, and the most wonderful Blood Purifier ever discovered; cleanses the most vitiated system, and SUPPLIES NEW AND RICH PURE BLOOD.

FREEMAN'S SYRUP OF PHOSPHORUS.

PHOSPHORUS is now acknowledged by the highest medical authorities to be the only cure for Consumption, Wasting Diseases, Mental Depression, Loss of Energy, Stomach and Liver Complaints, and many other dreadful maladies at one time thought incurable.

FREEMAN'S SYRUP OF PHOSPHORUS.

THE climax of Chemical discovery, supplying the long-felt want of a perfect cure and reliable Solution of Phosphorus. It is very pleasant to the taste, and may be taken by the most delicately-constituted female or infant. It thoroughly revitalizes the human frame, and BUILDS UP A NEW AND HEALTHY CONSTITUTION.

FREEMAN'S SYRUP OF PHOSPHORUS.

INDIGESTION, CONSTIPATION, LOSS OF ENERGY, MENTAL DEPRESSION, especially when caused by excessive brain-work in general, are quickly and permanently relieved by a few doses of FREEMAN'S SYRUP OF PHOSPHORUS. Highly and confidently recommended TO ALL WHO ARE ENGAGED IN EXCESSIVE BRAIN-WORK.

FREEMAN'S SYRUP OF PHOSPHORUS.

CONSUMPTION and WASTING DISEASES, hitherto pronounced incurable, *can be cured* by a course of FREEMAN'S SYRUP OF PHOSPHORUS. Quickly supplies the system with *new*, *rich*, and *pure blood*, *restoring the failing functions of life*; the Appetite returns, the long-lost colour once more appears giving a healthful sparkle to the eye, the true sign of a return of *Health, Strength and Vitality*. *No More Cod-Liver Oil.*—One dose of FREEMAN'S SYRUP OF PHOSPHORUS is equal to twenty doses of Cod-Liver Oil.

FREEMAN'S SYRUP OF PHOSPHORUS.

NONE NOW NEED DESPAIR OF LIFE—With FREEMAN'S SYRUP OF PHOSPHORUS a man may easily *add twenty years to his life*. Thousands have been snatched from the brink of the grave by an early use of FREEMAN'S SYRUP OF PHOSPHORUS. The most extreme cases need not despair.

FREEMAN'S SYRUP OF PHOSPHORUS.

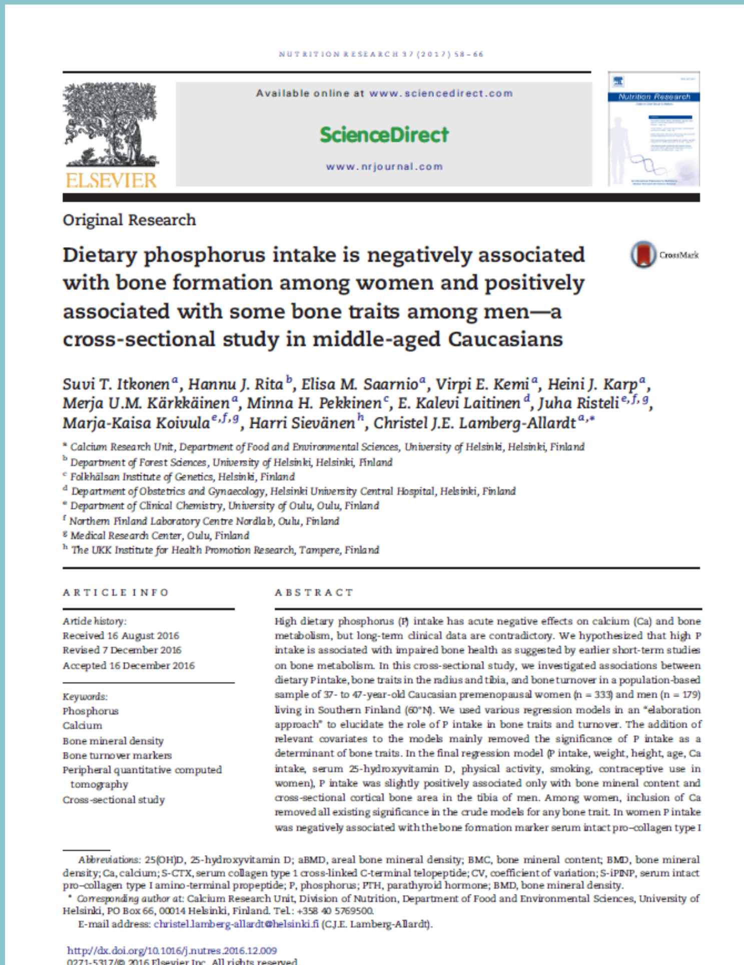
ORDER it of any Chemist. Should there be any difficulty in procuring it from your Chemist, our Special Agents will, upon receipt of Stamps or Post Office Order for the amount, forward it to any part, packed securely.

Sold in Bottles at 2s. 9d., 4s. 6d., 11s. and 33s. each, by Chemists and Patent Medicine Dealers.

Special Agents: GOODALL, BACKHOUSE & Co., Leeds.

http://skittishlibrary.co.uk/freemans-syrup-of-phosphorus-1884/

An English advertisement in 1884



NUTRITION RESEARCH 37 (2017) 58–66

Available online at www.sciencedirect.com

ScienceDirect

www.nrjournal.com

Original Research

Dietary phosphorus intake is negatively associated with bone formation among women and positively associated with some bone traits among men—a cross-sectional study in middle-aged Caucasians

Suvi T. Itkonen[a], *Hannu J. Rita*[b], *Elisa M. Saarnio*[a], *Virpi E. Kemi*[a], *Heini J. Karp*[a], *Merja U.M. Kärkkäinen*[a], *Minna H. Pekkinen*[c], *E. Kalevi Laitinen*[d], *Juha Risteli*[e,f,g], *Marja-Kaisa Koivula*[e,f,g], *Harri Sievänen*[h], *Christel J.E. Lamberg-Allardt*[a,*]

[a] *Calcium Research Unit, Department of Food and Environmental Sciences, University of Helsinki, Helsinki, Finland*
[b] *Department of Forest Sciences, University of Helsinki, Helsinki, Finland*
[c] *Folkhälsan Institute of Genetics, Helsinki, Finland*
[d] *Department of Obstetrics and Gynaecology, Helsinki University Central Hospital, Helsinki, Finland*
[e] *Department of Clinical Chemistry, University of Oulu, Oulu, Finland*
[f] *Northern Finland Laboratory Centre Nordlab, Oulu, Finland*
[g] *Medical Research Center, Oulu, Finland*
[h] *The UKK Institute for Health Promotion Research, Tampere, Finland*

ARTICLE INFO

Article history:
Received 16 August 2016
Revised 7 December 2016
Accepted 16 December 2016

Keywords:
Phosphorus
Calcium
Bone mineral density
Bone turnover markers
Peripheral quantitative computed tomography
Cross-sectional study

ABSTRACT

High dietary phosphorus (P) intake has acute negative effects on calcium (Ca) and bone metabolism, but long-term clinical data are contradictory. We hypothesized that high P intake is associated with impaired bone health as suggested by earlier short-term studies on bone metabolism. In this cross-sectional study, we investigated associations between dietary P intake, bone traits in the radius and tibia, and bone turnover in a population-based sample of 37- to 47-year-old Caucasian premenopausal women (n = 333) and men (n = 179) living in Southern Finland (60°N). We used various regression models in an "elaboration approach" to elucidate the role of P intake in bone traits and turnover. The addition of relevant covariates to the models mainly removed the significance of P intake as a determinant of bone traits. In the final regression model (P intake, weight, height, age, Ca intake, serum 25-hydroxyvitamin D, physical activity, smoking, contraceptive use in women), P intake was slightly positively associated only with bone mineral content and cross-sectional cortical bone area in the tibia of men. Among women, inclusion of Ca removed all existing significance in the crude models for any bone trait. In women P intake was negatively associated with the bone formation marker serum intact pro–collagen type I

Abbreviations: 25(OH)D, 25-hydroxyvitamin D; aBMD, areal bone mineral density; BMC, bone mineral content; BMD, bone mineral density; Ca, calcium; S-CTX, serum collagen type 1 cross-linked C-terminal telopeptide; CV, coefficient of variation; S-iPINP, serum intact pro–collagen type I amino-terminal propeptide; P, phosphorus; PTH, parathyroid hormone; BMD, bone mineral density.

* *Corresponding author at:* Calcium Research Unit, Division of Nutrition, Department of Food and Environmental Sciences, University of Helsinki, PO Box 66, 00014 Helsinki, Finland. Tel.: +358 40 5769500.
E-mail address: christel.lamberg-allardt@helsinki.fi (C.J.E. Lamberg-Allardt).

http://dx.doi.org/10.1016/j.nutres.2016.12.009

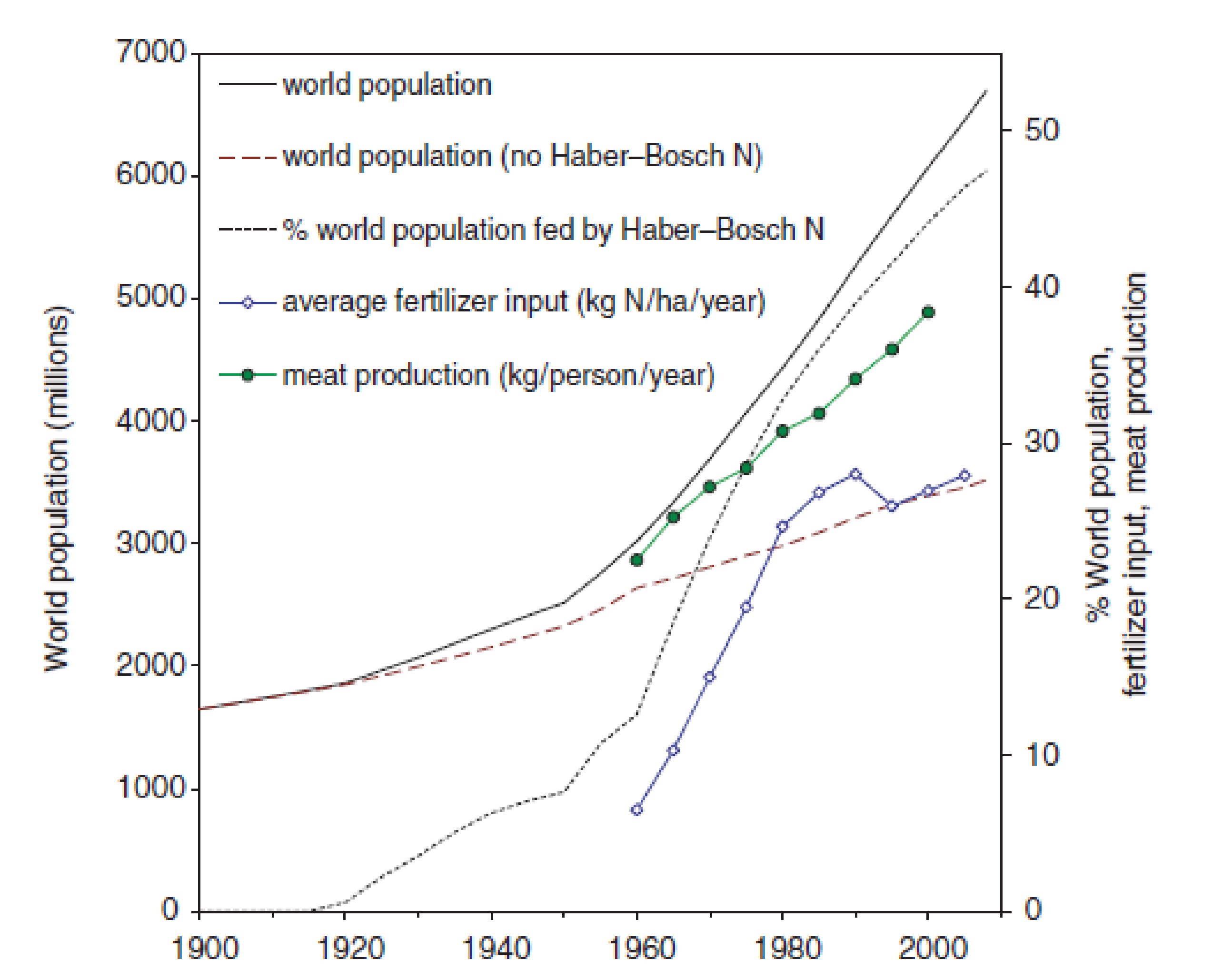
Nitrogen (N)

- No major geological source
- Concentration in Earth's crust 0.002%
- Synthesis of ammonia (Fritz Haber, Nobel 1918)

  $N_2 + 3\ H_2 \leftrightarrow 2\ NH_3$

  - Requires a lot of energy
- Production of 'reactive N'
  - 1860: 15 Tg y^{-1} N
  - 1990: 156 Tg y^{-1} N
  - More than 100 Tg y^{-1} N in fertilizers
- Plants <2% DW
  - Plants take up NO_3^- and NH_4^+
- Humans 2.6 %

Nitrogen fertilizers and world population



Sutton et al. (2011)

Apatite mineral
$Ca_{10}(X)(PO_4)_6$, $X = 2OH^-, 2F^-, 2Cl^-, CO_3^{2-}$

απατείν (apatein, Greek) = to deceive or to be misleading

1. **Magmatic apatite**
   - **Russia, Finland, South Africa, Zimbabwe, Brazil**
   - **Weak fertilizer value as such, mycorrhizae can solubilize to small extent**
   - **Finnish (young) soils contain a high concentration of apatite**

2. **Sedimentary apatite**
   - **80% of production**
   - **USA (Florida), Morocco, China**
   - **Higher reactivity**
   - **Cd, U**

Apatity, Russia

Western Sahara

https://www.theatlantic.com/science/archive/2016/11/the-desert-rock-that-feeds-the-world/508853/ + Wkipedia

Phosphoric acid and its anions

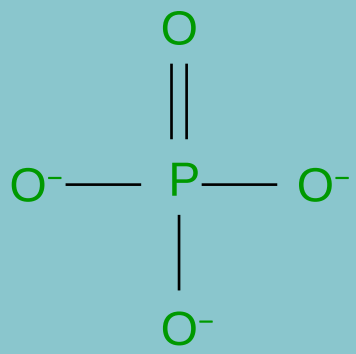
Orthophosphoric acid

- **Weak triprotic acid**

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \quad (pK_a = 2.12)$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \quad (pK_a = 7.21)$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-} \quad (pK_a = 12.67)$$

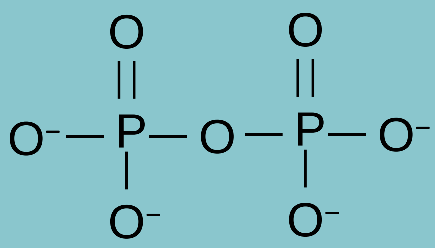


Anion of phosphoric acid = dissolved orthophosphate

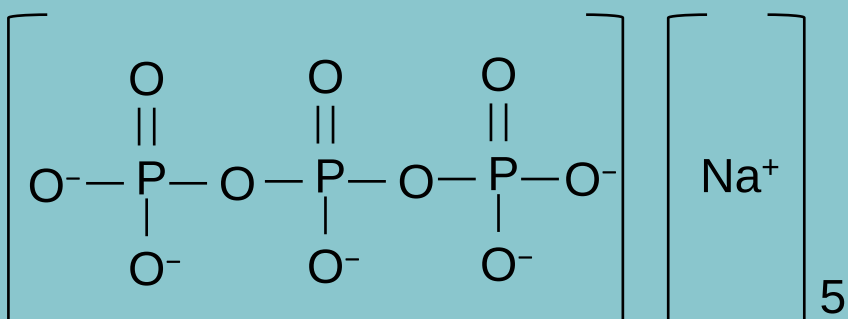
- **The only P-compound that ubiquitously can pass the cell wall, that is the only directly available P form**
- **Highly reactive**

Other P-compounds

Phosphate can be condensed:

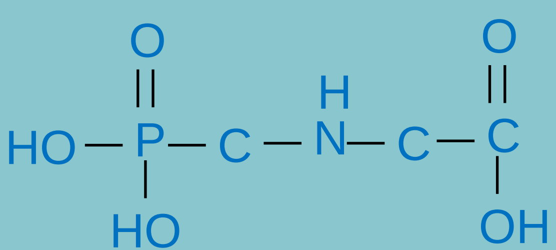


Pyrophosphate



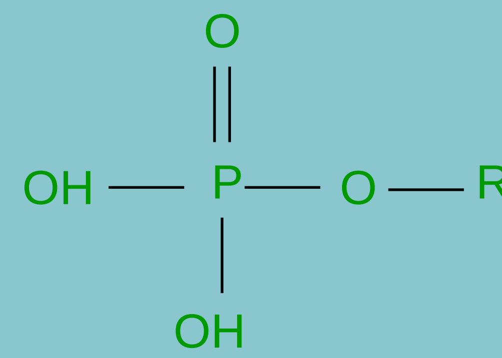
Sodiumtripolyphosphate

Form P–C bonds:



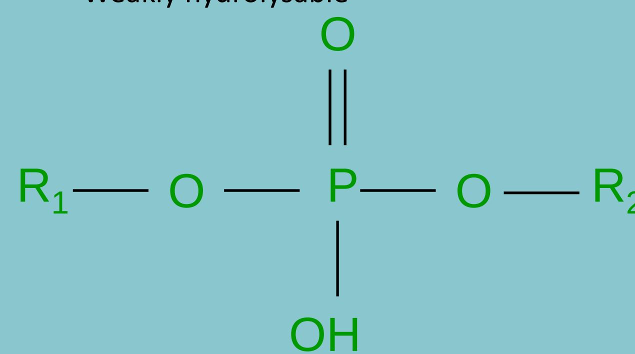
Glyphosate – a phosphonate

Bind with an organyl group:



Phosphate monoester (P–O–C)

- E.g. phytic acid
- Weakly hydrolysable

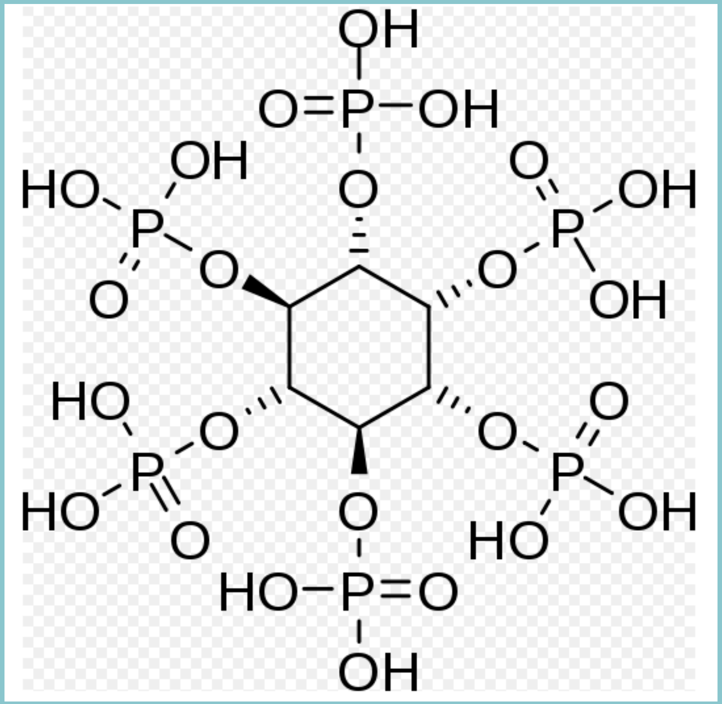


Phosphate diester (C–O–P–O–C)

- E.g. nucleotides and phospholipides
- Easily hydrolysable

Phytic acid (myo-inositol hexakis phosphoric acid)

- Salts of phytic acid: phytates
- Storage form of P in bran and seeds
- Stable, weakly hydrolysable monoester
- Fungi can exrete phytase and utilise inositol P
- Nonruminants cannot utilise, only rumen microorganism produce phytase
- Can be bound to same sorption sites as orhophosphate

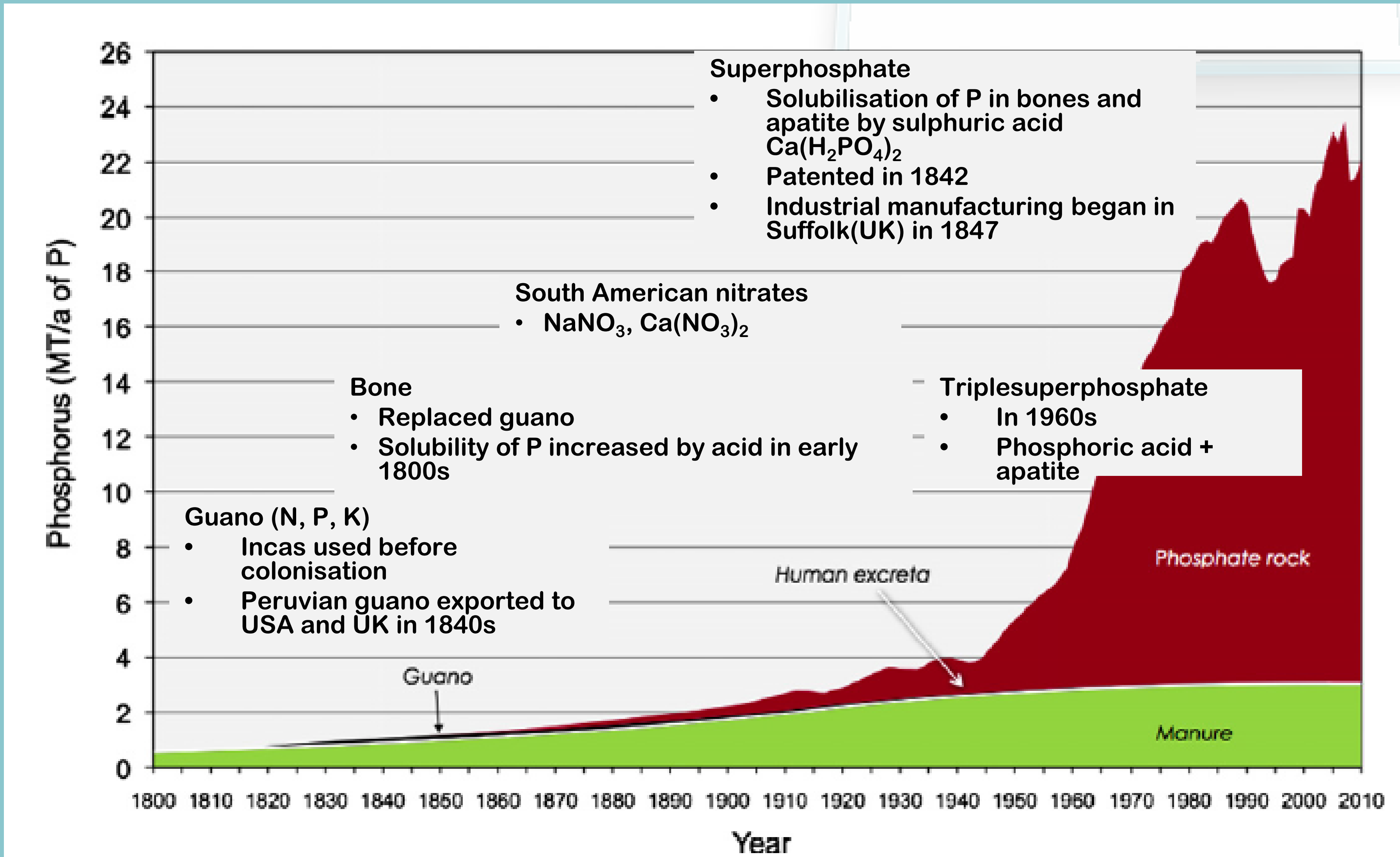


Wikipedia

Phosphates in detergents

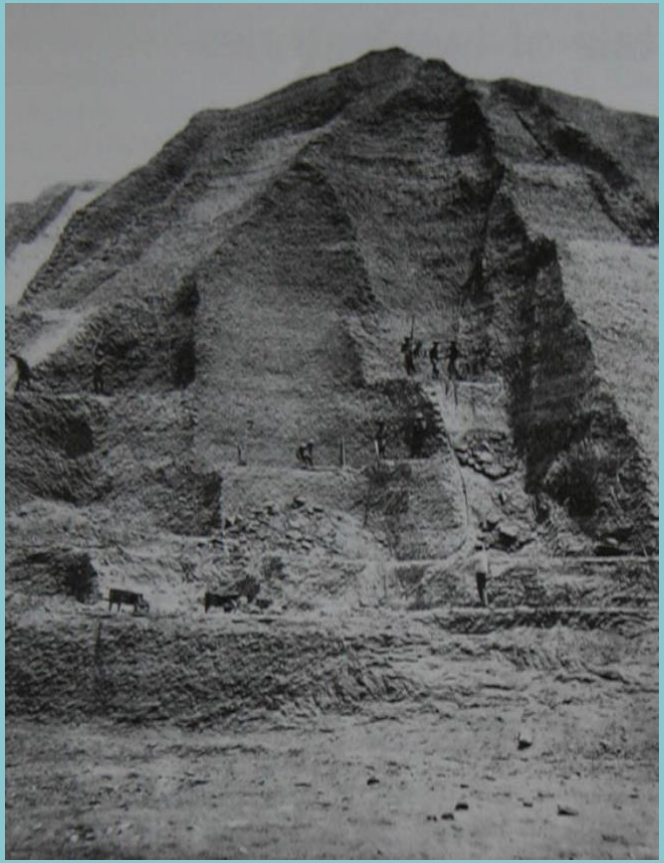
- Sodium tripolyphosphate ($Na_5P_3O_{10}$)
  - Chelates Ca^{2+} and Mg^{2+}, which would react with surfactants, ”water softener”
  - Used to be as much as 40% of ingredients
  - Hydrolyses easily to orthophosphate
- EU regulation
  - No phosphate in laundry detergents for consumer use after 30.6.2013
  - No phosphate in dish machine detergents for consumer use after 1.1.2017
- Phosphate replaced by zeolite, citrate, polycarboxylates, phosphonates
- SCOPE Newsletter
  - http://phosphorusplatform.eu/

Phosphorus fertilizers

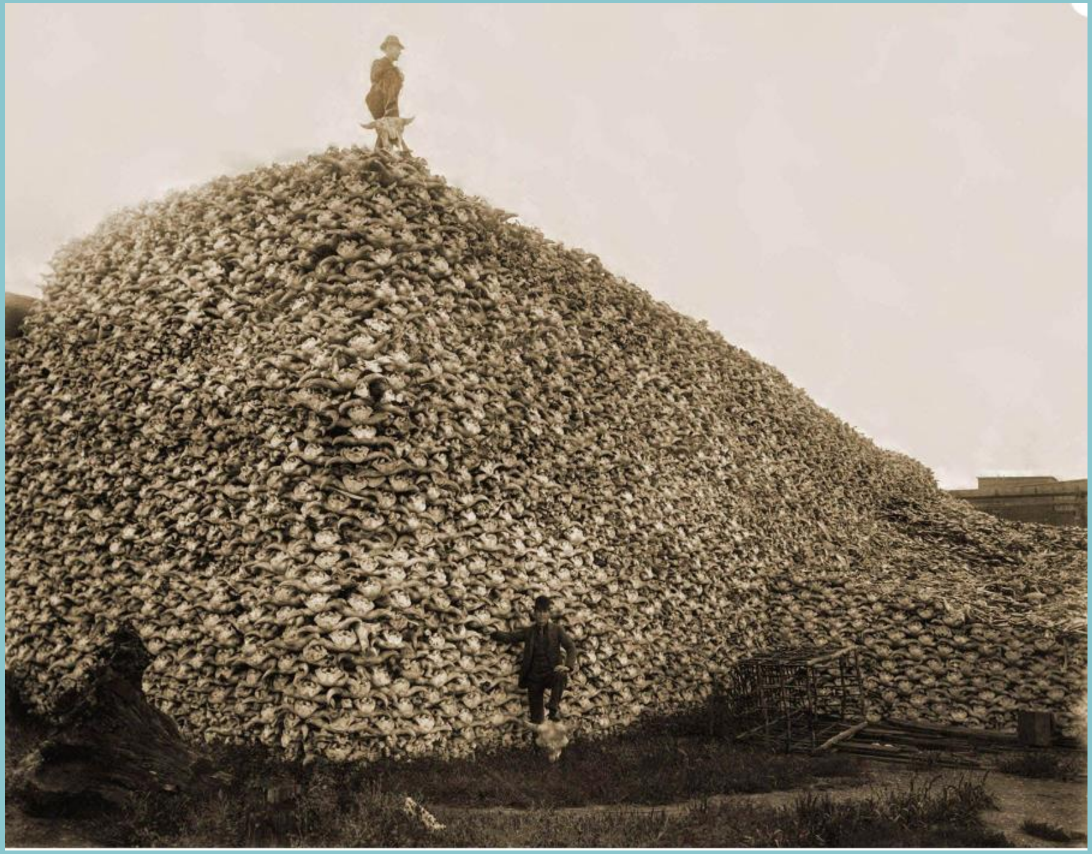


Ashley et al. (2011)

Ancient P sources



Guano mine in Peru in about 1860 (Wikipedia)



Skulls of bisons for manufacturing fertilizers in 1870s
(https://rarehistoricalphotos.com/bison-skulls-pile-used-fertilizer-1870/)

Future P sources?

- Mineable P reserves will last for 40–400–X years
- China forbade P export in 2008, price of rock P increased by 700%
- EU has defined P as a critical raw material

”Trilemma” (Obersteiner et al. 2013)

1. Rich P consumers
   - Use too much P
   - Try to secure import
2. Poor and food unsecure P consumers
   - 30% cultivated land suffers from P deficiency
3. P producers
   - Known reserves: Morocco 75%, China 6%, Algeria 3.3 %, Syria 2.7 %, South Africa 2.2 %, Russia 1.9%, Jordan 1.9%, USA 1.6% (USGS 2015)
   - Try to control the price of P
   - High price would secure P reserves but cause problems for the developing countries

➢ P reserves should be known better, P should be used in moderation and recycled

Siilinjärvi open mine – The only phosphate mine in western Europe



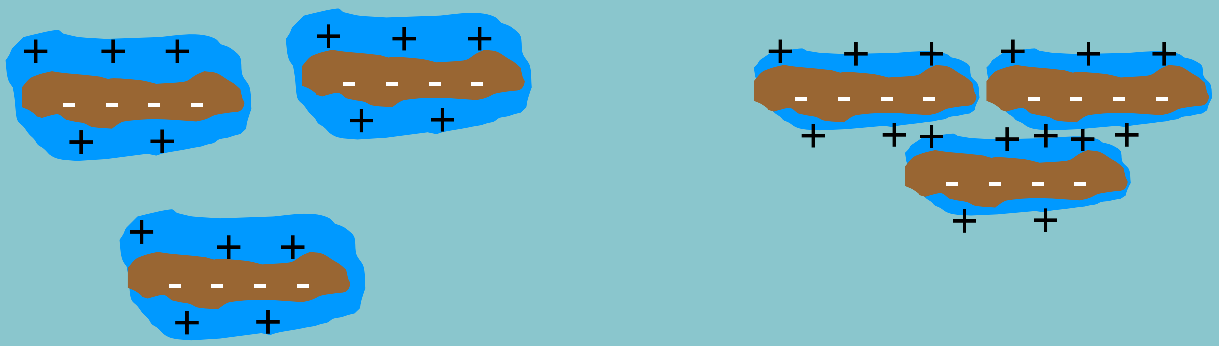


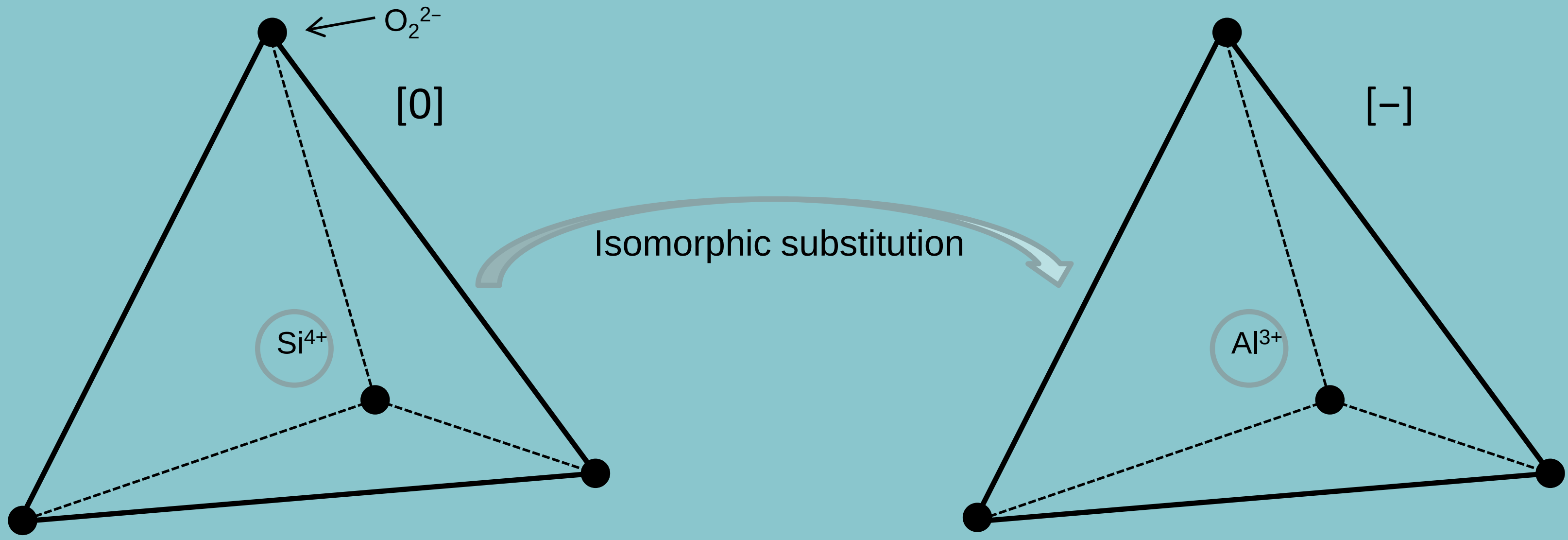

14

Gypsum heap in Siilinjärvi ($CaSO_4 \cdot 2H_2O$)

$$Ca_5(PO_4)_3X + 5\ H_2SO_4 + 10\ H_2O \rightarrow 3\ H_3PO_4 + 5\ CaSO_4 \cdot 2\ H_2O + HX$$

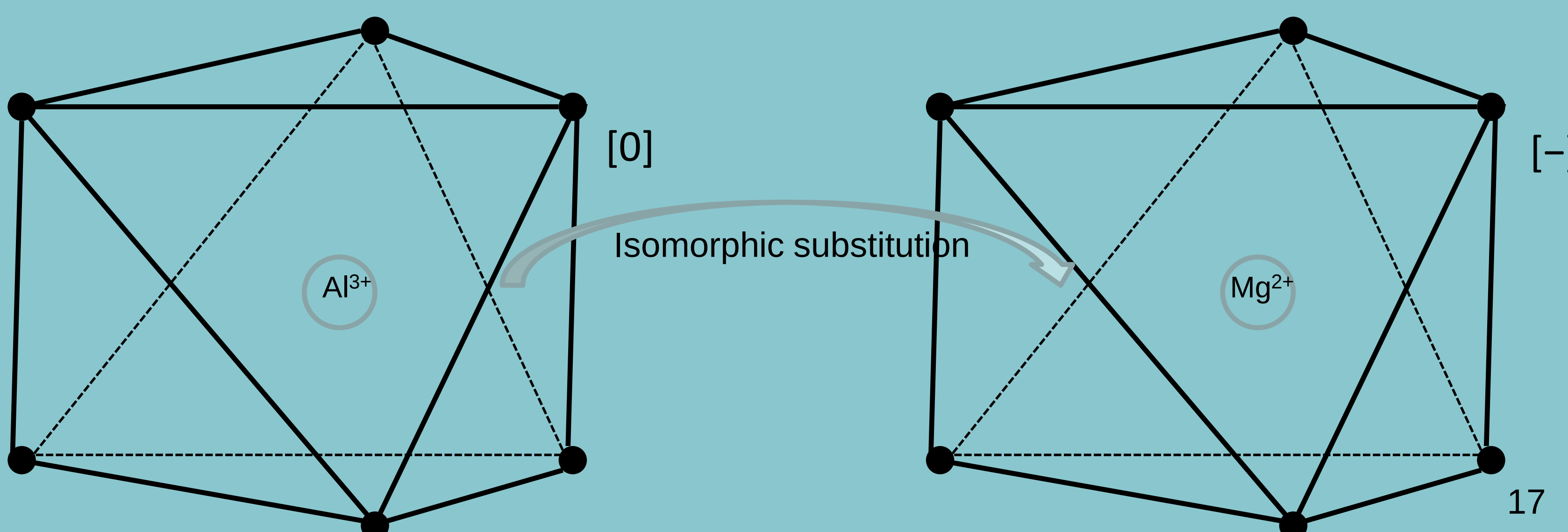
Soil particles are negatively charged…





Silicon tetrahedron

…due to isomorphic substitution



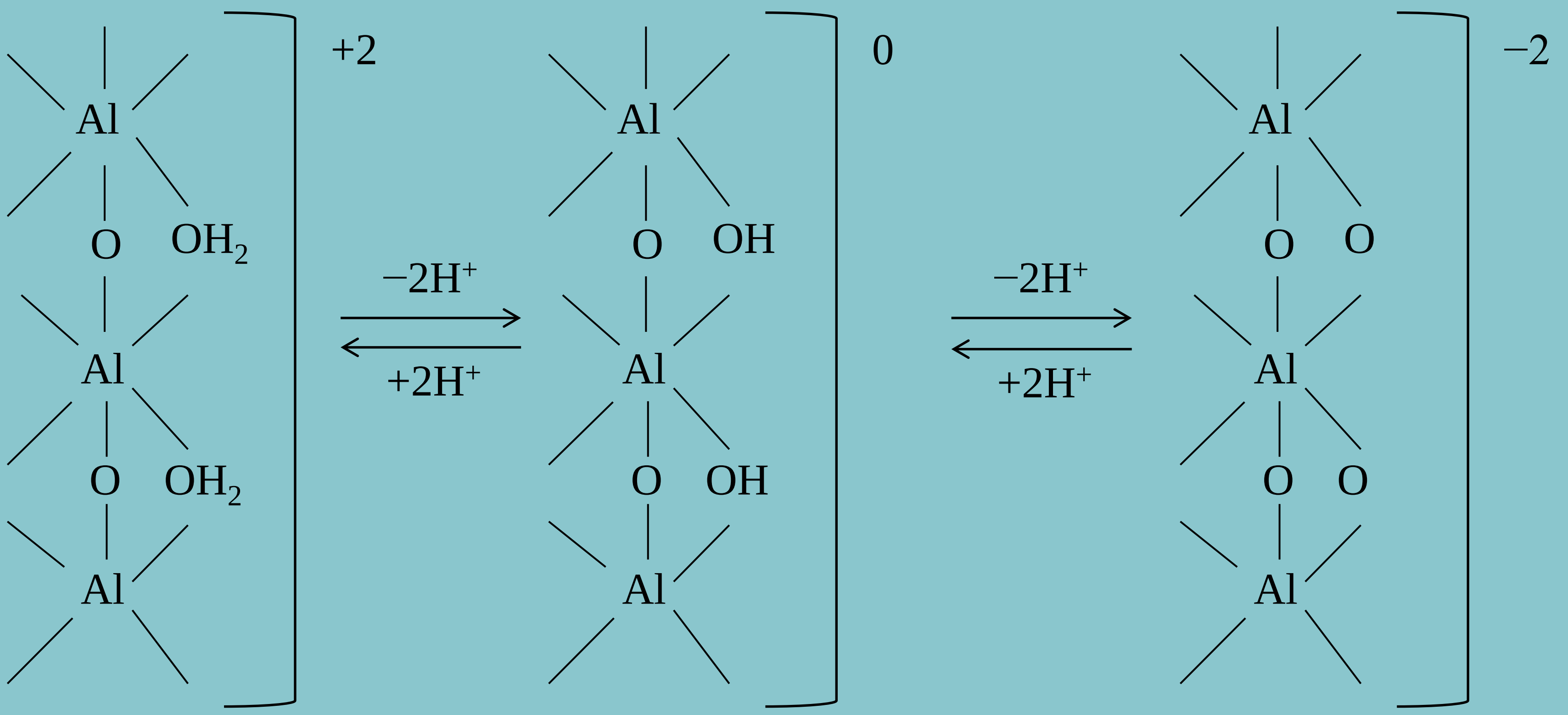
Aluminium octahedron

Recap I

- What is apatite?
  - $Ca_{10}(X)(PO_4)_6$, X = $2OH^-$, $2F^-$, $2Cl^-$, CO_3^{2-}
- Orthophosphoric acid?
  - H_3PO_4
- Dissolved orthophosphate?
  - $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}
- Why it is important?
  - Only P-compound that passes the cell wall
- What is the charge of soil particles?
  - Mostly negative

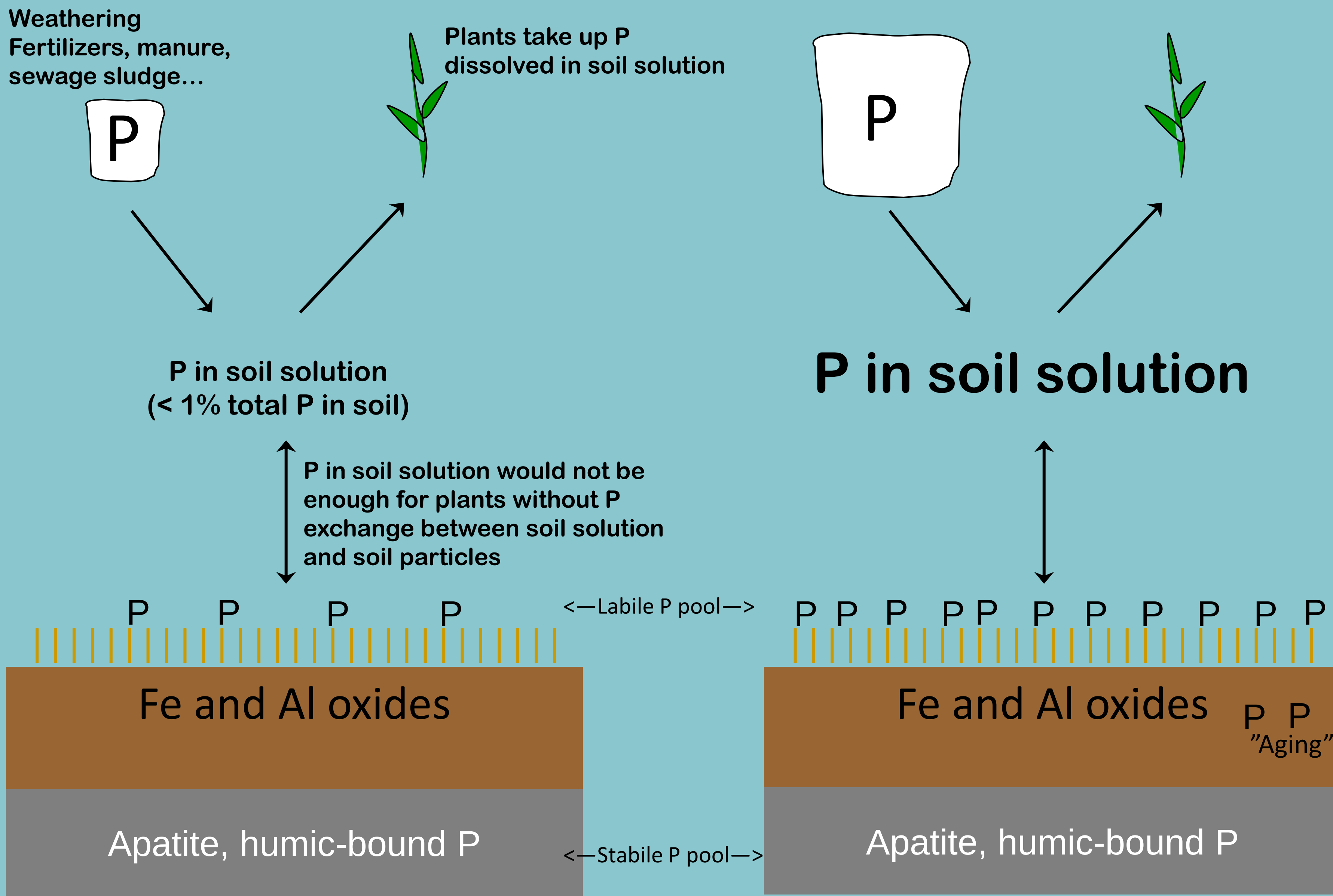
Iron and aluminium oxides

- Aluminium 3rd commonest element in Earth crust (8%)
- Iron 4th commonest (5%)
- Weathering produces Fe and Al hydroxides, oxyhydroxides, hydrated oxides, poorly crystalline oxides, amorphous oxides, sesquioxides..
- Charge depends on pH, positive at low pH



Picture: Hartikainen (2017, Modified)

Sorption-desorption reactions



Binding of anions

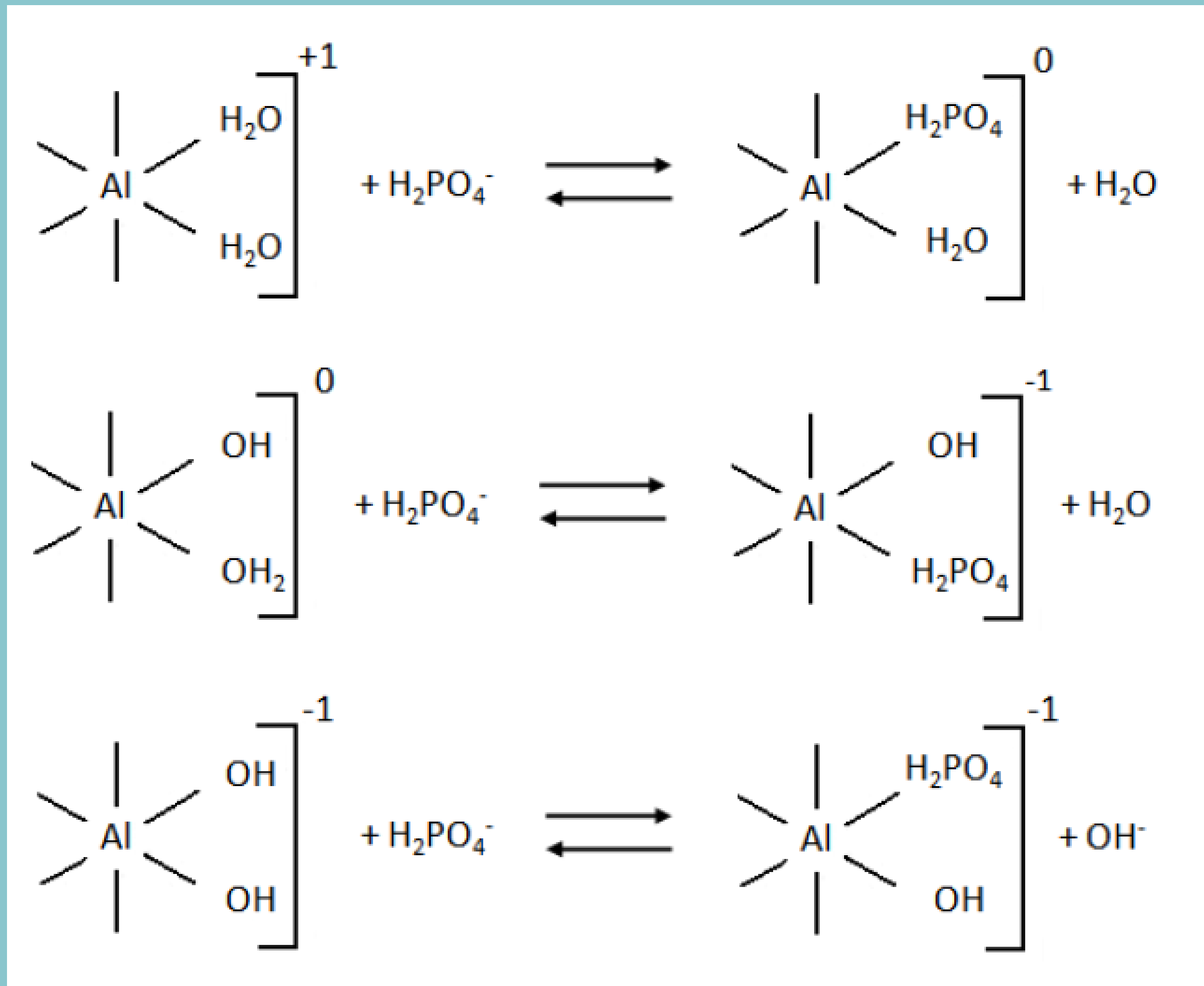
- An electrostatic repulsion between a negatively charged soil particle and a negatively charged anion
- Unspecific binding
  - Possible to positive surfaces, which only occur in Finland under very acidic conditions
- Spesific binding
  - Spesific ligand exchange reaction (Hingston et al. 1967)
    - Some anions can bind chemically to the central cation of Al and Fe oxides
  - Charge of Al and Fe oxides depend on the pH
  - Anion (e.g. $H_2PO_4^-$) replaces H_2O or OH^- group and binds by its O_2 to the central cation

Binding tendency of anions

Anion of the acid	OH^- Hydroxide	>	$H_2PO_4^-$ Phosphate	>>	SO_4^{2-} Sulfate	>	Cl^- Chloride	= NO_3^- Nitrate
Acid	H_2O		H_3PO_4		H_2SO_4		HCl	HNO_3

Central cation can be compared to H^+
Acids donate H^+ the more eagerly the stronger the acid
The stronger the acid, the weaker the corresponding base
Weak base does not take H^+ or bind to central cation

Phosphate binding to Al oxide



With lowering pH the surface charge of oxides becomes more positive -> binding tendency increases as the electrostatic repulsion decreases and H_2O group is more easily replaced than OH

Negative charge increases upon binding of an anion -> binding tendency decreases

Picture: Hartikainen (2009)

Sorption desorption reactions are not fully reversible

- Sorption initially fast (min, h), followed by a slow reaction (d)
- Binding may first occur binuclearly, i.e. anion is bound to two central cations
- With the increase in anion saturation, binding becomes monodental and weaker
- In time, binding may become stronger
  - Binding is changed from monodental to bidental
  - Adsorption is followed by absorption (P is diffused into a soil particle)
  - Adsorbed P is covered by Al ja Fe oxides (occlusion)
- In addition to sorption, secondary P minerals may be formed, if concentrations exceed solubility product, e.g. after fertilising

23

Characteristics affecting P binding

	Sorption promoted	**Desorption promoted**
Sorptive components	Plenty	Little
Saturation of sorptive components	Low	High
Ionic strength	High	Low
Competing anions	Little	Plenty
pH	Low	High

Development of soil P reserves over time

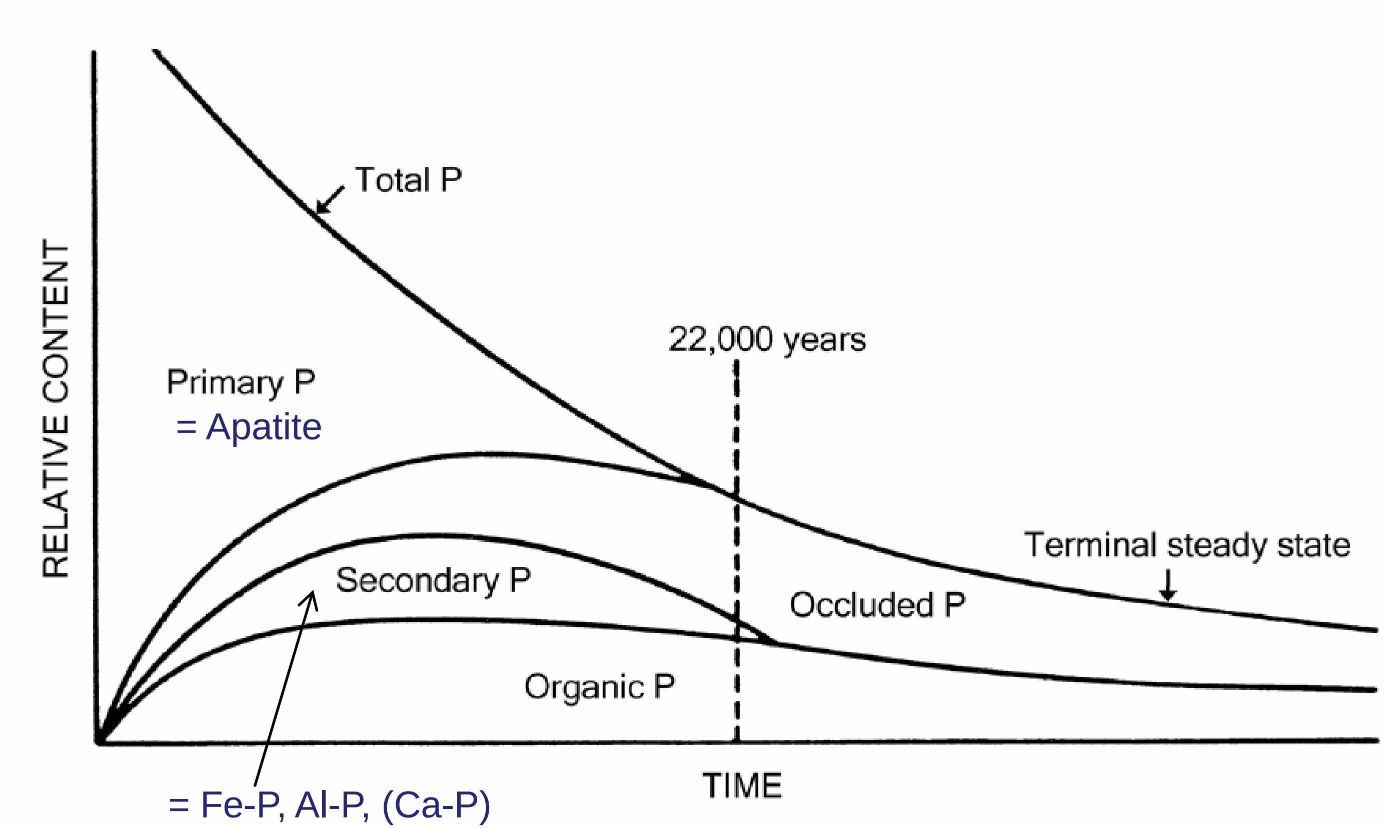
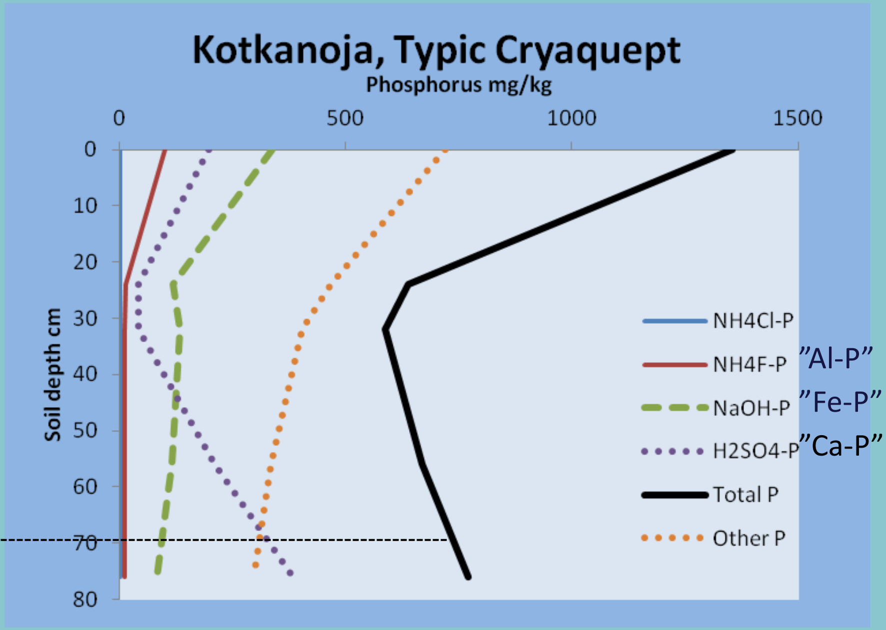


Figure 1.1 Changes in the amount and composition of soil P over time (Walker and Syers, 1976. © Elsevier, reproduced with permission).

An example on vertical P stratification in a cultivated soil

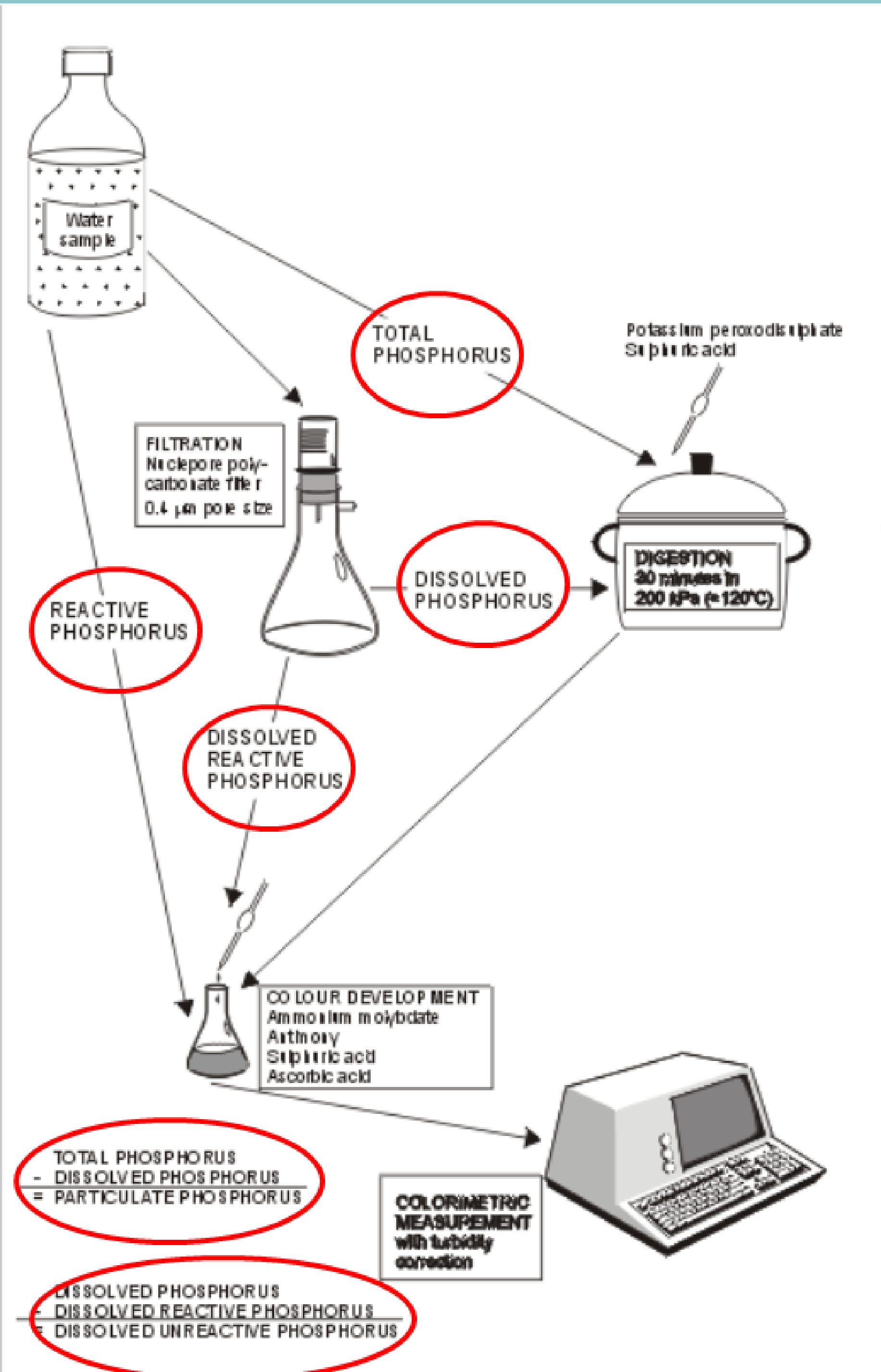
Ap horizon
- Plough layer
- Enriched with P
- P mainly as secondary P forms and organic P
- Degree of P saturation: 8–36%
- Source of dissolved P

B horizon
- Apatitic P weathered and transformed to secondary P forms
- Degree of P saturation: <7%
- Sink for dissolved P



C horizon
- Apatitic P dominates

Peltovuori (2006)



Phosphorus determination

PERUSMÄÄRITYKSET:

1. Kokonais-P, *Total P* (TP, PTOT, P_{tot},...)
2. Liuennut (kokonais-) P, *Total dissolved P* (TDP)
3. Liuennut reaktiivinen P, *Dissolved reactive P* (DRP, SRP)
4. Reaktiivinen P, *Reactive P* (RP)

LASKENNALLISET JAKEET:

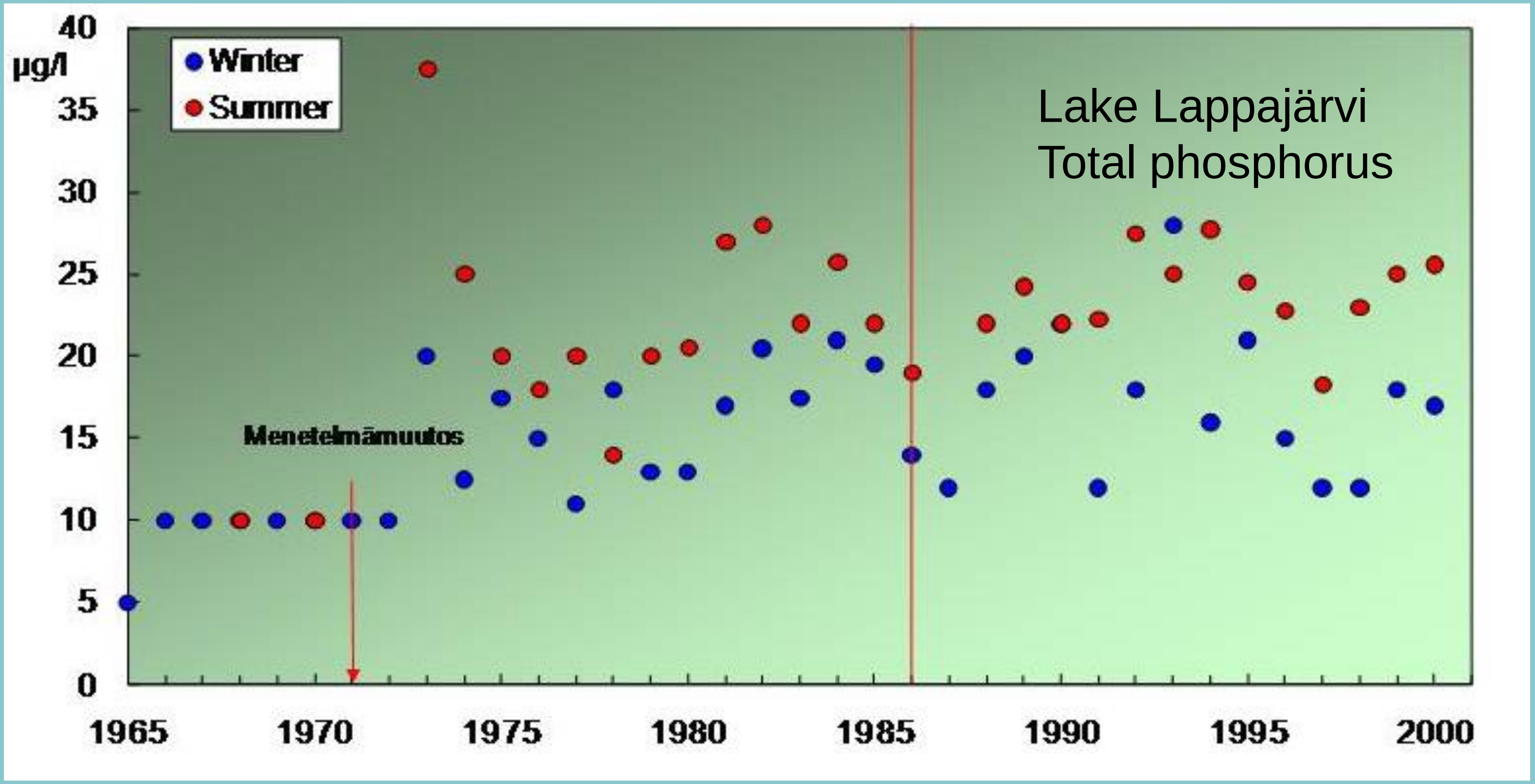
1. Hiukkasmainen P, *Particulate P* (PP)
2. Liuennut ei-reaktiivinen P, *Dissolved unreactive P* (DUP)

Operational P forms

- DRP ≠ dissolved orthophosphate!!
  - In acid conditions labile esters and polyphosphates will be hydrolysed
  - Complexes between phosphate and metals will be degraded
  - Colloidal metal oxides will be dissolved
  - Silicate, germanium and arsenate interfere with the determination
- DUP
  - P forms that go through the filter, but require digestion to react with molybdate
  - e.g. RNA, DNA, AMP, phospholipids, inositol phosphate
- RP
  - ?

28

Changes in the phosphorus determination

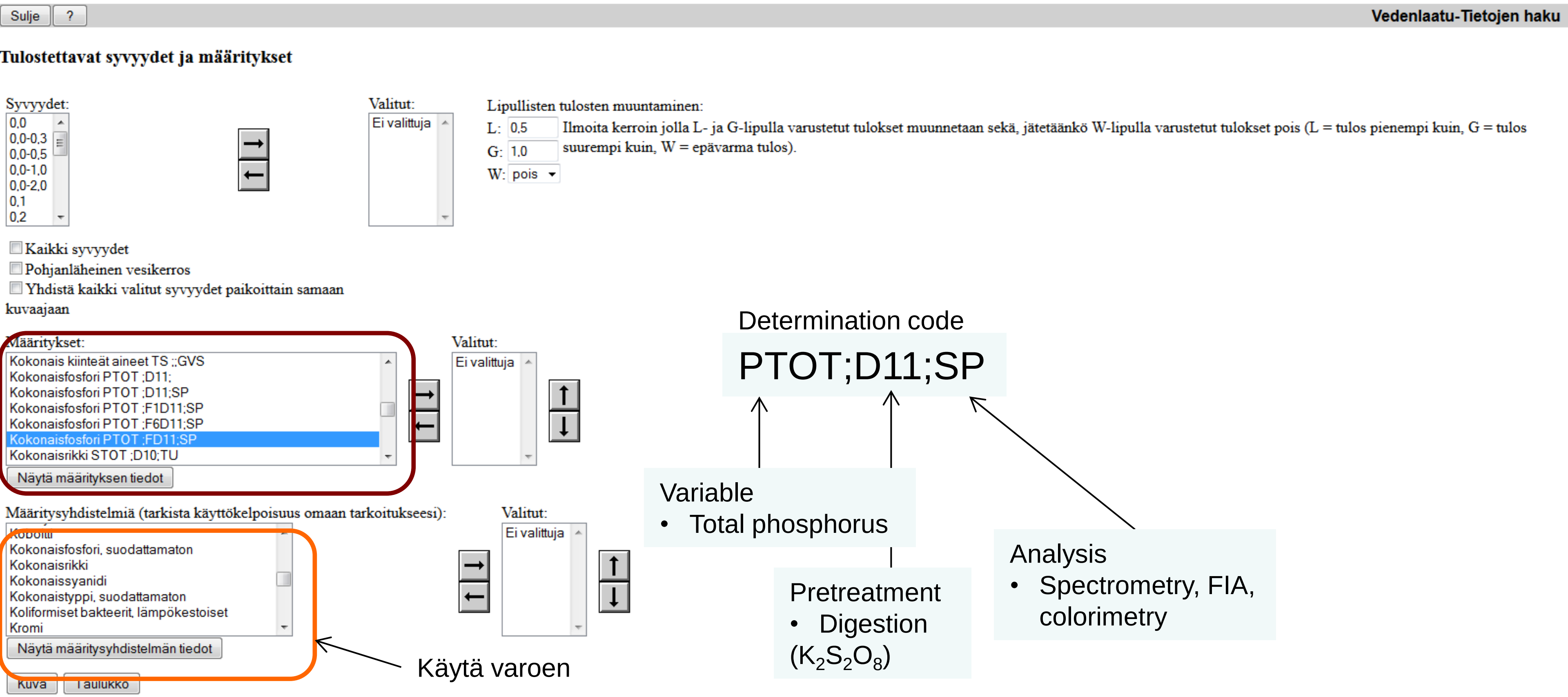


- Digestion with sulphuric acid and hydrogen peroxide, reduction with stannochloride
- Larger results (precision 10 µg l^{-1})

- Digestion with peroxodisulfate, molybdenum blue method

- Acidity increased
- Somewhat larger results

Be careful with the P varieties in HERTTA!



PTOT;; = Unspecified and probably an old total P determination (*use with care*)… **TP**
PTOT;D11; = Total P determination with a peroxodisulfate digestion (*probably OK*)… **TP**
PTOT;D11;SP = Total P determination with a peroxodisulfate digestion and a spectrometric analysis (*OK*)… **TP**
PTOT;FD11;SP = Dissolved total P, filtered but no information how (*use with utmost care*)… **TDP**
PTOT;F1D11;SP = Dissolved total P, filtered through an unspecified membrane with a 0.45 µm pore size (*result may be too high*)… **TDP**
PTOT;F6D11;SP = Dissolved total P, filtered through a Nuclepore, polycarbonate membrane with a 0.4 µm pore size (*OK*)…**TDP**
PO4P;; = Unspecified phosphate P determination, probably old (*use with utmost care*)… **RP**
PO4P;;SP = Unspecified phosphate P determination, probably old (*use with utmost care*)… **RP?**
PO4P;F6;SP = Phosphate P analysed from a sample filtered through a Nuclepore polycarbonate membrane, 0.4 µm (*OK*)… **DRP**

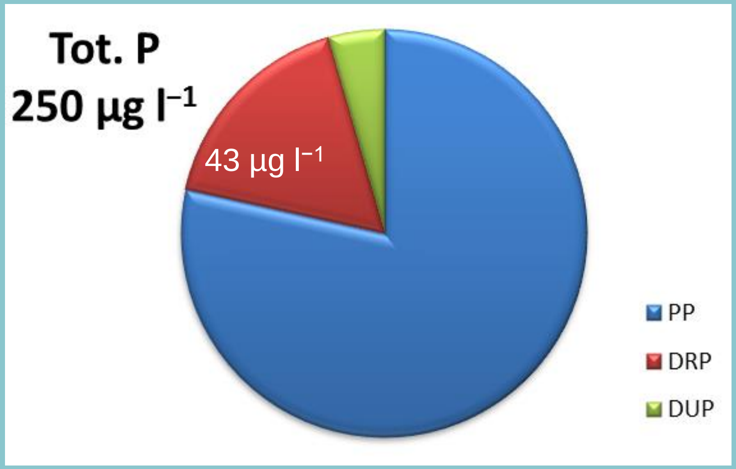
Difference between phosphorus and nitrogen

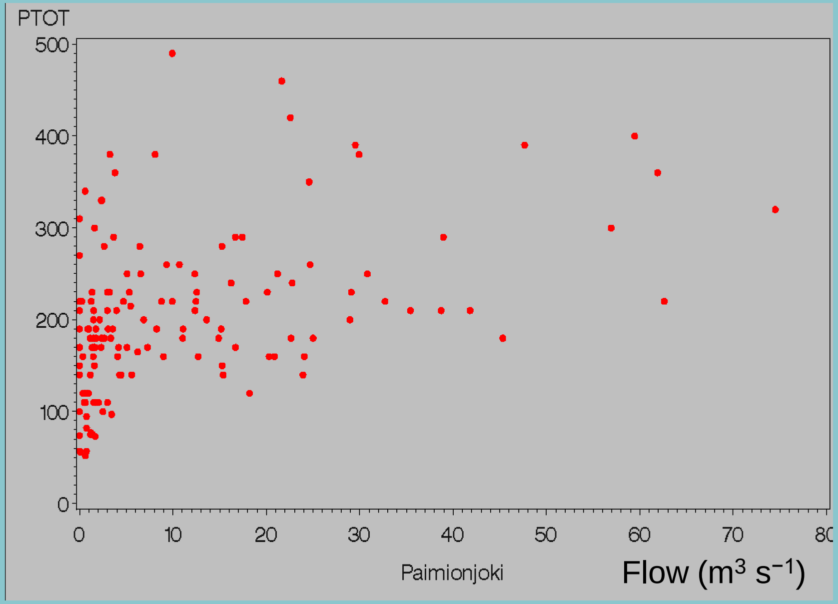
	Phosphorus	Nitrogen
Origin	Rock	Atmosphere
Main species	PO_4^{3-} as bound in various ways	NO_3^- NH_4^+ Organic N
Binding	Onto surfaces	Organic matter NH_4^+ on surfaces
Redox sensivity	No	Yes
Directly available forms	$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}	NO_3-N NH_4-N Low molecular weight organic compounds
Losses are governed by	Sorption-desorption reactions, i.e. ’chemistry’	Mineralisation, i.e. ’[micro]biology’
Is transported as	With soil particles and in a dissolved form Surface runoff, drainage flow	Mainly in a dissolved form Especially in drainage flow Atmospheric deposition

Phosphorus forms in two agricultural rivers in Finland

The Paimionjoki

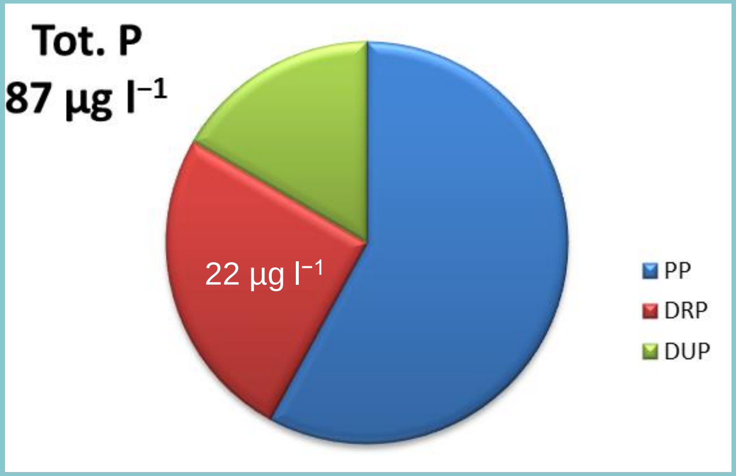
Field percentage 43, of which 12% grassland, Clayey soil

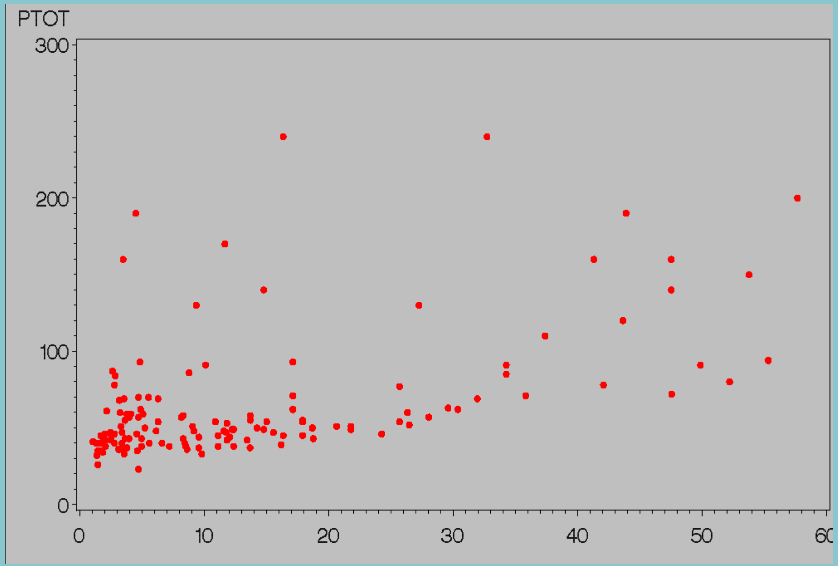




The Lestijoki

Field-% 11, of which 31% grassland, coarse mineral and organic soils

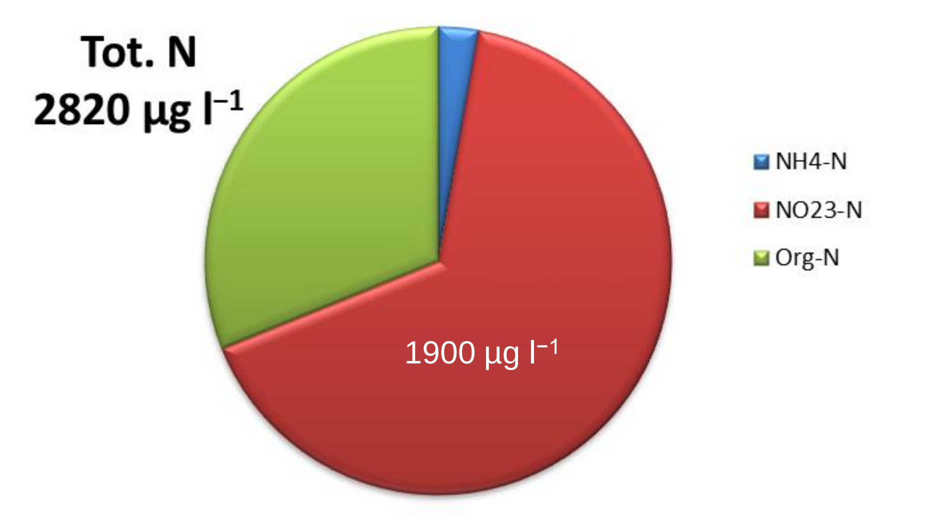


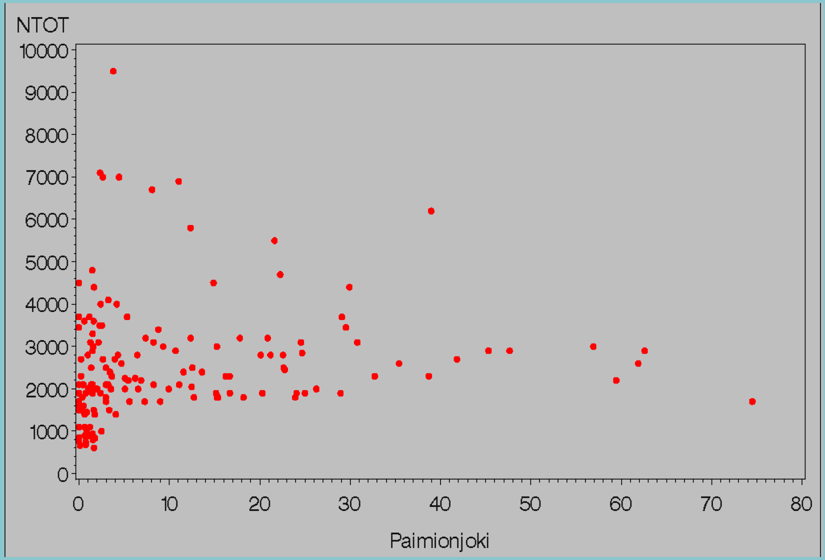


Nitrogen forms in two agricultural rivers in Finland

The Paimionjoki

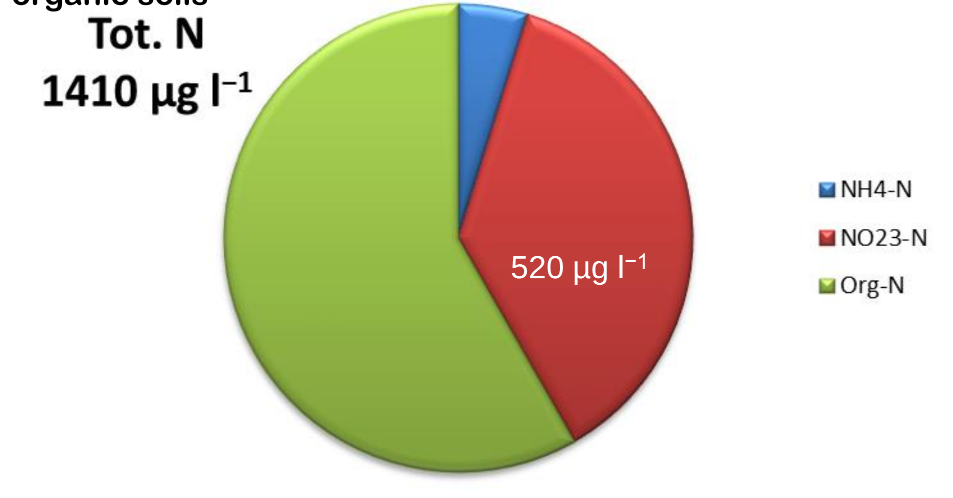
Field percentage 43, of which 12% grassland,
Clayey soil

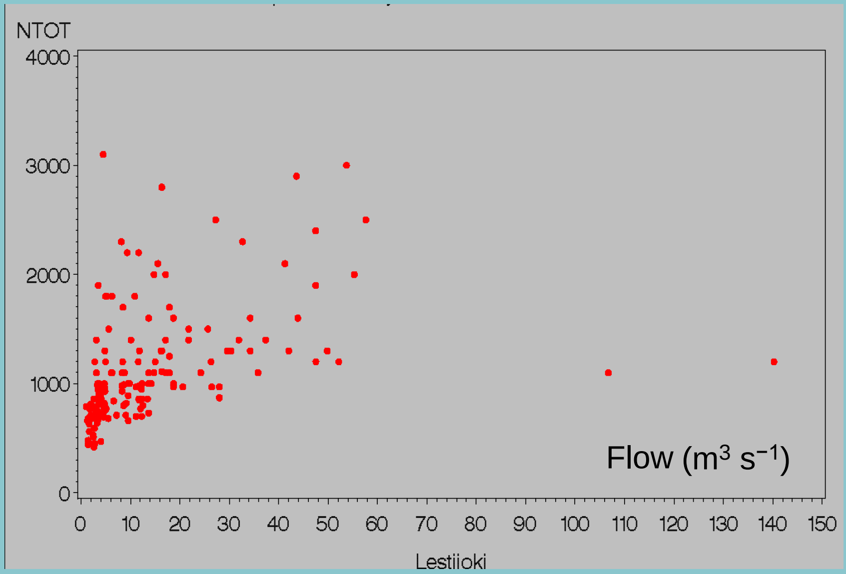




The Lestijoki

Field-% 11, of which 31% grassland, coarse mineral and organic soils

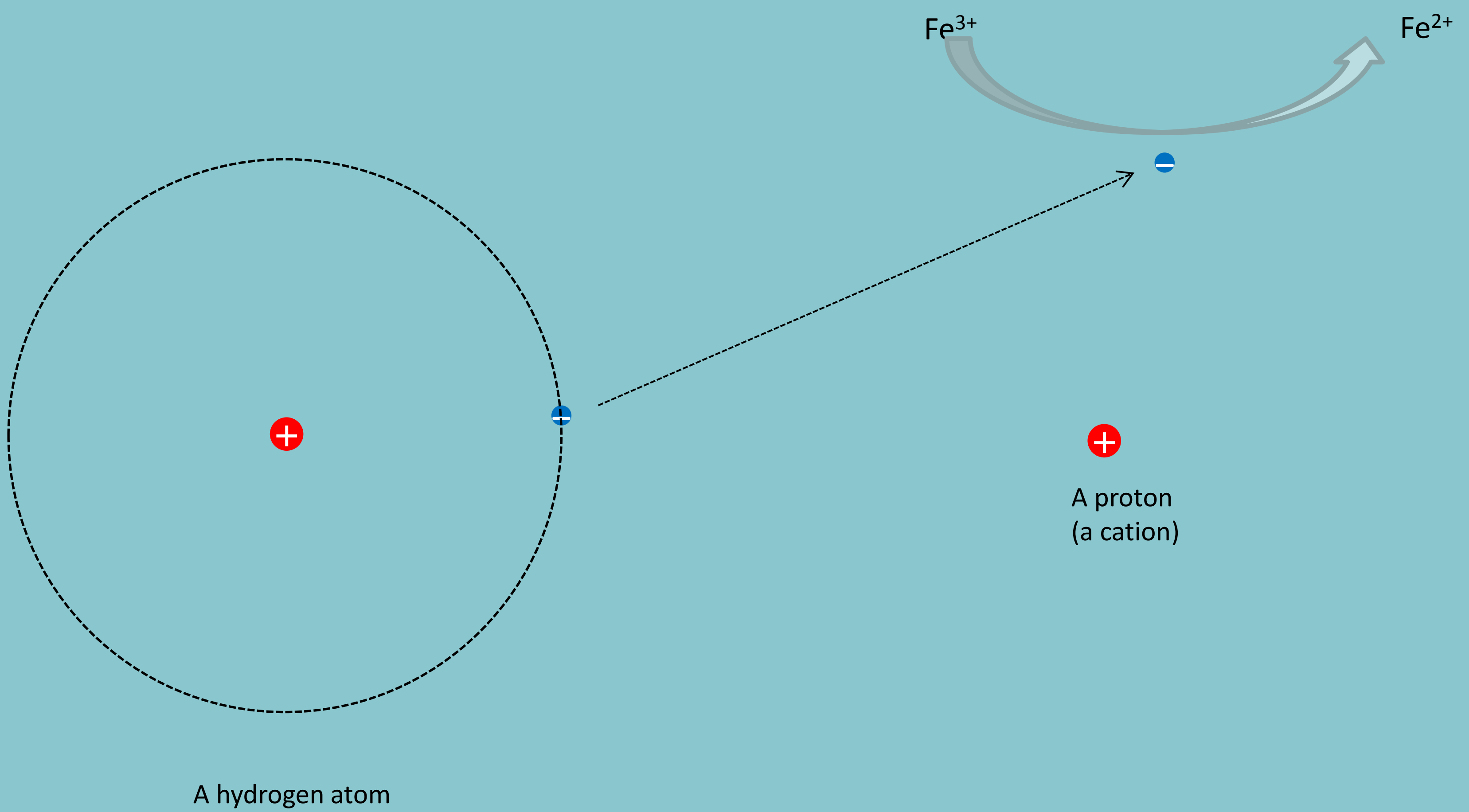




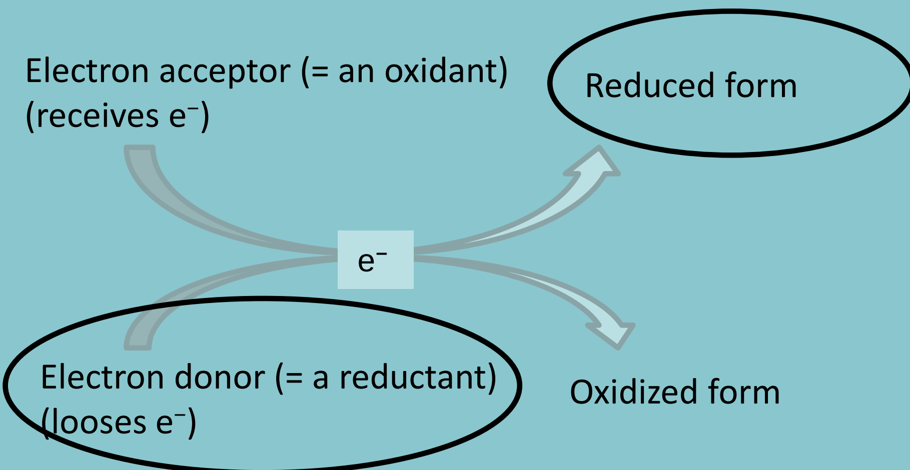
Recap II

- What happens to the surface charge of Al and Fe oxides when pH increases?
  - It becomes more negative
- Is NO_3^- attached to Al and Fe oxides?
  - No
- Does an increase in pH promote sorption or desorption of dissolved orthophoshate?
  - Desorption
- What about an increase in ionic strenght?
  - Promotes sorption
- Is dissolved reactive P = dissolved orthophosphate?
  - No
- What is the dominant P fraction in agricultural rivers?
  - Particulate P
- What is the dominant N fraction in agricultural rivers?
  - NO_3-N

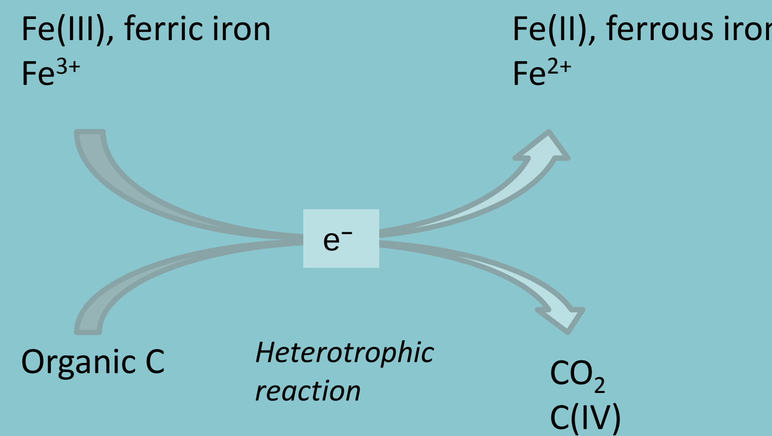
Back to school

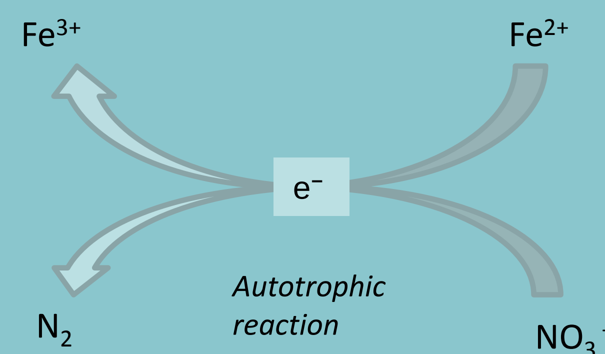


“The chemistry of life, however, is based on redox reactions, i.e., successive transfers of electrons and protons from a relatively limited set of chemical elements.” (Falkowski et al. 2008)



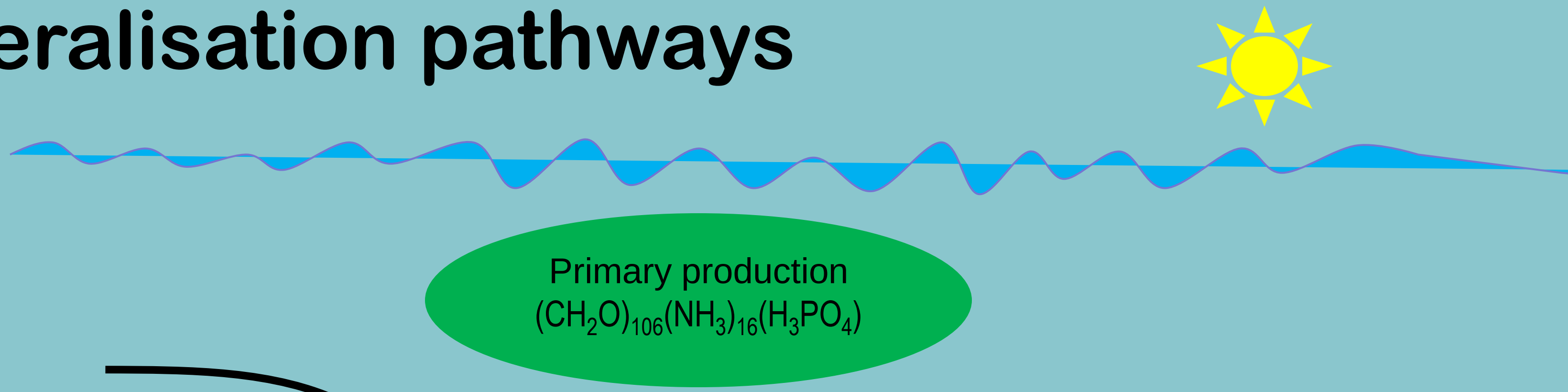
Chemical energy





Burgin et al. (2011)

Mineralisation pathways



Aerobic mineralisation(23%)*

$\mathbf{O_2} + {}^{1}/_{2}\,C_2H_3O_2^- \rightarrow HC\mathbf{O_3^-} + {}^{1}/_{2}\,H^+$

$C_2H_3O_2^-$ = acetate = electron donor

Denitrification (5%)*

${}^{4}/_{5}\,\mathbf{NO_3^-}(\mathbf{l}) + {}^{3}/_{5}\,H^+ + {}^{1}/_{2}\,C_2H_3O_2^- \rightarrow {}^{2}/_{5}\,\mathbf{N_2}(\mathbf{g}) + HCO_3^- + {}^{1}/_{5}\,H_2O$

Manganese reduction

${}^{7}/_{2}\,H^+ + 2\mathbf{MnO_2}(\mathbf{s}) + {}^{1}/_{2}\,C_2H_3O_2^- \rightarrow 2\mathbf{Mn^{2+}}(\mathbf{l}) + HCO_3^- + 2H_2O$

Iron reduction(17%)*

${}^{15}/_{2}\,H^+ + 4\mathbf{FeOOH}\ (\mathbf{s}) + {}^{1}/_{2}\,C_2H_3O_2^- \rightarrow HCO_3^- + 4\mathbf{Fe^{2+}}(\mathbf{l}) + 6H_2O$

Sulfate reduction (55%)*

${}^{1}/_{2}\,H^+ + {}^{1}/_{2}\,\mathbf{SO_4^{2-}}(\mathbf{l}) + {}^{1}/_{2}\,C_2H_3O_2^- \rightarrow {}^{1}/_{2}\,\mathbf{H_2S}(\mathbf{g}) + HCO_3^-$

Methane

${}^{1}/_{2}\,H_2O + {}^{1}/_{2}\,C_2H_3O_2^- \rightarrow CH_4 + {}^{1}/_{2}\,HCO_3^-$

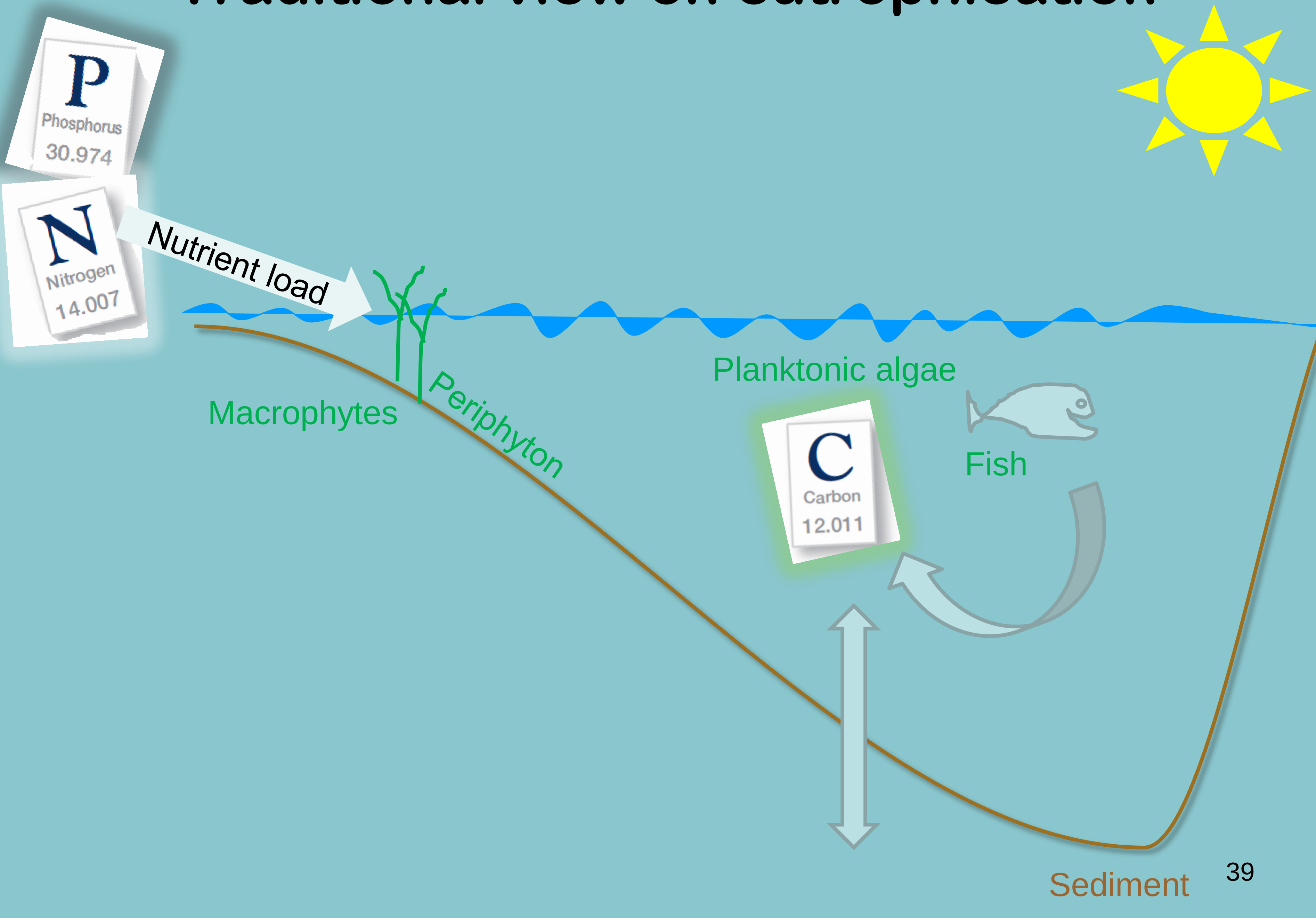
*Percents refer to marine systems (Canfield ym. 2005), sulfate reduction has lower role in freshwaters

Iron, the most abundant redox-sensitive metal

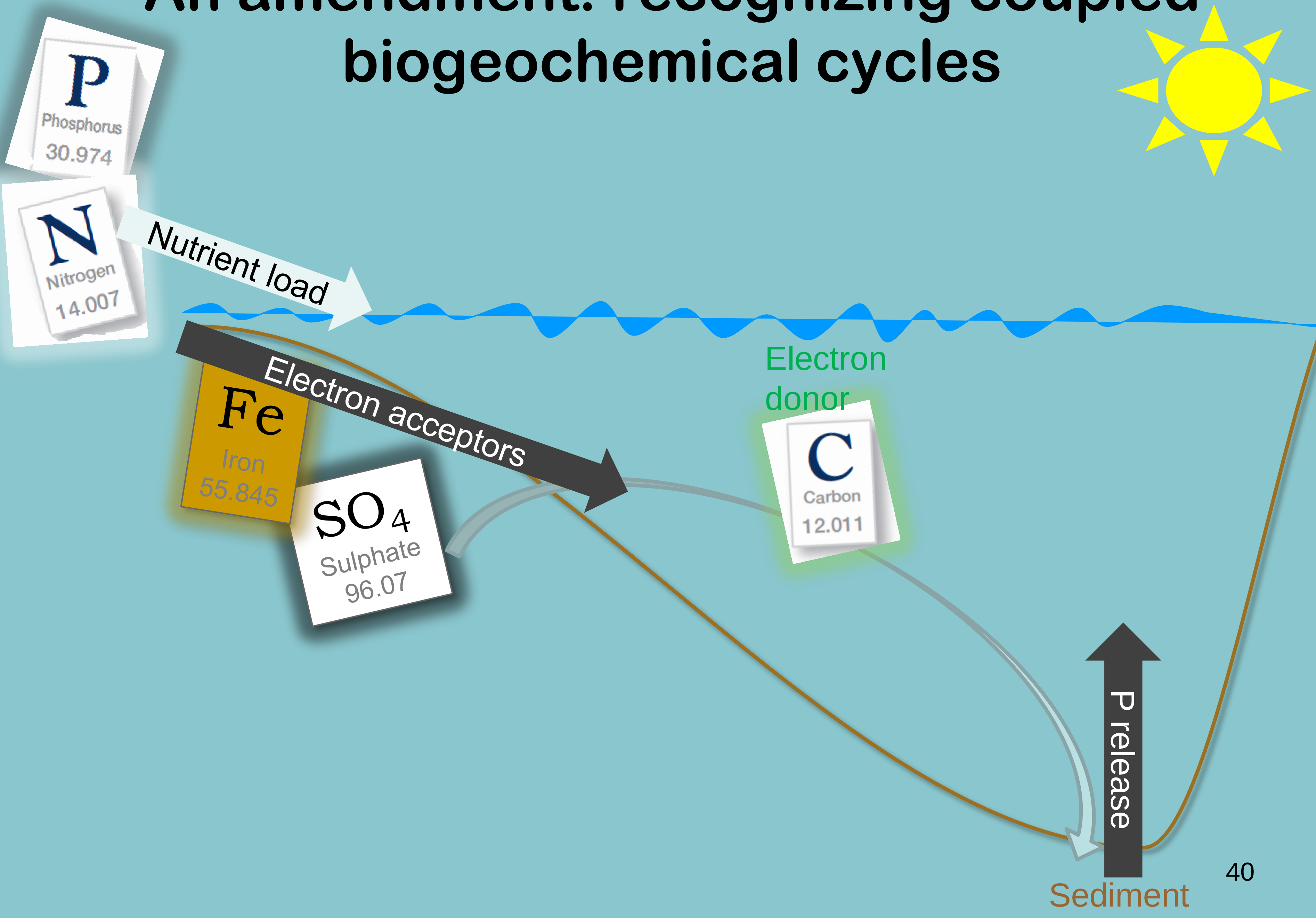
Oxidation of iron (chemically or microbiologically)

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightarrow 4\,Fe^{3+} + 2\,H_2O$$

Traditional view on eutrophication

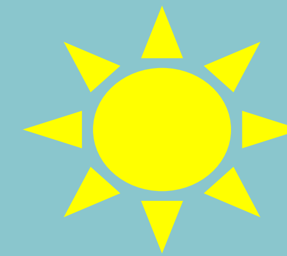


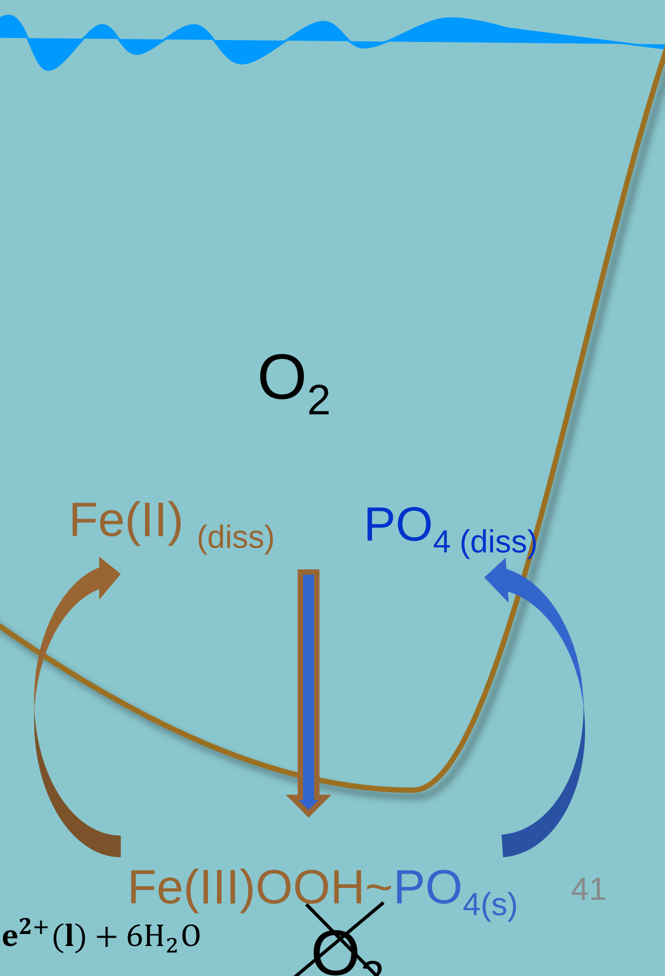
An amendment: recognizing coupled biogeochemical cycles



P release from sediments

1. Prevalence of microbial Fe reduction and a coupled Fe and P cycling





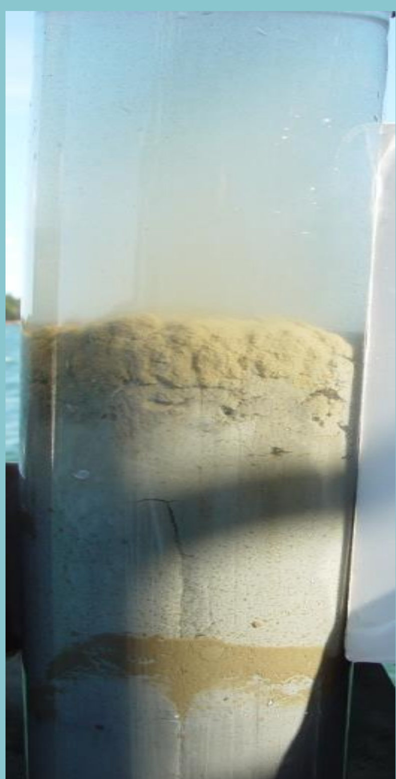


Photo: Seppo Knuuttila

Dominates when

- **Microbially available Fe(III) oxides present**
- **Sediment surface oxygenated allowing the oxidation of Fe(II)**
- **Bottom fauna bioturbates surface sediment**

$$^{15}/_2\,H^+ + 4\mathbf{FeOOH}\,(\mathbf{s}) + {}^1/_2\,C_2H_3O_2^- \rightarrow HCO_3^- + 4\mathbf{Fe^{2+}}(\mathbf{l}) + 6H_2O$$

P release from marine sediments

2. Prevalence of microbial SO_4 reduction and an uncoupled Fe and P cycling

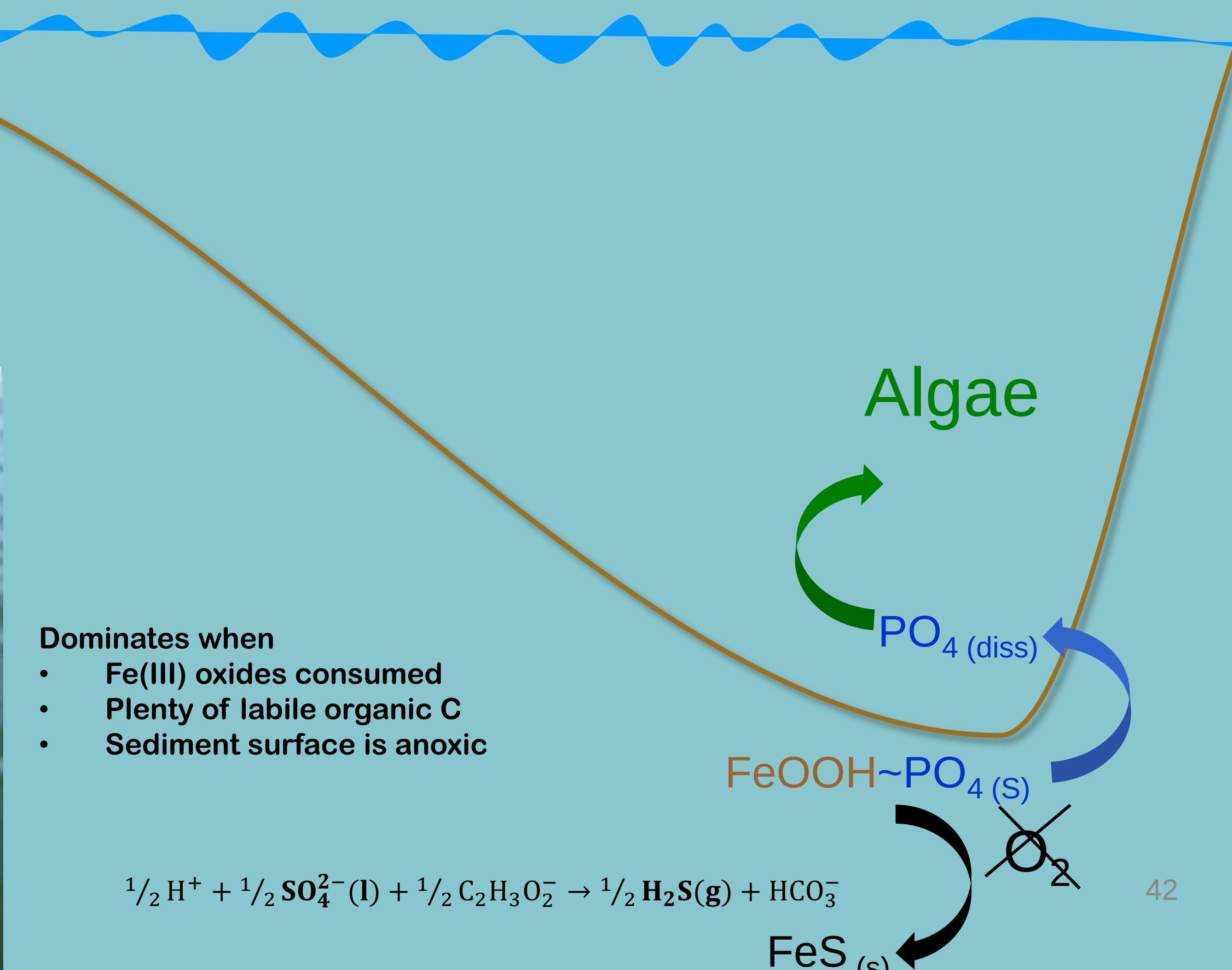


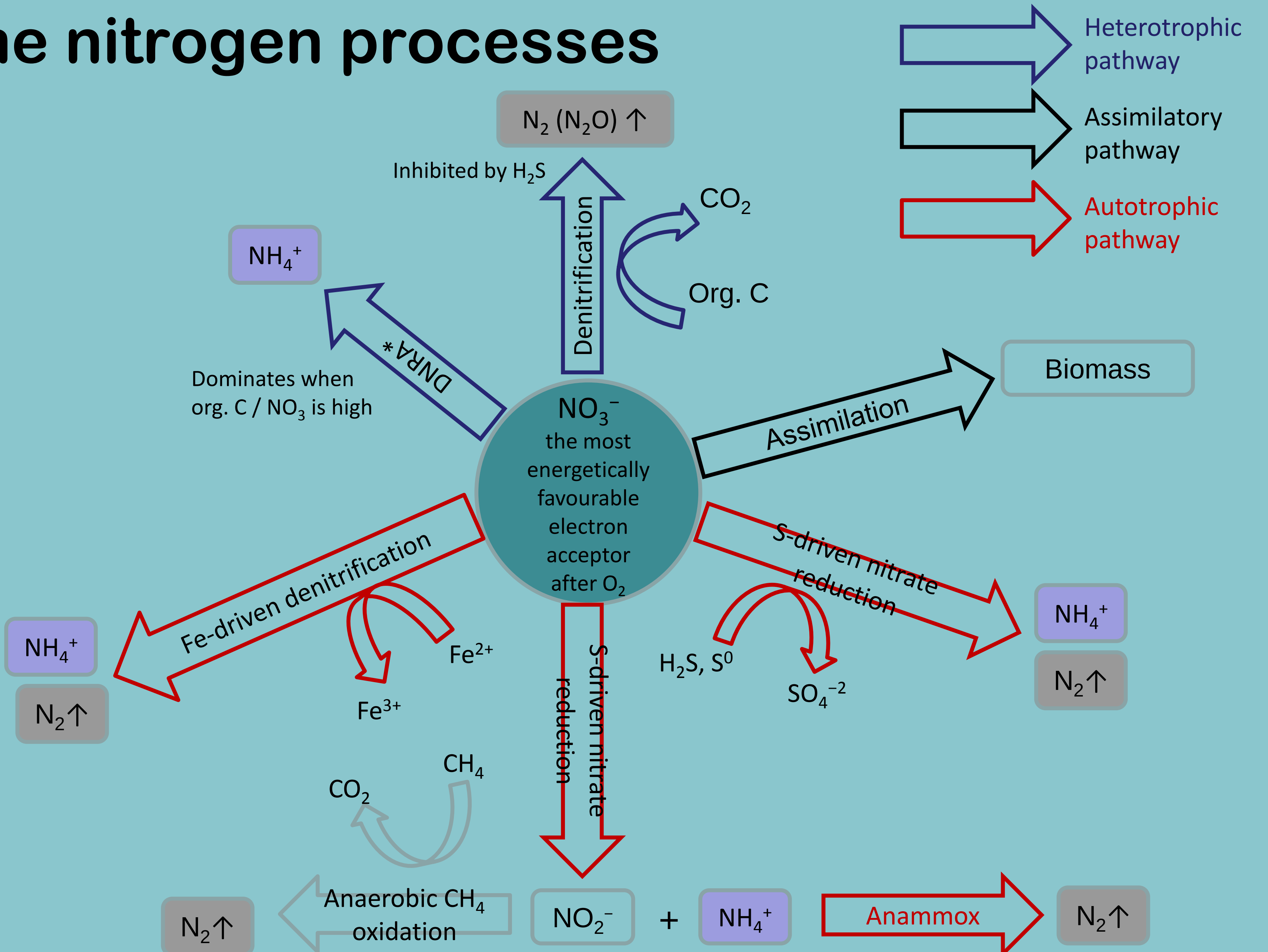
Photo: Seppo Knuuttila

Dominates when

- **Fe(III) oxides consumed**
- **Plenty of labile organic C**
- **Sediment surface is anoxic**

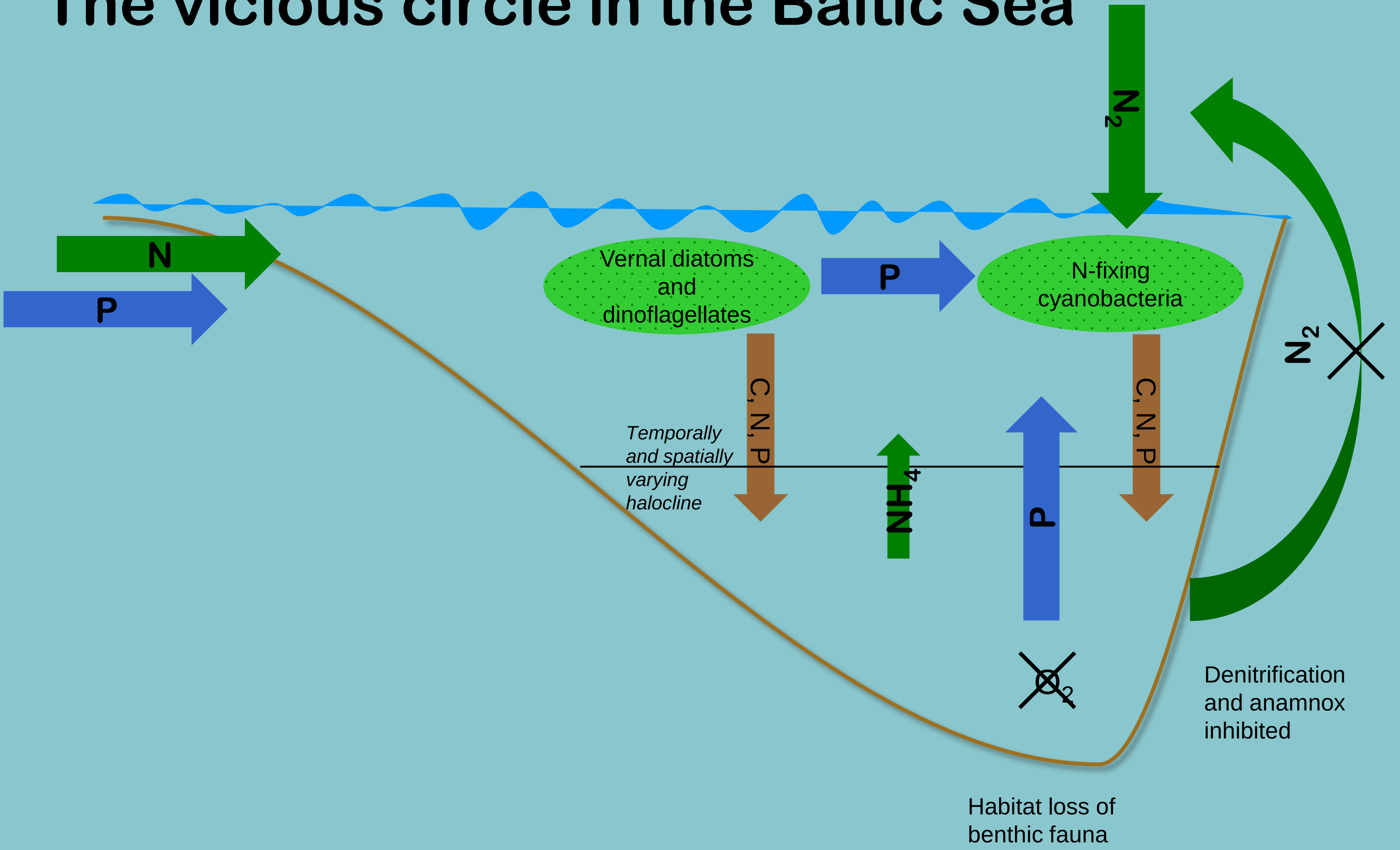
$$\tfrac{1}{2}\,\mathrm{H^+} + \tfrac{1}{2}\,\mathbf{SO_4^{2-}(l)} + \tfrac{1}{2}\,\mathrm{C_2H_3O_2^-} \rightarrow \tfrac{1}{2}\,\mathbf{H_2S(g)} + \mathrm{HCO_3^-}$$

Some nitrogen processes



* Dissimilatory nitrate reduction to ammonium
Modified from Burgin & Hamilton (2007)

The vicious circle in the Baltic Sea



References

Ashley et al. 2011. A brief history of phosphorus: From Philosopher's stone to nutrient recovery and reuse. Chemosphere 84:737-746.

Burgin, Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Frontiers in Ecology and Environment 5:89–96

Burgin, Yang, Hamilton, Silver. 2011. Beyond carbon and nitrogen: how the microbial energy economy couples elemental cycles in diverse ecosystems. www.frontiersinecology.org

Falkowski et al. 2008. The microbial engines that drive Earth's biogeochemical cycles. Science 320:1034-1038.

Hartikainen 2017. 4.2 Maaperän reaktiot. Paasonen-Kivekäs, Peltomaa, Vakkilainen, Äijö (toim.).Maan vesi- ja ravinnetalous. Ojitus, kastelu ja ympäristö. Salaojayhdistys, 2. täydennetty painos.

Hingston, Atkinson, Posner, Quirk.1967. Specific adsorption of anions. Nature 215:1459–1461.

Obersteiner et al. 2013. The phosphorus trilemma. Nature Geoscience 6: 897–898.

Peltovuori 2016. Phosphorus in agricultural soils of Finland – characterization of reserves and retention in mineral soil profiles. Pro Terra 26.

Sutton et al. (Eds.) 2011. The European nitrogen assessment. Sources, Effects and Policy Perspectives.