Aquatic Nutrient Cycles II

Plankton Bacteria

Particulate Nutrients

Dissolved Nutrients:
HPO_4^{2-}, PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+, H_4SiO_4
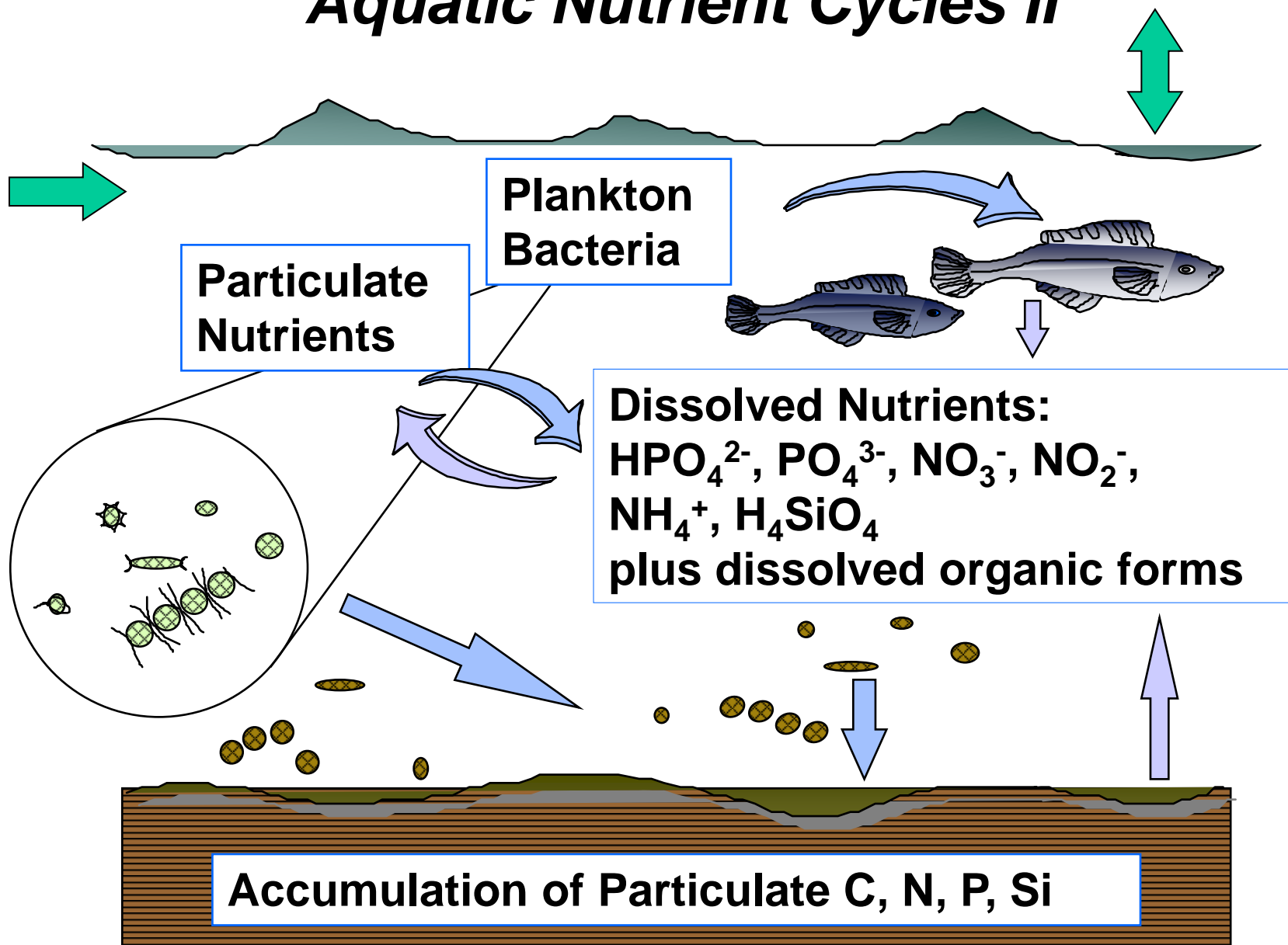**plus dissolved organic forms**

Accumulation of Particulate C, N, P, Si

Different forms of P in the sea.

PO4 = phosphate

DIP = dissolved inorganic phosphorus = phosphate

SRP = soluble reactive phosphorus = measured phosphate (subject to error, some organic phosphates and other substances included inadvertently)
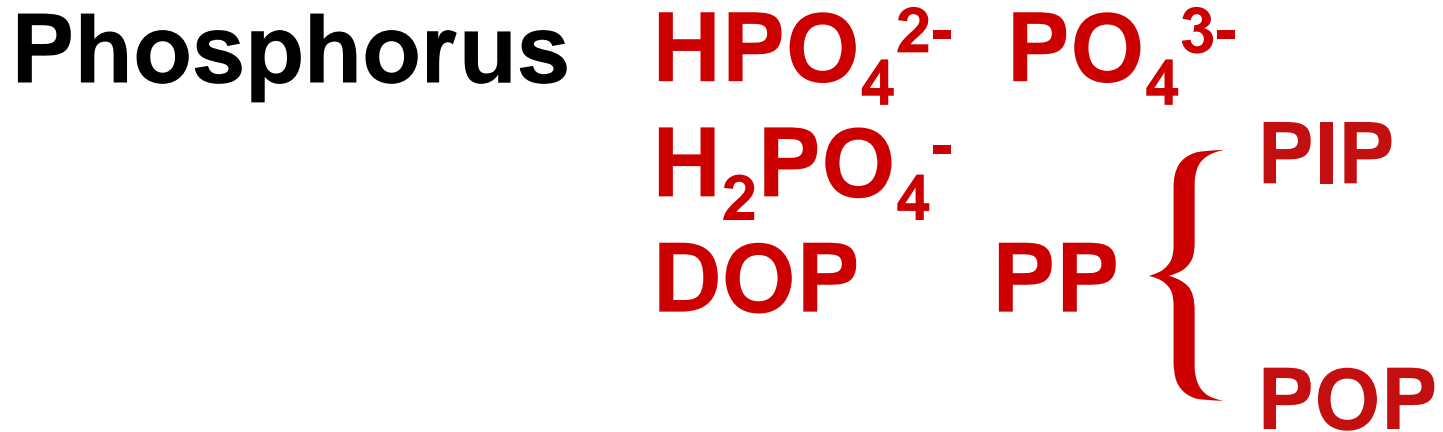
DOP = dissolved organic phosphorus
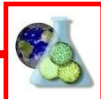
SNP = soluble non-reactive phosphorus (mostly DOP)

TDP = total dissolved phosphorus = DIP+DOP

The major nutrients

Phosphorus HPO_4^{2-} PO_4^{3-}
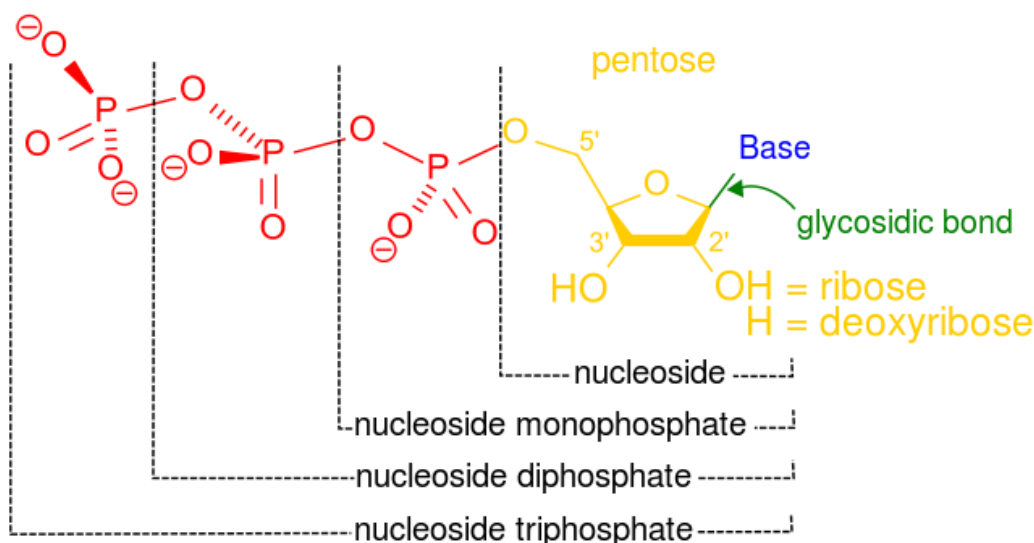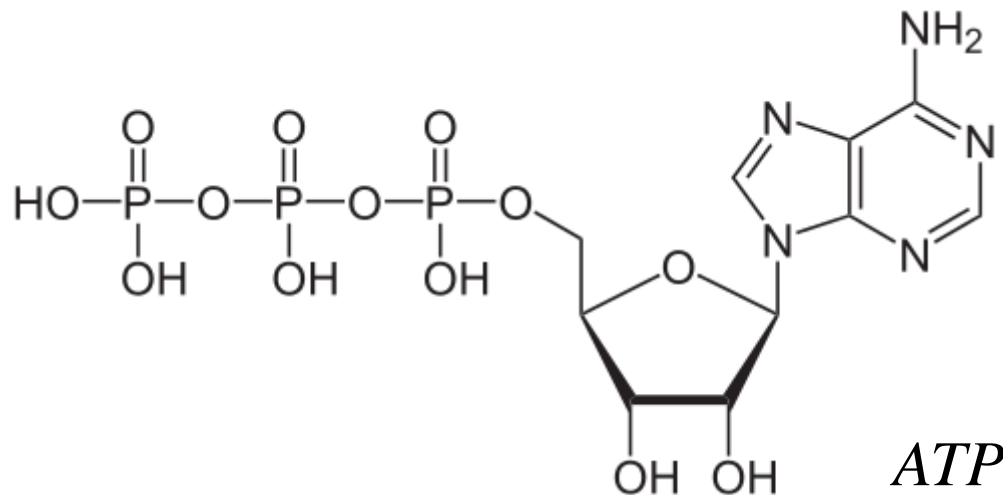$H_2PO_4^-$
DOP   PP $\Big\{$ PIP

POP

Phosphate has a potential of adsorption to inorganic phases:
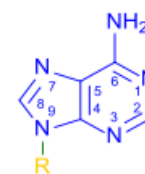forms insoluble compounds with some metals (typically Fe oxides)
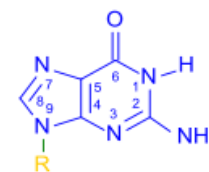
Phosphorus in the Ocean

- Essential element for life (2-4% dry weight of cells)

- DNA and RNA

- ATP for energy transmission

- phospholipid for cell membranes

- skeletal material, teeth, etc.

- often biolimiting in ocean (and lakes)

ATP

pentose

5'

3'   2'

HO   OH = ribose
      H = deoxyribose

Base

glycosidic bond

----- nucleoside ------
nucleoside monophosphate ----
nucleoside diphosphate ---------
nucleoside triphosphate ---------

Purines

NH$_2$

Adenine

Guanine

Pyrimidines

NH$_2$

H$_3$C
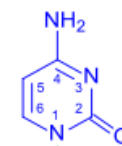
Cytosine
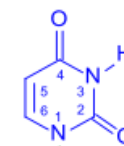
Uracil
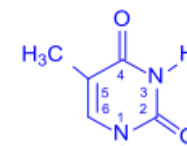
Thymine

Mineral Forms

- <u>Apatite</u>: $Ca_{10}(PO_4)_6X_2$ where $X=OH^-$, F^-, Cl^-
  - 95 % of all P in earth's crust
  - main constituent of phosphorites
  - main P-bearing mineral in igneous rocks
  - teeth, bones, scales

- <u>Vivianite</u>: $Fe_3(PO_4)_2 \cdot 8\ H_2O$ in reducing fresh-water sediments

Forms of P in the Water Column

- In the open ocean, most P is 'dissolved': either inorganic or organic.

- In deep ocean waters, inorganic forms ("orthophosphate") dominate.

- In surface waters, dissolved organic forms can exceed measured "orthophosphate" concentrations.

- In surface waters with very low orthophosphate concentrations (e.g. <0.02 μM), there may be analytical limitations to determining 'true' concentrations when using standard nutrient measurement systems. Concentrations may be overestimated.

- Now: we use nanomolar nutrient measurement systems with a 2 m pathlength cell for colourimetric nanomolar phosphate and nitrate/nitrite measurements.

Inorganic Speciation

Inorganic P found mainly as ionic forms of phosphoric acid, H_3PO_4

Phosphoric Acid dissociates in seawater:

$H_3PO_4 \Leftrightarrow H_2PO_4^- + H^+$ $\qquad\qquad$ ($K_1^* = 2 \times 10^{-2}$)

$H_2PO_4^- \Leftrightarrow HPO_4^{2-} + H^+$ $\qquad\qquad$ ($K_2^* = 7.4 \times 10^{-7}$)

$HPO_4^{2-} \Leftrightarrow PO_4^{3-} + H^+$ $\qquad\qquad$ ($K_3^* = 9 \times 10^{-10}$)

(K^*-values for seawater at $S = 35$, $T = 20°C$, atmospheric pressure. These seawater values are significantly greater than those for freshwater and even greater than those for sodium chloride solution.)

Inorganic Speciation
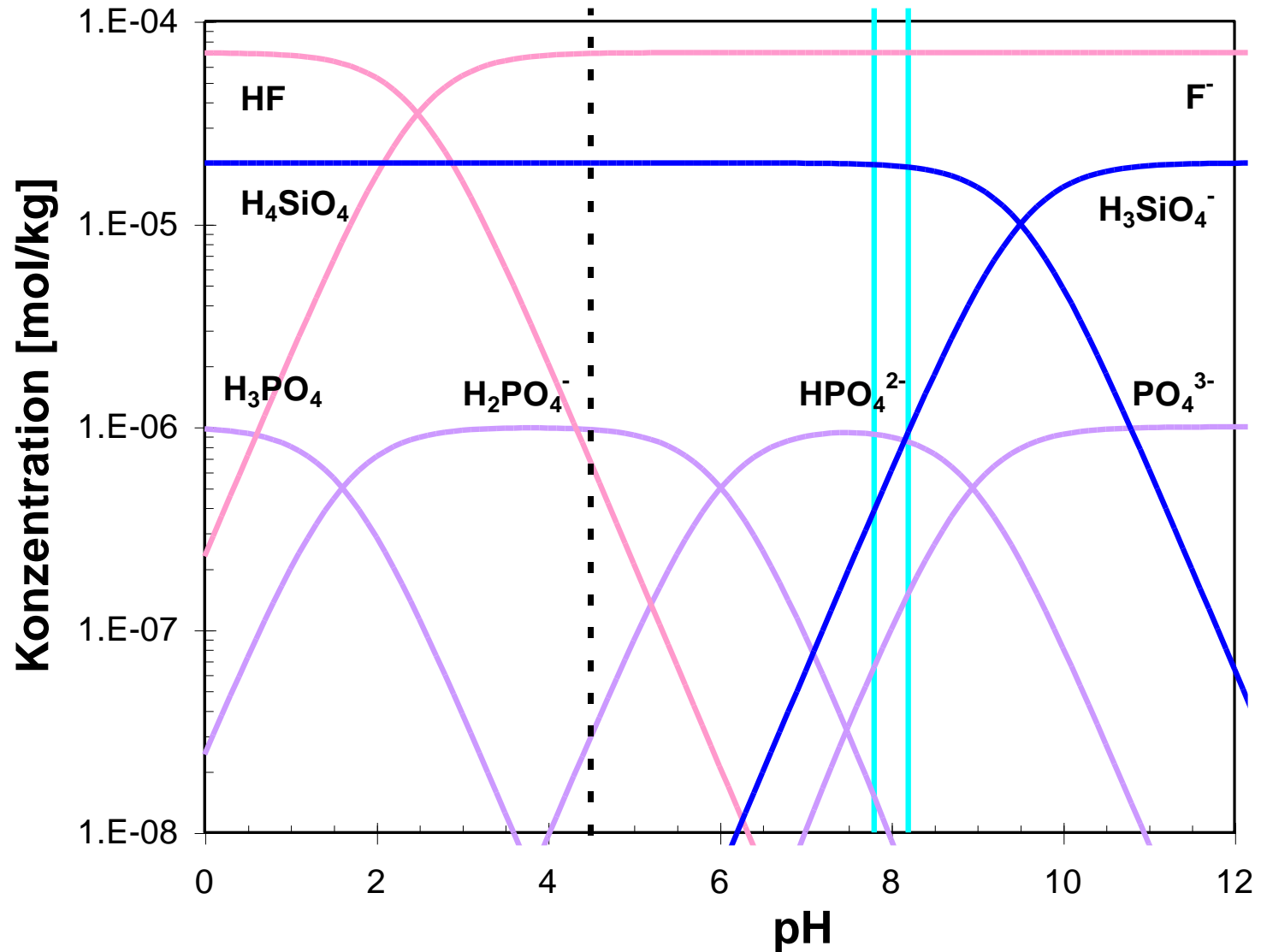
Inorganic Speciation

The K^*-values are "apparent dissociation constants" and vary with:
*   Temperature
*   Salinity
*   Pressure

Knowing: 'total' inorganic P concentration,
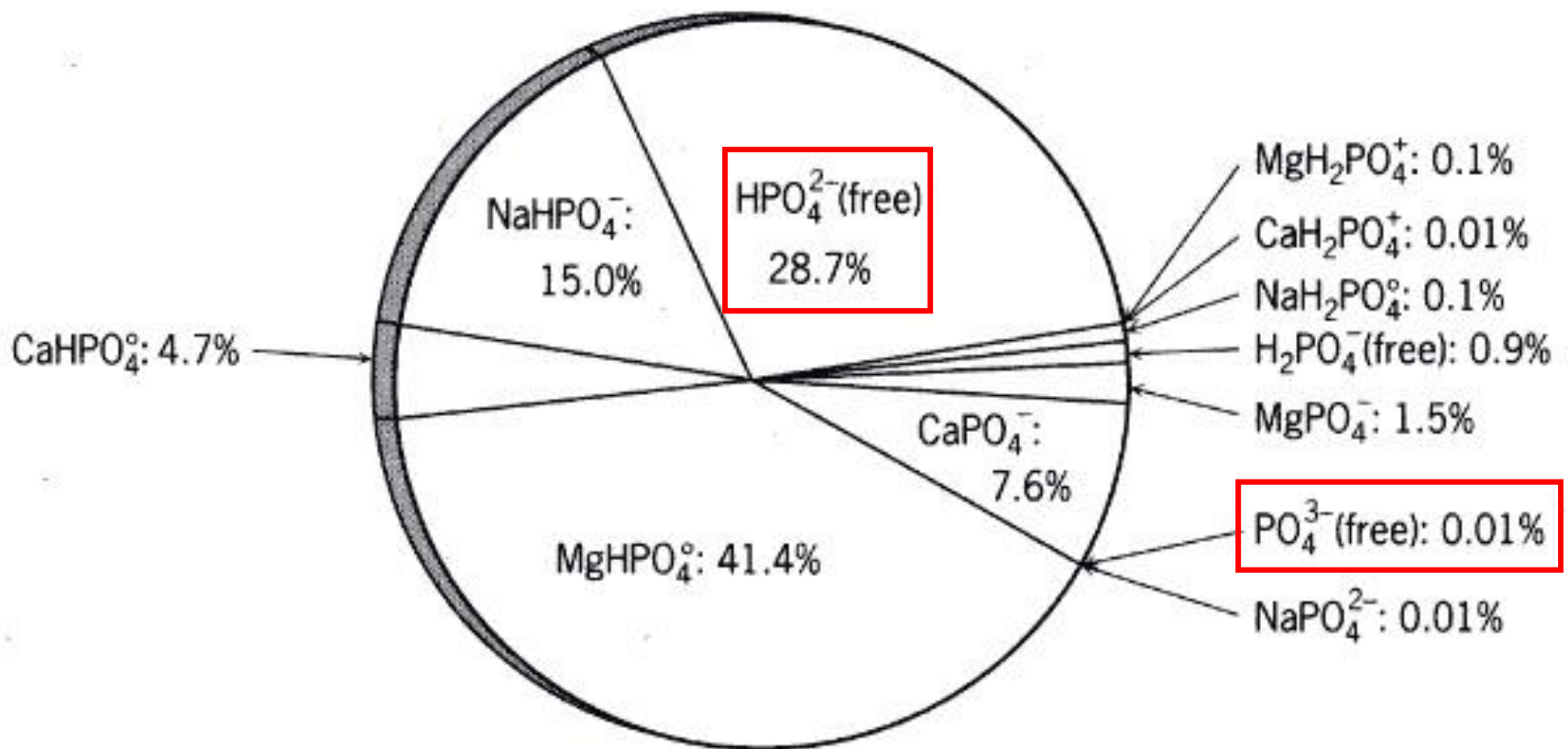pH and the K^*-values,
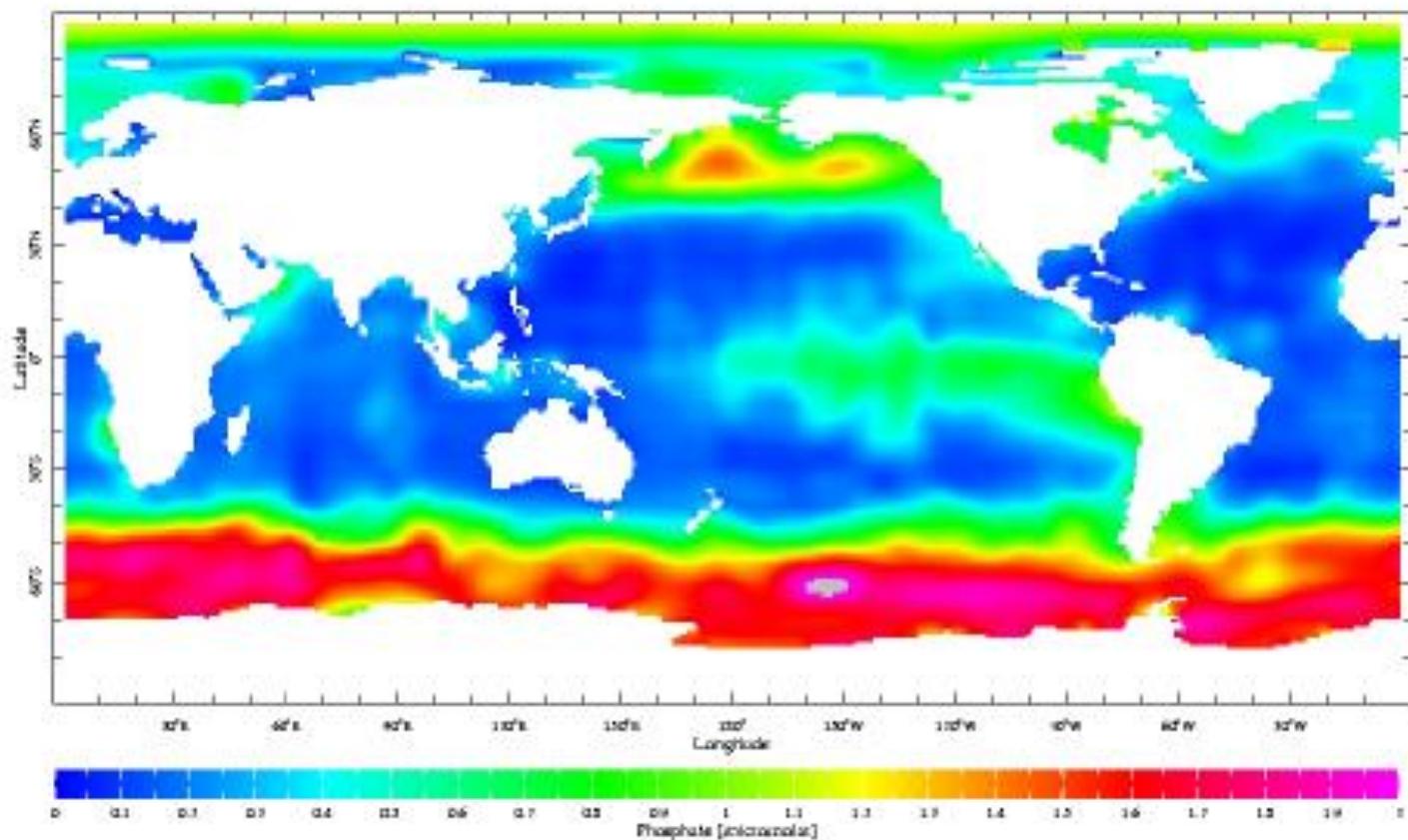the speciation of P can be calculated.

For „typical" seawater:

Species	% of total	% ion pairs
H_3PO_4	Almost zero	
$H_2PO_4^-$	1.2%	21%
HPO_4^{2-}	90.3%	68%
PO_4^{3-}	8.4%	99.9%

Importance of Ion-Pairing

In seawater, ionized forms of P are ion-paired with Ca^{2+} and Mg^{2+}
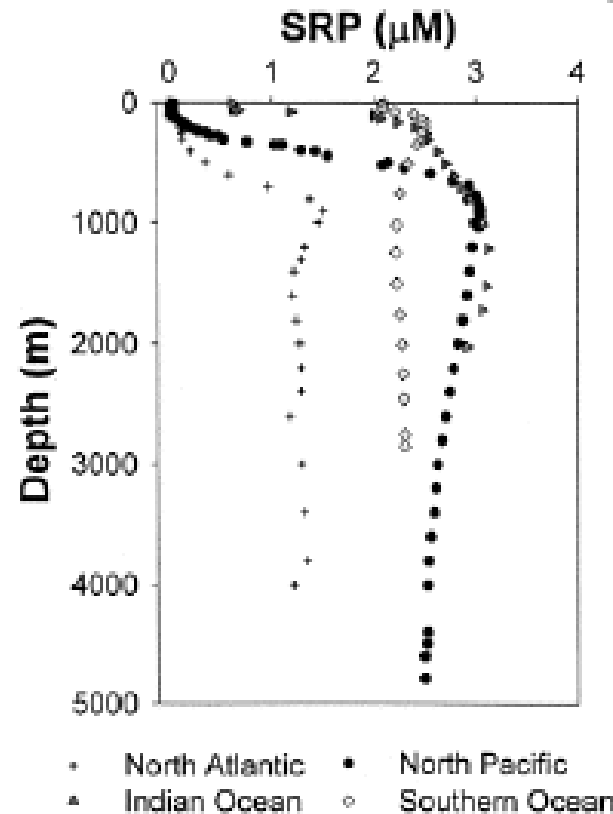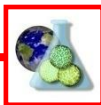
Surface Phosphate Concentration (World Ocean Atlas)

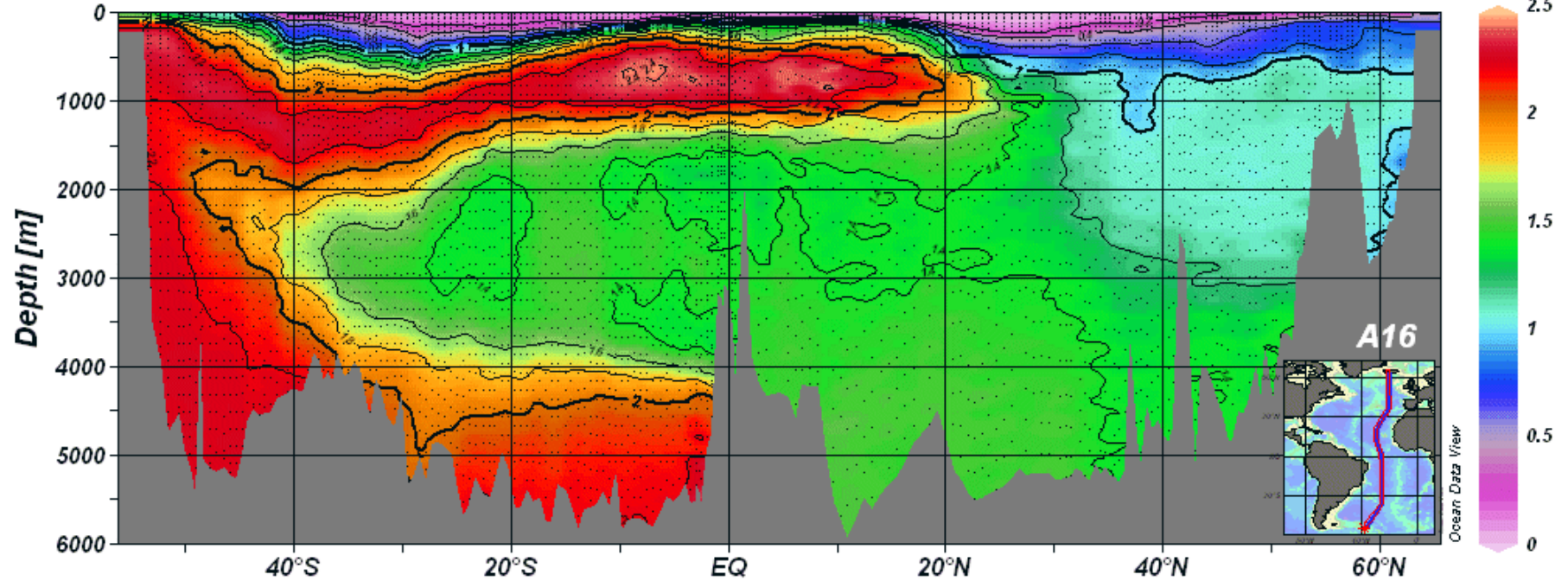**Typical SRP Distributions in the Open Ocean**

Typical depth profiles of SRP (= soluble reactive P)

(C.R. Benitez-Nelson, 2000, "The biogeochemical cycling of phosphorus in marine systems," *Earth-Sci. Rev.*, 51: 109-135)
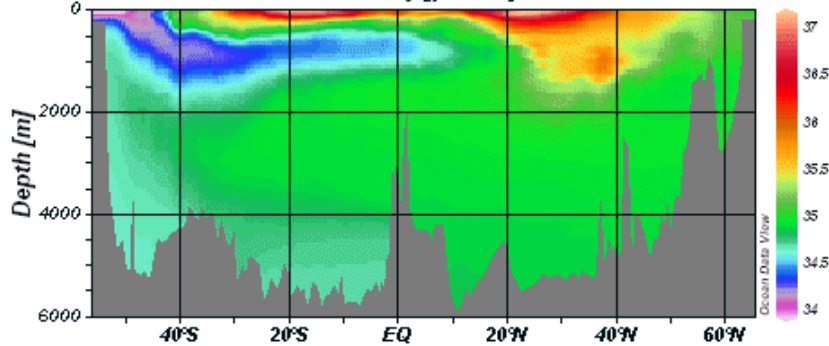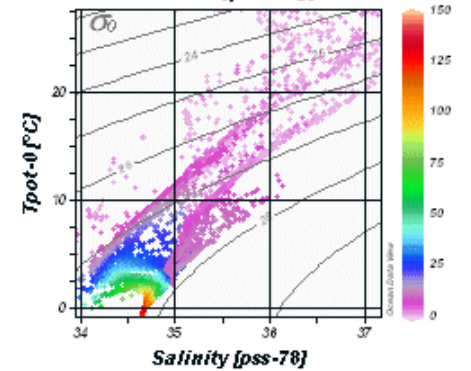
eWOCE

Phosphate [µmol/kg]

A16

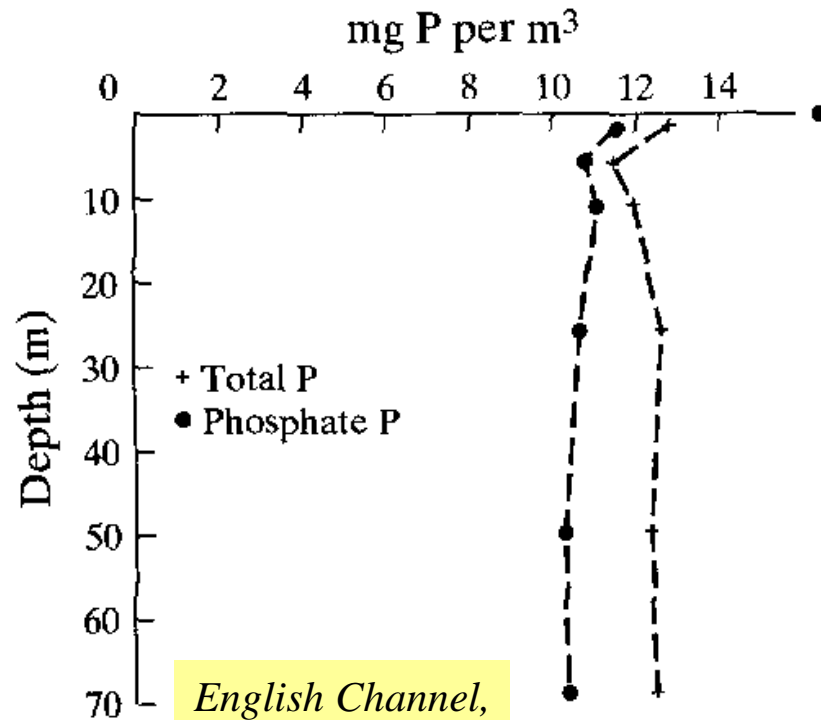Salinity [pss-78]

Nitrate [µmol/kg]
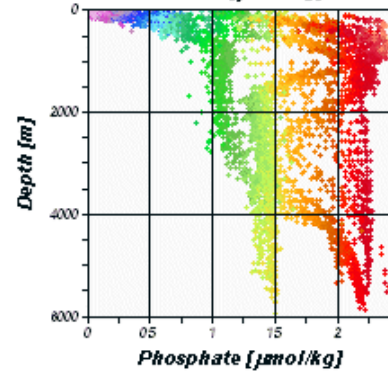
Silicate [µmol/kg]

Dissolved Organic P
(Soluble Non-Reactive P)

Generally not well characterized, includes:
- Phospholipids
- Phosphoproteins
- Nucleic acids

Seasonal Cycle!!!
Labile!

English Channel, Jan. 1949
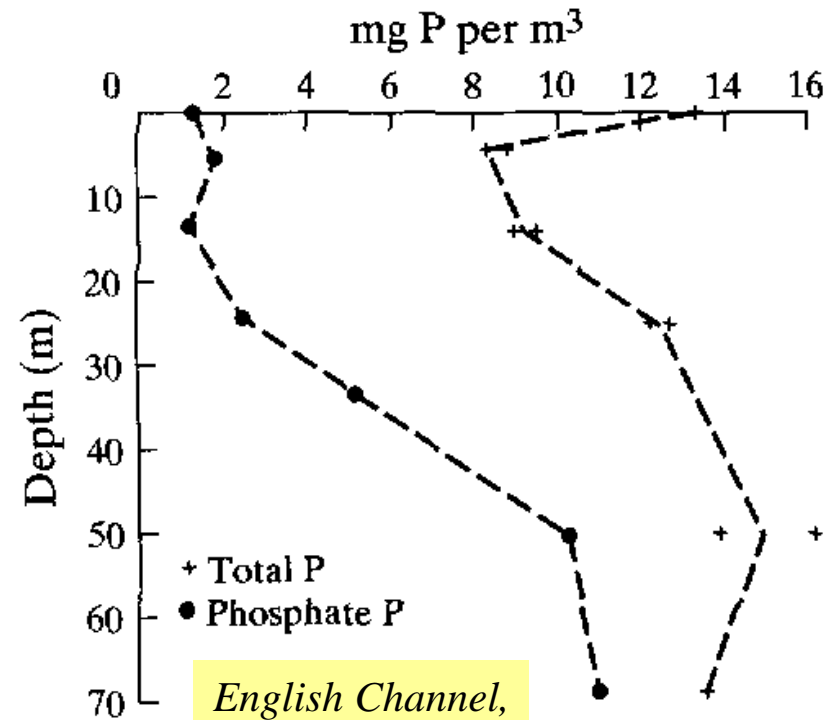
English Channel, Aug. 1949

Dissolved Organic P

Figure 8.4 *Variations during one annual cycle of the concentrations of various components of total phosphorus in the water of Departure Bay, Vancouver Island, British Columbia. Samples were taken at a depth of 5 m. (a) Particulate phosphorus (b) Total dissolved phosphorus (c) Proportions of inorganic and organic components of the dissolved total phosphorus.* (From Strickland and Austin 1960.)

Phosphorus Cycling:

- Simpler than N-cycle. No (direct) REDOX chemistry!

- Almost all P found in +5 oxidation state.

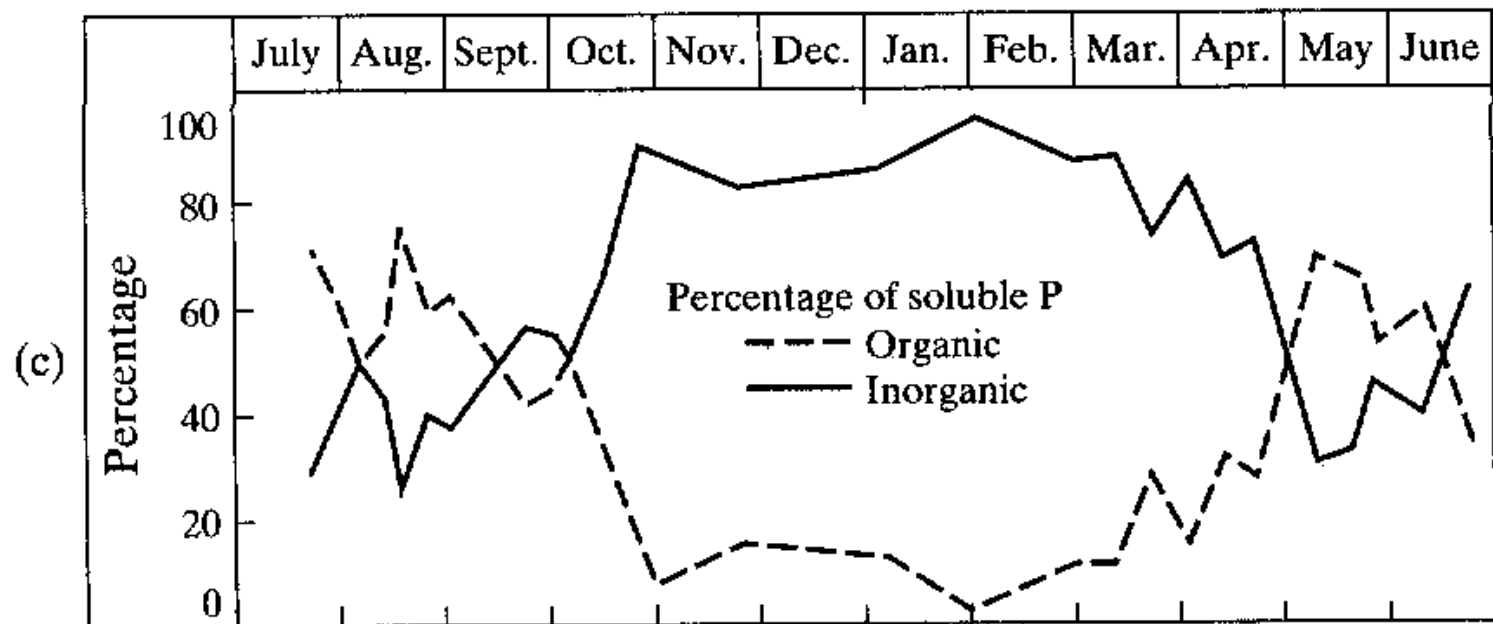- PO_4^{3-} is subject to strong adsorption onto particle surfaces (e.g. iron oxides or $CaCO_3$ surfaces)

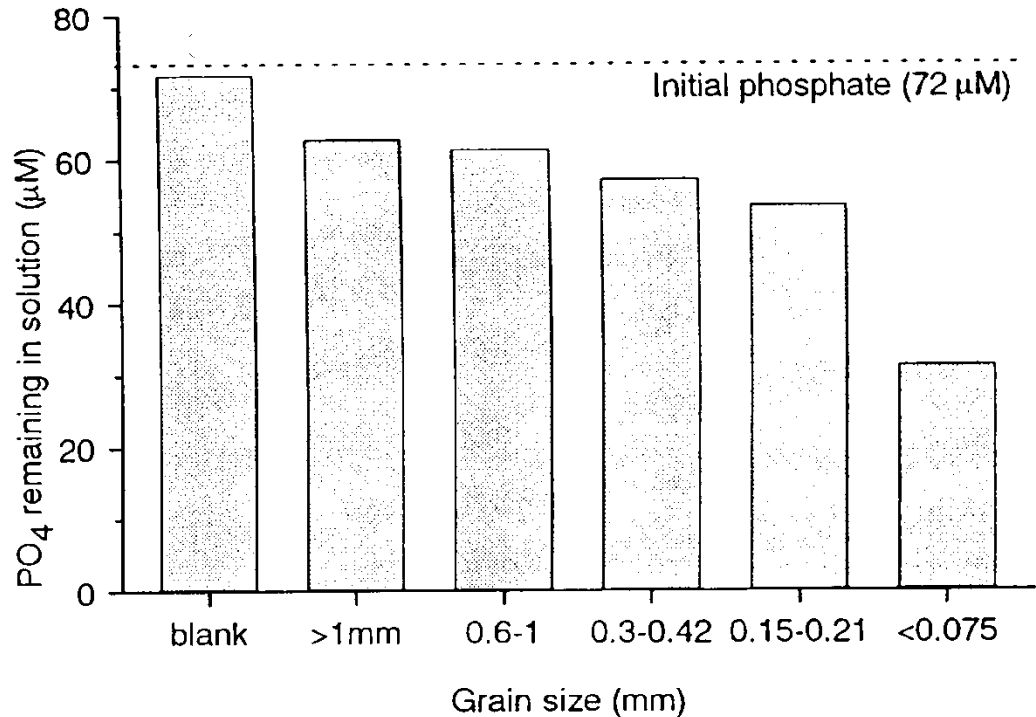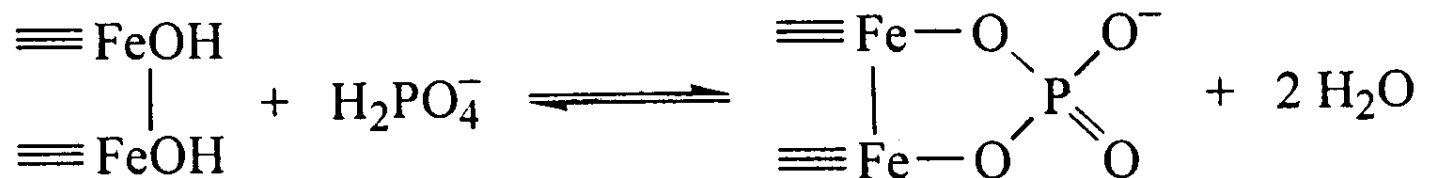Fig. 7. Phosphate adsorption by calcium carbonate sediment (Barang Lompo) of different grain-size categories after 3 h incubation in an initial PO_4 solution of 72 μM (experimental procedure: see text). (Maximum SD < 2 μM)

$$\equiv FeOH \atop | \atop \equiv FeOH \quad + \quad H_2PO_4^- \quad \rightleftharpoons \quad \equiv Fe-O \diagdown \atop | \atop \equiv Fe-O \diagup P \diagdown O^- \diagup O \quad + \quad 2\,H_2O$$

Special chemistry of phosphorus

- Adsorption onto particles and formation of insoluble complexes with metals (typically Fe) under aerobic conditions

- Generally, P does not travel far in the sediment

- Under reducing conditions P can be desorbed from iron oxides and released into pore water or water column

- Hence P has an "indirect" redox chemistry (via the redox chemistry of iron)

- "phosphorites" can be formed in sediments under reducing conditions and with large supply of organic material to sediments (e.g. in upwelling regions). Phosphate in phosphorites is present as fluorapatite $Ca_5(PO_4)_3F$, and hydroxyapatite $Ca_5(PO_4)_3OH$ or $Ca_{10}(PO_4)_6(OH)_2$
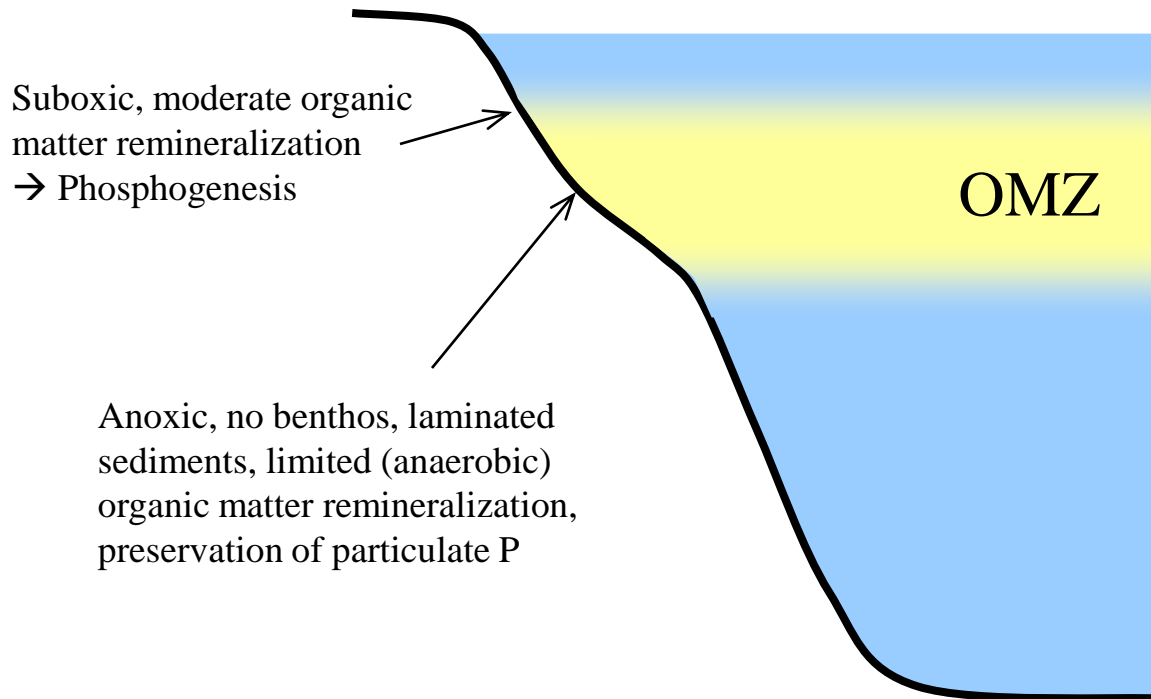
Special aspect of phosphorus cycle

- No major atmospheric component to the P cycle

Phosphorite formation

→ Francolite (carbonate-fluorapatite): $(Ca)_5[F/(PO_4, CO_3)_3]$

→ Formation in sediment or at sediment surface under specific conditions:
  - under high POC and adequate P and Ca contents,
  - under weakly reducing conditions,
  - often at boundary of Oxygen Minimum Zones
    → Upwelling areas

Loss of phosphorus from oceanic nutrient pool!

Suboxic, moderate organic matter remineralization
→ Phosphogenesis

OMZ

Anoxic, no benthos, laminated sediments, limited (anaerobic) organic matter remineralization, preservation of particulate P

F^- Ca^{2+}

Water
Sediment

Weakly reducing

Phosphogenese

PO_4^{3-} A_T
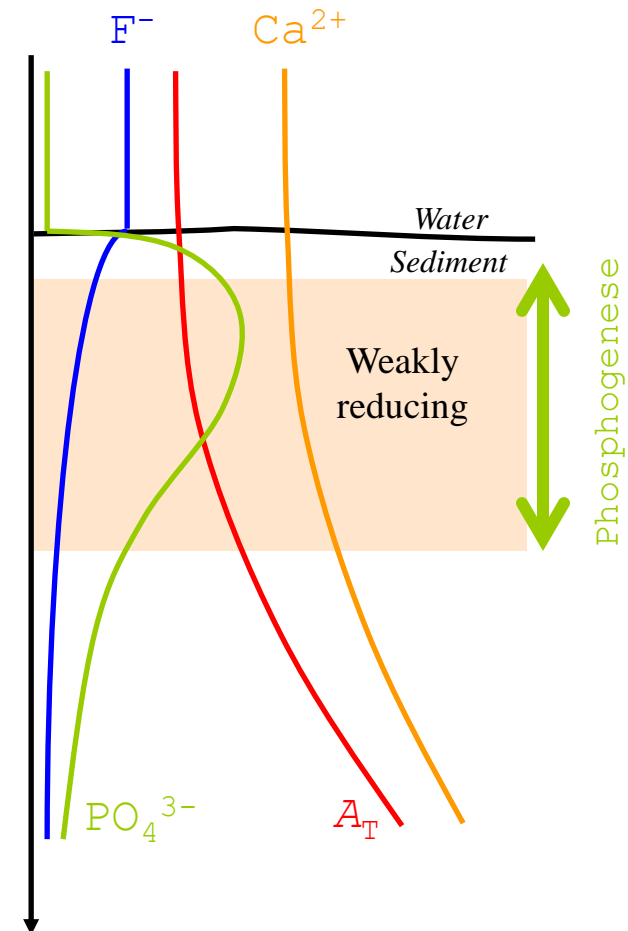
Sources of P

River Inputs

<u>Dissolved P (<0.45 μm):</u>   Organic
                                     Inorganic (mainly 'orthophosphate')

                                     → Both together are called
                                        "Total dissolved P" or TDP

Pre-Anthropogenic TDP Flux   ~ 1×10^{12} g yr^{-1}
TDP Flux NOW   ~ 2×10^{12} g yr^{-1}

<u>Particulate (>0.45 μm).</u>   Organic
                                     Inorganic
                                     Includes adsorbed P

Particulate Flux (poorly known)   ~ 14×10^{12} g yr^{-1}
Pre-Anthropogenic particulate 'reactive' P   ~ 1.5×10^{12} g yr^{-1}

Sinks of P

Organic matter burial $1 - 2 \times 10^{12}$ g yr^{-1}

Burial of apatite in sediments 1×10^{12} g yr^{-1}

$Ca_5(PO_4)_3(X)$ X = Cl or F or OH

Adsorption on Fe oxides 0.7×10^{12} g yr^{-1}

(volcanic rock – seawater interaction)
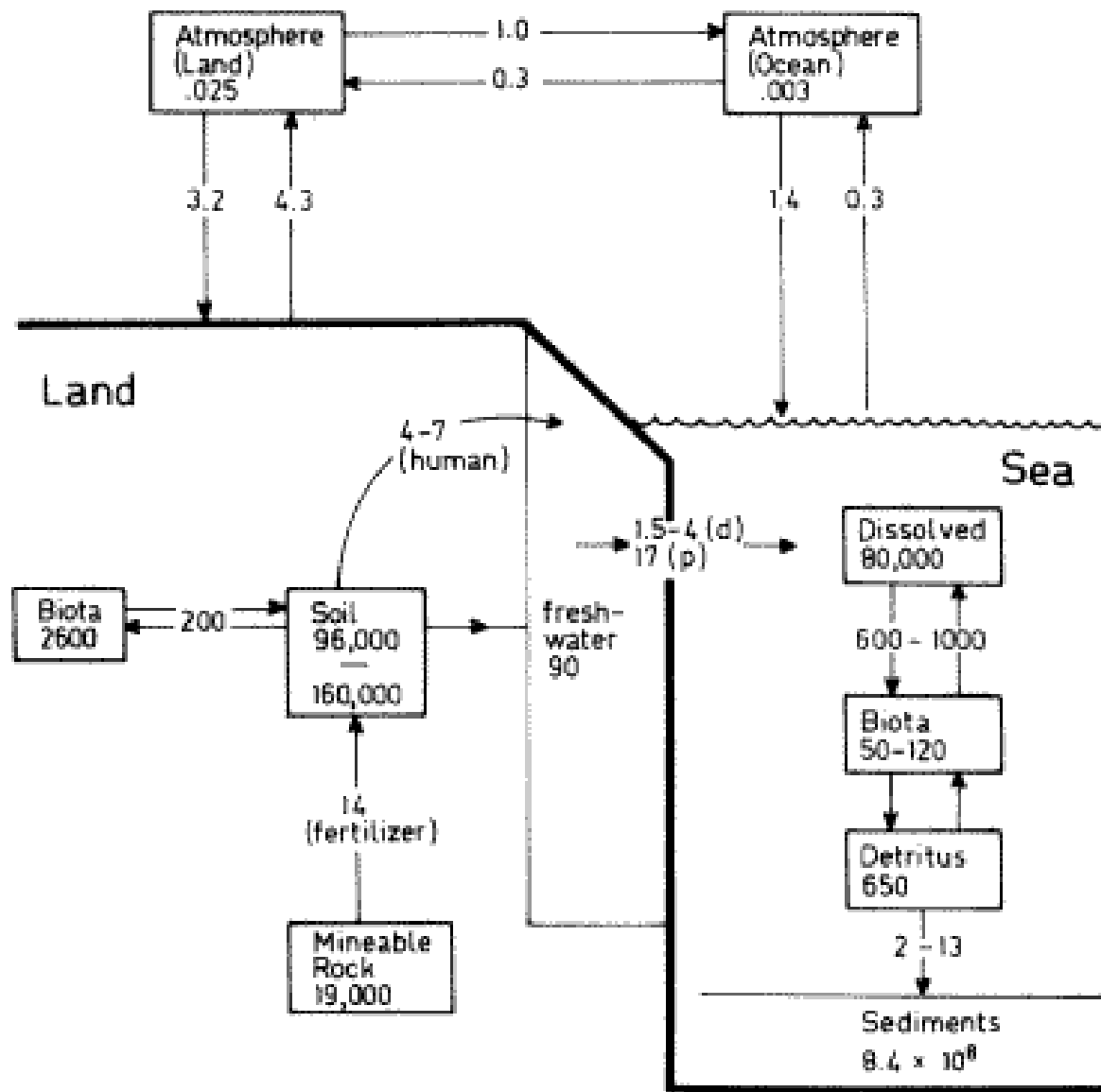
Transformations of phosphorus
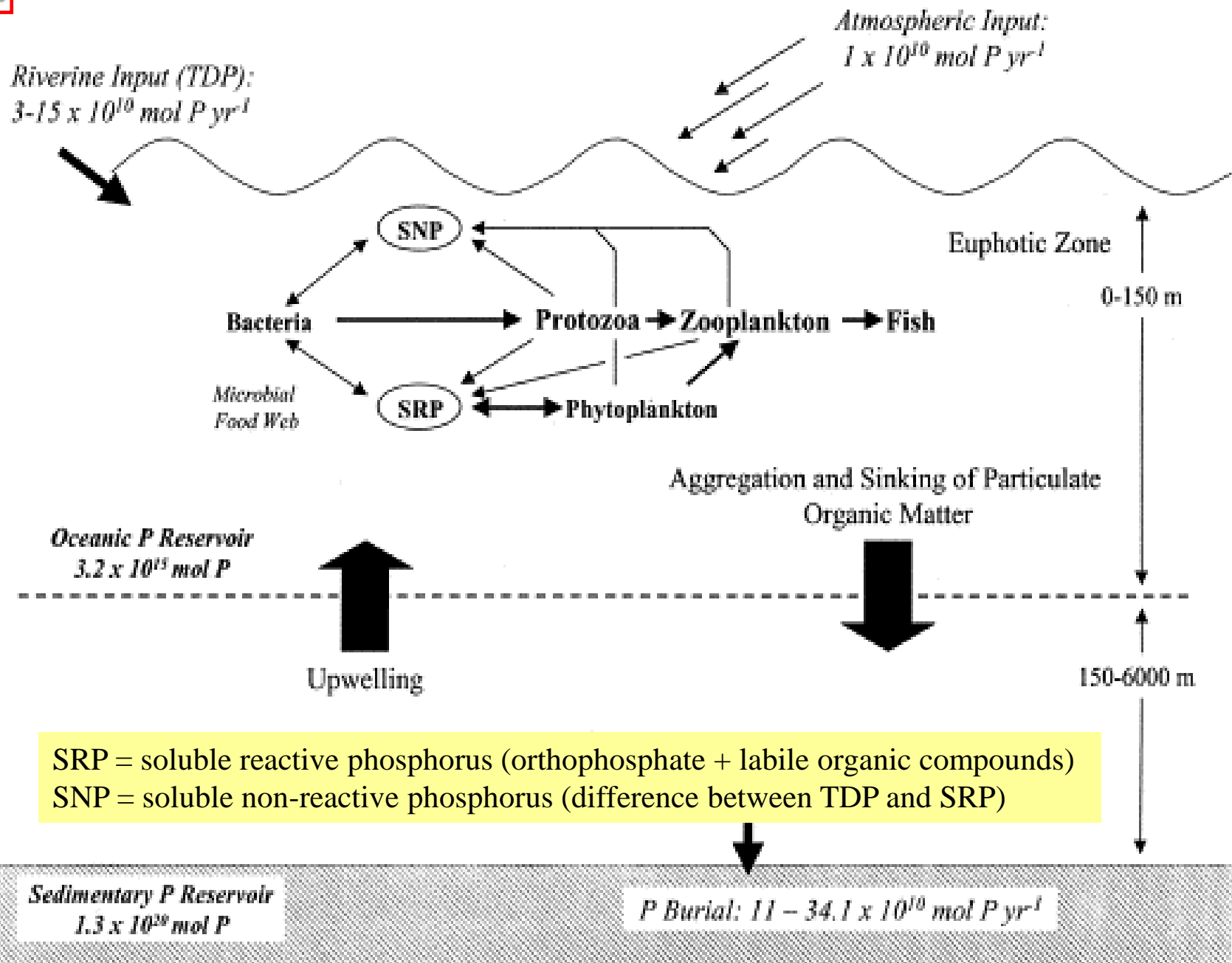
<u>Fast parts of the cycle:</u>

- Uptake by algae

- Uptake by bacteria

- Regeneration by bacteria

- Regeneration by other heterotrophs

- Interaction with solid phases
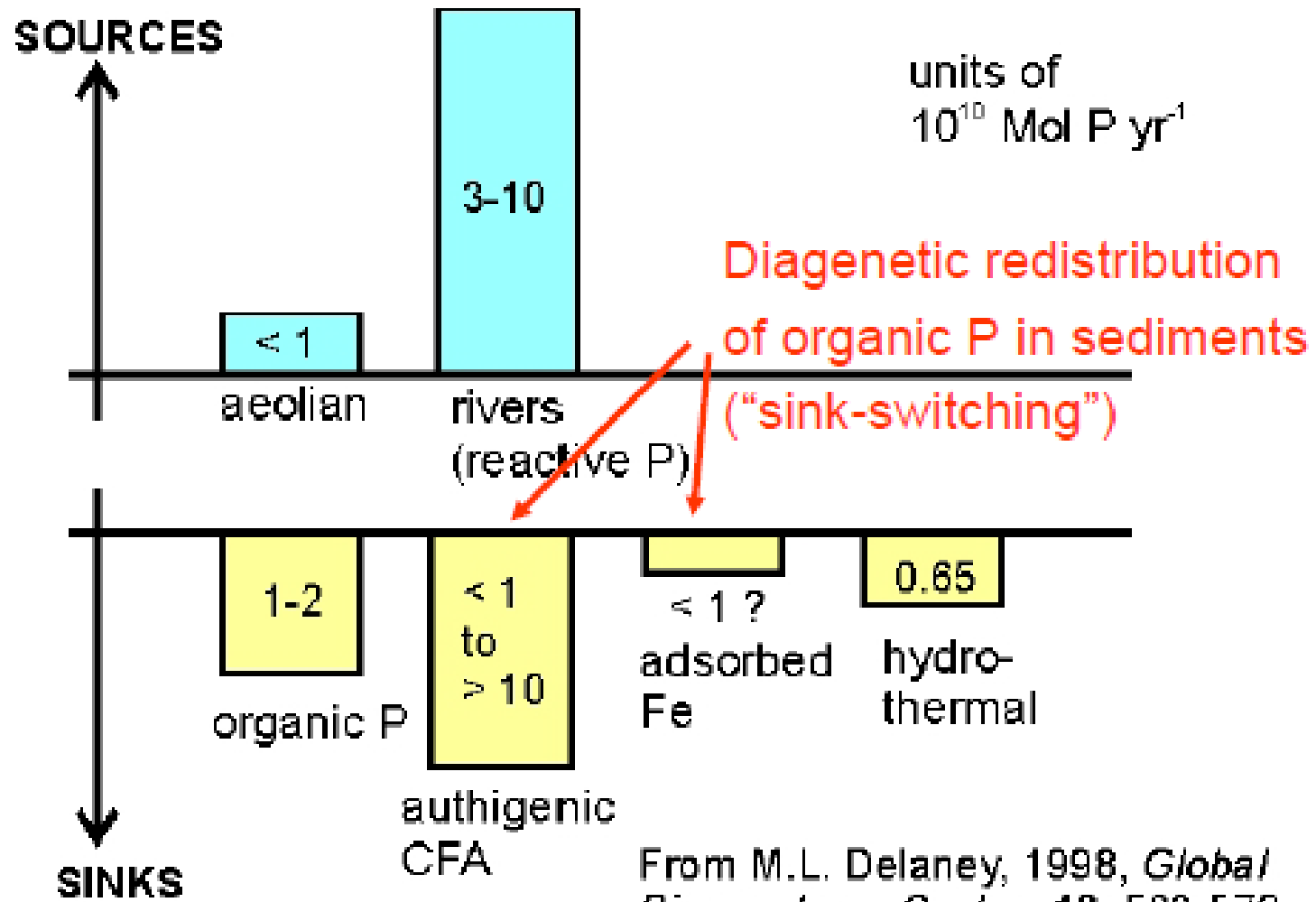
<u>Slow part of the cycle:</u>

- uplifting of sedimentary rock, occurs over geological timescale

- Rock weathering provides P back to the oceans

Global phosphorus cycle. Fluxes are in Tg P yr^{-1} and reservoirs are in Tg P
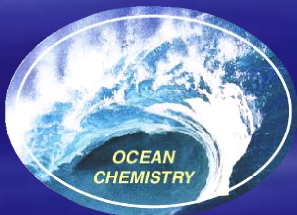
Atmospheric Input:
1×10^{10} mol P yr^{-1}

Riverine Input (TDP):
$3-15 \times 10^{10}$ mol P yr^{-1}

SNP

Euphotic Zone

0-150 m

Bacteria → Protozoa → Zooplankton → Fish

Microbial Food Web

SRP → Phytoplankton

Aggregation and Sinking of Particulate Organic Matter

Oceanic P Reservoir
3.2×10^{15} mol P

Upwelling

150-6000 m

SRP = soluble reactive phosphorus (orthophosphate + labile organic compounds)
SNP = soluble non-reactive phosphorus (difference between TDP and SRP)

Sedimentary P Reservoir
1.3×10^{20} mol P

P Burial: $11 - 34.1 \times 10^{10}$ mol P yr^{-1}

Magnitude of P fluxes in the ocean.

From M.L. Delaney, 1998, *Global Biogeochem. Cycles*, **12**: 563-572.

Nutrient Cycles

- The distribution of nutrients
  – profiles and patterns

- **Controls on nutrient distributions**
  – **nutrient ratios**

OCEAN
CHEMISTRY

Redfield ratio

C:N:P = 106:16:1 marine plankton

$$(CH_2O)_{106} (NH_3)_{16} H_3PO_4$$

"Redfield Molecule"
Originally described by Redfield *et al*.
from work in the Gulf of Maine

Nutrient ratios in the deep sea

<u>IF:</u>
- all organic matter has the Redfield Ratio
- all organic matter is decomposed in the deep sea

<u>THEN:</u>
- slope of measured $NO_3:PO_4$ and $AOU:PO_4$ should equal the Redfield Ratios
- e.g. slope of $NO_3:PO_4$ concentrations should equal 16

- NOT ALWAYS TRUE
- Possible Reasons:
  - preferential decomposition of different types of organic material?
  - non-Redfield organic material is produced?
  - non-aerobic oxidation of the organic material

Nitrate and Phosphate look remarkably similar:
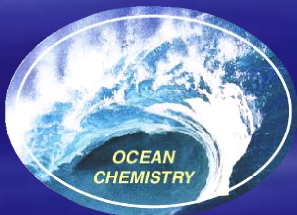
$NO_3:PO_4 \sim 15/16$
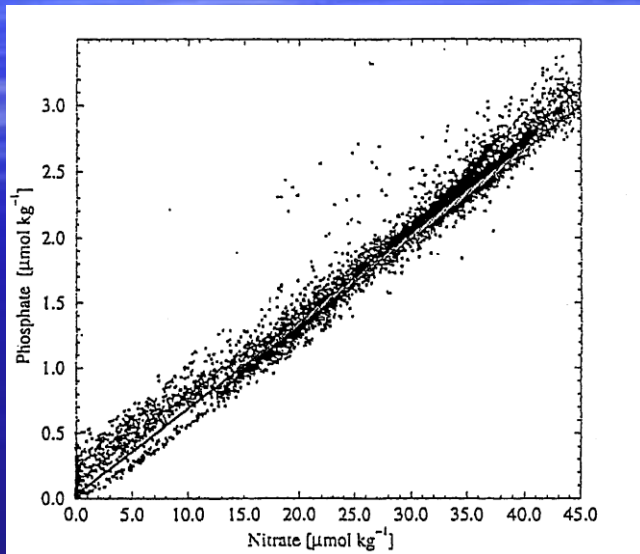
*Anderson and Sarmiento, 1993
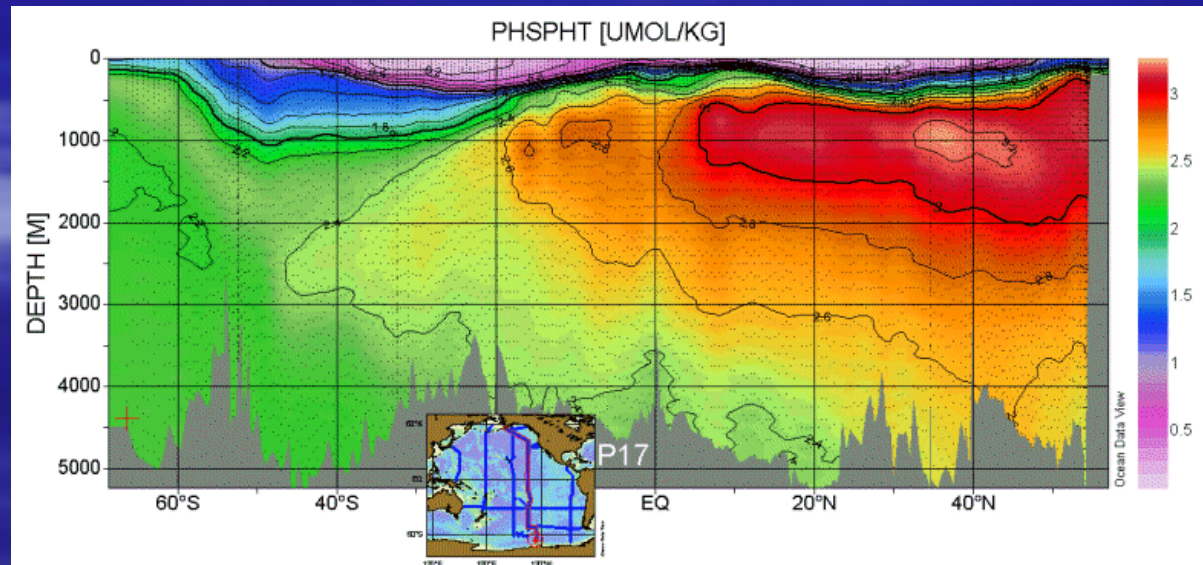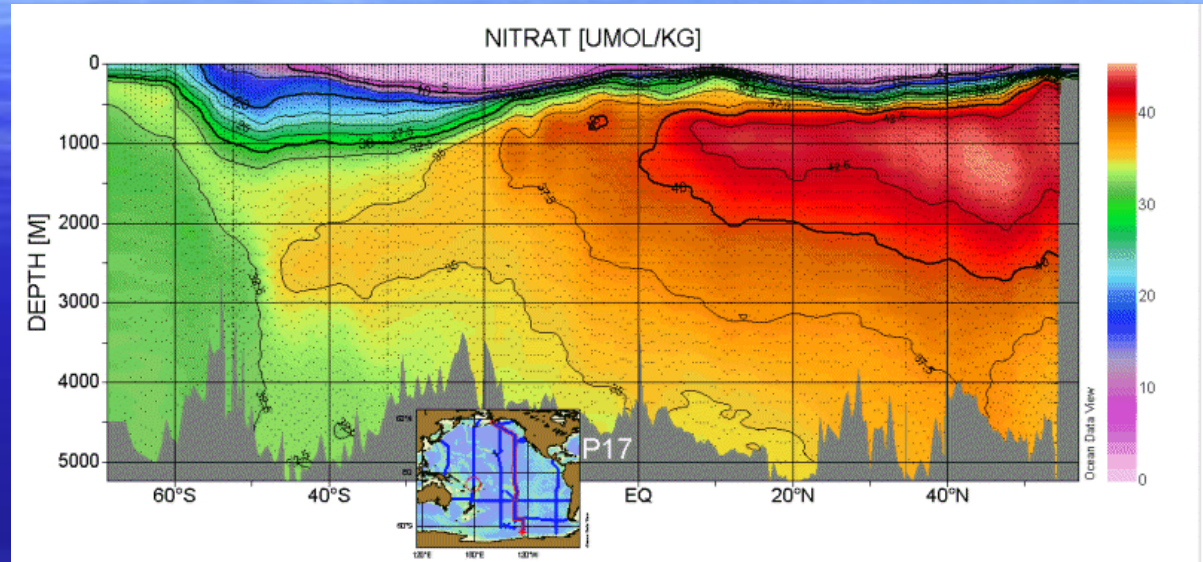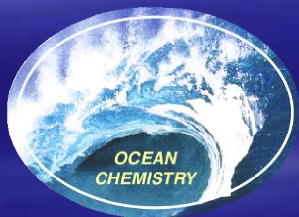
N:P Ratios

- Nitrate and Phosphate look remarkably similar
  - "Redfield Ratio" for recycled N and P is about 15:1
    - as determined by co-variation along water mass trajectories
  - bulk decomposition of Redfield material
    essentially inverse of bulk organic matter formation

  there's only so many ways to "building" living material

Deviations from ideal N:P Ratios

- Note scatter in diagram
- Regional Variations in the composition of the organic material supply
- Differences in recycling rates between the constituents
- Additional biogeochemical processes (e.g., nitrification/denitrification)
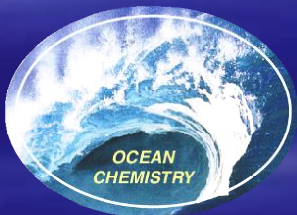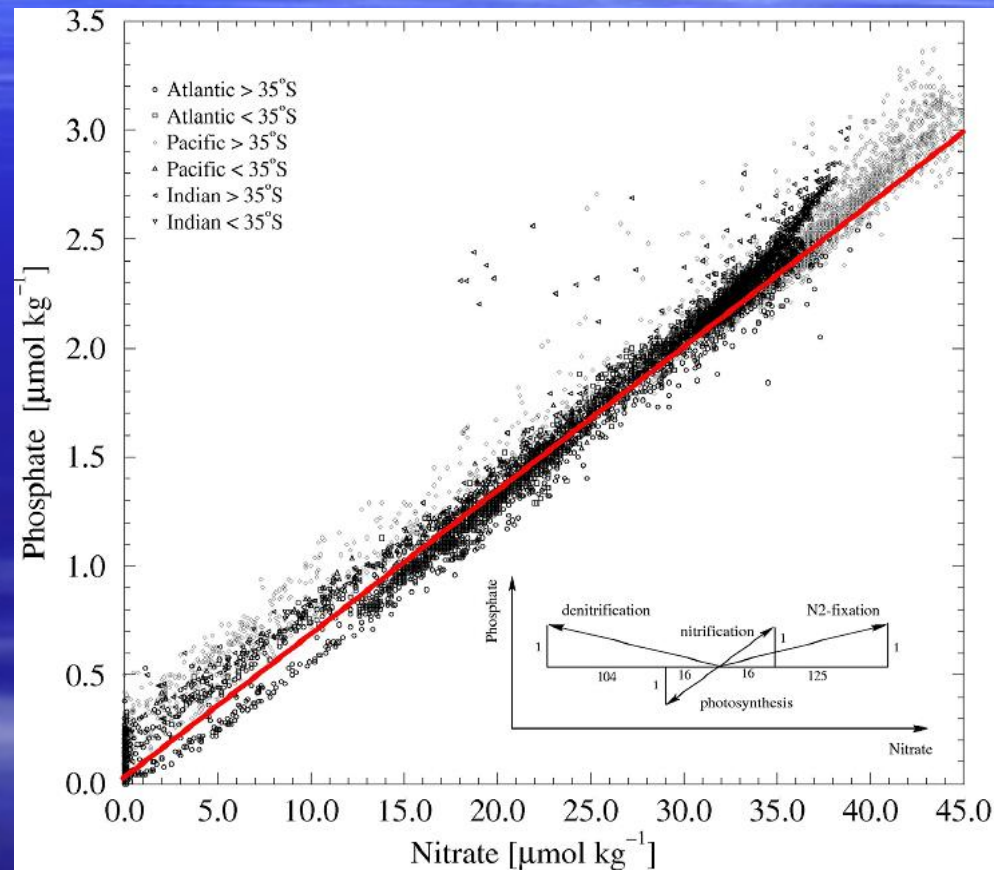
Nitrate vertical profile in O_2–deficient areas
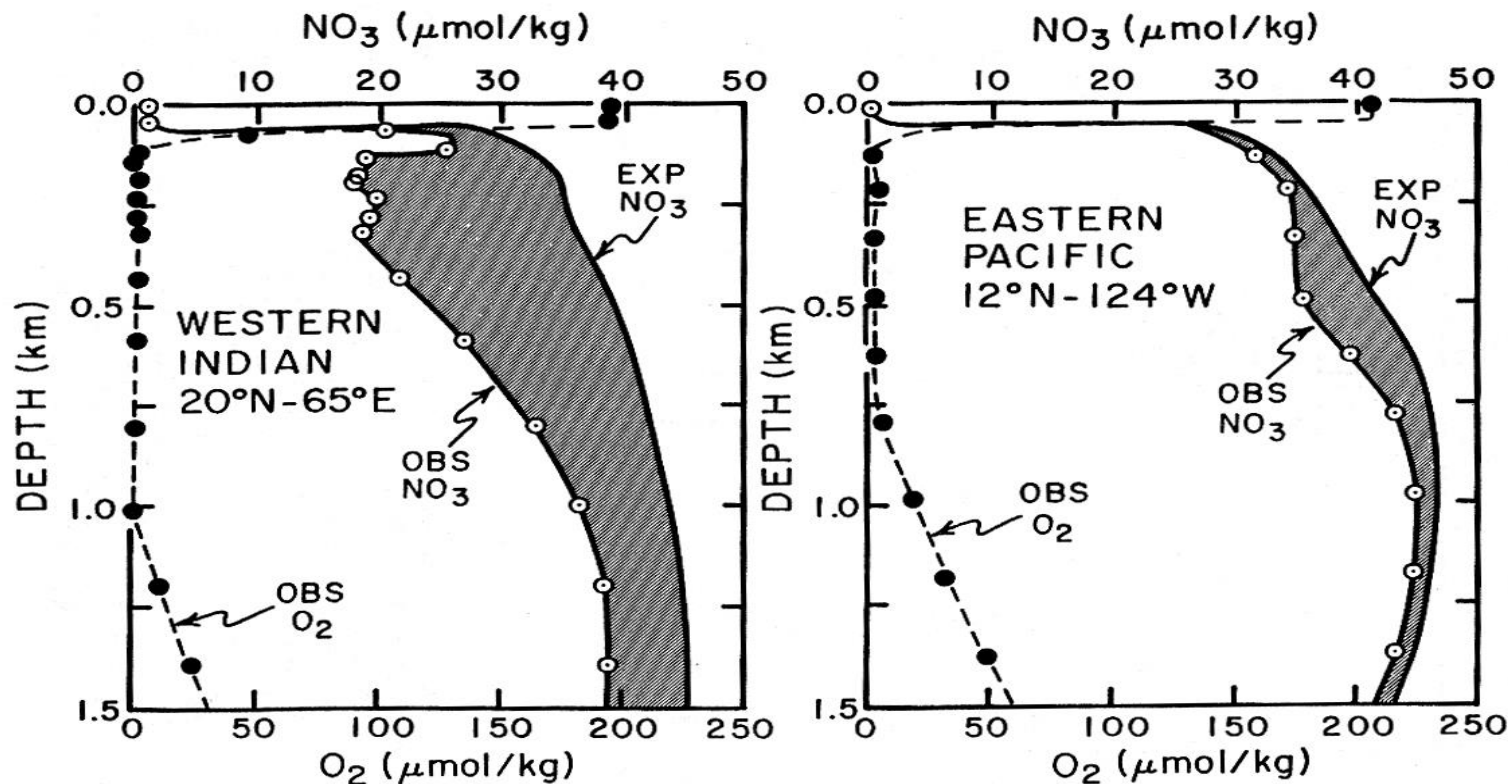## « expected nitrate » = $16 \cdot [PO_4^{3-}]$

Figure 3–16. Plots of the dissolved oxygen and of the nitrate concentration versus depth in the northern part of the western Indian Ocean and in the eastern part of the equatorial Pacific. Both areas have thermoclines in which the dissolved oxygen content goes to zero. In these waters nitrate is utilized by bacteria as an oxidizing agent leading to nitrate deficiencies in the water column (see the shaded area between the measured and the expected nitrate concentration curves). The expected nitrate concentration is calculated by multiplying the measured PO_4 concentration by 15. These results were obtained as part of the GEOSECS program (425, 426).

Denitrification: ($NO_3 \rightarrow NO_2 \rightarrow N_2$)

$\Rightarrow$ evidence for 'missing' nutrients
e.g. in Indian Ocean thermocline
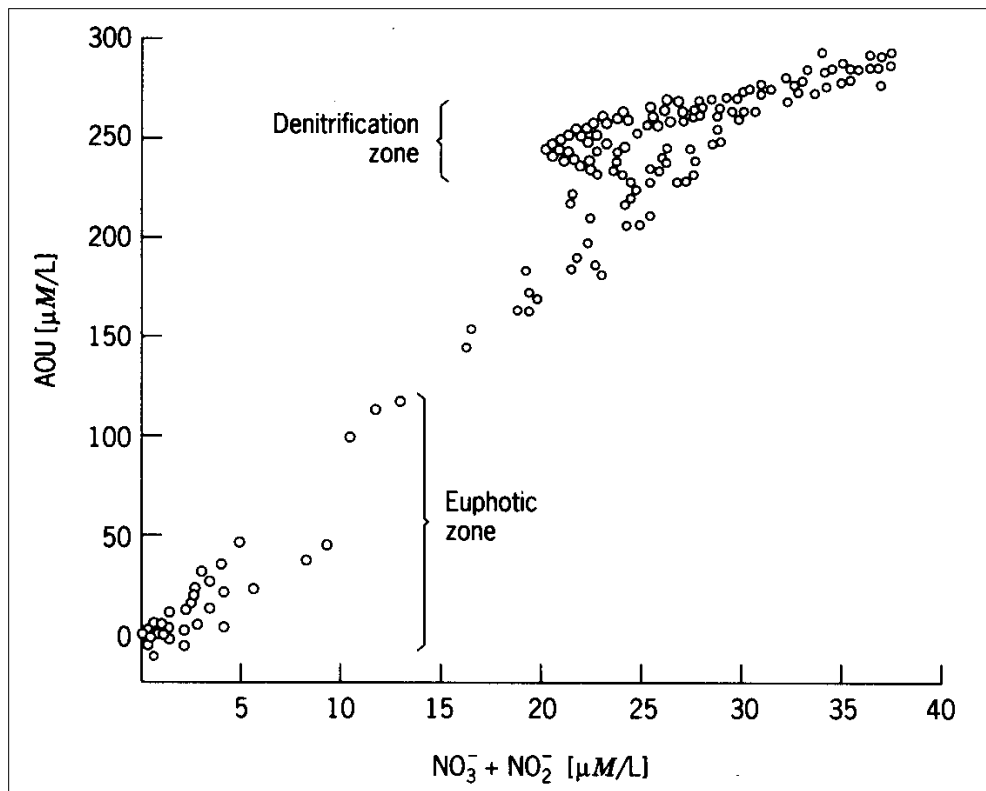
AOU versus [NO_3^-] + [NO_2^-] in the waters of the Arabian Sea

So… nitrogen containing nutrients can be removed…. not only recycled within the ocean.