

Nutrients

Nutrients are generally considered to be elements or compounds (e.g. N is a nutrient, NO₃ and NH₄ are types of N compound that are also nutrients) that are needed for biological growth.

Classification of Elements or Nutrients (Wally Broecker):

Bio-unlimiting—their distribution is determined solely by physics

- generally show no vertical structure in the ocean
- or they covary with sodium, etc.
- may be necessary for biology, but so abundant that they never run out...for example, sodium and potassium are used by cells, but the distribution has nothing to do with biology

Bio-intermediate—they are needed for biological processes, but they aren't entirely controlled by biology

- typically covary with Phosphorous with depth, to some point
- this may be because they are actually biologically used in small quantities (e.g. carbon, nickel, calcium, selenium) or because they mimic bio-active elements (e.g. germanium)

Bio-limiting—essentially zero in the surface waters, increase with depth
-subdivided into **Macronutrients** and **Micronutrients**

- macronutrients make up the gross composition of organisms:
- P, C, N, Si, O, H
- Generally used to make up the skeleton, major pools, etc.
- micronutrients are needed in trace quantities, and are often found in trace quantities
 - Zn, Fe, Se, Mn, Co
 - often used in enzyme reactions

Non-Cyclic—so reactive, they are immediately “scavenged” or removed by attachment to particles

- Th, Pb, Fe
- Can use this principal to look at sedimentation rates
 - Th²³⁴ equilibrium values

UNITS: we usually refer to nutrient values in terms of their molar quantities. This is typically expressed as $\mu\text{g-at}$ or mg-at per unit volume, or as μM or mM . These are typically interchangeable but if there's more than one atom per molecule, this is NOT true! Carbon is unusual in that we sometimes refer to it in terms of grams.

1 Mol = 6.02×10^{23} atoms of substance

1 Molar = 1 Mol/Liter

mM = 1/1000 (Total carbon)
 $\mu\text{M} = 1\text{E}-6$ (most macronutrients)
nM = 1E-9 (micronutrients such as iron)
 $\text{pM} = 1\text{E}-12$ (micronutrients, trace organics such as pesticides)

1 $\mu\text{g-at L}^{-1}$ equals 1 mg-at m^{-3} , so when we integrate, $\mu\text{g-at L}^{-1}$ becomes mg m^{-2}

Biolimiting Nutrients

We are interested in these because they control production and biomass.

Liebig Limitation: the nutrient that controls the absolute accumulation of biomass.

Blackman Limitation: we need to consider not only the nutrient that limits absolute accumulation, but how fast we get there (rate-limiting factors)

Distribution:

Vertically: obviously more in the deep water than in the surface waters

BIOLOGICAL PUMP—Phytoplankton take up C, Nutrients, die, sink out (about 90% stays in euphotic zone and is recycled)...pumps C and nuts towards the bottom

Globally:

PO_4 is low in the Atlantic, high in the Indian and Pacific (1.2, 2.5, 3)

NO_3 is low in Atlantic, higher in Indian and highest in Pacific (20, 35, 40)

Si shows strong gradient between Atlantic, Indian, Pacific (30, 120, 160)

A.C.Redfield – 1930's at WHOI, noticed a relationship between $\text{NO}_3:\text{PO}_4$, then later between $\text{NO}_3:\text{PO}_4:\text{O}$. This has since then been extended to include all biolimiting nutrients. In general, inorganic nutrients are found at a constant ratio, throughout the world's oceans.

Shuter (1979) Formally extended this by stating that phytoplankton take up nutrients in constant proportions...e.g. organisms also have a Redfield Ratio for uptake rates

Is this true? More or less...phytoplankton generally have Redfield proportions.

Exceptions: Dinoflagellates often have 9:1 C:N

Bacteria typically have C:N of about 2-4:1

Soft tissue: 105:15:1

Hard Parts (shells): 26:0:0 (26:50 Ca:Si)

Deep Water: 1000:15:1, 5000:50
(C=CO₂+HCO₃+H₂CO₃)
Shallow Water: 869:0:0 (974:0)

BIOLOGICAL UTILIZATION:

- Biology is generally considered to be controlled by N, P, or Si (now also Fe)
- Fresh water, P is almost always limiting...this is because P is extremely particle-reactive, and freshwater has a high surface area to volume ratio
- In the oceans, we generally assume that N is limiting

Phosphorous Cycle:

- Only place it can come from is outside the oceans, or from internal recycling
- Turns over very quickly...
- Primary type is PO₄, but DOP is also important
- Used in DNA, RNA, phospholipid bilayer, ATP, ADP, etc.

Silica Cycle

- most abundant element in continental crust
- also has to come from outside the oceans
- very abundant in the older ocean basins, also high in freshwater runoff
- used as silicic acid (SiOH₄)
- primarily used by diatoms (and silicoflagellates) as skeletal structure
- used to think it had an extremely slow dissolution rate, because diatoms cover the skeleton with a membrane, and essentially a chemical reaction that dissolves it, so slows down at cold temperatures

Iron Cycle

- extremely reactive, also extremely bio-reactive
- most of it comes from 3 sources: biological turnover, upwelling (from continental crusts), and aeolian deposition
- bacteria make compounds called **siderophores** that react with Fe, make it available...appears that diatoms can also access that form of iron

Nitrogen Cycle

- Much more complicated than P or Si
- About 70% of the atmosphere is N₂ gas, but this gas is inert
- There are many forms of N available to oceanic phytoplankton:
- Inorganic (NO₃, NO₂, N₂)
- Organic (NH₄, urea, DFAA, other DON compounds)
- Nitrifying Bacteria: oxidize NH₄→NO₂→NO₃
- Denitrifying Bacteria: reverse process (mostly occurs in anoxic sediments...they are using NO₃ and NO₂ as electron donors)

- Nitrogen Fixation: can directly utilize N₂ gas by “fixing” it into organic compounds....this is extremely energy inefficient, and can't occur in the presence of oxygen

UPTAKE MEASUREMENTS

We can measure nutrient uptake in 3 ways:

- 1) Nutrient depletion...this is cheap and easy, but only as sensitive as the method you use, and can't account for transformation to different compounds (e.g uptake of NO₃, release of NH₄)
- 2) Radio-isotopes...these are extremely sensitive, but they are radioactive, and not all compounds have them (e.g. Nitrogen)
- 3) Stable-Isotopes...primarily N, C, and Si

When we use isotopes, we measure two different things:

V: the velocity of uptake, time dependent

Rho: the absolute uptake rate (volume or biomass dependent)

Radioisotopes measure Rho, need to measure biomass to get V

Stable Isotopes measure V, need biomass to get Rho

Note that we can increase uptake rates by either having a low V and high biomass (so high Rho), or having low biomass but high V.

Kinetics of Nutrient Transport:

We are interested in the rate processes of how nutrients are taken up. Most nutrients are taken up by active transport, meaning that they have to take it up against a gradient....typically, cells have 100x more nutrients inside the cell than they do outside the cell. This results in a hyperbolic function similar to the PvsE curve

Michaelis-Menten Curve: derived from enzyme kinetics

$$V = V_{max} * S / K_s + S$$

Monod Curve: same thing, except we use growth instead of nutrient uptake

Lineweaver-Burke Analysis: reciprocal plot of uptake vs. concentration, which linearizes the curve and makes it easier to calculate V_{max} and K_s .

NOTE: It takes about 10x more nutrients than the K_s to saturate uptake!

Healey (1980) pointed out that the *slope* is much more important than the K_s value, since two species can have the same slope but different V_{max} values...at low nutrients, they are equally competitive.

Droop Kinetics: Similar to Michaelis-Menten, but we assume that phytoplankton can take up excess nutrients and store them in internal pools. So we need to know the cell Quota:

Cell Quota (Q) is the amount of nutrient that cell wants to achieve (optimal concentration)

This allows for “surge uptake” by nutrient-starved populations, which does not fit the classic definition of a Michaelis-Menten curve.

Population Ecology:

Combining all of these things, it is clear that multiple species can compete by having different V_{max} , α , K_s , and Q's for varying nutrients. In general, picoplankton have very high affinity, but low capacity (bacteria will always outcompete diatoms at low concentrations).

Size is also important: small cells have a much smaller surface:volume ratio, so can more easily overcome diffusion limitation. Large cells sink faster, though, possibly increasing their opportunity to interact with nutrient fields.

When we add adaptations to light (and to some extent temperature), we get another dimension of variability...so there can be a very large number of adaptations based on light, nutrients, and temperature to growth rates, suggesting that it should not be at all surprising that there are so many species and ecotypes of phytoplankton.