

Lecture 20

Nutrients in Fresh Water Systems

Reading for this week: BB Ch6 (236-263)

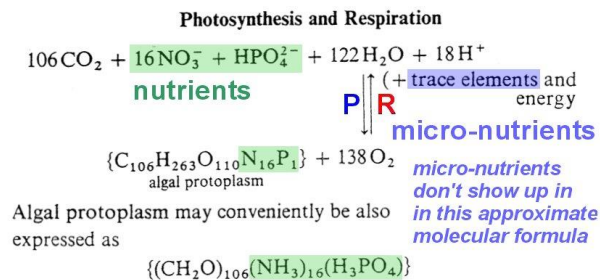
Today –

1. Nutrients, eutrophism in lakes and rivers

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The Terrestrial Aquatic N and P cycles, revisited.

The concentrations of N, P C and O in the hydrosphere are intricately related by the Redfield relationship.



$\Delta \text{N (+)} / \Delta \text{P (+)} = 16$	$\Delta \text{CO}_2 (+) / \Delta \text{P (+)} = 106$
$\Delta \text{CO}_2 (+) / \Delta \text{N (+)} = 6.6$	$\Delta \text{O}_2 (+) / \Delta \text{P (-)} = 138$
$\Delta \text{O}_2 (+) / \Delta \text{N (-)} = 8.6$	$\Delta \text{O}_2 (+) / \Delta \text{CO}_2 (-) = 1.3$

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Atmosphere exchanges.

Nitrogen:

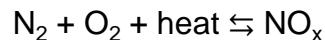
“fixed” N occurs in a number of gaseous forms that are easily exchanged to the atmosphere.

Natural sources of atmospheric "fixed" N (NO_x and NH_3) are:

- direct emission by the biosphere and from soils
- minor NO_x production by lightening

Anthropogenic sources:

- NO_x production by pollution (especially internal combustion)



Phosphorous:

occurs mostly in insoluble, inorganic forms (not easily exchanged to the atmosphere).

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Atmosphere exchanges – recall from last lecture....

NH_3 vapor dissolves in rain to produce NH_4^+ and OH^- (*base*)

NO_x vapor dissolves in rain to produce NO_3^- and H^+ (*acid*)

But, the rain flux of [N] and [P] to the landscape is very small.

- ♣ Marine rain: [N] and [P] of surface sea water are VERY low (consumed during photosynthesis), so [N] = [P] ~ 0 in marine aerosols.
- ♣ N in terrestrial rain derives from atmospheric gasses primarily, with particulates running a distant second
- ♣ P in terrestrial rain derives primarily from terrestrial particulates; $[\text{P}]_{\text{rain}}$ is very low.

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[N] and [P] in terrestrial surface fresh waters (Rivers and Lakes):

- The [N] cycle has significant gas phase and biological components, with a large modern anthropogenic perturbation.

[N] enters rivers and lakes primarily through discharged soil waters. Soils are an important source of NH_4^+ and NO_3^- to the hydrosphere and biosphere.

- The [P] cycle has no significant gaseous components.

[P] enters rivers and lakes primarily as particulate matter and secondarily as dissolved inorganic phosphorous (DIP) also known as "ortho-P" (H_3PO_4 and its conjugate base forms).

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The terrestrial N and P cycles summarized

- ✓ Because "free" (aka "mineralized") N and P are utilized quickly by autotrophs, they have low T_{res} in most aquatic systems.
- ✓ N and P are transported and reside in inorganic and organic forms (bound in organic compounds).
- ✓ N and P transported and reside in dissolved and particulate forms.
- ✓ **Today, anthropogenic (pollutive) fluxes of both elements are ~50% of the total N and P cycle.**
- ✓ See the tables on the next 3 slides

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The terrestrial N cycle

TABLE 5.15 Terrestrial Nitrogen Cycle

Process	Total Flux (Tg N/yr)	Percent of Total Input or Output	Anthropogenic Flux (Tg N/yr)	Reference
<i>Land input</i>				
Biological fixation	139	49	44	Burns and Hardy 1975
Fertilizers & industry	85	30	85	FAO 1989
Precipitation and dry deposition	61	21	37	Table 3.15
Total input	285	100	166	
<i>Land output</i>				
River N	49–62	19	13–27	Table 5.16
Denitrification to N ₂ , N ₂ O	179	63	?	To balance (see text)
NH ₃ gas loss	37	13	27	(See Chapter 3)
NO _x : soil gas loss and biomass burning	14	5	5	(See Chapter 3)
Total output	279–292	100	>45	

Note: Tg = 10⁶ metric tons = 10¹² g.

Berner and Berner, "Global Environment"

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The terrestrial N cycle

TABLE 5.16 River Nitrogen Transport (in Tg N/yr)

	Natural	Pollution	Total
<i>Dissolved N</i>			
DIN			
NO ₃ ⁻ N	4.0	Inorganic	
NH ₄ ⁺ N	0.5		
DON	10.0	Organic	
Total dissolved	14.5	7 ^a –21 ^b	22 ^a –36 ^b
Particulate N (PN)	21	6 ^b	27–33 ^c
Total N (TN)		Inorg + Org	49–63
Reactive N ^d			28–42

Note: ^a Meybeck 1993.

^b Wollast 1993.

^c Meybeck (1993), 21 Tg; Ittekkot and Zhang (1989), 33 Tg; Wollast (1993), 27 Tg.

^d Total dissolved N plus 22% of PN; see text.

Source: Meybeck 1982; 1993, except where noted.

Berner and Berner, "Global Environment"

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The terrestrial P cycle

TABLE 5.17 Phosphorus Fluxes in Rivers and Rain (in Tg P/yr)

Source	Total Flux		Polluted Part	Reference
<i>P in river runoff</i>				
Dissolved ortho-P	0.8	Inorg Org	0.4	Meybeck 1982; 1993
Dissolved organic P ^a	1.2		0.6	
Total dissolved P	2.0		1.0	Meybeck 1982; 1993
Particulate organic-P	8.0	Inorg Org	?	Meybeck 1982; 1993
Particulate inorganic-P ^a	12.		?	
Total particulate P	20.0		?	Meybeck 1982; 1993
Total output	22		>1	
Reactive P output ^b	5			See text
<i>P in rain + dry deposition to land</i>				
Soil particle origin	3.0		0.2	Graham and Duce 1979
Industry, combustion	0.21		0.21	Graham and Duce 1979
Sea salt	0.03			Graham and Duce 1979
Total rain and dry deposition	3.2		0.41	
Rain only to land	1.0		—	Meybeck 1982

^a Calculated by difference from total; no data.

Berner and Berner, "Global Environment"

^b Total dissolved P plus 15% of particulate P (after Berner and Rao 1994).

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Summary of the terrestrial N and P cycles, continued.

- [N] DIN : DON = ~30% of total : ~70% of total = 4 : 10 ~ 2 : 5
- [P] DIP : DOP = ~40% of total : ~60% of total = 8 : 12 ~ 2 : 3
- [N] Dissolved : Particulate = 14.5 : 21 ~ 5 : 7
- [P] Dissolved : Particulate = 2 : 22 ~ 1 : 10
(where, i = inorganic, o = organic, d = dissolved)

Human activity has significantly increased the rate at which these elements move through the hydrosphere, with specific consequences for various parts of it.

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The perturbed terrestrial N Cycle in Terrestrial watersheds:

Because N cycles more quickly than P (significant dissolved N fluxes of its mobile forms), ecosystems have developed methods of "holding" N deposited on the landscape in rain more efficiently than P.

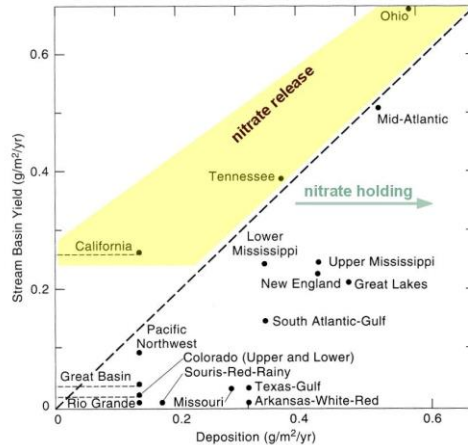


Figure 5.10. Median yield of nitrate ($\text{g}/\text{m}^2/\text{yr}$) in relation to the atmospheric deposition rate of nitrate ($\text{g}/\text{m}^2/\text{yr}$) in U.S. river basins grouped by region. (After R. A. Smith, R. B. Alexander, and M. G. Wolman, "Water Quality Trends in the Nation's Rivers," *Science* 235: 1612. Copyright © 1987 by the American Association for the Advancement of Science, reprinted by permission of the publisher.)

Berner and Berner, "Global Environment"

Pollutive N inputs can be "held" by high biomass ecosystems (e.g., forests), in which case N deposition on the landscape far outweighs the runoff yield.

Notice the few "N-saturated" systems (where runoff exceeds deposition). As an ecosystem becomes "saturated", then rapid N outflow may occur over a few seasons even at constant N input.

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N and P in polluted rivers:

☀ Agricultural Environments:

Excess N is almost always applied to soils in agricultural landscapes to increase plant yield because N fluxes quickly through the ecosystem.

P cycles more slowly through the hydrosphere (primarily in particulate form) and such soil waters have low [P]

Deforestation or agricultural soil erosion are types of anthropogenic events that can perturb an environment, increasing P flux into a watershed's rivers.

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N and P in polluted rivers:

☀ Urban Environments:

industrial and household use of detergents and cleaners leads to a dissolved pollutive P flux to rivers that is generally proportional to watershed population.

Careful management has allowed this source of pollution to be reduced significantly in recent decades in much of the world.

Anthropogenic "forcing" of N and P have led to 2 types of rivers that deviate significantly from Redfield ratio control on N : P, as we see on the next slide.

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N and P in polluted rivers:

☀ "Agricultural rivers" have N : P > 16

☀ "Industrial rivers" have N : P < 16 : 1

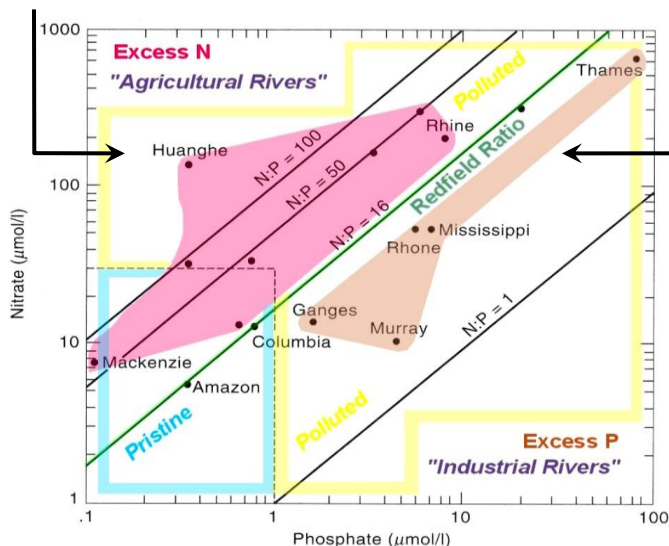


Figure 5.11. Mean nitrate concentration versus mean phosphate concentration for various world rivers. Pristine rivers are enclosed by the dashed line. The diagonals are lines of equal N/P ratio (in mol/mol). (Data from Kempe 1984 and Meybeck 1993.) Modified from Berner and Berner, "Global Environment"

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Nutrient cycles in Lakes

Photosynthesis and Respiration in stratified bodies of waters result in **Nutrient Profile** relationships.

Lake stratification causes concentration gradients in DIN, DIP and DOx from excess **photosynthesis** in surface waters and excess **respiration** in light-limited deep waters

Rivers typically don't show similar concentration profiles because they are *well-mixed* during flow.

Lake outflow and inflow tells us about the net effect of that lake on watershed output.

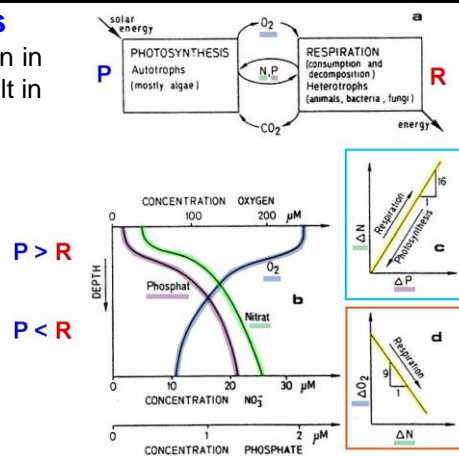
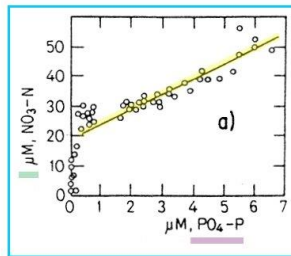
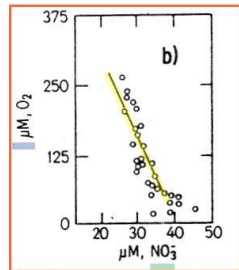


Figure 9.13 Photosynthesis and respiration. A well-balanced ecosystem may be characterized by a stationary state between photosynthetic production, P (rate of production of organic material) and heterotrophic respiration, R (rate of destruction of organic matter) (a). Photosynthetic functions and respiratory functions may become vertically segregated in a lake or in the sea. In the surface waters the nutrients become exhausted by photosynthesis. The subsequent destruction (respiration) of organism-produced particles after settling leads to enrichment of the deeper water layers with these nutrient elements and a depletion of dissolved oxygen [schematic representation in (b)]. The relative compositional constancy of the aquatic biomass and the uptake (P) and release (R) of nutritional elements in relatively constant proportions (see equation 24) is responsible for a covariance of carbon, nitrate, and phosphate in lakes (during stagnation periods) and in the ocean; an increase in the concentration of these elements is accompanied by a decrease in dissolved oxygen. The constant proportions $\Delta C : \Delta N : \Delta P : \Delta O_2$ typically observed in these waters are caused by the stoichiometry of the P - R processes (c and d). **Strumm and Morgan, Aquatic Chemistry**

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N, P and O content of natural waters often covary by the Redfield ratio, as in this example of DIN, DIP and DOx (= dissolved O₂) in Lake Zurich.



(solid yellow lines are Redfield ratio stoichiometry).

Waters from a range of lake depths sampled before overturn display correlated nutrient contents and anti-correlated nutrient-DOx.

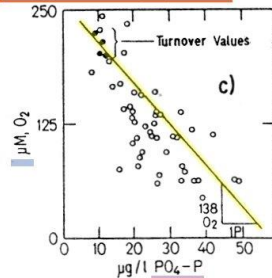


Figure 11.13 Stoichiometric correlations among concentrations of Nitrate, Phosphate, and Oxygen. (a and b) Lake Zürich. [Data from P. Zimmermann, *Schweiz. Z. Hydrol.*, 23, 342 (1962) and I. Ahlgren, *Schweiz. Z. Hydrol.*, 29, 53 (1967).] (c) Lake Gersau. [From H. Ambühl, *Schweiz. Z. Hydrol.*, 37, 35 (1975).] For (b) and (c) only results from the deeper water layers were considered.

Strumm and Morgan, Aquatic Chemistry

"turnover" values = shallow water characteristics introduced into the deep waters during lake turnover.

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Nutrient cycles in the Oceans

Redfield ratios are also applicable to nutrient regeneration in marine systems. In fact Redfield originally developed this quantification of respiration-mediated nutrient recycling by for marine systems.

Recall that unlike lakes, marine stratification reflects a slow churning of the oceans that distribute water masses around the globe and isolate deep waters from the atmosphere.

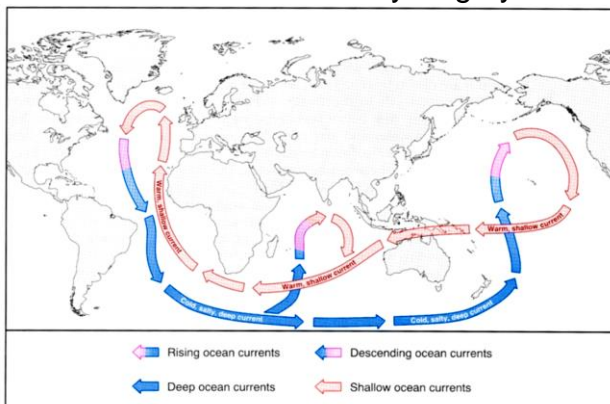


FIGURE 3.7
The conveyor belt circulation pattern of the world's oceans. Cold, salty water in the North Atlantic sinks to the deep ocean and moves southward to resurface and be warmed in the Indian and Pacific oceans. Surface currents then return the water to the Atlantic. A complete passage takes about one thousand years. Currently, this conveyor belt circulation pattern is driven to some extent by an imbalance between the loss of water from the Atlantic by evaporation and its gain by precipitation and continental runoff.
(After Dickinsen and Monastersky, 1991.)

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Redfield Ratio predicted changes in C, N and P due to photosynthesis and respiration in the oceans are shown in this plot.

The slowness of ocean circulation (in their current configuration they complete one "cycle in about 2000 yrs"), means that most of the oceans are isolated from the atmosphere on 100-1000 year time scales.

They thus have plenty of time to develop the signature of excess respiration in deep water masses

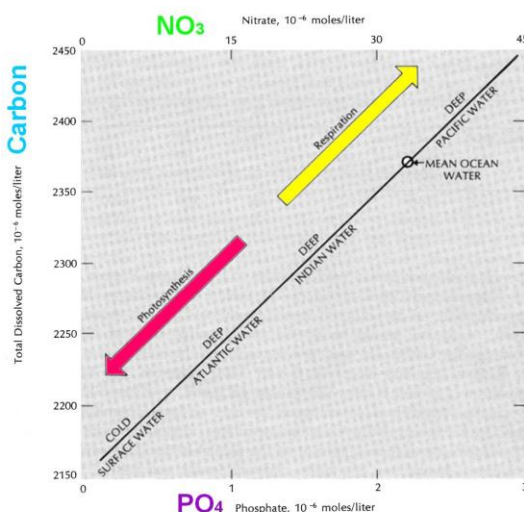
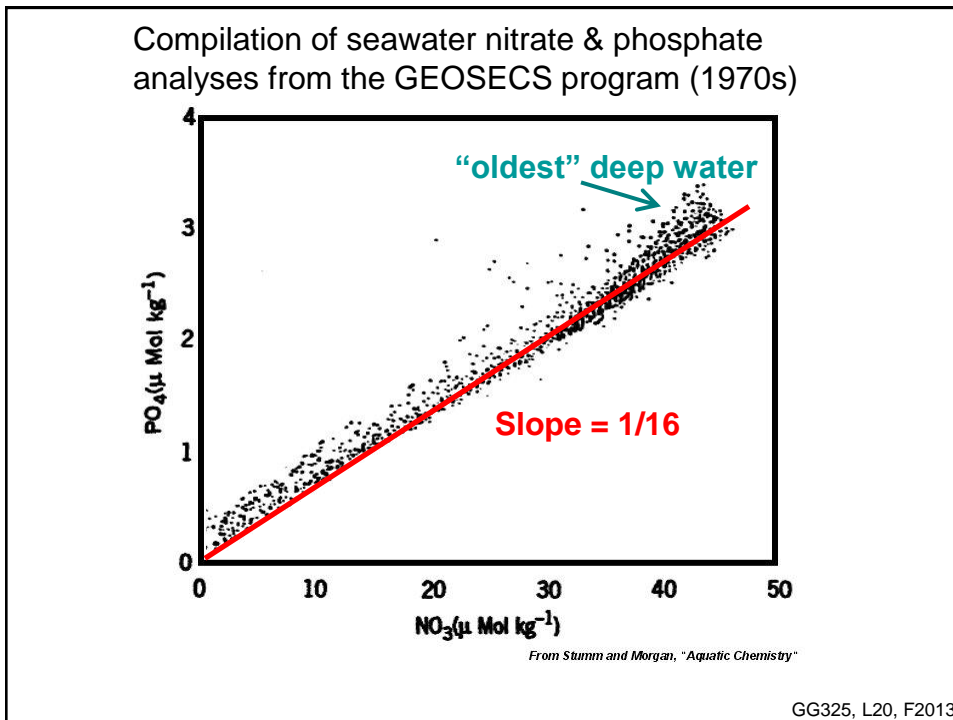
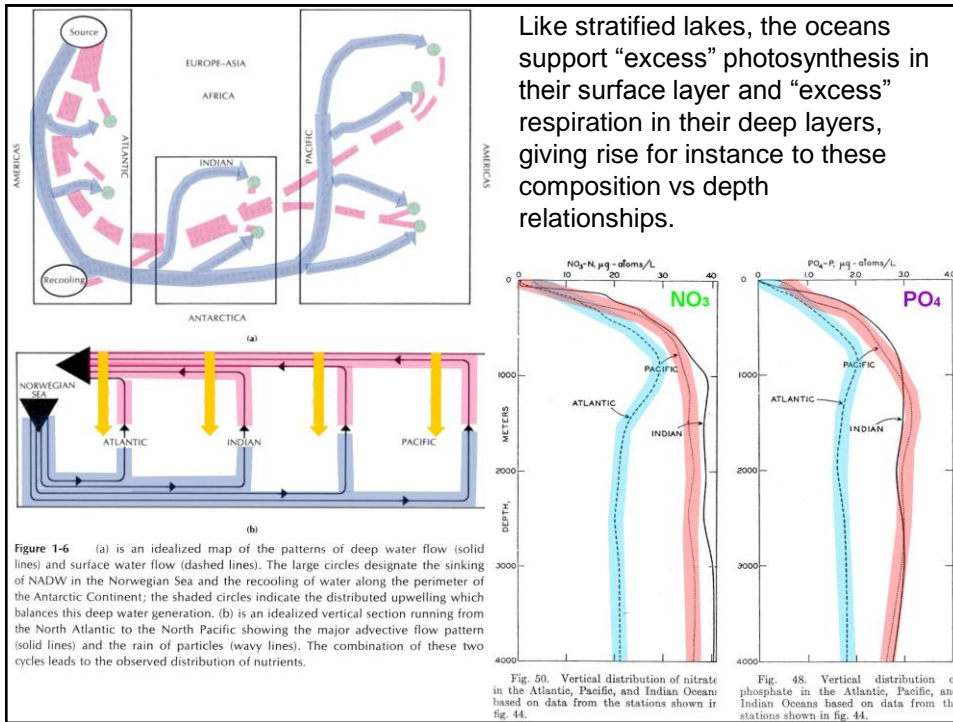


Figure 1-3 Ideal covariance of carbon, nitrate, and phosphate within the ocean. Conditions at the lower (surface water) end of the line are achieved when the limiting nutrients have been exhausted by photosynthesis. The other extreme is fixed by the degree of horizontal enrichment of the nutrient elements within the deep sea. Intermediate values are produced by mixing these end members in varying proportions.

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Lake data fit the Redfield paradigm less well than marine data because in the open ocean the particulate organic carbon of the surface oceans is dominated by phytoplankton that follow Redfield stoichiometry and there are few other sources of N or P

Terrigenous organic matter with higher C/P and C/N can contribute significantly to the pool of organic carbon available for remineralization to offset the C:N:P ratio in some lakes.

Also, bacterial denitrification and N-fixation can affect N/P ratios.

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Nutrient limitation

- The least available nutrient in any system is considered to be the limiting nutrient for the total amount of photosynthetic C-fixation a system can sustain.
- This is a stoichiometric concept that presumes that one nutrient is totally consumed before other nutrients - not a rate of photosynthesis
- Prevailing wisdom holds that **P is limiting in lakes**, while **N is usually limiting in the marine environment**, although there are exceptions.
- Plus, in complex ecosystems even if one nutrient is depleted other organisms that need little to none of this nutrient can be favored and still flourish.

Nutrient overloading (especially P) by "industrial" human activities can enhance photosynthesis greatly in an urbanized watershed.

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TABLE 6.5 Concentrations of Essential Elements for Plant Growth in Living Tissues of Freshwater Plants (Demand), in Mean World River Water (Supply), and the Plant/Water (Demand/Supply) Ratio of Concentrations

Element	Symbol	Demanded by Plants (%)	Supplied by Water (%)	Demand/Supply (Plant/Water) Ratio (approx.)
Oxygen	O	80.5	89	1
Hydrogen	H	9.7	11	1
Carbon ^a	C	6.5	0.0012	5,000
Silicon	Si	1.3	0.00065	2,000
Nitrogen ^a	N	0.7	0.000023	30,000
Calcium	Ca	0.4	0.0015	<1,000
Potassium	K	0.3	0.00023	1,300
Phosphorus ^a	P	0.08	0.000001	80,000
Magnesium	Mg	0.07	0.0004	<1,000
Sulfur	S	0.06	0.0004	<1,000
Chlorine	Cl	0.06	0.0008	<1,000
Sodium	Na	0.04	0.0006	<1,000
Iron	Fe	0.02	0.00007	<1,000
Boron	B	0.001	0.00001	<1,000
Manganese	Mn	0.0007	0.0000015	<1,000
Zinc	Zn	0.0003	0.000001	<1,000
Copper	Cu	0.0001	0.000001	<1,000
Molybdenum	Mo	0.00005	0.0000003	<1,000
Cobalt	Co	0.000002	0.00000005	<1,000

Source: J. R. Vallentyne, *The Algal Bowl: Lakes and Man*. Copyright © 1974. Environment Canada. Reprinted by permission of the publisher.

^aConcentrations in water for inorganic forms only.

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P-limitation and Eutrophism



<http://www.umanitoba.ca/institutes/fisheries/eutro.html>

View from above (left) of an experimental lake in Canada with a divider curtain separating it from another lake. P was added to the near side of the curtain. The bright green color results from the ensuing bloom of bluegreen algae (Cyanobacteria).



Aerial view (above) of another experimental lake in which algae were stimulated by P addition for 26 consecutive years. The lake in the background is unfertilized.

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P-limitation and the “Life cycles” of Lakes

Biologically-related chemical components (both nutrients and trace elements) do not flux through lakes as quickly as water does because *their residence times exceed that of lake water.*

An expression for determining how fast a particular constituent moves relative to lake water is:

$$(T_{rel})_i = (T_{res})_i / (T_{res})_{water}$$

$(T_{rel})_i > 1$ means the constituent is held back

$(T_{rel})_i = 1$ the constituent moves at the same rate as water

$(T_{rel})_i < 1$ the constituent moves faster than the water.

At steady state volume and composition, this becomes:

$$(T_{rel})_i = \frac{(T_{res})_i}{(T_{res})_{water}} = \frac{(\text{grams } i_{lake}) / (\delta i / \delta t)}{(\text{liters of } H_2O_{lake}) / (\delta H_2O / \delta t)}$$

$$(T_{rel})_i = (\text{conc } i_{lake}) * (\delta i / \delta t) / (\delta H_2O / \delta t)$$

$(\delta i / \delta t) / (\delta H_2O / \delta t) = \text{rate of change of } i / \text{rate of change of } H_2O$
 $= (\text{conc } i_{stream} / \text{unit of water flow}) / \text{unit of water flow}$

$$(T_{rel})_i = \frac{(C_{lake})_i}{(C_{stream\ inflow})_i}$$

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“Life cycles” of Lakes

The retention of biologically-related chemicals makes them subject to a natural “lifecycle”:

1. Lakes usually begin life with clear, nutrient-poor waters.
2. Photosynthesis proceeds at a limited rate. Respirative decomposition of algal biomass consumes O_2 in the deep part of the lake, yet we find fairly oxygenated bottom waters in a young lake.
3. Biological activity increases over its “lifetime” until it gets choked with organic matter and fills-in with sediment.

The stages are given names, although there is a continuum between them:

oligotrophic: $[O_2] > 25\%$ saturation at that temperature. (*young lake*)

mesotrophic: $25\% > [O_2] > 10\%$ saturation (*middle-aged*)

These waters support more photosynthesis/respiration and will be more turbid than oligotrophic waters.

eutrophic: $[O_2] < 10\%$ saturation (*old-aged*)

These lakes support large amounts of photosynthesis in their turbid shallow waters. Large amounts of respiration in their deep waters leads to high nutrient concentrations in deep water and very low $[O_2]$.

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DOx and T profiles in oligotrophic and eutrophic lakes that turn over 2x/year.

We looked at this plot earlier in the semester

In an oligotrophic lake:
Bottom waters are oxygenated.

There is little photosynthesis occurring in the upper waters and little respiration in the deep waters. O₂ is lost from the warm surface waters by gas exchange with the atmosphere and DOx can actually increase with depth after the spring overturn (a temperature effect).

In an eutrophic lake:

A steep decline in DOx with depth occurs after both overturns from large amounts of photosynthesis in upper waters and large amounts of respiration in deep waters.

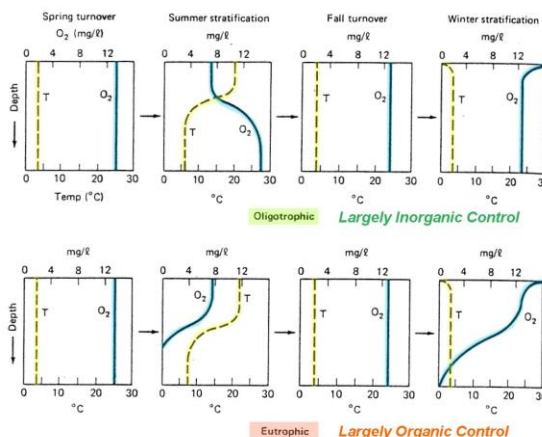


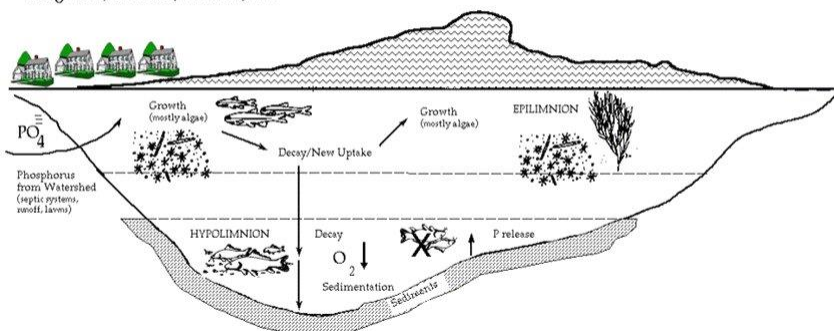
Figure 14-8 Idealized distributions of temperature and dissolved oxygen in oligotrophic and eutrophic lakes. The increase in dissolved O₂ with depth in the oligotrophic case in summer is due to the greater solubility of O₂ at lower temperatures (after Wetzel, 1975)

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We also looked at this illustration earlier in the semester

Generalized Eutrophication

Long Pond, Brewster/Harwich, MA



www.capecodcommission.org/water/eutrocycle.gif

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In an oligotrophic lake: Well oxygenated bottom waters causes pe to remain fairly high: Fe and Mn are in their oxidized states (e.g., Fe^{3+} , Mn^{4+}). Fe^{3+} forms an insoluble phosphate compound FePO_4 (the mineral vivianite); some PO_4^{3-} remineralized by respiring organisms into deep lake waters is exported from the lake to the sediments

Remember Reduced Fe diffuses out of the sediments towards the overlying oxidizing waters

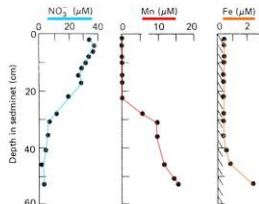
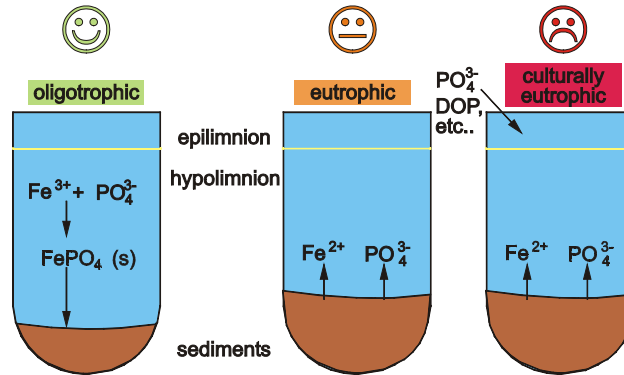


Figure 14-4 Profiles of nitrate, manganese, and iron in interstitial water from a sediment core from the eastern equatorial Atlantic (Froelich et al., 1979)



In an eutrophic lake: High BOD sediment flux causes bottom waters to not be oxygenated. Significant Fe^{2+} and PO_4^{3-} can diffuse out from the sediments and provide "extra" phosphorous to surface water algae. Once this occurs, the lake is unable to control the rate at which photosynthesis occurs and it eventually becomes overwhelmed by biological activity

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The **Natural** oligotrophic → eutrophic → "lake fill-in" life cycle may take 100s to 10000s of years, depending on:

- the size of the lake
- its overturn characteristics
- the watershed load of nutrients coming into the lake.

Human activities can increase this rate by orders of magnitude, causing "cultural eutrophism" (leading to rapid death of a lake in just decades).

This was particularly so in lakes on heavily phosphorous loaded industrial rivers of the Northeastern US and Western Europe in the 1970s and 1980s, and subsequently led to efforts to limit the release of phosphorus-bearing compounds into the environment.

Better knowledge of the P and N cycles has allowed watershed resource managers to better control nutrient loading in the major waterways of industrialized countries.

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The pollution fluxes of various forms of P to three US great lakes since 1800 is shown below:

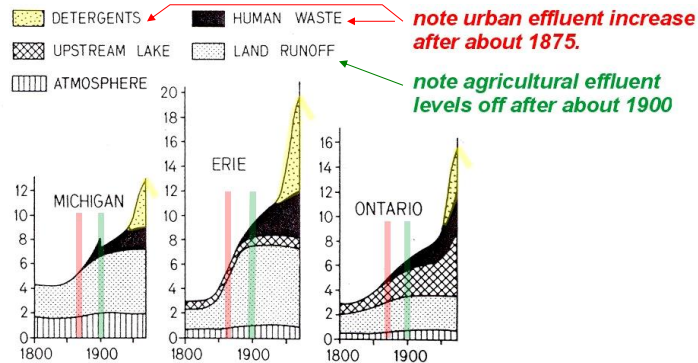


Figure 11.15 Historical loadings of total phosphorus in some Great Lakes, in thousands of tons per year, as calculated by a model. (From St. C. Chapra [34].)

Strumm and Morgan, Aquatic Chemistry

Notice that much of the P entered these lakes as inorganic and organic materials in dissolved and particulate forms, as well as DIP (ortho-P).

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Given flux and speciation data, one can estimate at what point lakes would become eutrophic at the current P input rate.

A simple Box model for lake [P] and [O] uses Redfield ratio stoichiometry, converted to mass quantities:

Each mg of P consumed in the Epilimnion produces:

100 mg of Algae plus 140 mg of O₂

If all of this P is recycled into the water by respiring organisms in the Hypolimnion, 140 mg of O₂ must be consumed there.

We can write an equation for the oxygen consumption in the Hypolimnion as a function of river-borne P load to the lake, stagnation duration between overturn events, and the lake depth:

$$\Delta O_2 = \frac{140 \text{ mg } O_2}{-4 \text{ mg P}} \cdot \frac{C T_{\text{stagnation}}}{z_{\text{hypo}}} \cdot \frac{C L_P \text{ in mg/yr}}{C \cdot 365 \text{ day/yr}}$$

There is a theoretical relationship between lake depth and P load that separates oligotrophic from eutrophic conditions, allowing one to calculate acceptable P load levels to avoid cultural eutrophism (see plots next slide).

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The annual P loading per lake surface, L_t ($\text{mg P m}^{-2} \text{ year}^{-1}$) causes (under the simplifying assumption that all L_t becomes phosphorus of oxidative origin, P_{ox}) during the stagnation period, T_{st} (days), an approximate oxygen consumption, $\Delta[\text{O}_2]$ (mg m^{-3}) of the hypolimnion assumed to be homogeneously mixed of depth $z_H(m)$ that is given by

$$\Delta[\text{O}_2] = 140 \frac{T_{st} L_t}{365 z_H} \quad L_t \text{ is per year} \quad (i)$$

Correspondingly, a maximum P loading L_{\max} could be estimated for a tolerable oxygen consumption $[\text{O}_2]_{\max}$:

$$\text{time in days } L_{\max} = \frac{[\text{O}_2]_{\max}}{\Delta[\text{O}_2]_{\max}} \times 7 \times 10^{-3} \times \frac{365}{T_{st}} z_H \quad (ii)$$

e.g., maximum acceptable O_2 loss.

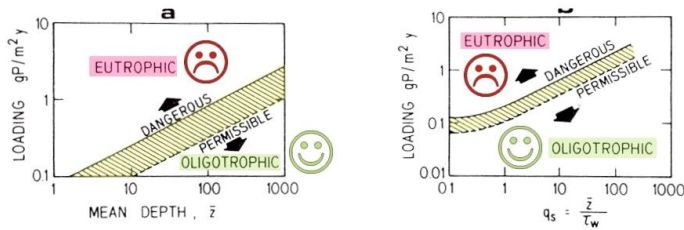


Figure 11.14 Vollenweider's model. (a) The relationship between areal phosphorus loading and mean depth provides estimates of dangerous or permissible loadings. (b) Vollenweider [Schweiz. Z. Hydrol., 37, 53 (1975)] later modified his loading concept to consider hydraulic residence time, τ_w (yv).

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