

Phosphorus

An overview of nutrient cycles.

It is useful to distinguish between "resources" and "conditions" which influence the ecology of organisms. A condition is any environmental factor which influences the ecological success of a population but which is not altered by the activity of the organisms in the population. Examples might include: temperature, pressure (in the sea), wind or currents. A resource is any material which influences the success of a population of organisms, and which is consumed and therefore potentially depleted by the organisms when the population increases. Examples might be light, food (for heterotrophs) or nesting sites. The elements required as nutrients for plants to grow are clearly "resources" since they are assimilated by plants as they grow. Commonly, it is the availability of N or P that controls the size of the standing crop of phytoplankton.

Elements of interest

The elements and Redfield ratios

Macronutrients

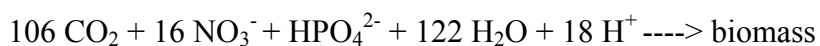
Macronutrients are those elements which constitute more than 0.1 % of the biomass of living phytoplankton. These elements include: C, O, H, N, P, S, K, Mg, Ca, Na, Cl. Of these, O, H, S, K, Mg, Ca, Na, and Cl are ordinarily of little importance in the ecology of phytoplankton and other primary producers because these elements are almost always present in vast excess compared to the requirements of the organisms. C can be important under some circumstances. These elements are consumed (assimilated) but not depleted. The macronutrients of greatest interest are N and P.

Micronutrients

Micronutrients are those elements which are essential for primary producers, but are not required in amounts greater than 0.1 % of biomass. The micronutrients include: Fe, Mn, Cu, Zn, B, Si, Mo, V, Co. With the exception of Si and possibly Fe and Mo, there is little evidence that any of the micronutrients are of any significance in regulating the success of the phytoplankton. (Note that the lack of evidence is probably as much a lack of sufficient investigation as it is the possibility that the trace elements are simply of little importance.)

Ratios

As a rough guide, the composition of the plankton may be used as an estimator of the relative amounts of elements required. Using the formulation of Stumm and Morgan:



Redfield noted that the various elements are needed in particular ratios (which have come to be called "Redfield Ratios). Of greatest interest are the elements that frequently are in short supply, N and P. The Redfield ratios for these two elements, related to C in marine phytoplankton, are:

$$106\text{C}:16\text{N}:1\text{P} \text{ (molar ratio)}$$

$$42\text{C}:7.2\text{N}:1\text{P} \text{ (weight ratio)}$$

The variance in these ratios in marine plankton is small, typically <20%. This constancy has been attributed to the relative constancy of these nutrients in the oceans and the homogeneous and stable nature of the oceans (according to Goldman et al. 1979. [Growth rate influence on the chemical composition of phytoplankton in oceanic waters. Nature 279:210-214].

The ratio of C:N:P in phytoplankton in lakes is more variable. Ratios of nutrient loading to lakes are quite variable and are reflected in the phytoplankton ratios. The table below suggests guidelines for identifying nutrient limitation from stoichiometric ratios of phytoplankton in lakes.

TABLE 13-17 Stoichiometric Ratios of Phytoplankton-Dominated Seston of Lakes as Approximate Indicators of Relative Nutrient Limitations^a

Ratio	Deficiency	Degree of nutrient limitation ^b		
		None	Moderate	Severe
C:N	N	<8.3	8.3–14.6	>14.6
N:P	P	<23	—	>23
C:P	P	<133	133–258	>258
Si:P	Si	<20	—	>100
C:Chl <i>a</i>	General	<4.2	4.2–8.3	>8.3
APA:Chl <i>a</i>	P	<0.003	0.003–0.005	>0.005

^a After Healey and Hendzel (1980), Kilham (1990), and Hecky *et al.* (1993).

^b Composition ratios of C:N, N:P, C:P in $\mu\text{mol } \mu\text{mol}^{-1}$; C:Chl *a* ratios as $\mu\text{mol } \mu\text{g}^{-1}$; and physiological ratio of alkaline phosphatase activity (APA):Chl *a* in $(\mu\text{mol } \mu\text{g}^{-1})\text{h}^{-1}$.

From Wetzel

Liebig's "law"

Justus Liebig first clearly recognized (1840) that the supply of individual elements could limit the growth of a population of organisms. He was an agriculturist and stated his "law of the minimum" in agricultural terms..."the growth of a plant is dependent on the amount of foodstuff which is presented to it in minimum quantity...". Liebig recognized that the limitation depended on the demand by the plant relative to the supply available. Hence, in the list of macronutrients above, N and P are of significance because they are frequently depleted whereas C, O, H are required in greater amount but are seldom (C) or never (O, H) depleted in natural waters.

In contrast to some later critics, Liebig also recognized that there were species differences (hence his recommendation for crop rotation) and that a total community might not be limited by a single nutrient but by several.

If diatoms are included, Si(OH)_4 would be included as an important nutrient. If nitrogen fixation is significant, Fe and Mo might be important. (No doubt a complete accounting would identify many such idiosyncrasies; nevertheless, the generalization is useful.)

Reynold's analogy:

As an explanation of nutrient limitation: "...This may be conveniently be done by analogizing the production of 'algal' cells to the assembly of motor cars. So long as the specified selection and number of components are available, it is possible to assemble complete vehicles. As soon as the supply of one of the components (be it wheels or lights or ashtrays) is exhausted, the next motor car cannot be completed. It may arguably function quite well without ashtrays and, for part of the time, without lights, but with the exhaustion of the supply of wheels, further production of useful vehicles ceases; an absolute minimum has been reached. So with 'algae' the elaboration of new biomass cannot reasonably exceed the capacity of the environment to supply the nutrient which is effectively exhausted first: that element is then said to be 'limiting'...."

Value of the concept: There is reason to believe that to a first approximation the size of the phytoplankton crop which develops will be proportional to the supply of a limiting nutrient. As we shall see, this is evidently most often the rate of supply of phosphorus (but there are many complexities). The concept is also implicit in the most commonly applied scale for describing lakes: **oligotrophic** ("poorly fed") lakes have little plant growth, because of a restricted supply of nutrient, whereas **eutrophic** ("well fed") lakes support dense populations because they are well supplied with nutrients. The value of the concept is that it serves as a guide to understanding the major types of water bodies and serves as a conceptual framework for lake management (via nutrient controls). **Mesotrophic** lakes are intermediate in productivity.

The bottom line: Phosphorus is the nutrient element of greatest interest in the management of lakes because it is *most likely to be in short supply* in relation to demand by phytoplankton. The same may not be true for rooted aquatic plants.

Note: the single limiting nutrient concept of Leibig and the auto assembly analogy proposed by Reynolds are likely oversimplifications of the relationship between growth of autotrophs in relation to nutrient supply. The fact is that organisms are more adaptive than auto assembly lines; they can adapt to changes in a limiting nutrient by, for example, excreting alkaline phosphatase in the case of phytoplankton or, in the case of macrophytes, by growing more roots. In the end, organisms likely try to optimize growth by adapting to alleviate constraints by critically limiting resources so that all resources are simultaneously limiting. This would be a good strategy in a constant environment, but resource availability is not constant so what is optimal in one situation is suboptimal in another. So "optimal" conditions are short-lived and transitory.

As a practical matter, P concentration in lakes is a good predictor of phytoplankton abundance, as measured by **chlorophyll-a** concentration, and phytoplankton abundance is an important indicator of water quality.

Chlorophyll-a is one of several pigments in phytoplankton that capture light energy. The concentration of chlorophyll-a in a water sample (following extraction of the pigments from the cells) is correlated with phytoplankton biomass or density.

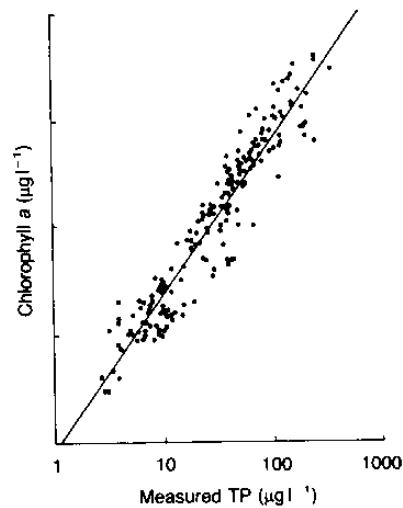


Figure 7.3 Relationship between summer levels of chl a and measured total phosphorus concentration for 143 lakes (Jones and Bachmann, 1976).

Trophic State

P and chlorophyll-a concentrations are two indicators of the trophic state of a lake. The table below provides qualitative descriptions of some other indicators.

Table 7.2 Qualitative characteristics of oligotrophic and eutrophic lakes

	<i>Oligotrophic</i>	<i>Eutrophic</i>
Depth	Deep	Shallow
Hypolimnion: epilimnion	> 1	< 1
Primary productivity	Low	High
Rooted macrophytes	Few	Abundant
Density of plankton algae	Low	High
Number of plankton algal species	Many	Few
Frequency of plankton blooms	Rare	Common
Depletion of hypolimnetic oxygen	No	Yes
Fish species	Cold water, slow growth, restricted to hypolimnion	Warm water, fast growth, tolerate low O ₂ in hypolimnion and high temperature of epilimnion
Nutrient supply	Low	High

A trophic state index (TSI) is a simple indicator of trophic state. Many indices have been developed, however, the most commonly used TSIs are those developed by Carlson that are

based on Secchi transparency, total P, and chlorophyll-a (1977. A trophic state index for lakes. L&O 22:361-368). Carlson used \log_2 transformations to interrelate these three indices of lake water quality, so that a doubling in total P (TP) concentration was related to a reduction in Secchi transparency by one half.

$$TSI_{SD} = 60 - 14.41 \ln (SD); \text{SD in m}$$

$$TSI_{Chl} = 9.81 \ln (Chl) + 30.6; \text{Chl in } \text{mg m}^{-3}$$

$$TSI_{TP} = 14.42 \ln (TP) + 4.15; \text{TP in } \text{mg m}^{-3}$$

Comparison of the TSIs for the three indicators provides an indication of the relative importance of zooplankton grazing, P-limitation, particle size, and non-algal turbidity.

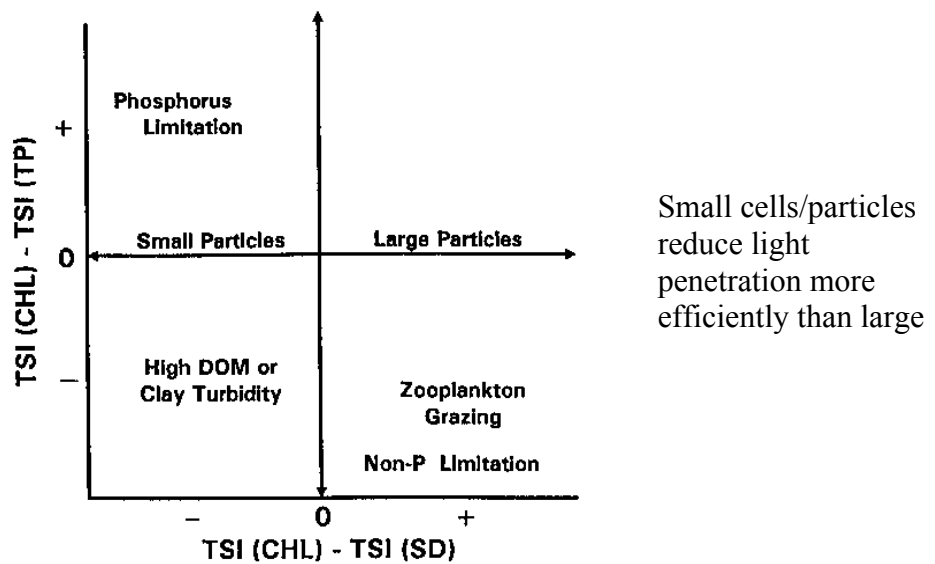


FIGURE 13-16 Potential nutrient-limited and nonnutrient-limited causes for deviation of biomass-based trophic state index (TSI). See text; based upon developments by Carlson (1992).

These TSIs and the parameters they are based upon are commonly used by lake managers to evaluate the condition of a lake and provide shortcut terminology for lake descriptions (You have to know the lingo to communicate in any science!).

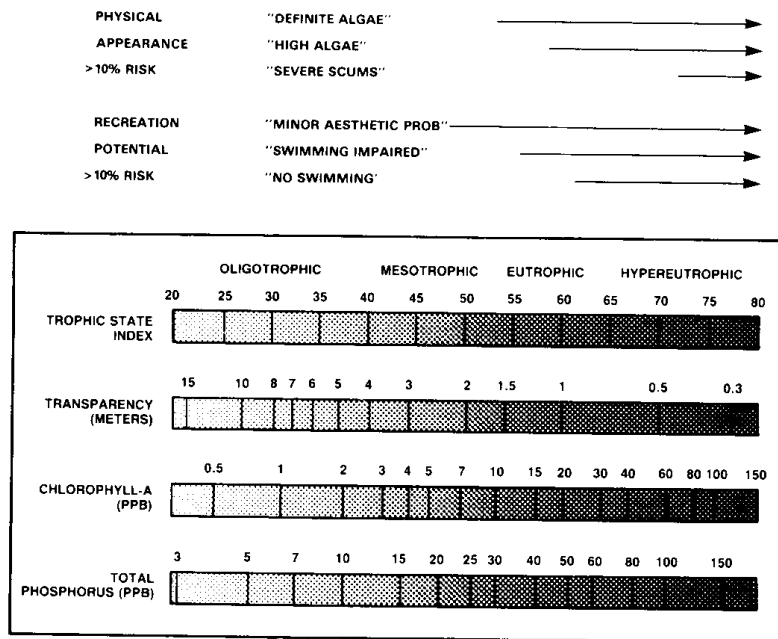


Figure 4-5.—Carlson's Trophic State Index related to perceived nuisance conditions (Heiskary and Walker, 1987). Length of arrows indicate range over which a greater than 10 percent probability exists that users will perceive a problem.

Some aspects of the chemical form of phosphorus and methods to analyze the various forms.

In natural waters, phosphorus is present in a fully oxidized state, as phosphate (PO_4^{-3}). Phosphate is present in various particulate (mineral, organic, biologic) and dissolved forms. There is no significant gas phase for phosphorus (in contrast to the other two major nutrients, C and N) and is therefor described as "rock-bound".

The cycling of phosphorus is complex, involving many different forms. Phosphorus is present in particulate forms (including phosphorus in living organisms and partially decomposed detritus, sorbed onto mineral particles, or part of the structure of specific inorganic minerals such as apatite), colloidal forms and dissolved forms (including inorganic PO_4^{-3} ions but also many other organic and in-organic chemical species).

Analytical methods

A variety of chemical analytical and filtration methods have been employed to measure the concentration of the various forms of phosphorus. Because of the great variety of chemical and biological forms of phosphorus present in natural water and the limited chemical methods available to measure the various forms, the current practice is to recognize *operational categories* of phosphorus, rather than attempt to measure individual chemical species. Two

means of separating phosphorus into operational categories are commonly used: (1) physical separation via filtration (sieving) and (2) chemical digestion procedures.

Physical separation. Filtration through specific filters is often a part of an analytical procedure for phosphorus. The commonest choice is the use of 0.45 μ filters (e.g. Millipore type HA cellulose acetate filters). [Wetzel and Likens favor the use of Whatman GF/F filters.] By definition, if the phosphorus is measured after passing through the filter, it is said to be "dissolved" (which of course contains some colloidal P), but if it is retained by the filter it is said to be "particulate" (including P in living organisms, detritus, etc.).

Chemical analytical methods. A variety of analytical methods have been employed to separate phosphorus into various operational categories. Three common ones are described in Wetzel and Likens "Limnological Analyses" (see p93ff). These 3 are:

Soluble Reactive Phosphate-Phosphorus (PO₄-P). This is the simplest and most direct procedure. Water samples are filtered (hence "soluble") and then a series of chemical reagents are added (see recipe in Wetzel and Likens). The amount of P is proportional to the intensity of color developed (measured against a standard curve with a spectrophotometer). In earlier literature, the result was often reported as "orthophosphate", or PO₄⁻³. However, it is clear that many different forms of P pass through the filters and react with the reagents, not just PO₄⁻³. Hence, the current practice is to report the results as "SRP", or soluble reactive phosphorus.

Dissolved organic phosphorus (DOP). The procedure is much the same as for SRP, except that H₂O₂ is added to the filtered sample followed by exposure for 2 hours to strong UV light. The *increase* in the amount of P measured by the SRP reagents (compared to SRP alone) is attributed to dissolved organic P.

Total Phosphorus. In this method, total phosphorus is oxidized by persulfate, which liberates organic phosphorus as inorganic phosphate. The sample is *not* filtered and hence represents total P.

Predicting P concentration in lakes

Phosphorus is a key ingredient in the ecology of lakes. It is the supply of phosphorus more than any other element that determines the fertility of lakes. [In some cases, other elements or light may be more important in a *particular* lake.] A very large literature has developed on the dynamics and significance of phosphorus in lakes. It is clear from this literature that a *complete* accounting of the dynamics of phosphorus in a lake is probably impossible. Accordingly, simplified models that emphasize important components of the biogeochemical cycle of phosphorus have been developed. For example, the PCLOOS model was developed by Janse et al. to describe the important processes involved in the cycling of P in a lake and its sediment. Some characteristics of the model:

Much of the P in a lake may in fact be in the sediment. To an extent, it is still part of the lake because it can be recycled to the water above. Sediments may be thought of as a short-term *reservoir* of P but a long-term *sink* for P. SRP plays a central role in the redistribution of P.

Phytoplankton represent a unique component: as primary producers they are responsible for the initial capture of sunlight energy as well as depending on the supply of nutrients to survive. The phytoplankton represent the linking of the production of organic carbon compounds and the assimilation of nutrients including P.

Phosphorus enters a lake primarily via inflow from the watershed. Dust fall may sometimes be significant as well. Together, these represent the "phosphorus load" to the lake [units: $\text{gm}^{-2} \text{yr}^{-1}$] Phosphorus leaves a lake via the outflow and possibly via fish harvest. P is also "lost" to the sediment, termed "retention". The net balance determines whether or not P is accumulating in a lake.

The classical model

Mortimer and Einsele independently noted the significance of redox events in the cycling of phosphorus. The model consists of a series of chemical events that influence the phosphorus balance between sediment and water column.

Basic concepts include:

As long as the water column is well oxygenated (orthograde oxygen curve), the surface of the sediment will also be oxidized. In particular, iron (Fe) will be in the ferric form (Fe^{+3}) and sorb or precipitate P. P remains *bound* in the sediment, so that the sediment acts as a *sink* for P.

If there is sufficient production (or import) of organic material to deplete oxygen supplies, redox potential will fall. When the redox is low enough, iron will be reduced to the ferrous form (Fe^{+2}), which is much more soluble. The dissolution of sediment Fe releases the bound P, which returns to the overlying water.

Once the hypolimnion has been deoxygenated, a lake is more likely to become "self-fertilizing": i.e. P in the sediment is no longer sequestered ("sink") but is recycled to fuel additional plant biomass and hence maintain the anoxia.

If redox potential is further reduced, SO_4 is used as an electron acceptor by sulfate reducing bacteria that produce sulfide (S^{-2}). The sulfide, in turn, precipitates the ferrous iron as insoluble FeS and FeS_2 , which reduces the P sorption by ferric iron oxyhydroxides under oxidizing conditions.

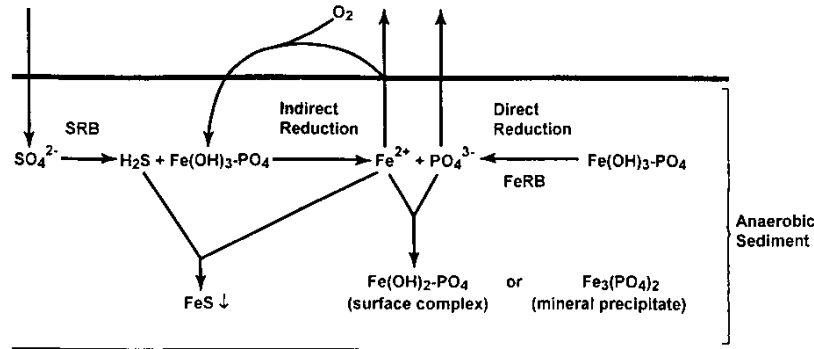


FIGURE 13-7 Interactions of sulfate on the reduction of Fe(III) and release of Fe(II) and phosphate. SRB = sulfate-reducing bacteria; FeRB = iron-reducing bacteria. (Modified from Roden and Edmonds, 1997.)

Current state of knowledge about phosphorus in natural water.

Biological processes are important in the processing of phosphorus. (see page 249, Kalff). "The bacteria are directly involved by releasing soluble reactive phosphorus (SRP) in the water following cell lysis and upon release during anaerobic conditions of polyphosphate granules accumulated under aerobic conditions. Whatever the precise mechanisms, biological release is important--with somewhere between 10 and 75 percent of the potentially soluble sediment phosphorus not sorbed but held within the cells of microbes."

Aerobic release mechanisms are also important (no just anaerobic, as implied by "classical model"). In particular, high temperature, high pH, and microbial activity can increase the release of sediment P. Bioturbation by the benthos, turbulence, and many other factors can influence retention or release of sediment P. Sediment-rooted aquatic macrophytes may "mobilize" sediment P and act as "nutrient pumps" moving P from sediments to the overlying water.

Some of our understanding of the dynamics of P in lakes may be an artifact of how we analyze P. Labile, organic P compounds that may contain P that is unavailable for plant uptake may be expressed as inorganic PO_4 because reagents used to analyze P breakdown these compounds.

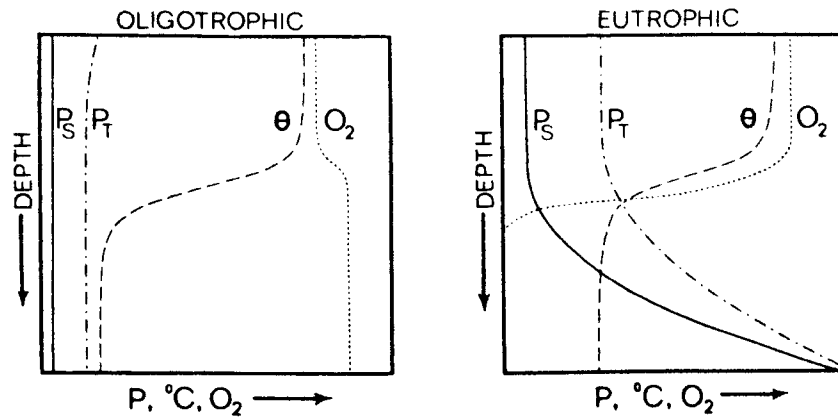


FIGURE 13-1 Generalized vertical distribution of soluble (P_S) and total (P_T) phosphorus in stratified lakes of very low (oligotrophic) and of high (eutrophic) productivity.

The correlation between the amount of P in the sediments and the productivity of the overlying water is weak. The P content of sediments can be several orders of magnitude greater than that in the water. The important factors are the 1) the ability of the sediments to retain P, 2) the conditions of the overlying water (pH, redox potential), and 3) the biota in the sediments.

Deposition of P into lake sediments occurs by:

- Sedimentation of P minerals imported from the watershed
- Absorption or precipitation of P with inorganic compounds
- Sedimentation of P with autochthonous organic matter
- Sedimentation of P with allochthonous organic matter
- Uptake of P by attached microbial communities and to a lesser extent by macrophytes and eventual transport back to the sediments by translocation and deposition of detritus

Once P is in the sediment, exchanges across the sediment-water interface are regulated by a number of biological and chemical processes.

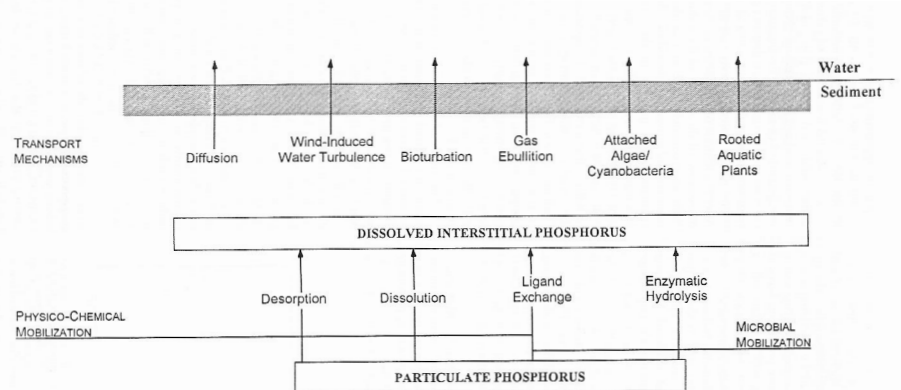


FIGURE 13-3 Processes involved in the mobilization of phosphorus from particulate stores into dissolved states of interstitial water of the sediments and transport across the sediment-water interface into the overlying water. (Modified extensively from Boström *et al.*, 1982, 1988, and Wetzell, 1999c.)

Phosphorus models

Comments on models in general: Models are commonly helpful in understanding the complexities of nature. Levins pointed out that the ideal model should be (1) general, (2) realistic, (3) precise and (4) simple. Obviously, not all these considerations can be met in a single model. The balance among the competing tradeoffs will depend on the specific situation. For example, a management model for a particular lake may sacrifice generality and simplicity in the interest of being more realistic and precise.

Mass balance models

A very little history: (from: Reckhow and Chapra, 1983, Engineering approaches for lake management, p206ff) "Biffi (1963) was among the first to apply the mass balance approach to chemical lake substances in lakes. ...Biffi's approach considers the lake to be a continuously stirred tank reactor with complete and instantaneous mixing and reaction...This is the basic form of the input-output [mass balance] phosphorus model...Unfortunately, phosphorus cannot be modeled successfully in this manner since, in many lakes, a large fraction of the input is deposited in the sediments. ...Piontelli and Tonolli (1964) proposed the first black, or input-output, model that included sedimentation..." [further discussion of the evolution of such models, including Vollenweider's early models..p209]. " For the input-output models, it seems considerably more important that the model form be selected on the basis of successful prediction as opposed to precise theoretical validity. (p211) ...Considering the simplicity of the models and the complexity of the lake system it is possible..[that any model] ...may predict well when fitted from a representative set of data."

Version in Kalff:

Mass balance models observe several simple assumptions:

- a conservative property (i.e. conservation of mass in the case of P)
- instantaneous and complete mixing of the lake
- (usually) a steady state, often with a specified yearly time frame to allow for seasonal variations.

The model:

$$\Delta M/\Delta t = I - O - (S_{\text{gross}} - R)$$

where: $\Delta M/\Delta t$ = storage or loss in lake

I = external load

O = outflow loss

S_{gross} = loss to the sediment

R = internal load

$(S_{\text{gross}} - R)$ = net sedimentation

Oxic vs. anoxic hypolimnia: p252ff

Oxic lakes tend to be deep, have a small watershed and therefore a long WRT (water residence time). P retained is high.

Anoxic lakes tend to be shallow, have a short WRT and low redox potential that promotes internal loading.

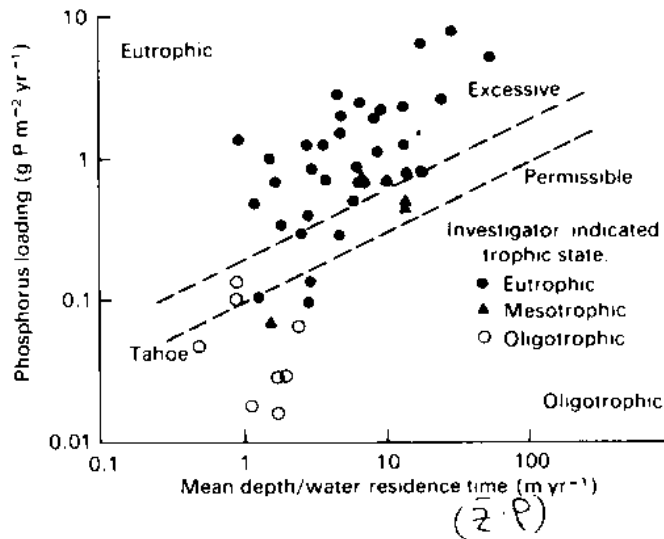
But note comment p254: Some empirical data suggests little difference by oxic vs. anoxic. Also, note the caution expressed about using laboratory experiments to estimate sediment release in whole lakes.

Empirical models

... "R.A. Vollenweider was the first to formulate drainage-basin loading criteria for phosphorus and nitrogen... The criteria he developed have their conceptual origin in a study of the input-output mass-balance of phosphorus and nitrogen.

"Under equilibrium conditions, there is a relationship between nutrient input/output and within-lake concentrations. The relationship changes systematically with loading ($\text{gm}^{-2}\text{yr}^{-1}$) and water residence time (WRT). WRT determines the extent incoming nutrients are sedimented (retained) rather than flushed. The resulting empirical models, or steady state statistical models, are widely used today in the management of lakes..." p261 Kalff.

Figure 75. U.S. OECD data applied to initial Vollenweider phosphorus loading and mean depth/hydraulic residence time relationship. (Rast and Lee 1978)



Based upon empirical data from many lakes, Vollenweider developed the following equation to predict P concentration in a lake:

$$P_{\text{water}} = P_{\text{inflow}} / (1 + \sqrt{\text{WRT}})$$

p252 "This equation indicates that among lakes, the P concentration of inflowing water rather than the actual P loading (Kg/year) is the single best indicator of the water concentration."

Table 17-1 p253 presents some data for a variety of lakes. [Note that negative N_{int} implies net adsorption by the sediment.]

Vollenweider developed a "critical loading" value from these empirical relationships to predict the external loading that would predict trophic state.

$$L_c = 10 \text{ or } 20 \bar{Z} (\rho + \rho^{0.5})$$

Where:

10 or 20 designates the steady-state P concentration in the lake that corresponds to mesotrophy (10) and eutrophy (20)

\bar{Z} = mean depth

ρ = flushing rate (1/water residence time)

Dynamic models (p265ff)

Dynamic models include mechanistic details of underlying chemical and biological processes in the cycling of phosphorus. Kalff discusses 3 such models. An example is the PCLOOS model. Although more complicated and data demanding than the Vollenweider style models, dynamic models have the advantage of addressing the mechanistic underpinning of phosphorus dynamics. In effect, the principal difference is the attempt to "go inside the black box."

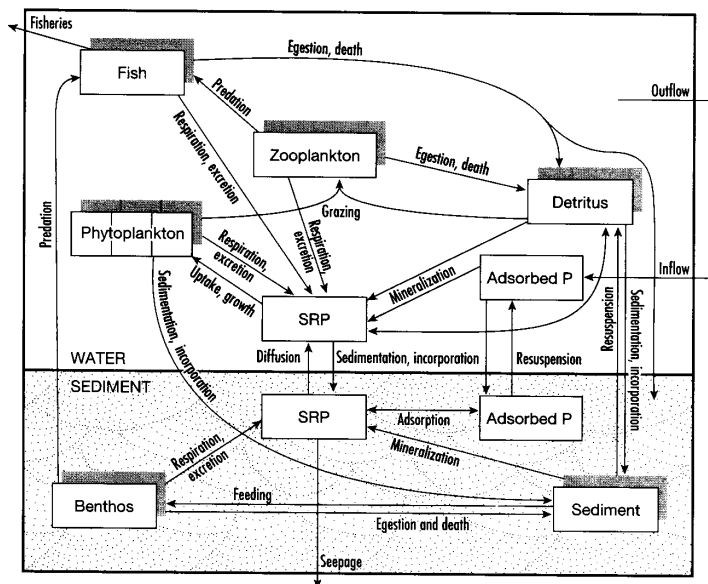


Figure 17-14 Overview of the PCLOOS model of phosphorus and carbon flow in aquatic systems. Compartments modeled in two units are indicated by two boxes, one behind the other. The phytoplankton compartment is composed of three functional groups: cyanobacteria, diatoms, and green algae. The arrows denote both carbon and phosphorus fluxes. (Modified from Janse et al. 1992.)

E. Phosphorus Control and Management

A variety of methods have been employed to limit anthropogenic increases in phosphorus loading. Such methods include:

- Removal of point sources. e.g. Sewage treatment plants with P removal, or so-called tertiary treatment.
- Diversion of P rich sources (e.g. Lake Washington).
- Wetlands, to intercept and sequester P and denitrify N.
- Maintaining riparian zones along streams to intercept particulate nutrients.
- Sediment inactivation in lake, using alum.

Examples:

An early success story was Lake Washington. The diversion of sewage away from the lake was very successful. Lake Washington lent itself to such a treatment because:

- The lake has a relatively rapid WRT (2 yrs or so) so P can be flushed or sedimented.
- Deep lake with an oxic hypolimnion, thus helping sediment and sequester P
- Diversion was possible because it was mostly point sources (sewage). (Non-point sources are much more difficult to control.)

Lake Washington has proven to be somewhat misleading. Other expensive projects have mostly been less successful, sometimes failing entirely. These failures have been attributed to a variety of causes, including:

- Nitrogen limitation
- Large sediment reservoir of P which extends internal loading
- Difficulty with non-point sources, notably, agriculture.

Various methods to palliate the effects of excess loading have also been attempted. In addition to sediment inactivation via alum or FeCl₃, lake aeration has been used. The purpose (typically) is to maintain an oxic hypolimnion and thereby reduce internal loading.

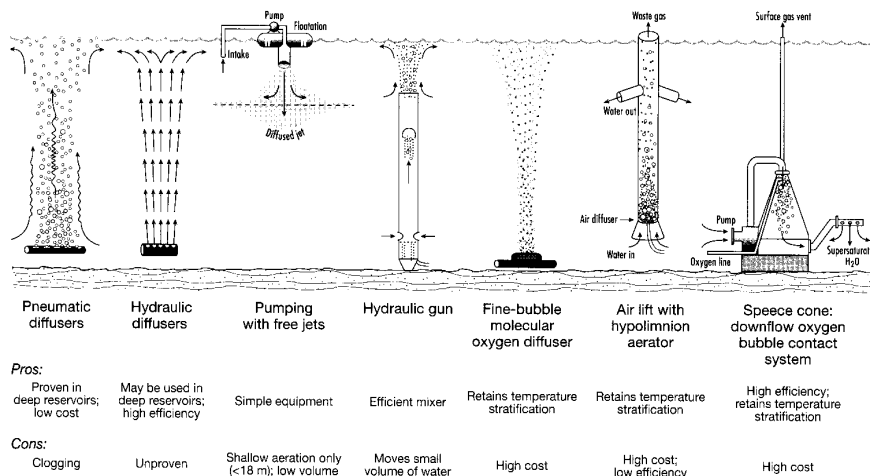


Figure 17-9 A variety of re-aeration devices and their advantages and disadvantages. (Largely after Johnson 1984, and Beutel and Horne 1999.)