## N:P RATIOS IN ESTIMATING NUTRIENT LIMITATION IN AQUATIC SYSTEMS

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# Description

The relative concentrations of N and P have been used to estimate which of these nutrients is limiting the growth of algae in aquatic systems. The approach is simple and easy to use provided that there are data on N and P concentrations. Yet, interpretation of the results should be done with caution as the N:P ratio may not correctly indicate the limiting nutrient of the system. The approach has mainly been used for standing waters, i.e. lakes and coastal areas, where nutrients rather than physical conditions tend to limit algal growth.

#### Rationale

Aquatic eutrophication results from excessive amounts of nutrients available for primary producers, such as planktonic algae, macroalgae and macrophytes. To successfully mitigate eutrophication, one should be able to identify which nutrient(s) is/are responsible for enhanced primary production so that management actions can be focused on nutrients having the highest impact.

Ecological stoichiometry is a discipline that seeks to understand the balance of multiple chemical elements in ecological interactions. As to freshwaters (lakes, rivers, reservoirs), it has traditionally been assumed that P is the nutrient present in lowest amount in relation to the requirements of phytoplankton. Therefore, when the flux of P entering a body of water is cut down, the biomass of algae is assumed to be reduced. In marine systems, N has been identified as the growth limiting nutrient, whereas in estuaries P may be limiting in the fresh-water part and N in the marine part [1]. Nitrogen limitation in marine systems has been attributed to (i) stronger N removal in coastal waters e.g. by denitrification, (ii) lower amount of N-fixing cyanobacteria ('blue-green algae') and (iii) to higher rates of microbial SO<sub>4</sub> reduction that makes Fe unable to sequester P [1, 2].

# Application

Since the observation of Redfield [3, 4] that marine phytoplankton contains a molecular C:N:P ratio of 106:16:1 (50:7:1 by weight), the use of elemental ratios has become widespread in marine and freshwater phytoplankton studies. A departure from this ratio has been assumed to imply nutrient deficiency. In such a case, there is not only sub-optimal growth of phytoplankton, but also substandard food resources for primary consumers of phytoplankton. For diatoms that need silicate for their frustules an optimal C:Si:N:P ratio of 106:15:16:1 has been suggested [5].

However, the nutrient content of phytoplankton is not constant but varies according to species, season and environmental conditions. For example, Redfield ratios are the exception rather than the rule in freshwater [6]. Therefore, a more accurate estimate of nutrient limitation is obtained when nutrient ratios are examined together with controlled biotests (bottle tests, mesocosms) with different levels of P and N amendments to natural phytoplankton community (e.g. [2]). Comparison of algal biotest results and chemical nutrient concentrations in lakes has suggested that a mass N:P ratio above 17 indicates P limitation, a ratio below 10 indicates N limitation and values between 10 and 17 indicate that either of the nutrients may be limiting [7–9]. The corresponding molecular ratios are > 38, < 22 and 22–38, respectively.

The above values were calculated using concentrations of total nutrients, i.e. nutrients largely bound by phytoplankton and other particles ('seston'). Inorganic nutrient fractions have been used in estimating the potential for nutrient limitation, for example by calculating the ratio of dissolved inorganic N and P in water (DIN:DIP, [10]) and the combination of total and inorganic nutrients [10, 11]. The absolute concentration level also plays a crucial role: if the concentration of DIP exceeds

ca.  $5 \mu g l^{-1}$  and DIN ca.  $300–500 \mu g l^{-1}$  neither P nor N may be limiting [12]. Thus, the limiting factor may depend on the level of nutrient concentrations.

In addition to a proxy of limiting nutrient, N:P ratio has been used in estimating the risk for cyanobacterial blooms. N-fixing cyanobacteria tend to dominate in lakes with a (total) mass N:P ratio below 22 [13]. Note that the growth of cyanobacteria is dependent on several other factors too, such as hydrodynamic and light conditions and the structure of food web [14–16].

## **Effectiveness**

Although N:P ratios may give valuable information on nutrient limitation, there are many restrictions and exceptions to this concept. In addition to N, P and Si, phytoplankton growth may be limited by Fe or C [e.g. 17]. Moreover, phytoplankton is not a uniform entity, but is composed of numerous taxa and species, each having specific nutrient requirements; increase in biomass is usually more easily detected than the change in species. Furthermore, other groups of primary producers have different elemental composition and requirements. As an example, benthic marine plants need more C and N in relation to P than phytoplankton (550:30:1, [18]). For macrophytes, nutrient availability may result in different growth strategy (horizontal/vertical) rather than in a clear change in biomass. Among the consumer organisms (that use primary producers as food), there is also a wide range in nutrient ratios. For example, the fast growing cladocera concentrate P [19], whereas the calanoids concentrate N [20]. Nitrogen limitation may thus be acerbated in a system having a high biomass of calanoids. Finally, in very nutrient-rich or turbid waters light rather than any of the nutrients may be in too short a supply. Physical conditions (morphology and hydrological regime) limit algal growth especially in rivers and creeks.

A problem related to the use of N:P ratio in estimating the limiting nutrient is brought about by the biological unavailability of some forms of nutrients. For example, P bound to eroded soil particles, forming a major P fraction in areas with arable farming and surface runoff, is not entirely available to algae. The same applies to dissolved organic N, although there is evidence that some of it is directly utilized by algae, or converted into algal-available forms by bacteria and UV radiation. By turn, there is also a preference of some species to utilize a specific form of a nutrient, e.g. NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>, or HCO<sub>3</sub><sup>-</sup> rather than CO<sub>2</sub>. On the other hand, the concentrations of dissolved nutrients may be below the detection limit, which prevents their use in calculations. Or the concentrations may show too much variation; N can be depleted very fast during the growing season, whereas there can be a large mobilization of P from the sediments. Thus, acute (instantaneous) growth limiting factors may show dynamic, even unpredictable variability over time. From the point of view of management, the maximum biomass (carrying capacity of the system) can be considered more important, and more stable, than the fluctuating instantaneous conditions.

A recent European compilation came up in a good correlation with chlorophyll *a* and total P [21], in line with the paradigm of P limitation in lakes. Such correlations may, however, be considered spurious as the chlorophyll *a* and P are not independent of each other. In addition, there is a lot of scatter in the chlorophyll *a* to P relationships making predictions for a single lake highly imprecise. The current view is that limitation of N can also be observed in freshwaters, both in productive and unproductive ones. Nitrogen limitation may be found when there is a high P level due to human perturbations or to P-rich soil type, or in low productive conditions with low N deposition.

# Time frame

Reversal of aquatic eutrophication following mitigation actions can be instantaneous, delayed, or impossible (see [22, 23]). Once the system has undergone a 'regime shift' with internal processes controlling the nutrient cycling, drastic measures are needed to abate eutrophication. A classic example of the mechanisms of inertia is formed by the P release from sediments; in pristine systems sediments act as a sink for P, but on increasing eutrophication the ability of sediments to capture P often decreases [24]. Past human activities often lead to legacy effects and can profoundly impact recent nutrient dynamics and, therefore, also interfere with expectations how fast measures lead to

improved situations [25]. Furthermore, measures can lead to different reactions of different water bodies within an area based on legacy effects of the sediment [26]. These temporal effects have to be considered to understand current nutrient conditions. Another example is the complex interactions among different species in the entire food web. As a consequence, the dominance of cyanobacteria, once started, may be difficult to be reversed. In conclusion, management has to acknowledge eutrophication history.

### Environmental side-effects

Management design should consider the entire water course/catchment. Nitrogen may be transported from a P limited lake to N limited coastal waters. Therefore, we should be able to estimate the retention of N in P-limited systems and vice versa. The biogeochemical cycling of N and P are closely linked to each other, and thus the measures focusing on one of the nutrients can affect the other. For example, the depletion of NO<sub>3</sub> in wetlands has been found to coincide with the release of P [27], probably as the mineralization pathway changed from denitrification to Fe reduction with the concomitant release of Fe-bound P. In such cases, increasing NO<sub>3</sub>, however, may not be the solution, since the underlying cause for P release is an excessive amount of labile organic C (eutrophication) rather than a shortage of NO<sub>3</sub>. As to the Baltic Sea, it has been suggested that decreasing N load may stimulate the growth of N-fixing cyanobacteria. By contrast, it has also been reasoned that a reduction in N load results in reductions in phytoplankton biomass, settling labile organic carbon and sediment release of P, and thereby reducing N load lowers the risk for cyanobacterial blooms [28].

#### Costs

In cases where there is enough reliable data on nutrient concentrations, the costs are incurred mainly by the statistical calculations. Obviously, the expenses increase if determinations on N and P have to be performed, and still more when biotests will be carried out to increase the evidence. Such costs may then be related to the costs of implementing mitigation measures that are inefficient due to focusing on less critical factors. By making a combined estimation of costs to reduce the load of N and P, the environmental goal to reduce eutrophication may become more feasible.

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