Limno.09.13.N

Nitrogen

A. Introduction

After phosphorus, nitrogen is the element most likely to limit plant productivity in fresh water. The Redfield ratio (N/P = 16) can serve as an indicator of the likelihood of nitrogen limitation: ratios much below 16 suggest that nitrogen may be limiting.

1. Redox ***species of interest***: NH_4^+, NO_3^-, NO_2^-, N_2 (gas), NO (gas), N_2O (gas), PON. Separate analytical methods are available for each of these species. [The sensitivity of several of the methods is good although sometimes insufficient to detect concentrations that are still meaningfully different for the organisms involved.] Nitrate is likely the most abundant species in oligotrophic lakes; ammonia most abundant in humic systems due to typically low DO and redox potential. Nitrogen in streams from undisturbed forests is mostly organic nitrogen. (Kalff, p280-281).

2. ***Processes*** involved in the transformations among these chemical species are mediated by *particular organisms*. The processes have been given names that are (partially) explanatory. Examples: *nitrification* = oxidation of ammonia to nitrate; *denitrification* = conversion of DIN (Nitrate or Nitrite) to gaseous species (e.g. N_2 or N_2O). To understand these processes it is useful to pay attention to the *organisms* involved, the *oxidation-reduction conditions* under which they occur, *where* (physical location) they occur (water column, sediment, shallow water, wetland) and the *linkage to other processes*.

3. The ***organisms*** involved include: plankton, periphyton, benthos, and macrophytes. Procaryotes are often of particular interest as they alone are capable of some key processes (e.g. nitrogen fixation, denitrification).

4. The "***vertical structure***" is often of particular interest. As noted in figure 18-2 there is often a "layer cake" of different zones within each of which characteristic processes take place. In the figure, for example, denitrification takes place in the (deeper) anaerobic zone of sediment.

B. Nitrification (see p273ff)

Nitrification takes place where there occur (simultaneously): reduced DIN (ammonia), sufficient oxygen and specific procaryotes capable of using oxygen as electron acceptor to convert ammonia to nitrate. The organisms harvest the energy associated with the reaction. [Aside: the term *nitrification* is an inheritance. It could be said to be a *misnomer* since by itself it does not alter DIN.]

1. The *organisms*. The organisms that catalyze these reactions are ***specific*** procaryotes, sometimes referred to as chemoautotrophs or chemolithotrophs. *Nitrosomonas*, and other genera, oxidize ammonia to nitrite; *Nitrobacter*, and

other genera, oxidize nitrite to nitrate. Typically the organisms occur together and nitrite does not accumulate to any extent.

2. *Rates* of nitrification. "Therefore, the ***observed rate of nitrification*** (and the coupled denitrification) is principally a function of three substrates: the NH_4^+ (or NO_2^-) pool available, the DO supply rate, the CO_2 available and the water temperature with its effect on rates of metabolism." Kalff, p274.

3. The *site* of nitrification is where *oxygen is available* (commonly by diffusion from the atmosphere or the epilimnion) and where *ammonia is present*, either by diffusion from a zone of reducing conditions (e.g. deep sediment) or excretion by animals. The site of this interface can vary from one ecosystem to another. Figure 18-2 is a general picture of what might happen in an oligotrophic lake. In Lake Rotoiti (figure 18-3) the interface coincides with the thermocline. In poorly mixed eutrophic wetlands, the interface might be close to the surface.

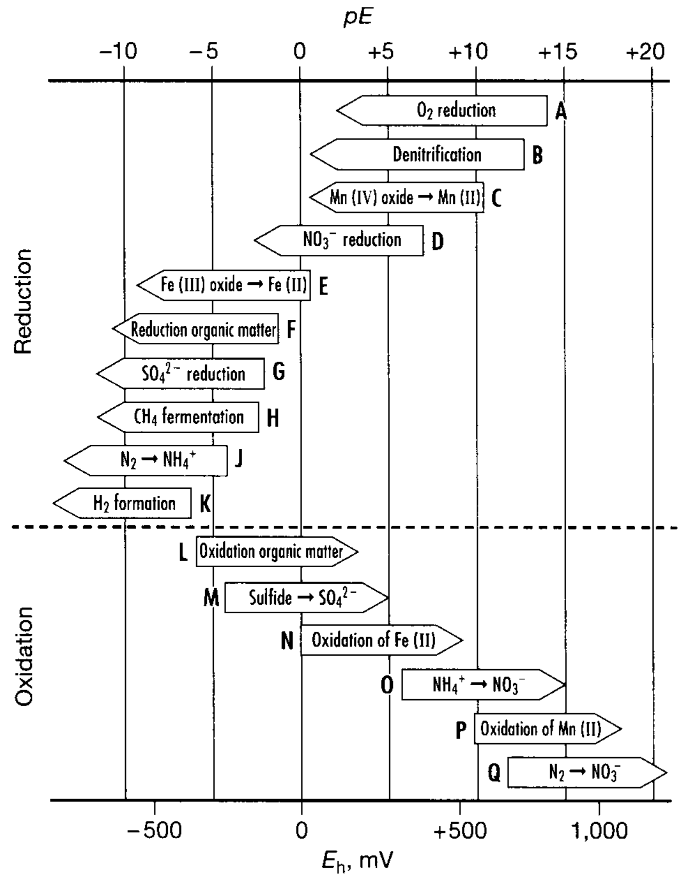
4. Relationship to *other environmental conditions*. Nitrification can consume a significant amount of oxygen (e.g. Table 18-1) and can lead to an "oxygen sag" in streams receiving wastewater with high ammonia concentration. In addition to the necessity for oxygen, nitrification can take place only where environmental conditions are appropriate. For example, studies of acid rain have revealed that nitrification does not occur where pH is below 5 (p274 Kalff).

C. Denitrification.

Under reducing conditions, DIN (NO_3^-, NO_2^-) may substitute for oxygen as a final electron acceptor (oxidizing agent) in the decomposition of organic matter. Because the end product of this process is a gas (N_2 or N_2O) that is lost from the ecosystem, the process has been named denitrification.

Nitrate (or nitrite) serves as final electron acceptor for a variety of facultative **anaerobic** heterotrophs (i.e. species that could also use oxygen if it were available) in the oxidation of organic matter. Because the organisms are not retaining the nitrogen involved, but only using it as an oxidizing agent, the process is "dissimilatory".

1. Kalff (p275) points out that denitrification is linked to the phosphorus cycle. As long as sufficient nitrate remains, the redox potential will remain high enough that diffusion of phosphorus from the sediment will be inhibited, as it is by oxygen. This mechanism has been used in lake restoration. Nitrate is injected into eutrophic lake sediments of oxidize them and keep iron in the ferric form (remember this figure from a previous lecture?)



2. Denitrification occurs extensively in wetlands and shallow lakes. Also, denitrification can be facilitated by macrophytes that conduct oxygen to their roots and nitrogen gas to the atmosphere. Accordingly, eutrophication due to excess nitrogen loading can be mitigated by managed wetlands. Nitrogen in runoff can be removed by routing flow through wetlands with the appropriate conditions.

Aquatic plant roots, where oxygenated environments are adjacent to anaerobic environments allow nitrification and denitrification to occur in close proximity and result in a net loss of nitrogen from the system.

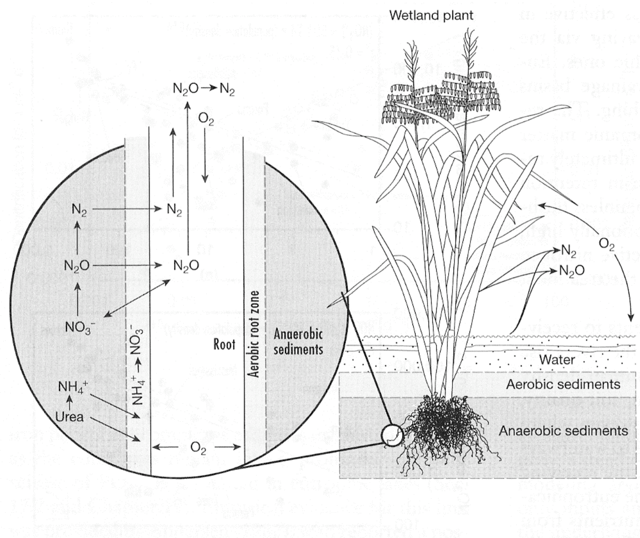


Figure 18–6 Schematic presentation of nitrification–denitrification in the root zone of rice and other emergent aquatic macrophytes. *(After Reddy et al. 1989.)*

D. Nitrogen fixation

1. ***When nitrogen fixation occurs***: Nitrogen fixation is an energetically expensive process. It only occurs when the N/P ratio is low and DIN is in short supply.

2. ***Organisms that fix nitrogen***: A wide variety of prokaryotes (and only prokaryotes) are capable of fixing N_2. A number of species of planktonic cyanophytes (see p278) are capable of fixing N_2. A characteristic feature is the presence of *heterocysts* that help isolate the key enzymes from environmental oxygen. Kalff (p280) points out that points out that rate of nitrogen fixation in the littoral zone is likely higher than in the pelagic zone.

3. ***Nitrogen fixation is expensive***: Nitrogen fixation requires metabolic energy. In cyanophytes, nitrogen fixation competes for the energy captured by photosynthesis, and therefore reduces growth rates. Nitrogen fixation by cyanophytes is proportional to light intensity. In the presence of DIN, even species capable of nitrogen fixation will preferentially assimilate ammonia (prefered), or nitrate (less preferred), rather than fix N_2.

D. Trophic classification system of lakes: N and P.

The table below presents a broad summary of the concentrations of P and N in relation to the trophic classification of lakes. Trophic state is by definition determined by the availability of nutrients, primarily P and N.

Table 18–3 **Summer near-surface average nutrient concentrations ($\mu g\ l^{-1}$) for classifying lakes and rivers into different trophic state categories.**

	Trophic State	Inorganic N	Total N	Total P	TN:TP	Chl-*a* Suspended	Chl-*a* Benthic
Lakes	Oligotrophic	< 200	< 350	< 10	~35	< 3.5	—
	Mesotrophic	200–400	350–650	10–30	~25	3.5–9	—
	Eutrophic	300–650	650–1200	30–100	~14	9–25	—
	Hypertrophic	500–1500	> 1200	> 100	~12	> 25	—
Rivers	Oligotrophic	—	<< 700	< 25	~28	< 10	< 20
	Mesotrophic	—	700–1500	25–75	~22	10–30	20–70
	Eutrophic	—	> 1500	> 75	~20	> 30	> 70

Source: After Vollenweider 1968, Forsberg and Ryding 1980, and Dodds et al. 1997.

E. Management issues.

Eutrophication is one of the primary problems for lakes. Reduction of sources of nitrogen and phosphorus are often the key to avoiding the detrimental effects of so-called "cultural eutrophication". As described above, wetlands and shallow lakes may sometimes support significant denitrification. In some cases, wetlands have been constructed and maintained for precisely this role.

Because of long distance transport via air pollution, local controls are sometimes not enough. Current estimates indicate that perhaps half of all the fixed nitrogen on the planet is the result of anthropogenic sources, both intentional (fertilizers) and unintentional (air pollution).

Furthermore, since there is an atmospheric source of N for nitrogen fixers that often dominate N-limited systems it is difficult to regulate phytoplankton production and reduce **cultural eutrophication**, anthropogenic enrichment of aquatic systems.