



Limnology
Lake and River Ecosystems

Third Edition

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TABLE 12-11 Estimates of the Nitrogen in Various Compartments in Lake Wingra, Wisconsin, Midsummer^a

Compartment	Nitrogen (metric tons)	Percentage of total N	
		A ^b	B ^c
Soluble and particulate N in water	3.2	0.5	50.6
Macrophyte N	1.2	0.2	19.3
Sediment, upper 10 cm			
Organic N	138	23.0	—
Interstitial water			
NH ₄ -N	0.74	0.1	11.5
Organic N	0.19	0.03	3.0
Exchangeable NH ₄ -N	1.0	0.2	15.6
Sediment, 10-30 cm			
Organic N	460	74.3	—
Interstitial water			
NH ₄ -N	4.6	0.8	—
Organic N	0.51	0.08	—
Exchangeable NH ₄ -N	5.4	0.9	—
Total			
Total N in system	615		
Total N excluding sediment organic N and all N below 10 cm in sediment	6.3		

^a Modified from Isirimah *et al.* (1976).

^b Total N in system.

^c Total N excluding sediment organic N and all N below 10 cm in sediment.

conditions (Table 12-11). Much (97%) of the total nitrogen occurred in the sediments as organic nitrogen (column A) but was not readily available for metabolism in the lake system (Isirimah *et al.*, 1976). Neglecting these relatively unreactive nitrogen reservoirs, about 50% of the "available" nitrogen existed in the water column, mostly in dissolved form, 20% in the macrophytes, and 30% in the interstitial water of surficial sediments (column B). Rapid turnover rates of NH₄-N occurred in the water but not in the sediments. NO₃-N turnover was slower in the water than in the sediments, where about 80% of the NO₃-N was rapidly denitrified to N₂.

VI. NITROGEN BUDGETS

Detailed evaluations of the nitrogen cycle that include close-interval quantitative measurements of inputs, metabolic dynamics, and outputs are available for only a few freshwater ecosystems. The cycle is obviously complex and requires accurate analyses of the dynamics of all components for several years. Only a few approximate mass balance analyses of the nitrogen budgets of lakes and streams are available. In these analyses, the rates of bacterial metabolism are obtained indirectly, by assumptions of microbial processing or

sedimentation by differences. Nonetheless, the approximate calculated budgets are instructive in characterizing the inputs, outputs, and retention of nutrients by ecosystems.

The nitrogen budget of Lake Mendota, Wisconsin, demonstrates the roughly equivalent contributions from runoff, ground water, and precipitation (Table 12-12). Major losses of nitrogen occur via sedimentation, denitrification, and outflow. Loss by seepage out of the basin was probably small, since most lake basins are well sealed (cf. Wetzel and Otsuki, 1974). In Table 12-13, the nitrogen budget for a large reservoir of complex morphometry accounts for inflows from all river influents and losses by sedimentation and outflow. Although the total nitrogen content of this reservoir decreased in 1962 because of low water levels, inputs of atmospherically derived nitrogen amounted to roughly 10,000 tons per year. About 1300 metric tons entered with rain and snow; the remainder may be attributed largely to biological fixation. Mirror Lake, a kettle lake located in a crystalline granitic bedrock region of the White Mountains of central New Hampshire, receives appreciable (half) nitrogen loading from atmospheric sources (Table 12-14). Primary outputs are via permanent sedimentation and river outflow in approximately equal quantities of inorganic and organic forms. Some 54% of the annual gross sedimentation of organic

TABLE 12-12 Estimated Nitrogen Budget of Lake Mendota, Wisconsin^a

Sources	Nitrogen income		Losses	Nitrogen losses	
	kg N yr ⁻¹	%		kg N yr ⁻¹	%
Municipal and industrial wastewater	21,200	10.4	Outflow	41,300	20.4
Urban runoff	13,700	6.8	Denitrification	28,100	13.9
Rural runoff	23,500	11.6	Fish catch	11,300	5.6
Precipitation on lake surface	43,900	21.6	Weed removal	3250	1.6
Ground water			Loss to ground water	^b	^b
Streams	35,900	17.7	Sedimentation and other ^c	118,850	58.6
Seepage	28,500	14.1		202,800	100
Nitrogen fixation	36,100	17.8			
Marsh drainage	^d	^d			
	202,800	100			

^a Modified from Brezonik and Lee (1968), with data improvements by Keeney (1972)

^b Unknown; likely very small in this lake.

^c By difference between total of other estimated losses and sum of income sources.

^d Considered significant, but data unavailable.

nitrogen was mineralized in a large, oligotrophic lake in Sweden (Jonsson and Jansson, 1997). About two-thirds of the nitrogen mineralized in the sediments, released to the overlying water, and transported out of the lake as nitrate via the outlet during turnovers in spring and autumn. Only ca. 4% of organic nitrogen remained in the sediments; the remainder was lost via denitrification at about 1 mg N m⁻² yr⁻¹.

Analyses of nitrogen budgets of some 40 lakes of very different states of productivity indicated that the removal of nitrogen is usually dominated by denitrification, which is directly correlated to organic matter loadings (Hellström, 1996). Where nitrogen fixation is significant, the increase in total nitrogen from N₂ fixation is generally proportional to the concentration of total phosphorus minus a fraction of the estimated nitrogen concentration without any N₂ fixation. General nitrogen budgets of this type leave much to be desired because they provide relatively little insight into the dy-

namics of internal processing or metabolic controls mechanisms. From an applied viewpoint, however, such mass balance information is useful in relation to nitrogen loading and the effects of this loading on alterations of productivity, as will be discussed in some detail with phosphorus (cf. Chap. 13).

Annual elemental mass balance budgets have also been used to characterize the inputs, outputs, and retention (i.e., the difference between nitrogen inputs and outputs) of stream ecosystems. Hydrological variations can be great in streams and they influence the fluxes. Even among more hydrologically stable streams, inter-annual variations in discharge can be large (Meyer and Likens, 1979; Meyer *et al.*, 1981; Grimm, 1987). In arid regions, flooding events can cause extreme variations in annual budgets.

Examination of representative nitrogen budgets of streams indicates that total nitrogen storage was similar even though the distributions among storage

TABLE 12-13 Estimated Nitrogen Budget of the Rybinsk Reservoir, Russia, in Metric Tons N per Year^a

Factors measured	Time			
	1 June 1960– 1 June 1961	1 April 1961– 1 April 1962	1 June 1962– 1 June 1963	
A	Measured nitrogen balance of water mass	+ 12,519	+ 5399	+ 12,170
B	Difference between inflow and outflow	- 180	- 7329	+ 1565
A - B = C	Increase in water mass	+ 12,699	+ 12,728	+ 10,605
D	Precipitated in sediments (20-yr average)	+ 12,500	+ 12,500	+ 12,500
C - D = E	Theoretical balance in water mass	+ 199	+ 228	- 1895
A - E	Nitrogen input from atmosphere and fixation	+ 12,320	+ 5171	+ 14,065

TABLE 12-14 Average Annual Nitrogen Budget for Mirror Lake, New Hampshire, 1970-1975^a

	kg yr ⁻¹ ± S _x
Inputs	
Precipitation	
Inorganic	112 ± 10.7
Organic	7
Litter	13.6
Dry deposition	~15
Fluvial	
Dissolved	
Inorganic	35 ± 7.2
Organic	46
Particulate, organic	9
Total	238
Outputs	
Gaseous flux	?
Fluvial	
Dissolved	
Inorganic	61 ± 8.8
Organic	54
Particulate, organic	11
Net insect emergence	13
Permanent sedimentation	127-139
Total	266-278
Change in lake storage (decrease in NO ₃ ⁻ storage)	-6

^a Modified from Likens (1985).

components differed (Table 12-15). Nitrogen storage was largely associated with woody debris (59-80%) in forested streams, whereas in an open desert stream as much as 93% was in algae and autochthonous detritus. Some nutrients are stored in consumer animals, although turnover rates in these organisms are relatively slow. Dissolved organic nitrogen exports are less than inputs and indicated biological utilization associated with mineralization and potentially some sorption and flocculation processes (Triska *et al.*, 1984). Most particulate organic inputs increased in nitrogen concentrations prior to export (Table 12-16).

It has been predicted that ecosystem nitrogen retention would increase as rates of net ecosystem production and biomass accumulation increase and then decline or increase at a slower rate as biomass approaches a steady state (Vitousek and Reiners, 1975; Grimm and Fisher, 1986). At steady state, nutrient inputs would equal outputs, even though the state and forms of the nutrients may change. This relationship has been generally verified in studies that evaluated the patterns of nitrogen retention during successional recovery of algal and macroinvertebrate communities after they were disturbed by flash-flooding events and reduced to virtual zero levels (Grimm, 1987). Biomass and stored nitrogen increased during the early to middle successional stages of recolonization and development and were followed by declines in late stages.

TABLE 12-15 Nitrogen Mass Balances of Five Streams in Percentage of Total in Each Category^a

	Watershed 10, Oregon	Beaver Creek Rifle, Quebec	Sycamore Creek, Arizona	Bear Brook, New Hampshire	Mare's Egg Spring, Oregon
Inputs (% of total)					
Dissolved inorganic N	3	15	16-58	73	(24)
Dissolved organic N	69	67	37-69	11	(24)
Particulate organic N	0	18	9-15	2	43.8
Precipitation and throughfall	2	0.02	0	3	4.2
Litter	19	0.12	—	11	0.2
N ₂ fixation	5	0.004	?	?	3.8
Pools retained N (% of total)					
Fine particulate inorganic nitrogen	40	19	0	—	—
Large particulate organic nitrogen	59	80	0	—	—
Producers	0.6	?	86-93	—	—
Consumers	0.2	?	6-14	—	—
Outputs (% of total)					
Dissolved inorganic N	4	15	18-58	84	(21)
Dissolved organic N	74	67	37-72	12	(21)
Particulate organic N	23	18	7-22	3.7	57 ^b
Coarse PON	8	0.1	0.1-6	3	
Fine PON	15	18	7-16	0.7	
Emergence	0.2	0.1	0.1-1	?	0.001
Denitrification	—	—	—	—	0.906

^a Data extracted from Meyer *et al.* (1981), Naiman and Melillo (1984), Triska *et al.* (1984), Dodds and Castenholz (1988), and Grimm (1987).^b Includes particulates (16%) and sedimented burial of PON (41%).

TABLE 12-16 Annual Nitrogen Budget for a Small Stream (Unnamed) in the Western Cascade Mountains, Oregon, Heavily Forested with Mature Conifer Trees^a

	$g\ m^{-2}$		$g\ m^{-2}$
			Sums
Total nitrogen inputs			15.25
Hydrologic inputs			11.06
Dissolved inorganic N (NO_3-N)	0.50		
Dissolved organic N	10.56	11.06	
Biological inputs			4.19
Terrestrial			
Throughfall	0.30	0.30	
Litterfall			
Needles	0.66		
Leaves	0.15		
Cones, bark, twigs, wood	0.17		
Coarse wood debris	0.11		
Microparticulate litterfall	0.18		
Miscellaneous	0.08	1.35	
Lateral movement			
Needles	0.31		
Leaves	0.29		
Cones, bark, twigs, wood	0.85		
Miscellaneous	0.33	1.78	
Aquatic			
N_2 -fixation			
Twigs	0.09		
Bark	0.17		
Chips	0.10		
Wood debris	0.34		
Moss	0.06	0.76	
Particulate organic N pool			11.93
Fine particulate organic matter			
1 mm–250 μm	0.58		
250 μm –80 μm	0.78		
<80 μm	3.41	4.77	
Large particulate organic matter			
Needles	0.27		
Leaves	0.08		
Cones, twigs, bark, wood	2.18		
Miscellaneous	0.74		
Coarse wood debris	3.80		
Moss	0.07		
Consumers	0.02	7.16	
Total nitrogen outputs			11.79
Particulate organic nitrogen		2.53	
Fine particulate organic matter			
1 mm–80 μm	0.28		
<80 μm	1.38	1.66	
Large particulate organic matter			
Needles	0.15		
Leaves	0.03		
Cones, twigs, bark, wood	0.46		
Miscellaneous	0.23		
Coarse wood debris	0.00	0.87	
Emergence of insects		0.02	
Drift of insects			
Dissolved organic nitrogen		8.81	
Dissolved inorganic nitrogen (NO_3-N)		0.43	
Denitrification		?	

^aData extracted from Triska *et al.* (1984).

A. Nitrogen Loading: Effects of Human Activities

Enrichment of fresh waters with nutrients needed for plant growth occurs commonly as a result of losses from agricultural fertilization, loading from sewage and industrial wastes, and enrichment via atmospheric pollutants (especially nitrate and ammonia). Sufficient information exists about the general responses of many lakes to loading of major nutrients, especially phosphorus and nitrogen, to predict the potential changes in their productivity. The phytoplankton productivity of infertile, oligotrophic lakes is often limited by the availability of phosphorus. As phosphorus loading to fresh waters increases and lakes become more productive, nitrogen often becomes the nutrient limiting to plant growth. Excessive loading of these nutrients permits increased plant growth until other nutrients or light availability become limiting.

The nitrogen loading concepts in relation to increased lake productivity are best discussed simultaneously with phosphorus loading and limitations. Both will be treated in the following chapter.

VII. NITROGEN DYNAMICS IN STREAMS AND RIVERS

A. General Nutrient Dynamics in Flowing Waters

Nutrients move unidirectionally within running waters. Dissolved substances move downstream, may be bound or assimilated for a period of time, and later be released for further movement downgradient. As materials and chemical mass cycle among biota and abiotic components of the stream ecosystem, they are transported downstream, in processes that resemble spirals and have been termed *nutrient spiraling* (Webster and Patten, 1979; Newbold *et al.*, 1981; Stream Solute Workshop, 1990). Although upstream movements of nutrients can occur in backflows from eddies, fish migration, and flight of adult aquatic insects, net fluxes are downstream.

Hydrological processes physically move water containing dissolved and particulate components to reactive sites. Exchanges at reactive sites include chemical ionic transformations, sorption and desorption, and metabolically mediated uptake and assimilation by biota (Fig. 12-13). Materials can be transferred from the water column to the stationary streambed. Some of these materials will be retained, utilized by incorporation into living organisms, potentially transferred to other organisms, and subsequently released by excretions or decomposition to the water column and further transported downstream.

Dissolved substances in running waters may be utilized extensively by biota or be reactive abiotically and

SURFACE EXCHANGES

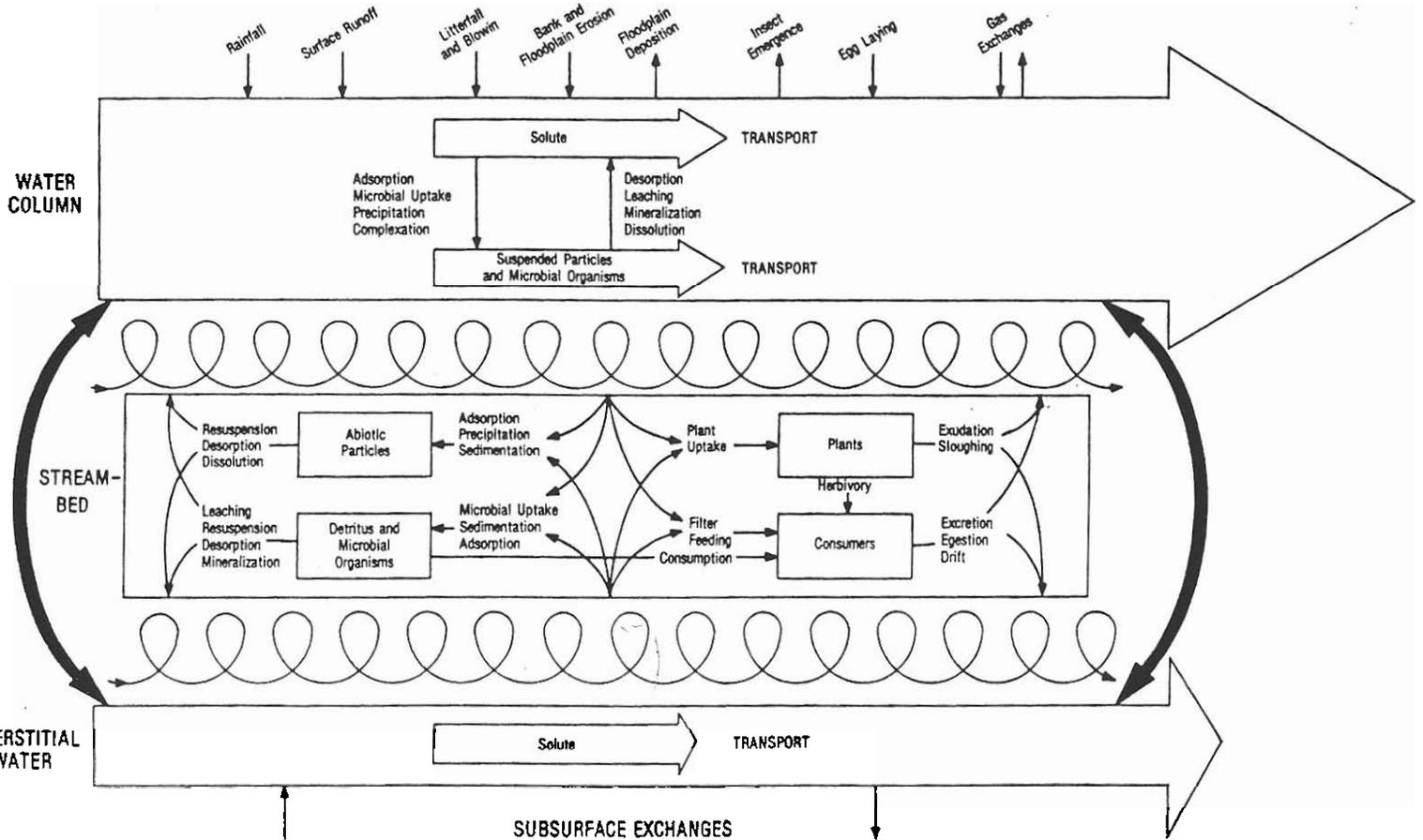


FIGURE 12-13 Solute processes in streams. The two spirals represent the continuous exchange of solutes and particle-bound chemical substances between the water column and the streambed and between the streambed and interstitial water. Materials in the water column and interstitial water are moving downstream, while the streambed materials are stationary. (From Stream Solute Workshop, 1990.)

are termed *nonconservative*. Other dissolved substances, termed *conservative*, are not generally modified chemically under normal limnological conditions or occur in such abundance that concentrations are not modified substantially by biological removal. Chloride ion is an essential nutrient that is nearly always conservative and is often used as a hydrological tracer. It should be noted, however, that differentiation between conservative and reactive solutes is relative; a solute may be conservative at one time or site and may become reactive at another place or time (Bencala and McKnight, 1987).

A nutrient atom may be used repeatedly as it passes downstream. The rate of utilization and release depends upon physical and biological retentiveness, largely by the microbiota associated with the streambed, that is, the extent to which the downstream transport of the nutrient is retarded relative to that of the water (Newbold, 1992). The objective is to quantify the average downstream distance (S , in meters) for the average nutrient atom to complete a cycle that takes an average time while it moves downstream at an average velocity. The average downstream velocity of the nutrient may be near that of the water in large rivers but is very much slower in streams and rivers where nutrients reside in the sediments and microbiota for a high proportion of the time.

Spiralling length (S) is the average distance a nutrient atom travels downstream during one cycle through the water and biotic compartment. The S equals the sum of distance traveled until uptake ("uptake length," S_w) and the downstream distance traveled within the biota until regeneration ("turnover length," S_b) (Fig. 12-14). The S can be calculated from the down-

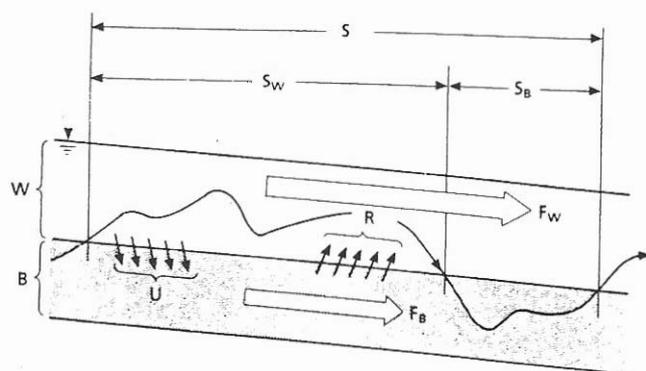


FIGURE 12-14 Spiralling in a river ecosystem of two compartments: water (W) and biota (B). The spiralling length (S) is the average distance a nutrient atom travels downstream during one cycle through the water and biotic compartments. $S =$ the sum of the uptake length (S_w) and the turnover length (S_b) estimated from the downstream nutrient fluxes (F_w and F_b) and the exchange fluxes of uptake (U) and retention (R). (From Newbold, 1992. *The Rivers Handbook*, vol. 1, Blackwell Science Ltd. Reproduced with permission.)

stream nutrient fluxes (mass per unit width of river per unit time in the water (W) component, F_w , and in the biota (B) component, F_b) and the exchange fluxes of biotic utilization (U) of nutrients from the water compartment or regeneration (R) from the biota in mass per unit area per unit time (Fig. 12-14). Details of the methodology, particularly to evaluate the uptake flux rates and release rates by the biotic compartments by use of isotopes of nutrients, are delineated in Newbold *et al.* (1981, 1983).

B. Nutrient Limitations and Retention

Nutrient limitations of primary producers and heterotrophic microbiota in streams and small rivers appear to be uncommon (cf. review of Newbold, 1992). Although cases of phosphorus limitations of both attached algal growth and production and of heterotrophic microbial activities have been determined in a number of streams and rivers, concentrations of soluble reactive phosphorus were consistently $< 15 \mu\text{g liter}^{-1}$ and often $< 5 \mu\text{g liter}^{-1}$. Similarly, increased microbial growth is found with inorganic nitrogen enrichments where natural concentrations were $< 50\text{--}60 \mu\text{g liter}^{-1}$, but rarely above this level. Evidence suggests that in lower-order streams with a greater dominance of biota attached to substrata, retention of nutrients is very high and that these nutrients are intensively recycled within the attached communities (cf. Paul and Duthie, 1989; Wetzel, 1993; Burns, 1998; Chap. 19). Removal of the attached microbial community, as was the case in a desert stream following a flood that eliminated most of the biota, reduced the retention of nitrogen to very low levels, slowed recycling rates, and increased spiralling length (Grimm, 1987). Nitrogen retention increased rapidly as the attached algal and bacterial community reestablished. As rivers become larger, nutrient retention is less and nutrient limitations can become more prevalent. Nutrient loadings to larger rivers, however, are often high because of human activities in the drainage basins. Coupled with high non-algal particulate turbidity and light reductions, nutrient availability is usually adequate to support microbial productivity within other environmental constraints.

The spiralling length of a nutrient suggests the extent of availability and utilization rates. A shorter spiralling length of one nutrient versus another could imply that the nutrient cycling more rapidly is in greater demand and is possibly limiting the potential growth and productivity of the community. For example, the shorter spiralling uptake length of nitrate nitrogen than that of phosphorus in a small stream of southern Spain was used as evidence of nitrogen limitation under different hydrological regimes (Maltchik *et al.*,

1994). Perhaps a more functional application is to determine the spiralling rates of nutrients among different dissolved, particulate, and animal consumer groups (e.g., Newbold *et al.*, 1983b). Such analyses demonstrate the rapid recycling rates and very short spiralling lengths of the attached microbiota in comparison to abiotic particulate materials and consumer metazoans.

C. Nitrogen Cycling in Running Waters

The inputs, transformations, and cycling of nitrogen in running waters are influenced, as in standing waters, to a large extent by bacterial, fungal, and other microbial metabolism. The transformation processes include both assimilation of nitrogen sources for utilization in synthesis of organic matter and growth, as well as utilization of inorganic and organic nitrogen compounds for energy in oxidation-reduction reactions. These processes have been discussed in detail in this chapter and are largely applicable to running water ecosystems as well as to lakes. Because many of these processes require anaerobic conditions, which are found less frequently in rivers, the subsequent discussion evaluates some of the quantitative differences in flowing waters on these processes. An important initial point of emphasis is that the assumptions that moving waters are fully oxygenated is not always true at even the macrolevel of bulk water volumes in streams and rivers and is often not the case in microenvironments within communities attached to surfaces and in interstitial waters of stream sediments.

D. Dissolved and Particulate Nitrogen in Rivers

The quantities of dissolved inorganic (NO_3^- , NO_2^- , and NH_4^+) and organic nitrogen compounds are highly diverse and variable because of marked differences in the inputs from surface and groundwater sources, particularly as affected by human activities (e.g., Spalding and Exner, 1993), and because of many competing reactions occurring in the nitrogen cycle. Ammonia concentrations tend to be low ($7\text{--}60\ \mu\text{g N liter}^{-1}$) in natural river waters, as is the condition in aerobic waters of reservoirs and lakes (Meybeck, 1982, 1993b). Ammonia nitrogen can constitute an appreciable portion (15 to $>80\%$) of the total dissolved inorganic nitrogen (DIN), particularly at low and, among polluted rivers, at very high DIN concentrations. As in lakes, nitrite nitrogen concentrations are very low ($<3\ \mu\text{g N liter}^{-1}$; $<1.5\%$ of total dissolved inorganic nitrogen, DIN) among well-oxygenated, unpolluted waters.

Among major rivers, nitrate concentrations range from $<25\ \mu\text{g N liter}^{-1}$ in subarctic environments and

TABLE 12-17 Distribution of Nitrogen Species (mg liter^{-1}) in Unpolluted Rivers^a

	Mean (min, max)
Values	
$\text{NH}_4\text{—N}$	0.018 (0.005–0.04)
$\text{NO}_2\text{—N}$	0.0012
$\text{NO}_3\text{—N}$	0.101 (0.05–0.2)
Dissolved organic N (DON)	0.260 (0.05–1.0)
Ratios	
DOC:DON	20 (8–41)
POC:PON	8.5 (7–10)

^aFrom many sources but particularly Malcolm and Durham (1976) and Meybeck (1982, 1993b).

in Amazonia to ca. $200\ \mu\text{g N liter}^{-1}$ in some temperate rivers (Meybeck, 1982, 1993b). Higher nitrate nitrogen concentrations are found among rivers influenced by agricultural runoff. An average $\text{NO}_3\text{—N}$ concentration of nearly $100\ \mu\text{g N liter}^{-1}$ is found in natural river waters (Table 12-17). Maximum nitrate concentrations during storm flows were directly related to the magnitude of the storms and resulting high discharge and inversely related to the frequency of storm events (Tate, 1990; Triska *et al.*, 1990a). The activity of terrestrial vegetation of the riparian zones influences the loadings of nitrate and ammonia to the streams; nitrogen concentrations are generally higher during periods of vegetation dormancy or following losses from harvesting or fire (e.g., Likens, 1985; Spencer and Hauer, 1991; McClain *et al.*, 1994). The extensive transformation reactions focused at the upland and stream margins of the riparian zone regulate and diminish transfers of inorganic nitrogen from ground water to stream water.

Dissolved organic nitrogen (DON) concentrations, although measured less frequently in natural river waters, nearly always constitutes a major part (world average ca. 40%) of the total dissolved nitrogen (Wetzel and Manny, 1977; Meybeck, 1982). In subarctic and humic tropical rivers, DON can constitute over 90% of the dissolved nitrogen. Although dissolved inorganic nitrogen concentrations and discharge can vary widely on a diurnal basis and seasonally, dissolved organic carbon and nitrogen are relatively constant (Manny and Wetzel, 1973). The ratio of dissolved organic carbon to dissolved organic nitrogen is, however, variable (8–41) and averages ca. 20 (Table 12-17).

Particulate nitrogen consists of particulate organic nitrogen (PON), adsorbed ammonia, and organic nitrogen adsorbed to particles (Table 12-17). On a weight ratio basis, the particulate organic carbon to

particulate organic nitrogen ratio is relatively constant at 8–10 (mean ca. 8.5).

E. Nitrogen Cycling in Sediments of Flowing Waters

Ammonium sorption to channel and riparian sediments can be extensive. For example, in granular sediments (0.5–2.0-mm grain size) of a third-order stream in California, exchangeable ammonium ranged from 10 $\mu\text{eq } 100 \text{ g}^{-1}$ of sediment where nitrification and subsurface exchange with stream water were high to 115 $\mu\text{eq } 100 \text{ g}^{-1}$ in the floodplain riparian sediments where channel water and groundwater mixing and nitrification potential were both low (Triska *et al.*, 1994). Sorbed ammonium was highest during summer/autumn base flow and lowest during winter storm flows. Similar results were found, with somewhat different seasonality, in a small temperate forest stream (Mulholland, 1992) and in the hyporheic zone of desert streams (Holmes *et al.*, 1994; Jones *et al.*, 1995). The riparian zone, when water-saturated, and parafluvial² and hyporheic zones are major sources of ammonium and dissolved organic nitrogen to the stream. Once within the stream, nitrogen uptake by at-

tached microbes (bacteria, fungi, and algae) was the primary mechanism controlling spatial and seasonal variations in the water. Diurnal daytime reductions in stream nitrate concentrations at base flow suggest that uptake by photoautotrophs can be an important retentive process (Burns, 1998), although the coupling of photosynthetic oxygen production within the sediment microbial communities to diurnal changes in denitrification are not clear in these environments.

The physical sorption of ammonia to sediment particles is dynamically coupled to sources from ground water and ammonification and transformations of dissolved inorganic nitrogen by nitrification, denitrification, and nitrate reduction (Fig. 12-15). Experimental studies of ammonium uptake by stream sediments indicated that biotic uptake by attached microflora was quantitatively much greater than physical adsorption (Newbold *et al.*, 1983b; Richey *et al.*, 1985; Aumen *et al.*, 1995). The duration of the storage of ammonium by sorptive processes is variable. Some studies indicate that appreciable retention can occur in summer months and contribute from 12–25% of nitrate released subsequently in winter by nitrification (e.g., Richey *et al.*, 1985), but in larger eutrophic river systems much of the ammonium is rapidly nitrified and exported downstream as nitrate (Lipschultz *et al.*, 1986).

The effectiveness of the denitrification and nitrification processes in the hyporheic zone of stream sedi-

²Parafluvial zone refers to the part of the active stream channel without surface water that is connected hydrologically with the surface stream water.

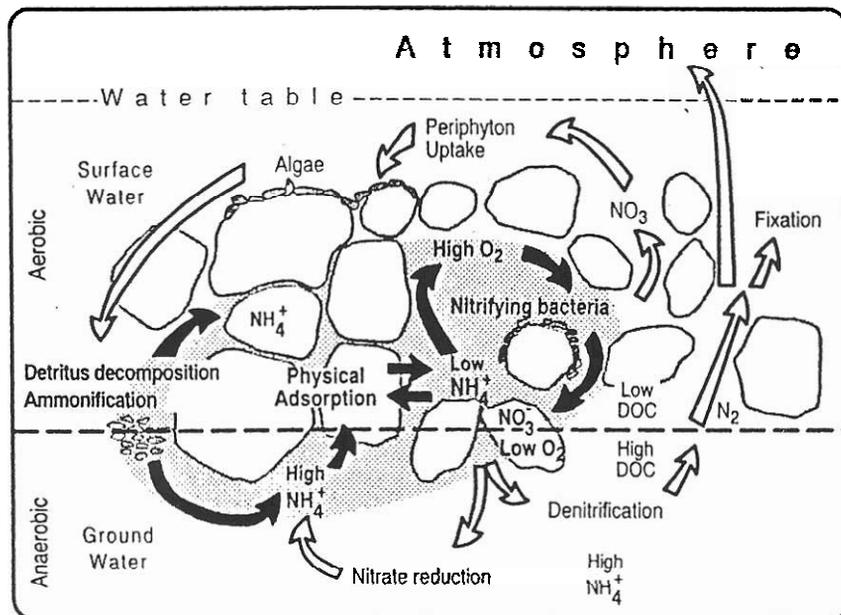


FIGURE 12-15 Linkages among physical sorption of ammonia to sediment particles, sources from ground water and ammonification, and transformations of dissolved inorganic nitrogen by nitrification, denitrification, and nitrate reduction at the groundwater–surface interface of a stream channel. (From Triska *et al.*, 1994.)

ments depends greatly upon the redox conditions within the interstitial water (Fig. 12-15). Flow conditions within the sediment interstices are quite variable spatially because of localized differences in sediment composition and textures. Internal flows also change over time between precipitation events, which lead to variations in both rates of groundwater inflow as well as rates of in-channel flows that penetrate down into the sediments (e.g., Triska *et al.*, 1990b). In organic-rich sediments, the redox profiles can be quite similar to those in lake sediments, in which the zone of nitrification can be restricted to the upper 2–3 mm and intensive denitrification occurs below the stratum of nitrifier activity (e.g., Cooke and White, 1987a,b; Birmingham *et al.*, 1994). Denitrification also occurs in shallow riparian sediments connected to the stream by the hyporheic zone (Duff and Triska, 1990). Denitrification increases with greater distance (10–15 m) from the stream channel were correlated with decreasing oxygen concentrations and increasing concentrations of reduced compounds.

Photosynthetic oxygen production by attached algae can diffuse for several millimeters into the sediments and reduce the rates of denitrification (Christensen *et al.*, 1990). Under shaded conditions or darkness, rates of denitrification increase rapidly as bacterial respiration depletes oxygen in the microzones. Clearly, the processes of nitrification and denitrification can be functioning simultaneously and reciprocally in the sediments, particularly where many microzones of steep redox gradients occur.

VIII. SUMMARY

1. Nitrogen, along with carbon, hydrogen, and phosphorus, is one of the major constituents of the cellular protoplasm of organisms. Nitrogen is a major nutrient that affects the productivity of fresh waters.
2. A major source of nitrogen of the biosphere originates from fixation of atmospheric molecular nitrogen (N_2). The nitrogen cycle is a complex biochemical process in which nitrogen in various forms is altered by nitrogen fixation, assimilation, and reduction of nitrate to N_2 by denitrification. For all practical purposes, the nitrogen cycle of lakes is microbial in nature: Bacterial oxidation and reduction of nitrogen compounds are coupled with photosynthetic assimilation and utilization by algae, photosynthetic bacteria, and larger aquatic plants. The direct role of animals in the nitrogen cycle is certainly very small; under certain conditions, however, their grazing activities can influ-

ence microbial populations and nitrogen transformation rates as well as nitrogen utilization rates by photosynthetic organisms. Although the nitrogen cycle of fresh waters is understood qualitatively in appreciable detail, the complex dynamics of quantitative transformation rates have not been clearly delineated, especially at the sediment–water interface, where intensive bacterial metabolism occurs.

3. Dominant forms of nitrogen in fresh waters include (a) dissolved molecular N_2 , (b) ammonia nitrogen (NH_4^+), (c) nitrite (NO_2^-), (d) nitrate (NO_3^-), and (e) a large number of organic compounds (e.g., amino acids, amines, nucleotides, proteins, and refractory humic compounds of low nitrogen content).
4. The nitrogen cycle consists of a balance between nitrogen inputs to and nitrogen losses from an aquatic ecosystem.
 - a. Sources of nitrogen include (i) nitrogen contained in particulate “dry fallout” and precipitation falling directly on the lake surface, (ii) nitrogen fixation both in the water and the sediments, and (iii) inputs of nitrogen from surface and groundwater drainage.
 - b. Losses of nitrogen occur by (i) outflow from the basin, (ii) reduction of NO_3^- to N_2 by bacterial denitrification with loss of N_2 to the atmosphere, and (iii) sedimentation of inorganic and organic nitrogen-containing compounds to the sediments.
5. Microbial fixation of molecular N_2 in soils by bacteria is a major source of nitrogen. In lakes and streams, N_2 fixation by heterotrophic bacteria and certain cyanobacteria is quantitatively less significant, except under certain conditions of severe depletion of combined inorganic nitrogen compounds.
 - a. The N_2 content of water is usually in equilibrium with the N_2 of the atmosphere during periods of turbulent mixing. In stratified, productive lakes, concentrations of N_2 may decline in the epilimnion because of reduced solubility as temperatures rise and increase in the hypolimnion from denitrification of NO_3^- -N.
 - b. N_2 fixation by cyanobacteria is usually much greater than fixation by heterotrophic bacteria. In cyanobacteria, N_2 fixation is light-dependent and usually coincides with the spatial and temporal distribution of these microbes. NH_4^+ -N assimilation requires less energy expenditure than NO_3^- -N, and NO_3^- -N less than N_2 -N. N_2 fixation by cyanobacteria increases when NH_4^+ -N and NO_3^- -N concentrations decrease in the trophogenic zone.

- c. Bacterial N_2 fixation in wetlands surrounding lakes or adjacent to streams can add significant amounts of combined nitrogen to freshwater ecosystems.
6. Ammonia is generated by heterotrophic bacteria as the primary nitrogenous end product of decomposition of proteins and other nitrogenous organic compounds. Ammonia is present primarily as NH_4^+ ions and is readily assimilated by plants in the trophogenic zone.
- a. NH_4-N concentrations are usually low in aerobic waters because of utilization by plants in the photic zone. Additionally, bacterial nitrification occurs, in which NH_4^+ is oxidized through several intermediate compounds to NO_2^- and NO_3^- .
- b. When the hypolimnion of a eutrophic lake becomes anaerobic, bacterial nitrification of ammonia ceases. The oxidized microzone at the sediment-water interface is also lost, which reduces the adsorptive capacity of the sediments for NH_4-N . A marked increase in the release of NH_4^+ from the sediments then occurs. As a result, the NH_4-N concentrations of the hypolimnion increase (Fig. 12-4).
- c. Bacterial nitrification proceeds in two stages: (i) the oxidation of $NH_4^+ \rightarrow NO_2^-$, largely by *Nitrosomonas* but also by other bacteria, including methane oxidizers; and (ii) the oxidation $NO_2^- \rightarrow NO_3^-$, in which *Nitrobacter* is the dominant bacterial genus involved.
- d. Nitrite (NO_2^-) is readily oxidized and rarely accumulates except in the metalimnion, upper hypolimnion, or interstitial water of sediments of eutrophic lakes. Concentrations are usually very low ($< 100 \mu\text{g liter}^{-1}$) unless organic pollution is high.
7. Nitrate is assimilated and aminated into organic nitrogenous compounds within organisms. This organic nitrogen is bound and cycled in photosynthetic and microbial organisms. During the normal metabolism of these organisms, and at death, much of their nitrogen is liberated as ammonia. Additionally, organisms release a variety of organic nitrogenous compounds that are resistant to proteolytic deamination and ammonification by heterotrophic bacteria to varying degrees.
- a. Nitrate (NO_3^-) is the common form of inorganic nitrogen entering fresh waters from the drainage basin in surface waters, ground water, and precipitation. In certain oligotrophic waters in basaltic rock formations, nitrate loading from atmospheric sources, especially if contaminated by human-produced combustion emission products, can dominate nitrogen loading.
- b. Bacterial denitrification is the biochemical reduction of oxidized nitrogen anions (NO_3^- and NO_2^-) concomitant with the oxidation of organic matter: $NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$. Nitrous oxide (N_2O) is rapidly reduced to N_2 and has rarely been found in lakes in appreciable quantities. Denitrification is accomplished by many genera of facultative anaerobic bacteria, which utilize nitrate as an exogenous terminal hydrogen acceptor in the oxidation of organic substrates. Denitrification occurs in anaerobic environments, such as in the hypolimnion of eutrophic lakes (Fig. 12-4) or in anoxic sediments, where oxidizable substrates are relatively abundant.
8. Dissolved organic nitrogen (DON) often constitutes over 50% of the total soluble nitrogen in fresh waters.
- a. Over half of the DON occurs as amino nitrogen compounds, mostly as polypeptides and complex nitrogen compounds.
- b. The ratios of DON to particulate organic nitrogen (PON) of streams and lakes are usually from 5:1 to 10:1. As lakes become more eutrophic, DON:PON ratios decrease.
9. The distribution of nitrogen in a lake can change rapidly. Examples of the depth-time distributions of the different forms of nitrogen demonstrate that as lakes become more productive from nutrient loading, concentrations of NO_3-N and NH_4-N in the trophogenic zone can be severely reduced and depleted by photosynthetic assimilation. Cyanobacteria with the capability of nitrogen fixation may then come to dominate. In anaerobic hypolimnion, NO_3-N is rapidly denitrified to N_2 , which is either fixed or lost to the atmosphere. NH_4-N concentrations accumulate from decomposition of organic matter and release of NH_4-N from sediments under anaerobic conditions.
10. Organic carbon-to-nitrogen ratios (C:N) indicate an approximate state of resistance of complex mixtures of organic compounds to decomposition, because proteolytic metabolism by fungi and bacteria removes proportionally more nitrogen than carbon. Higher C:N ratios commonly occur in residual organic compounds, which are more resistant to decomposition.
- a. Organic materials from allochthonous and wetland sources commonly have C:N ratios from 45:1 to 50:1 and contain many humic compounds of low nitrogen content.
- b. Autochthonous organic matter produced by the decomposition of plankton tends to have higher

protein content and C:N ratios of about 12:1.

c. Alterations in the protein-carbohydrate-lipid ratios alter the particulate C:N ratio as a result of phosphorus or nitrogen limitation. A C:N ratio of >14.6 often indicates a severe nitrogen deficiency in phytoplankton, between 8.3 and 14.6, a moderate deficiency, and <8.3 , no nitrogen deficiency.

11. Much of the total nitrogen occurs in the sediments in forms that are relatively unavailable for biotic utilization. Of the readily available nitrogen, a majority occurs in soluble form in the water and in the interstitial water of surficial sediments (and in littoral vegetation in shallow, productive lakes). Turnover rates of $\text{NH}_4\text{-N}$ are rapid in water but slower in the sediments. In contrast, $\text{NO}_3\text{-N}$ turnover is slower in the water than in sediments, where, under anoxic conditions in eutrophic lakes, $\text{NO}_3\text{-N}$ is rapidly denitrified to N_2 .
12. Increased loading of inorganic nitrogen to rivers and lakes frequently results from agricultural activities, sewage, and anthropogenic atmospheric pollution. In unproductive oligotrophic lakes, phosphorus availability is often the principal limiting nutrient for plant growth. As phosphorus loading to fresh waters increases and they become more productive, nitrogen becomes more important as a growth-limiting nutrient.
13. In running waters, nitrogen is used repeatedly as it passes downstream. The rate of utilization and release depends upon physical and biological retentiveness, largely by the microbiota attached to the streambed. The average distance a nutrient atom travels downstream during one cycle through the water, biotic, and substrata compartments is referred to as the *spiralling length* (Figs. 12-13 and 12-14).
14. Nutrient limitations for biotic productivity are uncommon in small rivers and streams, where nutrients are efficiently retained and recycled. As rivers become larger, nutrient retention is less and nutrient limitations can become more prevalent.
15. The processes of nitrogen cycling in the water of streams and rivers are similar to those of lakes and are influenced to a large extent by bacterial, fungal, and other microbial metabolism. Attached bacteria, fungi, and algae are the primary organisms controlling the seasonal spatial and temporal variations within the water. The processes of nitrification and denitrification often function simultaneously and reciprocally in running water sediments, where many microzones of steep redox gradients occur in the hyporheic zone of the streambed.