

Denitrification as a Nitrogen Sink in Lake Mendota, Wis.

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■ The significance of denitrification as a sink in the nitrogen budget has been determined for Lake Mendota, Wis. About 28,100 kg. of nitrogen were lost from the lake hypolimnion during the summer of 1966. However, this relatively large amount represented only about 11% of the estimated total annual nitrogen input. Denitrification rates ranged from 8 to 26 $\mu\text{g. of N per liter per day}$, while rates of nitrate reduction (to ammonia and organic nitrogen) were found by ¹⁵N tracer techniques to range from 1.4 to 13.4 $\mu\text{g. of N per liter per day}$ in the hypolimnion of the lake. Nitrate depletion is more than an order of magnitude slower than oxygen depletion in the hypolimnion of Lake Mendota, and denitrification is probably not significant with respect to respiration and catabolic processes in the lake hypolimnion. There is some evidence to indicate that dissolved nitrogen gas concentrations increase above those expected on the basis of solubility as the result of denitrification. Evaluation of various nitrogen sinks for Lake Mendota has revealed that only about one third of the estimated annual nitrogen input can be accounted for by currently evaluated sinks. Sediment deposition probably accounts for most of the remaining two thirds.

Denitrification probably occurs in stratified lakes which lose their hypolimnetic oxygen, but the significance of this has not been properly assessed. Hutchinson (1957) has reviewed many examples of lakes in which the late summer nitrate distribution is dichotomic as the result of depletion by nitrate assimilation in the surface waters and by denitrification and nitrate reduction in the anoxic bottom waters. Only recently (Goering and Dugdale, 1966a, 1966b) have estimates been made of in situ denitrification rates in natural waters. However, these rates do not necessarily define the quantitative significance of denitrification as a sink in the nitrogen budget of a water body. A recent investigation of nitrogen cycle dynamics in natural waters (Brezonik, 1967) permits an estimate of this sort for Lake Mendota, Wis.

Lake Mendota has been one of the most frequently studied lakes in the world, and descriptions of its characteristics are numerous in the limnological literature. A few facts germane to the following study should be mentioned. The lake covers 3938 hectares and has a maximum depth of about 24 meters. The lake is moderately eutrophic and loses its dissolved oxygen below about 10 meters during summer stratification. A heavy influx of nutrient compounds results from the lake's

location in a basin of fertile crop and pasture land and partially from the urban influence of the city of Madison, which now nearly surrounds the lake. Lee *et al.* (1966) have recently estimated nitrogen and phosphorus sources for the lake which show an annual input of nitrogen equivalent to 0.50 mg. of N per liter of lake water and an annual phosphorus input equivalent to 0.047 mg. of P per liter of the lake. This raises questions concerning the fate of this large amount of nutrient material in the lake. Obviously, very little of it can be accounted for by increased concentration in the lake itself. This paper represents an evaluation of denitrification as a sink for nitrogen in the lake and discusses the possible importance of some other nitrogen sinks.

Procedures

The ¹⁵N incubation method to determine nitrogen cycle reaction rates has been described in detail by Brezonik (1967) and is similar to the procedures of Neess, Dugdale, *et al.* (1962) and Dugdale and Dugdale (1965). In brief, the following procedure was used to determine rates of nitrate reduction to ammonia and organic nitrogen in the anoxic hypolimnion of Lake Mendota. Samples were taken at various depths with a Van Dorn sampler and added to 1-liter polyethylene bottles. Special care was taken to avoid dissolved oxygen additions during transfer from the sampler to the incubation bottle. After addition of 0.10 mg. of ¹⁵NO₃⁻-N per liter (95 atom % ¹⁵N), the samples were sealed with a rubber stopper, again avoiding air entrainment, and were incubated in situ for several days. Following incubation, activity was stopped with 1 ml. of saturated mercuric chloride, and a total Kjeldahl analysis was made on a 500-ml. sample according to standard methods (Am. Public Health Assoc., 1965). The ammonia recovered by Kjeldahl procedure was concentrated, converted to molecular nitrogen by reaction with alkaline hypobromite in a Toepler pump apparatus, and subjected to mass spectrometric isotope ratio analysis for ¹⁵N enrichment according to procedures described by Brezonik (1967). A Consolidated-Neir Model 21-201 isotope ratio mass spectrometer was used for these measurements.

Nitrate, nitrite, and ammonia determinations were made on samples preserved with 1 ml. of saturated mercuric chloride per liter of sample using the Technicon AutoAnalyzer. Ammonia was determined by the phenol-hypochlorite procedure, nitrite by the sulfanilic acid-2-naphthylamine diazotization procedure, and nitrate by zinc reduction to nitrite and subsequent diazotization. These were standard AutoAnalyzer methodologies, modified as necessary to obtain optimum results with Lake Mendota water. Dissolved oxygen was measured by the Winkler-azide procedure (Am. Public Health Assoc., 1965). Dissolved gas concentrations were determined

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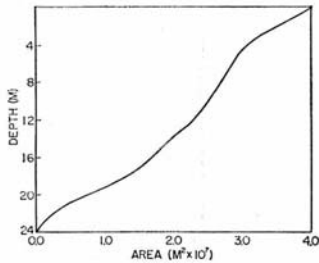


Figure 1. Lake Mendota surface area vs. depth

by a gas chromatographic procedure (Swinnerton, Linnembom, *et al.*, 1962; Brezonik, 1965) using Fisher Model 25 gas partitioner.

Results and Discussion

Calculation of the total denitrification in Lake Mendota requires volume estimates for the water in each level of the lake. This was computed from a hydrographic map of the lake by weighing the area contained within each contour on a Sauter single-pan balance after cutting away the excess paper. Water volumes contained between successive contours were obtained according to the method of Hutchinson (1957), using the formula

$$V_{n-m} = 1/3 (A_m + A_n + \sqrt{A_m A_n}) (n - m)$$

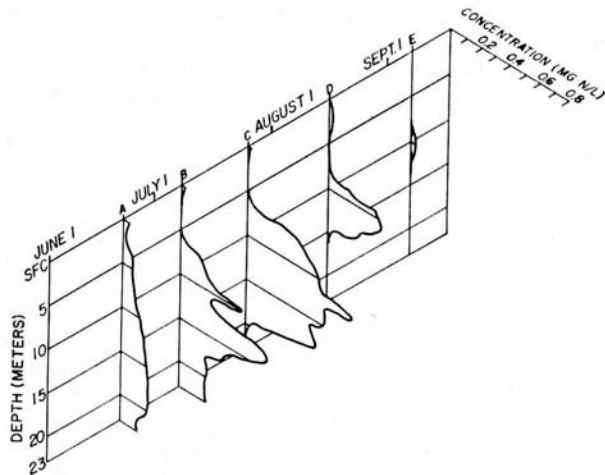


Figure 2. Nitrate distribution in Lake Mendota during the summer of 1966

Sampling dates as follows: A. June 22; B. July 8; C. July 26; D. August 17; E. September 8. Vertical profile on September 24 showed complete nitrate depletion throughout the water column

Areas enclosed by the various contours are shown *vs.* depth in Figure 1; volumes of the 1-meter strata *vs.* depth would give a similar curve. Summation of all the volume elements gives a total lake volume of 4.03×10^8 cu. meters. Figure 1 shows that a relatively small fraction of the total lake volume occurs in the hypolimnion. In 1966, the hypolimnion extended to a maximum of 10 meters from the surface. The volume of water contained below 10 meters is only 1.95×10^8 cu. meters, or less than 40% of the total volume. As shall be shown later, an even smaller volume of water was involved in denitrification.

Complete nitrogen profiles were taken at meter intervals from the deepest part of the lake at about 3-week intervals during the summer of 1966. The nitrate data (Figure 2) show changes in concentration with both depth and time. Apparently, the hypolimnetic nitrate content first increased, especially at mid-depths, presumably as the result of nitrification. Nitrate declined in the epilimnion because of algal assimilation early in the summer, and it later declined gradually to zero in the hypolimnion as the result of denitrification and nitrate reduction. Similar curves for nitrite concentrations (Figure 3) corroborate well with the nitrate changes. Dissolved oxygen was still present in the upper hypolimnion in early July, and the nitrite maximum at 14 meters reflects its role as an intermediate in nitrification. The nitrite maxima at 18 meters on July 26 and at 14 meters on August 17 indicate loci of denitrification and nitrate reduction after dissolved oxygen had disappeared at those levels.

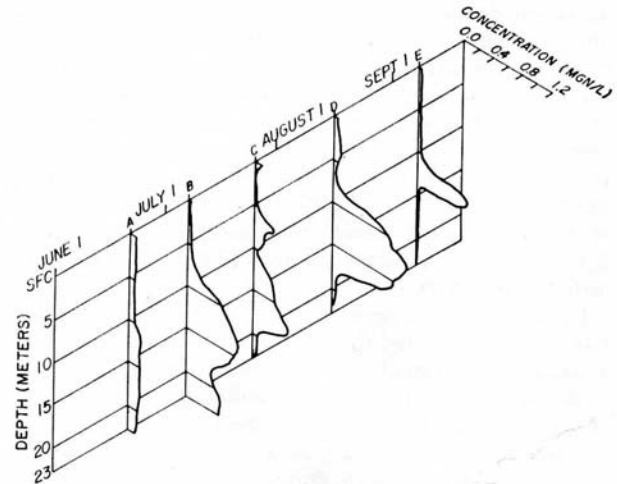


Figure 3. Nitrite distribution in Lake Mendota during summer of 1966

Sampling dates are same as listed for Figure 2. Vertical profile on September 24 showed complete nitrite depletion throughout the water column

The extent and duration of anoxic conditions in the hypolimnion obviously will affect the extent of denitrification. Figure 4 has been drawn from a large number of dissolved oxygen profiles in the lake during the summer of 1966 and shows the extent and duration of anoxic conditions in the deepest part of the lake. Also shown in Figure 4 is the approximate date of nitrate disappearance at various depths in the hypolimnion as determined from nitrate profiles measured during this period. These data indicate that anoxia prevailed at and below 14 meters long enough for denitrification and anaerobic nitrate reduction to completely deplete nitrate. Some denitrification probably occurred in the hypolimnion above 14 meters long enough for denitrification and anaerobic nitrate reduction to completely deplete nitrate. Some denitrification probably occurred in the hypolimnion above 14 meters, up to about 11 meters, but anoxia was not maintained long enough for it to be completed.

The maximum nitrate concentrations found at the various depths during summer stratification are assumed to be the nitrate concentrations when nitrification ceased and denitrification began. These values are shown in Table I with the total nitrate content of each stratum. The water from 14 meters to the lake bottom thus had a total nitrate content of 4.43×10^7 grams of NO_3^- -N. All this nitrate disappeared during stratification. Assuming no replacement of hypolimnetic water by physical transport, the only nitrate sinks are denitrification and reduction to ammonia and organic nitrogen.

The amount of nitrate lost by denitrification can be determined if the significance of nitrate reduction can be estimated. Rates of this reaction were measured at various depths in the hypolimnion periodically during the summer of 1966 using ^{15}N tracer techniques (Table II). The range of the reduction rates was 0.06 to 0.56 $\mu\text{g. of N per liter per hour}$, but most of the rates were between 0.20 and 0.40 $\mu\text{g. per liter per hour}$. The average of all measurements is 0.307 $\mu\text{g. per liter per hour}$. Assuming this average rate occurred throughout the hypolimnion during the period of denitrification, multiplication of the rate by the time required for nitrate depletion at

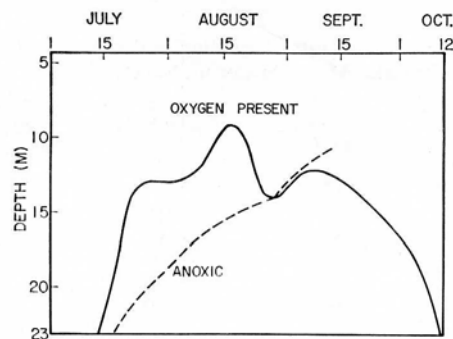


Figure 4. Extent of anoxic conditions in Lake Mendota during summer of 1966

— oxygen depletion - - - - - date of nitrate depletion

each depth will give the total nitrate lost by reduction to ammonia and organic nitrogen. The time required to deplete nitrate at each level was obtained from Figure 4 as the difference between the oxygen and nitrate depletion curves. These time intervals, with the nitrate lost by reduction to ammonia and organic nitrogen, are also given in Table I. The nitrate lost by denitrification (in milligrams of N per liter) was obtained by subtracting the nitrate lost by reduction from the maximum nitrate concentration at each depth (the second last column of Table I). Finally, multiplication of this concentration by the volume of each stratum gives the total denitrified nitrogen in each level of the lake. Summation of these totals in the final column of Table I shows that 2.81×10^7 grams of nitrate-nitrogen were lost from Lake Mendota by denitrification during summer stratification in 1966.

The above figure probably represents a slight underestimate of denitrification in the lake. Some denitrification undoubtedly occurred at 13 meters and, probably, 12 and 11 meters as well. But anoxic conditions weren't maintained long enough for complete nitrate depletion by anaerobic processes. Samples taken on August 26, 1966, had viable zooplankton at 13 meters; a small amount of dissolved oxygen (about 1 mg. per liter) further indicated some epilimnetic mixing had occurred down to this depth. The nitrate content at 13 meters was near 0.10 mg. of N per liter, indicating considerable depletion had

Table I. Denitrification in Lake Mendota

Depth, M.	Volume, Cu M. $\times 10^7$	Maximum Nitrate, Mg. N/L.	Total Nitrates, G. $\times 10^7$	Time to Deplete Nitrate, Days	Nitrate Lost by Reduction, Mg. N/L.	Nitrate Lost by Denitrification, Mg. N/L.	Total N Denitrified, G. $\times 10^7$
14	1.92	0.60	1.15	38	0.280	0.32	0.614
15	1.78	0.53	0.945	28	0.206	0.32	0.570
16	1.63	0.43	0.700	24	0.177	0.25	0.408
17	1.48	0.44	0.652	20	0.147	0.29	0.429
18	1.27	0.49	0.622	17	0.125	0.37	0.470
19	1.02	0.26	0.265	14	0.103	0.16	0.163
20	0.70	0.18	0.126	9	0.066	0.11	0.077
21	0.42	0.16	0.0672	8	0.059	0.10	0.042-
22	0.21	0.17	0.0357	5	0.037	0.13	0.027
23	0.08	0.17	0.0136	5	0.037	0.13	0.010
Total	10.51		4.43				2.81

Table II. Rates of Nitrate Reduction under Anoxic Conditions in Lake Mendota during Summer, 1966

Date	Depth, Meters	Total Kjeldahl N, Mg./L.	Nitrate Reduction, $\mu\text{g./L./Hour}$
7-19	18	1.26	0.39
	20	1.38	0.48
	23	1.51	0.27
7-25	14	0.75	0.46
	16	0.85	0.30
	20	1.40	0.06
	21.5	1.45	0.19
	23	1.60	0.13
8-1	12	0.69	0.35
	14	0.95	0.37
	16	1.00	0.37
	20	1.43	0.26
	21.5	1.57	0.15
	23	1.73	0.37
8-9	12	0.85	0.20
	14	1.12	0.41
	16	1.27	0.56
	18	1.46	0.21
	20	1.50	0.31

occurred. However, it is not possible to evaluate the amount of depletion caused by mixing with nutrient poor epilimnetic water. The amount of denitrification at 13 meters (and also 11 and 12 meters) cannot, therefore, be determined, but it is estimated that the total denitrification at these levels would not greatly change the estimate for denitrification in the entire lake.

Rates of denitrification in different levels of the lake can be estimated by dividing the nitrate concentration lost via denitrification by the length of time needed to deplete nitrate at each level. These rates range from 26 $\mu\text{g. of N per liter per day}$ at 22 and 23 meters to 8.4 $\mu\text{g. of N per liter per day}$ at 14 meters. Higher rates in the bottom waters seem reasonable, considering the influence of sediments on denitrification. Goering and Dugdale (1966b) found that 500 $\mu\text{g. of } ^{15}\text{NO}_3^- \text{-N per liter}$ was depleted in 6 days from an anoxic sediment water mixture from Smith Lake, Alaska. This suggests a denitrification rate near 80 $\mu\text{g. of N per liter per day}$. A much lower rate, 15 of N per liter per day, was observed in anoxic water from 1 meter below the ice in Smith Lake. Goering and Dugdale (1966a) found rates from 12 to 18 $\mu\text{g. of N per liter per day}$ in the anoxic hypolimnion of an island bay in the equatorial Pacific. The ecological significance of the latter rates is not entirely clear since nitrate and nitrite were absent, or nearly so, in the depths where denitrification occurred. The physical and chemical characteristics of the bay suggest limited vertical exchange and a stagnant hypolimnion. Denitrification would thus seem to be limited to the narrow zone at the thermocline between the oxygen and

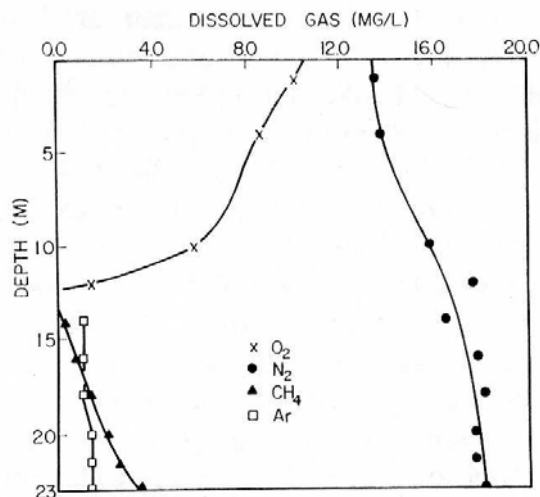


Figure 5. Dissolved gas concentration in Lake Mendota on September 1, 1966

sulfide bearing waters, where renewal of nitrate in the anoxic water can occur by diffusion and mass transport. The estimated denitrification rates for Lake Mendota compare surprisingly closely with those measured in the ocean and in Smith Lake, especially when the diverse natures of the waters are considered.

Compared with oxygen consumption, denitrification is a slow process in the lake. Hypolimnetic oxygen depletion occurs at least an order of magnitude faster than nitrate depletion by denitrification in Lake Mendota. However, other factors besides bacterial respiration exert an oxygen demand, including reduced inorganic ions as sulfide and ferrous iron in the sediments (Gardner and Lee, 1965). Nitrification exerts a considerable oxygen demand, nearly 4.5 mg. of O_2 per mg. of N nitrified. Nitrification caused 0.3 to 0.4 mg. of N per liter increases in the nitrate content of the 13- to 15-meter stratum during late June and early July; this would exert an oxygen demand of 1.4 to 1.8 mg. per liter in that stratum. A wider variety of microorganisms can use molecular oxygen as a terminal electron acceptor than can use nitrate. Thus, even considering the action of other oxygen sinks, bacterial respiration probably depletes the hypolimnetic oxygen considerably faster than the nitrate. Denitrification is relatively unimportant from the standpoint of respiration and catabolic processes in the hypolimnion, but it may be important as a nutrient sink.

Goering and Dugdale (1966b) have shown that denitrification in lakes produces molecular nitrogen rather than nitrous or nitric oxides. Denitrification will thus tend to increase the dissolved molecular nitrogen content of the hypolimnion above that expected only on the basis of solubility. Dissolved gas concentrations were measured by a gas chromatographic procedure in a midlake vertical profile on September 1, 1966, when denitrification was nearly complete. The results (Figure 5) indicate an inverse clinograde distribution of molecular nitrogen, which resulted predominantly from the lower temperature of the hypolimnetic water when it was in equilibrium with the atmosphere. The hypolimnion temperature was about 11 ° C. when thermal stratification began and isolated the bottom water from the atmosphere. Table III presents the measured nitrogen gas concentrations and the theoretical

concentrations in the lake based on solubility. The theoretical content likewise results in an inverse clinograde distribution because of increased gas solubility at lower temperatures. Deviations of the measured concentrations from theoretical concentrations are shown in Table III, and apparently, the upper water tended toward slight undersaturation, while the hypolimnion tended toward supersaturation with nitrogen gas. The average N_2 in the hypolimnion (14 meters and below) was 0.25 mg. of N_2 per liter more than predicted by solubility based on the Fox (1909) solubility data and about 0.2 mg. of N_2 per liter more based on the Hamberg (1886) values preferred by Benson and Parker (1961). These average increases are of the general size expected from the denitrification calculated earlier. However, several error factors must be considered. The solubility of nitrogen gas in water can still be debated, although the values must be close to those mentioned above. The determination of dissolved gas concentrations by gas chromatography is relatively imprecise with the apparatus used, and there exists the possibility that the hypolimnetic water did not reach equilibrium with the atmosphere at 11 ° C. Considering these aspects, dissolved nitrogen gas measurements seem to be insufficient to enable a quantitative estimate of denitrification in a lake, although they will permit a qualitative detection of denitrification.

Finally, an approximate budget of the nitrogen sinks for Lake Mendota can be obtained from this and previous studies. A recent estimate (Lee *et al.*, 1966) places the total nitrogen input to Lake Mendota at 252,000 kg. annually. The estimated contributions from individual sources are shown in Table IV. The denitrification estimate reported above accounts for only 11 % of the total annual input. Even considering possible denitrification at 11, 12, and 13 meters, which may occur especially in years when those depths remain anoxic for longer periods, the estimate would not be more than 15% of the total nitrogen input.

Other sinks for nitrogen in the lake include loss through the outlet, weed and algal harvesting, fish removal, evaporation, insect emergence, and sediment uptake. An earlier estimate of the total nitrogen leaving Lake Mendota through its outlet, the Yahara River, was 4200 kg. (Rohlich and Lea, 1949). The concentrations of nitrogen compounds in the lake have not markedly increased since 1949; therefore, losses through the outlet have probably remained relatively constant. Loss through the outlet would thus account for about 16% of the estimated nitrogen input.

Herman, Wisby, *et al.* (1959) estimated the harvest of yellow perch during the ice fishing season to be 44.7 kg. per ha. for Lake Mendota. Schraufnagel, Corey, *et al.* (1967) have estimated that

Table III. Dissolved Nitrogen Gas in Lake Mendota, September 1, 1966

Depth, Meters	Temp., ° C.	N_2 , Mg./L.	$S_{N_2}^{a,b}$, Mg./L.	$N_2^{b,c}$, Mg./L.	$S_{N_2}^{a,d}$, Mg./L.	$N_2^{c,d}$, Mg./L.
1	24.4	13.5	13.8	- 0.3	13.8	- 0.3
4	22.4	13.7	14.3	- 0.6	14.3	- 0.6
10	20.5	15.9	14.8	+ 1.1	14.8	+ 1.1
12	14.6	17.7	16.4	+ 1.3	16.4	+ 1.3
14	12.9	16.5	16.8	- 0.3	16.9	- 0.4
16	12.1	17.9	17.5	+ 0.4	17.6	+ 0.3
18	11.8	18.1	17.5	+ 0.6	17.6	+ 0.5
20	11.4	17.7	17.5	+ 0.2	17.6	+ 0.1
21.5	11.3	17.7	17.5	0.2	17.6	+ 0.1
23	11.1	18.1	17.5	0.6	17.6	+ 0.5

^a Solubility of molecular nitrogen at the given temperature; all water below 14 meters assumed to be at 11° C. when stratification began.

^b Solubility values from Fox (1909).

^c Measured molecular nitrogen concentration minus solubility at the given temperature.

^d Solubility values from Hamberg (1886).

Table IV. Estimated Sources and Sinks for Nitrogen in Lake Mendota

Source	Nitrogen ^a Contribution, Kg.	Contribution, %	Sink	Nitrogen Lost, Kg.	Lost, %
Municipal and industrial wastewater	21,200	8	Outlet loss	41,300	16.4
Urban runoff	13,700	5	Denitrification	28,000	11.1
Rural runoff	23,500	9	Fish catch	11,300	4.5
Precipitation on lake surface	43,900	17	Weed removal	3,250	1.3
Ground water	113,000	45	Ground water recharge	?	
Nitrogen fixation	36,100	14	Sediments and other losses ^b	168,000	66.7
Marsh drainage	?				
Approximate total	252,000	100	Approximate total	252,000	100

^a From Lee *et al.*, 1966.

^b By difference between total sinks (assumed to equal total sources) and sum of all other calculated sinks. Other sinks are probably small, and sediment deposition accounts for most of the nitrogen in this category.

the catch of other species and the summer catch of yellow perch would likely boost this figure to 89.4 kg. per ha. annually. Assuming a nitrogen content of fish flesh of 2.5 % (wet weight), as reported by Mackenthun (1959), about 11,300 kg. of nitrogen would be removed by fishing, or roughly 4.5 of the total income (Schraufnagel, Corey *et al.*, 1967). Removal of Lake Mendota aquatic plants and weeds by machine harvesting is practiced by the city of Madison, but thus far only about 454 kg. of plants are removed per year. An average nitrogen content of 3.6 grams per kg. of rooted aquatics (Schraufnagel, Corey, *et al.*, 1967), this sink accounts for only 1.3 % of the total nitrogen input.

The significance of insect removal is thought to be similarly small, but quantitative data are lacking. Probably a large fraction of emerging insects remains in the Lake Mendota watershed and much of their nitrogen eventually recycles into the lake. Net removal of nitrogen by this sink is presumably insignificant.

Some nitrogen losses may also occur by ground water recharge through the lake sediments in the eastern part of Lake Mendota. Pumping of ground water from wells located east of the lake by the city of Madison has lowered the water table in this area, and subsurface flows from the lake may partially recharge the aquifer. However, the magnitude of flow from the lake is uncertain and the concentration of nitrogen compounds in the outflowing water unknown, so the significance of this sink cannot presently be assessed.

Nitrogen losses to the atmosphere represent a potential nitrogen sink, the significance of which is neither appreciated nor understood. Two mechanisms for atmospheric loss are possible. Diffusion of ammonia and possibly other volatile nitrogen compounds from the lake surface could be significant under appropriate conditions. In natural waters near neutral pH, nearly all the ammonia is present as NH_4^+ ; pK_B for ammonia is 9.24. However, in eutrophic lakes algal blooms often raise the pH to 9 or above, and a significant fraction of the ammonia is thus present as volatile NH_3 . The pH of the Lake Mendota surface water is generally 8.9 to 9.0 during the summer. However, ammonia is depleted to trace concentrations (0.01 to 0.05 mg. of N per liter) by algal assimilation in early spring and remains low in concentration until late fall. During periods when the surface water ammonia content is high (0.3 to 0.4 mg. of N per liter) the pH is near 8.0, and during much of the period of high ammonia values, the lake is ice covered. Considering these factors, the authors feel that ammonia diffusion from the lake surface is probably a rather minor nitrogen sink.

Aerosol formation from surface foam concentrates is a second possible nitrogen sink to the atmosphere. Wilson (1959) concluded that the origin of organic nitrogen and ammonia in New Zealand snow is aerosol formation from oceanic surface foam. Nitrogen-potassium ratios in the snow and oceanic foam concentrates were similar, but the ratio in the bulk oceanic water was different. Foam lines appear commonly on the surface of Lake Mendota during periods of high winds, and the foam probably contains high organic nitrogen and phosphorus concentrations. Overall, aerosol formation from foam is probably a small sink for nitrogen; however, present information is insufficient to evaluate its true significance. Data is lacking regarding both the rates of aerosol formation from lake foam (and the bulk water) and the concentrations of nitrogen in aerosol particles.

Altogether, the above nitrogen sinks account for only about 32 % of the total annual nitrogen input to Lake Mendota. Approximately two thirds of the nitrogen remains to be accounted. The total nitrogen compounds dissolved or suspended in the lake water have remained constant or increased only slightly in recent years. Certainly any tendency for higher nitrogen concentrations would account for an insignificant fraction of the remaining nitrogen input, which represents over 300 μg . of N per liter of lake water. While certain sinks cannot be properly assessed, their significance is likely to be small. The most likely conclusion is that nearly two thirds of the annual nitrogen input, or about 163,000 kg., is deposited annually in the sediments of the lake.

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