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Several investigations have been undertaken in the vicinity of Kingsport, Tenn., on the Holston River to determine the existing water quality conditions and to develop a mathematical model to estimate conditions that may occur with reduced waste loads. This paper presents some of the results of these studies concerning the nitrogenous components: the behavior of various forms of nitrogen in the receiving river and downstream reservoir, some factors that affect this behavior, and some effects that nitrogen had on other environmental factors. The results are discussed in light of information reported in the literature. The paper first addresses nitrification in the free-flowing river environment and then the impact of nitrogen on the Cherokee Reservoir.

The studies took place on the South Fork Holston and Holston Rivers (Figure 1). Kingsport, which is located primarily on the South Fork Holston River, is the center of a major industrial complex that includes a large chemical industry, an ammunition plant, a paper mill, and a large number of smaller industries. Although Kingsport has a population of only 30 000, carbonaceous wastes equivalent to over 900 000 people are discharged to the river. Nitrogenous waste discharge characteristics of the major discharges are presented in Table I.

The river reach to be discussed extends from South Fork Holston River Mile (SFHRM) 5.6 to Holston River Mile (HRM) 53 (Figure 1). The station at SFHRM 5.6 is upstream from all sources of pollution from Kingsport. The next station downstream, SFHRM 1.2, is downstream from the main sources of pollution in the immediate Kingsport area, which includes all the major industrial waste discharges except those from Area B of the Holston Army Ammunition Plant. The North Fork Holston River was also sampled at NFHRM 0.2 because of its effect on water quality in the Holston River. A mathematical model for dissolved oxygen (DO) has been developed for the stream reach from SFHRM 1.2 to HRM 118.9.

There are two distinct reaches within this 151.3-km stretch: 64.4 km of free-flowing stream below Kingsport and 86.9 km of reservoir. Factors that have been analyzed and modeled mathematically in the first 64.4-km river reach below Kingsport include carbonaceous biological oxygen demand (BOD), nitrogenous oxygen demand, benthic oxygen demand, aquatic plant photosynthesis and respiration, and reaeration. Results show that carbonaceous BOD is important only for 16.1 km below Kingsport, that nitrification is an appreciable demand in the lower 49.9 km, and that aquatic weeds exert the greatest influence on the DO concentrations. Benthic oxygen demand was found to be the least important. The mathematical model indicates that aquatic plants exert such a tremendous demand that some solution other than secondary waste treatment and low flow augmentation from upstream reservoirs will be needed to alleviate the DO problem in the first 64.4-km reach.

Cherokee Reservoir is a eutrophic multipurpose impoundment. Field surveys have shown that shortly after spring temperature-density stratification occurs, the DO in the reservoir hypolimnion is quickly depleted. The anaerobic hypolimnion often extends to within 6.1 m of the surface of the 45.7-m-deep reservoir, resulting in considerable loss of desirable aquatic habitat.

FACTORS AFFECTING NITRIFICATION

Nitrogenous BOD has become recognized as a major factor in the oxygen balance of some streams. Courchaine,[2] Wezernak and Gan-

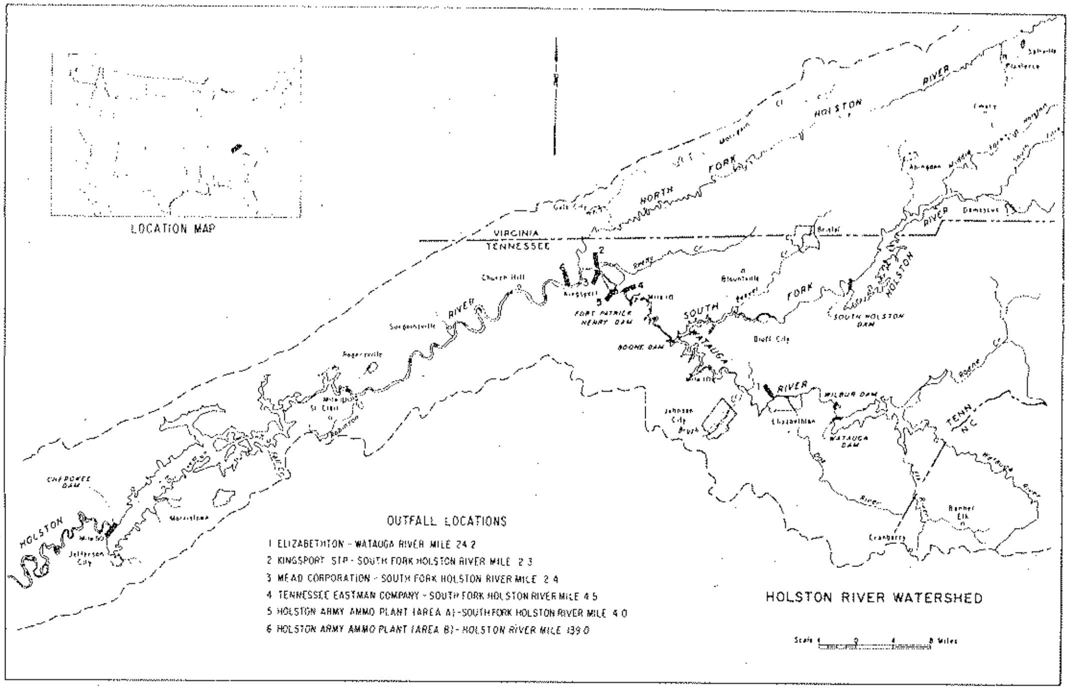

FIGURE 1. The study area.

non,[3] and Torpey[4] have reported three cases in which the nitrogenous BOD has been reported to be more significant than the carbonaceous BOD. The importance of nitrification in streams has resulted in a considerable amount of research.[5-8] In an investigation on the Thames River, Torpey[4] determined that nitrification was the reason for very little DO improvement following a considerable reduction of the carbonaceous waste being discharged to the river.

Factors affecting nitrification in rivers. For the purpose of this paper, nitrification is defined as the oxidation of ammonia and nitrite nitrogen to nitrate nitrogen. In the aquatic environment, this oxidation is usually accomplished by special autotrophic bacteria called nitrifiers. Of the few bacteria capable of this oxidation, *Nitrosomonas* is the most important in the conversion of ammonia to nitrite and *Nitrobacter* is the most important in the conversion of nitrite to nitrate. The biochemical reactions are

$$NH_4^+ + (3/2)O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + 2H^+ + H_2O \quad (1)$$

$$NO_2^- + (1/2)O_2 \xrightarrow{\text{Nitrobacter}} NO_3^-. \quad (2)$$

Stoichiometrically, 4.57 mg/l of DO are required in the oxidation of 1 mg/l of NH_4^+ to NO_3; however, Wezernak and Gannon,[5] using biological procedures, showed that 4.33 mg/l of DO are required for this oxidation. Apparently, some oxygen is produced during CO_2 fixation in protoplasm synthesis:

$$4CO_2 + HCO_3^- + NH_4^+ + H_2O \rightarrow C_5H_7NO_2 + 5O_2. \quad (3)$$

Others[6, 9-11] also have determined oxygen requirements for oxidizing ammonia and nitrite nitrogen. Their results differ, but not more than 10 percent.

The oxidation rate for the nitrogenous BOD, K_n, is generally determined by one of two ways: (1) long-term BOD analyses conducted in the same fashion as the determination of the bottle BOD deoxygenation coefficient for the carbonaceous BOD or (2) analysis of the rate of change in the downstream direction of the individual nitrogen compounds.

The first procedure has been reviewed and reported by Whipple *et al.*[12] and, therefore, will not be presented here. The determination of K_n by this procedure is questionable because of the experiences associated with the determination of the oxidation coefficient for carbonaceous BOD. De Marco *et al.*[13] has shown that the determination of K_n is de-

TABLE I. Waste discharges upper Holston River—Nitrogenous material.*

Waste Source	Total Kjeldahl-N kg/d	Ammonia N. kg/d	Nitrite + Nitrate-N kg/d	Total N kg/d	Total N PE‡
Tennessee Eastman Corp.	7 312	4 890	†	7 312	304 819
Mead Paper Co.	27	†	†	27	1 134
Kingsport Sewage Treatment Plant	23	50	20	82	3 402
Holston Army Ammunition Plant					
A. Area A	5	5	‡		
B. Area B	1 381	1 279	1 116	2 497	10 432

* From EPA.[1]
† Not significantly above raw water intake amounts.
‡ One population equivalent = 10.89 grams per capita per day.

pendent on turbulence and the initial nitrifying seed concentration. In addition, further evidence that K_n determined by the bottle procedure is not representative of stream conditions is the fact that, while nitrification is occurring in the stream from which the sample is collected, nitrification does not begin in the long-term BOD analysis for an appreciable time lag, usually 3 to 10 days. Also, the standard adjustment of pH to 7 for the BOD analysis introduces more error.

Nitrification rates, therefore, should be determined on the basis of actual stream data. Oxidation rates have been determined by a number of investigators. O'Connor[7] proposed a model including nitrification as a first-order reaction; Stratton and McCarty[6] proposed a model based on Monod's equation; Wezernak and Gannon[3] proposed a model based on the autocatalytic growth reaction; and Huang and Hopson[8] concluded on the basis of laboratory data that nitrification follows a zero-order reaction. Lopez-Bernal[14] evaluated the first-order, zero-order, and autocatalytic models using actual stream data and found the first- and zero-order models to be statistically equivalent to the autocatalytic model.

The determination of K_n is best accomplished by plotting on graph paper the masses (kilograms per day) of the individual nitrogen compounds versus the time of travel in the stream. The nitrogen compounds that reflect the rate of nitrification are total Kjeldahl, ammonia, nitrite, and nitrate nitrogen. To adequately analyze nitrification within the stream, the rate of change of each compound should be evaluated. The rate of change of the compounds is dependent on not only nitrification, but also other processes involved in the nitrogen cycle. Each compound, or combination of compounds, is affected by different biological processes, discussed in the following paragraphs.

Nitrification causes a decrease in ammonia concentration and an increase in nitrate concentration. However, ammonia concentrations in the stream may increase as a result of the oxidation of organic nitrogen or the reduction of nitrate nitrogen, or they may decrease as a result or (1) aquatic plant consumption, either macrophytic or microphytic, (2) equilibration, or (3) conversion to organic nitrogen for cell synthesis by heterotrophic bacteria. The addition of ammonia to the stream by oxidation of organic material is represented by:

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right) O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right) H_2O + cNH_3. \quad (4)$$

The use of ammonia by heterotrophic bacteria for cell synthesis is represented by the following relationship developed by Eckenfelder[15]:

$$\text{Organic matter} + O_2 + NH_3 \xrightarrow{\text{cells}} \text{new cells} + CO_2 + H_2O. \quad (5)$$

Stratton[16] reports that the rate of ammonia loss from the stream to the atmosphere is proportional to pH, temperature, surface turbulence, and air velocity above the water surface.

Factors other than nitrification that affect the change in nitrate concentration in a stream are denitrification, respiratory reduction, and assimilatory reduction. The process of denitrification is represented by

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-. \quad (6)$$

Biological denitrification is technically an anaerobic process, but in most cases, it is carried out by aerobic bacteria. Many aerobic bacteria contain nitrate reductases, the enzymes that mediate the reaction,

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2 + H_2O. \quad (7)$$

The ability to reduce nitrate to nitrite does not, however, permit normal growth under anaerobic conditions, since (1) a large amount of nitrate must be reduced to oxidize a small amount of substrate and (2) the reduction product, nitrite, is highly toxic. A few normally aerobic bacteria (principally *Pseudomonas* and *Bacillae* species) can use nitrate as a physiologically useful terminal electron acceptor by reducing it beyond the level of nitrite to molecular nitrogen. As stated by Mechalas *et al.*,[17] " . . . the nitrate ion fulfills the role normally occupied by oxygen in aerobic respiration—that of hydrogen ion acceptor in the electron transport system." The nitrogen gas formed by this reaction may be transferred from the water to the atmosphere if the nitrogen concentration in the water exceeds the saturation concentration; thus, this process can result in a loss in the total nitrogen concentration.

Denitrification resulting in the production of nitrogen gas has been observed by one researcher[18] in a case in which the DO was apparently high. It was hypothesized that the denitrification occurred in the mud deposits in which anaerobic conditions existed. Respiratory reduction, which reduces nitrate to ammonia, is also dependent on oxygen concentration. Bandurski[19] and Bonner and Varner[20] report that assimilatory reduction also involves reducing nitrate to ammonia, but the ammonia is assimilated into cellular, organic compounds. Both of these reduction processes can be represented by

$$HNO_3 + 8[H] \rightarrow NH_3 + 3H_2O. \quad (8)$$

According to Bandurski,[19] the mechanisms of respiratory and assimilatory reduction are different, but this difference does not imply that the respiratory mechanism is not available for assimilation nor that the assimilatory reductive mechanisms do not reduce nitrate as a source of oxygen under extreme environmental conditions. Nicholas[21] states that the suppression of nitrate assimilatory reduction by ammonia is common in many fungi and algae and is believed to occur in higher plants.

Very little work has been done on the absorption and assimilation of nitrate and ammonium by aquatic plants, but it is evident that this process is sensitive to many environmental factors and that the known types of behavior give some idea of the range that occurs. Comparison of the results of different studies is a problem because of the varying degree to which environmental conditions have been controlled or even recorded. Most of the research has been on nonaquatic plants. McKee[22] reports that some workers have found plants to grow better with nitrate than with ammonia, whereas others have reported just the opposite. He reports that one worker found better growth of sugar beets with ammonia than with nitrate at pH 7, but the situation was reversed at pH 5. Some workers have reported certain species to grow better with nitrate and ammonium together than with either alone. McKee[22] hypothesizes that, since no plant is known to require both ions separately, the use of both compounds together is probably an indirect benefit. He feels "their simultaneous use avoids changes in acidity due to preferential absorption of a single ion." Margolis and Steward[23] compared the use of nitrate with that of ammonia for fertilizing tomato plants. They stated that when nitrate is used, little more than enough nitrogen is stored for protein synthesis, whereas the use of ammonium salts leads to a high accumulation of soluble nitrogen in the leaves, much more than that needed for protein synthesis.

In general, nitrogen in almost any form probably can be used by plants. Very little information can be found in the literature, and no conclusions have been drawn for aquatic vascular plants such as potamogeton, which is common in the Holston River. A considerable amount of research[24-27] has been conducted on the preferred form of nitrogen by algae; however, the results of this research are probably not applicable to higher plants. This hypothesis is based on the fact that the preferred form of nitrogen is different for different species of algae and that higher plants have root systems that distinguish higher plants from the algal microorganisms.

Nitrification in the Holston River. Nitrification in the free-flowing portion of the Holston River was determined from data collected during a survey in 1969. Water samples were collected with time-of-travel in the river. Over a 24-hour period, seven masses of water were followed and sampled as they moved downstream. Some of the water quality conditions that were observed during this survey and that usually affect nitrification are presented in Figure 2. The average benthic oxygen demand and average standing crop of attached aquatic plants for the same survey are shown in Fig-

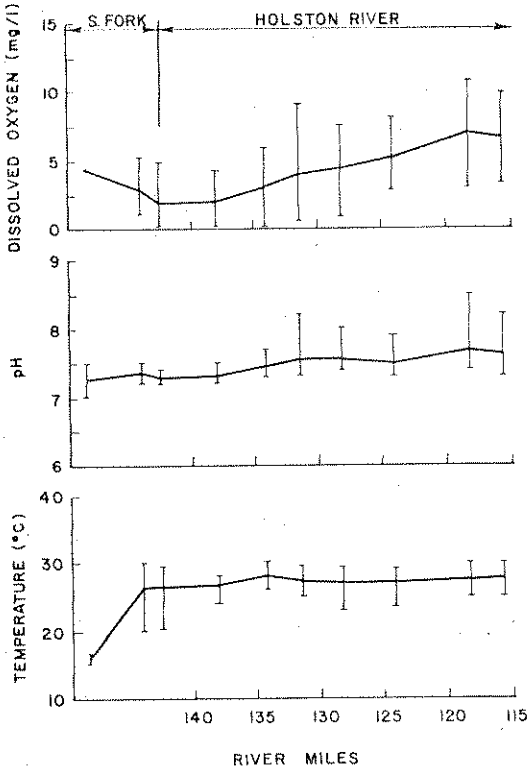

FIGURE 2. Observed DO, pH, and temperature conditions during the 1969 Holston River study.

ure 3. Average streamflow velocity during the survey was 0.23 m/s, and average depth was 1.3 m.

The oxidation rate for nitrogenous BOD was determined from the rates of change of ammonium and nitrate plus nitrite within the various stream reaches. The oxidation rates were determined on the basis of each of these compounds and then averaged because, as discussed above, the form in which nitrogen is consumed by the plants in the Holston River is not known. The rate of change was essentially the same for total Kjeldahl nitrogen and ammonia (Figure 4). Nitrate and nitrite formation could not be handled separately in this analysis because laboratory analyses in this case yielded only the summation of the two compounds. Because the oxidation of nitrite is usually rapid, it was assumed that the summation of the two compounds was essentially all nitrate.

In the Holston River, nitrification is considered significant only downstream from HRM 137.9 even though high concentrations of ammonia exist upstream from this point (Figure 2). The downstream nitrification is obvious because of the increase in nitrate plus nitrite nitrogen concentration, most of which is probably nitrate. Upstream from HRM 137.9, significant denitrification obviously occurred, as shown in Figure 4. Nitrification may have

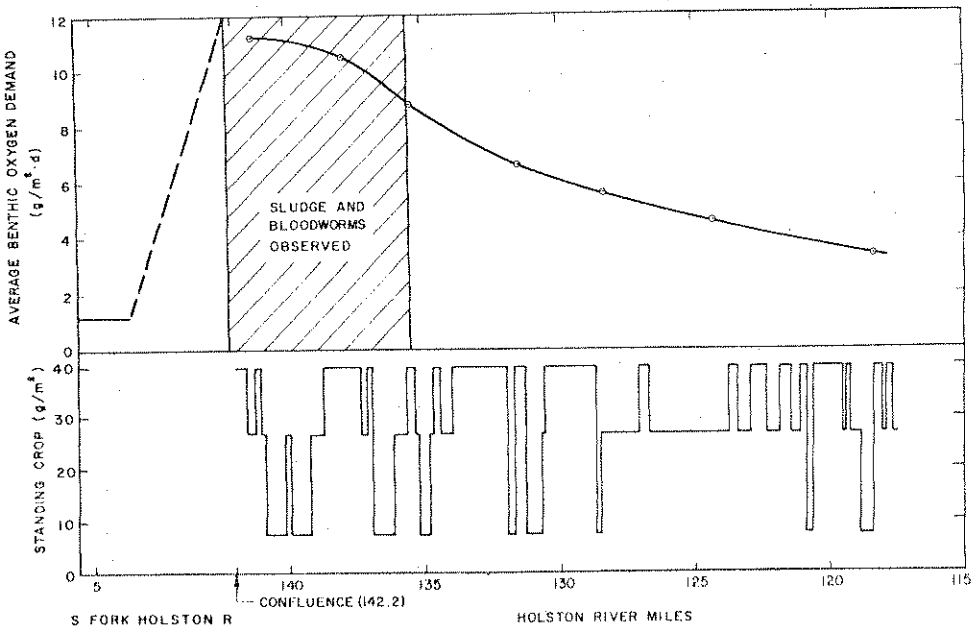

FIGURE 3. Observed benthic oxygen demand and standing crop of attached aquatic plants during the 1969 Holston River study (standing crop data provided by EPA[1]).

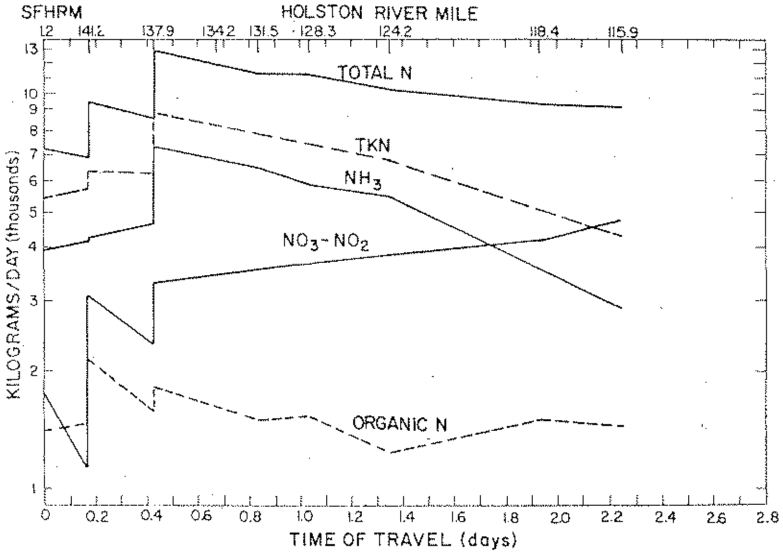

FIGURE 4. **Nitrogen conditions in the Holston River during the 1969 study. The values shown are mean values based on seven data points. All values are as nitrogen. Average streamflow in the South Fork Holston River was about 22 m³/s and in the Holston River about 41 m³/s.**

occurred upstream from HRM 137.9, but could not be measured by the methods used.

The coefficient of oxidation for nitrogenous BOD was determined for the entire stream reach from HRM 137.9 to 118.4. Nitrification was assumed to fit a first-order, linear differential equation. The coefficient, based only on ammonia reduction, was 0.30 per day; based only on nitrate-nitrite increase, the coefficient was 0.15 per day; and the average coefficient was

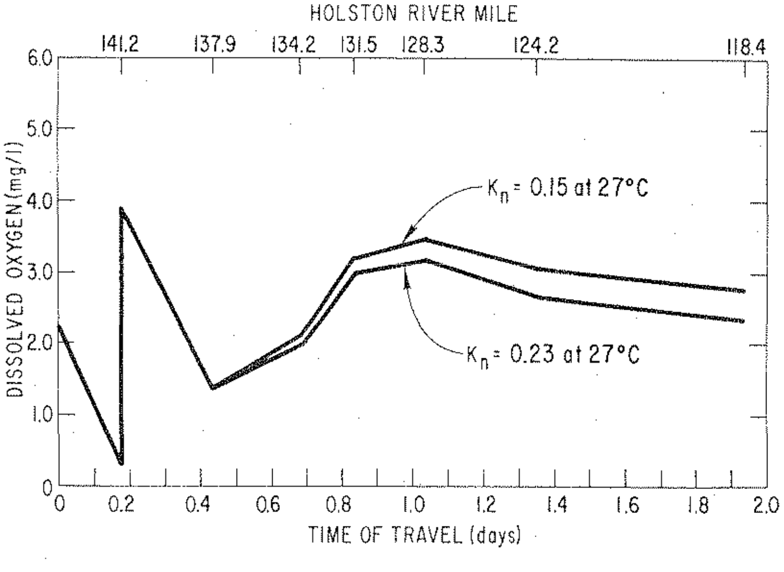

FIGURE 5. **Sensitivity of DO prediction model to range of nitrification coefficients calculated for the 1969 Holston River study.**

TABLE II. Summary of nitrification coefficients determined for free-flowing streams.*

Stream	Maximum Within Reach	Average for Reach Studied	Minimum Within Reach	Source of Data
Grand River, Michigan	3.9	2.6	1.9	Courchaine[2]
Clinton River, Michigan	15.8	5.7	2.2	Wezernak and Gannon[3]
	4.0	1.9	0.4	
Truckee River, Nevada	—	1.9	—	O'Connell and Thomas[28]
South Chickamauga Creek, Tennessee	1.9	—	1.1	TVA
Oostanaula Creek, Tennessee	0.8	—	0.1	TVA
Town Branch, Alabama	—	0.7	—	TVA

* Coefficients in this table were calculated by assuming a first-order reaction and are reported for base e, 20°C.

0.23 per day (all values are reported at 27°C base e). To determine the sensitivity of the difference in the two coefficients on modeling DO concentration in the river, the DO concentration was computed with two coefficients for Run 6 of the survey (the effects of aquatic plants were omitted). As shown in Figure 5, the maximum accumulated difference between the DO computed with the average coefficient (0.23 per day) and that using the lower coefficient (0.15 per day) is only 0.5 mg/l. In the Holston River, this difference in coefficients is also insignificant because nitrification apparently did not occur upstream from the critical DO sag and therefore affected DO only in the recovery portion of the DO sag curve. The coefficient determined for the Holston River is low in comparison with values reported by most other investigators [2, 3, 28] (Table II). However, the value determined for the Holston River is within the range of reported values.

Total nitrogen decreased in the downstream direction. This decrease may have resulted [illegible] equilibration of ammonia, or [illegible] conversion of the nitrogen compounds to nitrogen gas, which may remain in solution or be transferred to the atmosphere. Reduction of nitrate to nitrogen gas probably occurred at least in the first four reaches, but especially in the first two reaches, because of the low DO concentrations. As stated above, in the presence of low DO concentrations, some organisms may use nitrate as a source of oxygen. The transfer of ammonia to the atmosphere is not believed to be significant in the Holston River because of the relatively low pH; however, during the hours of high photosynthetic activity, some of the total nitrogen lost could be attributed to this process. The uptake of nitrogen by the aquatic plants is not believed to have been significant during the 1969 study. In 1969, the Environmental Protection Agency [1] (EPA) estimated the total standing crop of attached aquatic plants to be 154 224 kg. In 1967, Peltier and Welch [29] analyzed the aquatic plants at three stations and found them to contain an average of 2.5 percent nitrogen. If 1967 and 1969 conditions were comparable, the estimated total amount of nitrogen in the plants would have been 3 855 kg. Even with a turnover rate of 10 percent of the nitrogen per day, the rate of uptake by the plants would be minimal compared with the amount of total nitrogen decrease in the river.

On the basis of available data, it cannot be determined whether nitrification occurred in the first two reaches. The ammonia actually increased in the first two reaches. This increase could have resulted from the oxidation of organic nitrogen material or the reduction of nitrate to ammonia. However, this increase [illegible] not necessarily indicate that [illegible]

Nitrification probably is carried out mainly by attached organisms in the river reaches investigated because of the time required for the generation of nitrifying bacteria. Long-term BOD analyses conducted on samples collected in May 1969 indicated that nitrification did not occur until about the tenth day of the BOD analysis. Urea was used as a nitrification inhibitor to determine when nitrification occurred. This result is in contrast to the results of long-term BOD analyses conducted on samples from Cherokee Lake, in which nitrification was determined to occur immediately. Therefore, it may be concluded that nitrifiers

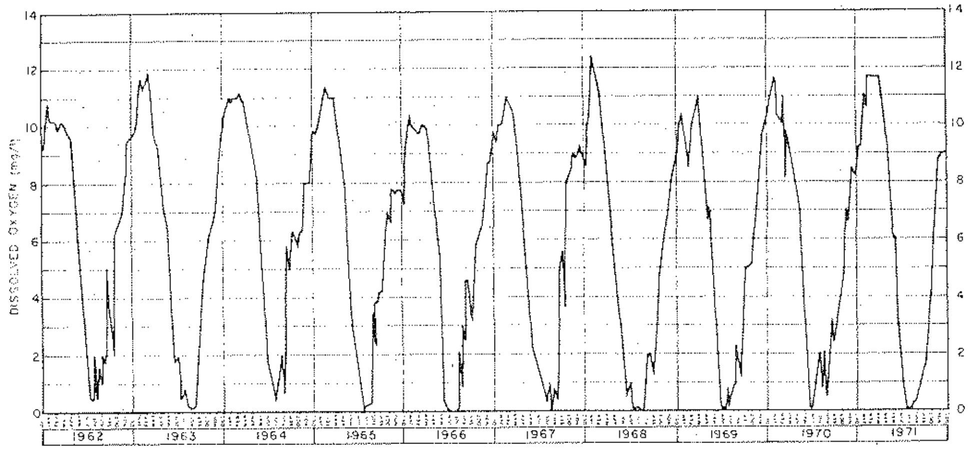

FIGURE 6. History of DO in Cherokee Reservoir. Data is for samples from turbine releases (Nicholas and Gordon[30]).

may not be present in the flowing water, especially in the upper reaches of the Holston River.

IMPACT OF NITROGEN DISCHARGES INTO CHEROKEE RESERVOIR

As is the case with many storage impoundments in the southeastern U. S., Cherokee Reservoir has demonstrated low DO concentrations since its closure and has been the subject of several investigations. Nicholas and Gordon[30] presented the results of several detailed analyses of DO in the reservoir, including the effect of ammonia nitrogen. The oxygen concentrations were shown to be somewhat diminished in the hypolimnion portions of Cherokee Reservoir during certain periods of the year (Figure 6). These conditions occur during summer and fall stratification and are apparently dynamic in nature. They concluded that the oxygen depletion was caused by pollution in the Holston River.

The effect of reducing upstream pollutants may reduce the rate of oxygen depletion and mass of oxygen consumed in the reservoir, but it is unlikely that the low DO problem in the turbine releases will be significantly alleviated.

Under stratified flow conditions, most eutrophic lakes will exhibit low oxygen concentration and, in certain cases, anaerobic conditions in the hypolimnion. Such observations are frequently recorded in reservoirs in the southeastern U. S. during the summer and fall months.

Figure 7 illustrates the oxygen conditions that occur in other reservoirs in the Tennessee River drainage area. Although the examples presented are not the best years for a given reservoir, the oxygen concentrations in the discharge are below desirable levels. In all, low DO conditions have been observed in 19 of the 33 major Tennessee Valley Authority (TVA) impoundments and have been observed consistently year after year in 14 of these reservoirs.

Factors affecting nitrogen in reservoirs. Before further discussion of the role of nitrogen in Cherokee Lake, the significance of nitrates, nitrites, organic nitrogen, and ammonia will be discussed. Investigators are not in agreement as to the effects of these compounds on eutrophication.

In spite of years of research on freshwater nitrogenous pathways, it is still not certain which form of nitrogen is preferable to aquatic organisms. Hutchinson[31] quotes examples of both total preference for nitrates and total preference for ammonia. Obviously, in a eutrophic body of water, intermediate levels of preference will exist. Gates[24] reported that "all chlorophyll-bearing algae can apparently use either ammonium salts or nitrates as nitrogen sources when they are available at suitable concentrations. At low light intensities, synthesis is faster with ammonium than with nitrate. Ammonium ion is often used preferentially when both are available."[25]

The complex nature of the nitrogen cycle is illustrated in Figure 8, and the various sources and sinks are listed in Table III. Although both aerobic and anaerobic transformations are shown in the hypolimnion, they would not occur simultaneously. The major reactions depicted are ammonia assimilation, nitrate assimi-

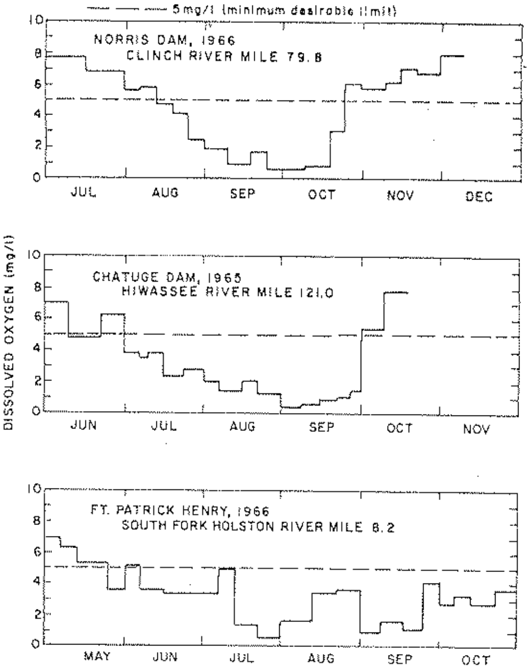

FIGURE 7. The DO history of some Tennessee reservoirs in critical periods. Data is for samples collected from turbine releases.

lation, ammonification, nitrification, denitrification and nitrogen fixation. Ammonification occurs when organic nitrogen is converted to ammonia, and nitrogen fixation is the phenomenon occurring when molecular (atmospheric) nitrogen is reduced to ammonia and then to cellular (organic) nitrogen. The other processes were defined in the previous system.

Obviously, a nitrogen balance is needed to place the various sinks and sources of nitrogen in their proper perspective. The lack of success in performing a nitrogen balance serves to illustrate the lack of knowledge of the phenomena involved. It is possible, however, to present experimental data that will give some insight into the relative magnitude of some of the variables involved, as discussed by Brezonik.[32]

For example, Dugdale and Dugdale[33] reported a maximum rate of ammonia fixation as 110 mg N/l·d and a maximum rate of nitrate fixation of 40 mg N/l·d. Brezonik[32] also found the rate of ammonia fixation to be higher than that of nitrate fixation. Ammonia can be dissipated into the atmosphere if the pH is sufficiently high, as found by Stratton.[34] In a lake with a pH of 9.1, he measured the loss of ammonia to be 97.95 mg/m²·d.

Studies by Brezonik and Lee[35] showed that, of 4.43×10^7 g of nitrate nitrogen present in Lake Mendota in 1966 below 14 m, an estimated 2.81×10^7 g were converted to dissolved nitrogen; the balance was reduced to ammonia and organic nitrogen. These estimates were made in the hypolimnion during midsummer.

Studies of nitrogen fixation in Florida lakes revealed rates varying from 93 to 2 450 mg N/l·h. Significantly, nitrogen fixation occurred in water containing concentrations of ammonia as high as 0.6 N/l. According to Brezonik,[32] nitrogen fixation occurred in the sediments at rates as high as 59 mg N/g·h.

While sediments are usually thought of as nutrient "traps," nitrogen can be released by burrowing animals, biological ammonia production from organic nitrogen, and ammonia desorption. The sources of nitrogen in sediments include deposition of detritus and silt, original deposits, and sorption. Obviously, the high concentrations of ammonia that typically occur in the hypolimnion of anaerobic lakes can be explained by the release of ammonia from sediments and the decomposition of settling organisms and detritus.

Effects of nitrogen and other nutrients on Cherokee Reservoir. Inasmuch as nitrifica-

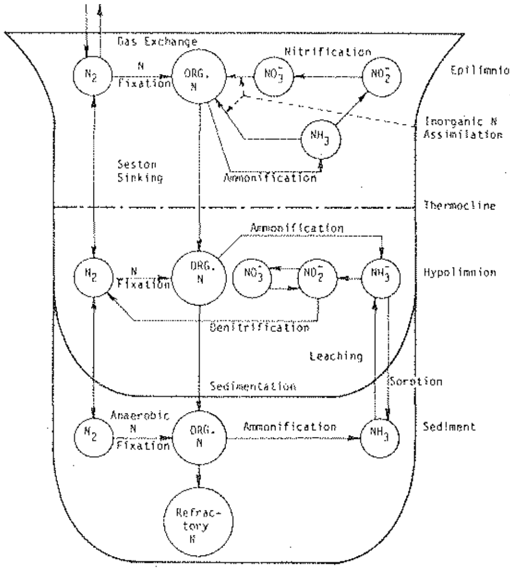

FIGURE 8. Nitrogen cycle reactions in an idealized stratified lake. Note that both aerobic and anaerobic transformations are shown in the hypolimnion. In a real lake they would, of course, not occur simultaneously. (Brezonik[32]).

tion occurs upstream from the reservoir, it would be interesting to determine the degree of oxidation occurring from the backwaters to the "plunge" point in Cherokee Reservoir. Before this determination, it would be somewhat premature to directly relate seasonal oxygen depletions in Cherokee Reservoir to the soluble nitrogen present in the inflow and, in particular, to individual contributors of nitrogenous material.

These conditions occur only during stratification and stagnation of the lake. Furthermore, oxygen is depleted more rapidly in the entrance portion of the basin. Several hypotheses, discussed in the following paragraphs, could be offered.

Frequent and sudden flow changes may tear away attached and rooted plants and sludge particles carrying them to Cherokee Reservoir. Even if only the soluble and light solids were transported, they would end up in the Cherokee hypolimnion because the incoming water is colder than the surface layers of the lake and thus enters the lake as an interflow. This is because sudden high flows originate from colder hypolimnion waters of upstream reservoirs. As stated previously, the rooted aquatic plants also contain nutrients.

Deposited debris and sludge would be converted, initially and aerobically, to ammonia, nitrite, and nitrates. These compounds would be carried into the reservoir by density currents, and oxidation of ammonia and nitrite would further deplete the reservoir oxygen supply which, at this time, is fixed and limited by stagnant stratification. Under the aerobic conditions that exist before stratification, ammonia would be rapidly added to the sediments and converted into organic nitrogen, as indicated by Byrnes[36] and Keeney.[37] Then, under subsequent anaerobic conditions, the organic nitrogen would be converted into ammonium, which under favorable physicochemical conditions may be released into the water in the form of ammonia nitrogen.

The importance of bottom sediments in the oxygen budget of eutrophic reservoirs cannot be overemphasized and, according to Hutchinson,[31] is particularly pertinent under stratified flow conditions. Some authors consider aquatic animals to be dominant in the nutrient regeneration processes. Herbivorous zooplankton, because of their rapid food consumption and high metabolic rates, consume and release back into the water nutrients many times greater in excess of their body content. Nitrogen is excreted as ammonium, free amino acids, and other organic compounds, which are then available for use by phytoplankton and bacteria, as reported by Keeney[37] and Dugdale and Doering.[38]

TABLE III. Sources and sinks for the nitrogen budget of a lake.[32]

Sources

- Surface
  - Agricultural (cropland) runoff and drainage
  - Animal waste runoff
  - Marsh drainage
  - Runoff from uncultivated and forest land
  - Urban storm water runoff
  - Domestic waste effluents
  - Wastes from boating activities
- In situ
  - Nitrogen fixation
  - Sediment leaching
- Airborne
  - Rainwater
  - Aerosols and dust
  - Leaves and miscellaneous debris
- Underground
  - Natural ground
  - Subsurface agriculture and urban drainage
  - Subsurface drainage from septic tanks near lake shore

Sinks

- Effluent loss
- Groundwater recharge
- Fish harvest
- Weed harvest
- Insect emergence
- Volatilization (of NH_3)
- Evaporation (aerosol) formation from surface foam
- Denitrification
- Sediment deposition of detritus
- Sorption of ammonia onto sediments

Materials are consumed by animals, and the animals themselves eventually die. At this point bacteria become more important, but Keeney[37] reports that nutrients released by autolysis and solubilization can rapidly release from 25 to 75 percent of the nutrients contained in animals. Although almost no information is available on the role of fishes in nitrogen cycling in lakes, the effects may be considerable. Fish urine accounts for about 7 to 25 percent of their total nitrogen excretion, mainly as creatinine, creatine, urea, ammonia, and amino acids.

Finally, oxygen conditions in conjunction with nitrogen and phosphorus variables were compared for other southeastern reservoirs in the hope that some conclusions could be drawn as to possible interrelationships among them. Unfortunately, there have been very few samplings that record both sets of variables for a reservoir similar to Cherokee. Inflow nutrient concentrations do not seem to directly affect the DO concentrations. This may be documented by Figure 7, which plots data for two relatively unpolluted reservoirs—Norris and Chatuge. During early summer, spring, and winter, ammonia and total Kjeldahl nitrogen concentrations are relatively high, with apparently negligible effects on the DO conditions. Reservoir operation and temperature may play a decisive role here, however.

Although ammonia appears to significantly affect the oxygen balance in Cherokee Reservoir, further investigation will be required to establish the reason(s) for the more acute oxygen conditions in Cherokee than in other southeastern reservoirs. Insufficient data exist on similar reservoirs, as well as for the Holston River system, that would allow one to directly relate nitrogen data with oxygen depletion. At least two other factors need to be considered, carbon and phosphorus content. Recent studies on the effects of carbon indicate that it seems quite possible that carbon could be limiting growth and controlling the algal mass in systems in which other nutrients are considerably in excess or in special situations, according to Goldman,[39] where alkalinity is low. However, carbon dioxide appears to be abundant in the Holston River inflow, and alkalinity was greater than 60 mg/l in the epilimnion of Cherokee Reservoir during the year 1970.

Lee[40] reports that phosphorus is almost unquestionably regarded as a key element in limiting and determining aquatic plant populations. However, a much better understanding of the relationship between the phosphorus input to a reservoir and the excessive growth of aquatic life accompanied by depletion of oxygen resources is required.

Some very recent experiments on the synergistic effects of phosphates and nitrates in the stimulation of phytoplankton growth indicate that nitrates enhanced the productivity response considerably. Jordan *et al.*[41] found that phosphate was the key substance in all of the positive treatment effects and that its omission from the treatment mixture essentially eliminated all growth response. Both phosphates and nitrates are abundant in the Holston River drainage area upstream (as well as downstream) from the Kingsport discharges. It has been found throughout this study that the phosphate content in all drainage streams and rivers, including the main trunk of the Holston River, is significantly high.

Another possibility is the benthic oxygen demand, which may be particularly acute in stagnant, stratified reservoirs and which may become a dominant factor, as indicated by several limnologists.[30, 31] This may be one more factor in the fertilizing processes that may be determining the extent of oxygen depletion in Cherokee Reservoir.

CONCLUSIONS

1. The nitrification coefficient is best determined by using nitrogen data from field studies, as opposed to using long-term oxygen demand data from BOD bottle studies.

2. Nitrogen balance in streams is very complex. Ammonia variation in streams is affected by nitrification, oxidation of organic nitrogen, reduction of nitrate nitrogen, aquatic plant uptake, equilibrium, and/or conversion to organic nitrogen for cell synthesis. Nitrate variation is affected by nitrification, denitrification, respiratory reduction, and assimilatory reduction. The effect of many of these factors is dependent on other variables such as temperature, DO, and pH. The variation in these two nitrogen compounds may be complicated by the fact that both aerobic and anaerobic processes can simultaneously occur in a stream—aerobic in the flowing stream and at the sediment surface and anaerobic within the sediments.

3. The determination of the nitrification coefficient from ammonia and nitrate data from field studies may not be valid unless the effects of the other factors affecting these nitrogen compounds are determined. In a portion of the Holston River, possible nitrification could *not* be detected because other factors were more important. In the downstream portion of the river, the nitrification coefficient based on ammonia variation was found to be twice that based on nitrate increase. The difference in these two rates cannot be explained quantitatively. For the Holston River, the difference in these two coefficients did not significantly affect the predicted DO sag curve using a mathematical model. However, in other cases, this difference in coefficients could be significant.

4. The nitrification coefficients calculated for the Holston River are lower than those reported for other free-flowing streams.

5. Many impoundments in the southeastern U. S. exhibit low DO concentrations in their hypolimnions. Some of these impoundments do not have any point-source waste discharges in their upstream watersheds.

6. To determine the effect of nitrification on the DO resource of a reservoir, the nitrogen balance needs to be defined. However, with streams, more research is needed to place the

various sinks and sources of nitrogen in their proper perspective. Some data on the various mechanisms affecting nitrogen balance have been reported in the literature, but these mechanisms are affected by many other variables and, therefore, their variation is essentially site-specific.

7. Factors affecting oxygen depletion in Cherokee Reservoir include, in addition to the normal oxygen demand of the inflow, decomposition of the aquatic weeds entering the reservoir, ammonia regeneration by zooplankton, fish wastes, and overall biological community respiration.

8. Although DO concentrations in Cherokee Reservoir have remained similar over the last 10 years, the fishing has improved.

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