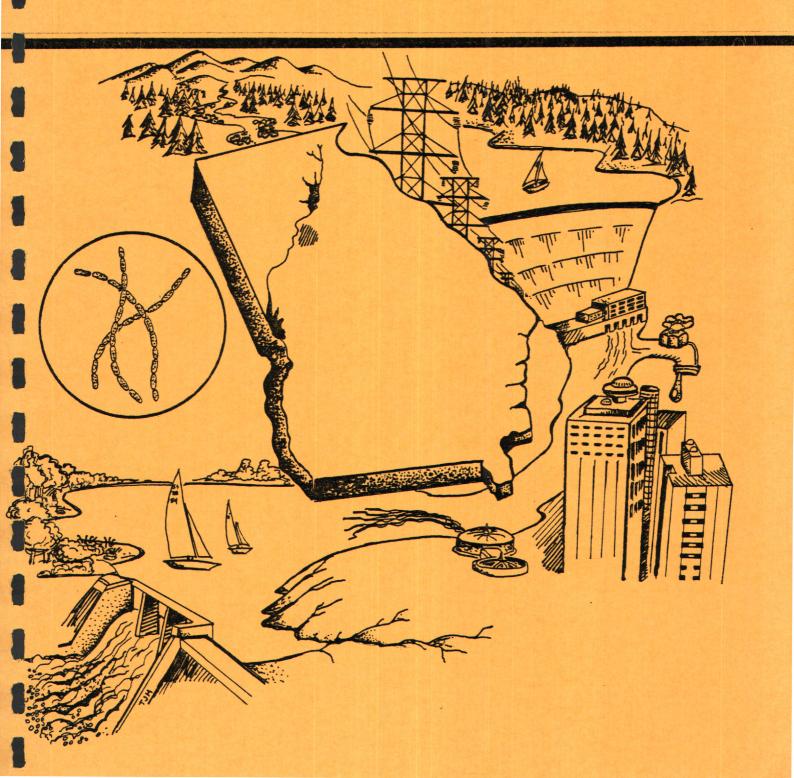
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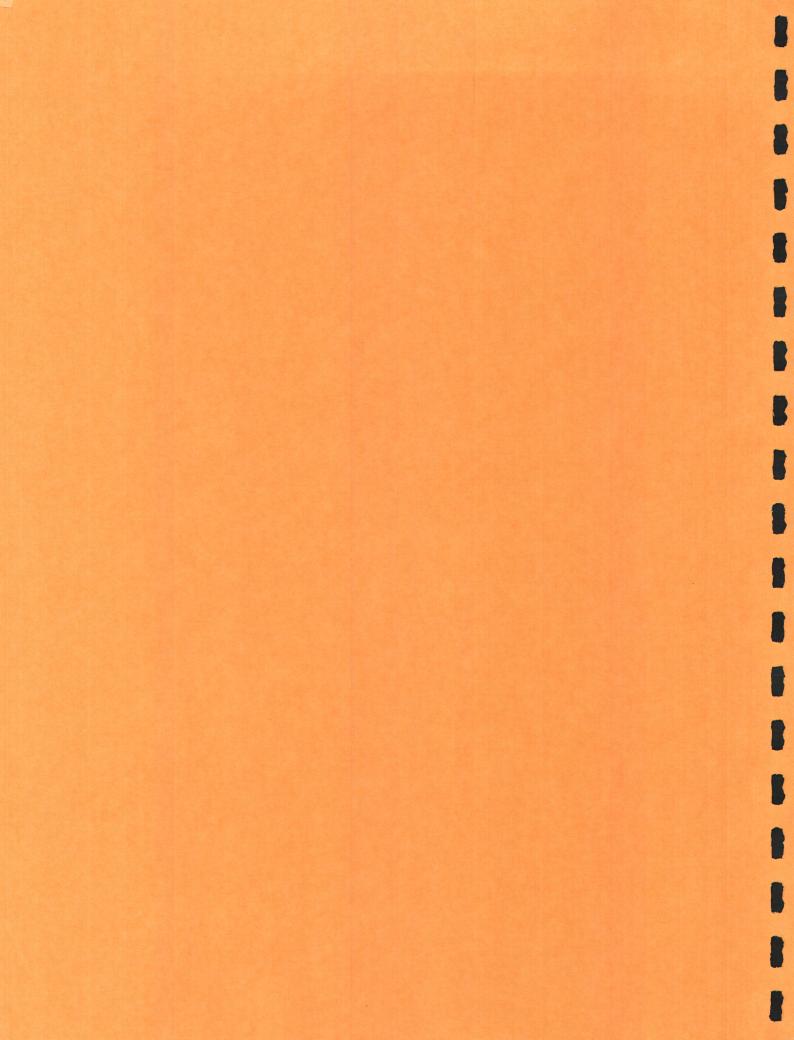
THE EFFECTS OF NITRIFICATION ON THE OXYGEN BALANCE OF THE UPPER CHATTAHOOCHEE RIVER, GEORGIA

by

Theodore A. Ehlke

River Quality Assessment of the Upper Chattahoochee River Basin, Georgia





UNITED STATES DEPARTMENT OF THE INTERIOR CECIL D. ANDRUS, Secretary

GEOLOGICAL SURVEY
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ABSTRACT

Oxygen consumption as a result of nitrification, and carbonaceous bacterial oxidation were compared in a 108 km reach of the Chattahoochee River, Georgia. Nitrogenous and carbonaceous oxygen consumption were separated by using an inhibitor of nitrification, 1-ally1-2-thiourea. The comparison was conducted in the laboratory using samples collected from the water column. Nitrification accounted for 38 to 52 percent of the total oxygen consumption.

Nitrifying bacteria were enumerated from the same reach of the river. The population of Nitrosomonas ranged from 10^1 to 10^3 per mL in the water column and 10^2 to 10^5 per g of benthic sediment. The Nitrobacter population ranged from 10^1 to 10^2 per mL in the water column and 10^2 to 10^3 per g in the benthic sediment. The concentration of ammonium, nitrite, and nitrate as N was determined from water samples collected throughout the study reach. The average rate of ammonium disappearance and of nitrate appearance was 0.02 mg/L/hour of flow time.

The effect of nitrification on the oxygen balance of the Upper Chattahoochee River, Georgia

by

T. A. Ehlke¹

Introduction

Nitrification can be important in the oxygen balance of waterways which receive wastewaters containing NH_4 -N. The oxidation of NH_4 + to NO_3 -proceeds in two steps, catalyzed by the chemoautotrophic bacteria Nitrosomonas and Nitrobacter:

$$NH_4^+ + 1 \frac{1}{2} O_2 \xrightarrow{\underline{Nitrosomonas}} NO_2^- + 2H^+ + H_2O$$
 $NO_2^- + \frac{1}{2} O_2 \xrightarrow{\underline{Nitrobacter}} NO_3^-$

The oxidation of 1.0 g of $\mathrm{NH_4}^+$ to $\mathrm{NO_2}^-$ by <u>Nitrosomonas</u> requires 3.43 g of $\mathrm{O_2}$. Similarly, the oxidation of 1.0 g of $\mathrm{NO_2}^-$ by <u>Nitrobacter</u> requires 1.14 g of $\mathrm{O_2}$. Thus oxidation of 1.0 g of $\mathrm{NH_4}$ + to $\mathrm{NO_3}$ - requires approximately 4.57 g of $\mathrm{O_2}$. Although conventional secondary waste treatment greatly reduces the utilizable carbonaceous content in the wastewater, little reduction in ammonia nitrogen usually occurs. The contribution of nitrification to the total oxygen demand of wastewaters can be significant. 1, 2 A study of the Grand River near Lansing, Michigan indicated that nitrification was responsible for 75 percent of the total BOD in a 16 km reach downstream of

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the municipal wastewater treatment plant. 2 Nitrification occurs in both the water column and in benthic sediments, but most investigators 1 , 3 , 4 have indicated that nitrification in benthic sediments is predominant. Stream temperature, pH 4 , time of travel, and wetted perimeter 5 are some variables affecting the rate of nitrification.

This study examines the contribution of nitrification to the total oxygen demand in a 108 km section of the Chattahoochee River near Atlanta, Georgia. The Chattahoochee River originates on the southern slopes of the Blue Ridge Mountains in northeast Georgia (fig. 1) and flows southwestward through metropolitan Atlanta to the Georgia-Alabama State line, then southward to the Gulf of Mexico. Many municipalities, including the city of Atlanta, use the waters of the river for water supply.

Impoundments on the river are used for hydroelectric power generation, recreation, and flood control. Streamflow is highly regulated and it is common for the river stage to rise or fall several feet during a day owing to variation in power generation at the Buford Dam.

Methods

Water and benthic sediment samples were collected at the sites shown in figure 1 following three days of steady flow during the summer of 1977. Streamflow at the upstream end of the study area (km 0) was maintained at 1,150 ft 3 /s.

The sample collection site at Atlanta (km 0) is upstream from the metropolitan Atlanta wastewater treatment facilities (WTF). All other sampling sites are downstream of the major Atlanta WTF. The time of travel from the Atlanta to Franklin, Georgia was determined using the techniques described by Velz.⁶

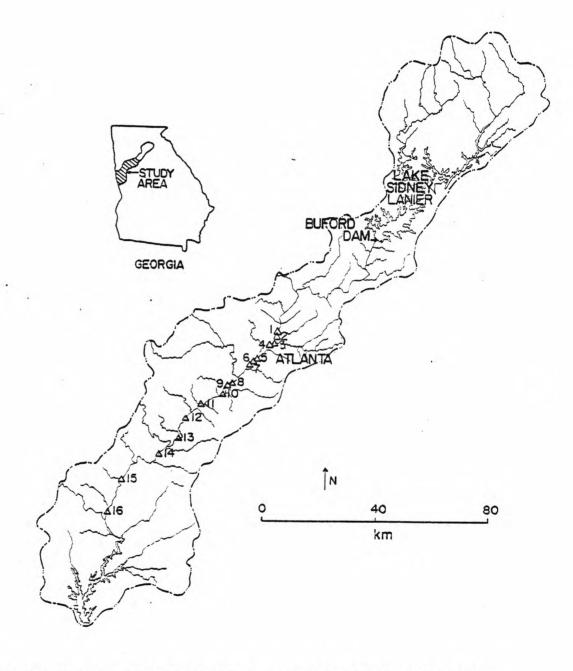


Figure 1.--The Chattahoochee River basin showing streamflow and water quality measuring sites.

Table I.--Key to collection sites shown in figure \boldsymbol{l}

Key number		ice downstream tlanta (km)
1	Chattahoochee River at Atlanta	0
2	Cobb Chattahoochee WTF near Atlanta	3.94
3	R. M. Clayton WTF at Atlanta	4.39
4	Chattahoochee River at U. S. 280	6.76
5	Chattahoochee River at Ga. 139	13.32
6	South Cobb Chattahoochee WTF near Mableton	13.98
7	Utoy Creek WTF near Atlanta	18.29
8	Chattahoochee River at Ga. 166	27.24
9	Camp Creek WTF near Atlanta	30.88
10	Chattahoochee River near Fairburn	33.93
11	Chattahoochee River above Bear Creek	43.54
12	Chattahoochee River at Capps Ferry Bridge	51.13
13	Chattahoochee River at Hutchison's Ferry	60.0
14	Chattahoochee River near Whitesburg	69.38
15	Chattahoochee River at Bush Head Shoals	90.17
16	Chattahoochee River near Franklin	108.62

Water samples for chemical and microbiological analysis were collected hourly near the center of river flow in 1-liter, autoclaved, polypropylene containers using the depth integrated technique. A narrow neck bottle was lowered to the river bottom in a weighted sleeve and retrieved at equal ascending and descending rate until the bottle was filled. Benthic sediment samples were collected for microbiological analyses using a United States Geological Survey BM 60 sampler. This apparatus collects a 12.8 cm x 5.1 cm x 3.7 cm sampler. Benthic sediment was subsampled in the field using preweighed, sterile 16 x 100 mm glass test tubes. The test tubes were inserted into the sediment to obtain the top 1 cm. Sample and test tubes were placed in sterile plastic bags and kept chilled to 4°C while enroute to the laboratory. At the laboratory a sediment wet weight was determined, then the sample was used for the enumeration of nitrifying bacteria. All sample analyses were completed within 8 hours of collection.

The populations of <u>Nitrosomonas</u> and <u>Nitrobacter</u> were determined from water and benthic sediment samples using a three-tube, most-probable-number (MPN) method. The presence of <u>Nitrosomonas</u> was indicated by the appearance of nitrite in an ammonium-containing medium. <u>Nitrobacter</u> populations were indicated by the disappearance of nitrite from a nitrite containing medium. Inoculated cultures were tested for the presence of nitrite after 30 days incubation at 28° C and at 2-week intervals thereafter up to 60 days.

Ammonium, nitrite, and nitrate concentrations as nitrogen were determined in the laboratory using methods described by Brown and others 9 . Carbonaceous and nitrogenous oxygen demands were determined separately using methods described by Stamer and Scott 10 and by Young. 11 In this procedure, the

carbonaceous oxygen demand was determined during a 20-day period while maintaining a 2-mg/L concentration of 1 ally1-2 thiourea (ATU, Eastman Kodak) to inhibit nitrification. ATU is a specific inhibitor of the oxidation of NH₄+ by Nitrosomonas. 12 The total oxygen demand was determined similarly without the inclusion of ATU. The amount of oxygen consumption resulting from nitrification was calculated as the difference between the total and carbonaceous oxygen demands.

Results and discussion

The log mean MPN populations of <u>Nitrosomonas</u> and <u>Nitrosomonas</u> in both in figures 2 and 3 respectively. The population of <u>Nitrosomonas</u> in both water and benthic sediments was lowest upstream of the metropolitan Atlanta WTF. Downstream of the WTF, the population of <u>Nitrosomonas</u> ranged from approximately 10^3 to $10^5/g$ of benthic sediment which generally is less than has been reported for other rivers.³, ¹², ¹³ <u>Nitrosomonas</u> populations in several New Jersey rivers and streams ranged from approximately 10^5 to $10^6/g$ of benthic material.⁴ The lower nitrifying bacteria populations observed in the Chattahoochee River than in other rivers may be a result of the relatively low NH₄+ concentration, as discussed below.

Within the study reach the population of <u>Nitrosomonas</u> exceeded that of <u>Nitrobacter</u> at almost every site. The <u>Nitrosomonas/Nitrobacter</u> ratio in benthic sediment (table II) ranged from 3 to 1 upstream of Atlanta to 414 to 1 just downstream of the metropolitan Atlanta WTF (km 33.93).

The NH₄-N concentration was also maximum at km 33.93 (figure 4). The <u>Nitrosomonas/</u>
<u>Nitrobacter</u> ratio and NH₄-N concentration generally decreased downstream of km 33.93.

Comparison of the <u>Nitrosomonas</u> and <u>Nitrobacter</u> populations (figs. 2 and 3) indicates that the Nitrosomonas population increased more rapidly than the

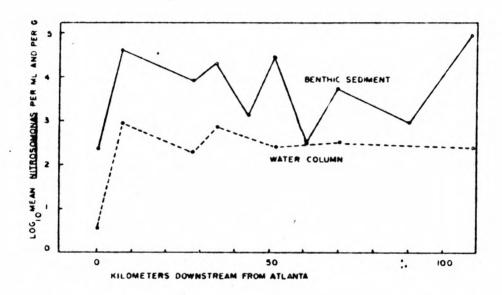


Figure 2.--Log $_{10}$ mean MPN Nitrosomonas per g of sediment and per ml from the Chattahoochee River.

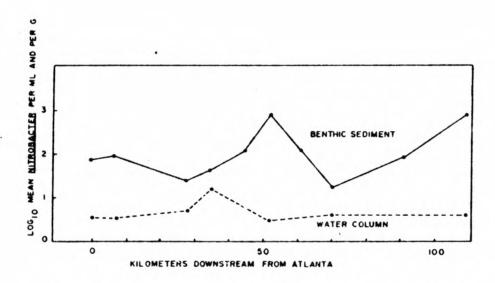


Figure 3.--Log₁₀ mean MPN Nitrobacter per g of sediment and per ml from the Chattahoochee River.

Table II.--Summary of <u>Nitrosomonas</u> and <u>Nitrobacter</u> populations in Chattahoochee River water and benthic sediment

km downstream	Mean N	itrosomonas	Mean Nitr	obacter	Nitr	osomonas
from Atlanta	MPN per ml	MPN per g	MPN per ml	MPN per g	Nitr	obacter
					water	benthic sedimen
0	3	191	3	68	1	3
6.76	830	33,000	3	83	237	399
27.24	190	7,100	5	23	37	308
33.93	710	17,000	17	42	43	414
51.13	260	23,000	3	630	80	37
69.38	320	4,700	4	20	70	234
90.17	ND	790	ND	74	ND	11
108.62	220	71,000	4	710	56	100

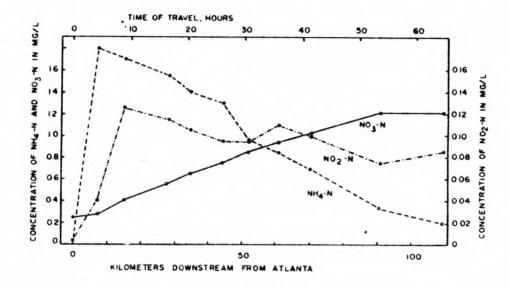


Figure 4.--Mean concentration of NH_4-N , NO_2-N , NO_3-N and flow time in the Chattahoochee River during the summer of 1977.

Nitrobacter population in the reach of the river from directly above to just below the major Atlanta WTF (km 0 to km 6.76). The observed rapid increase in the $\mathrm{NO}_{2}-\mathrm{N}$ concentration (fig. 4) directly downstream of the major Atlanta WTF probably results from the large Nitrosomonas population and the 414:1 Nitrosomonas/ Nitrobacter ratio. Similar responses in other rivers were reported by White and others. 1 The mean concentrations of NH₄-N. NO₂-N and NO₃-N in the Chattahoochee River are summarized in figure 4. The mean $\mathrm{NH_4-N}$ concentrations at km 6.76 and km 108.62 were 1.8 mg/L and 0.2 mg/L. The mean concentrations of NO_2 -N at 6.76 and km 108.62 were 0.31 mg/L and 1.28 mg/L respectively. Based on a travel time of 65.07 hr., the average rate of decrease in NH_Δ -N concentration and the average rate of increase in NO_2 -N plus NO_3 -N concentration was approximately 0.02 mg/L/hr. In the reach of the river from km 6.76 to km 43.54 the increase in the NO_{2} -N plus ${\rm NO_3-N}$ concentration was about equal to the decrease in ${\rm NH_4-N}$ concentration (table III). In the reach from km 43.54 to km 108.62 the decrease in $NH_{\Delta}-N$ concentration .03mg/L/hr. while the increase in the NO_3-N plus NO_2-N concentration was .Olmg/L/hr.This apparent loss of ammonium without a concomitant increase in the concentration of $\mathrm{NO_2-N}$ and $\mathrm{NO_3-N}$ was observed in other streams. 1 , 4 It may be attributed to ion exchange with benthic sediments or uptake by various aquatic plants. None of these were measured in this study.

The low rate of nitrification in the Chattahoochee River during this study does not appear to be related to temperature. Nitrification in wastewater treatment plants was reported to be most rapid from 20 to 30°C ¹⁴ but the precise temperature requirements for nitrification in natural streams is less well known. White and others reported negligible nitrification in a tributary to the Allegheny River when water temperatures were 17°C or lower. The water temperature in the Chattahoochee River during this study ranged from 20.8°C to 27.1°C.

Table III.--Downstream changes in the concentration of $\rm NH_4-N$, $\rm NO_2-N$, and $\rm NO_3-N$ in the Chattahoochee River

each (km downstream rom Atlanta)	ΔNH ₄ -N (mg/L)	△ NO ₂ -N (mg/L)	△ NO ₃ -N (mg/L)
6.76 - 13.32	-0.10	+0.08	+0.13
13.32 - 27.24	-0.15	-0.01	+0.15
27.24 - 33.93	-0.15	-0.01.	+0.10
33.93 - 43.54	-0.10	-0.01	+0.10
43.54 - 51.13	-0.34	0.00	+0.10
51.13 - 60.00	-0.11	+0.01	+0.09
60.00 - 69.38	-0.15	-0.01	+0.08
69.38 - 90.17	-0.37	-0.02	+0.19
90.17 - 108.62	-0.13	+0.01	0.00

The rate of $\mathrm{NH_4}$ -N oxidation in a polluted stream in New Jersey was reported by Tuffey and others to be $1\,\mathrm{mg/L/hr}$ of travel time. The initial concentration of $\mathrm{NH_4}$ -N was approximately 4 times that of $\mathrm{NH_4}$ -N in the Chattahoochee River. The rate of $\mathrm{NH_4}$ -N oxidation was reported by White and others as 0.50 mg $\mathrm{NH_4}$ -N/L/hr in a tributary to the Allegheny River, where the initial $\mathrm{NH_4}$ -N concentration was 7.1 mg/L. The lesser rate of nitrification in the Chattahoochee River does not appear to be limited by temperature in the range 20.8° to 27.1°C but rather by the concentration of $\mathrm{NH_4}$ -N.

The proportion of nitrifying bacteria in the water column and in the benthic sediment can be determined knowing the mean depth of water within the study reach. The mean depth in the Chattahoochee River on May 28, 1977 at 41 river sites from Atlanta downstream to Whitesburg was 1.42 m. Streamflow at the same time was 1150 ft³/s at Atlanta. Using the data in table II, 53 percent of the Nitrosomonas were present in the water column, (1.42 m in depth) and 47 percent in the top 1 cm of benthic sediment. Similarly, 72 percent of the Nitrobacter were in the water column and 28 percent in the top 1 cm of benthic sediment. These results suggest that a substantial part of the nitrification in the Chattahoochee River from Atlanta to Whitesburg may occur in the water column. Generally, other investigators have indicated that the majority of nitrifying bacteria occurred in the upper 1 cm of benthic sediment. Related studies on the Chattahoochee River suggest that the scarcity of nitrifying bacteria in the benthic sediment may be related to the particle size distribution of streambottom material. (Robert E. Faye, oral communication, 1978).

Carbonaceous and nitrogenous oxygen consumption

Laboratory analysis indicated that carbonaceous and nitrogenous oxygen consumption were nearly equal in the upper reaches of the Chattahoochee River (table IV). The calculation of oxygen consumption by this method is an approximation of the potential oxygen uptake because in situ conditions cannot be duplicated in the laboratory. Nevertheless, it provides a method for comparing potential oxygen consumption at different sites.

The magnitudes of nitrogenous and carbonaceous oxygen consumption were 2.75 mg/L and 2.71 mg/L respectively, in the reach from Atlanta to Capps's Ferry (15 km). In a related study, J. K. Stamer (written communication, 1978) determined that the nitrogenous and carbonaceous oxygen consumption in the water column would be 11.1 and 10.2 tons per day in the same reach, assuming similar flow conditions.

The importance of nitrification to total oxygen consumption in the Chatta-hoochee River declined downstream from Capps Ferry. Overall, nitrification accounted for 43 percent of all oxygen consumption between Capps Ferry and Franklin (15 km, flow time 36 hours). In the furthest reach downstream (Bush Head shoals to Franklin), the relative importance of nitrification was the least, 38 percent of all oxygen consumption. Previously, Courchaine² reported that nitrification accounted for more than 75 percent of all oxygen consumpton in a 16 km reach of the Grand River near Lansing, Michigan. This study indicates the potential importance of autotrophic nitrification to the oxygen balance in the Chattahoochee River, a situation where the initial ammonium concentration was relatively low.

Table IV.--Oxygen consumption in the Chattahoochee River due to nitrifying bacteria and to all other sources on June 1, 1977

Reach (km downstream from Atlanta)		on in mg/L due to: non-nitrifying sources
0 - 6.76	0.02	0.02
6.76 - 13.32	0.50	0.47
13.32 - 27.24	0.89	0.84
27.24 - 33.93	0.43	0.43
33.93 - 43.54	0.55	0.57
43.54 - 51.13	0.35	0.37
51.13 - 60.00	0.35	0.41
60.00 - 69.38	0.28	0.32
69.38 - 90.17	0.56	0.75
90.17 - 108.62	0.53	0.86

CONCLUSIONS

The Chattahoochee River, although comparatively unpolluted, undergoes measurable nitrification in a 108 km section downstream of Atlanta Georgia. Nitrosomonas and Nitrobacter populations were more numerous in the water column, considering its entire depth, than in the top 1 cm of benthic sediment. The population of nitrifying bacteria and the rate of nitrification were far lower than that reported in other rivers. The low rate of nitrification may be a result of the lesser concentration of ammonium in the Chattahoochee River. Laboratory analyses of Chattahoochee River waters indicated that nitrification accounted for approximately 38 to 52 percent of all oxygen consumed over a 20-day period.

The in situ measurement of nitrification may differ to a greater or lesser degree from the amount measured in this study. The inclusion of benthic nitrification in the overall rate will improve the accuracy of nitrification estimates. These are planned as future studies.

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