Nitrogen availability in urban runoff

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THE AVAILABILITY TO ALGAE OF PHOSPHORUS in urban stormwater runoff has been discussed.[1] In addition to phosphorus, high concentrations of nitrogen compounds have also been found in urban runoff. Inorganic N in the form of ammonia, nitrite, and nitrate has been reported in Cincinnati, Ohio, runoff at an average concentration of about 1.0 mg N/L for the sum of the three N forms.[2,3] This concentration was about three times the critical level of 0.3 mg N/L of inorganic N, which was suggested by Sawyer[4] for algal growth problems in lakes. The same Cincinnati runoff carried an average total N concentration of 3.1 mg N/L, which included the organic as well as the inorganic N forms. Thus, about 65 percent of the total N in the runoff was present as organic N. Similarly, Kluesener and Lee[5] found that organic N forms were responsible for about 77 percent of the total N input to Lake Wingra, Madison, Wis., from urban runoff.

Because inorganic N forms such as ammonia, nitrite, and nitrate are readily available for algal growth in lake waters, the availability of the total N in a runoff stream will depend on the relative amount of organic N in the runoff and on the availability of the organic N to algae.

$$\text{Available Total N} = \text{Inorganic N} + (\text{Organic N}) \times (\text{Percentage of Organic N available}) \quad (1)$$

The availability of organic N is a function of the rate at which the organic N can be mineralized to form inorganic N in the following reactions:

$$\text{Organic N} \rightarrow \text{Ammonia N} \quad (2)$$
$$\text{Ammonia N} \rightarrow \text{Nitrite N} \quad (3)$$
$$\text{Nitrite N} \rightarrow \text{Nitrate N} \quad (4)$$

This paper describes the results of a series of mineralization tests in which the reactions in Equations 2 to 4 were allowed to proceed in urban runoff under the influence of the bacteria in the runoff for the purpose of estimating the availability of the N loads transported by urban runoff. With such estimates, it was hoped that nutrient budget calculations might be modified to reflect the biological availability of the N loads.

METHODS

Runoff sampling. Thirteen grab samples of urban runoff were collected in Madison, Wis., from October 1972 to March 1973 as part of a phosphorus availability study.[1] The sampling stations included a low density residential area (Station A), a medium density area (Station B), and the University of Wisconsin-Madison campus (Station D). A single sample was also collected from a residential area that had previously been under construction and had been sodded to prevent erosion before collection of the sample (Station F). All samples were taken with plastic bottles from street gutter or open storm sewer flows and were stored at 4°C in darkness until they were analyzed.

Chemical analyses. Ammonia N was determined by the automated alkaline phenol hypochlorite method,[6] while nitrate N was measured by the modified brucine method of Jenkins and Medsker.[7] Both ammonia N and nitrate N were determined after filtration of the runoff through a 0.45-μ pore size membrane filter. Total Kjeldahl N (TKN) was measured with an ammonia electrode* after manual digestion of 20 ml of unfiltered runoff in a 100-m1 micro-Kjeldahl flask with 5 ml of digestion reagent, described in "Standard Methods,"[8] to convert organic N to ammonia N. After cooling the digestion residue, 50 ml of 4°C

* Model 95-10, Orion Research, Inc., Cambridge, Mass.

ammonia-free water were added to the residue and the resulting solution was transferred to a small jar containing a stirring bar. Five ml of alkaline reagent (40 g NaOH + 33.2 g KI/100 ml water) were added to the sample immediately before reading of the dissolved ammonia concentration with the electrode. Soluble Kjeldahl N (SKN) was determined by the same procedure, with a filtered (0.45-μ) sample. The following N forms were calculated from the chemical analyses:

Soluble organic N

$$= \text{SKN} - \text{ammonia N} \quad (5)$$

Particulate organic N

$$= \text{TKN} - \text{SKN} \quad (6)$$

Total organic N

$$= \text{TKN} - \text{ammonia N} \quad (7)$$

$$\text{Total N} = \text{TKN} + \text{nitrate N} \quad (8)$$

Algal-available N

$$= \text{ammonia N} + \text{nitrate N} \quad (9)$$

In computing total N or available N, the concentration of nitrite N was assumed to be negligible, based on earlier reports,[9] and this species was not measured in the tests reported herein.

Mineralization tests. Triplicate 1-L glass bottles containing 400 ml of unfiltered runoff were incubated at 21° ± 1°C in darkness for 82 to 100 days inside a constant temperature walk-in incubator. The bottles were stoppered with plastic foam plugs and swirled daily by hand to ensure aerobic conditions in the samples. Aliquots of well-mixed sample were removed at intervals during the incubations for analysis of ammonia N and nitrate N. The sum of these two species was used to estimate the concentration of algal-available N in the bottles (by Equation 9). The percentage of total N in algal-available N forms was computed by the equation:

$$\text{Percentage of total N available} = \frac{\text{Ammonia N + Nitrate N}}{\text{TKN + Nitrate N}} \times 100 \quad (10)$$

The TKN and SKN values of each sample bottle were determined before and after the dark incubation in order to follow the changes in organic N forms, as calculated by Equations 5 to 7.

RESULTS

Initial N availability. The initial pattern of N availability in the Madison runoff samples is given in Figure 1. The range of algal-available N (Equation 9) in these samples was 4 to 66 percent of total N, and 9 of 13 samples showed organic N concentrations greater than algal-available N concentrations. With respect to the organic N fraction of total N, 10 of 13 samples seemed to have more particulate organic N than soluble organic N. Absolute concentrations of total N varied from 1.87 to 4.99 mg N/L, and organic N ranged from 0.75 to 3.53 mg N/L in these samples.

Mineralization of organic N. The changes in the concentrations of ammonia N and nitrate N during dark aerobic incubation of a typical runoff sample (A-6) are shown in Figure 2. These data are representative of the characteristics of all the incubations, the detailed data of which are reported elsewhere.[10] As was expected from the sequential nature of the nitrogen mineralization reactions in Equations 2 to 4, the ammonia N concentrations increased first, then declined as the nitrate N levels began to increase. The initial rapid rise in nitrate N was followed by a slower rate of increase up to the end of the incubation. Ammonia N, in contrast, continued to decrease to levels close to the detection limit (0.05 mg N/L) of the analytical method used to determine this species.

One of the unexpected results of the dark incubations is illustrated in Figure 3, in which the average absolute concentrations of the runoff N fractions are given before and after 100 days of dark incubation of sample A-6. Although algal-available N increased from 0.15 to 1.70 mg N/L, the concentration of organic N forms in the sample—soluble plus particulate organic N—decreased from 1.72 to 0.62 mg N/L, a change of only -1.10 mg N/L. Thus, the apparent total N at the end of the incubation period was higher than the initial total

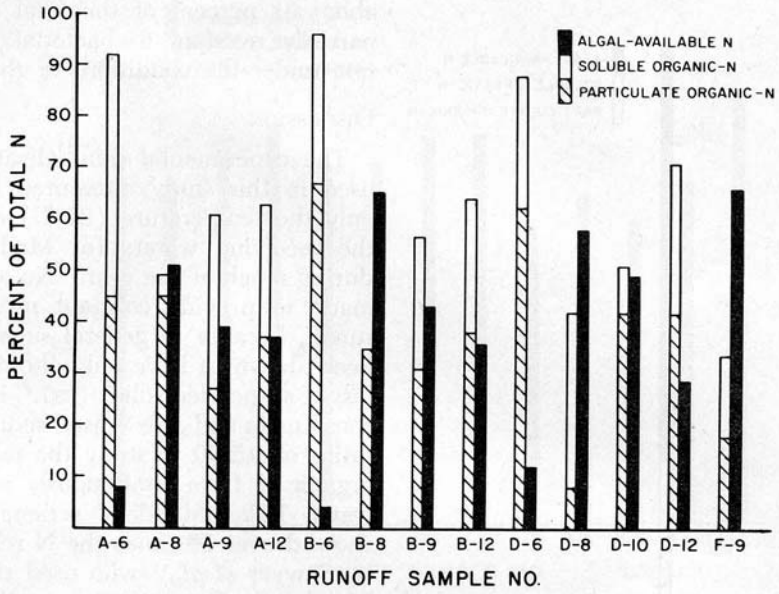

FIGURE 1.—Nitrogen availability pattern in fresh urban runoff samples.

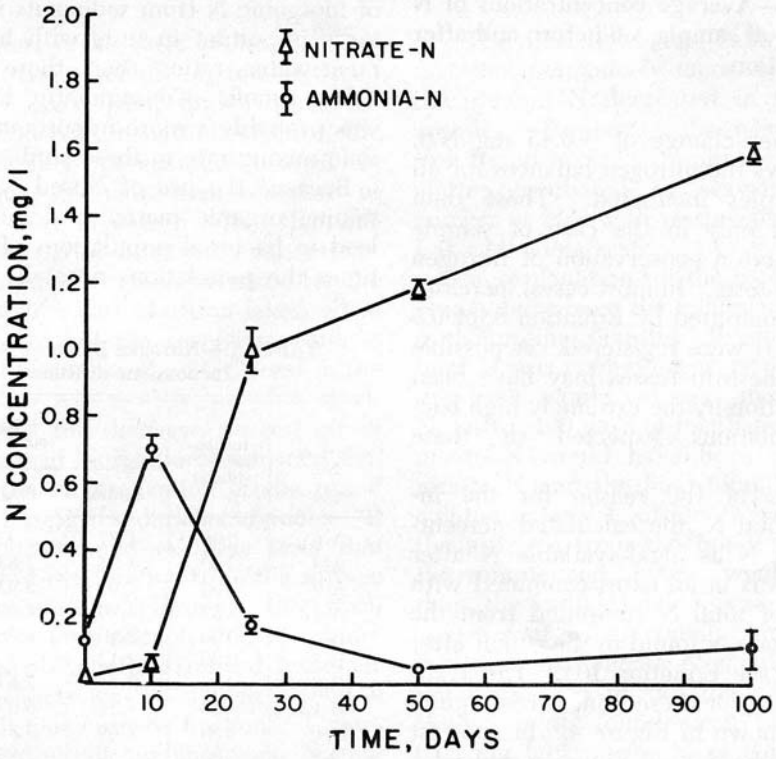

FIGURE 2.—Changes in ammonia N and nitrate N concentrations during dark incubation of runoff sample A-6 showing both the ranges and mean values from triplicate incubations.

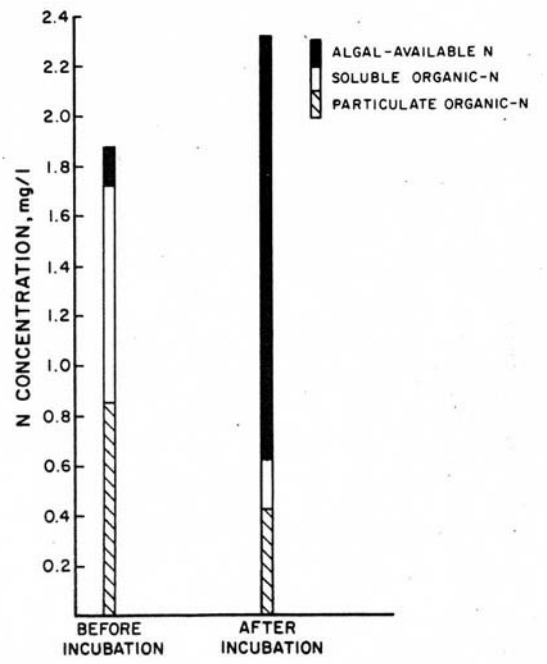

FIGURE 3.—Average concentrations of N forms in runoff sample A-6 before and after dark incubation.

N by the net change of +0.45 mg N/L. Table I shows the nitrogen balances for all of the samples incubated. These data showed that only in the case of sample A-12 was there a conservation of nitrogen during these tests. In most cases, increases in total N, computed by Equation 8, of 0.5 to 1.5 mg N/L were registered. A possible reason for these increases may have been nitrogen fixation by the extremely high bacterial populations expected in these samples.

Regardless of the reason for the increases in total N, the calculated percentage of total N as algal-available N after incubation was in all cases computed with the values of total N computed from the TKN and nitrate N found in the runoff after incubation (see Equation 10). The availability pattern for these mineralized runoff samples is shown in Figure 4. In contrast to Figure 1, the data in Figure 4 showed a range of algal-available N of 57 to 82 percent of the final total N values, with an overall average of 69 percent. Conversely, about 31 percent of the total N was apparently resistant to bacterial mineralization under the conditions of these tests.

DISCUSSION

The experimental mineralization system used in this study attempted to simulate only the temperature (21°C) expected in the receiving waters for Madison runoff during much of the year. No attempt was made to provide constant mixing of the runoff, because in general such runoff has been shown to have only about 1 mg/L or less of suspended solids (ss).[5] By comparison, Austin and Lee[11] used sediment:water ratios of 0.5:20 to study the release of inorganic N from continuously mixed, deep water Lake Mendota sediments. They showed over 50 times the N release found by Sawyer *et al.*,[12] who used similar Lake Mendota sediments at a sediment:water ratio of 1:3 and quiescent laboratory conditions. The effect of mixing on the release of inorganic N from sediments is probably more important in tests with higher sediment:water ratios than those found in urban runoff. Consequently, temperature was probably a more important parameter than mixing rate in these studies.

Because the use of closed systems containing organic matter and bacteria may lead to bacterial populations of 10^3 to 10^5 times the populations normally present in

TABLE I.—Nitrogen Balances for Dark Incubations of Runoff

Sample No.	Incubation Time (days)	TKN + Nitrate N (mg N/l)		
		Initial	Final	Change
A-6	100	1.87	2.32	+0.45
A-8	100	2.05	2.83	+0.75
A-9	100	2.61	3.93	+1.50
A-12	82	4.99	4.99	0.00
B-6	100	3.60	4.05	+0.45
B-8	100	2.12	2.85	+0.73
B-9	100	2.61	3.63	+1.02
B-12	82	4.54	6.03	+1.49
D-6	100	2.69	3.36	+0.67
D-8	100	2.50	2.95	+0.45
D-10	100	4.26	5.25	+0.99
D-12	100	4.94	5.68	+0.74
F-9	100	2.23	2.92	+0.69

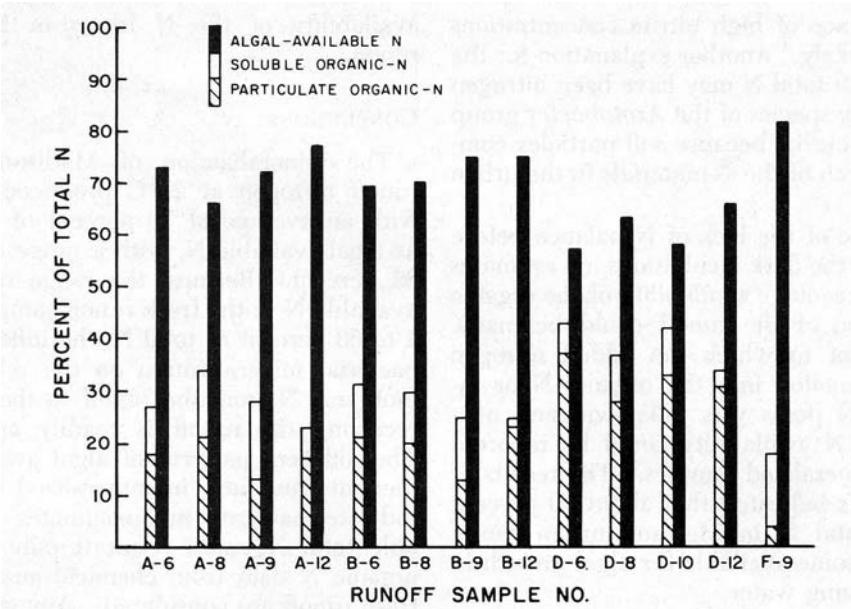

FIGURE 4.—Nitrogen availability pattern in mineralized urban runoff samples.

natural waters,[13] the rates of inorganic N production from runoff organic N seen herein may have been higher than the mineralization rate in nature. Hence, the final availability percentages shown in Figure 4 may be more representative of 200 to 300 days in nature rather than the 82 to 100 day period used in the laboratory. The same statement could be made for the winter periods in the Madison lakes, when the temperature of the receiving water is considerably less than the 21°C used in the tests.

In all tests, the decreases in organic N and increases in inorganic N provided evidence for the mineralization of the runoff organic N during the dark incubations. It was initially assumed in these tests that the amount of evaporation from the surface of the suspensions (through the foam plugs) was not significant; that no photosynthetic algal growths removed inorganic N; and that there was no change in total N because of bacterial N fixation. Consequently, the initial and final total N concentrations should have been equal, as a decrease in organic N was expected to be balanced by an equal increase in inorganic N. The data, however (Table I), showed that the inorganic N increased more than the organic N decreased in most of the samples. Similar results were found by Von Brand *et al.*[14] with nitrogenous organic matter incubated in seawater and by Sawyer *et al.*[12] with wastewater effluent in Lake Mendota water.

One explanation for the increase in total N may have been the influence of nitrite N in the original samples. Because the initial total N was computed as TKN + nitrate N, this value would not have included nitrite N. After 100 days of incubation, all of the nitrite N would have been converted to nitrate N and the final total N value calculated as TKN + nitrate N would include the nitrogen from the initial nitrate N in the sample and, hence, would be larger than the initial total N value. Previous analyses of urban runoff, however, have indicated that nitrite N should only be a minor fraction of the total N in runoff. Weibel *et al.*[9] found mean values of only 0.05 mg/L of nitrite N as compared with 2.7 mg/L of total N in Cincinnati runoff. Also, the high populations of aerobic bacteria reported for urban runoff [2, 3] make

the presence of high nitrite concentrations seem unlikely. Another explanation for the increase in total N may have been nitrogen fixation by species of the *Azotobacter* group of soil bacteria, because soil particles composed much of the ss materials in the urban runoff.

Because of the lack of N balance before and after the dark incubations, no estimates of the percentage availability of the organic N fraction of the runoff could be made. The extent to which the added nitrogen was channelled into the organic N or inorganic N pools was unknown, and only the total N availability could be reported in the mineralized samples. The results of these tests indicated that about 70 percent of the total N in Madison urban runoff could become available for algal growth in the receiving water.

Similar tests with river waters tributary to Lake Ontario[15] have shown that about 62 to 78 percent of the total N in these waters could be converted to algal-available N in 35 to 50 days. In contrast, Austin and Lee[11] reported that about 44 percent of total N was released as algal-available N from Lake Mendota deep water sediments after 200 days of aerobic incubation. The higher value of N release in the urban runoff or river water tests is probably related to the relatively short residence time of the eroded soil-bound or vegetable organic matter in contact with decomposing organisms as compared with the deep water lake sediments, which have been subjected to long periods of bacterial attack. Keeney [16] has stated that the organic matter in lake sediments is more stable towards decomposition than that present in dead plant and animal remains, probably because of protection by reaction with organic compounds and clay minerals, formation of resistant heterocyclic material, and physical inaccessibility. If such reactions occurred between the organic N forms in urban runoff and lake sediments, the values reported in this study would be overestimates of the eventual availability of the runoff nitrogen. Consequently, the average value of 70 percent should probably be viewed as an upper limit on the availability of the N forms in Madison runoff.

CONCLUSIONS

The mineralization of Madison urban runoff nitrogen at 21°C produced waters with an average of 70 percent of total N as algal-available N, with a range of 57 to 82 percent. Because the range of algal-available N in the fresh runoff samples was 4 to 66 percent of total N, the influence of bacterial mineralization on the release of inorganic N from the runoff to the waters receiving the runoff is readily apparent. The different patterns of algal availability seen in fresh and in mineralized samples indicate that gross underestimates of available total N could result if only the inorganic N data from chemical analyses of fresh runoff are considered. Any estimates of the true, biologically important nitrogen loadings from urban runoff should also consider the mineralization of organic N forms.

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Authors. At the time that this study was made, William F. Cowen, Kannikar Sirisinha, and G. Fred Lee were, respecttively, graduate student, graduate student and author of the M.S. thesis from which this paper was prepared, and director, Water Chemistry Program, University of Wisconsin, Madison. At the present time, Cowen is research chemist, U. S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Md., Sirisinha is on the faculty of Public Health, Mahidol University, Bangkok, Thailand, and Lee is director, Center for Environmental Studies, University of Texas at Dallas, Richardson.

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