NITROGEN AND PHOSPHORUS IN LAKE ONTARIO TRIBUTARY WATERS

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(Received 18 May, 1978; revised 10 July, 1978)

Abstract. During the Spring of 1972 through the Spring of 1973 samples of rivers tributary to Lake Ontario and streams in the Genesee River Basin (New York) were analyzed for N and P forms by chemical methods, then incubated in darkness or bioassayed with algae to estimate the percentage of total N, organic N, total P or particulate P which could eventually become available for algal growth in Lake Ontario. The total available P in the river water samples could be estimated by adding to the soluble orthophosphate 0.2 of the difference between the soluble orthophosphate and the total phosphate. The total available N can be estimated from the sum of the inorganic N (NH_3 and NO_3^-) plus 0.5 times the total organic N concentration of the river water sample.

1. Introduction

The Chemistry–Biology Panel of the International Field Year for the Great Lakes (IFYGL) chose as one of its objectives the development of an aquatic plant nutrient budget for Lake Ontario. This panel and others concerned with management of excessive fertilization of natural waters are frequently faced with the question of what forms of N and P should be measured and how much of the non-readily available (to algae) N and P should be considered as potentially available in the receiving water. The research presented here is an attempt to estimate the nutrient availability of the organic N and particulate P forms in tributaries to Lake Ontario.

2. Sample Collection

Samples of Niagara, Genesee, Oswego, and Black River water were collected from 0 to 1 m depth in the rivers, near Lake Ontario (Figure 1). For the P studies, additional samples were taken from the Niagara River and the southern tip of Grand Island. The samples were collected from August 1972 to June 1973, although most were collected from February to June 1973. Genesee River basin streams draining a variety of land uses were sampled from October 1972 to June 1973 for the P studies. Samples were received 2 to 9 d after collection and were stored at 4°C in darkness until analyzed for N and P forms, generally after 2 to 7 d. This period of storage is

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Water, Air, and Soil Pollution **10** (1978) 343–350.

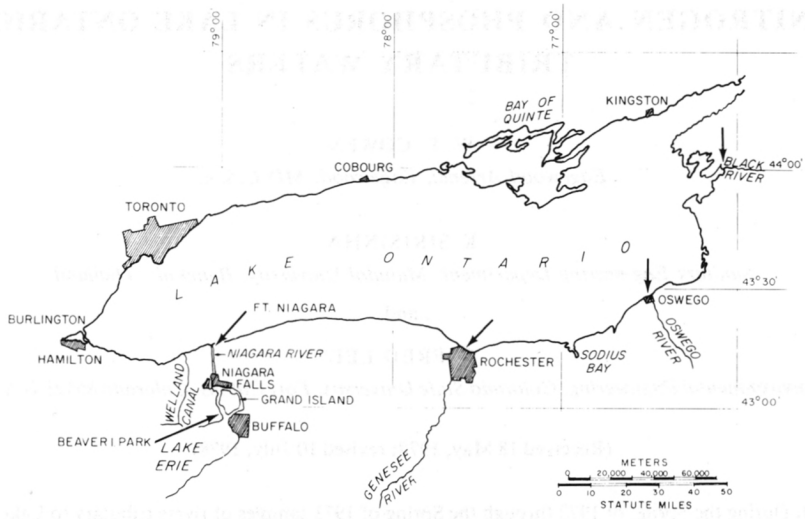

Fig. 1. Lake Ontario and major tributaries.

not considered significant in affecting the conclusions from this study, in that any changes that took place in the form of N and P in the samples during storage would likely have occurred in the river water and/or lake water to a similar extent.

3. Analytical Methods

All analyses were by procedures given in *Standard Methods* (APHA *et al.*, 1971) with the exception of total Kjeldahl nitrogen (TKN), where an Orion ammonia electrode was used for analysis of the digested solutions, and dissolved reactive phosphate (DRP), where the method of Murphy and Riley (1962) was used. For the purpose of this study the readily available P was defined as equal to the dissolved reactive phosphate. The readily available forms of N were assumed to be equal to NH_3–N plus NO_3^-–N. Nitrite was not determined, as it was assumed to be negligible compared to total N or the sum of NH_3–N + NO_3^-–N. Particulate P (PP) concentrations were derived as the difference between total phosphate (TP) and total soluble phosphate (TSP) or were determined directly by persulfate digestion of particles retained on a 0.45 μm millipore membrane filter, then scraped off into distilled water. 'Particulate' or 'soluble' forms were defined by 0.45 μm membrane filtration in these studies.

Attempts were made to model the aerobic mineralization of organic N and P forms in Lake Ontario by various experimental conditions, and to follow the changes in 'readily available' N by analyzing for NH_3–N + NO_3^-–N and the changes in 'readily available' P by determining DRP in the water sample or DRP recovered

from anion exchange resin added to a water sample plus the DRP in the solution phase of the sample.

Algal-available P from PP forms was bioassayed with *Selenastrum capricornutum* Algal Assay Procedure methods (US EPA, 1971) using the PP forms isolated by membrane filters as the source of P and hemocytometer cell counts for growth measurement. Total P availability was bioassayed using whole water samples which were autoclaved and filtered before assay, with cell growth measured by light (750 nm) 'absorbance'-scattering.

Chemically defined available P from PP forms was measured by the DRP found in dilute acid extracts, base extracts and anion exchange equilibrations of PP forms isolated by membrane filtration. The detailed procedures for each type of test are discussed along with the results of the tests.

This paper presents a summary of the key results of this study. The complete data and additional information on experimental procedures are presented in Cowen and Lee (1976) and Cowen *et al.* (1977).

4. Results

4.1. TOTAL N MINERALIZATION

To model the aerobic bacterial mineralization of the total N in the tributary waters, triplicate samples were stored in foam stoppered flasks in darkness at 20°C for periods of 35 to 50 days. Since the temperature of Lake Ontario at various depths and times of the year is lower than 20°C, the mineralization seen in these tests was expected to be upper estimates of that actually occurring in the lake as a whole. The ammonia levels were generally negligible and the nitrate levels constant after about 25 days of incubation, so that the 35 to 50 day period was sufficient for an estimation of final mineralization. Comparison of initial and final average TKN + NO_3^-–N values for nine samples showed agreement of better than 10% in five samples and better than 15% in eight of the samples, indicating that the assumption of negligible nitrite in the initial samples and assumed zero absorption of ammonia from the incubator atmosphere was essentially correct. Table I shows that in each river the

TABLE I

Mineralization of total N to ammonia and nitrate in 35 to 50 days[1]

River	No. of samples	Range of total N (mg N l^{-1})	Range of % of total N as NH_3–N + NO_3^-–N	
			Initially	After incubation
Niagara	3	0.45 – 1.13	30 – 67 (53)	54 – 91 (78)
Genesee	4	1.26 – 2.26	51 – 55 (54)	60 – 75 (67)
Oswego	8	1.01 – 2.30	44 – 69 (57)	58 – 91 (75)
Black	4	0.59 – 1.25	27 – 58 (44)	36 – 75 (62)

[1] Mean value in parentheses.

readily available N was increased by aerobic mineralization. The final average values were in the range of 62 to 78% of total N.

4.2. ORGANIC N AVAILABILITY

When the increases in NH_3–N + NO_3^-–N of the tributary samples were compared to the organic N fraction initially in the samples, the results were quite variable (Table II), even within each river group. Such variability may be related to the source inputs of organic N forms to the rivers.

TABLE II

Mineralization, expressed as a percentage of organic N, after 35 to 50 days[1]

River	No. of samples	Range of organic N (mg N l^{-1})	Range of Organic N mineralization (% of organic N)
Niagara	3	0.15 – 0.79	34 – 74 (60)
Genesee	4	0.59 – 1.08	11 – 48 (29)
Oswego	8	0.39 – 1.04	8 – 74 (42)
Black	4	0.25 – 0.91	12 – 48 (34)

[1] Mean value in parentheses.

4.3. TOTAL P MINERALIZATION

Total P aerobic mineralization to DRP was tested under similar conditions (15 to 22°C in darkness) to those used for N mineralization. Anion exchange resin (Dowex 1–X8, 20–50 mesh, chloride form) was added at a 1 g 100 ml^{-1} sample level to some of the bottles to trap DRP released to solution by microbial action or desorption from soil particles. The resin-bound DRP was recovered from the resin by leaching with 1 N Na_2SO_4 after isolating the resin from natural particles by passing the sample through a No. 60 wire sieve.

In an attempt to assess the contribution of available P derived from algal biomass, chloroform was added to lyse the algal cells and liberate phosphatase enzymes, which could then assist in the hydrolysis of condensed or organic P forms to DRP (Berman, 1970). These tests were allowed to run in darkness for 7 to 16 days under the same temperature conditions as the mineralizations. The maximum observed values of available P were recorded from each mineralization for the overall comparison.

Direct bioassays of algal-available P in the river waters were performed after autoclaving the samples in order to lyse microorganism cells. Any soluble P released in a form used by the test alga was measured in this test, whether soluble orthophosphate or soluble condensed or organic P forms. Since the samples were filtered prior to inoculation with test alga and algal assay medium salts minus P (US EPA, 1971), the algae did not have access to any particulate P forms except that fraction released

by autoclaving. Test cultures were quantified after 18 days of incubation and compared to standard cultures grown on orthophosphate.

It should be noted that in several cases long storage periods at 4°C (16 to 96 days) preceded the chloroform and dark incubation test. However, since the purpose of the tests was to estimate upper bounds of aerobic mineralization (at 15 to 20°C) the added mineralization during the long periods at 4°C was considered small compared to the eventual mineralization under the test conditions.

Table III shows that the average percent of TP estimated as available by the chloroform treatment was greater than the initial value in the Niagara, Oswego and Black Rivers but not in the Genesee River. A possible explanation for this observation was that the Genesee carried large loads of suspended soil particles, which may have adsorbed phosphate released by chloroform treatment, thus maintaining an equilibrium concentration (Taylor and Kunishi, 1971). Dark incubations were variable and did not appear to show any large difference in TP availability over that seen initially, except for the Oswego River samples. Algal bioassays of Niagara River water, in contrast, showed very low available TP compared to that initially observed as sample DRP. The bioassay results for the other rivers generally agreed with the results of the mineralizations and chloroform tests, indicating a range of about 30 to 67% TP availability in those rivers.

4.4. PP AVAILABILITY

The *Selenastrum* algal bioassays of PP forms from tributary waters indicated that less than 6% of the PP was available to the test algae in 18 days (Table IV). Microscopic cell counts of *Selenastrum* in these tests provided visible evidence of competition for available P by species of algae native to the rivers. When this competition was removed by autoclaving the suspensions of PP before bioassay, the resulting availability was increased to about 38% of PP. Much of the increase was probably also due to cell lysis and release of cellular P. Similar assays of PP forms from streams in the Genesee River basin showed less than 24% of PP available in

TABLE III

Comparison of tests used to estimate TP availability in Lake Ontario tributaries

River	No. of samples	Range of maximum observed TP available (% of TP)			
		Initially	After chloroform added	After dark incubation[7]	Algal bioassay
Niagara	9	4 – 44 (18)	26 – 91 (58)[1]	12 – 51 (28)[2]	5 – 15 (<11)
Genesee	4	7 – 60 (30)	9 – 71 (38)	16 – 64 (36)	8 – 72 (32)
Oswego	11	31 – 74 (48)	51 – 81 (67)[3]	46 – 74 (64)[4]	38 – 84 (60)[5]
Black	5	12 – 26 (20)	36 – 51 (45)	20 – 55 (30)	35 – 56 (43)[6]

[1] 8 samples tested
[2] 7 samples tested
[3] 10 samples tested
[4] 7 samples tested
[5] 8 samples tested
[6] 3 samples tested
[7] Combined results, with and without resin, with only the maximum observed value of the two tests reported.

TABLE IV

Algal biossays of PP availability

River	No. of samples	Algal-available P (% of PP)	
		Range	Mean
Niagara	1	<5	<5
	2 (Autoclaved)	33 – 57	45
Genesee	3	2 – <6	<6
	2 (Autoclaved)	36 – 41	38
Oswego	3	<1 – <2	<2
	2 (Autoclaved)	32 – 44	38
Black	2	3 – <5	<5
	2 (Autoclaved)	26 – 45	36
Genesee River Basin Streams[1]			
Spring Creek (cropland)	3	<3 – 16	<16
	1 (Autoclaved)	20	20
Allen Creek (urban)	7	<2 – 24	<24
	1 (Autoclaved)	34	34
Jaycox Creek (pasture)	1	7	7
Dansville (runoff – high density residential)	5	0 – 3	<3
	2 (Autoclaved)	8 – 10	9

[1] Predominant land use in parentheses.

natural particle suspensions and 8 to only 34% of PP available in autoclaved suspensions (Table IV), approximately the same qualitative behavior as seen in the rivers.

Chemical extractions of Genesee River basin PP forms by dilute $HCl–H_2SO_4$ (Wentz and Lee, 1969), 0.1N NaOH–0.1N NaCl (Williams *et al.*, 1967), and Dowex 1–X8 (20–50 mesh, chloride form in water – 1 g 100 ml^{-1} PP suspension) provided comparisons with biological assays of PP availability. The acid extraction was performed in 5 to 15 min at room temperature and the base and resin extractions were shaken mechanically at 20°C over night and for 24 h, respectively. The extracted DRP or resin-bound DRP was compared to the PP content in the text flasks to determine percent availability of PP. The results (Table V) indicated a range of group mean values of 6 to 50% of PP available. Comparison of the resin, base, and algal bioassay values (Table IV) showed an overall range of 0 to 34% of PP extracted. The acid extractions were generally higher than the values from the other tests. The relatively low values seen in some of the resin equilibrations were in agreement with the results of algal bioassays on natural (unautoclaved) PP suspensions, indicating that major factors regulating the P availability were probably physical-chemical reactions between eroded soil particles and soluble P forms.

TABLE V

Chemical extractions of Genesee River basin PP forms[1]

Sampling station	No of samples	Range of % of PP extracted by:		
		Acid	Base	Resin
Genesee River (at Rochester, N.Y.)	4	21 – 79 (50)	11 – 28 (17)	6 – 31 (17)
Spring Creek	3	18 – 25 (22)	10 – 18 (13)	1 – 11 (6)
Allen Creek	8	40 – 60 (48)[2]	25 – 37 (30)	18 – 27 (25)
Jaycox Creek	2	29 – 30 (30)	18 – 19 (18)	17 (17)
Dansville runoff	8	28 – 35 (30)[2]	10 – 32 (18)[3]	5 – 16 (11)

[1] Mean values in parentheses.
[2] 6 samples averaged.
[3] 7 samples averaged.

5. Discussion

Based on the results of this study, average total N availability in the aerobic mineralization tests was 62 to 78%, while average organic N availability varied from 29 to 60% in the river samples. Golterman (1960) found about 20 to 30% liberation of N forms to solution after lysis of *Scenedesmus* cells with UV irradiation or chloroform treatment. Further decomposition resulted in an overall mineralization of 55 to 70% in five days. Foree and Barrow (1970) found about 46% mineralization of algal-bacterial-zooplankton cells after 200 days.

Foree *et al.* (1970) found from 0 to 94% with an average of about 50% of the initial particulate N present in algal cells was converted to inorganic forms. These studies were conducted under both aerobic and anaerobic conditions. They concluded that about 50% of the N and P present in algal cells was in a refractory form which would not likely be converted to an available form. Based on the studies in this investigation as well as the studies of others it is concluded that a reasonable estimate of available N entering Lake Ontario from US tributaries would be NH_3–N plus (NO_3^-–N – NO_2^-–N) plus 0.5 (TKN – NH_3–N). An estimate of TP availability should be made by adding the soluble orthophosphorus (DRP) to 0.2 (TP-DRP), where DRP is approximately equal to TSP, so (TP – DRP) represents PP. Based on these studies the percent of PP available may vary by ±20% depending upon sample location and time.

It should be emphasized that the 0.2 and 0.5 factors suggested above governing the availability of particulate and organic forms of P and N, respectively, should be used as a guideline in those cases where there is a lack of reliable data on the available forms in a particular water. It is expected, based on these studies, that the specific factor will be highly variable from water to water and with time, for any particular source of nutrients. There is obvious need for studies of the type

conducted in this investigation on a wide variety of waters. Such studies would likely improve the ability to estimate the amount of algal available forms of N and P present in natural waters. Until such studies are conducted on a specific water, it is suggested that the relationships developed in this study be used to estimate the algal available amounts of N and P present in a natural water sample.

Acknowledgments

This research was funded by a grant from the US Environmental Protection Agency, Grant No. R–800537, in conjunction with the International Field Year for the Great Lakes (IFYGL). The authors wish to thank N. Halverson and E. Adamany for their technical aid with the nutrient analyses, P. Boulton and other personnel of the New York State Department of Environmental Conservation, R. Moore of the State University College, Oswego, N.Y., and R. Sweeney of State University College, Buffalo, N.Y. for their assistance in sample collection. The assistance and advice of G. P. Fitzgerald and the assistance of the US EPA personnel at Grosse Ile, Michigan, especially N. Thomas, and the EPA-Rochester, N.Y., especially D. Casey, is greatly appreciated.

This investigation was conducted at the University of Wisconsin-Madison. It received support from the Department of Civil and Environmental Engineering Experiment Station at the University of Wisconsin-Madison, Department of Civil Engineering – Environmental Engineering Program, Colorado State University, and EnviroQual Consultants and Laboratories, Fort Collins, Colorado.

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