TASK GROUP D (CANADIAN SECTION)

INTERNATIONAL REFERENCE GROUP

ON

POLLUTION FROM LAND USE ACTIVITIES

AVAILABILITY OF PHOSPHORUS IN DIFFERENT SOURCES ENTERING THE GREAT LAKES FOR ALGAL GROWTH

by

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3.0 DISCLAIMER

The study discussed in this document was carried out as part of the efforts of the Pollution from Land Use Activities Reference Group, an organization of the International Joint Commission, established under the Canada-U.S. Water Quality Agreement in 1972. Funding was provided through Fisheries and Environment Canada. Findings and conclusions are those of the authors and do not necessarily represent the views of the Reference Group or its recommendations to the Commission.

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8.0 SUMMARY

The bioavailability of phosphorus in various sources contributing to loadings of this element to the Great Lakes was studied in lake column simulators. Loading of total phosphorus was equivalent between treatments that included river water, tertiary-treated sewage effluent, shoreline bluff material and Grand River suspended particulates. Growth response of algal communities to treatments was compared to the response to phosphoric acid. A background response due to phosphorus in the water used to fill the columns and contaminating sources was also measured. Averages for total and soluble reactive phosphorus concentrations were similar between treatments although obvious differences in growth response were observed. Sewage effluent produced an overall growth response equivalent to the phosphoric acid control while river water had an overall response of 65% of the control. Response to bluff material was indistinguishable from that due to background sources. An inverse relationship existed between nitrate concentrations and phosphorus availability. The full response to the Grand River particulates and its control was probably limited by zooplankton grazing pressure. All other columns had declines in algal standing crops coincident with increases in numbers of *Bosmina* spp.

In bluff material the high density of particles containing apatite phosphorus and the poor solubility of this compound led to a short residence time in the upper layer and low bioavailability of the phosphorus in this treatment. The impact of shoreline erosion on the

Great Lakes in terms of phosphorus loading is negligible compared to municipal point-source and diffuse tributary loads of phosphorus. The cost-effectiveness of phosphorus control strategies proposed by PLUARG is increased in a relative sense when bioavailability of phosphorus is considered.

9.0 INTRODUCTION

Eutrophication was cited a decade ago as "the most serious water pollution problem having long-term, international significance" (Anon., 1969). It is generally accepted that eutrophication in most lakes is the result of excessive loadings of phosphorus and results in prolific growth of attached and planktonic algae (Vollenweider, 1968).

Phosphorus loadings to the lower Great Lakes originate from a variety of sources such as discharge of municipal and industrial wastes, agricultural runoff and shoreline erosion. A cost-effective management strategy for phosphorus loadings was proposed by PLUARG (1978) where finances would be directed towards management programs that could remove the greatest amount of phosphorus load per unit cost. Although tributary loads in the lower lakes are important with 48 and 28 percent of the total phosphorus loading to Lake Erie and Ontario originating from this source, costs per unit amount of phosphorus removed vary widely for rural programs. Control of urban non-point source phosphorus loadings is also extremely expensive (PLUARG, 1978). On the other hand, PLUARG (1978) designated municipal point sources as the most significant and controllable source of phosphorus entering the Great Lakes. Removal of phosphorus to a 0.5 mg•L^{-1} effluent concentration was designated as the most cost-effective control measure examined in their study. Availability of phosphorus in diverse sources can indicate differences in the relative cost-effectiveness between management practices that are not evident with comparisons based on total phosphorus.

The purpose of our experiment was to compare the availability of phosphorus for algal growth in the sources contributing most of the total phosphorus loading to the lower Great Lakes.

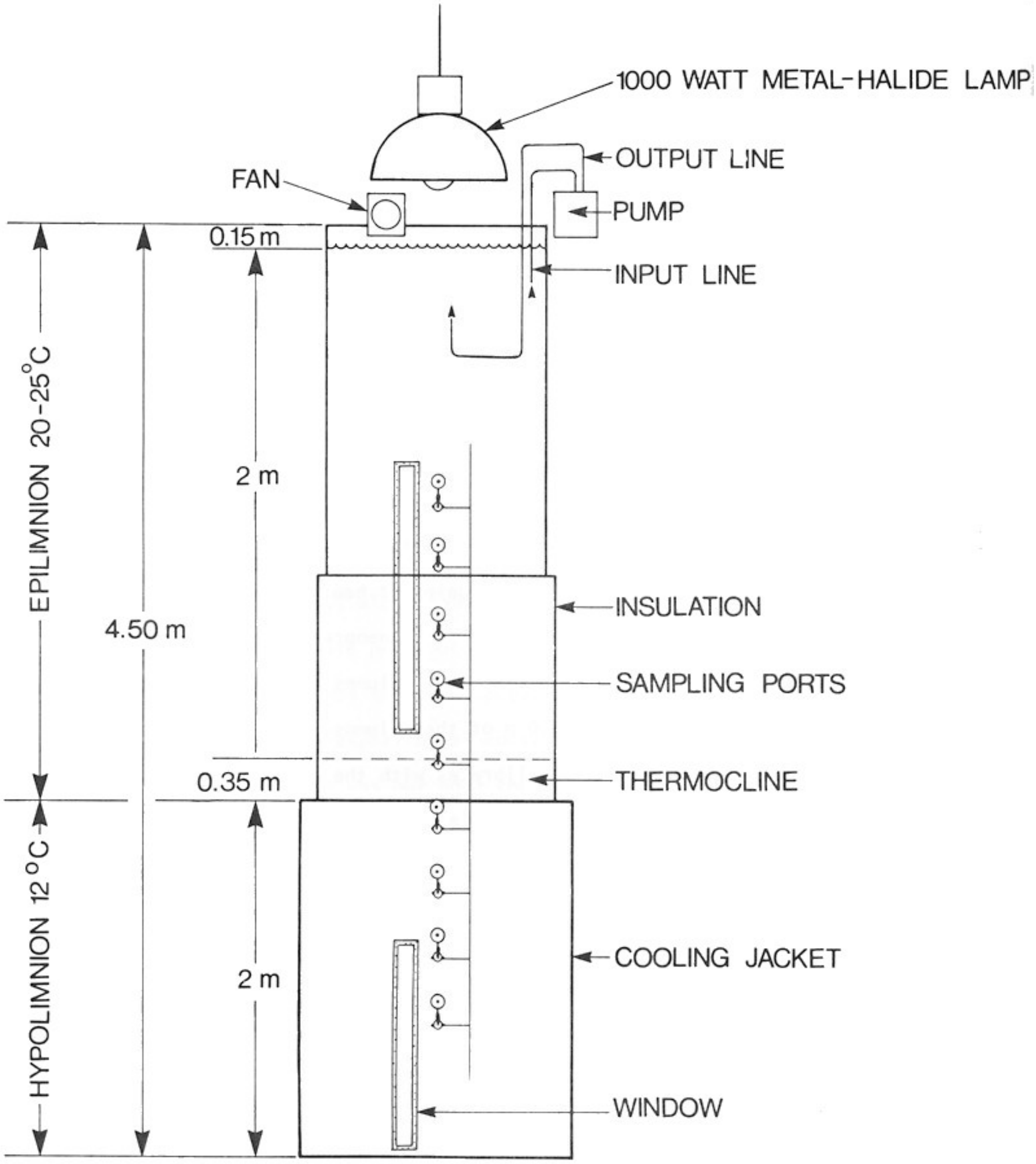
We assumed that algal communities would grow in some proportion to the supply of available phosphorus provided they were phosphorus-starved and that phosphorus was the only factor limiting growth. The study was carried out in large experimental ecosystems, referred to as Lake Column Simulators (LCS). It was our hope that these systems by virtue of their size, control of forcing variables (nutrients and light) and inclusion of ecosystem processes, such as sedimentation and zooplankton grazing, would offer more realism than laboratory bioassays carried out in small vessels.

10.0 MATERIALS AND METHODS

10.1 LAKE COLUMN SIMULATORS - CHARACTERISTICS AND CONTROL

The LCS are eight stainless steel columns, 4.5 m high, 1.0 m in diameter, with a volume of 3417 L when filled to 4.35 m. The LCS are located indoors in the wet-lab area of the Great Lakes Biolimnology Laboratory at the Canada Centre for Inland Waters, Burlington (Fig. 1). A one-thousand W, metal-halide lamp (CGE, 24754 Gl) suspended *ca.* 40 cm from the water surface, is the primary source of irradiance for each column. These lamps were on a 12h light, 12h dark cycle and provided a quantum flux just above the water surface of ca. 800 μ einsteins•m^{-2} •sec^{-1}.

A coil carrying a coolant mixture of ethylene glycol and water encircles the lower 2.0 m of the column (lower layer - LL) and is connected to a coolant reservoir equipped with a pump and refrigerating system. Temperature stratification can be established in the middle of the column with this system. Advective gains of heat to the LL through the steel walls are minimized by an insulative neoprene jacket. Temperature in the LL averaged 11-13°C in all eight columns during the experiment. Temperature in the upper 2.0 m of the columns (upper layer -UL) is not directly controlled but equilibrates with the ambient air temperature due to heat flux through the uninsulated steel walls of this portion of the column. Heat from the lamps is partially dissipated by a continuous flow of air over the water surface provided by fans. The low surface area of water to volume ratio also helps minimize heat gain from the lamps. High UL temperatures in this experiment (25-27°C) were the result of the high heat conductance of stainless steel, the large surface area of the uninsulated sides relative to the UL volume, the height of this part of the column relative to the room height and the high temperatures in the building at this time of the year (May-June). The region of temperature discontinuity was thin (0.35 m) and located



LAKE COLUMN SIMULATOR

2.0 - 2.5 m from the water surface. Vertical temperature difference within both UL and LL was usually less than 1°C, suggesting each compartment was vertically homogeneous. Continuous vertical mixing in the UL was provided by a centrifugal pump (Little Giant Corp. Model 2E-38NT). Surface water was drawn through a stainless steel tube into the pump and a second tube attached to the pump outflow extended 1.0 m down the inside of the column, 0.5 m toward the centre and was turned up at the tip to direct water flow toward the surface.

The growth of attached algae on the walls of containers is a problem common to all model ecosystems. Biomass of attached algae was controlled by frequently scrubbing the upper walls with abrasive pads. Attached algae was restricted to the upper 0.5 m of columns with high planktonic algal production due to shading by the latter.

Water loss due to evaporation was 10-30 L•day^{-1} from each column. Deionized water was added on a regular basis and always prior to sampling days to maintain a constant column volume, thus preventing artifacts in ion concentration.

10.2 NUTRIENT TREATMENTS

10.2.1 Phosphorus

Total phosphorus loadings were approximately equivalent for all treatments. Loading was based on the rate of 1.1 g P•m^{-2}•yr^{-1}, previously reported for Lake Erie (Anon., 1969). The volume or weight of the respective treatments required to achieve the desired loading was dependent on the form and concentration of phosphorus in each treatment. Samples of all treatments were analyzed for phosphorus and nitrogen (Tables 1 and 2).

River Water (RWT)

A bulk sample for RWT was collected from Twenty-Mile Creek near Smithville in PLUARG agricultural watershed AG-10. Total phosphorus (TP) averaged 0.197 $mg•L^{-1}$ with soluble reactive phosphorus (SRP) comprising about 50% of this total. Approximately 12.6 L of river water was added to two columns daily.

Sewage Effluent (SET)

Several batches of tertiary-treated, sewage effluent were collected from the Skyway Sewage Treatment Plant, Burlington. Total phosphorus concentrations varied considerably between batches but loading was equivalent to the other treatments for the important initial phase of the experiment. Loadings subsequently decreased because the volume of effluent added daily (0.95 L) was held constant although phosphorus concentrations had unknowingly decreased.

Total phosphorus concentration was 2.5 and 1.4 $mg•L^{-1}$ for batches a and b respectively that were used for most of the experiment. Soluble reactive phosphorus was 80% of the total in batch a and 32% in batch b.

Bluff Material (BMT)

Material was collected from clay bluffs several miles east of Port Stanley, Ontario.

Table 1. Concentrations and Loadings of Phosphorus in the Treatments

Aqueous Treatments	Concentration (µg P•L^{-1})		Amount of Treatment Added Daily	Loading (mg P•day^{-1})	Addition Period
	Total	Soluble Reactive			
Phosphoric Acid-Control [a]	5600	5600	0.35 ml	1.98	1 - 42
			0.70 ml	3.95	43 - 72
Sewage effluent a)	2.500	2.00	0.95 L	2.37	1 - 18
b)	1.400	0.45	0.95 L	1.33	19 - 38
c)	0.400	0.035	0.95 L	0.38	39 - 42
d) Same batch as c			1.69 L	0.68	43 - 59
River water	0.197	0.091	12.6 L	2.48	1 - 45
	Concentration (µg•g^{-1})				
Particulate Treatments [b]	Total	Inorganic			
Bluff Material	638	619	3.58 g	2.28	1 - 45
Grand R. particulates[c]	1767	1057	1.34 g	2.37	46 - 80
Yeast Extract Blank [d]	10000	5000	0.024 g	0.24	1 - 59

[a] Bluff material II switched to same loading on day 46

[b] Concentration as µg P•g^{-1} dry weight of solids; amounts added on dry weight basis

[c] Bluff material I switched to this treatment on day 46

[d] Approximate composition.

Table 2. Concentrations and Loadings of Nitrogen in the Treatments and Supplemental Loadings

Treatment	Concentration in Treatment (mg•L^{-1})			Amount of Treatment Added Daily	Treatment Loading (mg•day^{-1})			Supplemental Loading (mg•day^{-1})		Total Loading mg N•day^{-1}	N:P in Loading	Addition Period
	Total	NH_3-N	NO_2+NO_3-N		Total	NH_4-N	NO_3+NO_2-N	NH_4-N	NO_3+NO_2-N			
Phosphoric Acid-Control	nil			0.35 ml	nil			12.54	29.25	54.33	27.5	1 - 42
				0.70 ml				25.09	58.51	108.66	27.5	43 - 73
Sewage Effluent a)	14.82	12.0	0.02	0.95 L	14.08	11.38	0.02	-	29.25	43.30	18.3	1 - 18
b)	[a]	20.0	0.22	0.95 L	19.17	18.96	0.21	-	29.25	48.42	36.5	19 - 38
c)	12.10	2.4	6.50	0.95 L	11.50	2.28	6.18	-	29.25	40.75	107.2	39 - 42
d)	Same batch as c			1.69 L	20.45	4.06	10.99	-	29.25	49.70	73.1	42 - 59
River Water	3.65	0.16	2.35	12.6 L	45.99	2.02	29.61		-	45.99	18.5	1 - 45
Bluff Material	250 (µg•g^{-1}) [b]			3.58 g	0.908			6.27	35.92	43.10	18.90	1 - 80[c]
Yeast Extract-Blank [d]	14.50 (µg•g^{-1})	13.00	1.50	0.024 g	0.35	0.31	0.04	-	-	0.35	1.5	1 - 43
	14.50	13.00	1.50	0.024 g	0.35	0.31	0.04	6.27	35.92	42.54	177.3	43 - 59

[a] Kjeldahl-N not available; total N is NH_4-N + NO_3+NO_2-N

[b] Fixed, NH_4-N, considered unavailable

[c] Phosphorus treatments changed at day 46 but N additions unchanged

[d] Approximate composition

Dried samples contained 638 $\mu g \bullet g^{-1}$ phosphorus, 90% of which was inorganic and known to be apatite (Williams *et al*, 1976), A suspension of 3.6 g dried bluff material and water was added to two columns daily.

Grand River Particulates (GRPT)

A bulk sample of suspended particulate matter was collected from the Grand River in Dunnville, Ontario, by centrifugation through a Westfalia 4-bowl, continuous-flow centrifuge (Model KDD 605) (R.L. Thomas, unpublished method). The centrifuged particulates were resuspended in water and refrigerated. Total phosphorus in oven-dried samples of the particulates was three times that of the bluff material (1767 $\mu g \bullet g^{-1}$) and 40% of the total phosphorus was organic. On day 46 and thereafter, the treatment to BMT(I) was replaced with a volume of the Grand River particulate slurry, sufficient to yield an equivalent phosphorus loading. Moisture content of the slurry was checked regularly.

Phosphoric Acid Control (PAC)

One column received an equivalent loading of total phosphorus in a completely available form for algal growth (H_3PO_4). The results served for comparison as the maximum response that could be expected in the experiment. Loading was doubled after day 43 to determine if a maximum response had been obtained in the earlier part of this treatment.

Phosphoric Acid Control for Grand River Particulates (PAC-GRPT)

On day 46 and thereafter, BMT(II) was switched to an equivalent loading of phosphorus in the form of H_3PO_4. Response of this treatment was compared to GRPT to determine the potential response under the conditions for algal growth present at this time.

Yeast Extract Blank (YEB)

Previous work suggested yeast extract contained a nutrient or "growth factor" that increased algal growth in the presence of high loadings of all nutrients. Small additions of yeast extract were deemed essential to minimize growth limitations by any nutrient other than phosphorus. All treatment columns received 24 mg of yeast extract daily which supplied an additional 10-15% of the treatment phosphorus load. One column received 24 mg of yeast extract daily as its sole phosphorus source other than that received through fallout in the lab and the water used to fill the columns. This column served as a background response considered to be present in all treatments.

10.2.2 Nitrogen

Nitrogen limitation of algal growth was eliminated by supplemental additions of inorganic nitrogen to all treatments except RWT. RWT contained an adequate supply of nitrogen on its own (N:P, 18.5:1) and a reasonably good balance between ammonia (0.160 $mg \bullet L^{-1}$) and nitrate (2.35 $mg \bullet L^{-1}$). On the other hand, sewage effluent contained nitrogen primarily as ammonia, 12 and 20 $mg \bullet L^{-1}$ in batches a and b respectively. Supplemental additions of nitrogen as nitrate (29.25 $mg \bullet day^{-1}$) were made to SET to ensure both ions were present.

Nitrogen in SET did not vary as widely as phosphorus and supplemental additions of nitrate were kept constant resulting in high and fluctuating N:P ratios in the treatment. Nitrogen in the bluff material was in the form of fixed NH_4^+ (H. Wong, CCIW, personal communication) and considered to be unavailable. Columns receiving bluff material were given 6.27 mg N as ammonia and 35.92 mg N as nitrate daily. These nitrogen additions were continued unchanged when phosphorus treatments to these two columns were changed to Grand River particulates and phosphoric acid. After day 42, YEB received these same supplemental nitrogen additions. PAC required all its nitrogen as supplemental loading. Additions of 12.54 mg N as ammonia and 29.25 mg N as nitrate were made daily until day 42. After this date, nitrogen additions were doubled to maintain a constant N:P ratio when phosphorus additions were doubled.

10.2.3 Macro- and Micronutrients

Other major nutrients such as Ca, Mg, Na, C, Si and Fe were added in proportion to the phosphorus loading but in proportions relative to each other similar to the composition of Chu 10 culture medium (Table 3). Micronutrient solutions used in Bristol's medium were also added on a similar basis.

10.3 ALGAL INOCULUM

Approximately 20 L of a mixed species, algal culture were added to each column. The algae was previously grown as a batch culture at a phosphorus concentration of 5 $\mu g \bullet L^{-1}$ until signs of phosphorus limitation were evident, such as yellowing and rapid

Table 3. Supplemental Loadings of Macro- and Micronutrients

Element	Loading
Macronutrients (mg•day^{-1})	
Ca	41.79 (sewage effluent) 51 .32 (other treatments)[a]
Mg	3.84
Na	13.99
C	3.57
Si[b]	10.96
Fe	0.44
Micronutrients (µg•day^{-1})	
Co	20.87
Cu	84.40
B	425.49
Mn	102.65
Mo	99.40
Zn	419.49

[a] River water treatment received no additional Ca

uptake of radioactive phosphorus. Chlorophycean genera such as *Ankistrodesmus*, *Scenedesmus, Coelastrum, Chlamydomonas* and *Chlorella* were the most abundant algae in the inoculum.

10.4 NUTRIENT AND ALGAL BIOMASS PARAMETERS

Composite water samples were collected from the UL of each column with a tube sampler. Composite samples were collected from the LL by pooling aliquots taken from different sampling ports. Chemical analyses were performed by the Water Quality Laboratories at CCIW, Burlington. Analytical procedures are outlined in the Analytical Methods Manual (1975). Nutrient analyses included: total phosphorus, total dissolved phosphorus, soluble reactive phosphorus, Kjeldahl nitrogen, nitrate-nitrite, ammonia, particulate organic carbon and dissolved inorganic carbon. Water samples for chlorophyll a analyses were filtered through GF/C filters, frozen and later analyzed using dimethyl sulfoxide as an extractant (K. Burnison, unpublished manuscript). This method is more efficient when green algae are abundant than methods involving grinding and extraction with acetone. Samples for seston dry-weight were filtered through ashed, pre-weighed, GF/C filters, dried at 60°C and reweighed.

10.5 ZOOPLANKTON

Composite samples (250 ml) taken from the middle of each column were used for enumeration of *Bosmina* spp. The total number of animals in each sample was later enumerated under a dissecting microscope.

10.6 PRIMARY PRODUCTION

Three light and one dark bottle (130 ml) were filled with composite water from the epi, spiked with ca. 2 µCi each of $Na_2{}^{14}CO_3$ and suspended *in situ* for 2-4 h at 25 cm. Incubation at this depth had consistently yielded light-saturated primary production rates in previous work. At the end of the incubation, 25-50 ml from each bottle was filtered through a 0.45 µm membrane filter (Sartorius Co.) and immediately dissolved in PCS liquid scintillation cocktail (Amersham Co.). Radioactivity on filters was counted using liquid scintillation techniques and quench corrected using the sample channels ratio method. Rates of carbon uptake were calculated following the procedure of Vollenweider (1974) using direct estimates of total dissolved inorganic carbon.

10.7 SEDIMENTATION

A darkened glass jar 8 cm deep, 9 cm in diameter was suspended at 3.0 m in each column and retrieved every three to four days. The trap contents were shaken and aliquots filtered through dried, pre-weighed GF/C filters for determinations of dry weight, particulate carbon, nitrogen and phosphorus.

11.0 RESULTS

11.1 NUTRIENTS

11.1.1 Phosphorus

Concentrations of total phosphorus in the UL of several treatments (RWT, SET, GRPT and PAC) averaged 20-25 µg•L^{-1} while BMT and YEB averaged less at about 14 µg•L^{-1} over the respective experimental periods (Table 4). The highest concentrations (40-50 µg•L^{-1}) were in RWT and SET although these treatments also exhibited the largest fluctuations in total phosphorus concentrations while the PAC varied the least (Fig. 2). Concentrations of soluble reactive phosphorus were low in all treatments, averaging only 1-3 µg•L-^{1} over the various experimental periods.

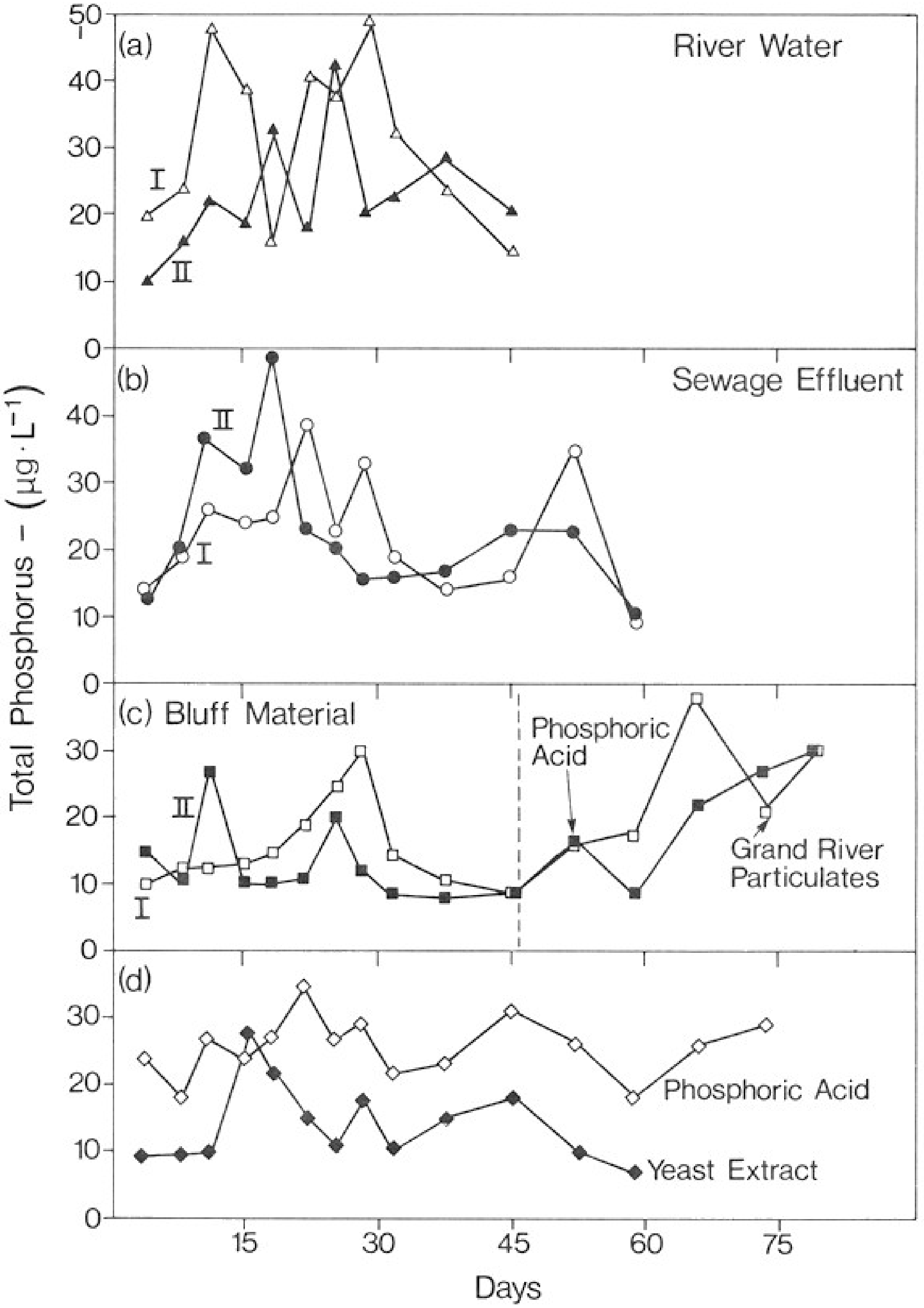
11.1.2 Nitrogen

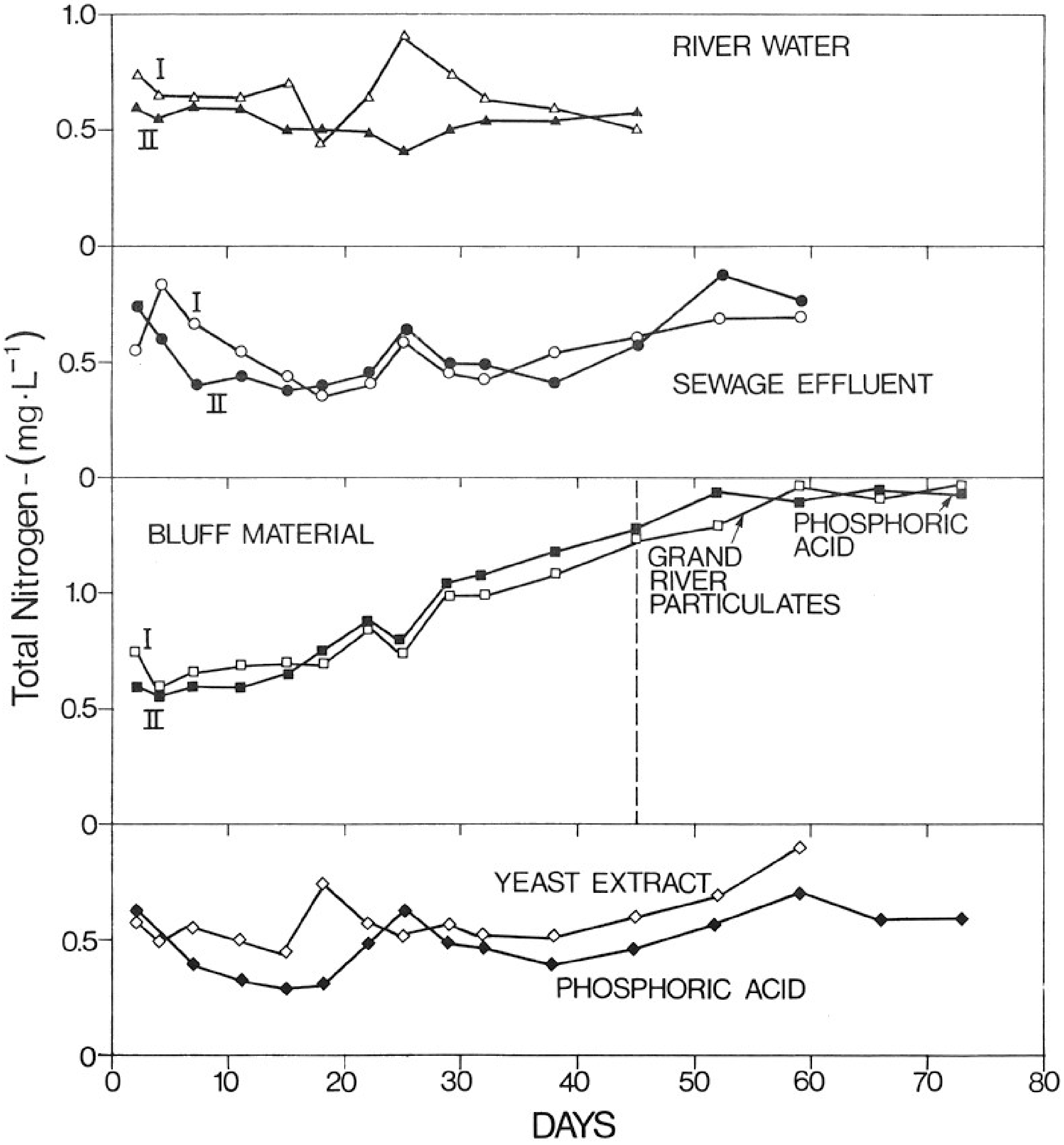
Total nitrogen in the UL averaged 0.500-0.600 mg•L^{-1} in PAC, RWT, SET and YEB over the entire experiment. BMT averaged higher at approximately 0.800 mg•L^{-1} and both PAC-GRPT and GRPT averaged yet higher at 1.40 mg•L^{-1}. The more productive treatments (RWT, SET and PAC) showed the least fluctuations in total nitrogen concentrations (Fig. 3). Nitrogen to phosphorus ratios were highest in YEB, BMT, GRPT and PAC-GRPT. Nitrate concentrations showed a negative relationship with chlorophyll a (Fig. 4). Treatments with the lowest chlorophyll concentrations accumulated nitrate in the UL. Concentrations of nitrate averaged 0.500-0.600 mg•L^{-1} in BMT, GRPT and GRPT accounting for an average of approximately 60% of the total nitrogen in the UL. The high concentration of nitrate in

TABLE 4. Average Concentrations of Total Phosphorus (TP), Soluble Reactive Phosphorus (SRP), Total Nitrogen (TN), Nitrate-Nitrogen (NO_3) and Total Nitrogen to Total Phosphorus Ratios (N:P) in the Upper Layer.

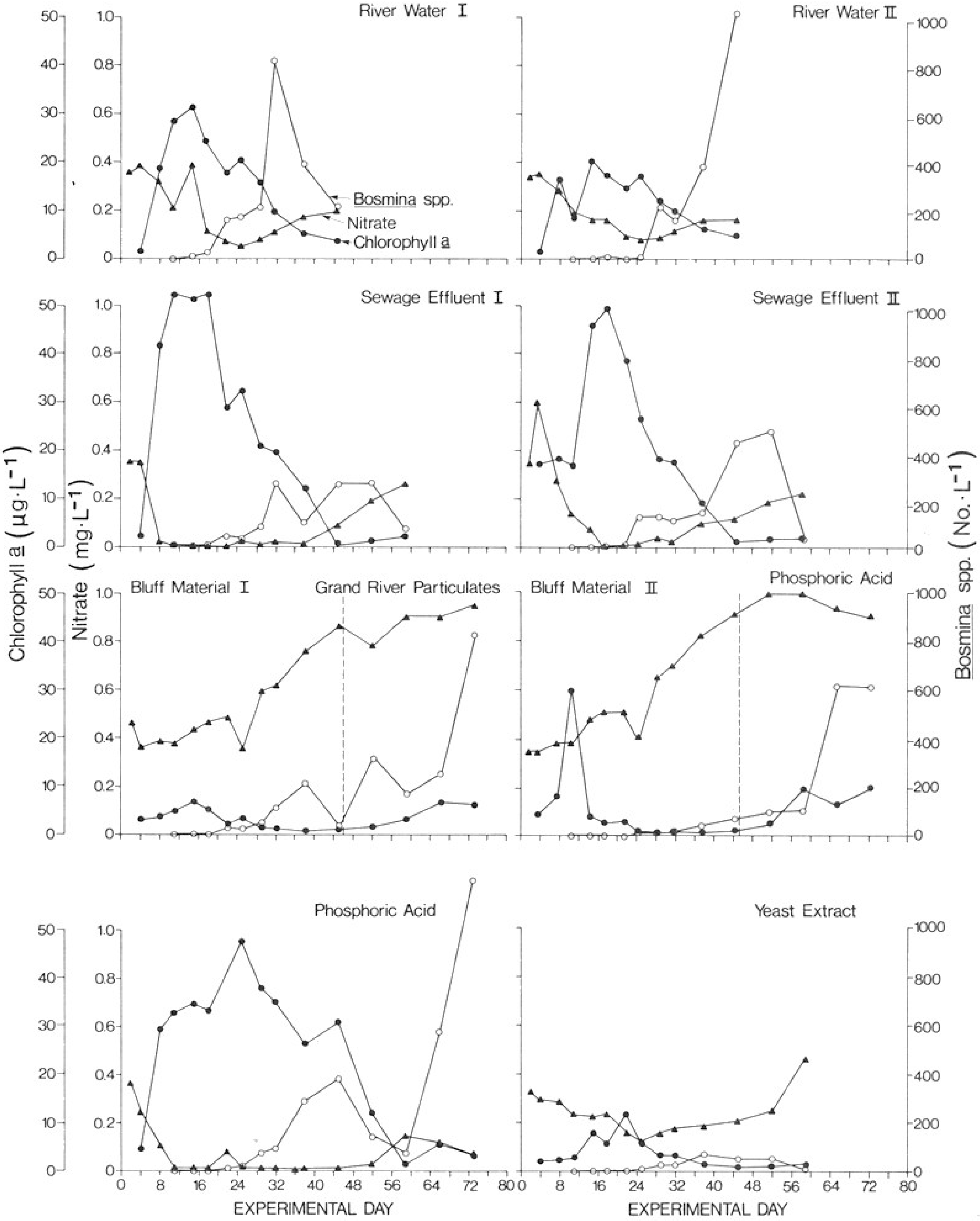
	Phosphorus ($\mu g \bullet L^{-1}$)		Nitrogen ($mg \bullet L^{-1}$)		
Treatment [a]	TP	SRP	TN	NO_3	N:P
Phosphoric Acid-Control for Grand River Particulates	24.9 ± 5.6	2.5 ± 2.5	0.500 ± 0.123	0.072 ± 0.102	22
Sewage Effluent	23.1 ± 10.4	3.0 ± 3.8	0.556 ± 0.144	0.125 ± 0.151	31
River Water	26.9 ± 11.8	3.4 ± 3.1	0.598 ± 0.109	0.190 ± 0.109	26
Bluff Material	14.2 ± 6.0	2.9 ± 2.7	0.835 ± 0.220	0.523 ± 0.078	70
Grand River Particulates	23.5 ± 10.2	0.9 ± 0.3	1.424 ± 0.072	0.883 ± 0.072	69
Phosphoric Acid-Control for Grand River particulate	18.5 ± 7.7	1.1 ± 0.6	1.438 ± 0.013	0.963 ± 0.045	92
Yeast Extract-Blank	14.0 ± 5.9	1.4 ± 0.8	0.584 ± 0.121	0.231 ± 0.088	49

[a] Average based on combined values where treatment replicated


Total Phosphorus – (µg·L⁻¹)
(a)
River Water
I
II
(b)
Sewage Effluent
II
I
(c) Bluff Material
II
I
Phosphoric Acid
Grand River Particulates
(d)
Phosphoric Acid
Yeast Extract
0
10
20
30
40
50
15
30
45
60
75
Days



Total Nitrogen - (mg·L⁻¹)
DAYS
0
10
20
30
40
50
60
70
80
1.0
0.5
0
RIVER WATER
I
II
SEWAGE EFFLUENT
BLUFF MATERIAL
GRAND RIVER PARTICULATES
PHOSPHORIC ACID
YEAST EXTRACT
PHOSPHORIC ACID


River Water I
River Water II
Bosmina spp.
Nitrate
Chlorophyll a
Sewage Effluent I
Sewage Effluent II
Bluff Material I
Grand River Particulates
Bluff Material II
Phosphoric Acid
Phosphoric Acid
Yeast Extract
Chlorophyll a (µg·L⁻¹)
Nitrate (mg·L⁻¹)
Bosmina spp. (No.·L⁻¹)
0
10
20
30
40
50
0
0.2
0.4
0.6
0.8
1.0
0
200
400
600
800
1000
0
8
16
24
32
40
48
56
64
72
80
EXPERIMENTAL DAY
EXPERIMENTAL DAY

the tap water used to fill the columns produced concentrations over 0.300 mg•L^{-1} in all columns immediately after filling. This source of inorganic nitrogen was apparently adequate to prevent nitrogen limitation in YEB because concentrations declined slowly and remained higher than in more productive treatments where nitrogen demand was high. Ammonia levels averaged less than 0.050 mg●L^{-1} in all treatments

11.2 ALGAL BIOMASS AND PRIMARY PRODUCTION

Maximum values attained by the various treatments for indices of algal biomass and primary production were used for comparison. Zooplankton grazing in later stages of many treatments was an unexpected additional variable that complicated comparison of means. Where treatments were replicated (RWT, SET and BMT) the maximum values from replicates were averaged.

11.2.1 Chlorophyll a

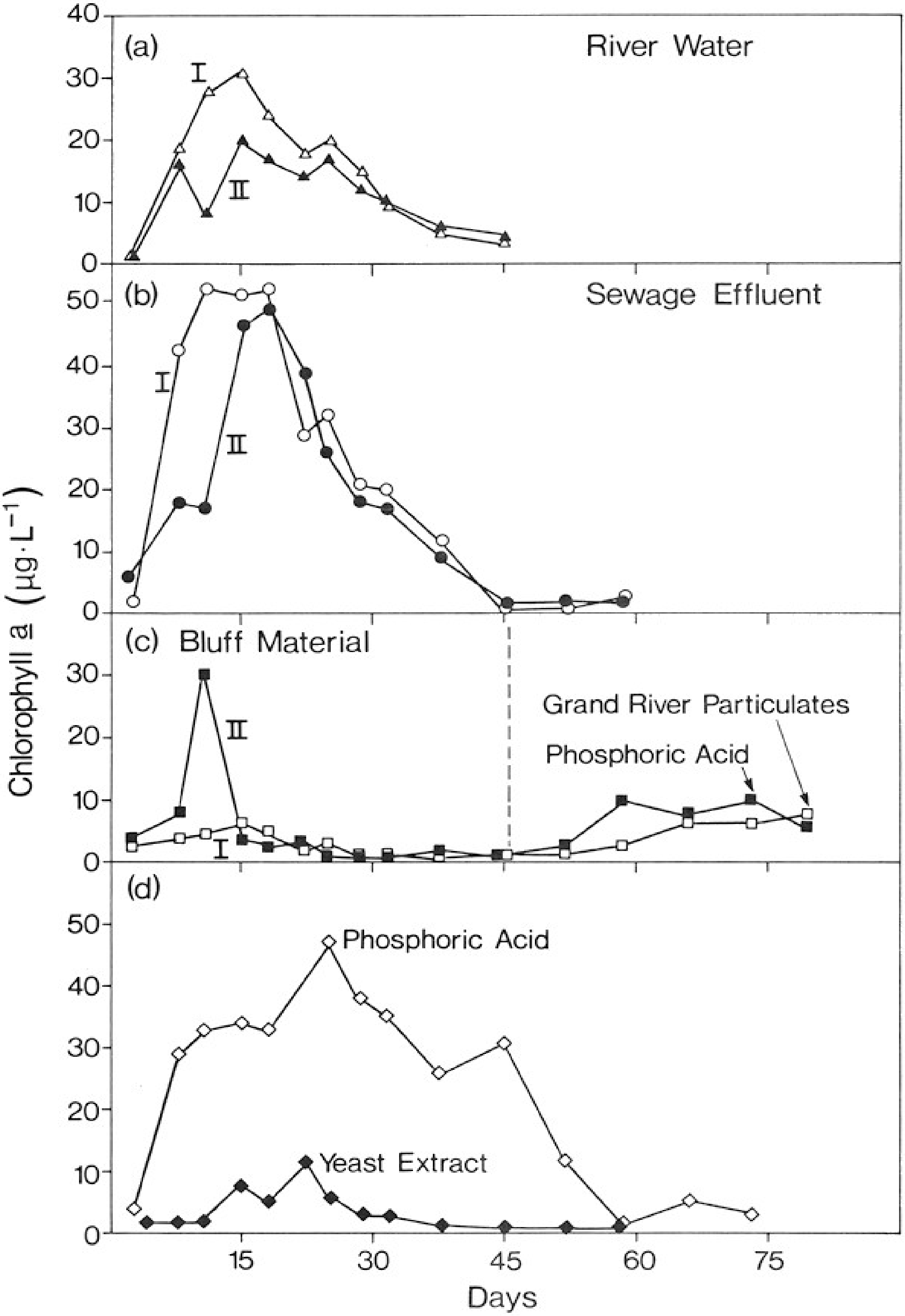
PAC and SET had similar maximum chlorophyll a concentrations of 47.3 and 50.7 µg•L^{-1} respectively (Table 5). The other treatment with high chlorophyll concentrations was RWT at 25.6 µg•L^{-1}. Deletion of an atypically high observation in one replicate reduced the maximum chlorophyll concentration in BMT from 18.1 to 7.2 µg•L^{-1}. Maximum concentrations for the other treatments (YEB and GRPT) were similar to BMT at 11.5 and 6.6 µg•L^{-1}, respectively, in SET, RWT and PAC maximum chlorophyll concentrations were reached by day 15 but declined rapidly thereafter, starting as early as day 20 in SET and RWT (Fig. 5). Concentrations of chlorophyll a declined during the middle portion of the

Table 5. Concentrations[a] of Various Indices of Algal Biomass (Chlorophyll a, Particulate Organic Carbon (POC), Seston Dry Weight and Ash-Free Dry Weight) and Primary Production Rates

Treatment	Chlorophyll a (µg•L^{-1})	POC (mg•L^{-1})	Seston		Primary Production (mg C•m^{-3}●h^{-1})
			Dry Weight (mg•L^{-1})	Ash-Free Dry Weight (mg•L^{-1})	
Phosphoric Acid-Control	47.3	5.50	11.15	9.99	156.4
Sewage Effluent	50.7	4.55	11.07	10.27	196.4
River Water	25.6	2.35	9.25	7.71	108.8
Bluff Material	18.1 (7.2)[b]	1.10	4.26	2.64	26.4
Grand River Particulates	6.6	1.40	3.30	2.43	45.7
Phosphoric Acid-Control for Grand River Particulates	9.8	1.40	3.17	3.11	101.3
Yeast Extract-Blank	11.5	1.40	2.80	2.57	20.0

[a] Maximum value for the various parameters presented; where treatments replicated maximum value from both columns averaged.

[b] Bracketed value is maximum if one value from one replicate deleted.



(a) River Water
I
II
(b) Sewage Effluent
I
II
(c) Bluff Material
II
I
Grand River Particulates
Phosphoric Acid
(d)
Phosphoric Acid
Yeast Extract
Chlorophyll a (μg·L⁻¹)
0
10
20
30
40
50
15
30
45
60
75
Days

experiment (day 20 to 45) to <1 µg•L^{-1} in BMT and YEB; however, concentrations increased when these two columns were switched to GRPT and PACGRPT.

11.2.2 Particulate Organic Carbon (POC)

The use of chlorophyll a concentrations alone as an indicator of algal biomass should be avoided because of the varying nature of chlorophyll content of algae (Steel, 1962; Munawar and Burns, 1976; Paerl *et al.*, 1976). Without direct estimates of biomass it was felt that several indices of algal biomass should be employed. Similar to chlorophyll a, PAC (5.50 mg•L^{-1}) and SET (4.55 mg•L^{-1}) had the highest maximum concentrations of POC of all treatments. While RWT had a maximum POC concentration of 2.35 mg•L^{-1}, BMT, GRPT and its control and YEB all had similar maximum POC concentrations of 1.10 - 1.40 mg•L^{-1}.

11.2.3 Seston Weight

Dry weight of suspended solids, or seston weight, is often used as a base of reference in productivity and physiological studies (Vollenweider, 1974). In our experiment this parameter was the least reliable of the various indices of biomass measured unless correction for ash content was made. Sufficient quantities of soil particles from BMT itself were kept in suspension in the UL of this treatment to contribute significantly to the seston weight (*ca.* 38% ash in BMT). Only several measurements of ash content were possible but the difference in ash content between BMT and other treatments was obvious. All other treatments and controls, except BMT and GRPT had ash contents of less than 20% of the seston weight. It is noteworthy that ash content of seston samples from RWT was slightly higher than some of the treatments at 16.6% and reflects the load of suspended sediment carried by rivers in the spring. The ash content of seston from BMT(I) fell markedly to 26% when the treatment was changed to GRPT, indicating an increase in the proportion of organic detritus in treatment material itself.

11.2.4 Primary Production

SET and PAC had the highest maximum primary production rates at 196 and 156 mg C•m•$^{-3}$h^{-1} respectively. RWT and PAC-GRPT also achieved rates in excess of 100 mg C•m•$^{-3}$ h^{-1}. Peak values in these two treatments and the control were achieved by day 15 (Fig. 6). Rates were on the decline by day 30 in RWT and SET while PAC sustained rates over 100 mg C•m•$^{-3}$ h^{-1} until day 45 but subsequently declined. In contrast to the indicators of algal biomass, the maximum primary production rate for GRPT was double that of BMT which had a maximum rate similar to the background response exhibited by YEB (20-25 mg C•m^{-3} h^{-1}).

11.3 RELATIVE RESPONSE TO TREATMENTS

The response to the various phosphorus treatments can be evaluated in a relative manner by comparison to the response of PAC. Maximum algal biomass should have been attained by the control for the experimental conditions imposed because phosphorus in this form readily dissociates to orthophosphate.

SET exhibited an overall response equivalent to PAC (Table 6).

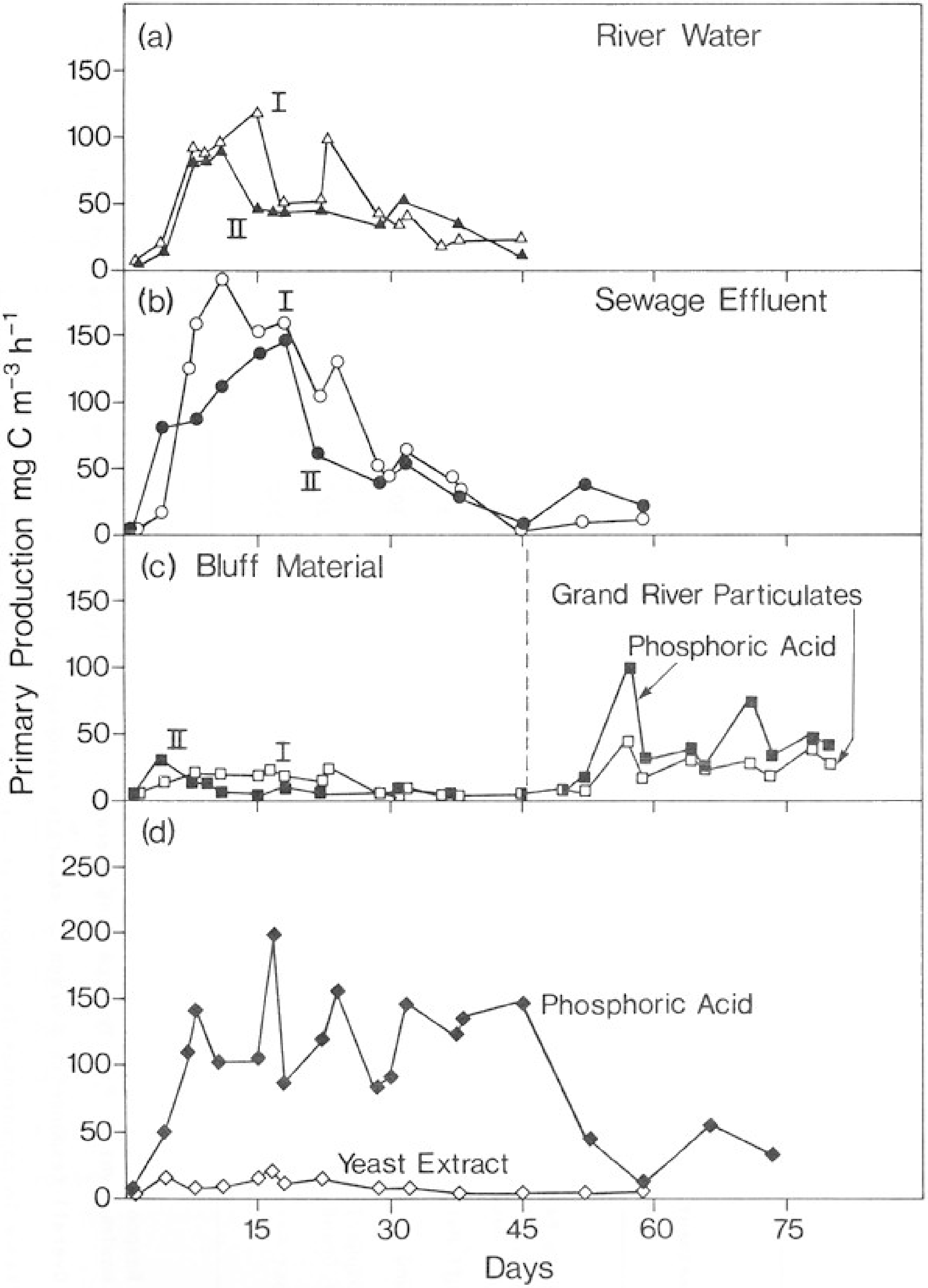

(a)
River Water
I
II
(b)
Sewage Effluent
I
II
(c) Bluff Material
II
I
Grand River Particulates
Phosphoric Acid
(d)
Phosphoric Acid
Yeast Extract
Primary Production mg C m⁻³ h⁻¹
0
50
100
150
200
250
15
30
45
60
75
Days

Table 6. Response[a] of Various Treatments in Indices of Algal Biomass and Primary Production Relative to the Control Response

Treatment	Chlorophyll a	POC	Seston		Primary Production	Overall [b]
			Dry Weight	Ash-Free Dry Weight		
Sewage Effluent	107	83	99	103	126	104
River Water	54	43	83	77	70	65
Bluff Material	38 (15)[c]	20	38	26	17	28
Grand River Particulates	14	25	30	24	29	24
Phosphoric Acid-Control for Grand River particulates	21	25	28	31	65	34
Yeast Extract-Blank	24	25	25	26	13	23

[a] Response based on maximum value reached for various parameters in each column; where treatments replicated maximum values from both columns averaged; response is treatment value as a percent of control value.

[b] Overall response is average of separate responses.

[c] Value in parentheses is response if a single value from one replicate is not used.

Maximum values for all standing crop parameters and primary production in SET either equalled or exceeded those achieved by PAC with the exception of a slightly lower POC value of 83%. RWT had the second highest overall response relative to the control of 65%. Relative response of the various parameters in RWT varied between 43 and 77% of the control for POC and ash-free dry weight respectively. The other treatments (BMT, GRPT) had overall relative responses very similar to the background response of 23%. The overall response of PAC-GRPT was higher at 34% but this was biased by the high relative response of 65% for primary production. The overall relative response of biomass parameters only as compared to PAC was similar to the blank at 26%. Relative response for most of the parameters in BMT, GRPT, PAC-GRPT and YEB were between 20 and 30% of the PAC. Correction of seston weight for ash content lowered the relative response of BMT for this parameter from 38 to 26% because of the misleading contribution the bluff material itself made to seston weight.

11.4 ZOOPLANKTON

Development of populations of *Bosmina* spp. followed a similar pattern of development in all treatments except YEB. Animals were present by day 25 in all columns and developed between days 30 and 50 in RWT, SET and PAC. Numbers were low in BMT (< 75 L^{-1}) until the treatment changed and subsequently increased several fold. Peak densities were highest in RWT and PAC at (800-1000 L^{-1}) intermediate in GRPT and its control (600-800 L ^{1}) and lower in SET (200-400 L^{-1}) and YEB (<50 L^{-1}).

11.5 SEDIMENTATION OF NUTRIENTS

The amount of particulate nitrogen and phosphorus sedimented in each column per day was expressed as a percentage of the total amount of that nutrient in the UL of each column (Table 7). This total was derived from two concentrations, one preceding, the other following the time period during which a sediment trap was suspended.

The three treatments showing the greatest response to phosphorus treatments in terms of algal biomass and primary production (PAC, SET, RWT) sedimented the highest percentages (4.2 - 5.5% day $^{-1}$) of the total nitrogen pool in the UL. All other treatments sedimented approximately (1% day^{-1}) of the nitrogen in the UL.

The reverse situation occurred with respect to sedimentation of phosphorus. BMT, which had the smallest standing crops of algae, sedimented the highest percentage of its UL phosphorus pool of all the treatments (8.8% day^{-1}). The more productive treatments (PAC, SET, RWT) as well as GRPT, all sedimented about 5% day^{-1} of their UL pool of phosphorus. PAC-GRPT and YEB sedimented slightly less phosphorus at 3.2 and 3.8% day^{-1} respectively. Sedimentation showed large unexpected increases at certain times in most treatments. The rather high standard deviations are the result of one or two high sedimentation periods of a few days duration in most cases.

12.0 DISCUSSION

Quantifying the supply of orthophosphate in our aqueous treatments, the most

Table 7. Percentages of the Total Phosphorus and Nitrogen in the Upper Layer Sedimented per Day

Treatment[a]	Phosphorus (%•day $^{-1}$)	Nitrogen (%•day $^{-1}$)
Phosphoric Acid-Control	4.9 ± 2.6	5.5 ± 5.2
Sewage Effluent	5.2 ± 2.3	4.3 ± 2.6
River Water	4.8 ± 3.6	4.2 ± 4.0
Bluff Material	8.8 ± 5.4	1.0 ± 0.8
Grand River Particulates	4.8 ± 2.3	1.1 ± 1.1
Phosphoric Acid-Control for Grand R. Particulates	3.2 ± 0.5	0.8 ± 0.6
Yeast Extract Blank	3.8 ± 2.2	1.1 ± 1.1

[a] Average based on combined values where treatment replicated

readily available form of phosphorus for algal growth, is plagued with difficulties. Unfortunately, analytical techniques presently employed to measure this ion, consistently overestimate its concentration as a methodologically defined compartment termed, soluble reactive phosphorus (SRP) (Rigler, 1966, 1968). Furthermore, orthophosphate is constantly and rapidly exchanged with the colloidal and particulate components of the total phosphorus pool, making measurements of concentration rather meaningless in terms of potential supply (Lean, 1974; Peters, 1978). Loading of SRP was equivalent between SET and PAC but it is uncertain, for the above reasons, whether loading of orthophosphate was the same. Both the high concentration of total phosphorus in the first batch of effluent (2.5 mg P•L^{-1}) and percentage of SRP (80%) indicate that orthophosphate was plentiful in SET. It was also apparent from the growth response to SET that this treatment and the control provided comparative supplies of bioavailable phosphorus.

High molecular weight forms of phosphorus often exist in dissolved fractions, test as soluble reactive phosphorus and show growth yields equivalent to orthophosphate in incubations longer than 96 h (Paerl and Downes, 1978). On the other hand, standing crops equivalent to those attained by PAC could possibly have occurred at lower phosphorus loadings if factors such as light or sedimentation had become limiting for either growth or accumulation of standing crops at the loading employed.

The comparatively lower standing crops of algae in RWT were likely the result of a decrease in the proportion of soluble phosphorus in this treatment. Suspended solids in this river do contain relatively high concentrations (493 µg•g-^{1}) of non-apatite phosphorus

(NAIP) (Williams *et al.*, 1979). A good correlation between algal growth and concentration of NAIP in sedimentary materials has been demonstrated by these researchers; however, in our experiment the river water supplied only 0.48 µg•day^{-1} of NAIP compared to 1.147 mg P•day^{-1} as SRP. Similar to SET it was likely orthophosphate and other dissolved phosphorus compounds supported algal growth.

The lack of increased algal growth in BMT over the background response of YEB, indicated that bluff material supplied negligible quantities of bioavailable phosphorus. Apatite phosphorus (AP) comprises 95%, but NAIP only 3%, of the total phosphorus in bluff material (Williams *et al.*, 1976). In addition, apatite is only sparingly soluble under the alkaline conditions of our experiment (Brown, 1966). Our daily addition of 3.6 g of bluff material would have supplied approximately 68 µg•day^{-1} of NAIP at a concentration of 19 µg•g^{-1} NAIP in bluff material. The supply of available phosphorus from this source was small considering that 240 µg of orthophosphate was supplied daily by yeast extract additions. In addition, the concentration of total phosphorus in the initial fill was 5-10 µg•L^{-1}.

Our results, and those of Williams and co-workers, are in conflict with the findings of Smith *et al.* (1977). These authors found substantial development of algal communities in 40 L glass tanks when ground apatite was supplied as the sole phosphorus source. This disparity in results may have arisen because the apatite in the latter study was very finely ground (crystals 38-100 µm) thereby enhancing solubility (Brown, 1966; Wier *et al.*, 1971.

The higher relative loss rates from the UL phosphorus pool in BMT, compared to other treatments and controls, was likely the result of rapid sedimentation of apatite crystals associated with soil particles in the treatment itself. A lower "steady state" concentration of total phosphorus in the UL should have resulted because loadings were equivalent between treatments yet relative loss rates differed. Although total phosphorus concentration fluctuated considerably in BMT, as it did in all treatments, the average concentration was considerably less (14 $mg{\bullet}m^{-3)}$ than the other treatments (20-25 $mg{\bullet}m^{-3}$). If higher relative loss rates were the cause of the lower average total phosphorus concentration then the absolute sedimentation rates of total phosphorus should have been higher in BMT compared to other treatments. In fact, the average sedimentation rate of phosphorus over the treatment period (replicates averaged) for BMT were similar to PAC at 1.77 ± 1.05 mg $P{\bullet}column^{-1}{\bullet}day^{-1}$ compared to 1.94 ± 1.01 mg $P{\bullet}column^{-1}{\bullet}day^{-1}$ for the control.

The reasons for this discrepancy are not entirely clear but the most plausible explanation is that sedimentation rates of the bluff material were underestimated with our method. The heterogeneous nature of both the material, in terms of particle size distribution, and the horizontal pattern of sedimentation were possible contributing factors. Visually we noted that when the slurry containing bluff material was added to the column, the distribution of large particles was patchy and their settling rate was very rapid compared to the cloud of smaller particles that was homogeneously dispersed. It is possible that a significant proportion of the phosphorus in the sample was contained in large particles that settled out in a patchy distribution and missed our sediment trap. Previous work on sedimentation in the column indicated that this method does underestimate sedimentation rates (K. Minns, personal communication).

Daily additions of inorganic nitrogen at N:P ratios high enough (>15:1) to preclude the possibility of nitrogen limitation on algal growth (Ryther and Dunstan, 1971; Claesson and Ryding, 1977) enables concentrations of inorganic nitrogen to show an inverse relationship with phosphorus availability. A phosphorus limitation of algal growth causes nitrate to accumulate if additions are sustained. Bioavailable phosphorus supports algal growth and nitrate concentrations will decrease due to uptake by algae.

The accumulation of nitrate in BMT, its rapid disappearance in SET and PAC, and intermediate levels in RWT show this inverse relationship with phosphorus availability. The amount of nitrogen taken up by algae and sedimented in PAC, SET and RWT must have been similar to the amount added daily because total nitrogen concentrations in the UL remained comparatively constant in these treatments. Total nitrogen did show a tendency to increase in the UL of SET and was probably a result of the increase in N:P ratios in the treatment itself. Total nitrogen increased in BMT because nitrate was continually added but not incorporated into algae and sedimented because phosphorus availability limited growth.

Chlorophyll concentrations failed to achieve the levels expected in both GRPT and the control for this treatment; however, the increased bioavailability of phosphorus in

GRPT compared to BMT was reflected in nitrate concentrations. In other treatments nitrate concentrations increased as zooplankton densities built up and cropped algal biomass, thereby decreasing the demand for nitrate. In GRPT, nitrate accumulated at a slower rate than in BMT(I) indicating increased bioavailability of phosphorus and uptake of nitrate for growth. Nitrate concentrations declined in GRPT-PAC indicating an even higher demand for inorganic nitrogen caused by the complete availability of phosphorus in this source.

Chemical analysis indicated GRPT should have supplied more bioavailable phosphorus than bluff material. Organic phosphorus and NAIP each constituted 40% of the total phosphorus in the Grand River particulates while these same two fractions had respective contributions to the total phosphorus of only 2 and 3% in the bluff material (PLUARG, 1978). Our addition rate of these particulates would have supplied approximately 0.948 mg NAIP .day^{-1} which was 48% of the phosphorus loading to the first PAC. If NAIP was readily available then chlorophyll concentrations of 20-30 mg•m^{-3} could have occurred in GRPT provided the relationship between chlorophyll and phosphorus loading was linear in this range. Grazing pressure by populations of *Bosmina* spp. likely limited accumulation of algal standing crop in GRPT and its control and was the probable cause of declines in standing crops in other treatments.

GENERAL DISCUSSION

Our results show that sources of phosphorus loading to the Great Lakes differ drastically in their potential to supply available phosphorus for algal growth. Phosphorus control strategies for municipal point sources have greater cost-effectiveness than originally proposed by PLUARG because of the high availability of phosphorus in this source. The availability of phosphorus in river water in our study has been attributed to the dissolved fraction. The cost-effectiveness of management practices for diffuse sources appears to be increased on the basis of phosphorus availability as well. Although control measures of phosphorus in diffuse sources are aimed at control of phosphorus associated with fine-grained sediment, if total loss of phosphorus from watersheds is reduced then the potential for desorption processes from suspended solids into the dissolved fraction, throughout the watercourse, is reduced.

The impact of phosphorus loading from shoreline erosion on the lower Great Lakes is probably minimal and loadings from this source should continue to be deleted from total phosphorus loading models. Efforts to control shoreline erosion from the standpoint of phosphorus management rather than soil conservation and shoreline protection are out of perspective. We conclude, as others have (Williams *et al.*, 1976, 1979), that low solubility and short residence time of apatite in the emphatic zone of lakes are the major factors limiting the supply of bioavailable phosphorus from eroding bluff material.

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