Metabolic Removal of Phosphate from Sewage Effluent

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Summary

Eutrophication, or fertilization, has become a major water pollution problem associated with the discharge of mineral-rich sewage effluent. A metabolic process to remove dissolved phosphate from sewage through the action of sewage microorganisms is, under development. The process, unlike other proposed solutions to the problem, would not require tertiary treatment of the sewage. Laboratory studies have produced promising data. Early reports from municipal sewage treatment plants confirm the expectation that the process may be feasible for widespread use.

Introduction

By virtue of its efficiency in degrading organic matter, conventional sewage treatment produces effluents relatively rich in dissolved phosphate and nitrate. Most of the suspended sewage matter is removed by the treatment process, and sunlight easily penetrates the fertilized water, promoting dense blooms of algae. These, upon dying, produce serious secondary pollution. The problem has attained such magnitude that it is featured prominently in a report of the President's Science Advisory Committee[1] dealing with all aspects of environmental pollution.

The denial of either nitrogen or phosphorus would preclude the growth of algae. However, some of the offending species can fix nitrogen directly from the atmosphere. Thus, the removal of phosphorus seems to offer the best control over algal growths promoted by sewage effluent.[2] It is believed that the chief, or only, form of phos-

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phorus available to microorganisms is dissolved, inorganic ortho-phosphate.[3] That the control of this phosphate concentration will have a regulating effect on algal growth has been reported by Shapiro and Ribeiro.[4]

To combat sewage fertilization, or eutrophication, pollution control authorities have begun taking action to limit the discharge of sewage phosphate. The first such instance occurred in 1964 when the State of Virginia refused to grant a permit for a new sewage treatment plant and its attendent subdivision unless the treatment process provided for the removal of phosphate. In 1966, the cities of Detroit, Michigan, and Cleveland, Ohio, became obligated to their respective state water pollution control agencies to remove 80% of the dissolved phosphate present in their sewages.

Metabolic Removal of Phosphate

Uptake of phosphate by intensively aerated mixed liquor had been reported by Srinath[5] and Alarcon.[6] In 1961, one of us (GVL), at the suggestion of his advisor, Dr. Joseph Shapiro, undertook to investigate and quantify the phenomenon as his thesis research project.[7] A novel sewage treatment process[8] resulted and was subsequently published.[9] Feng, concurrently and independently, exploring the use of phosphate as an index for operational control of the activated sludge process, reported[10] data on phosphate metabolism highly consistent with the thesis work.

One of the salient features of the phosphate removal process is that, at a rate of aeration in excess of that generally applied to sewage, an apparent "threshold" exists beyond which the rapid uptake of dissolved, inorganic orthophosphate is accomplished by the sewage microorganisms. Furthermore, uptake occurs even in the absence of microbial growth. The phosphate is not tightly bound within the microorganisms and, when the oxygen level falls, orthophosphate leaks out of the cells.

In essence, the process provides for the aeration of mixed liquor (composed of influent raw sewage and microorganisms returned from the process) at a rate sufficiently high to induce the rapid metabolic uptake of phosphate. The microorganisms are then removed in a small fraction of the total flow and are maintained without aeration. The dissolved oxygen content rapidly falls and the phosphate is secreted by the microorganisms into the suspending liquid. The

phosphate-depleted microorganisms constitute the sludge returned to the aeration basin where they take up additional phosphate from the influent raw sewage. The phosphate-rich liquor is conveyed to a basin for chemical precipitation.

As part of the thesis research, the District of Columbia Sewage Treatment Plant was operated for 1 week in a manner in which it could best approximate the desired process conditions. The available rate of aeration was limiting and no arrangement could be made to strip the phosphate from the microorganisms. Nonetheless, the test portion of the plant demonstrated sustained low-order phosphate removal.[7,9] The portion of the plant operated as a normal control discharged a higher concentration of orthophosphate from its aeration basin than was present in the influent end of the basin.

The aforementioned refusal of the State of Virginia to permit the discharge of sewage effluent unless treated for phosphate removal was directed at the Greater Manassas Sanitary District in Prince William County. The consulting engineers retained by the County, Wiley and Wilson of Lynchburg, Virginia, asked Hazleton Laboratories, Inc., to perform further research on the metabolic process so that it might be incorporated into the proposed sewage treatment plant.

In the course of this study,[11] a number of the proposed process parameters were investigated in detail. Some of the results follow.

Aeration

As stated, one of the most critical factors affecting the uptake of phosphate by sewage microorganisms is the rate of aeration. The thesis research determined the amounts of air *applied to*, not *consumed by*, the mixed liquor. Because of differences in geometry, it is impossible to extrapolate from the 2-liter research flasks to plant-scale aeration basins. Accordingly, the apparatus shown in Figure 1, a modified "oxyutilometer"[12] was constructed to permit measurement of rates and amounts of oxygen consumed by mixed liquor.

An extensive series of uptake experiments was conducted. The oxyutilometer revealed that the maximum rates of phosphate uptake obtained were accommodated by an hourly oxygen consumption rate of 100 ml. per liter of mixed liquor. This value, along with an assumed oxygen transfer efficiency of 5% was used to estimate plant-scale maximum air requirements at 3700 cfm per million gallons of sewage per day flowing through the aeration basin. This provides
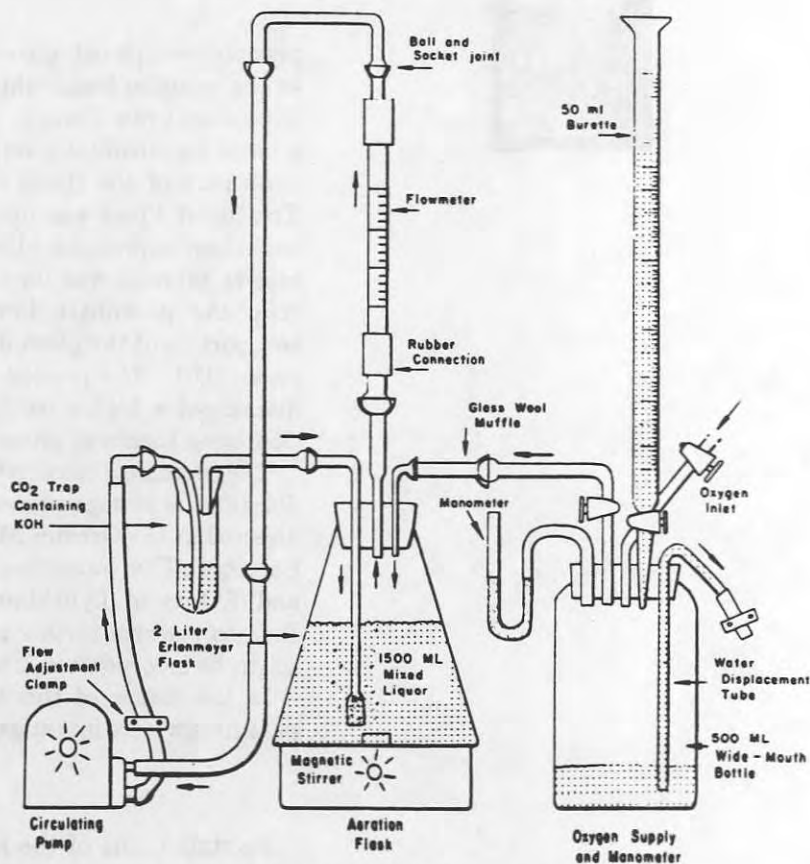
Fig. 1. Modified oxyutilometer.

for the consumption of 4725 lb. of oxygen per day. The maximum aeration period for phosphate and biochemical oxygen demand (BOD) removal was estimated at 4 hr. with considerable reduction in aeration rate in the effluent half of the basin deemed probable.

Suspended Solids

It was previously reported[7,9] that return sludge was necessary for phosphate uptake to occur in aerated sewage. A few per cent, by volume, of return sludge initiated uptake. Increasing the amount of sludge returned showed less than a proportional increase in uptake with marginal effects occurring beyond 40%. In the current work,

the mixed liquors were prepared on the basis of mg./l. suspended solids rather than per cent return by volume. Significant uptake occurred over a suspended solids range of 1075–4270 mg./l. Discussions with the Wiley and Wilson engineers concerned with pumping and tankage practicalities led to the selection of 2500–4000 mg./l. as the desired range.

Temperature

1-hr. oxyutilometer runs were conducted comparing identical mixed liquors in water baths at 15 and 25°C. in order to determine how the proposed process would operate in winter. Phosphate uptake and oxygen consumption dropped by 25–30% at the lower temperature. This decrease is considerably less than predicted by the Q_{10} law. While significant, the decline in activity would not critically impair the process during the winter months.

Rapid Sludge Removal

Rapid sludge removal from the secondary settling tanks is essential[7,9] if release of phosphate from the microorganisms into the clarified sewage is to be prevented. Rapid sludge removal might be accomplished by frequent or continuous mechanical action, or suction on settled sludge; or by froth flotation applied directly in the aeration basin.

Phosphate Stripping of Return Sludge

Phosphate stripping of the sludge organisms could not be practiced during the test run of the District of Columbia Sewage Treatment Plant. Continued uptake occurred throughout the test period without apparent phosphate saturation of the microorganisms. However, it seems likely that continuous, high percentage phosphate removals will require stripping phosphate from the sludge organisms. Otherwise, they will likely become phosphate-sated after a number of cycles through the aeration basin. Mixed liquor aerated in excess at 6 or 8 hr. begins to lose its phosphate back into solution.[7,9]

Several methods for stripping phosphate from return sludge were studied along with their effects on the subsequent ability of the sludge organisms to take up oxygen and phosphate. The influence of pH upon the rate of phosphate release from settling sludge is shown in Table I. Sludge adjusted to pH 3 immediately released large amounts

of phosphate to the supernatant. Uptake studies were conducted with acid-stripped sludge which had been readjusted to neutral pH. Contrary to earlier results,[7,9] this sludge continued to leak phosphate during aeration and its oxygen consumption was only a fraction of that of the controls. This indicated that the sudden change in pH induced a shock condition from which the organisms did not rapidly recover.

TABLE I
Effect of pH on Phosphate Stripping of Fresh Return Sludge

Settling time, hr.	Dissolved PO_4—P, mg./l.			
	pH 3	pH 5	pH 6.5	pH 9
0	32.0	19.5	12.3	11.4
1	29.0	21.3	14.6	11.8
2	35.0	23.8	16.8	15.6
3	36.2	30.4	19.0	26.4
4	37.6	35.8	20.8	30.2
5	37.6	30.2	19.0	24.4
6	32.4	33.0	25.0	26.8
7	35.0	34.4	28.4	32.0
12	41.4	47.6	36.6	45.2
23	42.4	66.8	57.6	58.4
Final pH	4.1	5.6	6.1	6.3

In other stripping studies, return sludge was allowed to settle anaerobically and the supernatant analyzed periodically for phosphate. Unexpectedly large quantities of phosphate were secreted as the culture aged, as is seen in Figure 2. It was noted that the rate of phosphate release dropped off sharply after about 60 hr. In another experiment, sludge was aged for 72 hr., washed with distilled water, and allowed to age an additional 28 hr. before measuring oxygen and phosphorus uptake in the oxyutilometer. Surprisingly, sludge stripped under these conditions retained good activity as evidenced by the uptake of 110.1 ml. of oxygen and 65% of the phosphate in 2 hr.

Mixed liquor prepared with washed sludge which had been aged for 26 hr. in distilled water showed about the same uptake of oxygen and phosphate as mixed liquor prepared with washed sludge aged for 50 hr. in distilled water. The phosphate uptake observed in these experiments was greater than 90% after 2 hr. of aeration. It appears
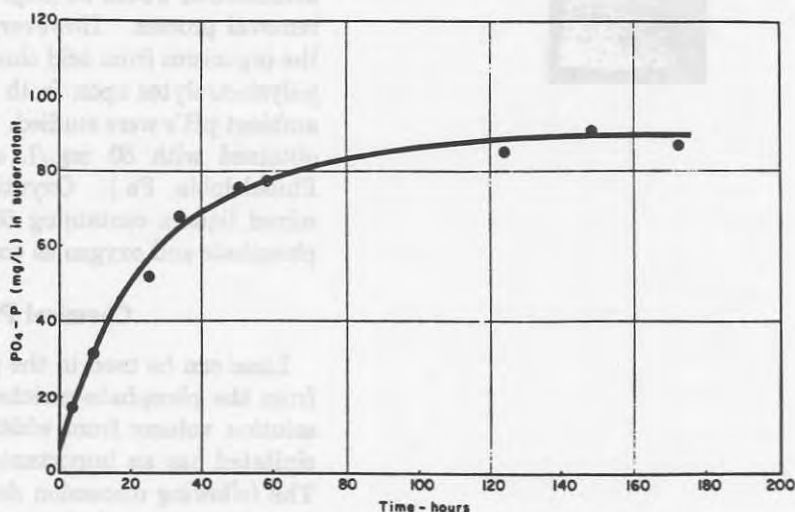
Fig. 2. Phosphate release by return sludge on standing.

that aging sludge for relatively long periods does not significantly reduce its ability to take up oxygen and phosphate.   Thus, anaerobic storage is preferable to acidification for phosphate stripping in that no chemicals need be added and the organisms, even after storage of 100 hr. are ready for immediate phosphate uptake upon aeration.

Removal of Phosphate-Depleted Sludge from Stripper

After yielding their phosphate, the sludge organisms are returned to the aeration basin. As little of the phosphate-rich suspending liquor as possible should be entrained with the organisms. Settling may possibly effect further concentration of the organisms. Froth flotation may offer an alternative.

Modified froth flotation experiments were performed based on a method developed for harvesting algae.[13,14] When mixed liquor containing 3950 mg./l. suspended solids was adjusted to pH 3 and aerated at the rate of 1.5 ml./l./sec. for 30 min., 95% of the solids was removed. Only about 15% of the original liquid volume was carried over in the process. Results were equal or better when the mixed liquor was maintained quiescent for purposes of phosphate stripping prior to harvesting by froth flotation. In harvesting phosphate-stripped sludge, any additional phosphate released by

acidification would be helpful rather than harmful to the phosphate removal process. However, because of the problem of recovery of the organisms from acid shock, the effects of several types of cationic polyelectrolytes upon froth flotation of nonaerated mixed liquors at ambient pH's were studied. Essentially complete solids removal was obtained with 50 mg./l. of Primafloc C7 (Rohm and Haas Co., Philadelphia, Pa.). Oxyutilometer experiments demonstrated that mixed liquors containing 50 mg./l. Primafloc C7 take up as much phosphate and oxygen as controls containing no polyelectrolyte.

Chemical Precipitation of Phosphate

Lime can be used in the precipitation of dissolved orthophosphate from the phosphate-enriched liquor produced in the stripper. The solution volume from which a given quantity of phosphate is precipitated has an important effect on the quantity of lime required. The following discussion demonstrates the advantage of the process in reducing the solution volume, i.e., increasing the phosphate concentration: Assume that the plant discharge is to be limited to a given quantity of orthophosphate, p_2, and that to accomplish this an amount of phosphate, p_1, must be precipitated as tricalcium phosphate.

The moles of calcium consumed in the precipitation of p_1 moles of phosphate as tricalcium phosphate is $^3/_2 p_1$ regardless of the volume from which it is precipitated or the calcium or phosphate ions remaining in solution. Expressions for the absolute and relative amounts of calcium ion required to maintain a particular amount of phosphorus in solution as a function of solution volume are derived as follows:

$$[Ca^{2+}]^3[PO_4^{3-}]^2 = k_{sp}$$

Total moles Ca^{2+} required = vol. $\times$ $[Ca^{2+}]$. Consider volumes of a, $10a$, and $100a$ liters:

a liters:

$$a[Ca^{2+}]_a = a\left[k_{sp}/\left(\frac{fp_2}{a}\right)^2 \right]^{1/3}$$

$10a$ liters:

$$10a[Ca^{2+}]_{10a} = 10a\left[k_{sp}/\left(\frac{fp_2}{a}\right)^2 \right]^{1/3} \times 100^{1/3}$$

$100a$ liters:

$$100a \, [\text{Ca}^{2+}]_{100a} = 100a \left[k_{sp} / \left(\frac{fp_2}{a} \right)^2 \right]^{1/3} \times 10{,}000^{1/3}$$

The relative amounts of Ca^{2+} required for order of magnitude changes in solution volume are:

$$\frac{10a \, [\text{Ca}^{2+}]_{10a}}{a \, [\text{Ca}^{2+}]_a} = 46$$

$$\frac{100a \, [\text{Ca}^{2+}]_{100a}}{a \, [\text{Ca}^{2+}]_a} = 2{,}150$$

$$\frac{1000a \, [\text{Ca}^{2+}]_{1000a}}{a \, [\text{Ca}^{2+}]_a} = 100{,}000$$

Where: p_1 = moles of phosphate precipitated as $\text{Ca}_3(\text{PO}_4)_2$; p_2 = moles of phosphate remaining in solution, a, $10a$, $100a$, $1000a$ = liters of solution to be treated; $[\text{Ca}^{2+}]$ = concentration of calcium ion in effluent; $[\text{PO}_4{}^{3-}]$ = concentration of phosphate ion in effluent; k_{sp} = solubility product of $\text{Ca}_3(\text{PO}_4)_2 = 1.2 \times 10^{-19}$; f = molar fraction of total phosphate phosphorus existing as $\text{PO}_4{}^{3-}$.[*]

$$f = \frac{[\text{PO}_4{}^{3-}]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4{}^{2-}] + [\text{HPO}_4{}^{2-}] + [\text{PO}_4{}^{3-}]}$$

$$= \frac{k_{a1} \times k_{a2} \times k_{a3}}{[\text{H}^+]^3 + k_{a1}[\text{H}^+]^2 + k_{a1} k_{a2}[\text{H}^+] + k_{a1} k_{a2} k_{a3}}$$

where: k_{a1}, k_{a2}, and k_{a3} are the respective equilibrium constants for the first, second, and third ionizations of phosphoric acid.

It is thus seen that, as solution volumes increase, the stoichiometric demand for lime rapidly diminishes in importance compared to the amount required to maintain the required precipitating concentration of calcium ion in solution. The latter's rapid increase with volume is shown in Figure 3. There is a 46-fold increase in the calcium requirement with each 10-fold increase in solution volume.

[*] f is a function of pH. These equilibrium considerations are assumed to have taken place at similar pH values for simplification.
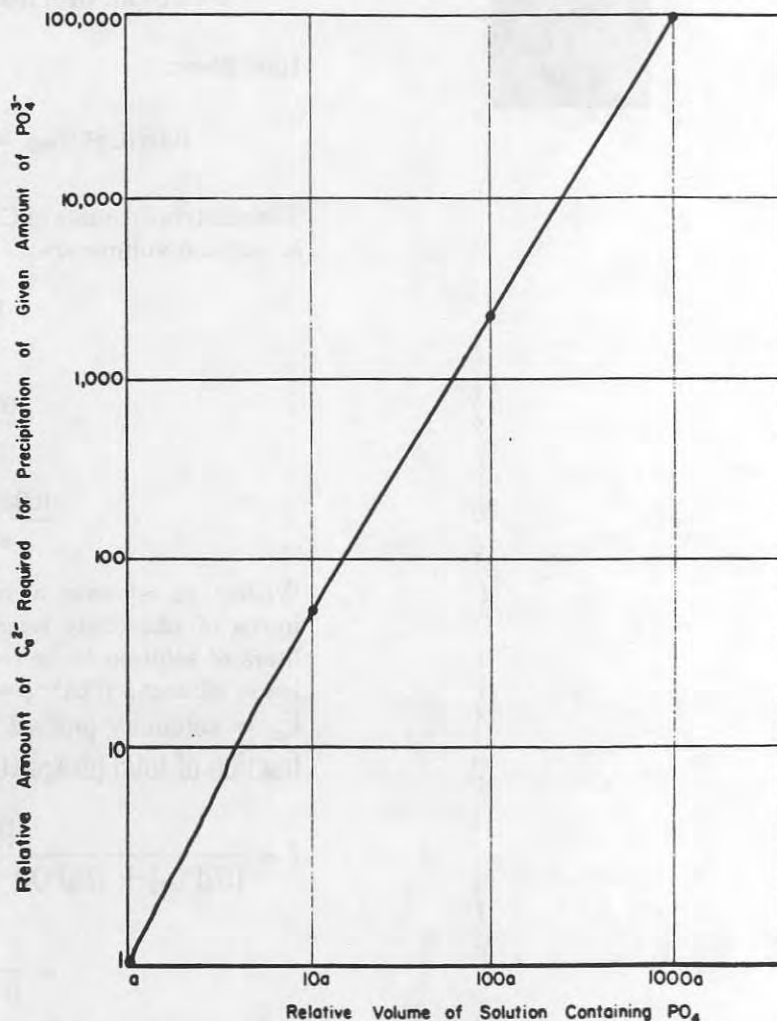
Fig. 3. Calcium concentration required to effect precipitation of given amount of phosphate from different solution volumes.

Laboratory Results

After the investigation of the parameters discussed, phosphate uptake experiments were conducted applying the information gained. Table II presents a summary of typical conditions and results. After two to 3 hr. of aeration, 73–95% of the dissolved orthophosphate was removed from the solution.

Fig. 4. Proposed phosphate removal flow sheet.

TABLE II
Phosphate Uptake Experiments

		Mixed liquor					
Sludge age, hr.	Suspended solids, mg./l.	Aeration rate, STP-ml./sec./l.	O₂ uptake during first hour, STP-ml./l.	Initial concentration, mg./l.	Final concentration, mg./l.	Per cent uptake	Aeration period, hr.
20	2650	83	89	10.7	2.8	74	2
6	3000	82	92	8.6	1.8	79	2
8	3000	83	95	7.4	2.1	72	1
26	2500	83	60	5.2	1.4	73	3
14	2500	83	65	3.8	0.2	95	3
12	2200	83	66	4.3	0.7	84	3
26ᵃ	2450	83	72	4.2	0.3	93	2
50ᵃ	2300	83	48	3.8	0.5	87	2

ᵃ Sludge washed prior to preparation of mixed liquor.

Process Schematic

As a result of the laboratory research, the process design shown in Figure 4 was recommended for the Manassas plant. Wiley and Wilson engineers used this schematic and the data obtained to design a one-million gallon/day sewage treatment plant for the Greater Manassas Sanitary District. The plans provide for a wide range of flexibility to permit considerable experimentation. It is hoped that the plant, or a variation thereof, will be built and operating in approximately 1 year.

Supporting Results

Encouraging new data supporting the prospects for the microbial removal of phosphate from sewage have accumulated. Full-scale tests at sewage treatment plants in San Antonio, Texas, by Vacker, Connell, and Wells demonstrated[15] a high degree of orthophosphate removal through the metabolic uptake by microorganisms and confirmed the findings reported by Levin and Shapiro.[7,9] The new Federal Water Pollution Administration of the Department of the Interior recently began an investigation of metabolic removal of

phosphate in San Antonio and elsewhere.   In July, the Department issued an announcement[16] confirming the process and calling it a "major breakthrough in pollution control."   Even more recently, last week, Sekikawa et al., in a paper[17] presented before the Third International Conference on Water Pollution Research, again confirmed the process principles and data.   It would thus seem that the near future may see the harnessing of microorganisms to perform another important industrial process.

The studies for the sewage treatment plant planned for the Greater Manassas Sanitary District were supported by Wiley and Wilson, consulting engineers, Lynchburg, Virginia.   Messrs. Martin Johnson and Garland Page, Jr., of that organization, who incorporated our results and process schematics into the design for the full-scale treatment plant, were most helpful.   Wiley and Wilson were retained, in turn, by Prince William County, Virginia.

Part of the studies for Wiley and Wilson were performed at the Baltimore Sewage Treatment Plant with the kind permission of Mr. Charles Hawthorne.

References

1. *Restoring the Quality of Our Environment*, report of The Environmental Pollution Panel, President's Science Advisory Committee, November, 1965.

2. *Investigation of the Odor Nuisance Occurring in the Madison Lakes, Particularly Lakes Monona, Waubesa, and Kegonsa from July 1943 to July 1944*, Governor's Committee Report No. 2, State of Wisconsin, Madison, Wisconsin, 1944.

3. B. J. Katchman, "Phosphates in Life Processes," in *Phosphorus and Its Compounds*, Vol. II, Interscience, New York, 1961.

4. J. Shapiro and R. Ribeiro, *J. Water Pollution Control Federation*, **37**, 1034 (1965).

5. E. G. Srinath, C. A. Sastry, and S. C. Pillai, *Experientia*, **15**, 339 (1959).

6. G. O. Alarcon, "Removal of Phosphorus from Sewage," Master's Essay, The Johns Hopkins Univ., Baltimore, Md., 1961.

7. G. V. Levin, "Metabolic Uptake of Phosphorus by Sewage Organisms," Doctoral dissertation, The Johns Hopkins Univ., Baltimore, Md., 1963.

8. G. V. Levin, "Sewage Treatment Process," U.S. Pat. 3,236,766, (Feb. 22, 1966).

9. G. V. Levin and J. Shapiro, *J. Water Pollution Control Federation*, **37**, 800 (1965).

10. T. H. Feng, *Water Sewage Works*, **109**, 431 (1962).

11. G. V. Levin and D. G. Shaheen, *Development of Sewage Treatment Process to Effect Metabolic Removal of Phosphorus*, Hazleton Laboratories' Final Report to Wiley and Wilson, Lynchburg, Va., September 30, 1965.

12. C. N. Sawyer and M. S. Nichols, *Sewage Works J.*, **11**, 51 (1939).

13. G. V. Levin, J. R. Clendenning, A. Gibor, and F. D. Bogar, *Appl. Microbiol.*, **10**, 169 (1962).

14. G. V. Levin and J. M. Barnes, "Froth Flotation for Harvesting Algae and its Possible Application to Sewage Treatment," Proc. 19th Ind. Waste Conf., Purdue Univ., 1965.

15. D. Vacker, C. H. Connell, and W. N. Wells, "Phosphate Removal through Municipal Wastewater Treatment at San Antonio, Texas," paper presented at the Annual Short School of the Texas Water and Sewage Works Association, Texas A & M University, March 9, 1966.

16. "Major Breakthrough in Pollution Control," U. S. Dept. of Interior News Release, Washington, D. C., July 28, 1966.

17. Y. Sekikawa, S. Nishikawa, M. Okazaki, and K. Kato, "Release of Soluble Ortho-Phosphate in the Activated Sludge Process," paper presented at Third International Conference on Water Pollution Control, Munich, Germany, September, 1966.