

PHOSPHATE REMOVAL BY ACTIVATED SLUDGE

Amenability Studies at
Mansfield, Ohio

by

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ABSTRACT

Biological phosphate removal was investigated in pilot and plant scale at Mansfield, Ohio, to determine waste and sludge amenability and the suitability of the activated sludge plant for a full-scale research or demonstration project. Pilot studies on the effect of MLSS, BOD, phosphate, and hardness concentrations showed only BOD exerted a significant change in phosphate removal. The addition of iron or aluminum salts effectively precipitated the phosphate. Amenability was established following sludge acclimatization when high levels of phosphate were removed from the primary effluent supplemented with a BOD material. Plant studies prior to and following manipulation of the operating conditions did not reveal phosphate removal. The plant is not suitable for full-scale research or demonstration studies without design modifications.

INTRODUCTION

This report describes investigations at the Mansfield, Ohio, Sewage Treatment Plant concerned with the removal of phosphate from municipal sewage by the activated sludge process. Field research conducted at San Antonio, Texas, established that high removals of orthophosphate from the liquid to the suspended solids were accomplished in the aeration tank. The efficiency of the process was found at San Antonio to be controlled by operational and design parameters including aeration detention times, mixed liquor suspended solids (MLSS) and dissolved oxygen (DO) concentrations, biochemical oxygen demand (BOD) and phosphate loads, rapid solid-liquid separation, minimum solids detention time in the final clarifiers, and separate disposal of the phosphate concentrates.

The purposes of the amenability studies conducted were:

1. To determine if biological phosphate removal is feasible in municipalities of various geographical locations, populations served, and sewage characteristics by pilot and plant investigations.
2. To locate activated sludge plants in various geographical regions to be used for demonstration of biological phosphate removal by operation in accordance with parameters identified at San Antonio.

3. To locate one activated sludge plant of suitable design and operational flexibility for use as a full-scale research plant to further specify, define, and optimize the biological phosphate removal process.

4. To verify on pilot scale that biological phosphate removal can be controlled by the parameters identified at San Antonio and/or isolate and identify additional controlling parameters.

Aerated jugs of mixed liquor have been previously shown to simulate an aeration tank. Aerated jugs circumvent many of the limitations exerted by normal operational characteristics in activated sludge plants, such as control of aeration rate, sewage flow, suspended solids concentration, and phosphate and BOD loadings. Sludge solids and waste from various points in the secondary system may be conveniently studied. Detention time of the mixed liquor in the aerated jug system is rigidly controlled. For these reasons, the method is selected for testing the amenability of the waste and activated sludge to phosphate removal.

By deliberate variation of the operational parameters, the conditions for sludge response and maximum phosphate removal can be established. These amenability studies indicate those waste and activated sludges most readily adaptable and, in conjunction with plant investigations, aid in specifying operational levels, design changes, or time for sludge adaptability necessary to attain phosphate removal in the full-scale plant.

Experimental Procedures

Plant Analysis

The plant was surveyed to determine pertinent design and operational characteristics. Programs of plant sampling and tracer studies were carried out in addition to jug studies to determine plant performance.

Plant records were examined for sewage flow, concentrations of BOD, suspended solids, and orthophosphate, other chemical and physical parameters, and performance characteristics. Typical data are presented in Appendix II. Plant personnel provided information on sampling practices, analytical procedures, anomalies of wastes being treated, and peculiarities of operational control. The schedule for wasting raw and activated sludges was determined. Disposal methods of waste activated sludge, primary sludge, digester supernatant, sludge thickener supernatant, drying bed underflow, and other waste streams were studied in anticipation of auxiliary, inhibitory, or latent effects on the phosphate removal process.

Tracer studies were conducted using Rhodamine WT dye on aeration tanks and final clarifiers to determine hydraulic characteristics such as detention, short circuiting, and degree of longitudinal mixing.

Grab samples were collected to determine the phosphate levels and degree of removal. These samples were analyzed for

concentration of orthophosphate and, occasionally, total phosphates, suspended solids, total oxygen demand (TOD), nonvolatile organic carbon (NVOC), and soluble nonvolatile organic carbon (SNVOC).

Chemically fixed samples were shipped to the Robert S. Kerr Water Research Center at Ada, Oklahoma for total phosphate analyses.

The sample sources were raw sewage, primary effluent, return sludge, aeration tank influent, aeration tank effluent, and final effluent.

Occasionally, supernatant samples were taken from digestion tanks and sludge thickeners. Dissolved oxygen was measured in conjunction with the sampling program. If phosphate was being removed, more detailed sampling on a slug-flow basis was undertaken to specify the magnitude of removal.

Aeration Jug Studies

Return sludge or mixed liquor from various points in the secondary system was mixed with primary effluent or raw sewage to obtain the desired test conditions. The mixtures were prepared in five-gallon polyethylene jugs for subsequent aeration.

A portable air compressor produced the air supply. Air was delivered through a manifold containing individual needle valves and rotometers for each jug. Polyethylene tee fittings were used as diffusers. The air flow was maintained constant throughout the experiment, except where noted.

The dissolved oxygen content and the temperature of the mixed liquor were monitored several times during each run.

Samples were withdrawn from the jugs usually at half-hour or hourly intervals. Preceding sample collection, approximately 200 ml of mixed liquor was siphoned through a plastic withdrawal tube for purging and returned to the original jug. A volume of 100 ml was sufficient for orthophosphate analysis, and 250 ml was taken when additional analyses were planned.

RESULTS AND DISCUSSIONS

Plant Characteristics

The Mansfield, Ohio, Sewage Treatment Plant shown in Figure 1 is an activated sludge system which treats an average of 8-9 million gallons per day (mgd). The system has three tanks for preaeration, grit, and grease removal; two primary clarifiers; six aeration tanks; and two final clarifiers. Approximately 90 and 95 percent of the BOD and suspended solids, respectively, are removed by these processes.

Four of the six aeration tanks were in operation during these studies. Compressed air at a rate of about 6.0 million cubic feet per day (mcfd) was supplied to these tanks by one of four blowers. (Another 0.5 mcfd of air was delivered to the preaeration tanks.) The aeration tanks were operated as a conventional activated sludge system; however, design of the tanks also permits operation of a step aeration process, reaeration, or combinations of these. Return sludge rates varied from about 20 to 50 percent of the sewage flow during these studies.

The primary sludge and excess activated sludge are pumped to one of two 0.15 million gallon sludge thickeners. Thickened sludge is pumped to three primary digesters and thence to a single secondary digester. Sludge from the secondary digester is dewatered by vacuum filtration for land disposal. The gas produced

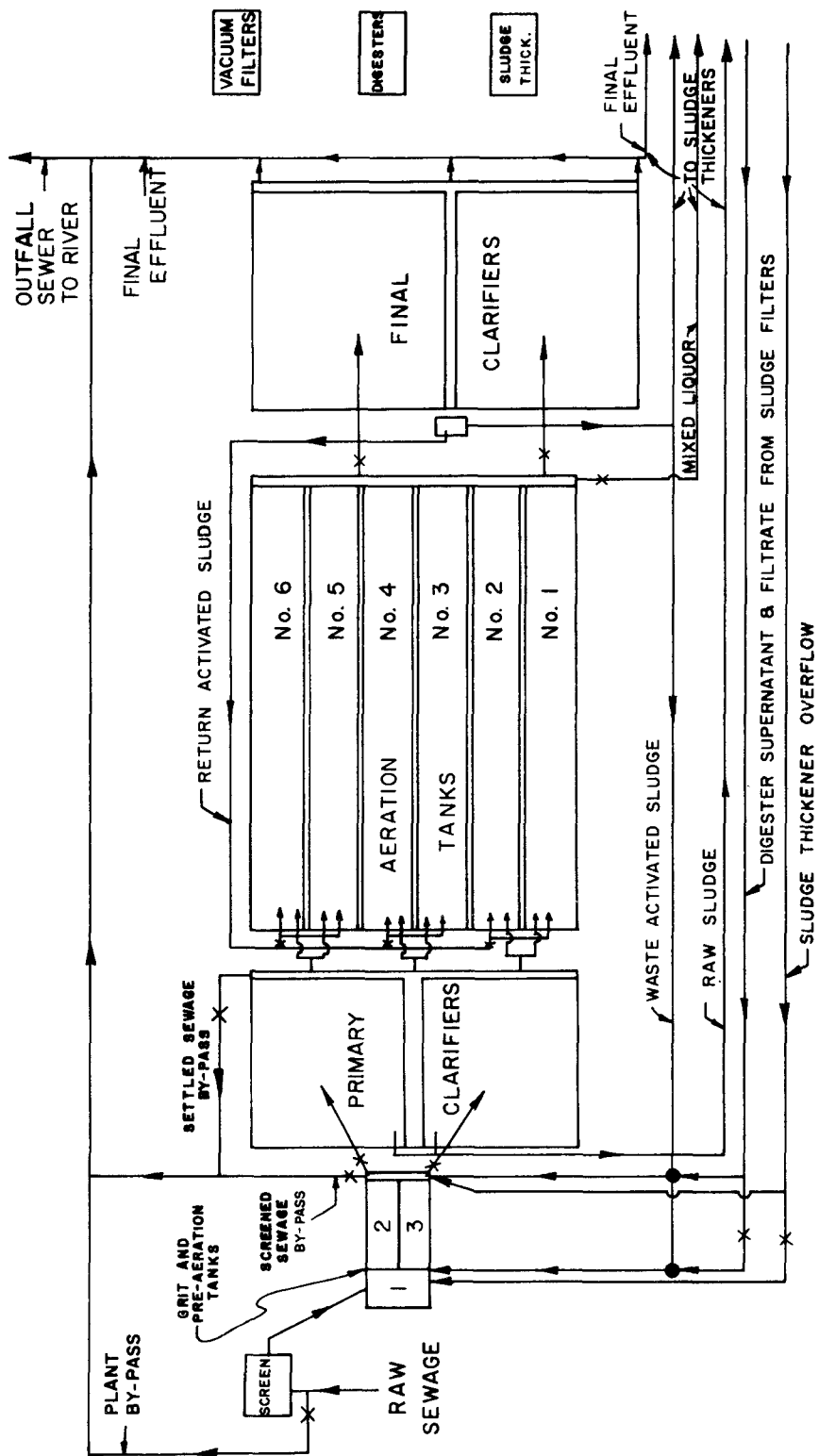


FIGURE 1 - MANSFIELD SEWAGE TREATMENT PLANT, MANSFIELD, OHIO

in the digesters is used as fuel for the boilers and gas engines that drive the blowers. Filtrate from vacuum filters and supernatant from thickeners and digesters are returned to the primary system.

Detention Studies

Tracer studies were conducted on two of the aeration tanks on May 16, 1967. Aeration Tanks No. 5 and 6 use longitudinally placed air diffusion tubes while Aeration Tanks No. 3 and 4 use transverse tubes. To determine the difference in the hydraulic efficiencies of the two systems, Tanks No. 4 and 5 were selected for dye tracing.

Two liters of 20 percent Rhodamine WT solution were introduced to the influent end of both aeration tanks, and dye concentrations were monitored at the effluent ends. Dye dispersion curves are presented in Figure 2.

Both tanks exhibited appreciable short circuiting with 90 percent of the tracer reaching the effluent within the theoretical displacement time. Tank No. 4, which has transverse diffusion tubes, demonstrated a peak tracer concentration at 30 percent of the theoretical detention time. Tank No. 5 with longitudinal diffusion tubes showed a peak concentration at 60 percent of the theoretical detention time. The tanks with longitudinal diffusion tubes were hydraulically nearer plug flow than the tanks with

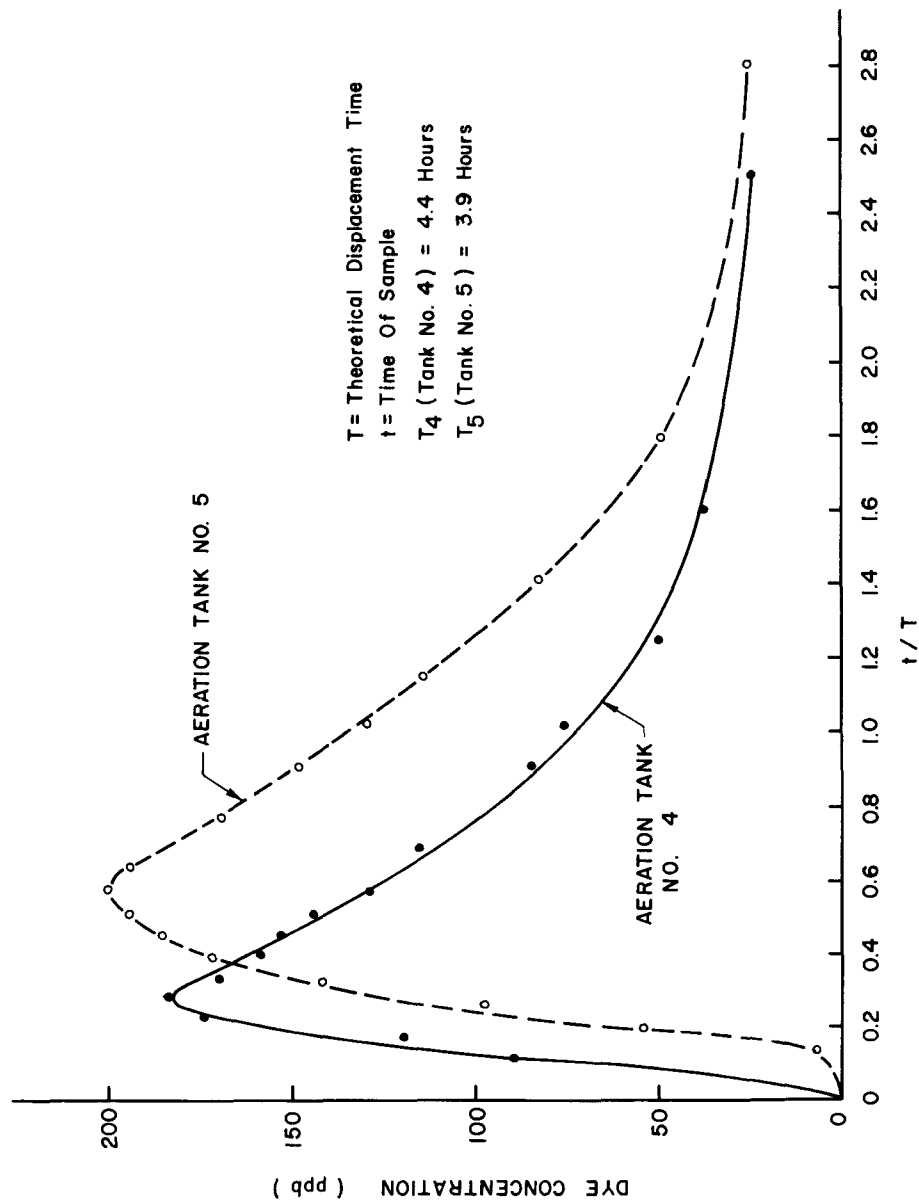


FIGURE 2 — DYE DETENTION IN AERATION TANKS

transverse tubes, but the dye studies indicate that much of the waste to both tanks receives less than three hours' detention time. These conditions are not considered conducive to good phosphate removal.

Plant Performance

Examination of plant records indicated that raw waste to the plant had an average BOD of about 190 mg/l. Approximately five hours' displacement time in the preaeration tanks and primary clarifiers reduces the BOD to less than 100 mg/l in the primary effluent. Further reduction in the aeration tanks and final clarifiers produces a final effluent with 15 to 20 mg/l BOD and suspended solids.

Dissolved oxygen concentrations were unusually high in the raw sewage and in the primary clarifiers, often 1 to 2 and 3 to 4 mg/l, respectively; however, about 6 mcf/d of compressed air or 0.7 cubic feet per gallon of waste was insufficient to maintain dissolved oxygen concentrations above 1.0 mg/l in the aeration tank effluent. As a result of the high primary effluent concentrations, dissolved oxygen was often significantly higher in aeration tank influents than effluents.

The plant was usually operated with mixed liquor suspended solids between 3,500 and 4,500 mg/l. The return sludge contained 0.5 percent total phosphate as P on a dry weight basis. Soluble

phosphate and BOD loadings were about 0.3 lb. P/day/100 lbs. MLSS and 9 lbs. BOD/day/100 lbs. MLSS, respectively.

Mansfield has a significant amount of industry including some metal plating. The waste to the sewage treatment plant formerly was subject to heavy concentrations of chromium and, on some occasions, still exhibits appreciable concentrations. On May 20, 1967, the raw waste was green, and a grab sample of the primary effluent contained 50 mg/l total chromium. Although the toxicity of this concentration of hexavalent chromium on activated sludge organisms has not been found significant,¹ other metals associated with the metal plating industry such as copper, cadmium, and zinc could be present in concentrations detrimental to biological activity.

Samples collected and analyzed during approximately 10 days of studies at the Mansfield Sewage Treatment Plant indicated that the plant did not remove significant amounts of phosphate either in the aeration tanks or through the plant as a whole. Soluble phosphate concentrations in the raw waste ranged from 2.7 to 4.3 mg/l-P and in the final effluent from 2.1 to 5.8 mg/l-P. Results of plant sampling are presented in Table 1.

Aeration Jug Studies

A series of experiments was devised to test the amenability of sewage and sludge to orthophosphate removal. Factors tested for their effect on the rate and magnitude of orthophosphate

¹ U. S. Department of Health, Education, and Welfare, Public Health Service, "Interaction of Heavy Metals and Biological Sewage Treatment Processes," Public Health Service Publication No. 999-WP-22. May 1965.

TABLE 1. PLANT MONITORING DATA

[illegible]

1/ > Denotes composite of two samples
 2/ Total Hardness - 270 mg/l CaCO₃
 3/ Chromium - 50 mg/l Cr
 4/ Total Hardness - 257 mg/l CaCO₃

removal were: suspended solids, BOD, and orthophosphate concentrations; metal precipitants; and sludge condition. Results from these experiments served as a guide to the utilization of plants for process demonstration.

Suspended Solids Variation

Studies at other activated sludge plants have shown that high orthophosphate removal occurs within a limited range of mixed liquor suspended solids concentrations; outside this range percent removal decreases.

To determine the optimum suspended solids concentration, a series of jug experiments was performed on May 17, 1967. Seven jugs were prepared for aeration with MLSS concentrations ranging from 450 to 4,300 mg/l. Jug components are recorded in Table 2 and results in Table 3.

The results were reasonably consistent with respect to initial and final orthophosphate concentration. There was a tendency for percent removal to increase (28 to 42 percent) with increasing suspended solids concentration; however, significant levels of removal were not obtained, and an optimum MLSS concentration was not determined. The remaining jug studies were run at a concentration range considered practical for the Mansfield Plant, i.e., 3,000 to 3,500 mg/l.

TABLE 2. Jug Components--Suspended Solids Variation

<u>Jug No.</u> ^{1/}	<u>Primary Effluent</u>	<u>Final Effluent</u>	<u>Return Sludge</u>	<u>Mixed Liquor</u> ^{2/}
(Liters of Component Added)				
1	10	4.6	0.4	--
2	10	4.2	0.8	--
3	10	3.8	1.2	--
4	10	3.4	1.6	--
5	10	3.4	2.0	--
6	--	--	--	15
7	10	1.3	3.7	--

^{1/}Aeration rate for all jugs - 15 liters per minute.
^{2/}Mixed liquor from aeration tank influent.

TABLE 3. Analytical Results--Suspended Solids Variation

<u>Aeration Time-Hrs</u>	<u>Jug No.</u>						
	1	2	3	4	5	6	7
	<u>Orthophosphate (mg/l P)</u>						
0 (11:15 am)	2.5	2.5	2.8	2.6	2.8	2.6	3.1
1	1.8	1.8	2.0	2.0	2.0	1.8	2.0
2	2.0	2.0	2.0	2.0	1.8	1.6	1.6
3	1.8	1.8	1.8	1.8	1.8	1.6	1.6
4	1.8	1.8	2.0	1.8	1.8	1.8	1.6
5	1.8	1.8	1.8	1.8	1.6	1.6	1.8
6	1.8	1.8	1.8	1.8	1.8	1.6	1.8
ML Settled (30 min)	1.8	1.8	2.0	2.0	1.8	1.8	1.8
% Removal	26.5	26.5	35.2	31.1	35.2	37.5	42.1
MLSS (mg/l)	454.0	937.0	1369.0	1794.0	2251.0	4300.0	3154.0

Note: During the aeration period, mixed liquor temperature increased from 14 to 18°C. Similarly, dissolved oxygen concentration fluctuated randomly between 8.5 and 10 mg/l.

Jug No. 6, composed of mixed liquor from the influent end of an aeration tank, served as a control for comparing removal efficiency between mixed liquor prepared in the plant and in the jugs. The removal efficiency of this jug was most comparable to that of Jug No. 7, which also had a comparable suspended solids concentration.

BOD Variation

Studies at other activated sludge plants have indicated that orthophosphate removal is also affected by primary effluent BOD concentration. On May 18, 1967, a set of jugs was prepared to determine the magnitude of this effect.

The components of the aeration jugs are shown in Table 4 and analytical results in Table 5. The BOD's of the jug components were not measured directly but were roughly estimated by adding to each jug a known quantity of Metrecal, which had a BOD of 290 mg/ml. Generally, the jug studies were based on a substrate or primary effluent volume of 10 liters with the remaining 5 liters a mixture of concentrated return sludge and final effluent to provide the desired solids concentration. In this experiment, Jug No. 1 was considered the base with 10 liters of primary effluent estimated to have a BOD equivalent to the "normal" or annual average, i.e., 95 mg/l. Metrecal was then added to the primary effluent for Jugs No. 2 through 5 to increase the BOD concentrations by a factor of 1.8, 2.3, 3.1, and 4.7, respectively.

TABLE 4. Jug Components--BOD Variation

<u>Jug No.</u> ^{1/}	<u>Substrate</u> (Est. BOD) mg/l	<u>Metrecal</u> ^{2/} ml	<u>Primary</u> <u>Effluent</u>	<u>Return</u> <u>Sludge</u>	<u>Final</u> <u>Effluent</u>	<u>Mixed</u> <u>Liquor</u>
Liters of Component Added						
1	95	--	10	2.7	2.3	--
2	173	2.7	10	2.7	2.3	--
3	220	4.3	10	2.7	2.3	--
4	295	6.9	10	2.7	2.3	--
5	440	12.0	10	2.7	2.3	--
6	95	--	-- ^{3/}	--	--	15
7	190	--	10	2.7	2.3	--

^{1/}Aeration rates for all jugs - 15 liters per minute.

^{2/}Metrecal contains 1.1 mg/ml O-PO₄ and BOD of 290 mg/ml.

^{3/}Raw sewage used in lieu of primary effluent.

TABLE 5. Analytical Results--BOD Variation

<u>Aeration</u> <u>Time</u> <u>Hrs.</u>	<u>Jug No.</u>						
	1	2	3	4	5	6	7
<u>Orthophosphate (mg/l P)</u>							
0 (10:00 am)	2.8	3.4	3.6	3.9	3.9	3.1	3.4
1	2.5	2.5	2.5	2.5	2.5	2.8	2.5
2	2.3	2.1	2.0	1.8	1.5	2.5	2.1
3	2.3	2.0	2.0	1.8	1.5	2.5	2.3
4	2.3	2.0	1.8	1.6	1.3	2.5	2.1
5	2.3	2.1	1.8	1.6	1.3	2.6	2.3
ML Settled (1 Hour)	2.5	2.1	2.0	1.6	1.3	2.6	--
% O-PO ₄ Removed	17.9	38.3	50.0	59.0	66.7	16.1	32.4
MLSS (mg/l)	3440.0	3214.0	3356.0	3434.0	3244.0	4374.0	3346.0

Note: During the aeration period, mixed liquor temperature increased from 14 to 17°C. Similarly, dissolved oxygen concentration increased from 4 to 8 mg/l.

Jug No. 6 was composed of mixed liquor from the effluent end of the aeration tanks. It served as a control for comparison of plant and synthetic jug mixed liquor. The removal efficiency of this jug was comparable to Jug No. 1 which contained no supplemental BOD.

The raw sewage, with an annual average BOD of 190 mg/l, was used in Jug No. 7 in lieu of primary effluent to increase the estimated BOD concentration of the substrate to twice that of the primary effluent. The orthophosphate removal efficiency in this jug was most comparable with Jug No. 2 which was supplemented with Metrecal to produce an estimated BOD 1.8 times that of a "normal" primary effluent.

Figure 3 presents percent orthophosphate removal versus estimated BOD concentration for the jugs in this experiment plus three other jugs aerated during a later study on orthophosphate variation. Orthophosphate removal generally increased with increased BOD with the greatest effect at estimated BOD concentrations less than about 300 mg/l. Thus, benefit from supplemental BOD would be limited at concentrations above 300 mg/l. Subsequent jug studies were run with supplemented BOD loading to obtain maximum phosphate removal.

Orthophosphate Variation

A set of six jugs was prepared on May 19, 1967, to determine the effect of orthophosphate concentration on its removal at the Mansfield Plant. Jug components are given in Table 6 and analytical results in Table 7.

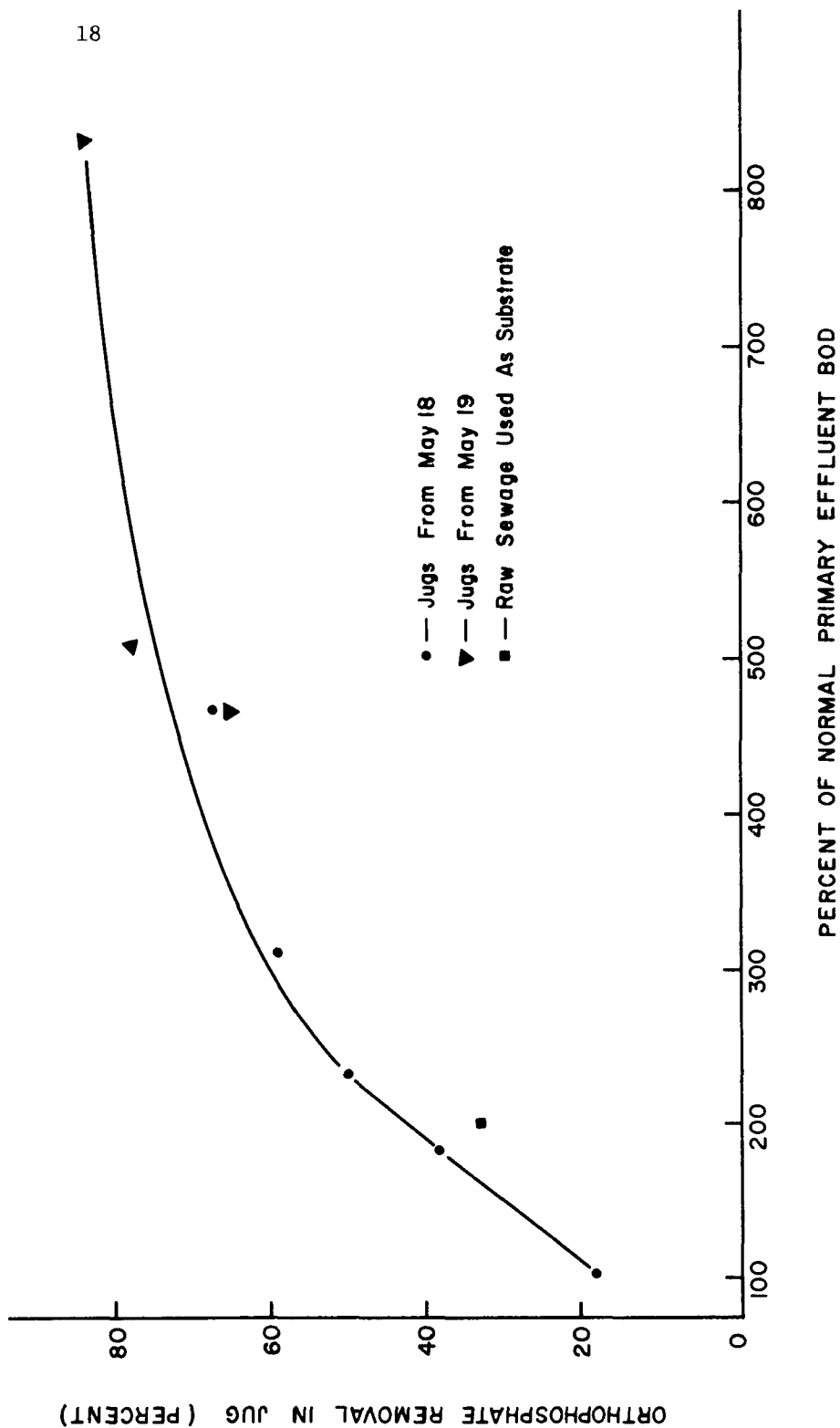


FIGURE 3 — EFFECT OF BOD ON PHOSPHATE REMOVAL

TABLE 6. Jug Components--Orthophosphate Variation

Jug No.	Substrate (Est. BOD) mg/l	Metrecal ml	KH_2PO_4 mg-P	Primary Effluent Liters	Return Sludge of Components	Final Effluent Added	Mixed Liquor
1	95	--	--	--	--	---	15
2	790	24	--	10	2.7	2.3 ^{2/}	--
3	480	15	--	5	2.7	7.3 ^{2/}	--
4	440	12	50	10	2.7	---	--
5	440	12	450	10	2.7	1.5 ^{3/}	--
6	440	12	--	10	2.7	2.3	--

^{1/}Aeration rate for all jugs - 15 liters per minute.

^{2/}City water in lieu of final effluent.

^{3/}0.4 liters each of thickener and digester supernatant added.

TABLE 7. Analytical Results--Orthophosphate Variation

Aeration Time-Hrs	Jug No.					
	1	2	3	4	5	6
	Orthophosphate (mg/l P)					
0 (11:00 am)	3.8	4.6	2.3	6.6	37	3.8
1	3.4	2.8	1.0	5.4	34	2.6
2	3.4	2.1	0.6	5.2	31	2.1
3	2.6	1.1	0.3	3.1	26	--
4	2.5	0.8	0.3	3.4	24	1.3
5	2.8	--	--	--	--	--
6	3.0	0.7	0.5	3.1	23	--
ML Settled (30 Min.)	3.0	0.7	0.5	3.4	22	1.3
O- PO_4 Removed (mg/l)	0.8	3.9	1.5	3.2	5.0	2.5
% O- PO_4 Removed	21.0	84.8	78.3	53.0	38.8	65.8
MLSS (mg/l)	4494.0	3595.0	3208.0	3464.0	3532.0	3366.0

Note: During the aeration period, mixed liquor temperature increased from 15 to 23°C. Similarly, dissolved oxygen concentration increased from 3 to 8 mg/l.

Jug No. 1 contained plant mixed liquor for removal efficiency comparison with phosphate and BOD supplemented and synthesized mixed liquor. Tap water was used in Jug No. 3 to reduce the orthophosphate concentration to approximately 50 percent of that in the control jug, and additional Metrecal was added to compensate for BOD reduction. Potassium dihydrogenphosphate was added to Jugs No. 4 and 5 to produce initial soluble phosphate concentrations of about 7 and 35 mg/l as P, respectively. In addition, 0.4 liter each of thickener and digester supernatant was added to Jug No. 5. The high orthophosphate load was added to simulate potential levels should thickener and digester supernatant streams be returned to the activated sludge system. Jug No. 6 served as a control for the study. Metrecal addition to Jugs No. 3 through 6 increased BOD loading to the level which gave highest phosphate removal in the BOD variation study. Jug No. 2 had twice the quantity of Metrecal used in the control jug to obtain supplemental data on BOD addition. Mixed liquor suspended solids concentrations ranged from about 3,200 to 4,500 mg/l.

Figure 4 indicates that supplemental orthophosphate (Jugs No. 4 and 5) increased the magnitude of removal but decreased the percent removal. Jug No. 3 with decreased phosphate showed decreased magnitude but increased percent removal, and a better quality effluent was obtained. Thus, supplemental phosphate was detrimental to the phosphate removal process in terms of both percent removal and effluent quality.

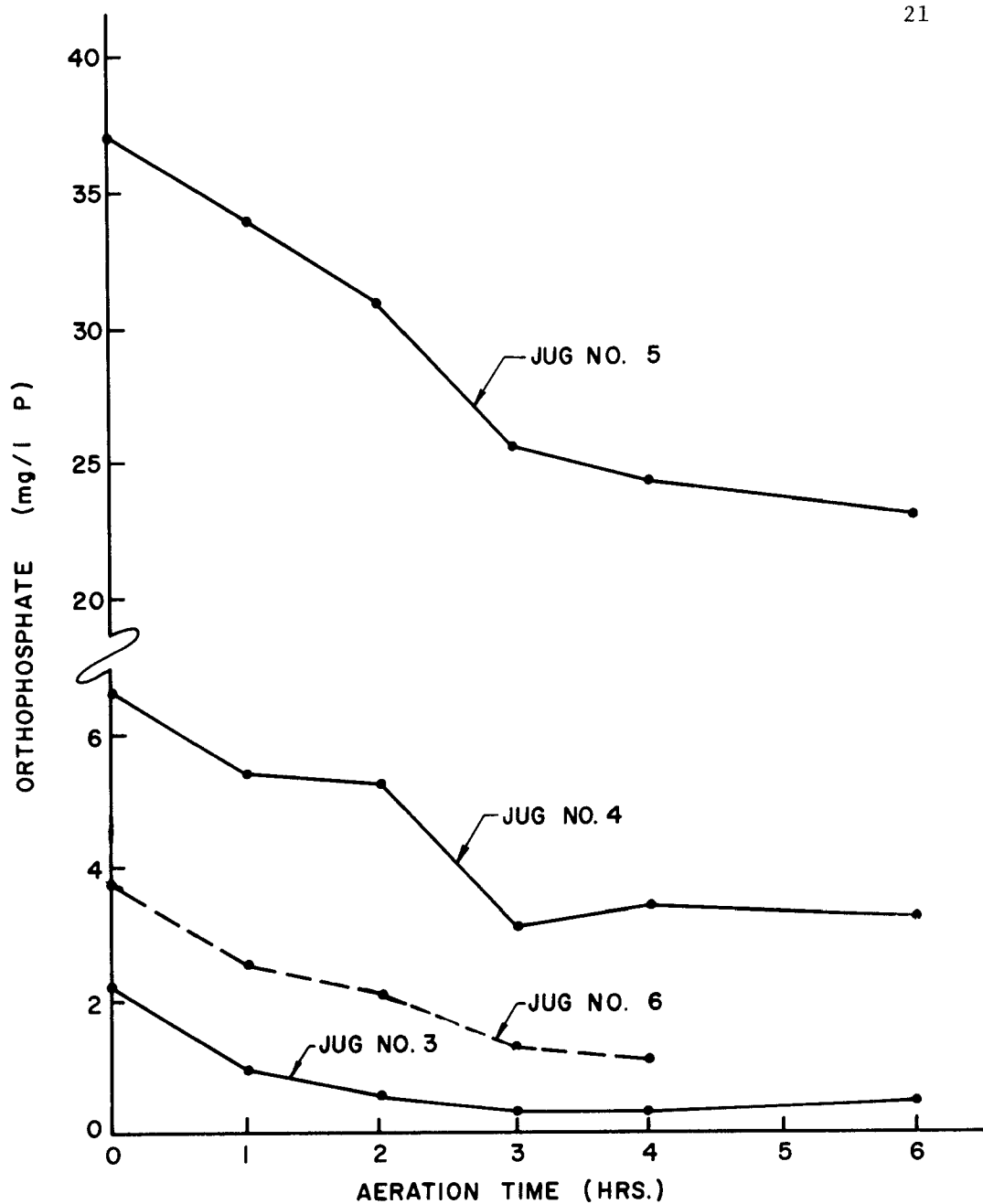


FIGURE 4 — EFFECT OF PHOSPHATE CONCENTRATION ON REMOVAL

Jug No. 2 with an estimated substrate BOD of 790 mg/l removed about 20 percent more orthophosphate than the control (Jug No. 6) which contained an estimated 440 mg/l substrate BOD. These results agree with those discussed in the previous experiment and are shown in Figure 3.

Chemical Addition

Three jugs were set up May 21, 1967, to determine the effect of iron and aluminum salts on orthophosphate removal. The mixed liquor was prepared using primary effluent, concentrated return sludge, and final effluent. Jug components are recorded in Table 8 and results in Table 9.

Jug No. 1 served as a control while Jugs No. 2 and 3 were dosed with 25 mg/l of ferric and aluminum ion, respectively. Aluminum sulfate and ferric chloride were the chemicals used; pH was not controlled. Orthophosphate concentrations of the primary effluent plus final effluent components before chemical and return sludge additions ranged from 4.0 to 4.2 mg/l as P. After chemical addition and thorough mixing, orthophosphate concentration was determined on the contents of Jugs No. 2 and 3 and before the return sludge was added and on all the jugs just after the addition of return sludge.

TABLE 8. Jug Components--Chemical Addition

Jug No.	^{1/} Primary Effluent Liters of	Return Sludge Components	Final Effluent Added	Fe ⁺³ mg/1	Al ⁺³ Added
1	10	2.7	2.3	--	--
2	10	2.7	2.3	25	--
3	10 ^{2/}	2.7	2.3	--	25
4	10 ^{2/3/}	2.7	2.3	--	--
5	10 ^{3/}	2.7	2.3	--	--

^{1/} Aeration rate for all jugs - 15 liters per minute. 12 milliliters of Metrecal was added to all jugs to increase the estimated substrate BOD to 440 mg/l.

^{2/} 8.6 liters of deionized PE plus 1.4 liters straight PE.

^{3/} 4.2 liters of deionized PE plus 5.8 liters straight PE.

TABLE 9. Analytical Results--Chemical Addition

Aeration Time-Hrs	Jug No.				
	1	2	3	4	5
	Orthophosphate (mg/1 P)				
0 (12:30 pm)	^{1/} --	0.7	0.4	--	--
0 ^{2/}	4.5	1.2	0.1	4.5	4.2
1	4.7	0.3	0.2 ^{3/}	5.1	5.5
2.5	3.9	0.2	--	4.8	4.6
3.5	3.9	0.2 ^{4/}	--	4.8	4.4
4	3.8	--	--	4.8	4.5
ML Settled (30 Min.)	4.4	0.2	0.2	5.7	5.1
% O-PO ₄ Removed	15.5	95.6	95.6	--	--
MLSS (mg/1)	2628.0	2836.0	2686.0	2740.0	2694.0

^{1/} Primary effluent plus chemical additive

^{2/} After return sludge addition.

^{3/} Aeration stopped at 1 hour and ML settled.

^{4/} Aeration stopped at 3.5 hours and ML settled.

Note: Temperature of the jug mixed liquor ranged from 14-18°C. Initial and final dissolved oxygen concentrations of the jug mixed liquor were about 4 and 8.5 mg/l.

Two additional jugs were prepared to determine the effect of hardness on orthophosphate removal. Primary effluent was passed through a cation exchange resin to reduce the hardness. The mixed liquor was prepared using concentrated return sludge, final effluent, and appropriate quantities of unaltered and deionized primary effluent. Jugs No. 4 and 5 were prepared with hardness concentrations of 75 and 250 mg/l, respectively.

Mixed liquor suspended solids in the five jugs ranged from about 2,500 to 3,000 mg/l. Metrecal was added to increase the BOD concentration to an estimated 300 mg/l.

Addition of iron and aluminum resulted in immediate orthophosphate removal. Aluminum produced the most dramatic effect in that greater than 90 percent of the orthophosphate was immediately precipitated. The jug containing iron removed 83 percent by precipitation and greater than 95 percent overall after two and one-half hours of aeration time. Only 16 percent orthophosphate removal occurred in the control jug compared to about 60 percent in previous jugs with similar contents.

Phosphate removal was not accomplished in Jugs No. 4 and 5. Both jugs indicated a greater quantity of orthophosphate at the end of the experiment than at the beginning. Decreasing the hardness was not beneficial to phosphate removal. However, the previous

high phosphate removals under conditions similar to the control jug suggest that the slug of metal waste in the sewage on May 20 may have altered the phosphate removal characteristics of the sludge.

Sludge Adaptation

On June 19, a study was begun to acclimate sludge microorganisms to environmental conditions suitable for phosphate removal. The activated sludge biota was maintained at a concentration of 2,000-4,000 mg/l suspended solids in the presence of sufficient supply of oxygen and food for several days.

Jug No. 6, which was used as a control during the phosphate concentration experiment on June 19, was used for the acclimatization procedure. Following the initial six hours of aeration when 65 percent of the soluble phosphate was removed, 400 milliliters of a Metrecal-phosphate-distilled water solution (174 mg/ml BOD; 0.3 mg/ml P) was fed continuously at a rate of 0.5 ml/min during overnight aeration. Decanting the supernatant from the settled mixed liquor in the jug and the addition of fresh primary effluent to the sludge were planned for the following day; however, because the primary effluent contained a high chromium concentration, no fresh primary was added. Instead, 600 milliliters of Metrecal-phosphate-distilled water solution was added during aeration throughout the next day and again overnight.

On May 21, the contents in the jug were allowed to settle, the supernatant was decanted and replaced with 10 liters of primary effluent and 12 milliliters of Metrecal. Five hours of aeration at 15 liters of air per minute reduced the soluble phosphate 58 percent from 5.9 to 2.5 mg/l as P. A control jug, with identical primary effluent but containing fresh sludge, was aerated simultaneously and removed less than 20 percent of the soluble phosphate. The contents of the test jug were again settled, decanted, and charged with 10 liters of fresh primary effluent. About 400 milliliters of the Metrecal feed solution was again added during overnight aeration.

On May 22, the jug was again decanted and fresh primary effluent with a 24 milliliter slug of Metrecal was added. During the subsequent 8 hours of aeration at 15 liters of air per minute, soluble phosphate was reduced 86 percent from 9.6 to 1.3 mg/l as P.

This acclimation test established that the activated sludge at Mansfield, Ohio, could be highly amenable to phosphate removal under optimum conditions of operation. Although increased removals resulted from operation at increased concentrations of suspended solids, dissolved oxygen, and BOD in addition to an adapted sludge, none of these parameters have been sufficiently specified for translation into plant operating criteria at Mansfield.

Plant Manipulation

Following the amenability studies at Mansfield, Ohio, minimal operational changes were made to induce phosphate removal in the plant. Although phosphate removal had not been obtained in the plant during these studies, high removals were accomplished in the jugs at high dissolved oxygen concentrations by increasing the BOD concentration. Therefore, operational modifications were designed to increase the BOD load to the plant and increase dissolved oxygen in the aeration tank effluents. The changes agreed upon by the city and plant officials were:

1. Increase rate of return sludge and wasting of sludge to reduce and maintain mixed liquor suspended solids concentrations at 2,000 to 3,000 mg/l.
2. Place all six aeration tanks in service and operate one blower at full capacity. If DO concentrations in aeration tank effluents remain below 1.0 mg/l, utilize two blowers at full capacity.
3. Discharge all digester supernatant and sludge filtrate to lagoons to prevent recirculation of phosphate.

These conditions were to be maintained for about two weeks before monitoring the plant again for phosphate removal. If no removal was occurring, it was agreed that one of the primary

clarifiers would be removed from operation to increase the BOD load to the secondary system. Following another stabilization period, the plant was to be monitored again for phosphate removal.

Grab samples collected on June 21, 1967, two weeks after initial changes were made, indicated that DO concentrations in the aeration tank effluents were consistently less than 1.0 mg/l. Analyses of samples collected also indicated that no significant phosphate removal was occurring in the plant.

Following failure of initial modifications to induce phosphate removal at Mansfield, two blowers were operated to increase the DO concentration. In addition, one of the primary clarifiers was taken out of service to increase the BOD load to the aeration tanks. After operation for one month under these conditions, the plant was again monitored on July 19, 1967. The DO levels had increased but were not consistently above 1.0 mg/l in the aeration tank effluent. Grab samples indicated that there was still no phosphate removal through the aeration tanks.

Following the July 19 visit, both blowers were increased to their full capacity for a two-week stabilization period. The last visit on July 30 and 31 showed dissolved oxygen concentrations at the effluent ends of the aeration tanks from 0.3 to 5.1 mg/l; however, grab samples collected continued to indicate no phosphate

removal as noted in Table 1. During this last monitoring, two previous days of rain had diluted the BOD concentration, and the raw and primary effluent exhibited a yellowish-green color of chromium waste.

Although dissolved oxygen concentrations in all the aeration tank effluents were not maintained at satisfactory levels for an extended period of study, it was concluded that modifications other than the increased air and BOD would be necessary for phosphate removal. The aeration tanks would require physical modification to reduce short circuiting and increase plug-flow conditions and mixed liquor detention time.

Sewage Characterization

A related purpose of the amenability analytical program was to characterize samples from the various unit processes of activated sludge plants with regard to selected chemical parameters. Additional samples from an aeration jug study were included in the characterization scheme. These samples were taken from a jug study whose operations and constituents were those which resulted in maximum phosphate removal. Primarily, the intention was to search for trends or correlatable functions within or between various chemical parameters which would be useful in defining the phosphate removal process. Frequently, phosphate removal realized from jug aeration was higher than that occurring in the

aeration tanks. During such instances, the probability of identifying gross differences of possible significance was greatly enhanced.

The samples were analyzed with and without solids to differentiate between the quantity of each respective chemical parameter associated with the solids and that associated with the liquid. Solids separation was accomplished by first decanting, then subjecting the resulting supernatant to further solids removal using a Sharples Super-Centrifuge. Samples resulting from such treatment are referred to as centrates of the original sample.

The samples characterized and the results therefrom will not be discussed in this report since the basic purpose was for comparison with similar data from other studies. Data and comparisons are made and reported under separate cover.²

Microbiological Studies

The microbiological studies conducted at the plants tested for amenability to phosphate removal were divided into two phases. Phase I consisted of selection of predominant colonial types, transfer of such to agar slants, and shipment to the Ada laboratory for identification. The final portion of this phase is under way. The results from Mansfield and the other amenability studies are a separate

²Lively, L. D., et al., "Phosphate Removal by Activated Sludge, Waste Characterization," Internal Report, USDI, FWPCA, Robert S. Kerr Water Research Center, Ada, Oklahoma. 1968.

report.³ Phase II consisted of determining bacterial number by the total plate count method from various plant and aeration jug samples. A correlation was sought relating bacterial population with phosphate removal and suspended solids concentration.

There is no apparent relationship between suspended solids content and bacterial contents. The bacterial counts remain essentially constant through the aeration tanks and during the course of the jug runs. Bacterial counts and phosphate removal, if related, were not detectable by the methods employed.

³Moyer, J. E., et al., "Survey of Activated Sludge Treatment Plants for Predominant Bacterial Types," Internal Report, USDI, FWPCA, Robert S. Kerr Water Research Center, Ada, Oklahoma. 1968.

SUMMARY

Studies conducted at the activated sludge plant of Mansfield Ohio, from May 16 to May 26, and follow-up investigations on three other occasions after plant manipulation during June and July 1967, revealed no phosphate removal by the plant.

Dye tracer studies conducted on the aeration tanks showed appreciable short-circuiting, especially those tanks containing transverse air diffusers. Air supplied to these tanks during the experimental periods was insufficient to maintain dissolved oxygen concentrations consistently above 1.0 mg/l.

The industry in Mansfield, including metal plating, subjected the waste influent to occasional high concentrations of metals. One grab sample had a chromium concentration of 50 mg/l indicating the presence of associated metals of the metal plating industry such as copper, cadmium, and zinc which could be detrimental to biological activity.

The plant usually operated within a mixed liquor suspended solids concentration range of 3,500 to 4,500 mg/l, and the return sludge rate varied from about 20 to 50 percent of the sewage flow. Air supplied averaged approximately 0.7 cubic foot of air per gallon of waste treated.

Phosphate concentrations in the waste streams during the study were:

<u>Source</u>	<u>Ortho (mg/l-P)</u>		<u>Total (mg/l-P)</u>		<u>Average Ratio (Ortho/Total)</u>
	<u>Min.</u>	<u>Max.</u>	<u>Min.</u>	<u>Max.</u>	
Raw Sewage	2.7	4.3	4.4	9.9	0.5
Pri. Effl.	2.1	3.8	3.7	13.4	0.5
Final Effl.	3.9	5.3	4.5	7.3	0.7

The return sludge contained 0.5 percent total phosphate as P on a dry weight basis. Soluble phosphate and BOD loadings were 0.3 lb. P/day/100 lbs. MLSS and 9 lbs. BOD/day/100 lbs. MLSS, respectively.

Pilot studies were conducted in aerated jugs to determine the effects of varying concentrations of MLSS, BOD, phosphate, hardness, and iron and aluminum salts. With the exception of iron and aluminum salts which precipitated the phosphate on contact, only BOD concentration exerted a significant effect on phosphate removal within the ranges studied.

Phosphate removal was increased in the aeration jugs from less than 20 percent where no supplemental BOD was added, to almost 85 percent when about 700 mg/l of supplemental BOD in the form of Metrecal was added to the substrate at the start of the aeration period.

An "acclimation" process produced a sludge which, with the addition of BOD, removed 86 percent of the soluble phosphate during an 8-hour aeration period.

CONCLUSIONS

1. The Mansfield, Ohio, activated sludge plant, at the time of these investigations, was not removing phosphate.
2. The aeration tanks exhibit a high degree of short-circuiting which is not conducive to good phosphate removal.
3. The aeration tanks with transverse diffuser systems exhibit greater short-circuiting than those tanks with longitudinal diffusers.
4. The air supplied and the hydraulic conditions in the aeration tanks are insufficient to maintain dissolved oxygen concentrations necessary for phosphorus removal.
5. The detention time in the preaeration and grit tanks and primary clarifiers is long, and the primary effluent BOD may contain insufficient substrate for the development and maintenance of a phosphate removing sludge.
6. The phosphate removal in jug studies is greatly increased by the addition of substrate in the form of Metrecal.
7. Varying mixed liquor suspended solids between about 1,300 and 4,300 mg/l has little effect on phosphate removal.
8. Within the ranges studied, increased hardness concentrations did not significantly increase phosphate removal.
9. Iron and aluminum salts were very effective in precipitating phosphate with aluminum having the most immediate effect.

10. The failure to induce phosphate removal in the plant by limited operational modifications was attributed to (a) the poor hydraulic conditions in the aeration tanks, (b) failure to maintain sufficient DO in the aeration tank effluent, (c) insufficient BOD load to the aeration tanks, and (d) the possibility that slugs of metal wastes were detrimental to biological activity.

RECOMMENDATIONS

The Mansfield, Ohio Sewage Treatment Plant is not recommended for demonstration of phosphorus removal without design modifications and operational changes. The changes necessary prior to such utilization are:

1. Convert the six single-pass aeration tanks into two three-pass tanks, all with longitudinal diffusers, to improve hydraulic efficiency.
2. Increase the air supplied to the aeration tanks, if necessary after tank modification, to maintain aeration tank effluent dissolved oxygen concentrations at 2 to 4 mg/l.
3. Prevent return of sludge thickener supernatant and digester supernatant to the system unless phosphate is chemically precipitated beforehand.

Another amenability study would be desirable before undertaking a full-scale program.

APPENDIXES

Appendix I

Analytical Procedures

by

B. L. DePrater

Sample Preparation

Samples collected for analyses in the field were processed as outlined in the respective analytical test procedures.

Samples returned to the Robert S. Kerr Water Research Center are referred to as whole, centrate, whole fixed, and centrate fixed.

The following table lists the treatment each type received prior to shipment to Ada.

<u>Sample</u>	<u>Treatment</u>
1. Whole	Shipped as is with no treatment.
2. Whole Fixed	Shipped as is plus 1 ml conc. sulfuric acid per liter of sample.
3. Centrate	The sample was passed through a Sharples motor driven laboratory model continuous centrifuge, equipped with a clarifier bowl driven at 23,000 rpm. The sample was delivered to the centrifuge by a peristaltic pump at a feed rate of 150 ml/min. The bowl was cleaned and rinsed with distilled water after each sample.
4. Centrate Fixed	The centrate sample plus 1 ml/l conc. sulfuric acid.

All samples were shipped in either 250 ml polyethylene bottles or 1,000 ml cubetainers.*

*Hedwin Corporation, 1600 Roland Heights Avenue, Baltimore, Maryland 21211.

Chemical Tests

1. Orthophosphate

In the field, initial samples for orthophosphate were filtered immediately using Schleicher and Schuell No. 588 paper. Subsequent analysis by the stannous chloride procedure in Standard Methods⁵ included the use of a B&L Spectronic 20 at 690m μ .

A continuous automatic sampling device, built specifically to support jug-study phosphate analyses, supplied whole samples to a Technicon AutoAnalyzer platformed according to the method by Gales and Julian.⁶ The Manifold and reagents were modified, however, to more closely approximate Standard Methods.⁵ The arrangement, in order of sequence, was as follows:

- a. A six-port peristaltic pump circulating jug mixed liquor continuously.
- b. An open-shut solenoid valve system selectively sampling the flow from a T-connection in each circulating jug line.
- c. A stepping relay alternately activating one of six jug sample solenoids or the solenoid to a distilled wash water supply.

⁵Standard Methods for the Examination of Water and Wastewater, 12th Edition, p. 234-236. 1965.

⁶M. E. Gales, Jr., and E. C. Julian, "Determination of Inorganic Phosphate or Total Phosphate in Water by Automatic Analysis." Presented at the 1966 Technicon Symposium on Automation in Analytical Chemistry.

d. A master timer regulating the stepping relay at two-minute intervals.

e. A Technicon proportioning pump providing the flow of samples and distilled water to a Technicon continuous filter. This pump also diluted filtered samples with distilled water in the ratio of 1:40, respectively.

Whole plant samples were run on the Technicon AutoAnalyzer using a Technicon Sampler II and a continuous filter with samples reaching the filter within thirty minutes. No significant orthophosphate bleedback occurred in unfiltered samples during this period.

2. Total Phosphate

Analyses were conducted on fixed whole samples at the Ada laboratory within 15 days of sample collection. Initially whole samples were blended for three to five minutes in a Waring Blendor and then analyzed by the persulfate procedure of Gales and Julian.⁶ The procedure was modified to more closely approximate the Standard Methods⁵ procedure for orthophosphate in that the samples were neutralized after digestion. Also the manifold design and reagents for the AutoAnalyzer were adjusted to deliver approximately the amount of reagents per sample outlined by Standard Methods.⁵

3. Total Carbon and Total Nonvolatile Organic Carbon

Whole samples were run in the field using the methods of Van Hall, Safranko, and Stenger⁷ and Van Hall, Barth, and Stenger.⁸ A Beckman Carbonaceous Analyzer was used. Preliminary homogenization with a Waring Blendor provided representative syringe sampling of whole samples. As the whole acidified sample was further purged with nitrogen gas for five minutes, results were reported as total nonvolatile organic carbon. Acetic acid standards were used for instrument calibration.

4. Total Oxygen Demand

Whole samples were run by the method of Stenger and Van Hall⁹ using the instrument and techniques described therein. Preliminary homogenization with a Waring Blendor was practiced. Sodium acetate standards were used.

5. Total Hardness

In the field, hardness was determined by EDTA titrimetry according to Standard Methods, Method B, p. 147-152.⁵

⁷C. E. Van Hall, J. Safranko, and V. A. Stenger, "Rapid Combustion Method for the Determination of Organic Substances in Aqueous Solutions," Anal. Chem. 35:3, p. 315-319. 1963.

⁸C. E. Van Hall, D. Barth, and V. A. Stenger, "Elimination of Carbonates from Aqueous Solutions Prior to Organic Carbon Determination," Anal. Chem. 37:6, 769. 1965.

⁹V. A. Stenger and C. E. Van Hall, "Rapid Method for Determination of Chemical Oxygen Demand," Anal. Chem. 39:2, 207. 1967.

6. Total Chromium

Chromium was determined in the field using the procedure of Standard Methods⁵ (Total Chromium Method B, p. 474-479).

Color was measured photometrically on a Beckman Model B Spectrophotometer.

Physical Tests

1. Solids

Tests for total suspended and total volatile suspended solids were conducted according to Standard Methods⁵ (Methods C & D, p. 424-425). Reeve Angel 2.4 cm glass fiber filters grade 934AH were used in lieu of asbestos mats. Gooch crucibles were fired at 600°C, cooled, and the mats placed in the crucibles and dried at 103°C for at least 1 hour before initial weighing. At intervals crucibles with filters were subjected to 600°C furnace temperatures to check for weight loss due to the filter. Total and total volatile solids were determined according to Standard Methods⁵ (Methods A & B, p. 423-424).

2. Dissolved Oxygen

Measurements were made in situ with a YSI Model 51 Oxygen Meter equipped with a Model 5103 oxygen/temperature probe. The meter was calibrated against the Azide Modification of the Winkler Method described in Standard Methods⁵ (Method A, p. 406-410). The meter was also calibrated against saturated air at the temperature at the test medium.

NOTE: Mention of products and manufacturers is for identification only and does not imply endorsement by the Federal Water Pollution Control Administration or the U. S. Department of the Interior.

Appendix II

PLANT OPERATIONAL DATA

Date 1967	Sewage Flow	Air			Return Sludge		Infl pH	Mixed Liquor TSS (mg/l)
		Pre-Aer. ³ (Thous. ft ³)	Air Lifts ³ (Thous. ft ³)	Aer. Tks. (mcf)	mgd	%		
5/15	9.80	585	645	5.94	2.28	23	7.6	2,887
5/16	10.46	615	912	5.78	2.97	28	7.5	3,212
5/17	10.41	582	1,108	5.58	3.60	35	7.4	3,783
5/18(rain)	9.65	583	1,108	5.39	3.65	38	7.5	3,458
5/19	8.94	581	1,114	5.43	3.64	40	7.5	--
5/20	8.09	587	1,126	5.70	3.72	45	7.5	--
5/21	7.26	582	1,111	5.65	3.72	51	7.4	3,491
5/22	8.24	581	1,110	5.63	3.67	44	7.5	4,069
5/23	8.03	595	1,111	5.69	3.70	46	7.3	3,879
5/24	7.84	582	1,107	5.70	3.69	47	7.3	3,934
5/25	7.82	586	1,105	5.72	3.71	47	7.3	3,692
5/26	7.69	581	1,091	5.69	3.64	47	7.4	--

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