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Ammonia Removal in a Physical-Chemical Wastewater Treatment Process

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November 1972

AMMONIA REMOVAL IN A PHYSICAL-CHEMICAL WASTEWATER TREATMENT PROCESS

By

Robert A. Barnes
Peter F. Atkins, Jr.
Dale A. Scherger

Contract No. 68-01-0049
Project 17010 HAM

Project Officer

Francis L. Evans III
Environmental Protection Agency
National Environmental Research Center
Cincinnati, Ohio 45268

Prepared for

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ABSTRACT

The pilot scale study at Owosso, Michigan, has demonstrated the feasibility of using chlorination followed by dechlorination with granular activated carbon for the removal of ammonia-nitrogen in a physical-chemical treatment facility. The pilot facility removed on the average 85 percent of the ammonia-nitrogen applied to the chlorination-dechlorination system. The study showed that ammonia-nitrogen removals as high as 98 percent can be obtained, if desired. The results from this pilot operation indicate that there was complete removal of free and combined chlorine in the dechlorination stage resulting in a dechlorinated effluent. The following overall average removal efficiencies were realized during the study: Ammonia-nitrogen - 85 percent or better; organic-nitrogen - 90 percent; biochemical oxygen demand - 94 to 96 percent; suspended solids - 90 percent; phosphorus - 80 percent or better.

This report was submitted by Ayres, Lewis, Norris, and May, Inc., Ann Arbor, Michigan, and Environmental Control Technology Corporation, Ann Arbor, Michigan, in fulfillment of Contract Number 68-01-0049 under the sponsorship of the Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. Ammonia-nitrogen can be removed to any desired level by the chlorination-dechlorination system.

2. Complete removal of ammonia-nitrogen from the wastewater would require a chlorine to ammonia-nitrogen feed rate of approximately 9 to 1.

3. The chlorination-dechlorination system can remove free chlorine and all forms of chloramines applied to the system.

4. There is an initial ammonia-nitrogen breakthrough during start up of the dechlorination process which stops after a brief lag or acclimation period.

5. The ammonia removal process tends to depress the pH in non-buffered systems and might necessitate pH adjustments in the final effluent.

6. The chloride content of the wastewater was increased, on the average, from 193 mg/l to 293 mg/l when employing the ammonia-nitrogen removal process.

7. Bacterial reductions in the ammonia-nitrogen removal process exceeded the normal effluent requirements as set forth by the State of Michigan. The chlorination-dechlorination process also provided a dechlorinated effluent.

8. The pilot facility has demonstrated that the physical-chemical treatment process can produce a final wastewater effluent with a BOD concentration of 7 mg/l and suspended solids levels less than 20 mg/l.

9. The dissolved oxygen level of the final effluent varied between 1 and 2 mg/l. Reaeration facilities would have to be provided if greater dissolved oxygen levels were required.

10. The carbon dosage required in the organic removal stage is approximately 500 pounds per million gallons of wastewater treated.

11. Low lime treatment (150 to 175 mg/l as $Ca(OH)_2$) - pH ranging between 8.8 and 9.4 - will, with proper coagulation and sedimentation, reduce the phosphorus level of the wastewater by over 80 per cent.

SECTION II

FUTURE WORK

Based on the experience gained in this study together with the results obtained, the following areas deserve further investigation.

1. The exact mechanism of chloramine removal should be defined.

2. The phenomena of acclimation noticed in the dechlorination system is worthy of further study as it most probably will add insight into the chloramine removal mechanism.

3. The composition of the effluent gases released during chlorination and also during dechlorination should be evaluated.

4. The minimum amount of carbon (pounds per gallon of wastewater treated) required in the dechlorination stage should be more adequately defined.

5. The ability to reverse the roles of the two carbon systems before regeneration should be investigated. That is to say, can the exhausted dechlorination carbon (before regeneration) be used in the organic removal phase or can the exhausted carbon from the organic removal stage prior to its being regenerated be used in the dechlorination stage.

6. A study should be initiated to determine whether the use of activated carbon as a dechlorinating agent precludes its subsequent use or reduces its effectiveness as an adsorbent for water soluble organics even after regeneration.

7. The bacterial reductions observed during the study are significant. A similar investigation into the ability of the process to reduce viral pollution should be undertaken.

8. The chlorination-dechlorination system should be studied operating under varying influent wastewater conditions of pH, alkalinity and organic loading.

9. The chlorination-dechlorination system, i.e., breakpoint chlorination followed by dechlorination using granular activated carbon is unique from other systems in that the process can be designed to remove all or part of the ammonia-nitrogen in the wastewater. When intermediate removals of ammonia-nitrogen (i.e., 50 to 75% removal) are required, the concept of split treatment and the use of the non-chlorinated stream to effect pH readjustment should be investigated.

10. The use of this ammonia removal system should be studied after conventional biological treatment process. This would be

of immediate benefit for biological treatment facilities presently facing immediate or anticipated ammonia-nitrogen removal orders.

11. The biological productivity of an effluent from a physical-chemical treatment process incorporating this type of ammonia removal system should be evaluated. These studies should be compared to the productivity of effluents from conventional biological systems, biological systems incorporating ammonia conversion (to nitrates) and biological systems where sand filtration is used as a tertiary step.

SECTION III

INTRODUCTION

This report discusses in detail the operation and performance of a pilot scale wastewater treatment facility utilizing breakpoint chlorination followed by dechlorination with granular activated carbon for the removal of ammonia-nitrogen from a domestic wastewater source. The study was performed at the wastewater treatment facility of the City of Owosso, Michigan.

The chlorination-dechlorination process was operated in conjunction with a complete physical-chemical wastewater pilot treatment facility. The total treatment scheme involved a number of chemical and physical processes operated in a sequential manner as follows: chemical coagulation and sedimentation, deep-bed filtration, carbon adsorption prior to chlorination (pre-adsorption), breakpoint chlorination, carbon adsorption for dechlorination (post-adsorption).

The main emphasis of this study was to evaluate the practical feasibility of using breakpoint chlorination followed by dechlorination using granular activated carbon for the removal of ammonia-nitrogen from a domestic wastewater within a standard physical-chemical treatment scheme. A secondary benefit of the investigation was the collection of data on the effectiveness of the overall process in removing biochemical oxygen demand (BOD), suspended solids (SS) and phosphates (PO_4) from the Owosso raw wastewater. This data can then be added to the data collected during a previous physical-chemical pilot scale study performed at Owosso, Michigan, during the summer of 1970.

SECTION IV

OBJECTIVES

The main objective of this study was to determine the engineering feasibility of incorporating an ammonia-nitrogen removal process into a conventional physical-chemical treatment process. To accomplish this objective, consideration was given to breakpoint chlorination followed by dechlorination using granular activated carbon and also to partial chlorination (chlorine application below that required for breakpoint) followed by chloramine removal by activated carbon.

The ammonia-nitrogen removal system was evaluated in terms of removal efficiency, chemical cost, process by-products and operational efficiency to evaluate the optimum mode of operation.

SECTION V

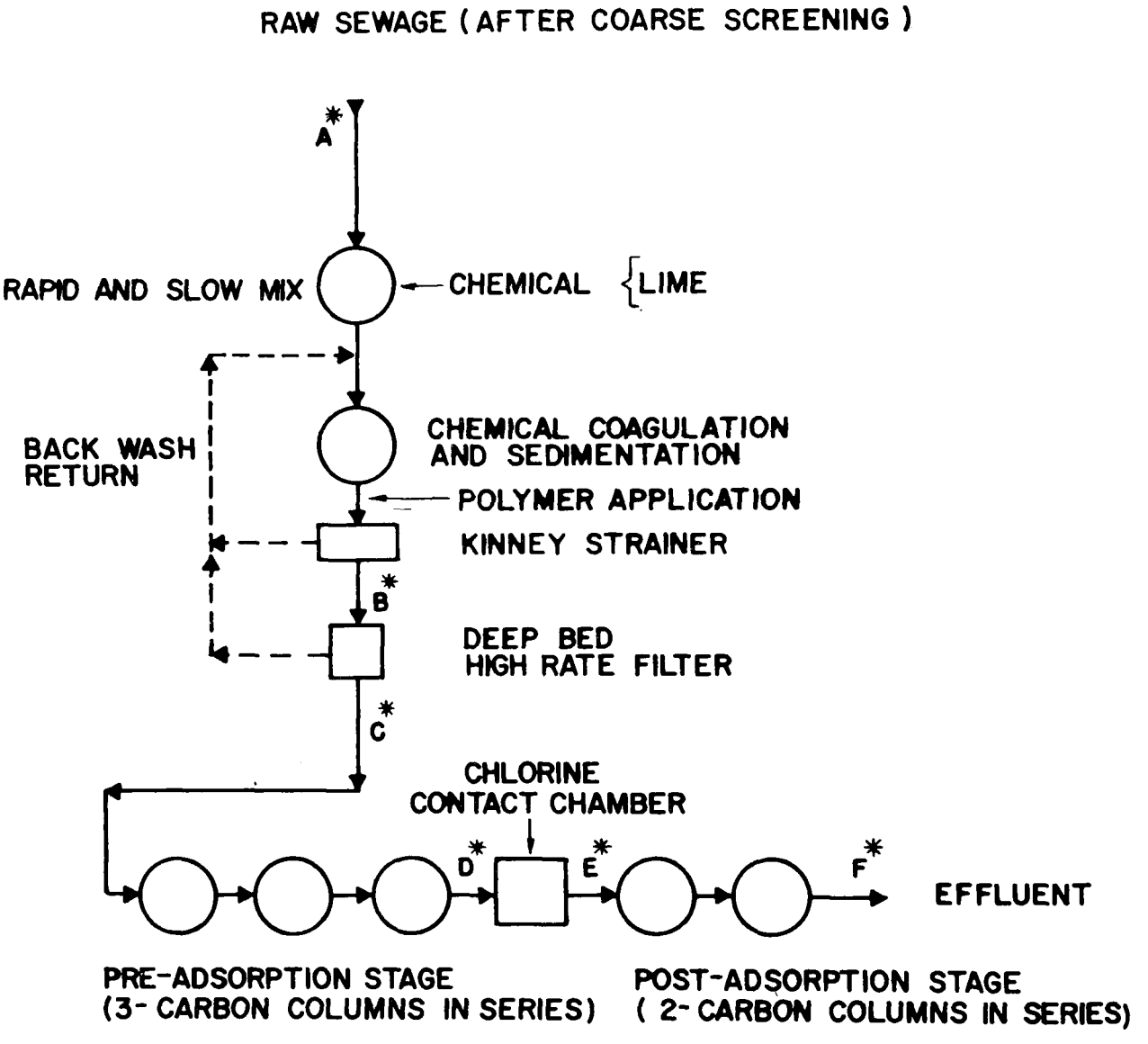
METHODOLOGY

Pilot Treatment Facility

The basic pilot plant configuration is shown in Figure 1. The pilot unit was a trailer mounted facility, completely self-contained, leased from Hydromation Engineering Company of Livonia, Michigan. The pilot unit received a raw wastewater flow varying between 10 and 15 gallons per minute (14,400 to 21,600 gallons per day) depending upon the detention desired in the sedimentation section. Once a flow rate was established, a constant rate was maintained by a head tank before the rapid mix chamber. In general, the unit was operated at an influent flow rate of 12 gallons per minute (gpm).

The incoming raw wastewater was chemically coagulated with lime (approximately 150 to 175 mg/l as $Ca(OH)_2$). This yielded a coagulation pH of 8.8 to 9.4. After chemical addition, the wastewater was rapid mixed for one minute and then allowed to slow mix for a period of 20 to 30 minutes. The coagulated waste was then settled for approximately two hours. The effluent from the coagulation-sedimentation section was then passed through a Kinney strainer (continuous backwash) at a rate of approximately 10 gpm, the remaining 2 gpm being wasted to drain. The Kinney strainer was used to remove fibrous or lint-like material which might cause surface loading of the deep-bed filter. After the Kinney strainer, the wastewater was filtered using a Hydromation deep-bed filter operating at a flow rate of 10 gallons per minute per square foot (10 gpm/ft^2). The deep-bed filter had a bed depth (PVC Class I media) of approximately 15 inches. The filter effluent was then pumped through three 12-inch diameter (I.D.) carbon contactors at a rate of six gallons per minute per square foot (6 gpm/ft^2). Each carbon contactor contained four feet of granular activated carbon (Calgon Filtrasorb 400, 14 to 40 mesh) in repose. All carbon contactors were operated under an up-flow, expanded-bed mode. The effluent from the third carbon contactor was then chlorinated using a Fischer and Porter vacuum-operated solution feed gas dispenser. No make-up water was used in the chlorination process; hence, there was no dilution of the wastewater as it underwent chlorination. The chlorinated wastewater was allowed to contact for a period of 15 minutes before the dechlorination step. The dechlorination process consisted of two 12-inch diameter (I.D.) carbon contactors operating in a manner analogous to the carbon contactors described earlier.

PILOT PLANT FLOW SCHEMATIC



NOTE:
A*, B*, C*, D*, E*, F* — INDICATE SAMPLING POINTS

FIGURE 1

The pilot plant was operated continuously on a twenty-four hour basis throughout the test period. Occasionly the system was shut down for equipment repair, replacement of exhausted carbon, or process modification as is normal when operating any pilot installation. Samples were taken automatically at selected locations every hour and composited based on flow to yield twenty-four hour composites. As indicated in Figure 1, samples were taken of the raw wastewater, Kinney strainer effluent, deep-bed filter effluent, after 15 minutes carbon contact (3rd carbon column effluent), chlorine contact chamber effluent, and the final effluent (25 minutes carbon contact - 5th carbon column effluent). Throughout most of the study the raw wastewater samples were taken by the Owosso treatment plant personnel because automatic monitoring of the raw wastewater in the pilot unit was prevented due to clogging of the automatic valves.

Twenty-four Hour Surveys

Periodically throughout the test period twenty-four hour continuous surveys were performed specifically to evaluate the ammonia removal process. During these surveys (totaling nine in number) grab samples were taken at the following locations: before chlorination (after either the second or third carbon contactor), after the chlorine contact chamber (15 minutes contact time), and after dechlorination (after either the fourth or fifth carbon contactor). These grab samples were taken in such a manner (sequential time samples) as to measure a particular mass (plug) of wastewater as it traveled through the various unit processes. All grab samples were analyzed immediately on site.

Samples taken before chlorination were analyzed for pH, ammonia-nitrogen and chlorides. The samples taken after the chlorine contact chamber were analyzed for pH, free chlorine, monochloramine, dichloramine, trichloramine and ammonia-nitrogen. Samples taken after carbon dechlorination were analyzed for pH, chlorides, ammonia-nitrogen, free chlorine, monochloramine, dichloramine, and trichloramine. On four survey days samples were also collected for bacteriological analyses to determine the magnitude of disinfection that might reasonably be expected from such a process.

Analytical Methods

All physical, chemical and bacteriological analyses performed during this study were in accordance with Standard Methods[1].

Free chlorine, monochloramine, dichloramine, and trichloramine were analyzed according to the procedure outlined by Palin[2]. It should be noted at this point that the determination of ammonia-nitrogen in the wastewater from the chlorine contact chamber is exceedingly difficult because of the inherent interferences (presence of chloramines) and at best is only of marginal value in assessing the quantitative amounts of unreacted ammonia-nitrogen present.

SECTION VI

RESULTS

Ammonia-Nitrogen Removal

The ammonia-nitrogen removal data collected throughout the study are tabulated in Table I and depicted graphically in Figure 2. In addition to these results are ammonia-nitrogen removal data generated by the twenty-four hour surveys which were performed to evaluate more stringently the chlorination-dechlorination process. These results are shown in Figures 3 through 13. The results on the chloride, ammonia-nitrogen, pH, free chlorine, monochloramine, dichloramine, and trichloramine levels for these surveys are tabulated in Appendix A (Tables A-1 to A-10). Chloride levels in the raw wastewater and final plant effluent at various times during some of the twenty-four hour survey periods are shown in Table II and Figure 14. The results obtained on bacteria reduction throughout the pilot facility during four twenty-four hour survey days are shown in Table III.

Overall Plant Performance

Figures 15 through 22 show the biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), and phosphate (PO_4) removal results obtained during the study. Table IV gives the results of organic nitrogen removal obtained during the testing program.

SECTION VII

DISCUSSION OF RESULTS

Ammonia-Nitrogen Removal

A review of Table I and Figure 2 shows that the chlorination-dechlorination process removed, on the average, 85 per cent of the ammonia-nitrogen applied to the system. The average level of ammonia-nitrogen in the wastewater prior to chlorination was 12.0 mg/l and the average effluent concentration from the pilot unit was 1.8 mg/l. This removal was accomplished using a mean chlorine feed rate of approximately 6.5 pounds per day (lbs./day) applied to a continuous wastewater flow of 5 gallons per minute (7200 gallons per day). Use of these mean values yields an average chlorine to incoming ammonia-nitrogen feed ratio of 108 mg/l to 12.0 mg/l respectively (a 9 to 1 ratio by weight).

The use of total averages serves no purpose other than being a gross method of analyzing data. A more realistic approach to evaluating the data is to examine the twenty-four hour survey data as shown in Figures 3 through 13.

A review of Figures 3 through 13 shows that the efficiency of the chlorination-dechlorination process in removing ammonia-nitrogen is directly proportional to the chlorine to ammonia-nitrogen feed ratio. The pilot facility at Owosso was operated using a constant chlorine feed, since the chlorine feed levels could only be altered manually. Therefore, the ratio of chlorine to ammonia-nitrogen varied depending on the incoming ammonia-nitrogen concentrations. Thus, there were times when the process was under-chlorinating, while at other times over-chlorination was taking place. If the process was under-chlorinating (below a certain optimum level--to be discussed later), then a certain portion of the ammonia-nitrogen in the incoming wastewater would be unreacted (not going off as nitrogen gas nor formed into one of the chloramines) and would pass through the dechlorination section and be recorded in the final plant effluent. Thus, any variation in the chlorine to ammonia-nitrogen feed ratios would be reflected by varying ammonia-nitrogen removal efficiencies in the overall process.

The dependency of ammonia-nitrogen removal on the chlorine to ammonia-nitrogen feed ratio is shown quite clearly in Figures 3 and 4. In Figure 3, at 10:00 AM the chlorine to ammonia-nitrogen feed ratio was approximately 7.5 to 1 and resulted in an ammonia-nitrogen level in the effluent of 0.7 mg/l or 91

Table I

Ammonia Nitrogen Data

Cumulative Throughput Volume (gallons)	Ammonia Nitrogen - mg/l: Raw	After Filtration	Before Chlorination (15 minute carbon contact)	After Chlorination-Dechlorination (15 min.-chlorine contact) (10 min.-dechlorination contact)	Remarks
0	15.6	5.9	----	---	
21,092	15.5	----	13.2	7.1	Cl_2 feed = #4/day
28,000	----	14.3	14.0	4.8	" "
42,100	----	15.9	15.5	7.0	" "
49,080	14.0	----	13.4	1.9	Cl_2 feed = 6.0#/day
56,041	12.7	12.8	12.7	2.8	7#/day= 10 am to 10 pm
63,272	15.7	13.3	14.0	4.5	4#/day= 10 pm to 10 am
70,722	13.7	18.0	13.7	2.2	Cl_2 feed = 6.0#/day
76,826	13.4	13.3	13.4	0.4	7#/day= 10 am to 2 am
84,600	----	5.6	5.5	0.25	4#/day= 2 am to 10 am
90,817	2.7	3.6	3.0	0.0	Cl_2 feed = 7#/day
97,789	7.5	8.1	----	0.0	" "
105,094	9.4	5.9	5.6	0.3	" "
111,106	8.9	9.6	10.5	---	" "
131,834	----	----	11.0	3.9	" "
138,093	----	6.7	6.9	1.4	" "
153,502	12.8	9.3	6.3	1.1	" "
160,819	10.5	10.7	7.0	1.2	" "
166,392	----	----	11.6	0.8	" "
176,814	9.4	5.9	8.7	0.4	" "
181,683	11.6	11.2	7.6	0.6	" "
185,072	9.6	----	----	3.3	Chlorinator Malfunction
189,441	13.1	7.3	9.1	2.9	" "
195,423	13.0	----	----	10.0	Chlorinator Off
201,923	9.9	7.4	7.2	1.4	Cl_2 feed = 7#/day
208,403	14.0	8.4	8.6	0.5	" "
214,836	15.8	8.5	8.8	0.4	" "
221,834	14.0	9.7	9.1	0.3	" "

Table I (continued)

Ammonia Nitrogen Data

Cumulative Throughput Volume (gallons)	Ammonia Nitrogen - mg/l: Raw	After Filtration	Before Chlorination (15 minute carbon contact)	After Chlorination-Dechlorination (15 min.-chlorine contact) (10 min.-dechlorination contact)	Remarks
229,286	15.8	----	----	0.4	Cl_2 feed = 7#/day
235,269	15.0	----	----	0.5	" "
260,930	15.4	10.5	10.6	10.5*	Chlorinator Off
267,842	14.1	----	----	13.1*	' '
274,754	14.6	12.7	----	2.6	Cl_2 feed = 6#/day
281,666	14.0	13.8	----	0.8	Cl_2 feed = 7#/day
288,578	14.7	15.1	15.2	3.2	" "
295,490	15.4	13.2	13.0	2.1	Cl_2 feed = 6#/day
316,266	----	----	14.1	0.8	Cl_2 feed = 7#/day
323,138	----	----	14.3	0.4	Cl_2 feed = 8#/day
330,050	----	----	14.7	3.8	Cl_2 feed = 5#/day
337,025	17.0	16.1	16.0	2.8	Cl_2 feed = 7#/day
344,000	14.0	14.4	14.6	4.2	Cl_2 feed = 4 1/2#/day
350,975	19.0	18.3	18.0	0.3	Cl_2 feed = 10#/day
357,948	17.2	14.8	15.5	0.9	" "
364,921	14.4	14.7	14.4	1.2	Cl_2 feed = 8#/day
371,894	----	----	13.4	1.5	" "
378,867	----	14.0	12.0	0.4	' "
385,840	14.9	14.8	14.9	0.8	'
455,714	----	----	18.0	4.5	" "
462,708	----	----	15.8	6.3	Cl_2 feed = 7#/day
469,702	----	----	14.1	0.5	Cl_2 feed = 10#/day
483,675	----	----	14.9	0.7	" "
490,654	----	----	17.1	1.3	' '
Average	13.3	11.3	12.0	1.8**	

Notes: *Values not included in column average

**Average effluent concentration over test period during variable chlorine feeds

FIG. 2 - DAILY AMMONIA REMOVAL DURING TEST PERIOD

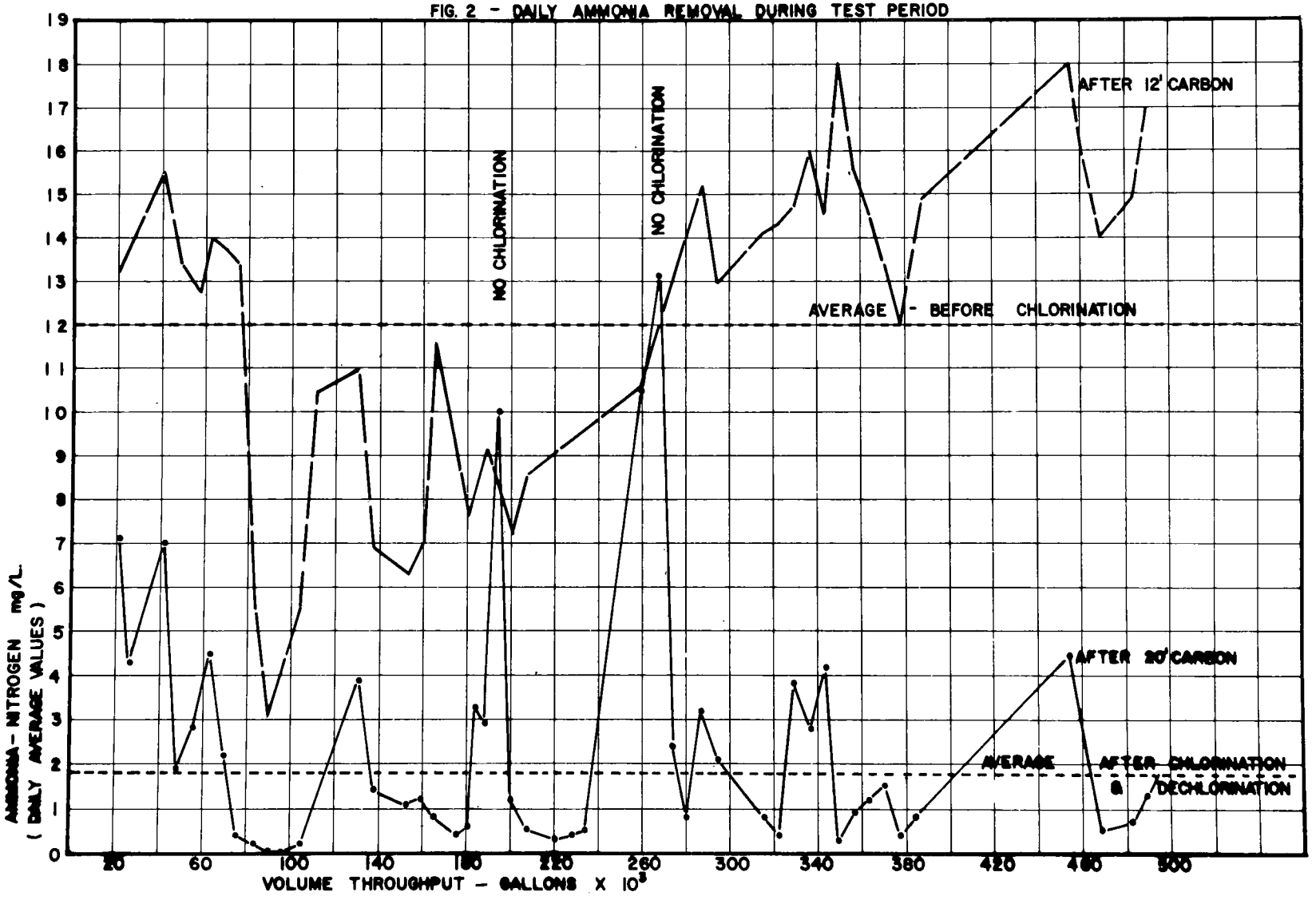


FIG. 3 - AMMONIA LEVELS BEFORE & AFTER CHLORINATION - DECHLORINATION

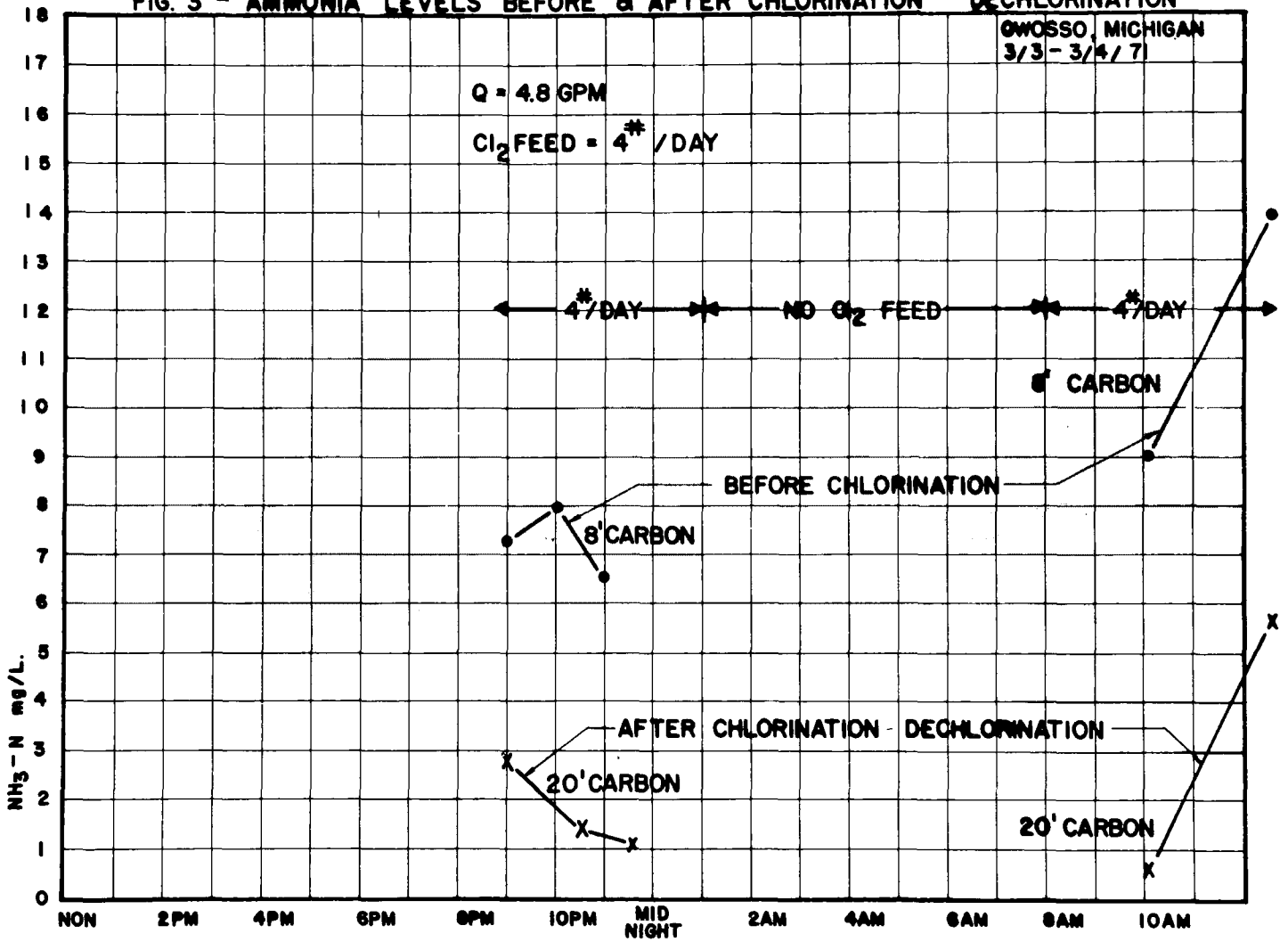
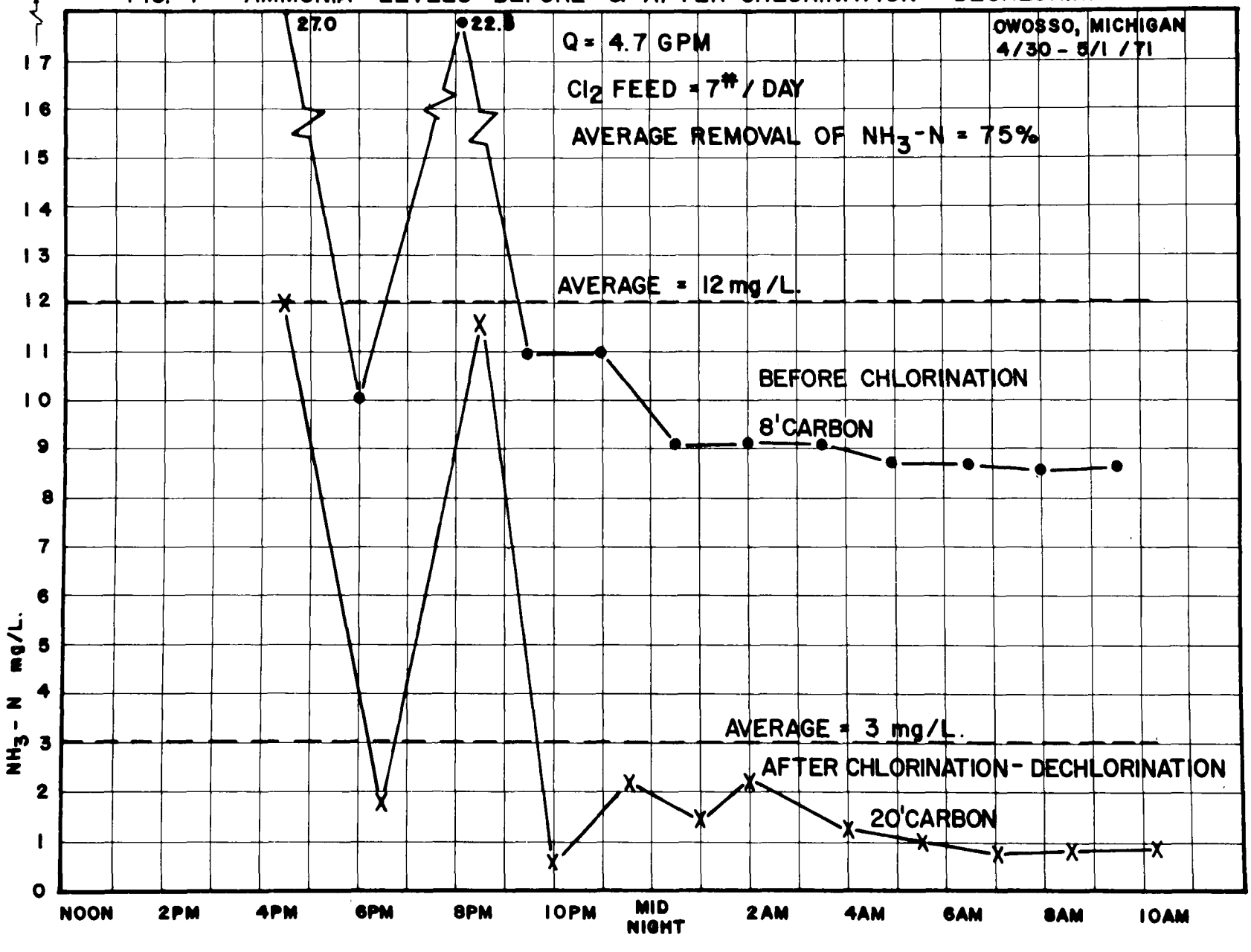


FIG. 4 – AMMONIA LEVELS BEFORE & AFTER CHLORINATION – DECHLORINATION



per cent removal efficiency. On the same day at 12:30 PM the incoming ammonia-nitrogen level increased to 14 mg/l and resulted in a chlorine to ammonia-nitrogen feed ratio of 4.7 to 1 and resulted in an ammonia-nitrogen level in the effluent of 5.7 mg/l or only a 59 per cent removal efficiency. The direct variation in ammonia-nitrogen removal efficiency with incoming ammonia-nitrogen concentrations, because of the constant chlorine feed rate, can be seen most vividly in Figure 4. Here extreme variations in ammonia-nitrogen levels were observed at two separate times. The chlorine feed rate on this particular survey day was fixed at 7 pounds per day. At a wastewater flow rate of 5 gpm, this amounts to a chlorine dosage of 116 mg/l in the wastewater. The 4:30 PM sample on this day showed an incoming ammonia-nitrogen concentration of 27.0 mg/l, resulting in a chlorine to ammonia-nitrogen feed ratio of 4.3 to 1. The resulting concentration of ammonia-nitrogen in the plant effluent was 12.0 mg/l, thus the process showed a removal efficiency of about 55 per cent. At 10:00 PM on this same day (Figure 4) the incoming ammonia-nitrogen concentration was 11.0 mg/l, thus making the chlorine to ammonia-nitrogen feed ratio 10 to 1. This resulted in a plant effluent having an ammonia-nitrogen level of 0.6 mg/l, and the process showed a 95 per cent level of efficiency.

The average incoming ammonia-nitrogen level for this particular day (Figure 4) was 12.0 mg/l with an average chlorine to ammonia-nitrogen feed ratio of approximately 10 to 1. The average ammonia-nitrogen removal was on the order of 75 per cent. This low daily average ammonia-nitrogen removal was caused by exceptionally high instantaneous ammonia-nitrogen concentrations, where, because of the experimental arrangement (constant chlorine feed), the wastewater was definitely being underchlorinated, thus high ammonia-nitrogen levels were observed in the plant effluent during these particular times. Again, it should be pointed out that these data were obtained from twenty-four hour composite samples which tend to mask the true efficiency of the ammonia-nitrogen removal process when a constant chlorine feed is being applied.

Figures 5, 6, and 7 show the results of a continuous monitoring of the ammonia-nitrogen removal system over a seventy-two hour period (May 13 through May 16, 1971). The results of these particular surveys are most interesting because during these three days the daily average ammonia-nitrogen levels were essentially constant, varying between 14.1 and 14.7 mg/l. The chlorine feed rate was varied on a daily basis between 5 and 8 pounds per day. When the chlorine feed rate was 7 pounds per day (116 mg/l chlorine) the pilot facility produced an average effluent ammonia-nitrogen concentration of 0.8 mg/l or 94 per

FIG. 5 - AMMONIA LEVELS BEFORE & AFTER CHLORINATION - DECHLORINATION

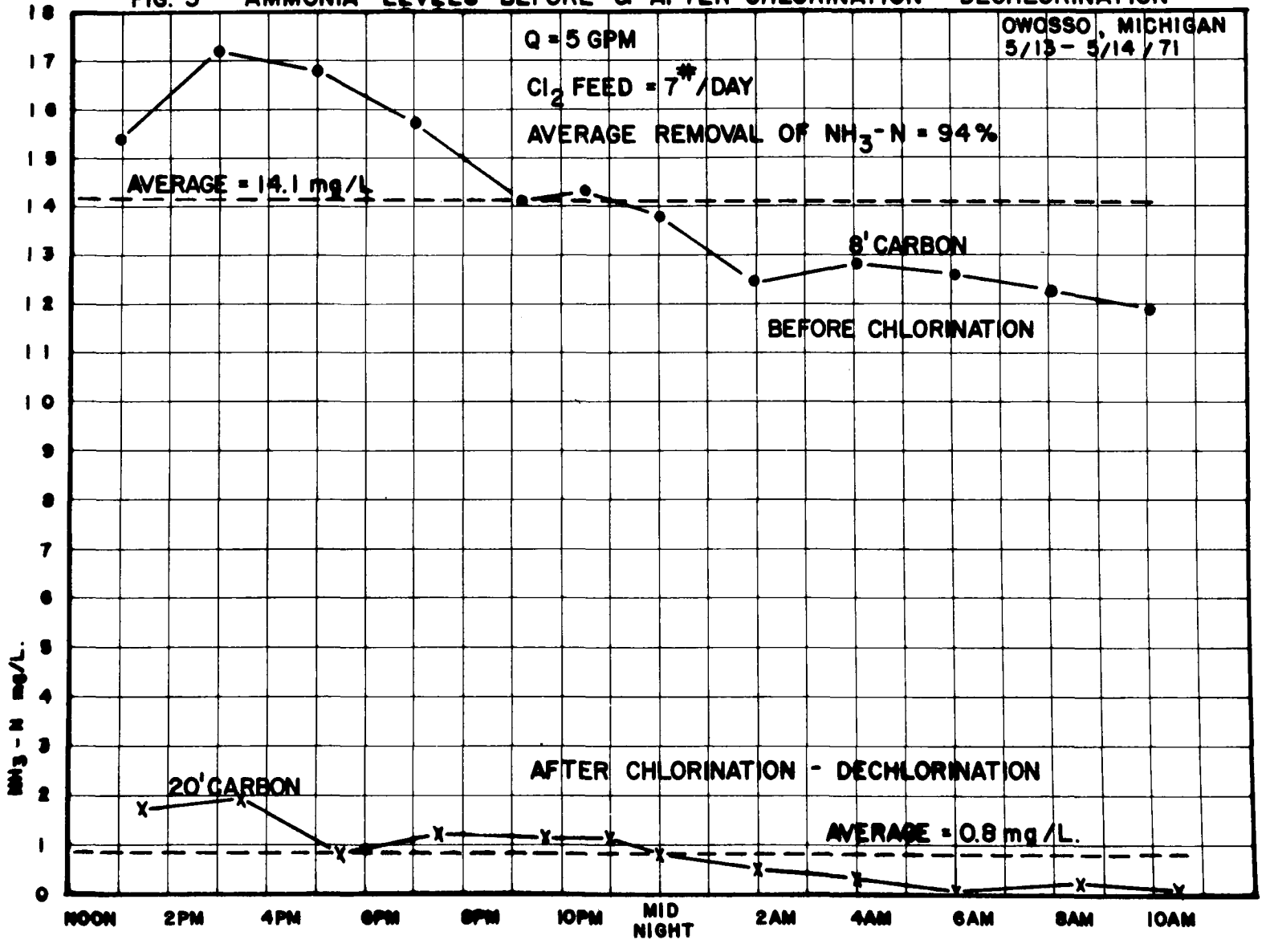


FIG. 6 – AMMONIA LEVELS BEFORE & AFTER CHLORINATION – DECHLORINATION

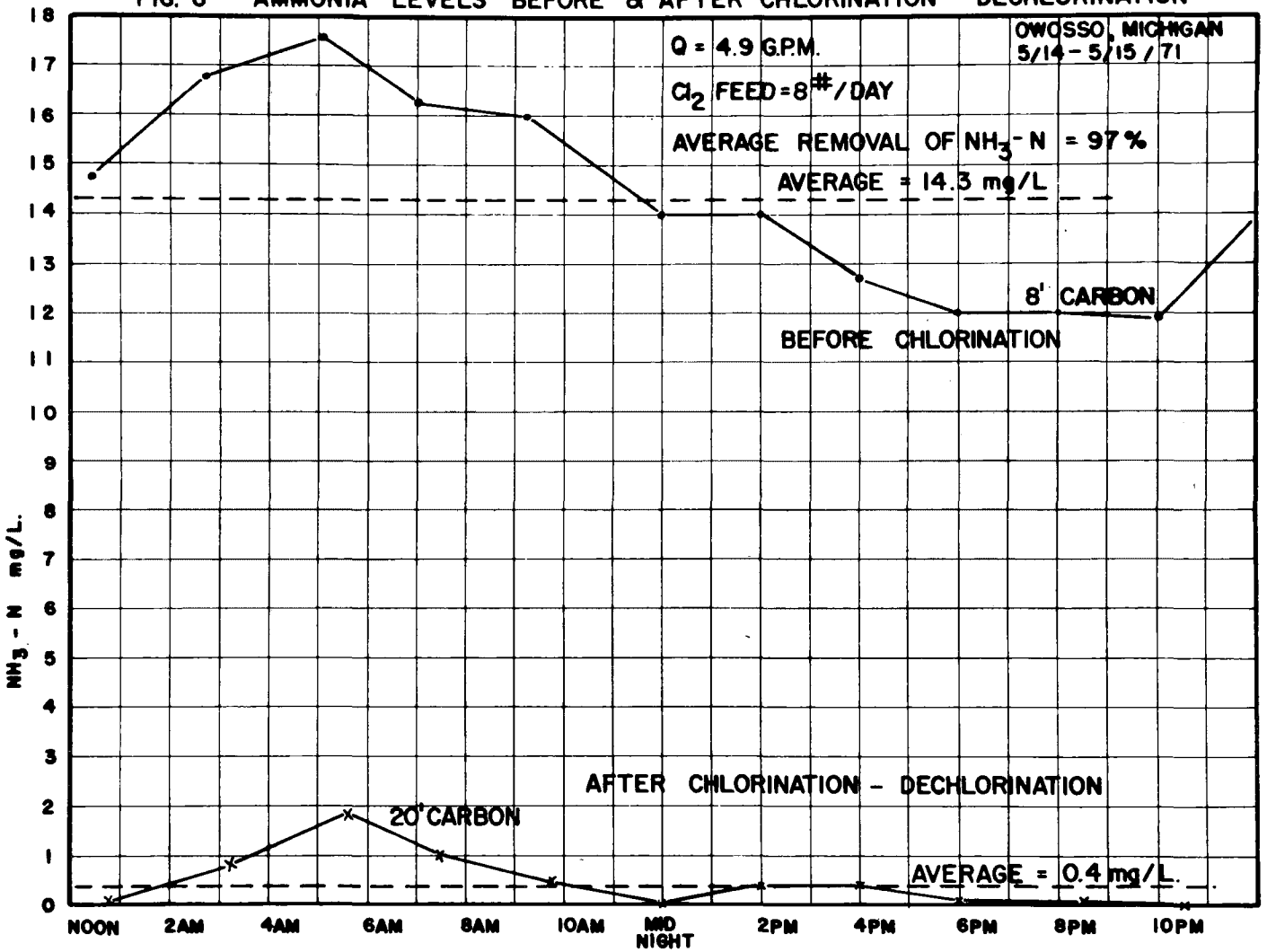
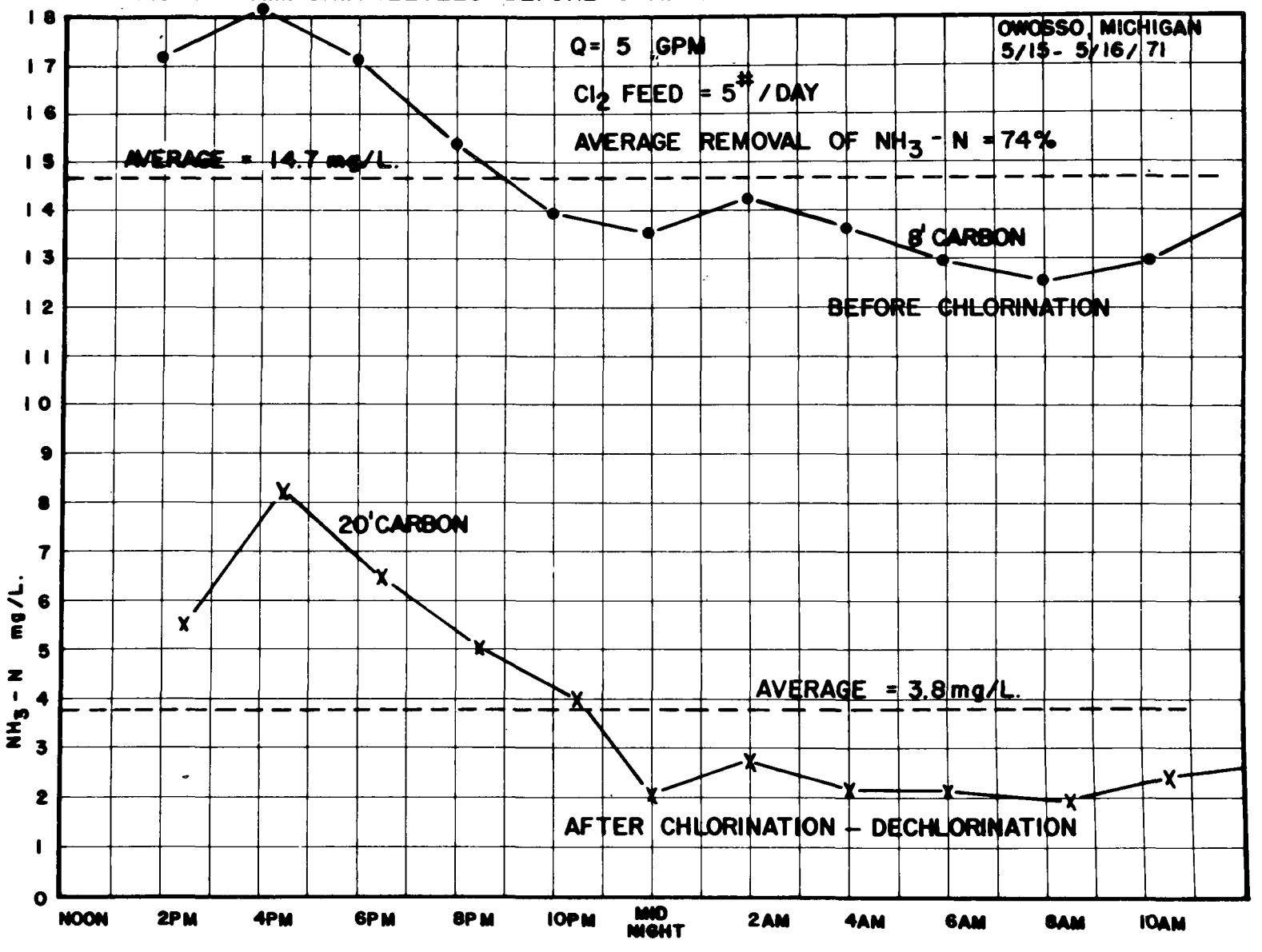


FIG. 7 – AMMONIA LEVELS BEFORE & AFTER CHLORINATION – DECHLORINATION



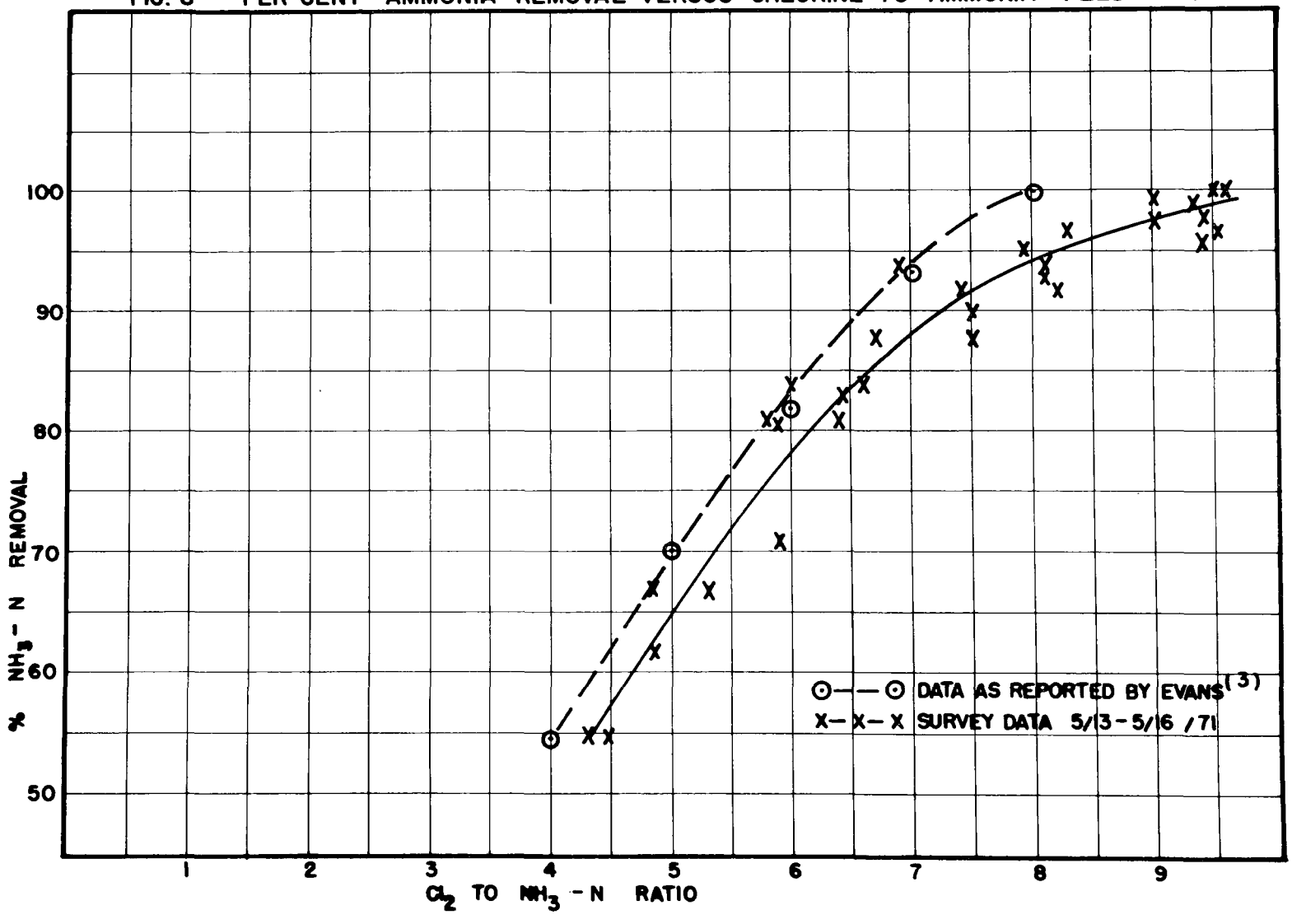
cent removal efficiency (see Figure 5). Figure 6 shows the results when the chlorine feed was increased to 8 pounds per day. Here the average effluent concentration was lowered to 0.4 mg/l for an overall ammonia-nitrogen removal efficiency of 97 per cent. On the last day of this test period (May 16, 1971), the chlorine feed rate was lowered to 5 pounds per day (Figure 7). This lower chlorine feed rate produced an effluent concentration of 3.8 mg/l of ammonia-nitrogen and showed an ammonia-nitrogen removal efficiency of 74 per cent.

Figure 8 is a summary plot of the data generated in the May 13 to 16, 1971, survey period (see Figures 5, 6, and 7). In this figure the per cent ammonia-nitrogen removed by the chlorination-dechlorination process is plotted versus the chlorine to ammonia-nitrogen feed ratio. This figure denotes in detail the fact that varying percent removal of ammonia-nitrogen was obtained as a function of the chlorine to ammonia-nitrogen feed ratio. The actual pilot plant data compares quite well with the experimental laboratory data as reported by Evans.[3] The only variation is that the field data indicates the need for a slightly higher chlorine to ammonia-nitrogen feed ratio to effect a given ammonia-nitrogen removal. Other data on chloramine formation, chlorides, pH, etc., generated during these three survey days are shown in Tables A-3 to Tables A-5 (see Appendix A). A review of these Tables (A-3 to A-5) indicate no breakthrough of free chlorine or chloramines during the test period. The apparent breakthrough of a slight amount of dichloramines will be discussed later in this report.

The data shown in Figures 5 through 8 were generated using the wastewater after it had undergone phosphate precipitation using low lime treatment ($Ca(OH)_2$ dosage of 175 to 200 mg/l, resulting in a pH of 8.8 to 9.4). Throughout the testing period no adjustment of pH or alkalinity was attempted. These data would indicate for the Owosso waste that stringent control of pH and alkalinity was not a prerequisite for ammonia-nitrogen removal. The data also indicate that with the proper monitoring and control equipment, as would be found in full-scale operation, any ammonia removal efficiency can be obtained if the chlorine feed is paced properly with the influent ammonia concentration. Tables A-1 to A-10 indicate that chlorine addition depressed the pH of the unbuffered, lime-clarified wastewater. Therefore, pH adjustment will be required at Owosso to meet the effluent pH requirement of 6.5 to 9.0.

It should be noted at this point that the dechlorination carbon employed during these survey days (May 13 to 16, 1971) was the original carbon placed in the unit at the outset of the study and exhibited no evidence of being exhausted (no free chlorine or chloramine breakthrough) even after 410,000 gallons of chlorinated wastewater had been applied to the system.

FIG. 8 - PER CENT AMMONIA REMOVAL VERSUS CHLORINE TO AMMONIA FEED RATIO



After the May 16, 1971 survey day the original dechlorination carbon (columns 4 and 5) was replaced by fresh carbon, and an investigation was undertaken to analyze an ammonia-nitrogen or chloramine breakthrough phenomena that has been observed by other investigators[4]. The results from these studies are shown in Figures 9 through 13. During this phase of the study, there was continuous monitoring of the chlorination-dechlorination system. Figures 9 through 12 show the ammonia-nitrogen removals achieved by the chlorination-dechlorination process during the initial days of operation using fresh dechlorination carbon. Figure 13 is a summary graph of per cent ammonia-nitrogen removal versus chlorine to ammonia-nitrogen feed ratio for these initial days together with a summary curve of previously discussed ammonia-nitrogen removal data obtained with dechlorination carbon exposed to 410,000 gallons of chlorinated wastewater.

As had been expected, Figure 13 indicates that the ammonia-nitrogen removal in the initial phase of operation of the dechlorination process is not as great as when the dechlorination carbon had been exposed to free chlorine or chloramines for a period of time (compare Curve A with Curve C). Curve B indicates transition of the system to ammonia-nitrogen removal levels approaching those shown in Curve C. Unfortunately, Curve B (see Figures 10, 11, and 12) was generated using high chlorine to ammonia-nitrogen ratios (9:1 and greater); hence, the points cluster around high removal efficiencies. Although the data are scattered, an inspection of Curves A, B, and C at the 9:1 chlorine to ammonia-nitrogen feed ratio suggests that there is substantial improvement in ammonia-nitrogen removal efficiencies after the carbon has been exposed to a chlorinated wastewater for a brief period of time. Thus, a phenomena of acclimation (rather than one of continual breakthrough) appears to be occurring. This observed acclimation period explains the relatively inefficient ammonia-nitrogen removals noticed at the outset of this study (see Table I), and might possibly explain the low ammonia-nitrogen removals reported by others[4] using laboratory test systems. The acclimation period for the dechlorination carbon appears to be on the order of three to five days under the test conditions experienced at Owosso.

An hypothesis will now be proposed to explain this acclimation phenomena, which if true, also defines the mechanisms by which the chloramines are broken down on the surface of the activated carbon. As is well known, the addition of near breakpoint doses of chlorine to ammonia-containing wastewater results in the reduction of the chlorine coupled with the oxidation of ammonia. The products of the reactions consist primarily of molecular nitrogen, various chloramines, chloride ions, and hydrated protons. It is hypothesized that different dechlorination

FIG. 9 — AMMONIA LEVELS BEFORE & AFTER CHLORINATION — DECHLORINATION

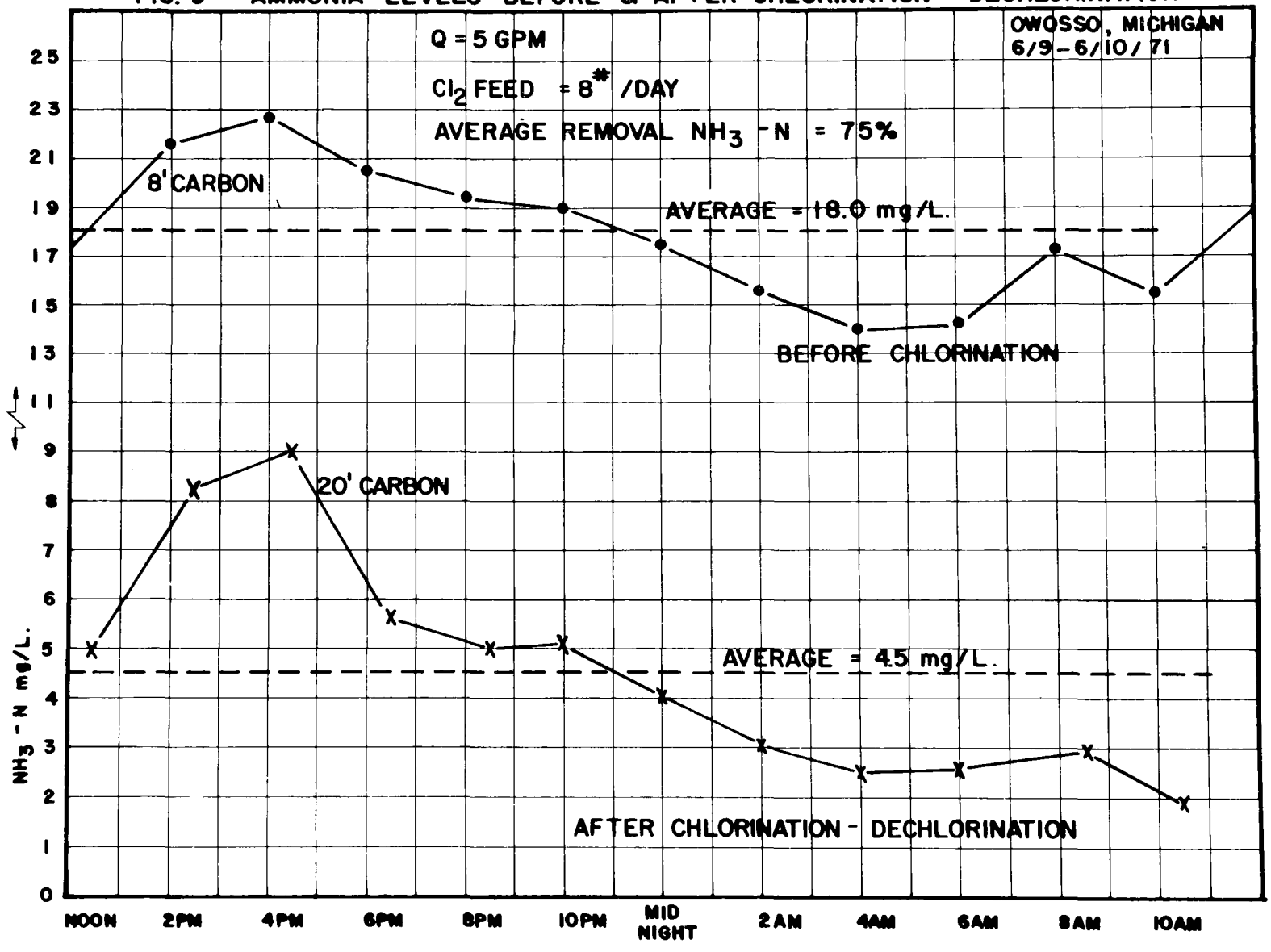


FIG. 10- AMMONIA LEVELS BEFORE & AFTER CHLORINATION - DECHLORINATION

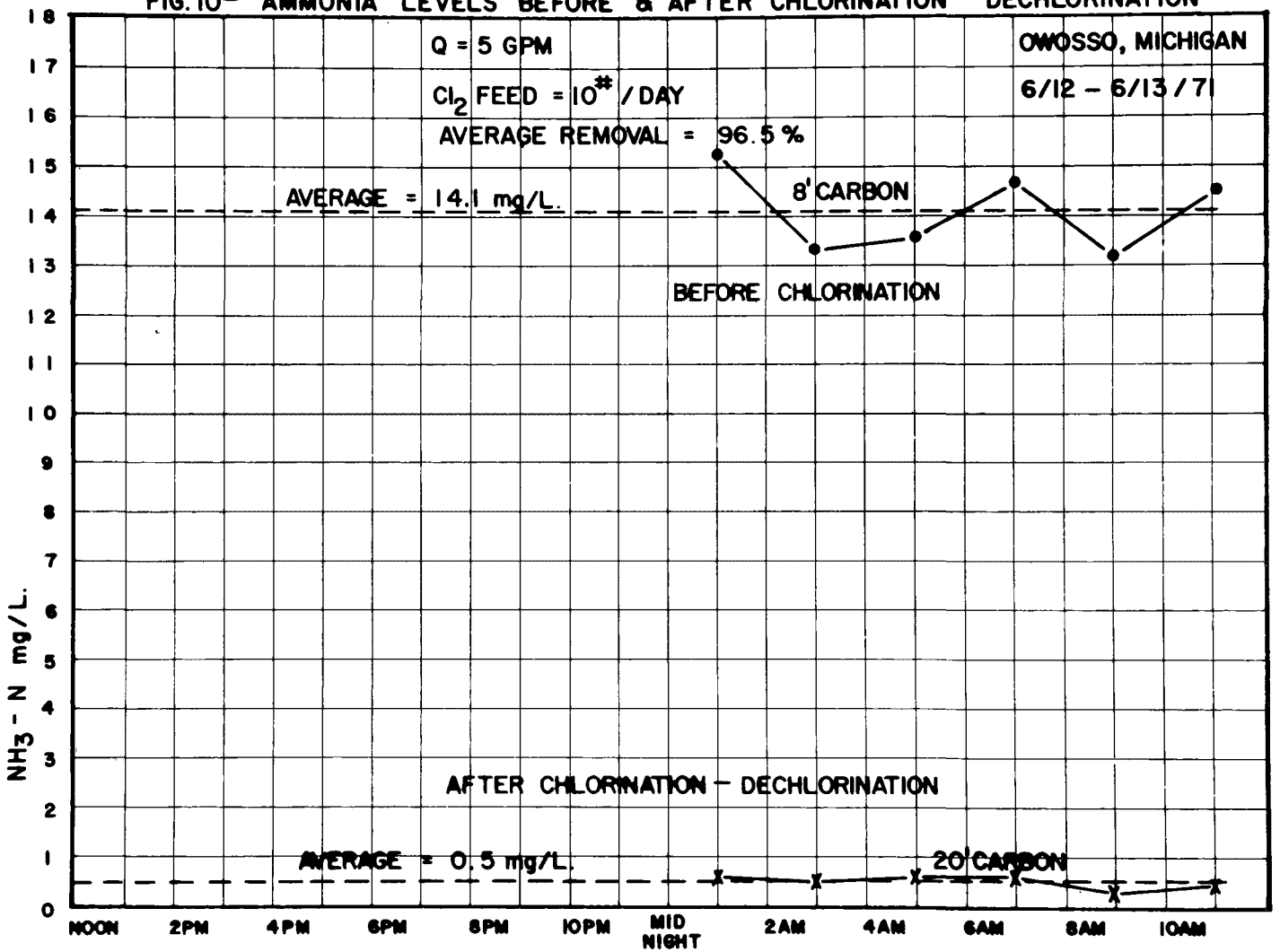


FIG. 11 — AMMONIA LEVELS BEFORE & AFTER CHLORINATION — DECHLORINATION

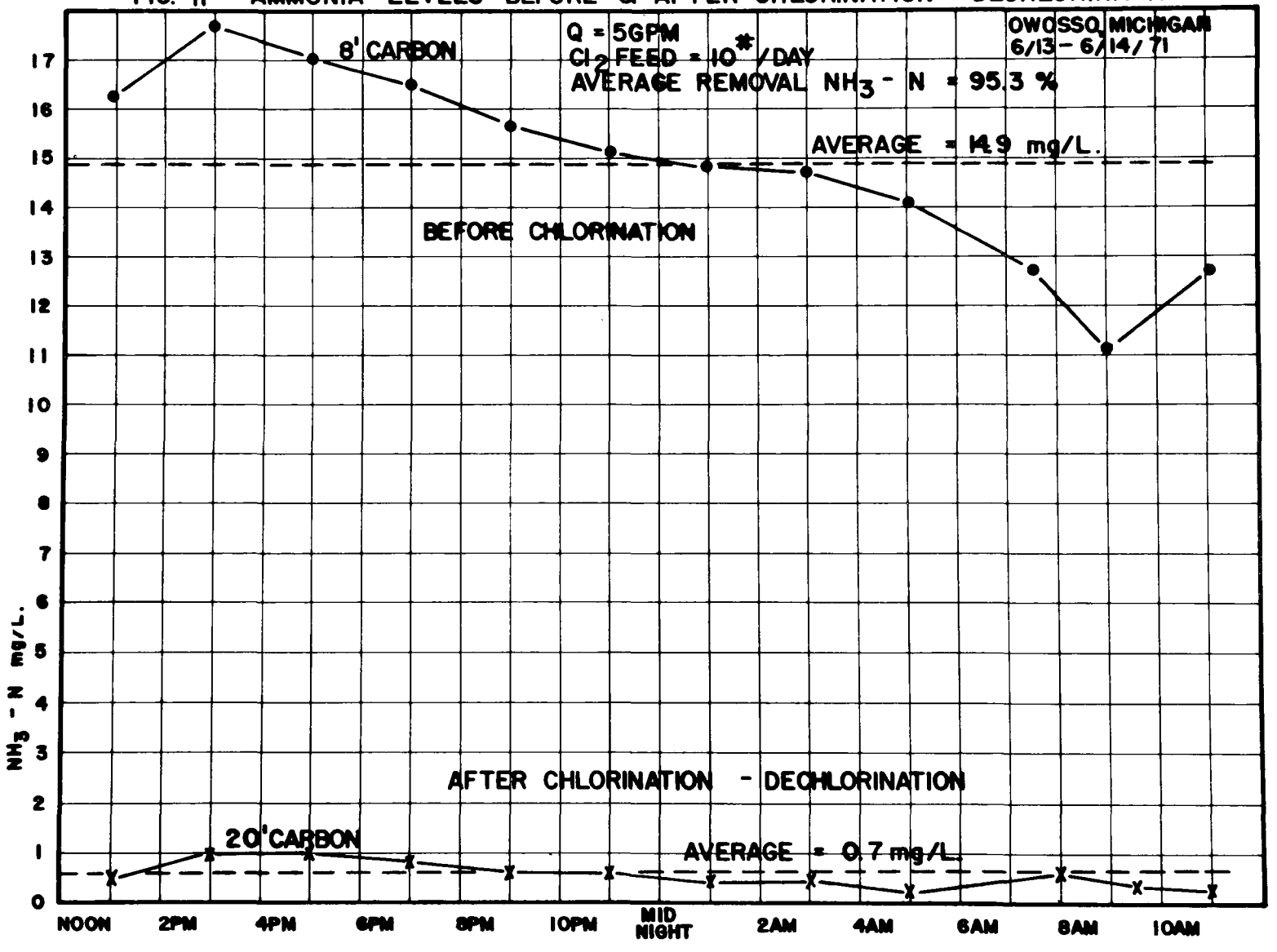


FIG. 12 - AMMONIA LEVELS BEFORE & AFTER CHLORINATION - DECHLORINATION

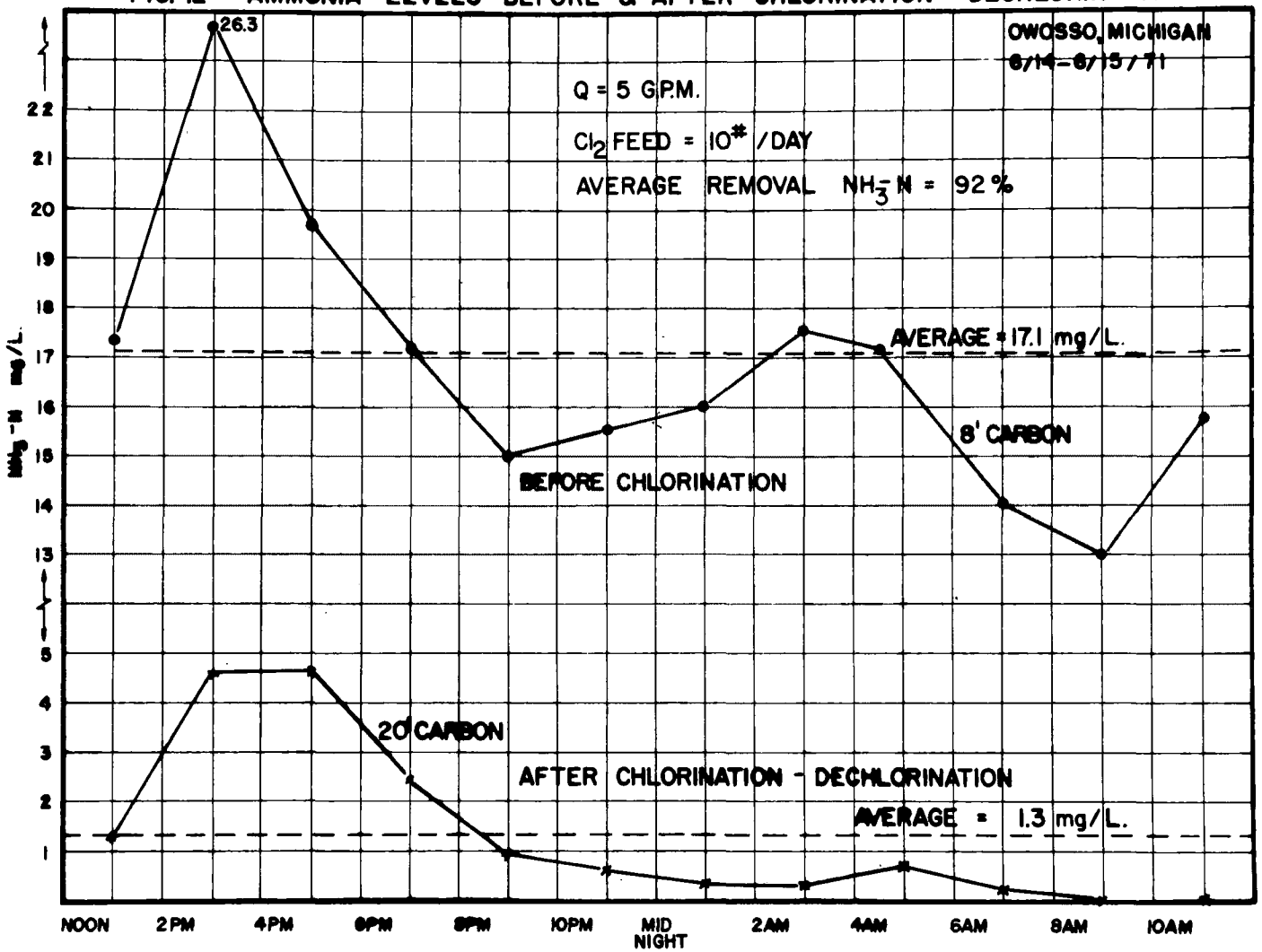
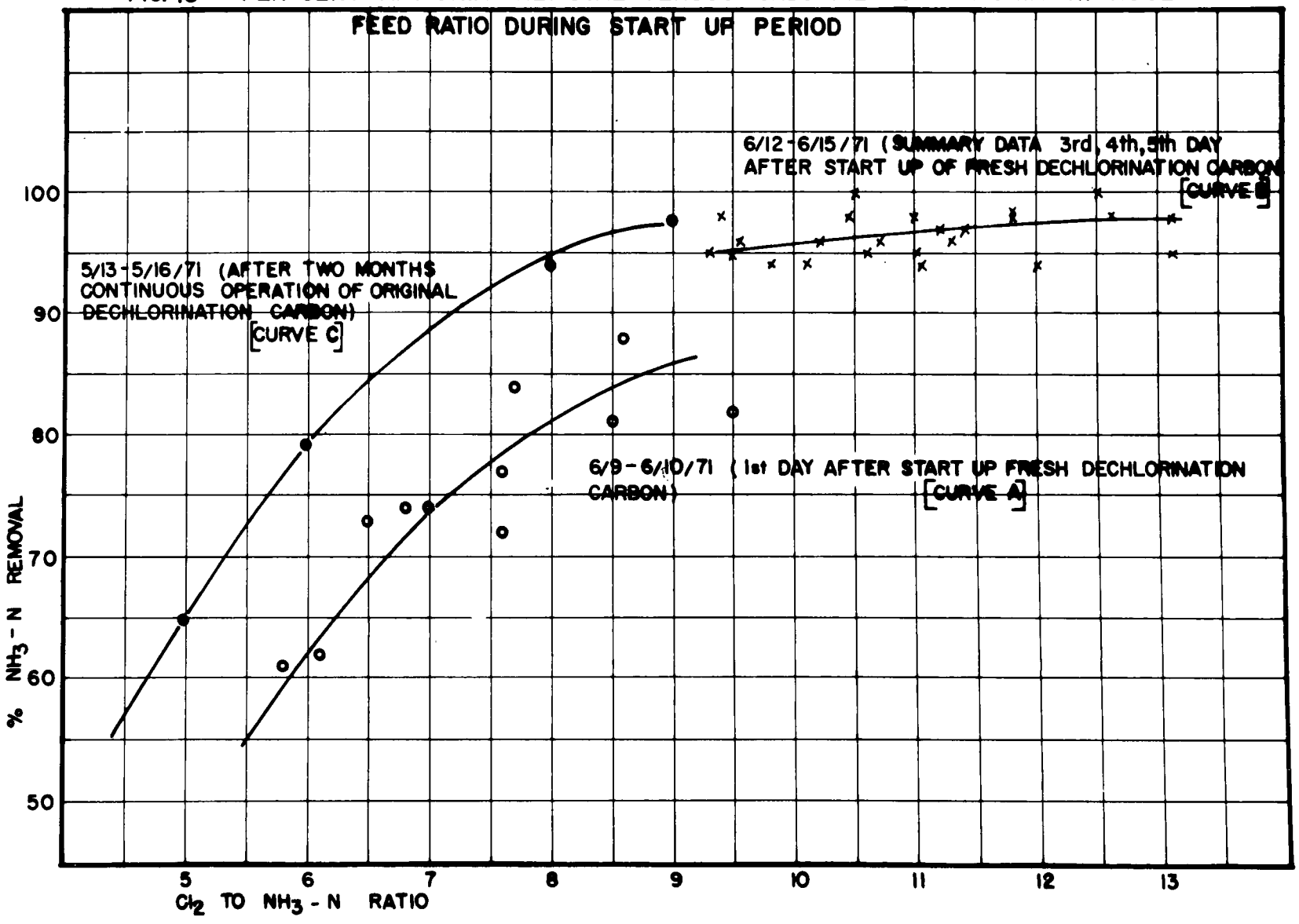


FIG. 13 — PER CENT AMMONIA REMOVAL VERSUS CHLORINE TO AMMONIA NITROGEN FEED RATIO DURING START UP PERIOD



reactions occur with respect to the chloramines, depending upon whether they come in contact with fresh or "acclimated" dechlorination carbon. When using fresh carbon, it is postulated that some of the chloramines are reduced back to ammonia while the carbon surface is oxidized. The hydrated protons released from the carbon surface as a result of this oxidation replace the chloride ions in the chloramines, resulting in a reversion of the nitrogen portion of the chloramine back to ammonia and release of chloride ions to solution. On the other hand, when using an "acclimated" carbon, the carbon surface is essentially devoid of available protons, which eliminates the possibility of the reversion of the chloramine back to ammonia. It is theorized in this case that the chloramines are adsorbed and/or catalytically oxidized on the carbon surface resulting primarily in the production of nitrogen gas, chloride ions released to the aqueous phase, and a further depression of the pH due to the release of hydrated protons from the breakdown of the chloramines.

Evidence to support this hypothesis is contained in the data on ammonia removal in the fresh versus acclimated carbon systems (Figure 13), the chloride mass balance data (Table II and Figure 14), and the chloramine and pH data (Tables A-3, A-5, and A-8) for both the fresh versus acclimated carbon systems.

As indicated previously (see Figure 13), there is a significant difference in the ammonia-nitrogen removal efficiencies when using fresh as compared to "acclimated" carbon in the dechlorination phase. This effect is independent of the chlorine to ammonia-nitrogen feed ratio in the chlorination stage. On the other hand, Table II and Figure 14 show that there is no significant difference in the chlorides released to the aqueous phase when using either fresh or "acclimated" carbon. These data were obtained during three consecutive twenty-four hour surveys (May 13 to May 16, 1971) when acclimated dechlorination carbon was being used, and during one twenty-four hour period (June 9 to June 10, 1971) when fresh carbon was used for dechlorination. These results indicate that the actual chloride concentrations measured during the survey days agree quite closely with the calculated chloride levels obtained from a theoretical mass balance, assuming all of the chlorine is reduced to chloride ion. The range of maximum and minimum values for the anticipated chloride concentrations was based on the accuracy with which the chlorinator could be set and held constant during the pilot operation.

The significant aspect of these results lies in the fact that a reasonable chloride mass balance (95 per cent confidence

TABLE II
EFFECT OF CHLORINATION-DECHLORINATION
ON CHLORIDE CONCENTRATIONS

OWOSSO, MICHIGAN

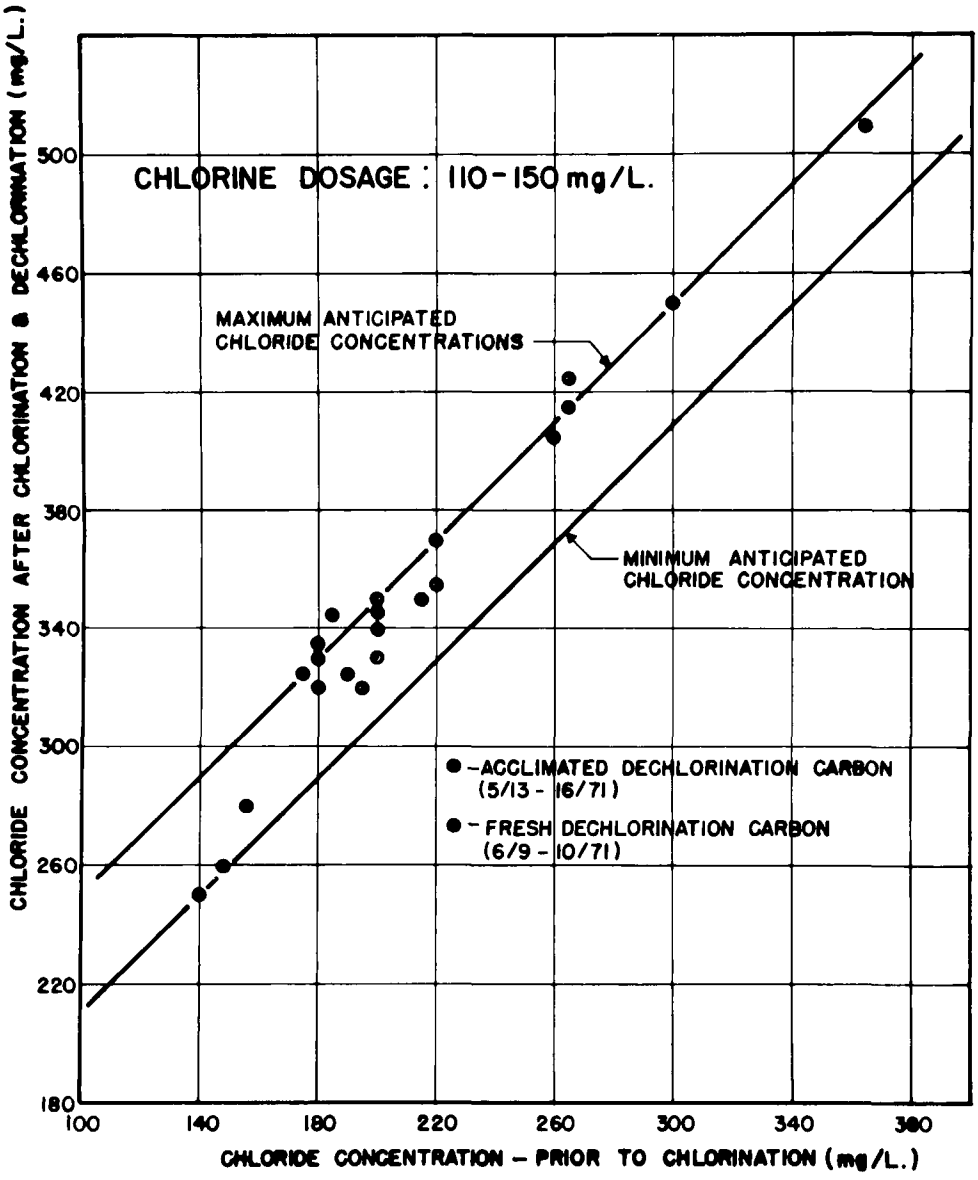
(1) Date and Sample		(2) Chloride Concentration Prior to Chlorination (mg/l)	(3) Chlorine Dosage (mg/l)	(4) Anticipated Chloride Concentration After Chlorination-Dechlorination (mg/l)	(5) Actual Chloride Concentration After Chlorination-Dechlorination (mg/l)
4/30/71					
A	Acclimated Carbon	156	112-136	268-292	280
B	" "	148	112-136	260-284	260
C	" "	140	112-136	252-276	250
5/13-14/71					
A	Acclimated Carbon	180	110-132	290-312	320
B	" "	190	110-132	300-322	325
C	" "	200	110-132	310-332	330
D	" "	195	110-132	305-327	320
E	" "	220	110-132	330-352	355
F	" "	215	110-132	325-347	350
5/14-15/71					
A	Acclimated Carbon	300	123-149	423-449	450
B	" "	265	123-149	388-414	415
C	" "	200	123-149	323-349	350
D	" "	175	123-149	298-324	325
E	" "	180	123-149	303-329	330
F	" "	185	123-149	308-334	345
G	" "	180	123-149	303-329	335
H	" "	265	123-149	388-414	425
6/9-10/71					
A	Fresh Carbon	200	121-147	321-347	340
B	" "	510	121-147	631-657	655
C	" "	365	121-147	486-512	510
D	" "	260	121-147	381-407	405
E	" "	220	121-147	341-367	370
F	" "	200	121-147	321-347	345

Note: Column 2 and 5 from Tables A-2, A-3, A-4
Column 3 from Figures 4,5, and 6
Column 4 = Column (2 + 3)

FIG. 14

EFFECTS OF CHLORINATION & DECHLORINATION ON CHLORIDE CONCENTRATIONS OF PLANT EFFLUENT

OWOSSO, MICHIGAN



limit) was attained even when the chlorine to ammonia-nitrogen feed ratio was below that required for breakpoint chlorination, in which case substantial amounts of chloramines are generated. It is also significant that this same phenomena occurs when fresh dechlorination carbon is utilized, even though a certain proportion of the ammonia is not removed by the chlorination-dechlorination process.

As is postulated and, apparently, supported by these data, once the carbon surface has undergone essentially total oxidation; the reversion of the chloramines to ammonia no longer occurs. After an "acclimation" of the carbon surface, the chloramine may be adsorbed and/or catalytically oxidized on the carbon surface. In this case, the catalytic oxidation of the chloramines release hydrated protons to the aqueous phase resulting in a depression of the pH of the wastewater during dechlorination. That this pH depression actually does occur is observed in Tables A-3 through A-5 for "acclimated" dechlorination carbon. In this case the pH of the effluent from the dechlorination system is on the order of 1 to 2 units lower than the chlorinated wastewater. Table A-8, for the case of fresh carbon in the dechlorination phase, shows no such reduction in pH after passage of the chlorinated wastewater through the dechlorination stage. In this case the hydrated protons released from the carbon surface are consumed in the reversion of chloramines to ammonia. A more rigorous experimental testing program--where all aqueous and gaseous inputs and outputs are measured--would be required to prove or disprove this hypothesis.

Table III shows the results of four bacteriological surveys performed between June 9 and June 15, 1971. Samples were taken every hour at various points and then composited into six-hour composites. The bacteriological surveys covered a twelve-hour period each day. Normally, the "A.M." labeled samples were taken between 5 AM and 11 AM, while the "P.M." samples were collected between 11 AM and 5 PM. Samples taken after the chlorine contact chamber were dechlorinated using sodium thiosulfate (8 - 10 mg/l thiosulfate per mg/l of free or combined chlorine). All samples were refrigerated immediately and transported under these conditions to the laboratory for analyses. Table III shows that there is a substantial reduction in total counts after chemical coagulation and sedimentation, then slightly more removal after filtration and passage through the first three carbon contactors. There is a significant reduction after the chlorine contact chamber, as would be expected. No total counts greater than 100 counts per 100 milliliters were observed after chlorination. The total coliform counts increased slightly in passage through the dechlorination stage. This increase was fairly high on June 9 and

TABLE III

Bacterial Removal in A Physical-Chemical System
by Chlorination - Dechlorination

Date	6/9/71 T.C.*	6/10/71 T.C.	6/14/71 T.C.	6/14/71 F.C.**	6/15/71 T.C.	6/15/71 F.C.
Raw A.M.	12 M***	10 M	13.5 M	10.5 M	14 M	12.5 M
Raw P.M.	14 M	11.16 M	13.0 M	5.4 M	22 M	16 M
Coagulated A.M.	1.6 M	4.17 M	1.1 M	1.0 M	4.6 M	
" " P.M.	3.3 M	4.65 M	1.1 M		4.2 M	
Filtered A.M.	1.05 M	4 M	0.53 M		4.2 M	
" " P.M.	3.1 M	3 M	1.65 M	1.27 M	3.9 M	3.0 M
12' Carbon A.M.	1.3 M	2 M	.28 M	0.15 M	3.9 M	
" " P.M.	0.93 M	1.67 M	.71 M	0.68 M	2.9 M	
Chlorinated A.M.	100	20	10	10	0	0
" " P.M.	100	20	10	10	0	0
Effluent A.M.	2200	250	530	500	25	50
" " P.M.	1700	325	830	200	25	50

Note: *T.C. - Total coliform per 100 ml of sample
**F.C. - Fecal coliform per 100 ml of sample
***M indicates million

decreased during the remaining days until the total counts in the plant effluent were below 25 per 100 milliliters. The reason for the increase in total coliform counts from the chlorination stage to the effluent was most probably due to the fact that prior to June 9 the dechlorination carbon had been exposed briefly to unchlorinated wastewater. On June 9 chlorination was initiated. Hence, a certain amount of flushing and exposure to chlorinated wastewater, which for all intents and purposes was sterile, was necessary before the total coliform counts in the effluent receded.

The increase in chloride content of the wastewater due to the chlorination-dechlorination process is shown in Table II. The average chloride level in the Owosso raw wastewater over the study period was 193 mg/l. This was increased to an average of approximately 293 mg/l after chlorination-dechlorination.

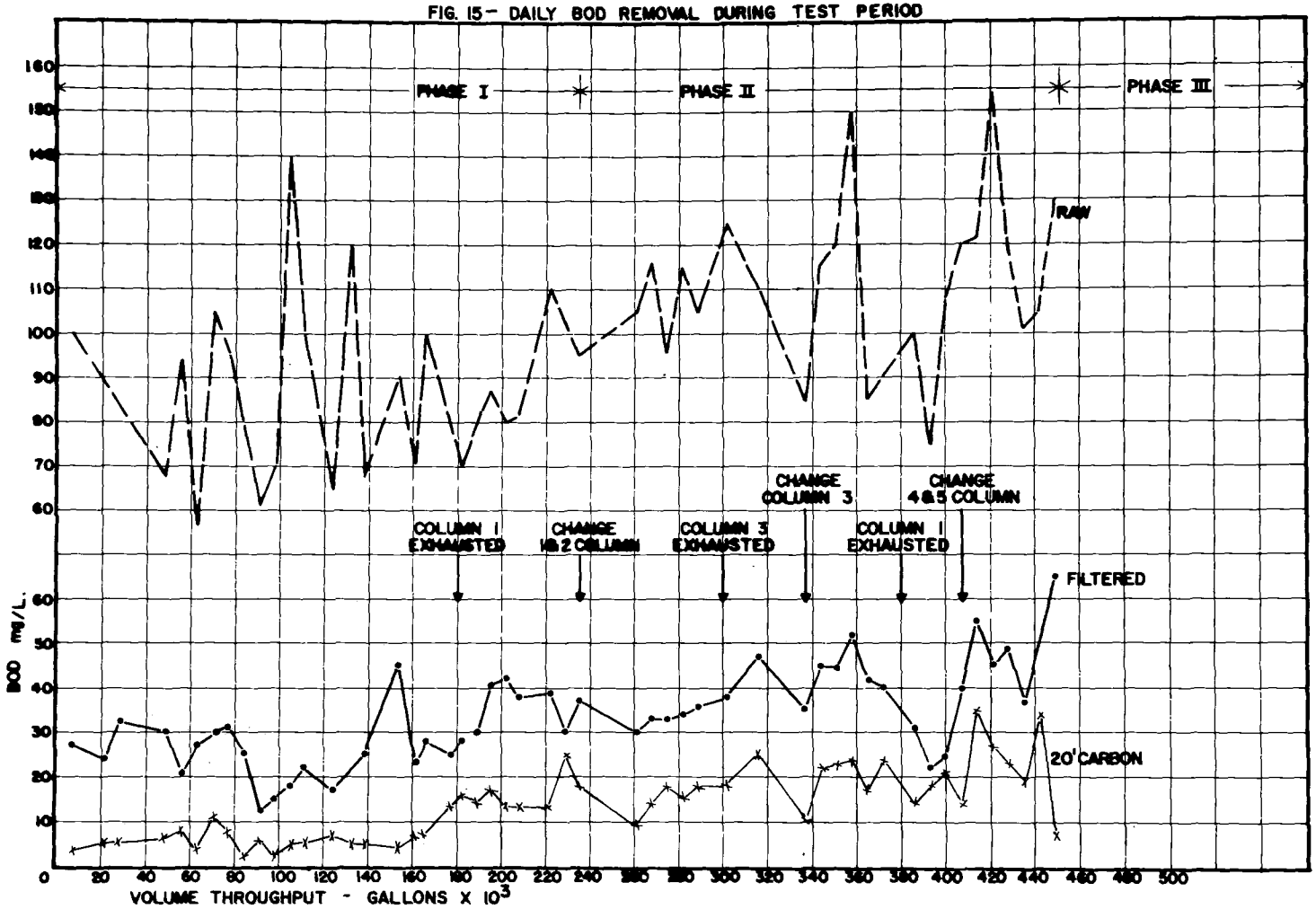
The results of all twenty-four hour surveys are tabulated in Appendix A (Tables A-1 through A-10). As noted by the data, there was no breakthrough of free chlorine or trichloramine on any of the samples taken. Periodically, the effluent from the fourth or fifth carbon contactors would yield trace amounts of mono- or dichloramines (0.1 to 0.4 mg/l). At times these trace amounts were also noticed in the wastewater prior to chlorination. The appearance of these trace amounts of chloramines seems to be an anomaly of the test rather than a true concentration. The data in Appendix A indicates, as anticipated, that the chlorination step causes a significant depression of the pH, indicating that some type of pH adjustment or split treatment arrangment may be necessary before the wastewater is discharged.

Organic Removal

The results on biochemical oxygen demand (BOD) removal are shown in Figures 15 and 16. This portion of the study was divided into three distinct phases. Phase I of the study was designed primarily to add support data to the existing pilot-plant BOD data as reported by Schenk[5] last summer at Owosso, Michigan. Phase II of the study involved the application of polymers prior to filtration (filter aid) in an attempt to increase the solids removal efficiency of the deep-bed filter. Phase III entailed a modification of the pilot facility (addition of eight more feet of carbon) to reflect more closely the envisioned full-scale carbon adsorption system.

Phase I (Figure 15) represents thirty-five days of operation during which the pilot facility treated 235,269 gallons of

FIG. 15 - DAILY BOD REMOVAL DURING TEST PERIOD



wastewater. Throughout Phase I, the carbon adsorption system had a total carbon contact depth of twenty feet resulting in a twenty-five minute contact period. The first twelve feet of carbon (fifteen minute contact time) were used before chlorination while the last eight feet of carbon in columns 4 and 5 (ten minutes contact) were operated after the chlorination section. A review of Figure 15 shows that during Phase I the pilot facility produced an effluent BOD which averaged 7 mg/l. On only seven days during this period did the daily average effluent BOD exceed 7 mg/l. The majority of these high BOD effluent values (greater than 7 mg/l) were observed after passage of approximately 180,000 gallons of wastewater through the system. At this through-put volume (180,000 gallons), analysis of the BOD data indicated that the first carbon column was at or near exhaustion. Operating at a reduced carbon contact time would explain the gradual rise in effluent BOD after this point (180,000 gallons). Evaluation of these data for Phase I yielded a carbon requirement of approximately 500 pounds per million gallons of wastewater treated (0.60 - 0.70 pounds of COD removed per pound of carbon). This substantiates the findings of Schenk.[5]

The lime-phosphate floc developed in the coagulation phase is a unique floc being light in substance and pin-point in nature, which caused some difficulty in the deep-bed filtration stage. Although the deep-bed filter reduced the suspended solids to between 20 and 25 mg/l, some operational difficulties within the expanded-bed carbon system were experienced even at these solids levels. The difficulties included among other things: clogged underdrains, solids deposition at the interface of the expanded carbon beds (these solids on top of the carbon contactors were removed periodically), and periodic wave-front movement of suspended solid material from carbon column to carbon column.

The solids accumulation at the carbon-water interface in no way interfered with the performance of the carbon unit, but was of concern from an operational viewpoint. Hence, it was deemed necessary to attempt to improve the deep-bed filter performance by use of a polymer as a filter aid. Figure 15 shows the results of these Phase II studies on the BOD removal through the system. The BOD removal efficiency of the carbon system did not increase and, in fact, appeared to deteriorate, while little or no improvement could be noted in the performance of the deep-bed filter (see Figure 19). In addition, the effluent from the deep-bed filter tended to foam, indicating some leakage of polymer through the filter.

Because of the problems encountered in Phase II, the polymer feed system was shut down and Phase III initiated. In order to provide a longer contact time, the carbon system was modified

by the addition of two small diameter carbon columns (5-1/2 inch I.D.) after the five large diameter carbon columns (12 inch I.D.). This resulted in a total carbon depth of twenty-eight feet and yielded a contact time of approximately thirty-five minutes. This mode of operation was more in line with the actual carbon contact depth (prior to chlorination) proposed for the full-scale Owosso system. The ammonia-nitrogen removal study was terminated at this point because the small carbon columns were not designed to operate as dechlorination columns (no air relief valves).

The results on BOD removal during Phase III are shown in Figure 16. The data reported during this phase of the study represent thirteen days of continuous operation. The average BOD of the raw waste for this period was 140 mg/l, the deep-bed filter effluent yielded an average BOD of 32 mg/l, and the average effluent BOD after thirty-five minutes carbon contact was 8 mg/l.

A summary of the chemical oxygen demand (COD) results for the total test period is shown in Figures 17 and 18. In Phases I and II (Figure 17), the average raw COD was 257 mg/l and the average effluent COD was 30 mg/l (after twenty-five minutes of carbon contact), resulting in an overall COD removal efficiency of 88 per cent. In Phase III (Figure 18) the average COD of the raw wastewater was 349 mg/l and the average COD in the effluent (after thirty-five minutes carbon contact) was 24 mg/l, for a total COD removal of 93 per cent.

Suspended Solids and Phosphate Removal

Suspended solids and phosphate removal observed during the study are shown in Figures 19-20 and 21-22 respectively. The average raw wastewater suspended solids during Phases I and II (see Figure 19) was 134 mg/l. The average suspended solids in the effluent was 14 mg/l. In Phase III (refer to Figure 20) the average raw suspended solids was 186 mg/l with a corresponding effluent suspended solids level of 20 mg/l.

Phosphate removal data are shown in Figures 21 and 22 for Phases I through III. Phosphate removal over the entire test period averaged approximately 82 per cent.

Organic Nitrogen

The system's ability to remove organic nitrogen is shown in Table IV. Organic nitrogen removals varied between 80 and 100 per cent and averaged 90 per cent during the observation period.

FIG. 16 - DAILY BOD REMOVAL DURING TEST PERIOD

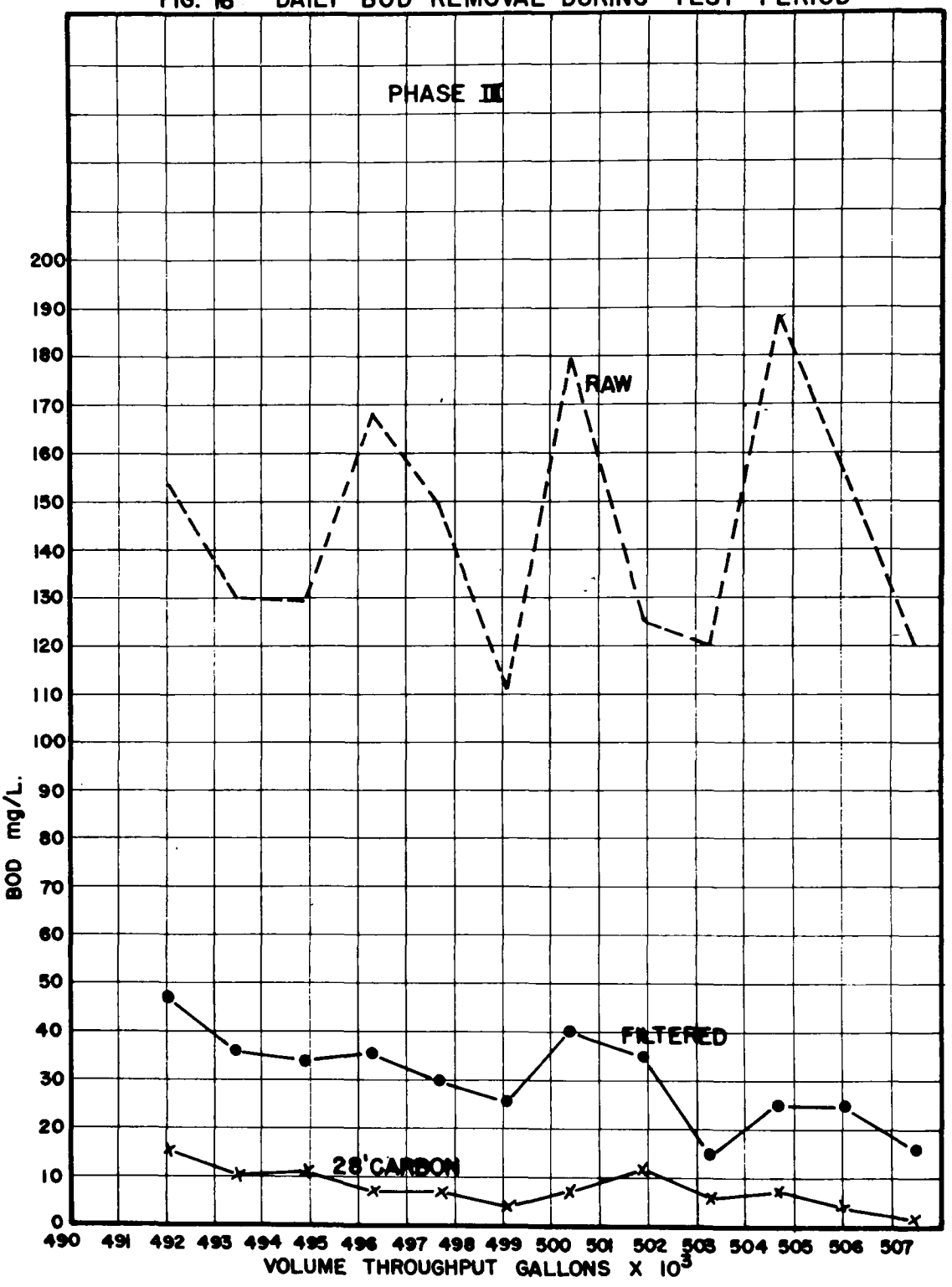


FIG. 17 – DAILY COD REMOVAL DURING TEST PERIOD

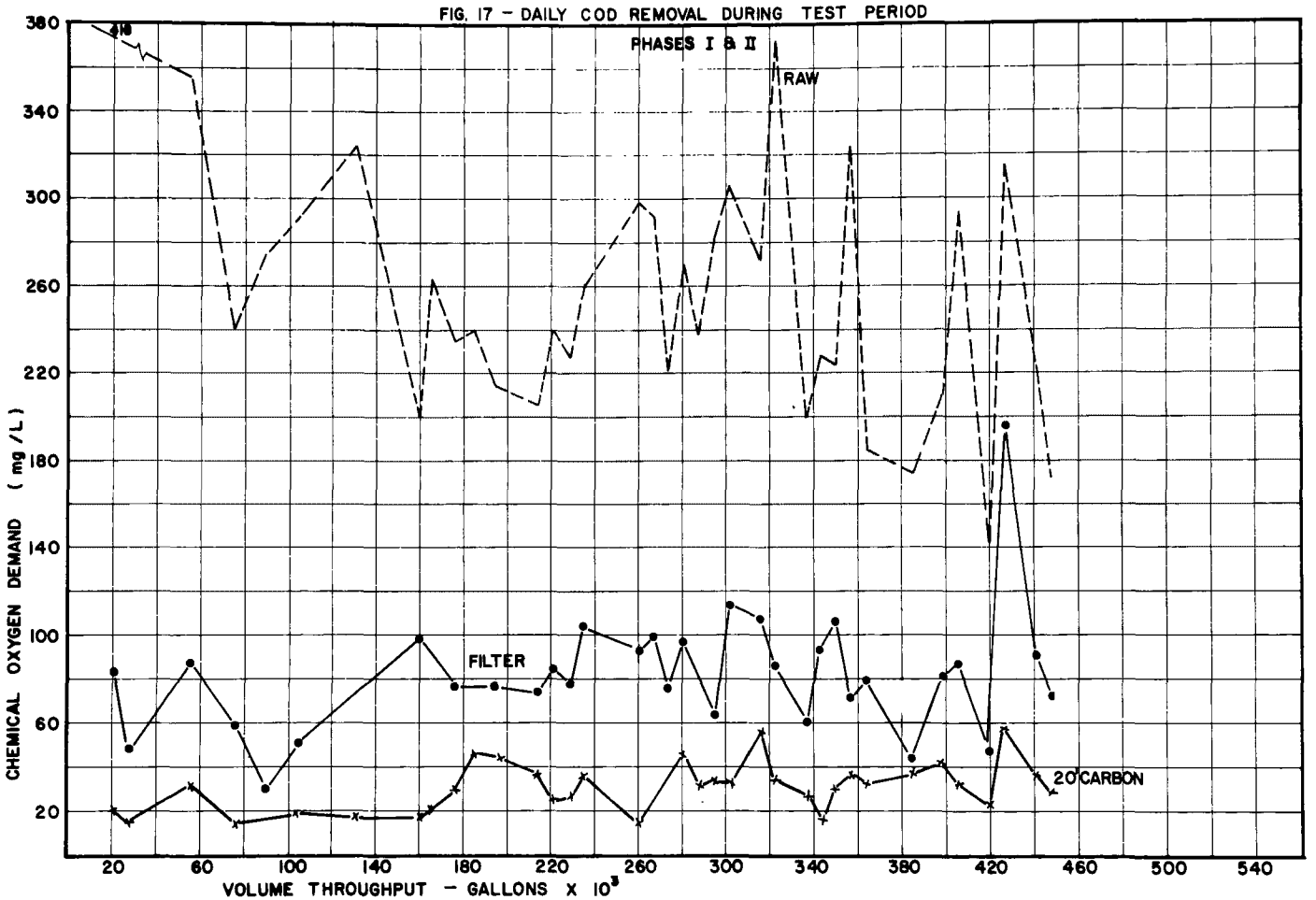


FIG. 18 - DAILY COD REMOVAL DURING TEST PERIOD

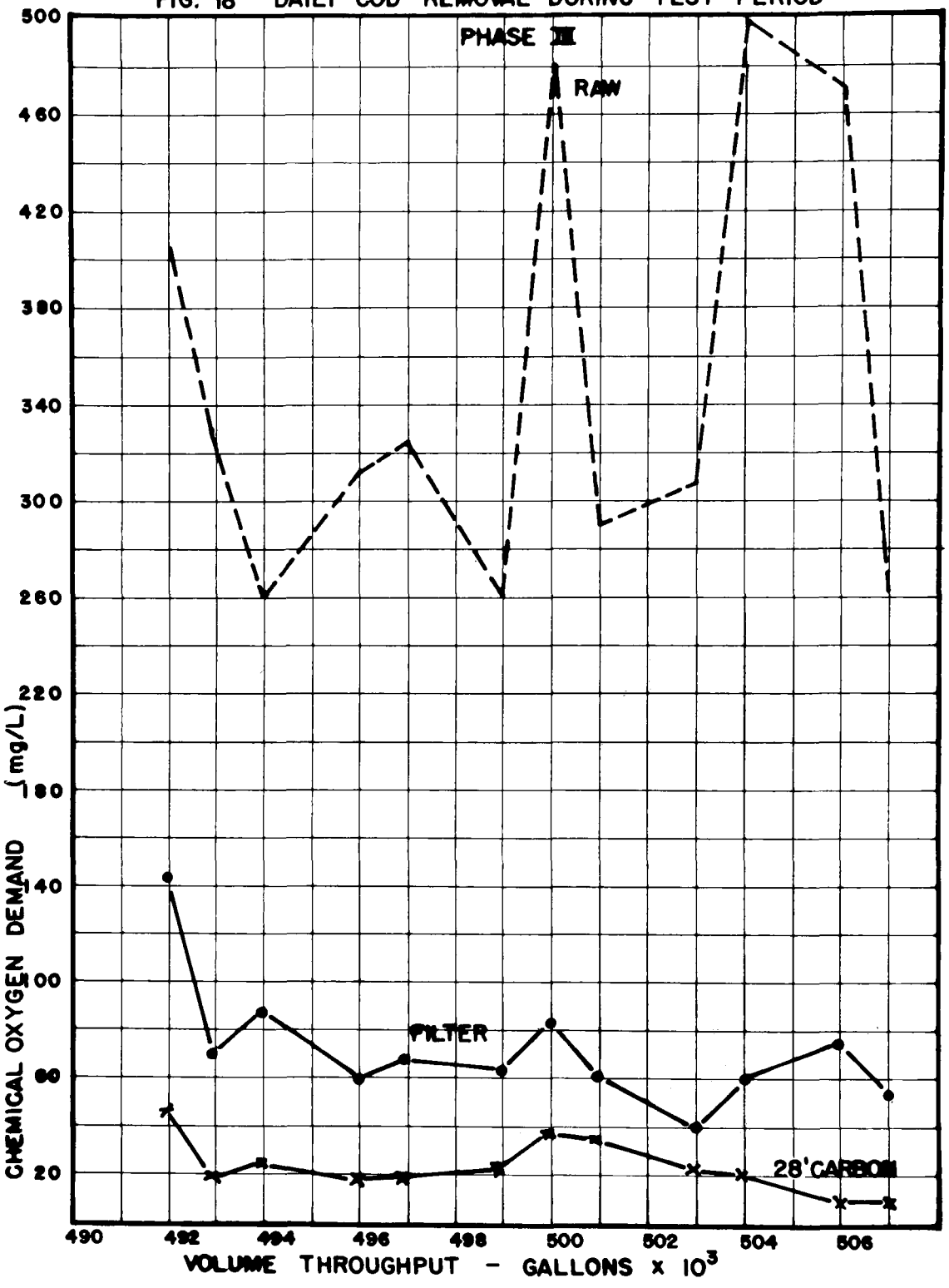


FIG. 19 - DAILY SUSPENDED SOLIDS REMOVAL DURING TEST PERIOD

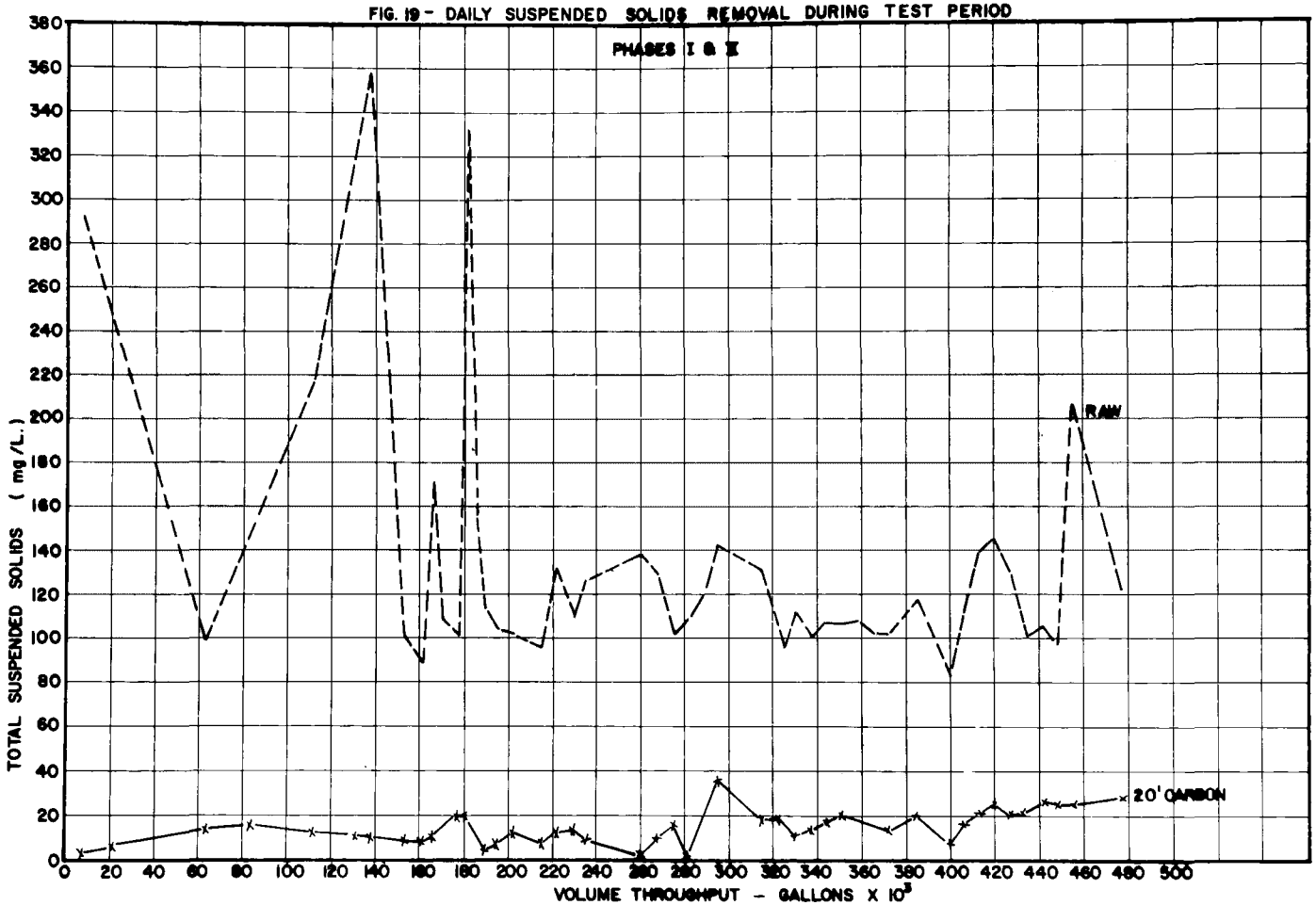


FIG. 20-DAILY SUSPENDED SOLIDS REMOVAL DURING TEST PERIOD

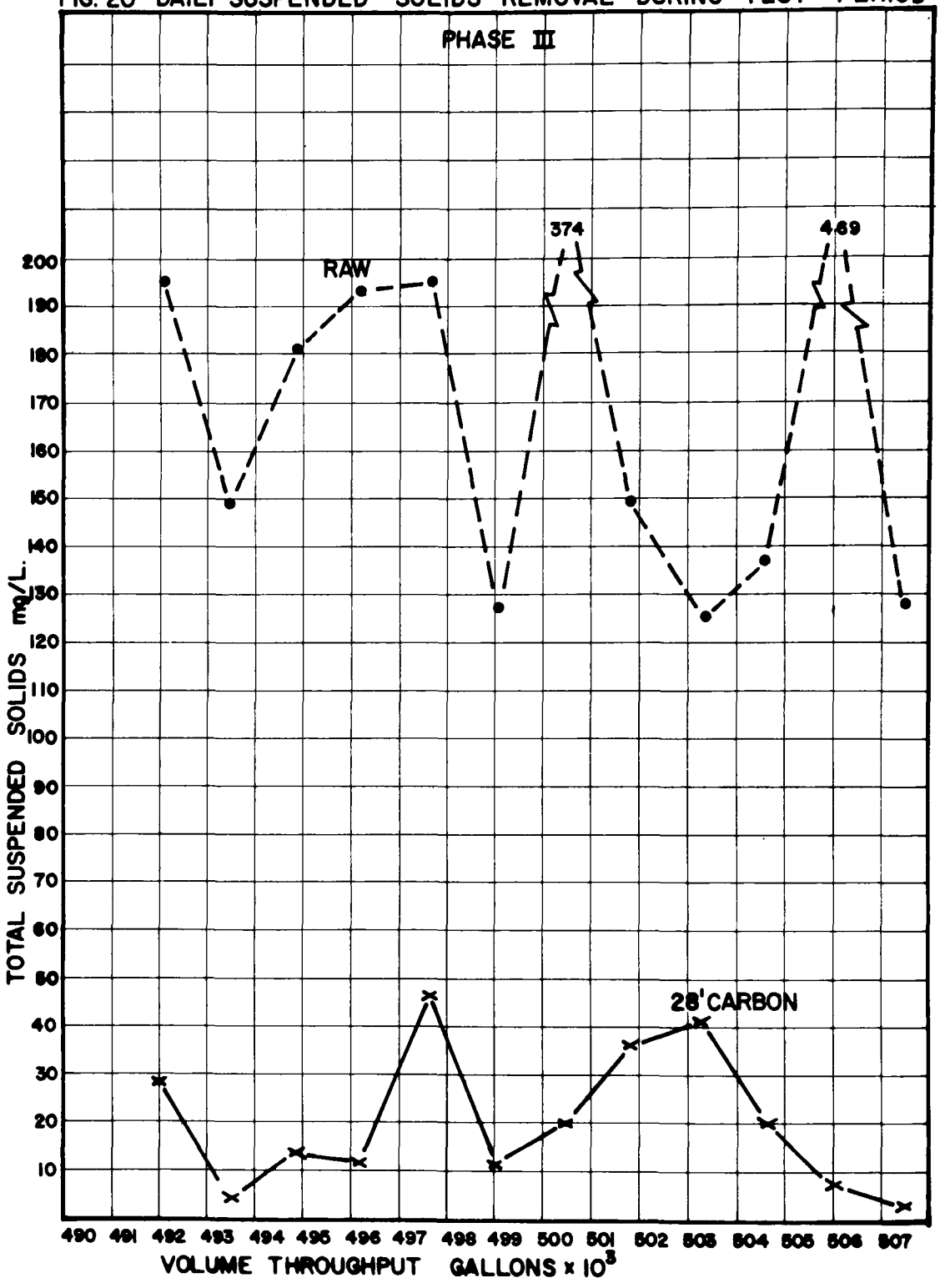


FIG. 21– DAILY PHOSPHATE REMOVAL DURING TEST PERIOD

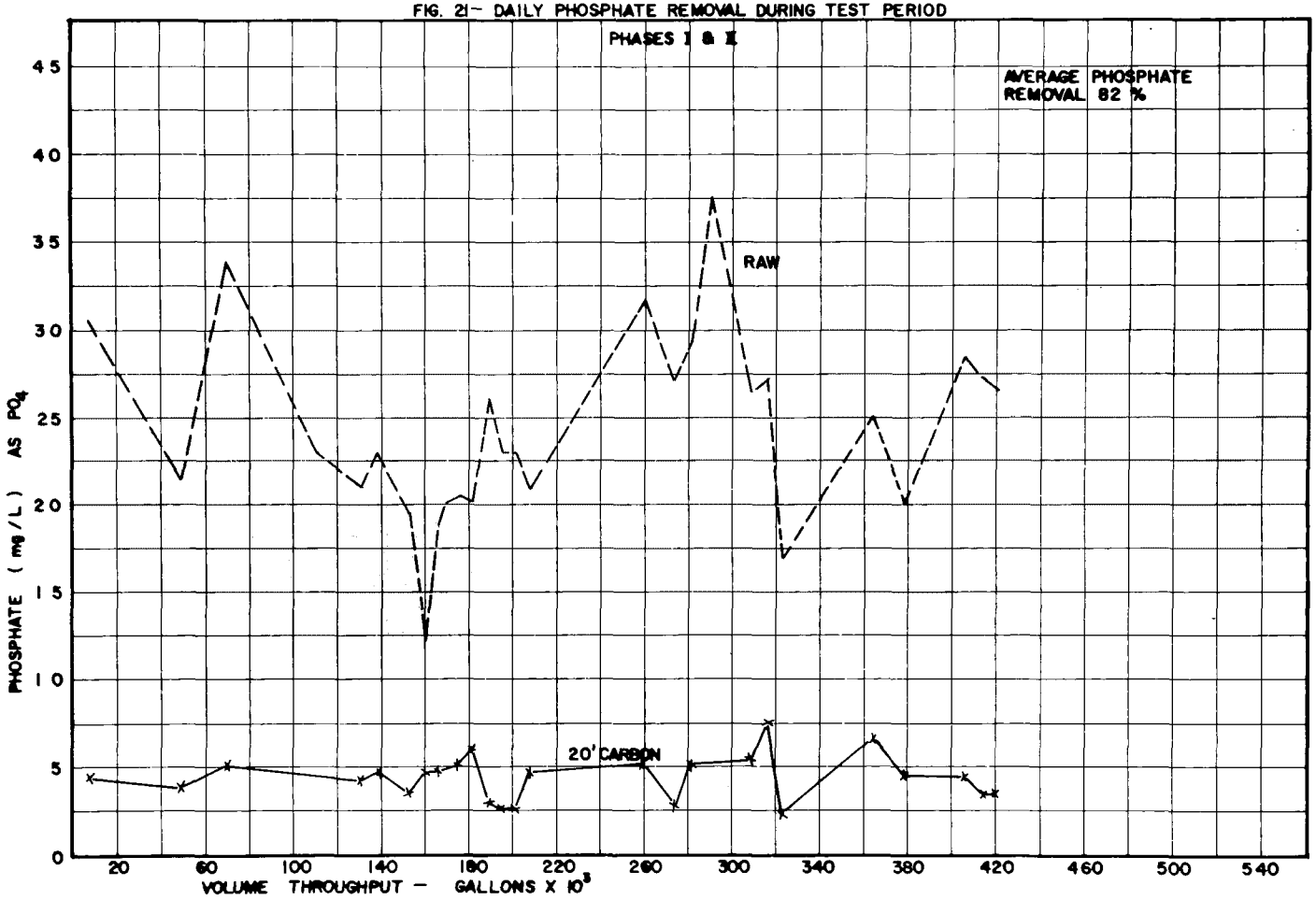


FIG. 22- DAILY PHOSPHATE REMOVAL DURING TEST PERIOD

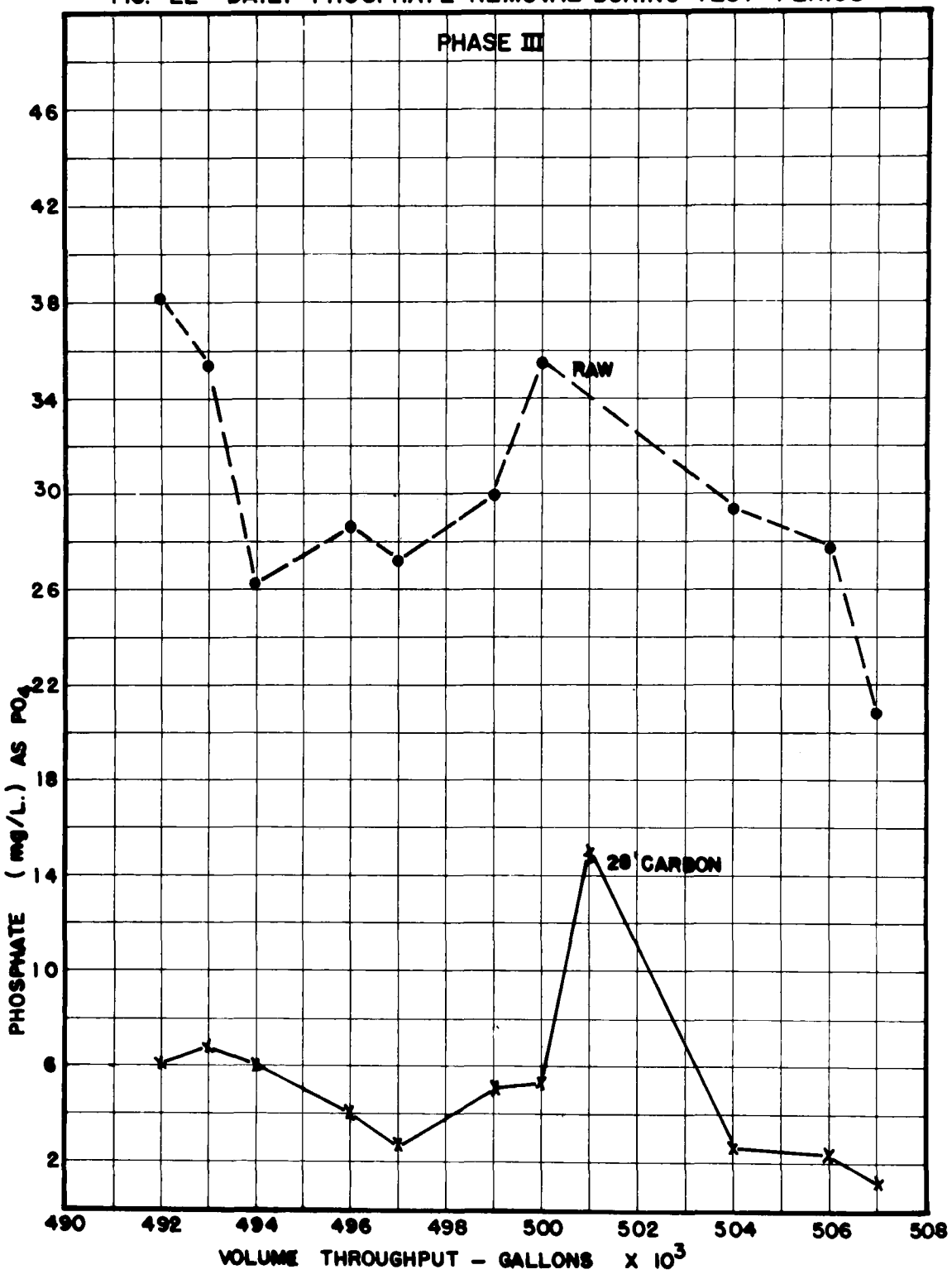


TABLE IV

Organic Nitrogen Data

Cumulative Throughput (gallons)	Raw*	After Filter*	After 12' Carbon* (15 min. of carbon contact)	After 20' Carbon* (25 min. of carbon contact)	Percent Removal
63,272	13.0	6.0	0.6	0.6	95
97,789	9.5	1.4	-	1.3	86
111,106	8.9	-	2.2	1.9	79
181,683	7.8	-	0.56	0.14	98
189,441	4.3	3.9	1.12	0.84	80
201,923	9.1	7.0	0	0	100

Average percent removal - 90%

*mg/l of Organic - N

SECTION VIII

ACKNOWLEDGEMENT

The cooperation and assistance of the Owosso wastewater treatment plant personnel, in particular Mr. Arnold VanPelt and Mr. Steve Hanzlovic, is gratefully acknowledged. Their assistance was of paramount importance in the successful operation of this pilot study.

A special acknowledgement is extended to Mr. Neil Jackson, City Manager, Mr. Ken Apsey, Director of Public Works and Mr. Paul Wesch, Director of Public Utilities, all of the City of Owosso, Michigan, whose far-sightedness, patience and persistence made this project possible.

SECTION IX

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SECTION X

APPENDICES

Appendix

A. Analytical Test Data During Twenty-Four Hour Survey Periods

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TABLE A-1

3/3/71 - 3/4/71

Sample	Time	NH_3 -N	Free Cl_2	Chloramines Mono	Di	Tri	pH
12' C	9:00 pm	7.3	0	0	0.2	0	9.0
Cl_2	9:20 "	-	0.8	22.0	11.6	0	6.9
20' C	9:30 "	3.8	0	0	0	0	8.6
12' C	10:00 pm	8.0	0	0	0	0	9.0
Cl_2	10:20 "	-	14.8	5.2	8.2	2.0	7.1
20' C	10:30 "	1.4	0	0.2	0	0	8.4
12' C	11.00 pm	6.6	0	0	0	0	9.0
Cl_2	11:20 "	-	1.6	16.8	12.2	3.6	6.2
20' C	11:30 "	1.1	0	0	0.4	0	7.6
4' C	10:00 am	9.0	0	0	0	0	8.8
Cl_2	10:20 "	-	1.2	15.0	20.0	1.1	6.7
20' C	10:30 "	0.6	0	0.4	0	0	7.0
12' C	1:30 pm	13.9	-	-	-	-	8.4
Cl_2	1:50 "	-	15.2	12.2	11.4	3.4	6.9

All values in mg/l except pH

TABLE A-2

4/30/71

Sample	Time	NH_3-N	Chlorides	Free Cl_2	Chloramines Mono	Di	Tri	pH
Raw	4:00 pm	23.7	-	-	-	-	-	-
8' C	4:30 "	27.0	156	-	-	0.2	-	-
cl_2	4:50 "	11.75	-	-	-	-	2.0	5.6
20' C	5:00 "	12.0	280	-	-	-	0	5.6
Raw	6:00 pm	22.5	-	-	-	-	-	7.0
8' C	6:00 "	10.0	148	-	-	-	-	9.2
Cl_2	6:20 "	1.0	-	-	-	-	-	5.5
20' C	6:30 "	1.8	260	0	-	-	0	6.2
Raw	8:00 pm	11.2	-	-	-	-	-	7.1
8' C	8:00 "	22.5	140	-	-	-	-	9.2
Cl_2	8:20 "	11.8	-	76.0	0	0	0.4	5.1
20' C	8:30 "	11.55	250	0	0	-	0	4.2
Raw	9:00 pm	10.0	-	-	-	-	-	7.1
8' C	9:30 "	11.0	-	-	-	-	-	9.1
Cl_2	9:50 "	0.5	-	76.0	0	0	0	5.2
20' C	10:00 "	0.6	-	0	0	38.0	0	4.3
Raw	10:00 pm	10.0	-	-	-	-	-	7.0
Raw	11:00 pm	12.0	-	-	-	-	-	6.8
8' C	11:00 "	11.0	-	-	-	-	-	9.1
Cl_2	11:20 "	2.3	-	76.0	0	0	0	6.4
20' C	11:30 "	-	-	0	0	37.0	0	4.1
Raw	12:00 mdnt	11.1	-	-	-	-	-	7.1
8' C	12:30 "	12.0	-	-	-	-	-	9.1
Cl_2	12:50 "	1.4	-	-	-	-	-	6.0
20' C	1:00 "	1.5	-	0	-	-	-	4.2
Raw	1:00 am	11.0	-	-	-	-	-	7.2

TABLE A-2 (continued)

Sample	Time	NH_3-N	Chlorides	Free Cl_2	Chloramines* Mono	Di	Tri	pH
Raw	2:00 am	11.5	-	-	-	-	-	7.2
8' C	2:00 "	13.0	-	-	-	-	-	9.2
Cl_2	2:20 "	2.1	-	-	-	-	-	6.2
20' C	2:30 "	2.2	-	0	-	-	-	4.3
Raw	3:00 am	10.0	-	-	-	-	-	7.2
8' C	3:30 "	10.5	-	-	-	-	-	9.1
Cl_2	3:50 "	1.5	-	-	-	-	-	6.0
20' C	4:00 "	1.4	-	0	-	-	-	4.3
Raw	4:00 am	9.0	-	-	-	-	-	6.7
Raw	5:00 am	9.5	-	-	-	-	-	6.8
8' C	5:00 "	9.5	-	-	-	-	-	8.7
Cl_2	5:20 "	1.0	-	-	-	-	-	5.3
20' C	5:30 "	1.0	-	0	-	-	-	4.3
Raw	6:00 am	8.0	-	-	-	-	-	6.8
8' C	6:30 "	8.0	-	-	-	-	-	8.7
Cl_2	6:50 "	0.95	-	-	-	-	-	5.4
20' C	7:00 "	0.9	-	0	-	-	-	4.3
Raw	7:00 am	-	-	-	-	-	-	6.6
Raw	8:00 am	6.5	-	-	-	-	-	6.8
8' C	8:00 "	7.5	-	-	-	-	-	8.6
Cl_2	8:20 "	0.98	-	-	-	-	-	5.4
20' C	8:30 "	0.95	-	0	-	-	-	4.3
Raw	9:30 am	8.0	-	-	-	-	-	6.7
8' C	9:35 "	6.0	-	-	-	-	-	8.6
Cl_2	9:55 "	1.0	-	-	-	-	-	5.4
20' C	10:05 "	1.0	-	0	-	-	-	4.4

All values in mg/l except pH

*Problem encountered in analyzing for chloramines due to contamination of chemicals - initial values invalid and chloramine analyses terminated.

TABLE A-3
5/13/71 - 5/14/71

Sample	Time	NH_3-N	Chlorides	Free Cl_2	Chloramines Mono	Chloramines Di	Chloramines Tri	pH
8' C	1:00 pm	15.4	-	-	-	-	-	9.2
Cl_2	1:20	-	-	1.6	4.4	8.0	24.8	5.0
20' C	1:30	1.7	-	0	0	0.2	0	5.2
8' C	3:30 pm	17.2	-	-	-	-	-	9.2
Cl_2	4:00	-	-	1.2	12.0	21.6	4.8	5.3
20' C	4:10	2.9	-	0	0	0.2	0	3.8
8' C	5:00 pm	16.8	180	-	-	-	-	8.9
Cl_2	5:20	-	-	0.4	6.0	21.6	14.4	5.4
20' C	5:30	0.84	320	0	0	0.2	0	4.3
8' C	7:00 pm	15.7	190	-	0	0.3	0	9.2
Cl_2	7:20	-	-	1.6	2.4	22.4	0	4.8
20' C	7:30	1.2	325	0	0	0.3	0	4.3
8' C	9:10 pm	14.1	200	-	-	-	-	9.1
Cl_2	9:30	-	-	0.8	7.2	22.8	1.6	4.9
20' C	9:40	1.1	330	0	0.3	0.3	0	4.1
8' C	10:30 pm	14.3	195	-	-	-	-	9.0
Cl_2	10:50	-	-	1.6	5.6	16.4	7.2	5.0
20' C	11:00	1.1	320	0	0.1	0.3	0	3.9
8' C	12:00 md	13.8	-	-	-	-	-	8.6
20' C	12:00	0.8	-	-	-	-	-	4.0
8' C	2:00 am	12.4	-	-	-	-	-	8.1
20' C	2:00	0.5	-	-	-	-	-	3.8
8' C	4:00 am	12.8	-	-	-	-	-	7.9
20' C	4:00	0.28	-	-	-	-	-	4.0
8' C	6:00 am	12.6	-	-	-	-	-	
25' C	6:00	0.0	-	-	-	-	-	
8' C	8:00 am	12.3	220	0	0.1	0.2	0	8.6
Cl_2	8:20	-	-	2.0	4.0	16.0	20	4.8
20' C	8:30	0.2	355	0	0	0.2	0	4.0
8' C	10:00 am	11.9	215	-	-	-	-	7.9
Cl_2	10:20	-	-	11.6	1.6	3.6	20.8	5.7
20' C	10:30	0.0	350	0	0.2	0.2	0.3	4.2

All values in mg/l except pH

TABLE A-4

5/14/71 - 5/15/71

Sample	Time	NH_3-N	Chlorides	Free Cl_2	Chloramines Mono	Chloramines Di	Chloramines Tri	pH
8' C	12:30 pm	14.8	300	0	0.2	0.3	0	8.6
Cl_2	12:50 "	-	-	1.6	2.0	28.4	1.6	5.7
20' C	1:00 "	0.14	450	0	0	0.2	0	4.8
8' C	2:45 pm	16.8	265	-	-	-	-	8.8
Cl_2	3:05 "	-	-	0.8	6.8	31.2	4.8	5.4
20' C	3:15 "	0.7	415	0	0.1	0.4	0	4.8
8' C	5:10 pm	17.6	200	-	-	-	-	9.0
Cl_2	5:30 "	-	-	10.0	0.8	20.4 34.4	0	5.0
20' C	5:40 pm	1.9	350	0	0	0.5	0	4.3
8' C	7:00 pm	16.3	175	-	-	-	-	9.1
Cl_2	7:20 "	-	-	1.6	3.2	19.2 24.8	1.4	4.8
20' C	7:30	1.0	325	0	0.1	0.2	0	4.5
8' C	9:15 pm	16.0	180	-	-	-	-	9.4
Cl_2	9:35 "	-	-	2.0	3.2	24.4 28.8	0	5.0
20' C	9:45	0.5	330	0	0	0.3	0	4.8
8' C	12:00mdnt	14.0	-	-	-	-	-	9.0
20' C	12:00 "	0.0	-	-	-	-	-	4.7
8' C	2:00 am	14.0	-	-	-	-	-	9.0
20' C	2:00 "	0.5	-	-	-	-	-	3.9
8' C	4:00 am	12.7	-	-	-	-	-	9.1
20' C	4:00 "	0.4	-	-	-	-	-	3.8
8' C	6:00 am	12.0	-	-	-	-	-	9.0
20' C	6:00 "	0.1	-	-	-	-	-	3.7
8' C	8:00 am	12.0	185	0	0	0.2	0	9.0
Cl_2	8:20 "	-	-	14.0	0	4.0	1.6	4.0
20' C	8:20 "	0.1	345	0	0	0.3	0	3.6
8' C	10:00 am	11.9	180	0	0.1	0	0	9.0
Cl_2	10:20 "	-	-	18.8	0.4	12	0.8	4.8
20' C	10:30 "	0.0	335	0	0	0.2	0	3.5
8' C	12:00noon	14.0	265	-	-	-	-	9.0
Cl_2	12:20	-	-	6.4	2.0	3.2	6.4	4.3
20' C	12:30	0.0	425	0	0	0.1	0	3.4

All values in mg/l except pH

TABLE A-5

5/15/71 - 5/16/71

Sample	Time	NH_3-N	Chlorides	Free Cl_2	Chloramines Mono	Chloramines Di	Chloramines Tri	pH
8' C	2:00 pm	17.2	-	-	-	-	-	9.1
Cl_2	2:20 "	-	-	1.6	20.4	19.6	0	6.1
20' C	2:30 "	5.5	-	0	0	0.1	0	3.5
8' C	4:00 pm	18.3	185	0	0	0.2	0	9.1
Cl_2	4:20 "	-	-	0.8	22.0	17.2	3.2	6.3
20' C	4:30 "	8.2	280	0	0	0.2	0	3.6
8' C	6:00 pm	17.2	180	-	-	-	-	9.0
Cl_2	6:20 "	-	-	0.4	22.4	16.8	0	6.3
20' C	6:30	6.5	280	0	0	0.1	0	3.9
8' C	8:00 pm	15.5	160	0	0.1	0.1	0	9.2
Cl_2	8:20 "	-	-	0.4	22.0	16.4	0	6.3
20' C	8:30 "	5.1	265	0	0	0	0	4.3
8' C	10:00 pm	14.0	185	-	-	-	-	9.1
Cl_2	10:20 "	-	-	0.4	20.0	12.0	0	6.1
20' C	10:30 "	4.1	275	0	0	0.1	0	4.2
8' C	12:00 mdnt	13.6	-	-	-	-	-	9.1
20' C	12:00 "	2.1	-	-	-	-	-	5.3
8' C	2:00 am	14.3	-	-	-	-	-	9.1
20' C	2:00 "	2.8	-	-	-	-	-	5.2
8' C	4:00 am	13.7	-	-	-	-	-	9.1
20' C	4:00 "	2.2	-	-	-	-	-	5.3
8' C	6:00 am	13.0	-	-	-	-	-	9.1
20' C	6:00 "	2.2	-	-	-	-	-	5.3
8' C	8:00 am	12.6	190	-	-	-	-	9.1
Cl_2	8:20 "	-	-	0.2	17.2	21.6	3.2	5.8
20' C	8:30 "	2.0	290	0	0	0.2	0	5.2
8' C	10:00 am	13.0	-	0	0	0.1	0	9.0
Cl_2	10:20 "	-	-	0.2	14.4	12.8	2.4	5.9
20' C	10:30 "	2.5	-	0	0	0.1	0	5.3
8' C	12:00noon	14.0	-	-	-	-	-	9.1
Cl_2	12:20	-	-	0.2	16.0	14.2	3.0	5.6
20' C	12:30	2.7	-	0	0	0.1	0	5.4

All values in mg/l except pH

TABLE A-6

5/23/71

Sample	Time	NH_3	Free Cl_2	Chloramines Mono	Chloramines Di	Chloramines Tri	pH
8' C	7:30 am	11.1	-	-	-	-	
Cl_2	7:50 "	-	4	7.2	16.8	3.0	
16' C	7:55 "	-	0	0	0.3	0	
20' C	8:00 "	0	0	0	0.2	0	
8' C	9:30 am	11.7	-	-	-	-	
Cl_2	9:50 "	-	3.5	8.0	17.0	2.0	
16' C	9:55 "	-	0	0	0.3	0	
20' C	10:00 "	0.2	0	0	0.1	0	
8' C	11:30 am	12.7	-	-	-	-	
Cl_2	11:50 "	-	3.0	8.1	17.2	2.4	
16' C	11:55 "	-	0	0	0.2	0	
20' C	12:00 "	0.8	0	0.1	0	0	
8' C	1:30 pm	13.5	-	-	-	-	
Cl_2	1:50 "	-	3.4	8.2	16.8	2.8	
16' C	1:55 "	-	0	0	0.3	0	
20' C	2:00 "	1.2	0	0	0.2	0	

All values in mg/l except pH

TABLE A-7

5/27/71

Sample	Time	NH_3	Free Cl_2	Chloramines Mono	Di	Tri	pH
8' C	9:00 am	11.6	-	-	-	-	8.8
Cl_2	9:20 "	-	4.0	0.4	9.2	0.8	4.8
16' C	9:20 "	-	0	0.2	0.8	0	4.4
20' C	9:30 "	0.7	0	0	0.2	0	4.4
8' C	11:00 am	14.4	0	0	0.1	0	8.8
Cl_2	11:20 "	-	9.6	2.8	8.0	0	4.5
16' C	11:20 "	-	0.2	1.3	1.4	0	4.3
20' C	11:30 "	0	0	0	0.1	0	4.2
8' C	1:00 pm	16.8	0	0	0.2	0	8.9
Cl_2	1:20 "	-	2.0	5.6	17.6	0.2	5.5
16' C	1:20 "	-	0.2	0.1	1.0	0	4.4
20' C	1:30 "	1.4	0	0	0.2	0	4.4
Cl_2	2:00 pm	-	0.4	11.2	17.2	0.8	6.0
16' C	2:00 "	-	0	0.1	0.8	0	4.4
20' C	2:10 "	-	0	0	0.1	0	4.4
8' C	3:00 pm	17.0	0	0	0.1	0	
Cl_2	3:20 "	-	2.4	11.6	20.4	0	6.0
16' C	3:20 "	-	0	0.1	0.8	0	4.2
20' C	3:30 "	2.6	0	0	0.2	0	4.2

All values in mg/l except pH

TABLE A-8

6/9/71

Sample	Time	NH_3	Chlorides	Free Cl_2	Chloramines Mono	Di	Tri	pH
8' C	8:00 am	12.8	200	-	-	-	-	9.0
Cl_2	8:20 "	-	-	1.6	10.4	20.0	1.6	4.8
16' C	8:20 "	-	-	0	0	0.4	0	5.0
20' C	8:30 "	3.0	340	0	0	0	0	5.2
8' C	10:00 am	15.5	510	0	0	0	0	9.0
Cl_2	10:20 "	-	-	0.8	7.2	18.0	1.6	4.7
16' C	10:20 "	-	-	0	0	0.3	0	5.0
20' C	10:30 "	3.0	655	0	0	0	0	5.1
8' C	12:00noon	17.4	365	-	-	-	-	8.9
Cl_2	12:20 pm	-	-	0.8	14.0	24.0	0	5.2
16' C	12:20 "	-	-	0	0	0.3	0	5.1
20' C	12:30 "	5.0	510	0	0	0	0	5.2
8' C	2:00 pm	21.6	260	-	0.1	0.1	0	9.0
Cl_2	2:20 "	-	-	1.2	14.0	28.0	0	5.3
16' C	2:20 "	-	-	0	0	0.4	0	5.3
20' C	2:30 "	8.4	405	0	0	0	0	5.3
8' C	4:00 pm	22.7	220	-	-	-	-	9.1
Cl_2	4:20 "	-	-	0.8	20.8	30	0	5.3
16' C	4:20 "	-	-	0	0	0.2	0	5.2
20' C	4:30 "	9.0	370	0	0	0	0	5.2
8' C	6:00 pm	20.5	-	-	-	-	-	9.0
Cl_2	6:20 "	-	-	0.6	20.0	23.2	0	5.7
16' C	6:20 "	-	-	0	0	0.3	0	5.4
20' C	6:30 "	5.6	-	0	0	0	0	5.4
8' C	8:00 pm	19.4	200	-	-	-	-	9.0
Cl_2	8:20 "	-	-	0.8	16.8	24.4	0	5.7
16' C	8:20 "	-	-	0	0	0.2	0	5.3
20' C	8:30 "	5.0	345	0	0	0	0	5.3
8' C	10:00 pm	19.0	-	-	-	-	-	9.0
Cl_2	10:20 "	-	-	0.6	16.0	22.4	0	5.7
16' C	10:20 "	-	-	0	0	0.3	0	5.4
20' C	10:30 "	5.1	-	0	0	0	0	5.4

All values in mg/l except pH

TABLE A-9

6/14/71

Sample	Time	NH_3	Chlorides	Free Cl_2	Chloramines Mono	Di	Tri	pH
8' C	7:30 am	12.7	180	0	0.1	0.3	0	9.0
Cl_2	7:30 "	-	-	4.8	3.2	20.8	4.0	4.2
16'C	7:40 "	-	-	0	0.1	0.6	0	3.7
20'C	7:40 "	0.8	370	0	0	0.4	0	3.6
8' C	9:00 am	11.1	200	-	-	-	-	9.1
Cl_2	9:20 "	-	-	6.8	2.0	7.2	8.0	4.4
16' C	9:20 "	-	-	0	0.2	0.3	0	3.7
20' C	9:30 "	0.4	400	0	0	0.2	0	3.7
8' C	11:00 am	12.7	220	0	0	0.1	0	9.0
Cl_2	11:20 "	-	-	6.0	1.2	6.0	10.2	4.8
16' C	11:20 "	-	-	0	0.1	0.4	0	3.7
20' C	11:30 "	0.3	415	0	0	0.3	0	3.6
8' C	1:00 pm	17.4	220	-	-	-	-	8.9
Cl_2	1:20 "	-	-	0.8	8.4	34.4	0	5.1
16' C	1:20 "	-	-	0	0	0.7	0	3.8
20' C	1:30 "	1.25	410	0	0	0.2	0	3.6
8' C	3:00 pm	26.3	210	0	0.2	0.2	0	9.0
Cl_2	3:20 "	-	-	0.2	16.4	28.2	0	5.6
16' C	3:20 "	-	-	0	0	0.6	0	3.8
20' C	3:30 "	4.6	395	0	0	0.1	0	3.7
8' C	5:00 pm	19.7	215	-	-	-	-	9.0
Cl_2	5:20 "	-	-	0.4	18.2	30.4	0	5.8
16' C	5:20 "	-	-	0	0	0.5	0	3.9
20' C	5:30 "	4.6	405	0	0	0.3	0	3.8

All values in mg/l except pH

TABLE A-10
6/15/71

Sample	Time	NH_3	Free Cl_2	Chloramines Mono	Chloramines Di	Chloramines Tri	pH
8' C	7:00 am	14	0	0	0.3	0	8.6
Cl_2	7:20 "	-	2.4	0.8	11.8	2.4	5.8
16' C	7:20 "	-	0	0	0.4	0	5.2
20' C	7:30 "	0.28	0	0	0.3	0	5.2
8' C	9:00 am	13.3	-	-	-	-	8.5
Cl_2	9:20 "	-	4.8	1.6	7.6	2.4	6.2
16' C	9:20 "	-	0	0	0.5	0	5.7
20' C	9:30 "	0	0	0	0.3	0	5.6
8' C	11:00 am	15.8	0	0	0.1	0	
Cl_2	11:20 "	-	6.4	2.8	18.2	2.0	6.3
16' C	11:20 "	-	0	0.1	0.5	0	5.6
20' C	11:30 "	0	0	0	0.2	0	5.6
8' C	1:00 pm	17.6	-	-	-	-	9.2
Cl_2	1:20 "	-	2.0	8.4	42.4	0	6.1
16' C	1:20 "	-	0	0.2	0.6	0	5.7
20' C	1:30 "	4.5	0	0	0.5	0	5.7
8' C	2:30 pm	17.2	-	-	-	-	9.2
Cl_2	2:50 "	-	2.4	10.0	38.2	0	6.2
16' C	2:50 "	-	0	0.1	0.7	0	5.8
20' C	3:00 "	7.6	0	0	0.3	0	5.8

All values in mg/l except pH

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16. Abstract The pilot scale study at Owosso, Michigan, was a physical-chemical wastewater treatment system consisting of chemical coagulation (lime to pH 8.8 to 9.4) sedimentation, deep bed filtration, carbon adsorption, chlorination to oxidize ammonia, and carbon dechlorination to remove free chlorine and chloramines.

Ammonia-nitrogen was removed to any desired level by the chlorination-dechlorination system. Complete removal from Owosso wastewater would require a chlorine to ammonia feed ratio of 9 to 1. The dechlorination carbon removed free chlorine and also the chloramines formed at less-than-breakpoint operation.

There is an initial ammonia-nitrogen breakthrough when using fresh dechlorination carbon which is attributed to acclimation rather than continuous leakage. After the period of acclimation, the dechlorination carbon removed free chlorine and all forms of chloramine without evidence of exhaustion. An hypothesis describing chloramine removal is presented. (Evans-EPA)

17a. Descriptors *Chlorination (Breakpoint), *Ammonia, *Chlorine Compounds, *Activated Carbon, Sewage Treatment, Oxidation

17b. Identifiers *Dechlorination (Activated Carbon), *Chloramine Removal (Carbon), Physical-Chemical Treatment, *Dechlorination Theory

17c. COWRR Field & Group

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Abstractor Francis L. Evans III

Institution Environmental Protection Agency, NERC, AWTRL

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