

OXYGEN RELATIONSHIPS IN OIL REFINERY  
EFFLUENT HOLDING PONDS

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## PREFACE

The purposes of the present study of oil refinery effluents in holding-pond series are to: (1) determine the magnitude of community metabolism; (2) determine the effects of light and temperature upon community metabolism of the oil refinery effluent community; (3) determine the annual course of community metabolism; (4) determine the efficiency of algae in oil refinery effluent in converting solar energy to chemical energy; (5) assess diffusion from the atmosphere in supplying oxygen for stabilization processes; (6) compare oil refinery effluent communities with other aquatic communities on the basis of community metabolism, chlorophyll, and suspended organic matter; and, (7) obtain design criteria for oil refinery effluent holding ponds.

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION. . . . .	1
1. Definitions. . . . .	2
<u>Photosynthetic Productivity and Community</u>	
<u>Respiration</u> . . . . .	2
<u>Production to Respiration Ratio</u> . . . . .	3
<u>Efficiency</u> . . . . .	3
<u>Eutrophication</u> . . . . .	4
<u>Autotrophic and Heterotrophic</u> . . . . .	4
<u>Assimilation Number</u> . . . . .	4
<u>Net Photosynthesis</u> . . . . .	4
<u>Light Saturation</u> . . . . .	4
<u>Holding Time or Retention Time</u> . . . . .	4
II. MATERIALS AND METHODS . . . . .	5
1. Description and Explanation of the Refining Processes and Waste Disposal . . . . .	5
2. Methods of Collection and Analyses of Samples. . .	6
3. Measurement of Community Metabolism. . . . .	8
4. Chlorophyll Analysis . . . . .	10
III. OXYGEN SUPPLY AND DEMAND. . . . .	12
1. Community Metabolism . . . . .	12
A. Seasonal Variations. . . . .	13
<u>Winter</u> . . . . .	13
<u>Spring</u> . . . . .	14
<u>Summer</u> . . . . .	19
<u>Fall</u> . . . . .	22
<u>Discussion</u> . . . . .	22
B. Comparison with Other Communities. . . . .	26
C. Annual Patterns. . . . .	31
<u>Refinery A</u> . . . . .	31
<u>Refinery B</u> . . . . .	34
2. Diffusion. . . . .	34
3. Light. . . . .	35
4. Temperature. . . . .	43
5. Productivity/Respiration Ratio . . . . .	44

Chapter	Page
IV. CHLOROPHYLL AND ORGANIC MATTER. . . . .	47
1. Chlorophyll in Oil Refinery Effluents. . . . .	47
2. Relationship of Chlorophyll to Photosynthesis. . . . .	52
3. Relationship of Chlorophyll, Organic Matter and Photosynthesis . . . . .	57
V. EFFECTIVENESS OF HOLDING PONDS. . . . .	61
1. Photosynthetic Production of Oxygen. . . . .	62
2. Reduction of Phenol. . . . .	65
3. Reduction of Biochemical Oxygen Demand . . . . .	68
4. Reduction of Chemical Oxygen Demand. . . . .	71
5. Reduction of Ammonia . . . . .	71
6. Evaluation of Retention Time . . . . .	71
VI. SUMMARY . . . . .	76
LITERATURE CITED . . . . .	79
APPENDIX . . . . .	83

## LIST OF TABLES

Table	Page
I. Comparison of Community Metabolism. . . . .	32
II. Percent Efficiency of the Algal Population in Converting Solar Energy into Chemical Energy at Refinery A . . . . .	42
III. Average Temperature in °F at Refinery A . . . . .	45
IV. Chlorophyll <u>a</u> in mg/l at Refinery A During Summer . . . . .	47
V. Chlorophyll <u>a</u> in mg/l at Refinery A During Fall . . . . .	48
VI. Chlorophyll <u>a</u> in mg/l at Refinery A During Winter . . . . .	49
VII. Chlorophyll <u>a</u> in mg/l at Refinery A During Spring . . . . .	50
VIII. Chlorophyll <u>a</u> in Various Phytoplankton Communities. . . . .	51
IX. Organic Matter Concentration in gm/m <sup>3</sup> at Refinery A . . . . .	57

### Appendix Tables

I. Community Metabolism at Refinery A. . . . .	84
II. Community Metabolism at Refinery B. . . . .	90

## LIST OF FIGURES

Figure	Page
1. Example of the diurnal curve for determination of community metabolism with calculations. . . . .	9
2. Average winter gross photosynthesis and community respiration at Refinery A. . . . .	15
3. Average winter gross photosynthesis and community respiration at Refinery B. . . . .	16
4. Average spring gross photosynthesis and community respiration at Refinery A. . . . .	17
5. Average spring gross photosynthesis and community respiration at Refinery B. . . . .	18
6. Average summer gross photosynthesis and community respiration at Refinery A. . . . .	20
7. Average summer gross photosynthesis and community respiration at Refinery B. . . . .	21
8. Average fall gross photosynthesis and community respiration at Refinery A. . . . .	23
9. Average fall gross photosynthesis and community respiration at Refinery B. . . . .	24
10. Comparison of community metabolism of an oil refinery effluent holding system with a sewage receiving stream . .	27
11. Community metabolism at Refinery A, 12 October 1961. . . . .	30
12. Solar intensity in langley's at Oklahoma City, Oklahoma on sampling dates (U.S. Weather Bureau, 1961 and 1962). . . .	37
13. Effect of solar radiation and light saturation on oxygen production . . . . .	39
14. Example of a diurnal oxygen curve with midday depression due to cloudiness. Nine days holding time, Refinery A, 18 July 1961 . . . . .	40

Figure	Page
15. Daily gross photosynthesis compared with chlorophyll concentration. . . . .	53
16. Assimilation number ( $\text{gm O}_2/\text{gm chlorophyll } \underline{a}/\text{m}^2/\text{hour}$ ) plotted against chlorophyll concentration in $\text{gm}/\text{m}^2$ . . .	54
17. Chlorophyll in $\text{gm}/\text{m}^3$ plotted against organic matter in $\text{gm}/\text{m}^3$ for Refinery A. . . . .	59
18. Annual course of photosynthesis at Refinery A for all stations during one year . . . . .	63
19. Annual course of photosynthesis at Refinery B for all stations during one year . . . . .	64
20. Reduction of phenol (0 to 10 days holding time) at Refinery A . . . . .	66
21. Reduction of phenol at Refinery B. . . . .	67
22. Reduction of biochemical oxygen demand (0 to 10 days holding time) at Refinery A. . . . .	69
23. Reduction of biochemical oxygen demand (0 to 60 days holding time) at Refinery B. . . . .	70
24. Reduction of chemical oxygen demand (0 to 10 days holding time) at Refinery A. . . . .	72
25. Reduction of chemical oxygen demand (0 to 60 days holding time) at Refinery B. . . . .	73
26. Reduction of ammonia (0 to 60 days holding time) at Refinery B . . . . .	74

Appendix Figures

1. Diagram of the holding pond system at Refinery A . . . . .	93
2. Diagram of the holding pond system at Refinery B . . . . .	94
3. Annual course of productivity (P) and community respiration (R) for Refinery A at the beginning of the system. . . .	95
4. Annual course of productivity (P) and community respiration (R) for Refinery A at one day holding time . . . . .	96



## CHAPTER I

### INTRODUCTION

A study of the photosynthetic production of oxygen in series of effluent holding ponds at two oil refineries in northern Oklahoma was conducted during the period June 30, 1961 to July 30, 1962. Clear, sunny days were selected as sampling dates so that communities could be studied under optimal climatic conditions. All four seasons of the year were considered and holding pond conditions were correlated with seasons.

Although the literature dealing with photosynthetic production of oxygen in aquatic communities is voluminous, there is little information on oxygen production in oil refinery effluent holding ponds. Copeland and Dorris (1962) reported photosynthetic productivity values as well as community oxygen demand for two oil refinery effluent holding pond systems in Oklahoma under summer conditions.

Considerable information exists for sewage ponds and streams polluted by sewage. Even though contents of sewage ponds are different than those of oil refinery effluent holding ponds, some principles may apply to both situations. Oswald, et al. (1957) reported results from a pilot-plant study of sewage ponds in California. They found that for the same degree of waste stabilization, more holding time was required in winter than in summer. It has been reported that shallow holding ponds result in a shorter holding period than relatively deep holding

ponds (Calvert, 1933; Bartsch and Allum, 1957; Oswald, et al., 1957; Farmer, 1960; Parker, 1962; and others). The same principles were found to apply in this study.

Some principles that apply to sewage ponds do not apply to oil refinery effluent-holding ponds. The number of days holding time necessary for stabilization of sewage effluents (Oswald, et al., 1957; and Parker, 1962) is much shorter than the number of days required to stabilize oil refinery effluents (Dorris, et al., 1961; and Copeland and Dorris, 1962). Although chlorophyll concentration is about the same in both sewage and oil refinery effluent, photosynthetic productivity is lower in oil refinery effluent. Efficiency of energy conversion by algae is lower in oil refinery effluent than in sewage.

#### Definitions

Terms used in the following discussion have been used by various authors in ecology with slightly different meanings.

Photosynthetic Productivity and Community Respiration. Light energy is degraded into heat, and carbon dioxide and an electron source are combined into reduced organic matter by photo-autotrophic organisms. A small portion of the light energy is stored in the reduced organic matter. The rate of energy storage is defined as gross photosynthetic productivity. The energy storage rate may be determined by measuring the rate of appearance or disappearance of one of the products in the chemical reaction which accompanies it. Some of the organic matter produced by photosynthesis is used directly and some must be oxidized to provide energy for life processes of the producer. This rate of energy change is also measured by the rate of change of one of the

products in the chemical reaction.

A community is composed of producers, various trophic levels of consumers, and decomposers. There is photosynthetic production in the system during daylight hours and continuous respiration both day and night. Gross photosynthesis of the community is the sum of the photosynthesis of all of the producer organisms. Total community respiration is the sum of the respiration of all of the organisms and the oxygen demand of inorganic and organic components of the community. If the community is to increase its biomass, products produced by photosynthesis must exceed the needs of total community respiration. When community respiration exceeds gross photosynthesis, the community decreases in biomass.

A community may exist in which organic matter with its stored energy is either exported or imported. A community may increase or decrease its biomass while photosynthesis and respiration remain equal, depending on whether organic matter is being added or removed from the community. In this study, organic matter was continuously imported in the oil refinery effluent. Thus the communities were provided with an energy source other than that produced by photosynthesis.

Production to Respiration Ratio. If no export or import of organic material occurs, the ratio of gross photosynthesis and community respiration must be unity. When import of organic material occurs, such as in the present study, the ratio is less than unity. However, the imported energy eventually may be utilized and the ratio tends to return to unity.

Efficiency. The ratio of quantity of potential energy produced during photosynthesis to quantity of light energy of suitable wave length which

falls on the surface of the water is efficiency. This ratio is expressed as percent.

Eutrophication. When photosynthetic productivity exceeds community respiration there is a net gain of energy by the community. A net gain of energy also occurs when organic matter is imported into the community. In either case, the community is said to be undergoing eutrophication.

Autotrophic and Heterotrophic. When the production to respiration ratio is unity or greater than unity, producer organisms are producing as much energy as is utilized by community respiration and the community is considered to be autotrophic. On the other hand, when production to respiration ratio is less than unity, the community is utilizing more energy than is provided by producer organisms and the community is considered to be heterotrophic.

Assimilation Number. The ratio of photosynthetic rate to weight of chlorophyll is termed the assimilation number.

Net Photosynthesis. The rate of storage of organic matter in excess of respiratory utilization is called net photosynthesis.

Light Saturation. When the rate of photosynthesis no longer increases with increased light intensity, the plant cell is considered to be light saturated. Photosynthetic rate may eventually decrease due to light inhibition of photosynthetic processes. This inhibition is brought about by photooxidation of critical enzyme systems and possibly by chlorophyll inactivation.

Holding Time or Retention Time. Length of time in days that effluent water remains in a pond or holding pond system is referred to as holding time or retention time. Holding time in the present study was calculated by dividing the volume of a pond by the average daily output of the refinery.

## CHAPTER II

### MATERIALS AND METHODS

#### Description and Explanation of the Refining Processes and Waste Disposal

Holding pond systems of two oil refineries were studied. Refining processes at Refinery A included atmospheric and vacuum crude distillation, solvent treating and dewaxing of lubricating oils, wax pressing and sweating, blending and compounding of oils and greases, thermal and catalytic cracking, catalytic reforming and polymerization, hydrogen fluoride alkylation with aromatic extraction, delayed coking, gasoline and distillate treating and blending operations, and cooling tower and boiler feed-water treatment.

Waste waters were segregated for treatment. A large part of the caustic solutions was sold for further refining, while the remaining strong caustic solutions and other potentially harmful chemical solutions were impounded in open pits. Sour water streams from cracking operations were treated in a steam stripping tower and an aeration chamber for removal of sulfides, phenol and ammonia. Oil was removed from the effluent water in conventional traps.

Combined effluents were passed through a settling basin for final removal of oil and solids and for overall improvement by oxidation and bacterial action. The effluents then passed through a series of ten

ponds connected by submerged pipes arranged end to end so that water traveled the entire length of each pond before entering the next (Appendix Figure 1). Each pond was approximately five feet deep. About ten days were required for water to travel from beginning to end of the pond system. Algae were present in all ponds at least during spring and summer.

Refining processes at Refinery B included crude distillation, vacuum distillation, catalytic cracking, hydrogen fluoride alkylation, propane deasphalting, and catalytic reforming. Caustic used in scrubbing catalytic gasoline was sold to a chemical company. Caustic used for removal of hydrogen sulfide was combined with the total refinery effluent and passed over an aeration tower. Oil was removed in conventional traps and in oil-settling basins.

Effluent water passed through a series of ponds for further improvement by oxidation and bacterial action. Effluents passed first through a series of three ponds, each about 14 feet deep. Upon leaving these ponds, effluent passed through a spray into four shallower ponds, about five feet deep (Appendix Figure 2). Water flowed from pond to pond through submerged pipes. However, in the last two ponds, which were larger than the others, dikes had been constructed to separate the ponds into bays. The first two ponds did not support algal populations and were anaerobic in the sense that they contained no free oxygen. Time required for passage of effluents through the entire pond system was about 60 days.

#### Methods of Collection and Analyses of Samples

Collecting stations were established at Refinery A at the inlet of

each pond, at the outlet of the last pond (Appendix Figure 1), and at the outlet of each pond at Refinery B (Appendix Figure 2). Thirteen series of samples were taken at Refinery A and eight at Refinery B between June 30, 1961 and July 31, 1962. Temperature was measured and duplicate dissolved oxygen samples were taken at each station at frequent intervals during a 24-hour period. Water samples for dissolved oxygen analysis were fixed by the Alsterburg (Azide) modification of the Winkler method (A.P.H.A., 1961). Liberated iodine was measured colorimetrically with a Bausch and Lomb Spectronic 20 photoelectric colorimeter at a wavelength of 450 millimicrons. Samples were measured soon after being fixed to avoid fading of iodine color. Optical density was converted to milligrams of dissolved oxygen per liter.

Water samples for chlorophyll and ash-free dry weight analyses were taken from ponds 1, 4, 7, and 10 at Refinery A. Aliquots of 100 ml. were filtered through Millipore filters of 0.45 millimicrons pore size for the chlorophyll analysis. The filtered residue was extracted in 90% acetone for 24 hours in the dark at about 5°C and centrifuged. Optical density of the liquid was determined with the Bausch and Lomb Spectronic 20 photoelectric colorimeter at a wave length of 663 millimicrons.

To determine ash-free dry weight, 100 ml. aliquots were filtered through Millipore filters of 0.45 millimicrons pore size. Filter and filtered residue was dried in an oven, cooled, weighed, and ashed at red heat in a muffle furnace. The ash was cooled in a dessicator and weighed. Weight of ash and filter paper was subtracted from the dried weight to determine ash-free dry weight.

### Measurement of Community Metabolism

The procedure of Odum (1956) and Odum and Hoskin (1958) was followed in measurement of photosynthetic productivity. Oxygen concentration and percent saturation at each sample period were plotted against time in hours as illustrated in Figure 1.

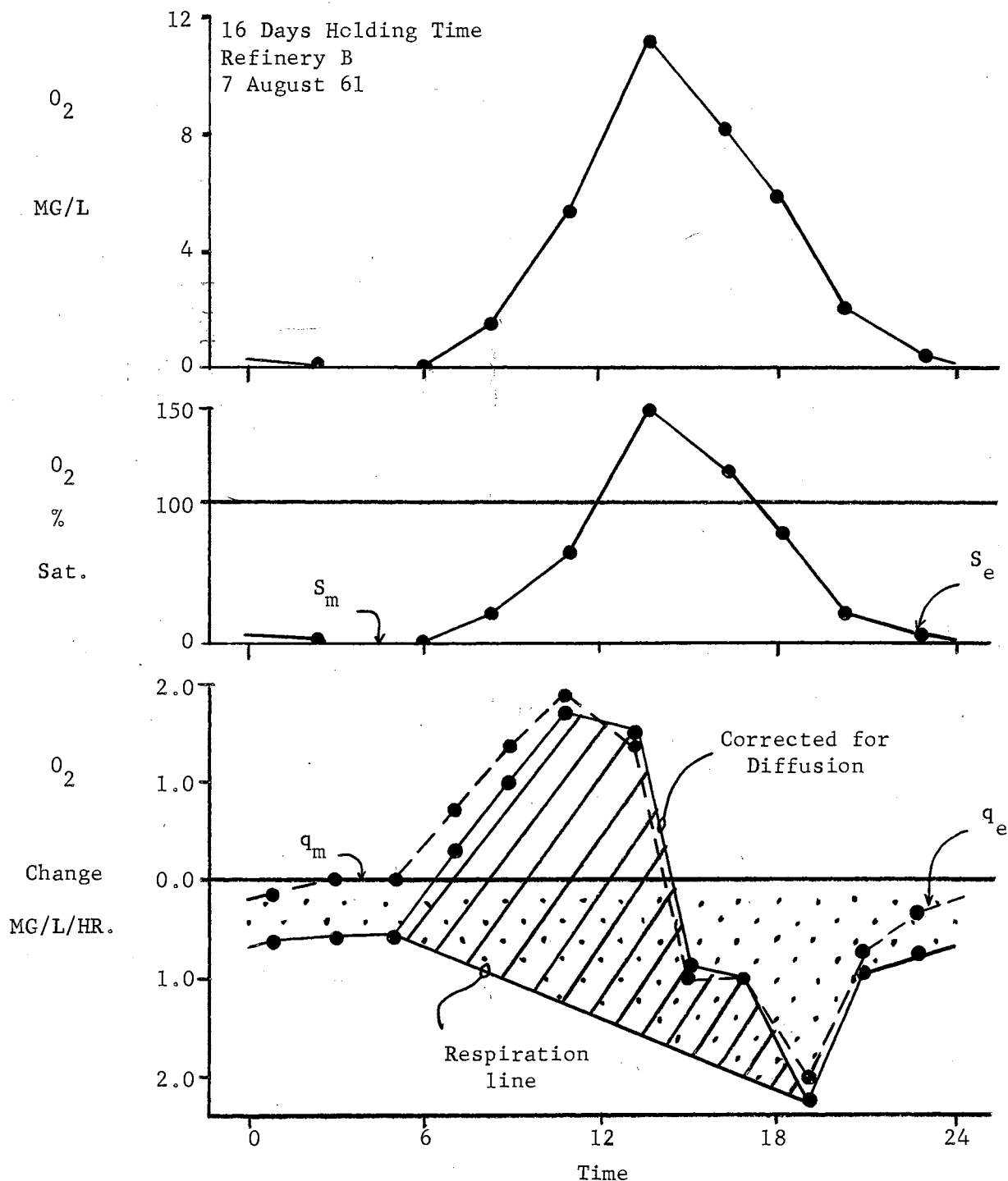
The rate of oxygen change in milligrams per liter per hour (mg/l/hr) was determined from the oxygen concentration curve and plotted on the same time scale (dashed curve in Figure 1). A rate-of-change point was plotted every two hours to make a smooth curve.

The original rate-of-change curve was corrected for diffusion by the method described by Odum (1956). The diffusion coefficient ( $k$ ) was obtained from the nighttime rate-of-change curve, since the only changes during the night are caused by diffusion and respiration. Gaseous exchange depends upon the saturation deficit of the water. The rate of change ( $q$ ) at any time during the night results from diffusion rate ( $k$ ) times saturation deficit ( $S$ ) minus respiration ( $r$ );  $q = kS - r$ . By subtracting the change at one time from that at another time, the effect of respiration was removed. Calculations were made from post-sunset and predawn determinations. The equations  $q_m = kS_m - r$ , and  $q_e = kS_e - r$ , where  $m$  = morning and  $e$  = evening, yield:

$$k = \frac{q_m - q_e}{S_m - S_e}$$

The calculated diffusion constant for Figure 1 was  $k = \frac{q_m - q_e}{S_m - S_e} = 0.9 \text{ mg/l/hr}$  ( $0.9 \text{ gm/m}^3/\text{hr}$ ) at 0% saturation. Saturation deficit at each period was multiplied by the diffusion constant ( $k$ ), and the product added to or subtracted from the original rate-of-change curve to correct for diffusion loss or gain (the solid curve at the bottom of Figure 1).





$$k = \frac{q_m - q_e}{S_m - S_e} = \frac{0.0 - (-0.42)}{0.0 - (-0.84)} = 0.5 \text{ gm/m}^3/\text{hr at } 0\% \text{ saturation.}$$

$$P_g = 18.24 \text{ gm/m}^3/\text{day} \times 0.54 \text{ M} = 14.3 \text{ gm/m}^2/\text{day.}$$

$$R = 24.56 \text{ gm/m}^3/\text{day} \times 0.54 \text{ M} = 9.8 \text{ gm/m}^2/\text{day.}$$

Figure 1: Example of the diurnal curve for determination of community metabolism with calculations.

On the corrected rate-of-change curve, the rate of community respiration was shown by drawing a straight line from the dawn point to the lowest point at night. The amount of community respiration ( $\text{gm}/\text{m}^3/\text{day}$ ) was determined by measuring the area between the respiration line and the zero rate-of-change line (stippled area in Figure 1). Gross photosynthesis, including simultaneous respiration, is represented by the cross-hatched area in Figure 1 between the respiration line and the daytime hump of the corrected rate-of-change curve. Amount of photosynthesis in  $\text{gm}/\text{m}^3/\text{day}$  was determined by measuring the enclosed area.

Since photosynthesis occurs on the basis of area exposed to sunlight, volumetric community photosynthesis and respiration values were converted to surface area. Depth of light penetration was determined with a submarine photometer. The euphotic zone was considered to extend to the depth at which light was 1% of surface intensity. Gross community photosynthesis and respiration in  $\text{gm}/\text{m}^3/\text{day}$  were multiplied by depth of the euphotic zone in meters to obtain gross photosynthesis and community respiration in  $\text{gm}/\text{m}^2/\text{day}$ .

#### Chlorophyll Analysis

Richards and Thompson (1952) developed a method for the spectrophotometric determination of chlorophyll a. In their procedure, optical densities were measured at wavelengths of 630, 645, and 665 millimicrons. Odum, et al. (1958) compared results based on optical density at wavelength 663 obtained with the Bausch and Lomb Spectronic 20 colorimeter with results obtained by the Richards and Thompson method. They found a straight line relationship, indicating a close agreement between the two methods. Pigments of green, red, and blue-green algae produced

different slopes. Algae under consideration in the present study were primarily green algae. The slope of the line for green algae was 15, and the following equation was derived.

$$\text{Chlorophyll } \underline{a} \text{ in mg/l} = 15.0 d_{663}, \text{ where } d = \text{optical density at } 663 \text{ millimicrons wavelength.} \quad (1)$$

Equation (1) is true if 10 ml. of extraction solution are used. High concentrations of chlorophyll in the effluent holding ponds made it necessary to use 20 ml. of 90% acetone for extraction. Since the dilution used in equation (1) was doubled, the slope of the line was changed to 7.5 and equation (1) became:

$$\text{Chlorophyll } \underline{a} \text{ in mg/l} = 7.5 d_{663}. \quad (2)$$

Only 100 ml. of water were filtered and chlorophyll a concentration determined by equation (2) had to be converted to the concentration in a liter of water. Equation (2) then became:  $7.5 d_{663} \times 0.02$  liters of acetone  $\times 10$  (10  $\times$  100 ml. = one liter of water), or

$$\text{Chlorophyll } \underline{a} \text{ in mg/l} = 1.5 d_{663}. \quad (3)$$

Equation (3) was used to compute chlorophyll a concentrations in the present study.

## CHAPTER III

### OXYGEN SUPPLY AND DEMAND

#### 1. Community Metabolism

Community metabolism involves production and respiration of oxygen by the community (Odum and Hoskin, 1958). Algae produce oxygen by photosynthesis. The oxygen may be used for chemical and bacterial oxidation of organic compounds as well as algal respiration. Approximately one gram of carbohydrate material is synthesized for every gram of oxygen produced. Conversely, for each gram of carbohydrate respired, approximately one gram of oxygen is required. Measurements of oxygen production and respiration gives a picture of energy relationships of the community.

Knowledge of community metabolism enables the scientist to better understand the nature of the aquatic community. For example, when productivity exceeds respiration, organic matter accumulates in the community, as at Silver Springs, Florida (Odum, 1957a). Silver Springs was barren at the beginning and accumulated organic matter as water proceeded downstream. At some point downstream, a balance between production and respiration was reached. When community respiration exceeds production of oxygen, there is a net loss of organic matter from the community. Odum and Hoskin (1958) indicate that it is necessary to have a steady inflow of organic matter into the community in order to

maintain conditions where respiration constantly exceeds productivity. Oil refinery effluent holding ponds are examples of such situations (Copeland and Dorris, 1962).

Magnitude of community metabolism may be used to describe community types. When a community is rich in nutrients oxygen production by photosynthesis will be high (Odum and Hoskin, 1958). When eutrophication is occurring, production will be relatively high (Copeland and Dorris, 1962). In organically polluted communities, such as oil refinery effluent holding ponds, both production and respiration are usually high (Copeland and Dorris, 1962). In deep lakes, productivity and respiration are usually low (Wisconsin Lakes, Manning and Juday, 1941; Verduin, 1956). Aquatic communities may be classified according to the production/respiration ratio (Odum, 1956). From the above discussion, it may be seen that community metabolism is an important aspect of the aquatic community.

#### A. Seasonal Variations.

Based upon water temperature, community metabolism data from Refinery A and Refinery B were assigned to the four seasons. Spring included data for late March and April (57° F. to 71° F.); summer extended from June through September (76° F. to 85° F.); fall included October and November (48° F. to 70° F.); and winter included December through early March (37° F. to 49° F.).

Winter. Measureable photosynthesis did not occur at any place in the system during the winter at Refinery A (Figure 2 and Appendix Table I). Average community respiration decreased from 27.3 gm/m<sup>2</sup>/day at the beginning of the system to 21.8 gm/m<sup>2</sup>/day at six days holding time and then increased to 31.9 gm/m<sup>2</sup>/day at ten days holding time.

At Refinery B (Figure 3 and Appendix Table II), average winter photosynthesis ranged from zero during the first 37 days holding time to  $3.0 \text{ gm/m}^2/\text{day}$  at 60 days holding time. Average community respiration was lowest at the beginning of the system and highest at 37 days holding time, ranging from 23.1 to  $32.4 \text{ gm/m}^2/\text{day}$ . The sharp decrease in respiration between 16 and 20 days holding time may have been caused by aeration at that point.

Dead and decaying algae exercise oxygen demand in decomposition. A major portion of community respiration during winter resulted from decomposition of sludges consisting chiefly of dead and decaying algae. This conclusion is supported by the fact that suspended organic matter was low (Table IX). Since winter community respiration was of about the same order of magnitude as summer (compare Figures 2 and 3 with 6 and 7), total community respiration is not dependent upon temperature (Beyers, 1962). Community respiration during winter proceeded at a rate limited by availability of oxygen and substrate.

Spring. At Refinery A (Figure 4 and Appendix Table I), average photosynthesis increased from zero at one day holding time to a maximum of  $20.7 \text{ gm/m}^2/\text{day}$  at seven days holding time, and decreased to  $12.7 \text{ gm/m}^2/\text{day}$  at ten days holding time. Average community respiration decreased steadily through the system, ranging from  $30.5 \text{ gm/m}^2/\text{day}$  in the first pond to  $8.2 \text{ gm/m}^2/\text{day}$  at ten days holding time.

At Refinery B (Figure 5 and Appendix Table II), average photosynthesis increased from zero at the beginning of the system to a maximum of  $14.2 \text{ gm/m}^2/\text{day}$  at 37 days holding time, and decreased to  $5.4 \text{ gm/m}^2/\text{day}$  at 60 days holding time. Average community respiration decreased continuously from  $27.0 \text{ gm/m}^2/\text{day}$  at zero days holding time to  $6.0 \text{ gm/m}^2/\text{day}$  at 60 days holding time.

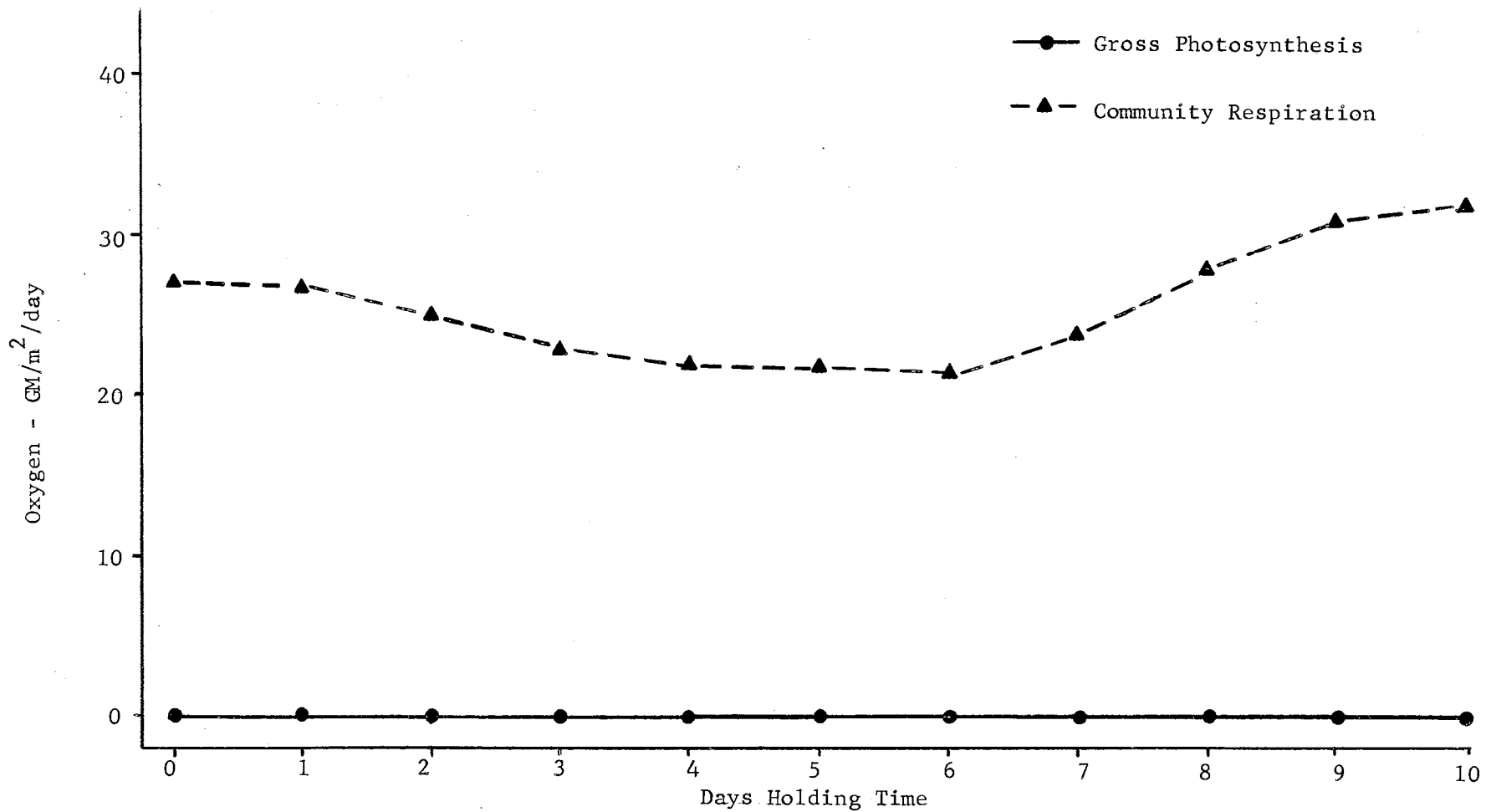


Figure 2: Average winter gross photosynthesis and community respiration at Refinery A.

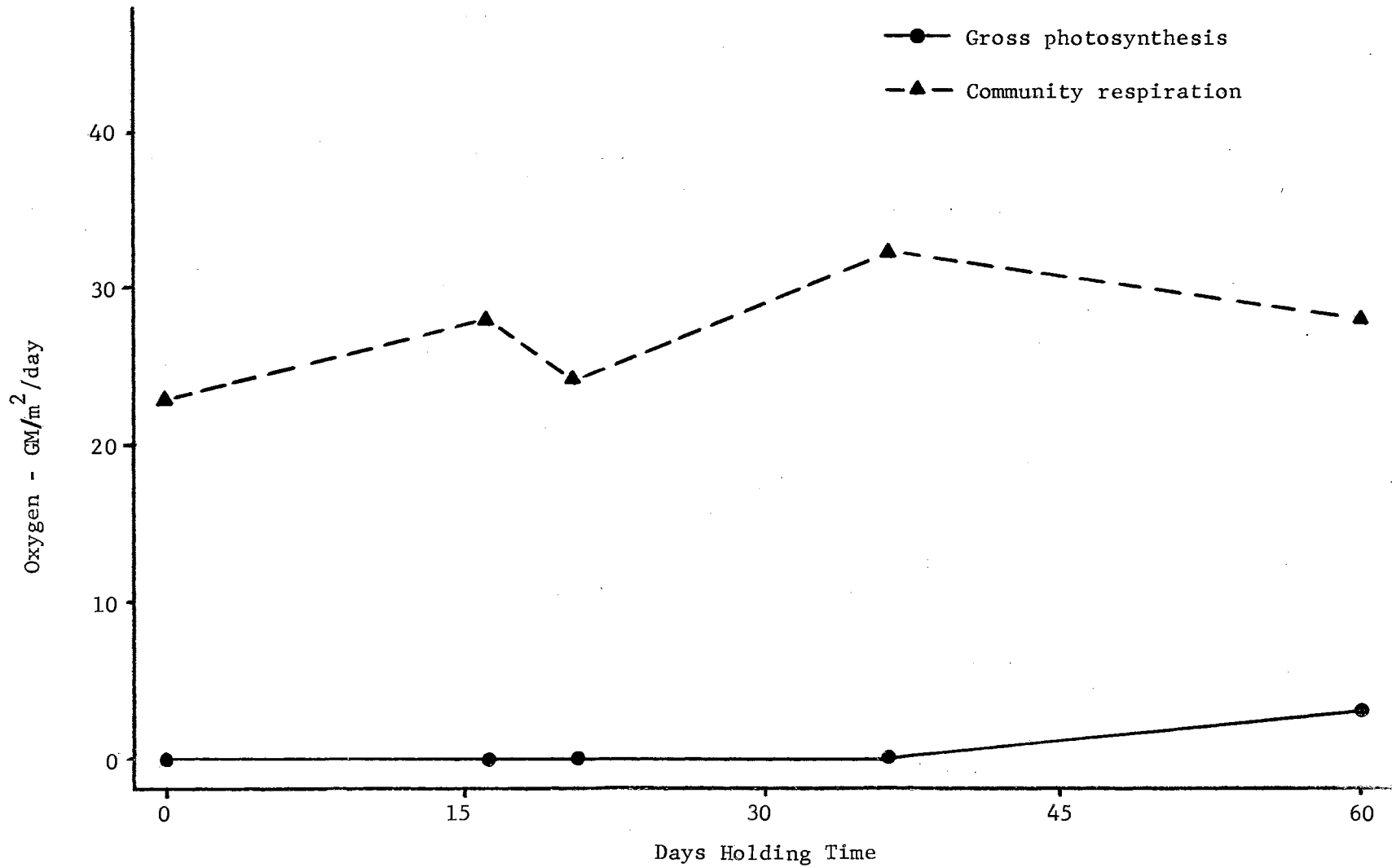


Figure 3: Average winter gross photosynthesis and community respiration at Refinery B.



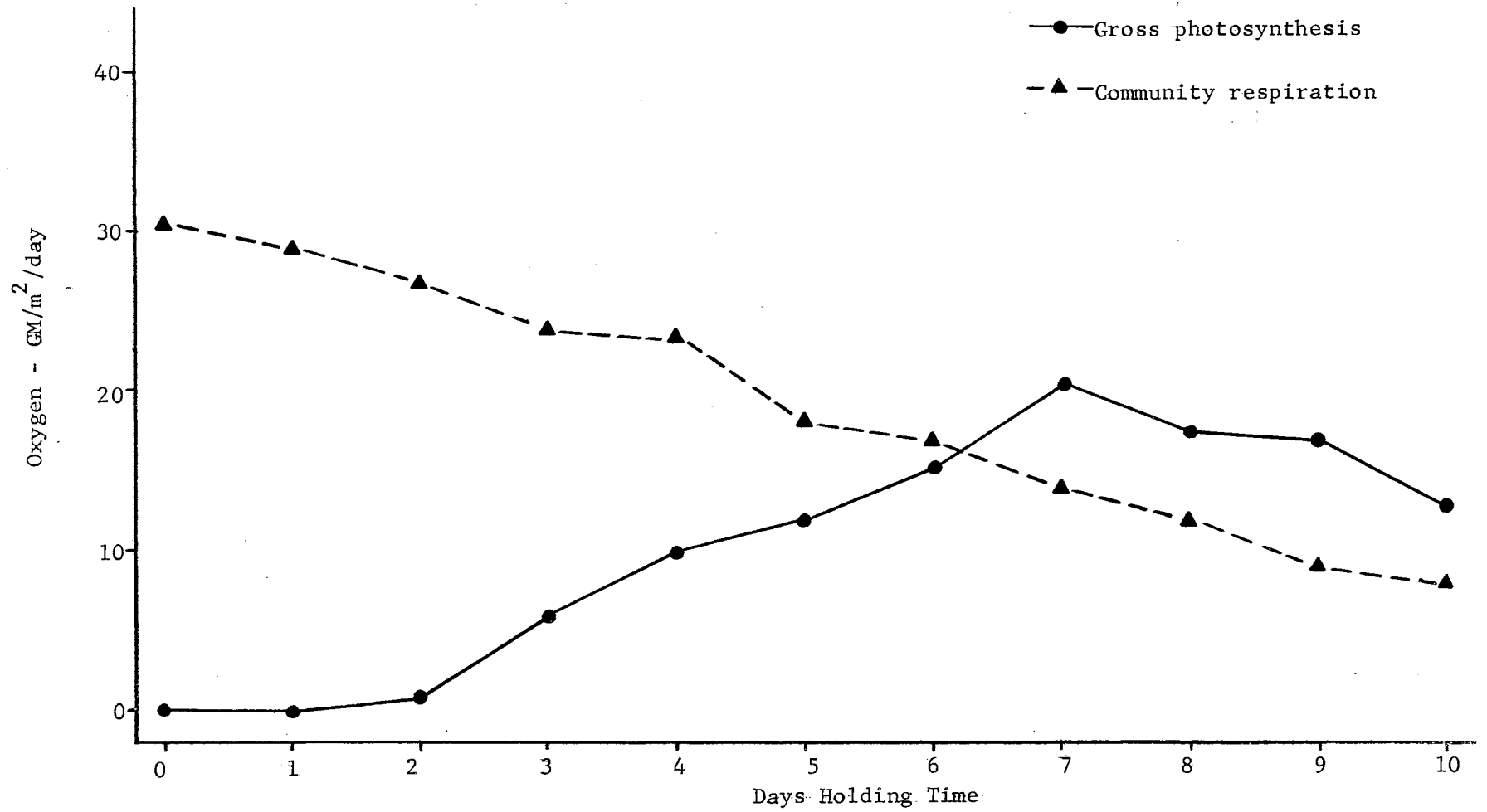


Figure 4: Average spring gross photosynthesis and community respiration at Refinery A.

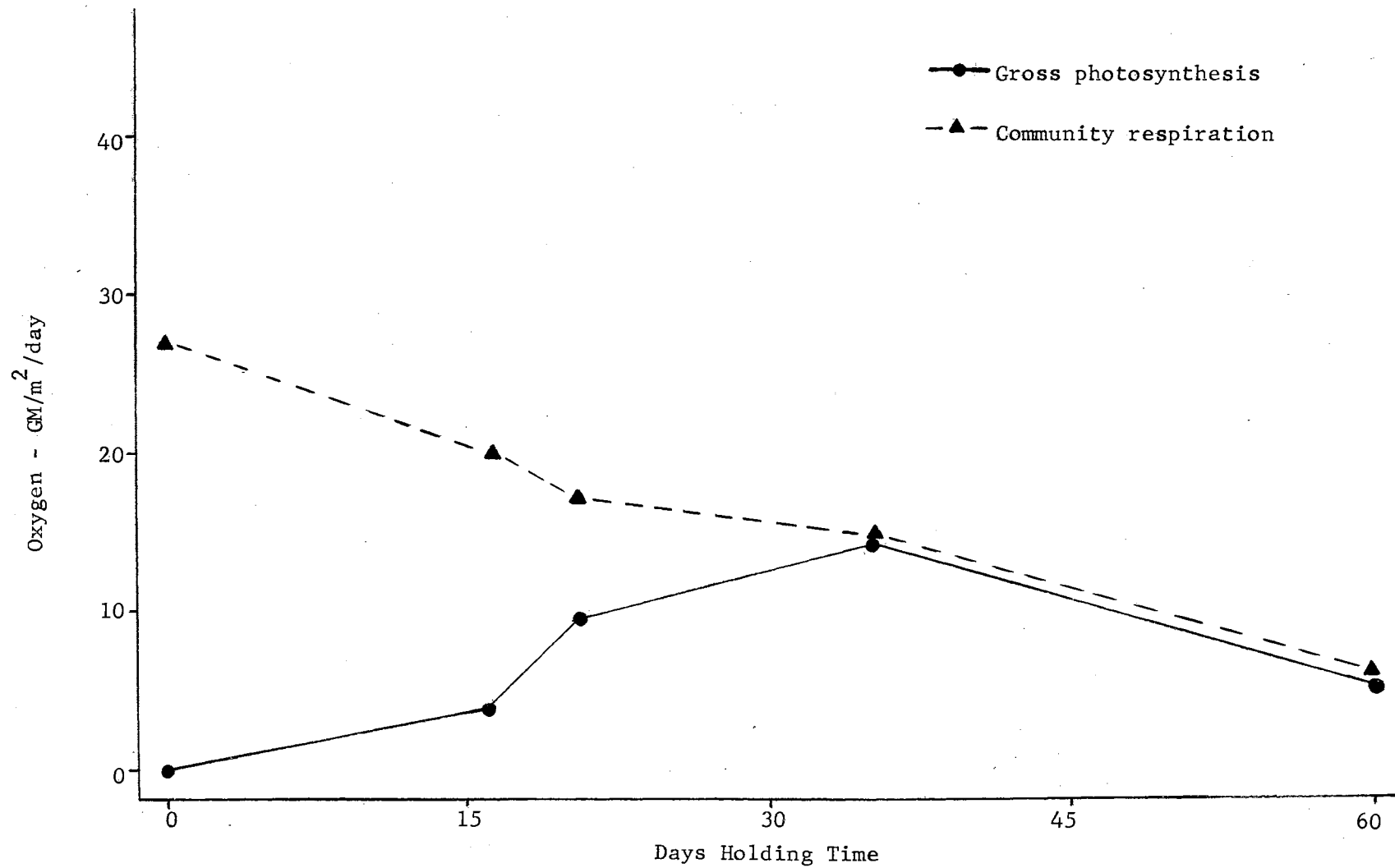


Figure 5: Average spring gross photosynthesis and community respiration at Refinery B.

Changes in photosynthesis within each pond system may be explained in terms of toxicity of effluent and availability of nutrients. Effluent decreases in toxicity as holding time increases (Dorris, et al., 1961). Raw materials progressively are made available by decomposition of organic contents of the effluent and decrease as holding time increases (Dorris, et al., 1962). Toxicity apparently inhibits utilization of raw materials by algae during the first few days holding time. However, a point is reached where toxicity is no longer limiting and maximal algal populations and photosynthesis occurs. Because of the decreased supply of raw materials with increased holding time, algae and photosynthesis decreased toward the end of the pond systems.

Summer. At Refinery A, average photosynthetic productivity during summer increased from 3.3 gm/m<sup>2</sup>/day at the beginning of the system to 16.8 gm/m<sup>2</sup>/day at nine days holding time, and decreased to 14.6 gm/m<sup>2</sup>/day at ten days holding time (Figure 6 and Appendix Table I). Community respiration was highest after one day holding time at 24.5 gm/m<sup>2</sup>/day. Respiration decreased to 9.0 gm/m<sup>2</sup>/day after seven days holding time, and increased to 16.7 gm/m<sup>2</sup>/day after ten days holding time.

Photosynthetic production of oxygen exceeded community demand from about five to nine days holding time. This means that the community accumulated new organic matter in about the last half of the pond system. It is possible that little or no decomposition of effluent-contained compounds occurred after about four days holding time.

At Refinery B, average photosynthetic productivity during summer increased from zero at the beginning of the system to 15.3 gm/m<sup>2</sup>/day after 20 days holding time, and decreased to 7.8 gm/m<sup>2</sup>/day after 60 days holding time (Figure 7 and Appendix Table II). Average community

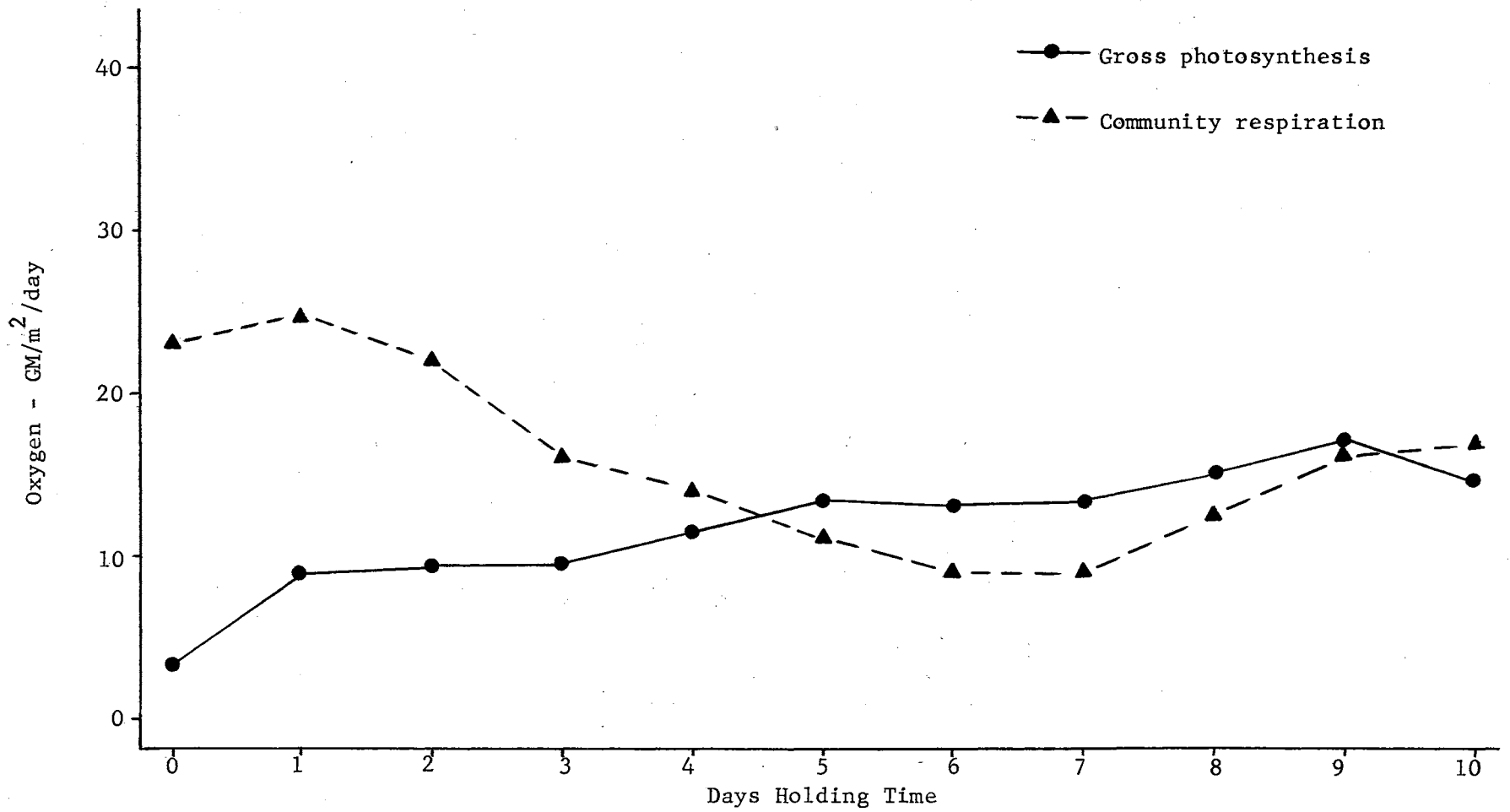


Figure 6: Average summer gross photosynthesis and community respiration at Refinery A.

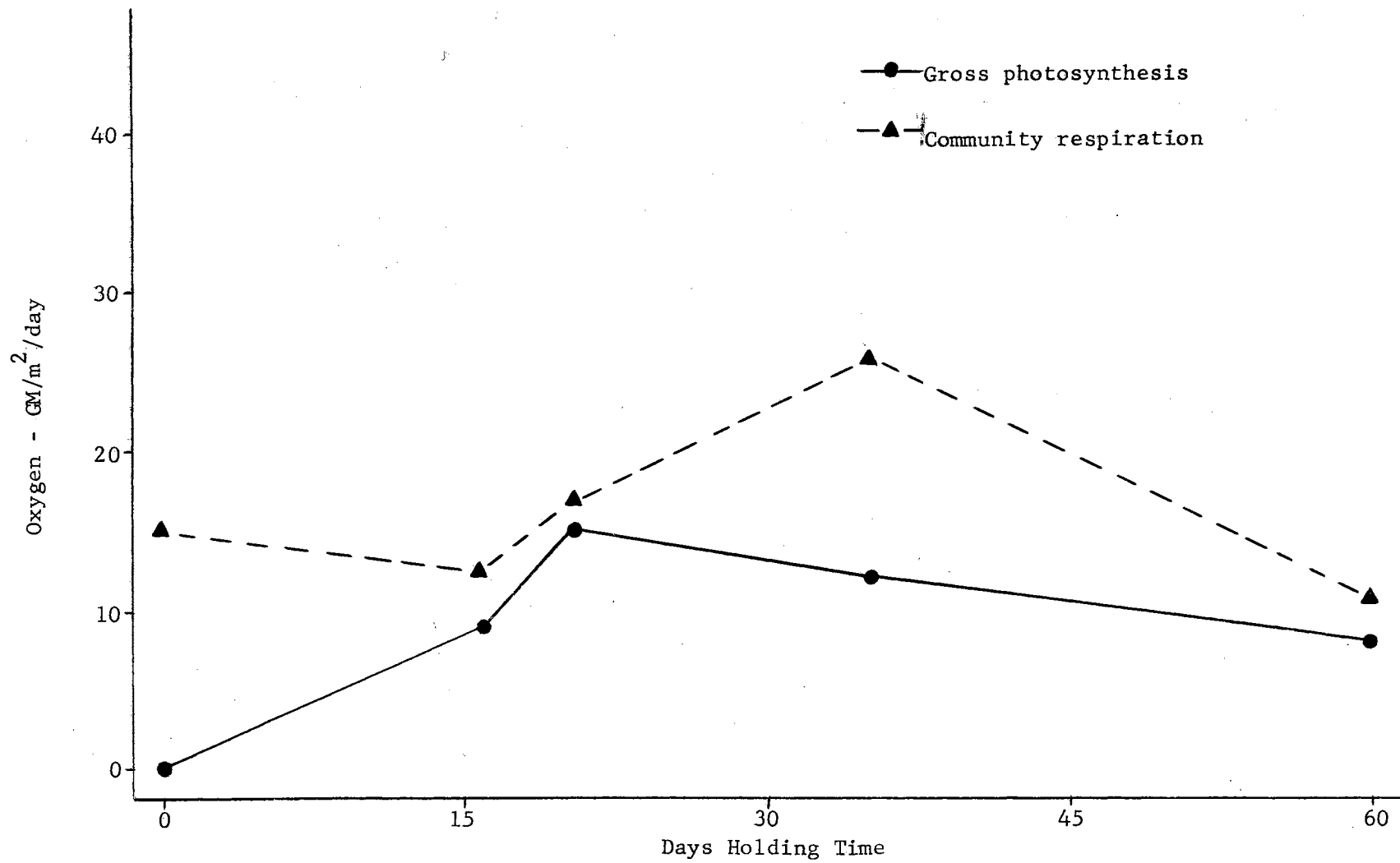


Figure 7: Average summer gross photosynthesis and community respiration at Refinery B.

respiration reached a peak of  $25.9 \text{ gm/m}^2/\text{day}$  after 37 days holding time and was lowest at  $11.0 \text{ gm/m}^2/\text{day}$  after 60 days holding time.

Community respiration exceeded photosynthetic productivity at all points in the system during summer at Refinery B. In other words, there was a net loss of organic matter from the community during summer.

Fall. Average community respiration was higher during fall than in any other season, presumably because of decomposition of sludges resulting from the summer algal population. At Refinery A, no photosynthetic productivity occurred in the first two days holding time during fall (Figure 8 and Appendix Table I). It reached a peak of  $12.0 \text{ gm/m}^2/\text{day}$  after five days holding time and decreased to  $7.4 \text{ gm/m}^2/\text{day}$  after nine days holding time. Community respiration ranged from  $34.8 \text{ gm/m}^2/\text{day}$  at the beginning of the system to  $42.4 \text{ gm/m}^2/\text{day}$  at four days holding time to  $30.6 \text{ gm/m}^2/\text{day}$  after nine days holding time.

At Refinery B, average photosynthetic productivity was zero for the first 16 days holding time (Figure 9 and Appendix Table II). Photosynthesis increased with holding time and reached a high of  $19.3 \text{ gm/m}^2/\text{day}$  after 60 days holding time. Average community respiration was lowest after 37 days holding time and highest after 60 days holding time. Respiration increased from  $17.2 \text{ gm/m}^2/\text{day}$  at zero holding time to  $19.4 \text{ gm/m}^2/\text{day}$  after 20 days holding time, decreased to  $4.9 \text{ gm/m}^2/\text{day}$  at 37 days holding time, and finally increased to  $29.8 \text{ gm/m}^2/\text{day}$  after 60 days holding time.

Discussion. As oil refinery effluent becomes progressively stabilized, oxygen demand of effluent-contributed materials decreases. After a low point in community respiration level based on effluent compounds is once

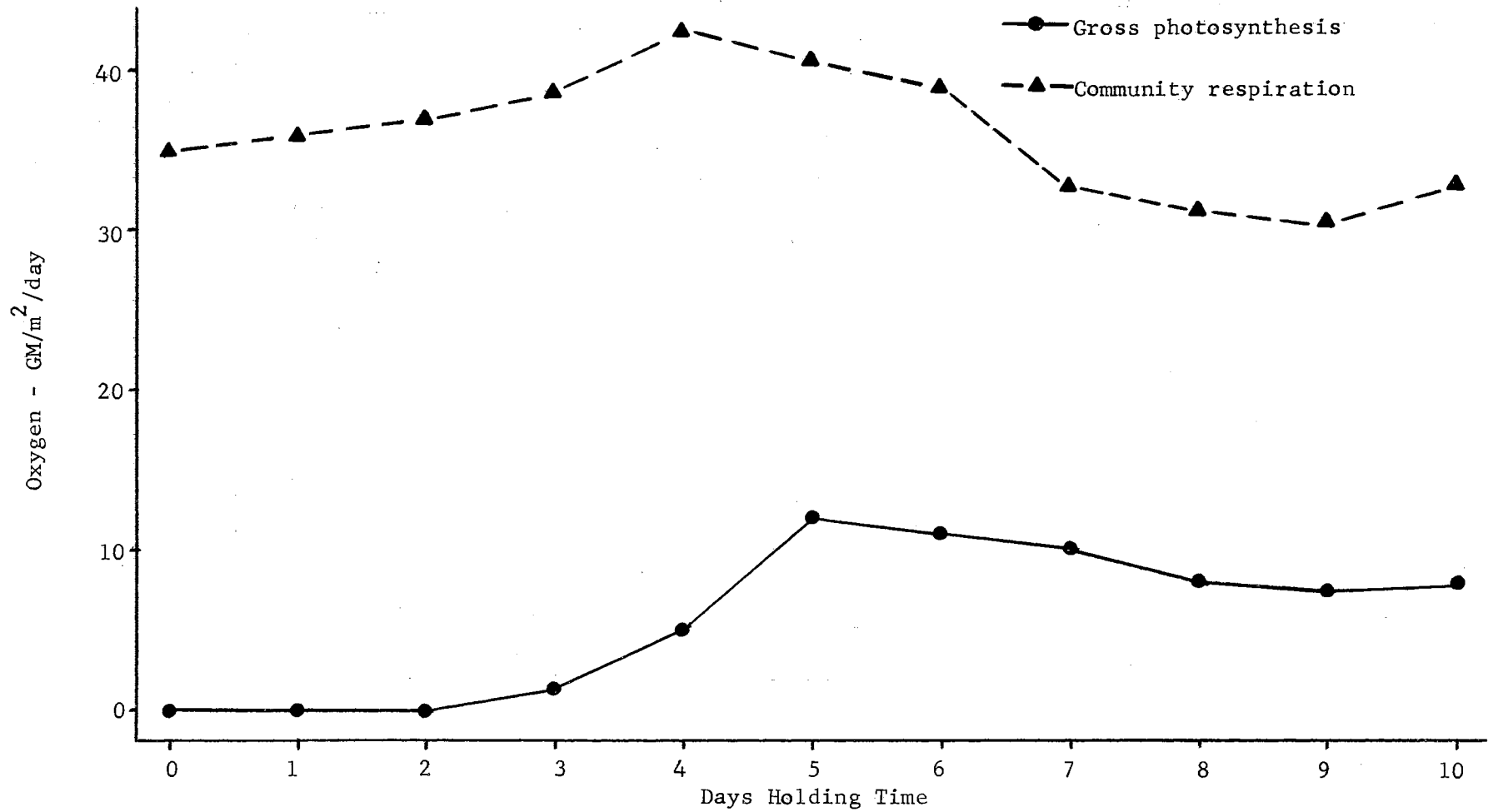


Figure 8: Average fall gross photosynthesis and community respiration at Refinery A.

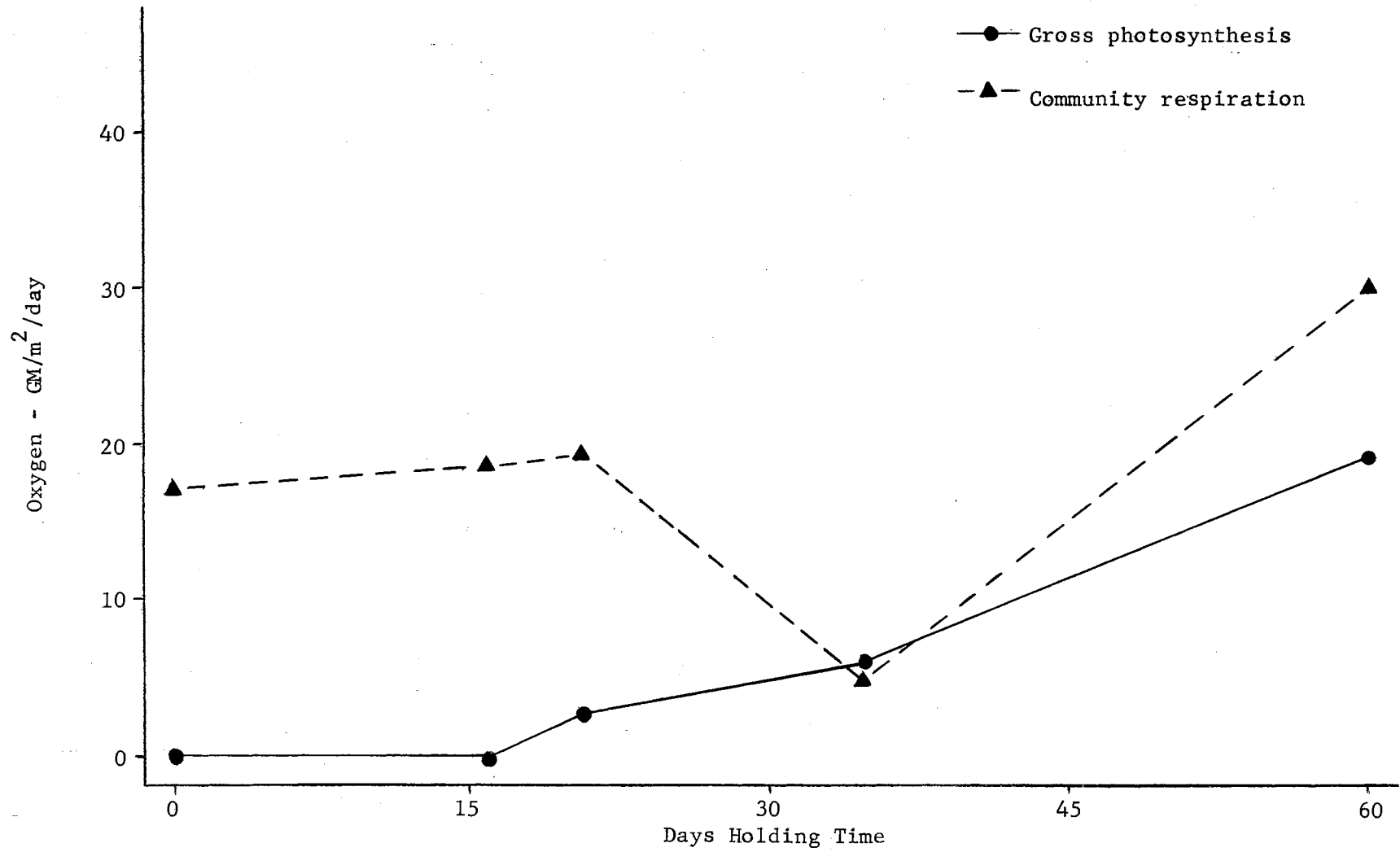


Figure 9: Average fall gross photosynthesis and community respiration at Refinery B.



reached, any later increase must be attributed to algal respiration or decomposition. This low point may correspond to the low point in the "oxygen sag curve" described by Streeter (1935).

Respiration "sag" occurred at different points in the holding pond systems during different seasons. During summer, the minimum was observed after seven days holding time at Refinery A (Figure 6) and after 16 days holding time at Refinery B (Figure 7). During fall, the minimum was observed after nine days holding time at Refinery A (Figure 8) and after 37 days holding time at Refinery B (Figure 9).

In spring, community respiration steadily decreased throughout the entire system at both refineries (Figures 4 and 5). Since there was a relative absence of algae and other organisms during winter, few dead algal cells were added to the community for about three months. During that time, remains of populations from the previous growing season decomposed. Community respiration was least affected during spring by algal populations because the remains of algal cells from the previous growing season had been decomposed during winter and the springtime algal population was composed of relatively new cells. During other seasons, dying algae settle to the bottom and must be decomposed. Also, older algal populations require a considerable amount of oxygen for respiration. Thus, after minimal respiration is attained, it may increase with continued holding because of algal decomposition and increased respiration.

During winter, respiration was almost the same in all ponds in the systems and no distinct minimum occurred. Wintertime community metabolism data are affected by the method of calculation. Since oxygen content of the water during winter was usually zero, diffusion constants

were used to calculate community metabolism. Therefore, community respiration and photosynthesis data are only indications of actual occurrences. However, since the only oxygen available for respiration was due to diffusion, diffusion constants should be close to the actual respiration.

A secondary peak in community respiration always followed the peak algal populations (compare Figures presented previously with chlorophyll data presented in Chapter IV). Apparently, decomposition of dead algal cells caused an increase in community respiration. The relation of toxicity and availability of nutrients affected the point at which peak algal populations occurred. Shifting of this point in the system from season to season is discussed in Chapter IV.

At Refinery A, during spring and summer, photosynthetic productivity exceeded community respiration in some part of the pond system (Figures 4 and 6). During other times of the year at Refinery A and during all seasons at Refinery B, community respiration exceeded photosynthetic productivity. Longer holding time at Refinery B and continuous excess of respiration over photosynthesis probably accounts for the greater reduction of effluent components at Refinery B than at Refinery A as discussed in Chapter V.

#### B. Comparison With Other Communities.

Odum (1956) discussed the community metabolism pattern of a sewage polluted river in Indiana (Figure 10B). In the septic zone (initial 20 miles), community respiration far exceeded productivity. In the early recovery zone (30 to 60 miles downstream), productivity increased rapidly until it exceeded respiration. Increase in respiration which

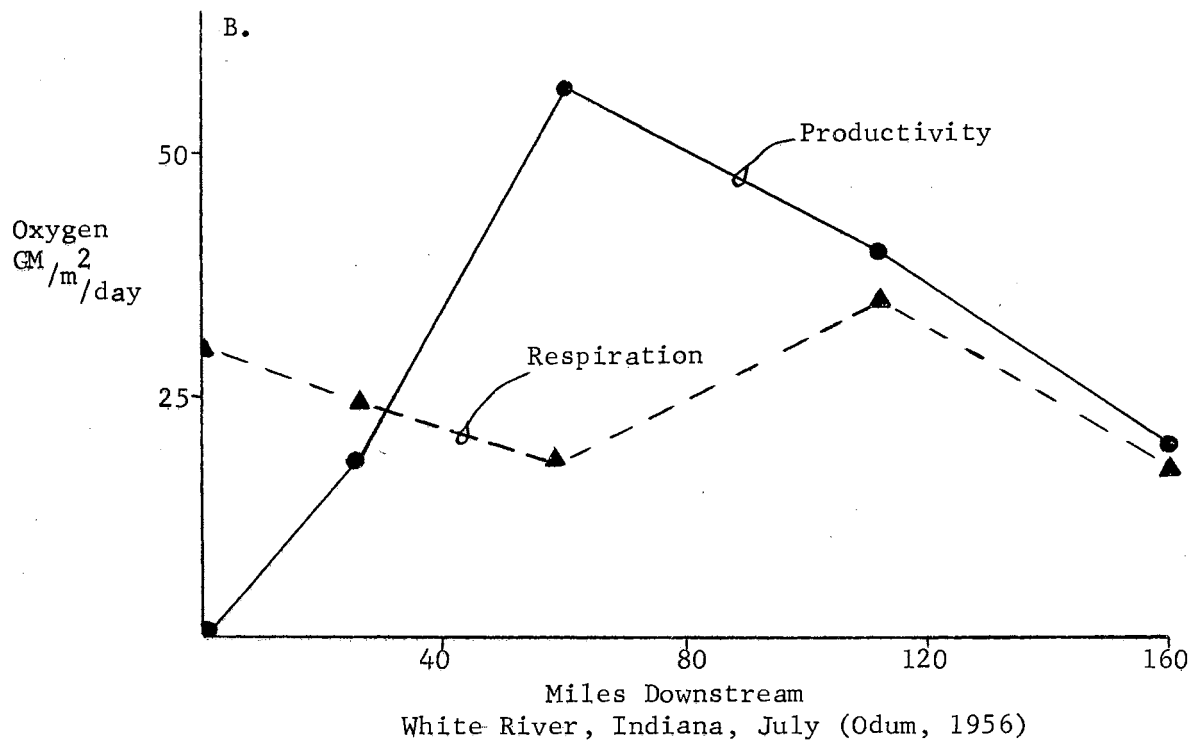
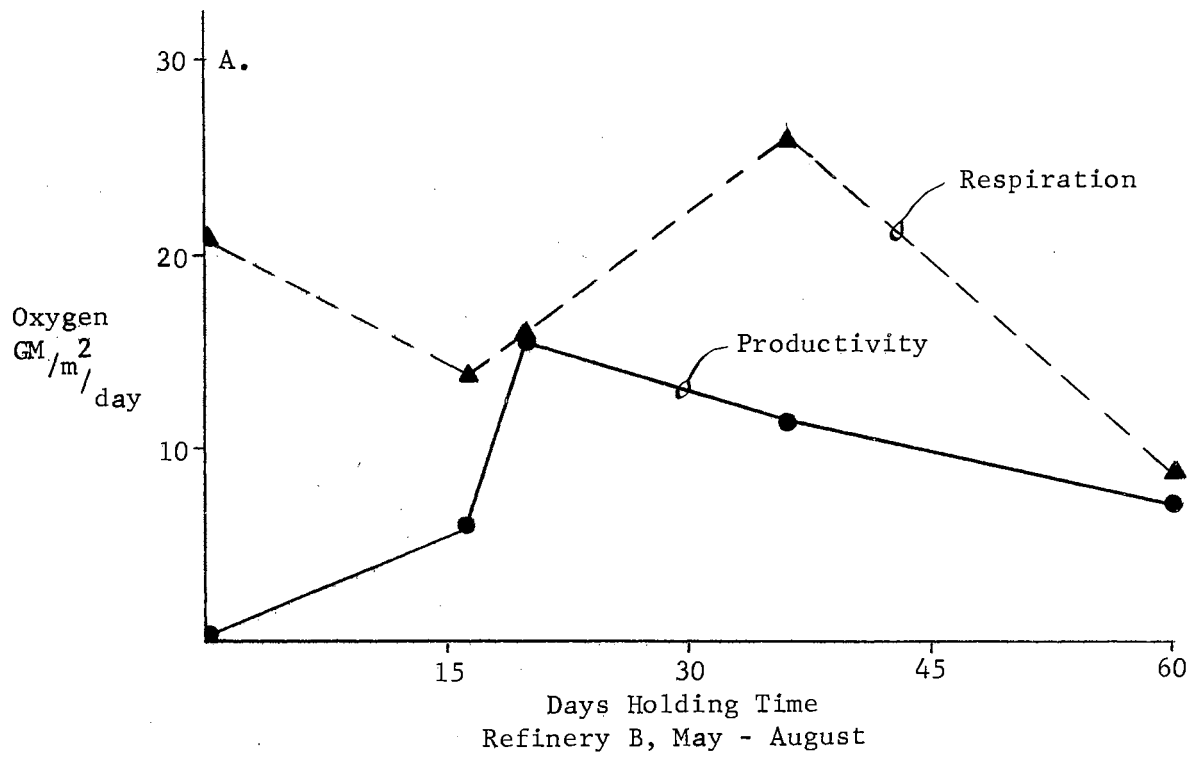


Figure 10: Comparison of community metabolism of an oil refinery effluent holding system with a sewage receiving stream.

followed resulted from decomposition of the organic matter added to the system by death of the large algal population. Algal population and productivity decreased downstream because nutrient release by decomposition of sewage was diminished. After the algal population had been decomposed, both respiration and productivity decreased simultaneously. The community became stabilized and a steady state was achieved at about mile 112.

The pattern of community metabolism at Refinery B resembled that in White River during summer (Figure 10A). Community respiration patterns were of the same shape and similar magnitude, with the first minimum occurring at 16 days holding time and a peak at 37 days holding time at Refinery B. Productivity at Refinery B exhibited the same pattern as that observed in the example, but of lower magnitude, with the peak occurring at 20 days holding time.

The pond system at Refinery A had only ten days holding time and did not exhibit complete zonation. The pattern (Figure 6) for the summer resembled only the first 112 miles of White River and the first 37 days holding time at Refinery B.

Lower productivity in oil refinery effluent may be explained by its different nature. Limiting factors in oil refinery effluent apparently held photosynthesis below the level attained in sewage.

If sufficient time were provided, it is possible that the pattern observed in Figure 10 might occur in any polluted situation. Odum (1956) reported similar relationships for the polluted River Trent and River Lark in England and Birs in Switzerland. Re-examination of data reported by Copeland and Dorris (1962) revealed similar patterns in other oil refinery effluent holding ponds.

During other seasons of the year, the pattern of community metabolism observed in the oil refinery effluent holding ponds exhibited variations of the pattern shown in Figure 10. Longer holding time is required during suboptimal seasons of the year in order to achieve complete stabilization. During fall only a short portion of the complete pattern was observed, and during winter only the septic zone was present. At Refinery B during fall (Figure 9), community metabolism resembled the first 112 miles downstream of the example presented in Figure 10B; whereas, the whole pattern was present during summer. At Refinery A on 12 October 1961 (Figure 11), community metabolism resembled only the first 60 to 80 miles downstream in the example. However, fall respiration data were affected somewhat by death and decomposition of large summer algal populations (see Appendix Figures 3 through 18).

Refinery A did not have sufficient holding time to complete the entire stabilization zone, even under the more optimal conditions of summer. Holding time at Refinery B was sufficient, at least during summer. Longer holding time is required during fall and winter, when environmental conditions are somewhat less than optimal.

In recent years, community metabolism has been studied in other types of communities throughout the world. Data obtained by the diel curve method may be used for comparison with the present study and are presented in part in Table I.

In unpolluted communities, community respiration was usually lower than the maximum in oil refinery ponds. Exceptions occurred when organic debris was washed into the community from the watershed (Copeland and Whitworth, 1962; and Minter and Copeland, 1962). In general, photosynthetic productivity was lower in unpolluted communities than in

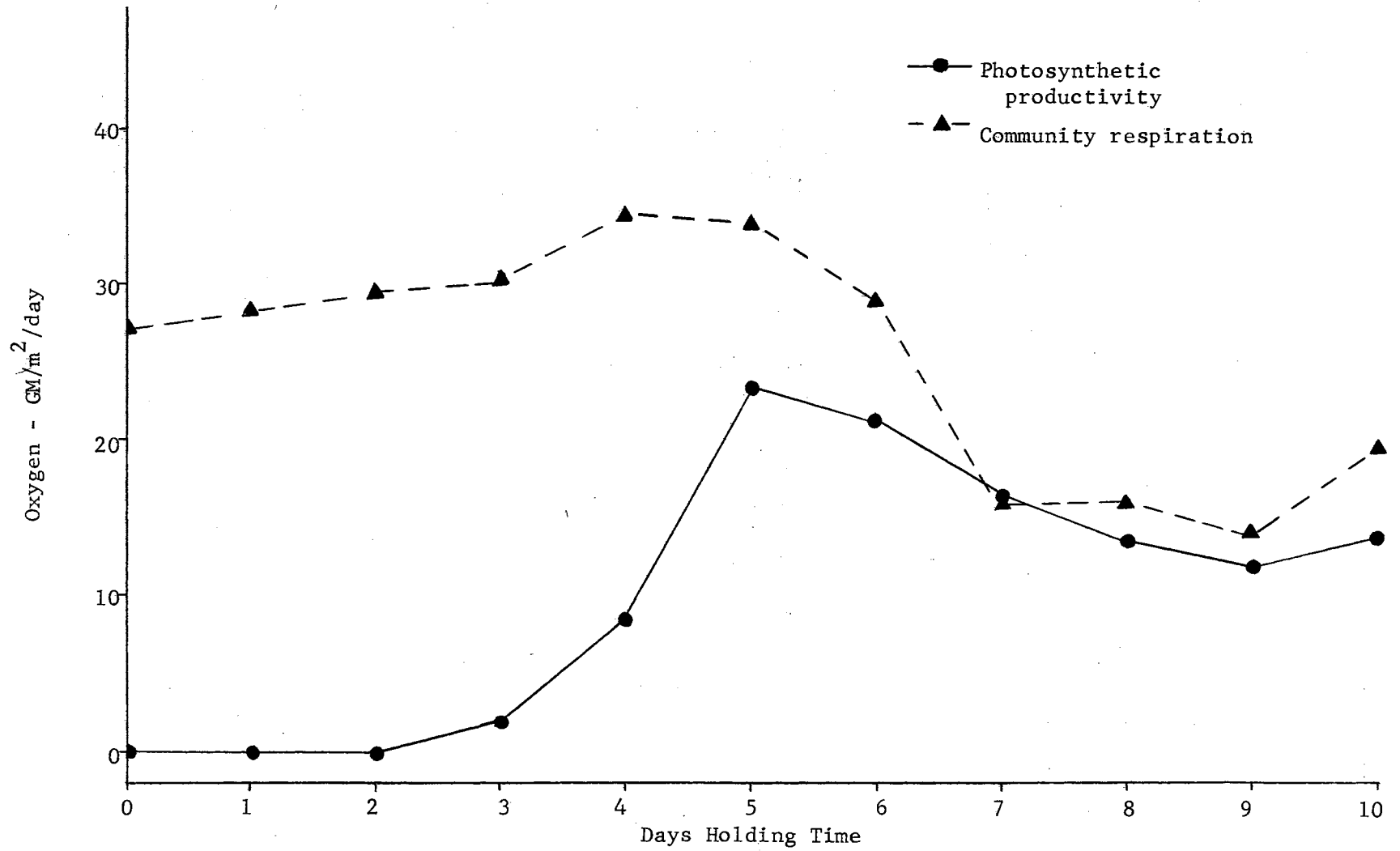


Figure 11: Community metabolism at Refinery A, 12 October 1961.

polluted ones. Only where nutrient material was high, did productivity approach that of the polluted community (Odum and Odum, 1955; Odum, 1957a and 1957b; and Copeland and Whitworth, 1962).

Sewage polluted communities supported higher productivity than those polluted with oil refinery effluent, possibly because of a larger yield of nutrients from sewage decomposition. Community respiration was of the same order of magnitude in both types of polluted communities.

### C. Annual Patterns of Metabolism.

The annual course of community metabolism for individual ponds is presented for Refinery A in Appendix Figures 3 through 13 and for Refinery B in Appendix Figures 14 through 18. Data were not available for Refinery B for November and December.

Refinery A. At the beginning of the pond system at Refinery A, the levels of community respiration fluctuated widely and no distinct pattern could be established (Appendix Figures 3 and 4). This is explained by the fact that the first pond served as a buffer zone against the incoming effluent for the pond system. Incoming effluent did not exert a constant oxygen demand because of variations in day-to-day activities of the refinery. Community respiration was a reflection of the effluent oxygen demand. Only during the warm months did photosynthesis occur, and then at a low level. Toxicity of the effluent was probably the limiting factor.

A distinct maximum in community respiration was observed during November at all other stations (Appendix Figures 5 through 13). This maximum occurred because the huge algal population present during the

TABLE I  
COMPARISON OF COMMUNITY METABOLISM

Source	gm/m <sup>2</sup> /day	
	P	R
<u>Unpolluted.</u>		
Ehiwetok Atoll, summer (Odum and Odum, 1955).....	24.0	24.0
Silver Springs, Florida (Odum, 1957a)		
Winter.....	8.0	2.8
Spring.....	35.0	5.0
Eleven Florida Springs, summer (Odum, 1957b).....	0.68 - 63.8	-----
Marine Turtle Grass, summer (Odum, 1957b).....	34.0	-----
Stewart Farm Pond, N.C., spring (Odum and Hoskin, 1958).....	2.2 - 4.5	2.1 - 5.2
Theta Pond, Oklahoma, summer (Copeland, et al., 1961).....	1.1 - 7.3	4.6 - 9.5
Oklahoma Farm Ponds (Copeland and Whitworth, 1962).....	4.4 - 27.4	4.9 - 26.4
Lake Wooster, Kansas, winter (Minter and Copeland, 1962).....	0.0 - 5.4	8.9 - 49.6
<u>Polluted.</u>		
River Lark, England (Butcher, et al., 1930, calculated by Odum, 1956)		
Fall.....	0.53	53.0
Spring.....	39.0	35.0
White River, Indiana, summer (Denham, 1938, calculated by Odum, 1956)....	0.24 - 57.0	18.0 - 29.0
Birs River, Switzerland, spring (Schmassman, 1951, calculated by Odum, 1956).....	50.0	18.0
Sewage Ponds, S.D., summer (Bartsch and Allum, 1957).....	19.0 - 36.0	22.0 - 36.0
Oil Refinery Effluent Holding Ponds, summer (Copeland and Dorris, 1962).....	6.0 - 23.4	8.5 - 30.2
Present Study (Appendix Tables I and II)		
Winter.....	0.0 - 3.9	15.6 - 36.0
Spring.....	0.0 - 29.2	2.1 - 38.6
Summer.....	0.0 - 25.0	2.2 - 30.9
Fall.....	0.0 - 23.3	4.9 - 50.5



growing season had died and was decomposing. Decomposition required a large amount of oxygen and caused community respiration to be higher than during other times of the year.

After the fall maximum, community respiration decreased throughout winter and spring, particularly at about four days holding time, after which time the system was more stable. During early summer (June) community respiration began to increase, probably because algae began to die and settle to the bottom.

Starting at about eight days holding time and continuing through the remainder of the pond system, extremely high community respiration was observed on August 1 (Appendix Figures 11 through 13). A "slug" of highly toxic material with high oxygen demand had been released into the pond system from the refinery. The "slug" had advanced through the system and was in the last pond at the time of sampling. Oxygen demand increased and caused community respiration to be higher than usual. Algae were killed, resulting in low photosynthetic productivity. Effect of the "slug" was traced back to four days holding time (Appendix Figure 7). The pond system rapidly recovered and algal growth and photosynthesis was back to normal at six days holding time (Compare Appendix Figures 9 and 10).

Photosynthetic productivity never exceeded community respiration in the first three days holding time (Appendix Figures 3 through 6). At five through eight days holding time, productivity exceeded community respiration from April through September (Appendix Figures 8 through 11), except on August 1 when the "slug" effect was observed. During spring and early summer, productivity exceeded community respiration at nine and ten days holding time (Appendix Figures 12 and 13).

Odum (1956) in an analysis of data presented by Butcher, et al. (1930) for the Itchen River, England, found a respiration peak during fall. Photosynthetic productivity was highest in summer and lowest in winter. Minter and Copeland (1962) found high community respiration in a pond on the college campus at Emporia, Kansas, during fall, just after a large leaf fall from surrounding trees.

Refinery B. Much the same pattern was observed at Refinery B as at Refinery A. At the beginning of the pond system, no photosynthesis was observed for the entire year and community respiration fluctuated widely (Appendix Figure 14). Again, the first pond was more or less a buffer zone.

Although data were not available for November and December, increase in community respiration during October indicated that a peak would occur in the fall as was observed at Refinery A (Appendix Figures 15 through 18). Community respiration decreased throughout winter to a low point in spring or early summer.

Photosynthetic productivity followed about the same pattern as that observed at Refinery A, except that it seldom exceeded community respiration (Appendix Figures 15 through 18). Photosynthesis occurred during the entire year at 60 days holding time.

## 2. Diffusion.

Oxygen diffuses into the water from the atmosphere when water is not saturated with oxygen. On the other hand, oxygen diffuses out of water at times of supersaturation. The amount of diffusion depends on saturation, but the speed depends on the rate at which the surface layer

is dispersed downward due to turbulent mixing (Odum, 1956).

Oxygen is most efficiently provided for bacterial decomposition processes through photosynthesis of planktonic algae, because photosynthesis provides oxygen under 1.0 atmosphere partial pressure while diffusion can only yield oxygen under 0.2 atmosphere partial pressure. At times of little or no photosynthesis, oxygen is supplied by slower, less effective, but nevertheless important, diffusion from the atmosphere. Rates of diffusion in the present study varied from 0.3 gm O<sub>2</sub>/m<sup>2</sup>/hour on calm days to as much as 3.0 gm O<sub>2</sub>/m<sup>2</sup>/hour on windy days (Appendix Tables I and II).

During winter, when no photosynthesis occurred, diffusion provided oxygen for community respiration. On calm days, when diffusion was lowest, free oxygen could not be detected in the first 9 days holding time at Refinery A. Respiration was more rapid than diffusion. Conversely, on a particularly windy day (March 3), oxygen was detected in all ponds; diffusion was more rapid than respiration.

Odum (1956) reported diffusion coefficients for various types of waters. He reported rates of 0.03 gm O<sub>2</sub>/m<sup>2</sup>/hour for absolutely still water to 34 gm O<sub>2</sub>/m<sup>2</sup>/hour for water drops. Diffusion rates of 0.3 to 3.0 gm O<sub>2</sub>/m<sup>2</sup>/hour found in the present study are consistent with 0.1 to 3.0 gm O<sub>2</sub>/m<sup>2</sup>/hour reported by Odum and Hoskin (1958) for still water and water with gentle circulation. Odum (1960) found that diffusion was a major contributor of oxygen in heavily polluted waters of Corpus Christi, Texas, boat harbor.

### 3. Light.

Light provides energy to drive photosynthetic processes. Carbon

dioxide is transformed into carbon-containing organic compounds of plants when light is absorbed by the photosensitive green pigment, chlorophyll. Over a considerable range, rate of photosynthesis is almost proportional to light intensity. However, at sufficient intensity, light saturation occurs, and rate of photosynthesis may slow or even decrease (Bonner and Galston, 1952). Some plants are shade adapted and become light saturated at relatively low intensity, while others are sun adapted and require relatively high intensity to become light saturated.

Not all sunlight that falls on the surface of effluent holding ponds enters the water, for some is reflected. Light that enters is absorbed rapidly and does not penetrate to great depths because of absorption by the dense population of algae and other particulate matter. Only a small portion of the available light can be utilized in photosynthesis. During winter, when algae were sparse, light penetrated to a depth of 1.8 m in the later ponds at Refinery A (Appendix Table I). However, particulate matter contained in the refinery effluent prevented light from penetrating below about 0.9 m during winter in the first ponds of the series. During summer, when algae were most dense, all light was absorbed in about one meter in the later ponds and about 0.67 m in the first ponds. The same relationship existed for Refinery B (Appendix Table II).

Solar intensity at the Oklahoma City weather station ranged from 297 langley's per day in December to 731 langley's per day in July (Figure 12). Highest photosynthetic rate occurred during July and August in the first three days holding time at Refinery A (Appendix Figures 3 through 6) and the first 20 days holding time at Refinery B (Appendix Figures 15 and 16). Photosynthesis at all other stations

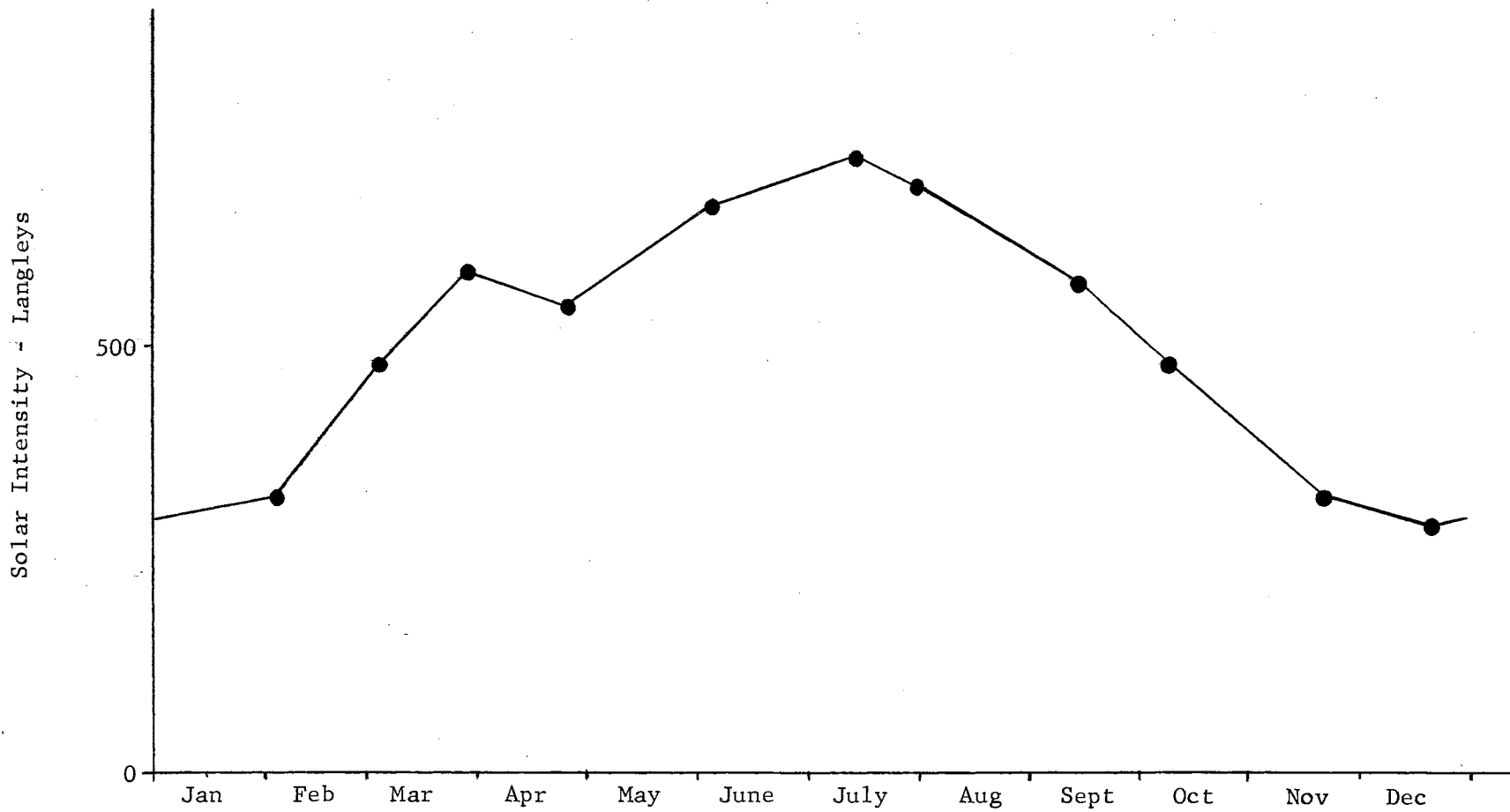


Figure 12: Solar intensity in langleys at Oklahoma City, Oklahoma on sampling dates (U. S. Weather Bureau, 1961 and 1962).

reached a maximum in spring or fall, or both (Appendix Figures 7 through 13, 17 and 18). It seems probable that light was more optimal in the first ponds, where particulate matter was greatest, when solar intensity was highest. On the other hand, in the later ponds where particulate matter was less, light was more optimal during spring and fall when algae were less dense. Algae may need a portion of the incoming solar energy to combat toxicity. In the first ponds, where toxicity is greatest, more light energy is required for photosynthesis than in the later ponds, where toxicity is least. Thus, maximum photosynthesis would occur during summer in the first ponds and during spring and fall in the later ponds.

Light saturation was found to occur on bright days. While photosynthesis was being measured at Refinery A, light intensity in foot candles was recorded at hourly intervals. Results of the simultaneous measurements are presented in Figure 13. During the morning hours, rate of oxygen production increased in proportion to light intensity. After an intensity of about 10,000 foot candles was reached, rate of oxygen production decreased, indicating that light saturation had occurred. It is probable that light saturation was reached at an intensity far below 10,000 foot candles since a large percentage of measureable light does not penetrate these waters.

Cloudiness causes depression in the daytime rate-of-change curve. An example of cloud effect is presented in Figure 14 for Refinery A at nine days holding time on 18 July 1961. Clouds obscured the sun between 1200 and 1400 o'clock on that date. Rate of oxygen production decreased during the cloudy period and increased after the sun came out again, causing a midday depression in the rate-of-change curve.

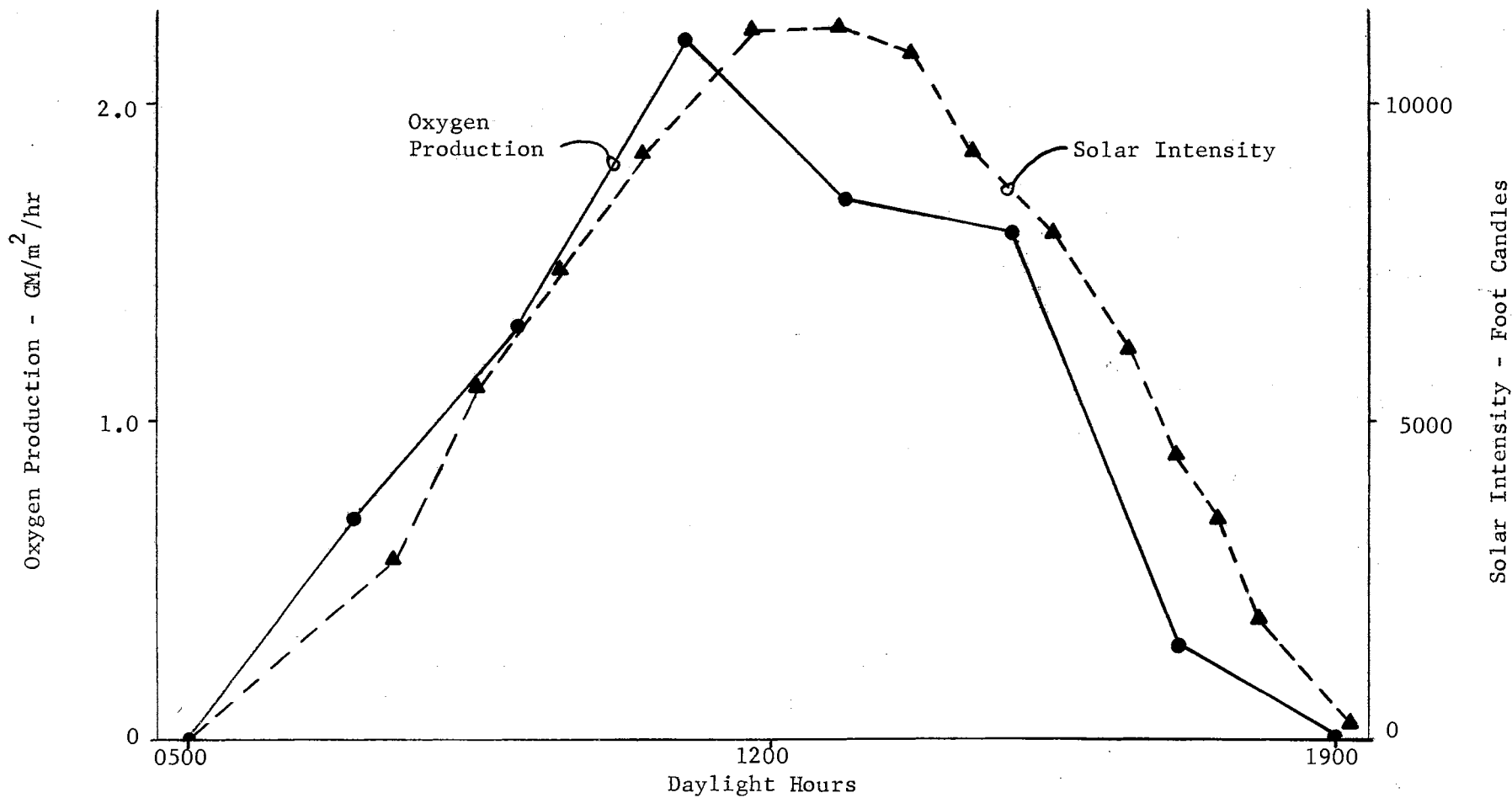


Figure 13: Effect of solar radiation and light saturation on oxygen production. Ten days holding time, Refinery A, 19 July 1962.

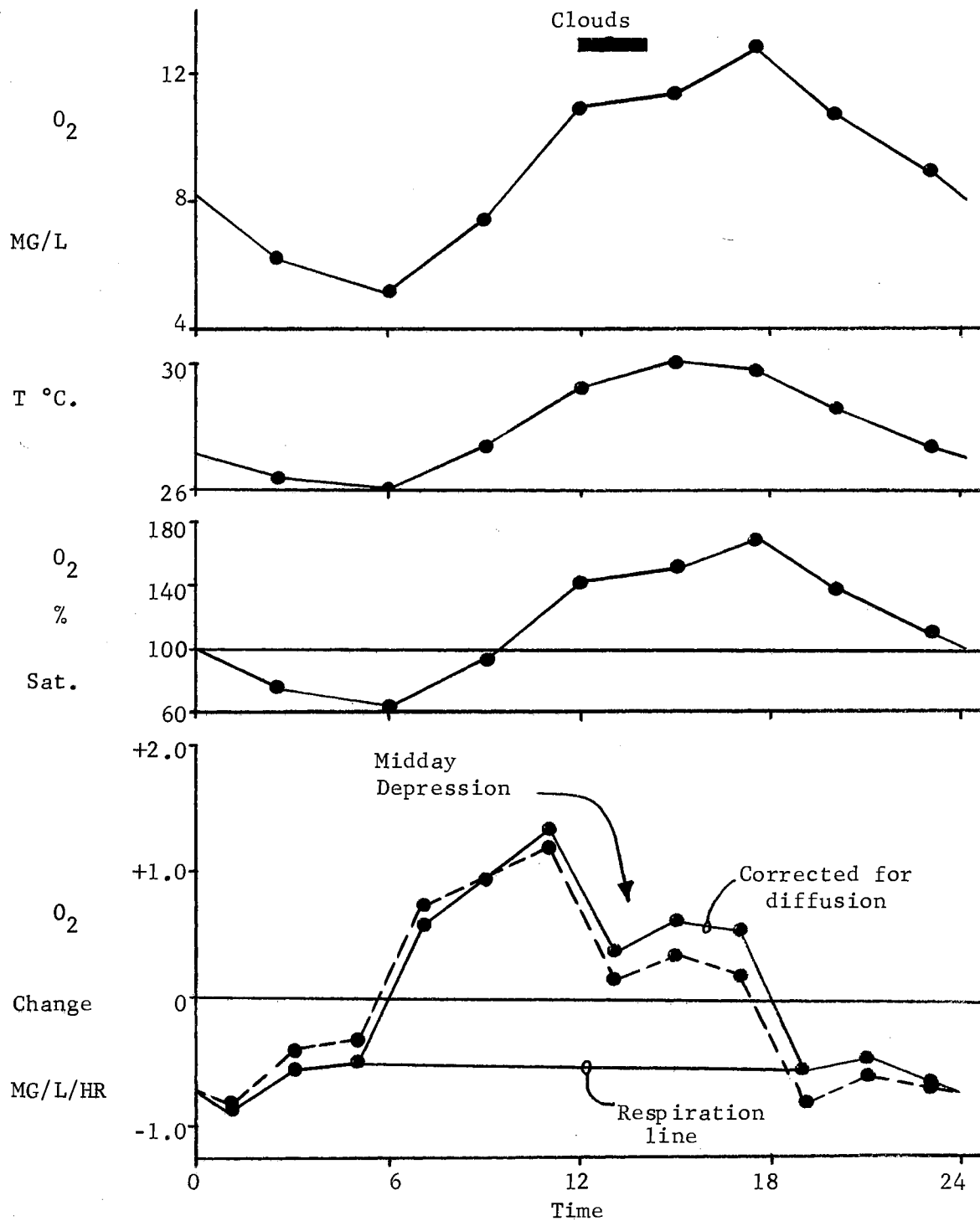


Figure 14: Example of a diurnal oxygen curve with a midday depression due to cloudiness. Nine days holding time, Refinery A, 18 July 1961.



Even though rate of oxygen production decreased, oxygen concentration increased, indicating that enough light was available for photosynthesis to exceed community respiration during the cloudy period.

Efficiency of algae at Refinery A in converting solar radiation into chemical energy is summarized in Table II. Considering glucose as the only product of photosynthesis, about 118,000 gram-calories of solar radiation is required to produce one mole of oxygen. However, according to Kok (1952) and Kraus (1956) about 112,000 gram-calories are required or about 3500 gram-calories per gram of oxygen, since the photosynthetic yield is not entirely glucose. Efficiency of the ecosystem was determined as the yield of potential chemical energy from the input of solar energy into the community (Clark, 1946; Stepanek, 1960). Total radiation data (Figure 12) from the U.S. Weather Bureau (1961 and 1962) at Oklahoma City, Oklahoma was used in the calculations. Efficiency was calculated by inserting gross photosynthesis and solar radiation data into the formula,

$$F = \frac{(3500 WO_2)}{10,000 S} 100 \quad (\text{modified from Oswald, et al., 1957}),$$

where F is percent efficiency,

$WO_2$  is weight of oxygen in gm/m<sup>2</sup>/day,

S is visible solar radiation in calories/cm<sup>2</sup>/day, and

10,000 is a factor converting cm<sup>2</sup> to m<sup>2</sup>.

Forsythe (1954) considered that 50.4 to 52.3% of solar radiation falls within the range of 4000 to 7700 A., while List (1951) maintains that 42.5 to 45.25% falls within the range of photosynthetically effective light. For the present study, a value of 50% used by Edmondson (1955) and Ryther (1956) was adopted.

TABLE II  
 PERCENT EFFICIENCY OF THE ALGAL POPULATION  
 IN CONVERTING SOLAR ENERGY INTO CHEMICAL  
 ENERGY AT REFINERY A

Date	Days Holding Time										
	0	1	2	3	4	5	6	7	8	9	10
<u>Winter</u>											
12/21/61	0	0	0	0	0	0	0	0	0	0	0
2/3/62	0	0	0	0	0	0	0	0	0	0	0
3/3/62	0	0	0	0	0	0	0	0	0	0	0
Average	0	0	0	0	0	0	0	0	0	0	0
<u>Spring</u>											
3/26/62	0	0	0	0	0	0	0.9	1.5	1.6	1.4	1.3
4/26/62	0	0	0.2	1.6	2.5	3.2	3.1	3.9	3.0	3.2	2.0
Average	0	0	0.1	0.8	1.2	1.6	2.0	2.7	2.3	2.3	1.7
<u>Summer</u>											
7/18/61	0.3	1.2	1.4	0.8	1.0	1.0	1.5	1.4	1.7	2.5	1.8
9/16/61	0	0.3	0.6	0.9	0.9	1.3	1.7	1.6	1.5	1.0	0.9
6/5/62	0.1	0.7	0.2	0.8	1.0	1.8	1.5	1.7	2.1	2.1	2.0
7/19/62	1.0	1.6	1.9	1.8	2.3	1.8	1.1	1.3	1.4	1.7	1.7
Average	0.4	1.0	1.0	1.1	1.3	1.5	1.5	1.5	1.7	1.8	1.6
<u>Fall</u>											
10/12/61	0	0	0	0.4	1.3	3.6	3.3	2.6	2.2	1.8	2.2
11/24/61	0	0	0	0	0.4	0.2	0.2	0.8	0.3	0.7	0.4
Average	0	0	0	0.2	0.9	1.9	1.8	1.7	1.3	1.3	1.3

Gross photosynthetic efficiencies ranged from 0 to 3.9%. The highest efficiency occurred in April at seven days holding time and the lowest in winter. It appears that algae are most efficient in conversion of solar energy during April and October, and least efficient during winter. Similar efficiencies were reported by Copeland and Dorris (1962) in oil refinery effluent holding ponds (1.0 to 3.6% for summer), by Odum and Hoskin (1957) in a flowing stream microcosm (3%), and by Beyers (1962a) in microecosystems (2 to 4%). Odum and Odum (1955) reported efficiency of 6% for Eniwetok Atoll. Odum (1957a)

reported 5.3% efficiency for Silver Springs, Florida. Odum (1957b) reported 0.5 to 10% for eleven Florida springs and a turtle grass community. Oswald, et al. (1957) reported efficiencies of 1 to 10% for sewage oxidation ponds.

Higher efficiencies occur in ecosystems with a more complete balance of flora and fauna (Silver Springs, Eniwetok Atoll, etc.). It may be that systems with a limited diversity of organisms have lower efficiency. Oil refinery effluent limits the variety of organisms that can survive. The microcosms of Beyers (1962a) were young geologically and species-limited. Thus, lower efficiencies occur where the ecosystem is not in balance or balanced out of phase. Odum (1956) contends that streams, with their varied biota and constant import-export mechanism are the most efficient ecosystems in existence.

#### 4. Temperature.

The direct effect of temperature upon the community metabolism is probably not nearly as important as the indirect effect. Beyers (1962b) has shown that lowered temperature does not greatly affect community respiration of a complex community. As was previously pointed out (Figures 2 and 3), cold weather did not appreciably lower respiration in the effluent holding ponds. Photosynthesis did not occur in the first few days holding time during spring, and fall and water temperature was higher than the last few days holding time, where photosynthesis was observed. Bartsch and Allum (1957) reported photosynthesis in water from 32° to 91° F in South Dakota sewage ponds. In essence, no correlation can be made between temperature and community metabolism.

Algae, during cold weather, generally settle to the bottom where some remain alive but dormant and others die. In these conditions, algae do not produce oxygen, but use it in respiration and decay.

Daily mean temperature at Refinery A for each pond is shown in Table III. Mean temperature ranged from 36° F in winter to 90° F in summer. Highest temperature occurred in the first holding pond and lowest occurred near the end of the holding pond system. Water temperature at Refinery B exhibited about the same pattern as at Refinery A.

#### 5. Productivity/Respiration Ratio.

Productivity/respiration (P/R) ratio is an index by which an aquatic community can be classified (Odum, 1956). When oxygen production equals or exceeds respiratory demands (P/R ratio of one or greater than one) the community is said to be autotrophic. When respiratory demands exceed oxygen production (P/R ratio of less than one) the community is said to be heterotrophic.

Successional changes in P/R ratios occur in oil refinery effluent holding pond series. There is a continual inflow of organic material, suspended or dissolved in refinery effluent, into the pond system. Decomposition of this mass of organic matter requires a considerable amount of oxygen and results in a low P/R ratio at the beginning of the pond system. As effluent progresses through the system, organic material is oxidized and the P/R ratio increases. If holding time is sufficiently long, the P/R ratio will increase to above one, and the community succeeds from heterotrophic to autotrophic condition. During the more optimal growing season, P/R ratio decreases in the last few days holding time because of decomposition of dead algae and the

TABLE III

AVERAGE TEMPERATURE IN °F AT REFINERY A

Date	Days Holding Time										
	0	1	2	3	4	5	6	7	8	9	10
<u>Winter</u>											
12/21/61			45.0	44.0	42.9	41.4	39.9	38.3	37.3	36.7	37.0
2/3/62				58.0	57.0	56.0	54.0	53.0	51.7	49.3	49.5
3/3/62	52.7	48.6	45.7	43.9	42.6	41.5	40.6	40.1	39.2	38.9	38.5
<u>Spring</u>											
3/26/62					58.5	59.3	57.3	56.6	56.8	56.6	56.6
4/26/62			73.0	72.4	70.7	71.0	70.7	71.0	69.0	70.8	71.2
<u>Summer</u>											
7/18/61	87.0	84.6	82.8	82.4	82.4	82.8	82.8	82.8	82.5	82.4	82.3
8/1/61	90.0	87.2	85.0	85.0	85.2	85.4	85.4	85.4	85.0	85.0	85.0
6/5/62	82.0	81.0	78.9	78.1	78.1	79.0	78.4	78.0	77.6	77.4	76.4
7/19/62	88.9	87.8	86.9	86.0	85.6	86.2	85.9	85.7	84.9	84.7	84.5
<u>Fall</u>											
10/12/61	73.0	72.0	72.0	72.1	71.5	71.4	70.9	70.8	70.5	70.1	70.0
11/25/61	54.0	52.0	52.0	52.0	51.5	51.0	50.0	49.6	48.9	48.4	48.0

community moves toward stabilization.

Productivity/respiration ratio was greatest during spring because spring algal populations exert very little respiratory demand (Odum, et al., 1958) and have high efficiency of assimilation (see Table II). Lowest P/R ratios occurred in winter when photosynthesis was very low or did not occur at all (Appendix Tables I and II).

In general, mean P/R ratio was higher at Refinery A than at Refinery B during spring and summer, but lower during fall and winter, since Refinery B had a longer holding time which allowed more complete stabilization of the community. It has been pointed out by Beyers (1962a), Odum (1957a), Odum and Odum (1959), Odum and Johnson (1955), and others, that a community tends to stabilize and P/R ratios of unity are achieved if sufficient time is allowed.

A P/R ratio of unity probably would be reached and maintained if the oil refinery effluent holding pond communities were allowed enough time for more complete stabilization. Data presented in Appendix Tables I and II show that the communities were moving toward that condition. During summer, when P/R ratio of greater than one was achieved before the end of the system, P/R decreased toward one in the remainder of the system. During less optimal seasons, such as fall, P/R increased toward one as holding time increased.

## CHAPTER IV

### CHLOROPHYLL AND ORGANIC MATTER

#### 1. Chlorophyll in Oil Refinery Effluents.

Chlorophyll data were obtained at Refinery A (Tables IV through VII). Average chlorophyll concentration was highest in summer with a range from 0.243 mg/l at 10 days holding time to 0.545 mg/l at six days holding time (Table IV). Water temperature (Table III) and photosynthetic production of oxygen (Appendix Table I) were high. In July, 1961, average daily water temperature in the ponds of the series was 82.3 to 87.0° F and maximum chlorophyll concentration was 0.675 mg/l at six days holding time. In August, maximum chlorophyll concentration

TABLE IV  
CHLOROPHYLL a IN MG/L AT REFINERY A DURING SUMMER

Date	Days Holding Time						
	1	3	4	6	7	9	10
7/18/61	0.266	0.146	0.172	0.675	0.588	0.243	0.260
8/1/61	0.831	0.356	0.505	0.174	0.128	0.121	0.035
9/16/61	0.208	0.382	0.410	0.703	0.606	0.200	0.190
6/5/62	0.090	0.285	0.245	0.240	0.401	0.188	0.266
7/19/62	0.457	0.675	0.757	0.937	0.915	0.495	0.465
Average	0.370	0.369	0.417	0.545	0.527	0.249	0.243

of 0.831 mg/l was observed after one day holding time and 0.505 mg/l at four days holding time when water temperature was 2 to 3° F warmer. In September, maximum chlorophyll concentration of 0.703 mg/l occurred at six days holding time. In June, when water temperature ranged from 76.4 to 82.0° F highest chlorophyll concentration was 0.401 mg/l at seven days holding time. Maximum concentration was 0.937 gm/l at six days holding time in July, 1962, with water temperature at 84.5 to 88.9° F.

Average fall chlorophyll concentrations (Table V) ranged from 0.007 mg/l at one day holding time to 0.138 mg/l at ten days holding time. A general increase was observed throughout the pond system. Chlorophyll concentration ranged from zero at one day holding time to 0.253 mg/l at ten days holding time in October and water temperature

TABLE V  
CHLOROPHYLL a IN MG/L AT REFINERY A DURING FALL

Date	Days Holding Time						
	1	3	4	6	7	9	10
10/12/61	0.000	0.094	0.064	0.171	0.169	0.222	0.253
11/24/61	0.015	0.015	0.015	0.018	0.023	0.021	0.023
Average	0.007	0.054	0.040	0.094	0.096	0.121	0.138

was 70 to 73° F. Water temperature was much lower (48 to 54° F) in November and chlorophyll concentration was extremely low at 0.015 to 0.023 mg/l.

Lowest chlorophyll concentrations occurred during winter (Table VI), and averaged from 0.019 mg/l at one day holding time to 0.087 mg/l at



three days holding time. In December, chlorophyll concentration ranged from zero at one day holding time to 0.100 mg/l at three days holding time with water temperature at 37.0 to 45.0° F. Chlorophyll concentration ranged from 0.038 mg/l at one day holding time to 0.074 mg/l at three days holding time in February, with water temperature at 49.5 to 58.0° F. However, because winter chlorophyll concentration was low and of the same order of magnitude no distinct maximum could be established.

TABLE VI  
CHLOROPHYLL a IN MG/L AT REFINERY A DURING WINTER

Date	Days Holding Time						
	1	3	4	6	7	9	10
12/21/61	0.000	0.100	0.078	0.068	0.084	0.036	0.052
2/3/62	0.038	0.074	0.049	0.041	0.045	0.040	0.039
Average	0.019	0.087	0.063	0.054	0.064	0.038	0.045

During spring months, average chlorophyll concentration ranged from 0.022 mg/l at one day holding time to 0.232 mg/l at four days holding time (Table VII). Chlorophyll concentration in March ranged from 0.015 mg/l at one day holding time to 0.134 mg/l at ten days holding time and formed a pattern more nearly like that of fall. Water temperature ranged from 56.6 to 58.5° F. By April, chlorophyll concentration was approaching the pattern indicative of summer conditions, although generally lower. Chlorophyll ranged from 0.030 mg/l at one day holding time to 0.424 mg/l at four days holding time, with water temperature at 69.0 to 73.0° F.

TABLE VII  
 CHLOROPHYLL a IN MG/L AT REFINERY A DURING SPRING

Date	Days Holding Time						
	1	3	4	6	7	9	10
3/26/62	0.015	0.021	0.040	0.026	0.030	0.053	0.134
4/26/62	0.030	0.289	0.424	0.282	0.186	0.128	0.097
Average	0.022	0.155	0.232	0.154	0.108	0.091	0.116

There is a wide variation of chlorophyll concentration among phytoplankton communities throughout the world (Table VIII). Chlorophyll concentration in marine and unpolluted fresh waters is much lower than in oil refinery effluent holding ponds. Chlorophyll concentration in sewage ponds is of the same order of magnitude as in oil refinery effluent holding ponds.

Chlorophyll concentration appeared to be closely correlated with sunlight and water temperature. Maximum chlorophyll concentration occurred at four to seven days holding time during summer and spring when the water was warmer and sunlight more intense. According to Emerson, et al. (1940), Bartsch and Allum (1957), Odum, et al. (1958), Wright (1960) and others, concentration of chlorophyll is dependent upon the amount of nutrients available. Since the amount of nutrients in effluent water partially depends on bacterial degradation of organic material, it may be that larger amounts of nutrients are available earlier in the pond system at higher temperatures. This hypothesis is somewhat substantiated by fall data where maximum chlorophyll concentration occurred at ten days holding time and was lower than spring or summer. Ion uptake by the algal cell may depend upon available energy.

TABLE VIII  
CHLOROPHYLL a IN VARIOUS PHYTOPLANKTON COMMUNITIES

Source	Chlorophyll <u>a</u> mg/l
<u>Unpolluted Freshwater</u>	
Linsley Pond (Riley, 1940).....	0.008 - 0.038
Wisconsin Lakes (Manning and Juday, 1941).....	0.0009 - 0.268
Lake Suwa, Japan (Ichimura, 1954)	
Summer.....	0.200
Winter.....	0.006
Canyon Ferry Reservoir, Montana (Wright, 1960).....	0.0058 - 0.021
<u>Marine</u>	
Fertilized sea water (Edmondson and Edmondson, 1947).....	0.020
East Sound, Washington (Ryther and Yentsch, 1957).....	0.015
Friday Harbor, Washington (Ryther and Yentsch, 1957).....	0.001
Gulf of Alaska (Ryther and Yentsch, 1957).....	0.0025
Woods Hole Harbor (Ryther and Yentsch, 1957).....	0.0017 - 0.0034
Baffin Bay, Texas (Odum, et al., 1958).....	0.021 - 0.066
Laguna Madre, Texas (Odum, et al., 1958)	
Winter, 1957.....	0.002 - 0.043
Summer, 1957.....	0.031
Pacific Ocean near Clarion Island (Shimada, 1958).....	0.00008 - 0.00015
Stagnant marine pool, Texas (Odum, et al., 1958).....	0.356
<u>Polluted</u>	
Sewage ponds, Denmark (Stemann Nielsen, 1957).....	0.300
Sewage ponds, Kadoka, S.D. (Bartsch and Allum, 1957).....	0.080 - 2.820
Oil refinery effluent holding ponds (present study, 1961 - 1962)	
Winter.....	0.000 - 0.100
Summer.....	0.035 - 0.937
Spring.....	0.015 - 0.424
Fall.....	0.000 - 0.253

During spring, when sunlight intensity was 110 to 150 langley's higher, assimilation was higher than during fall when solar intensity was lower, even though water temperatures were virtually the same.

## 2. Relationship of Chlorophyll to Photosynthesis.

Chlorophyll is involved in initial events of photosynthesis. Therefore, oxygen production per unit of chlorophyll is related to gross photosynthesis rather than to net photosynthesis (oxygen remaining after simultaneous community respiration). Ryther and Yentsch (1958) found wide variations in photosynthesis/chlorophyll ratio when only net photosynthesis was considered. Oxygen data discussed in the present study concern gross photosynthesis. The ratio of oxygen production to chlorophyll is referred to as assimilation number (Odum, et al., 1958).

Gross photosynthesis in  $\text{gm/m}^3/\text{day}$  was plotted against chlorophyll a in  $\text{gm/m}^3$  (Figure 15). Data for July through October, 1961 and June through July, 1962 were plotted on the same line, while April and November data were on separate plots. As chlorophyll concentration increased, oxygen production per day did not increase in a proportional manner. Although few data were available for April, chlorophyll-gross photosynthesis relationship was higher than in summer (upper dashed line in Figure 15). Chlorophyll-gross photosynthesis relationship during November, again with few data, was also linear but much lower than that of summer (lower dashed line in Figure 15).

Gross photosynthesis from July through October, 1961 and June through July, 1962 were converted to  $\text{gm O}_2/\text{gm chlorophyll/m}^2/\text{hour}$  and plotted against chlorophyll in  $\text{gm/m}^2$  (Figure 16). Assimilation numbers ranged from 13.8 to 1.0  $\text{gm O}_2/\text{gm chlorophyll/m}^2/\text{hour}$  and

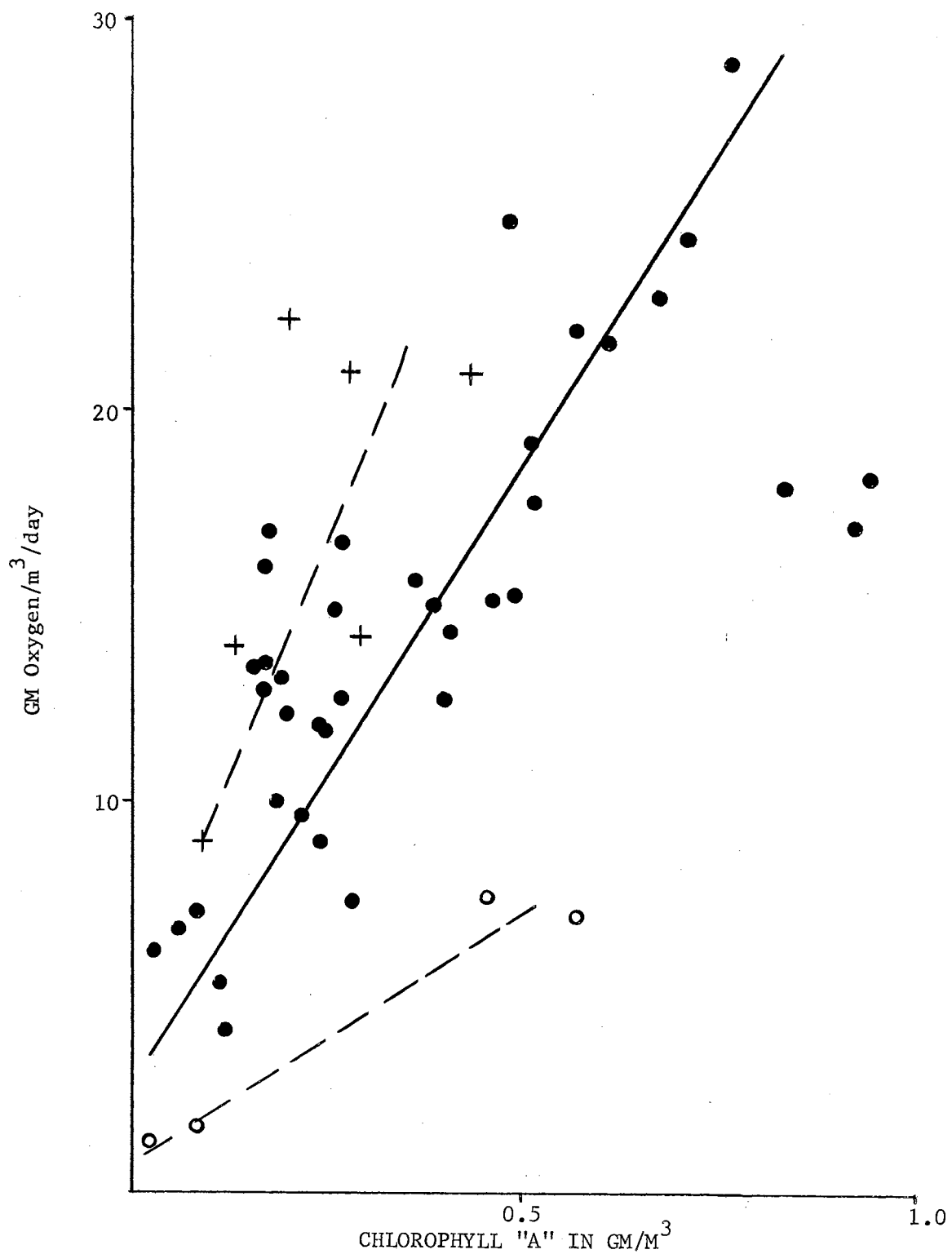


Figure 15: Daily gross photosynthesis compared with chlorophyll concentration. ● indicates data for July through October, 1961 and June through July 1962. + indicates data for April, 1962. ○ indicates data for November, 1961.

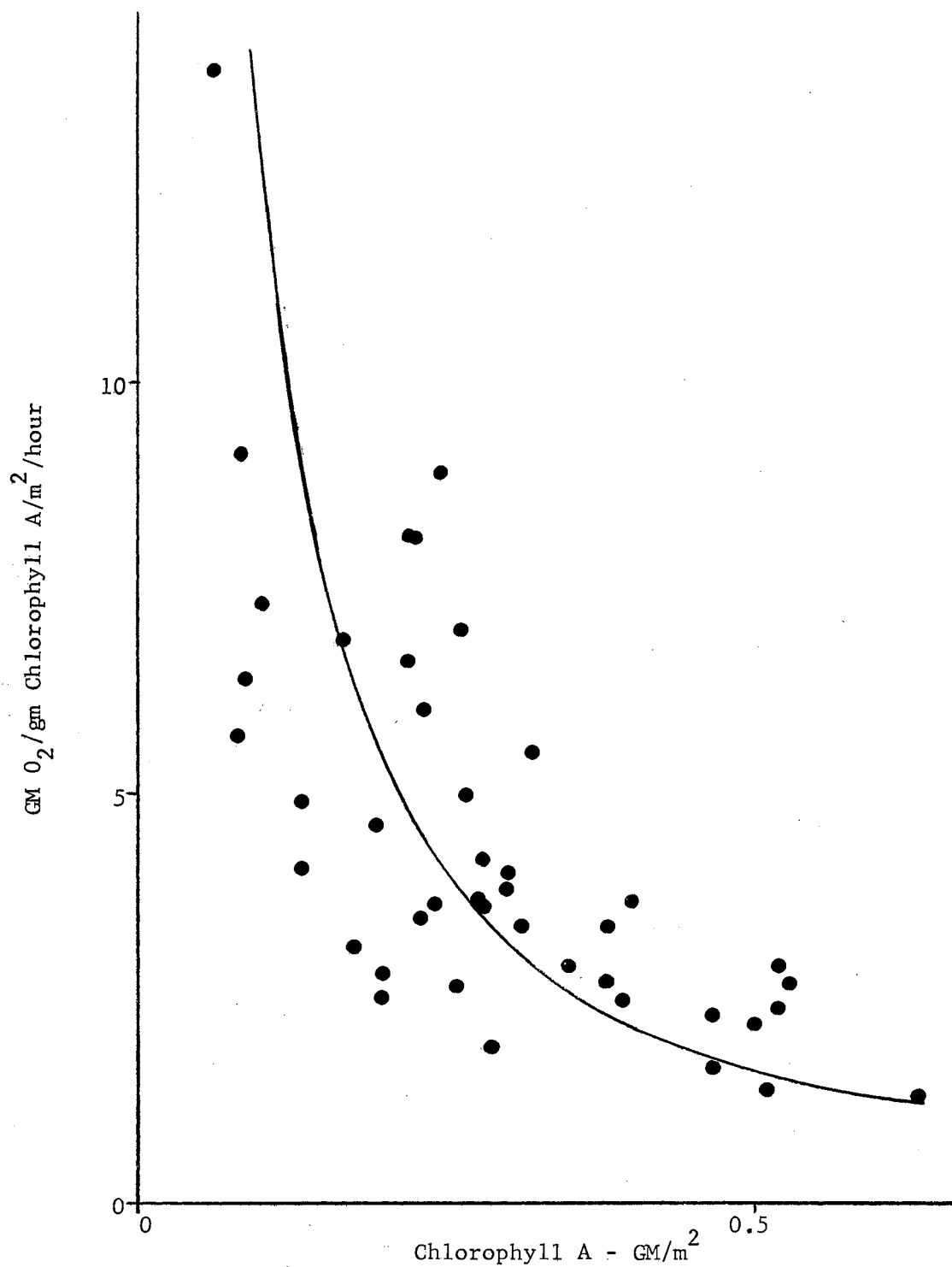


Figure 16: Assimilation number (gm O<sub>2</sub>/gm chlorophyll  $\frac{a}{m^2}$ /hour) plotted against chlorophyll concentration in gm/m<sup>2</sup>.

decreased as chlorophyll concentration increased. According to Wright (1960) three explanations are plausible:

1. apparent chlorophyll content may consist of products not distinguished colorimetrically from chlorophyll;

2. photosynthesis-inhibitors accumulate as population increases;  
or

3. nutrient content necessary for photosynthesis is depleted by large populations.

The last explanation is probably most logical for the present situation. Certain mineral elements and/or carbon dioxide supply probably were depleted by large populations of algae and photosynthesis was limited. This hypothesis is supported by relationship of the fall and spring data (Figure 15). Algal populations were lower and did not drain the supply of raw materials. In April, when temperature and sunlight were optimal, gross photosynthesis-chlorophyll relationship was linear and higher than in summer, and carbon dioxide was probably not limiting. In November, when temperature and sunlight were lower, the relationship was linear and lower than in summer. In November, temperature and sunlight, but not carbon dioxide, probably were the limiting factors.

Some writers have attempted to estimate the amount of algal photosynthesis from chlorophyll measurements by use of assimilation numbers (Strickland, 1960). To justify such a procedure, it was assumed that photosynthesis was proportional to amount of chlorophyll. Willstatter and Stoll (1918) related photosynthesis to chlorophyll concentrations and were among the first to use assimilation numbers. Ryther and Yentsch (1957) calculated an assimilation number for marine phytoplankton

and demonstrated its use to estimate photosynthesis.

Assimilation number has been shown to be affected by variations in environmental conditions. Ryther and Menzel (1959) showed that light adaptation affected estimates obtained by the use of an assimilation number. They found that phytoplankton adapted to low light intensity became light saturated at an intensity less than 1000 foot candles. Phytoplankton adapted to high light intensity became light saturated at an intensity of approximately 5000 foot candles. Odum, et al. (1958) pointed out that chlorophyll concentration diminished at times of light saturation. Unabsorbed light passed through the top layer of phytoplankton and was used by a lower layer, thereby increasing total photosynthesis. Thus, when light adaptations are unknown, use of assimilation numbers to estimate photosynthesis may be somewhat biased. Odum, et al. (1958) recognized that other factors affected use of assimilation numbers. Reduced rates of supply of nutrients reduced chlorophyll concentrations. Higher temperatures speeded up reactions and allowed a faster regeneration rate which probably caused a higher assimilation number. In conclusion, they pointed out that uniform assimilation numbers may not be assumed for all communities at every season unless information is available to permit corrections for light conditions, age of cells, nutrient abundance, and temperature.

The seasonal relationship noted in Figure 15 points out the effect of different conditions upon the use of an assimilation number to estimate photosynthesis. For example, if an assimilation number was calculated from November data, gross photosynthesis calculated by that number for July would be too low. On the other hand, if an assimilation



number was taken from April data it would yield a gross photosynthesis that would be too high for July.

Wright (1960) found that the relationship between photosynthesis and chlorophyll was not linear during early summer. He concluded that as chlorophyll concentration increased assimilation number decreased.

### 3. Relationship of Chlorophyll, Organic Matter and Photosynthesis.

Total suspended organic matter in  $\text{gm/m}^3$  at Refinery A is presented in Table IX. Organic matter concentration ranged from  $1.0 \text{ gm/m}^3$  after one day holding time in February to  $101.0 \text{ gm/m}^3$  after one day holding time in September. Organic matter concentration at one day holding

TABLE IX  
ORGANIC MATTER CONCENTRATION IN  $\text{GM/M}^3$  AT REFINERY A

Date	Days Holding Time						
	1	3	4	6	7	9	10
8/1/61	36.0	18.0	28.5	13.0	17.5	7.0	7.0
9/16/61	101.0	46.5	18.5	28.5	26.0	9.5	11.5
10/12/61	7.0	18.5	16.0	20.5	21.5	13.0	12.0
11/24/61	6.0	4.0	7.5	2.5	3.5	3.0	2.0
12/21/61	2.0	6.5	8.0	2.5	4.5	6.5	3.5
2/3/62	1.0	5.0	5.0	4.5	5.0	2.0	2.5
3/26/62	8.0	21.0	21.0	17.5	8.5	8.0	11.0
4/26/62	10.0	23.0	30.0	31.5	19.5	13.0	13.5
6/5/62	16.0	22.5	21.5	19.0	23.5	13.5	25.5
7/19/62	51.0	36.5	40.0	47.5	52.5	36.0	32.0

time was eliminated from consideration because the effluent contained varied amounts of suspended organic matter which usually settled during the first two or three days holding time. In September, for example, organic matter concentration of the water at one day holding time was unusually high and was still above the usual concentration after three days holding time. From November through February, when the algal population was very low, organic matter concentration was lowest and generally uniform throughout the pond system. From March through October, when algae were abundant, organic matter concentration was higher and usually reached a maximum near the middle of the system.

Chlorophyll in  $\text{gm/m}^3$  was plotted against organic matter in  $\text{gm/m}^3$  in Figure 17. Chlorophyll increased in straight-line proportion with organic matter. The apparent conclusion is that increase in organic matter toward the middle of the pond system during warm months was due to increase in algae. As algae died and settled to the bottom near the end of the pond system, organic matter concentration decreased proportionally. Concentrations of 1.0 to 8.0  $\text{gm/m}^3$  organic matter were present during winter when algae were absent or low in population. The effluent probably contributed approximately that amount.

Riley (1941) related chlorophyll concentration and ash-free dry weight to photosynthesis. Wright (1959) correlated photosynthesis to biomass and found that as biomass increased, photosynthesis per unit of biomass decreased. In the present study organic matter concentration was in direct proportion to chlorophyll concentration; therefore, the curvilinear relationship that existed for assimilation number (Figure 16) would be the same for gross photosynthesis-organic matter ratio.

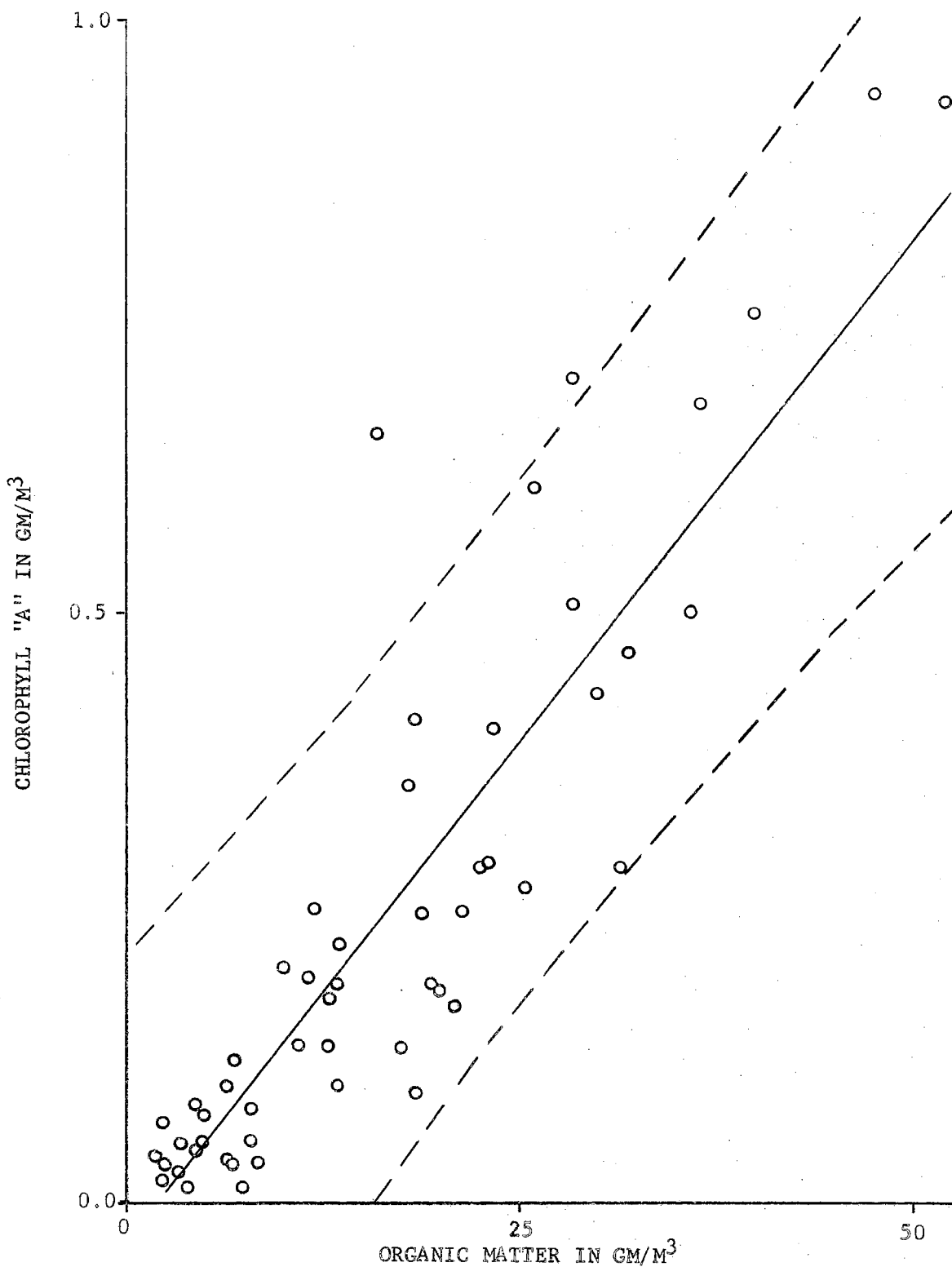


Figure 17: Chlorophyll in GM/M<sup>3</sup> plotted against organic matter in GM/M<sup>3</sup> for Refinery A. Dashed lines indicate the 95 % confidence belt. Solid line indicates the linear regression.

Manning and Juday (1941) found that the ratio of chlorophyll to organic matter increased in winter and was lowest in summer. In oil refinery ponds the ratio is constant throughout the year because of relative absence of zooplankton (K. W. Minter, personal communication), while in the Wisconsin lakes of Manning and Juday, zooplankton is reduced only in winter.

## CHAPTER V

### EFFECTIVENESS OF HOLDING PONDS

The most economical and efficient method of stabilizing organic wastes appears to be to hold waste water in a series of ponds for periods of several days (Allen, 1955). This method is particularly good if enough land is available to permit sufficient holding time. In such a holding-pond system, natural processes of stabilization by bacterial oxidation occurs. Algae utilize nutrients released by bacterial action and in return, through photosynthesis, provide oxygen that is necessary for the efficient bacterial degradation.

Oswald, et al. (1957) have provided information for design of sewage ponds. Although some criteria for design of sewage ponds might be used for other wastes, it is likely that other wastes may impose different criteria. One of the more important aspects is length of holding time. Information obtained at Refineries A and B may be used as an aid in pond design for oil refinery effluent.

Photosynthetic production of oxygen, reduction of phenol, chemical oxygen demand and biochemical oxygen demand at Refineries A and B, and reduction of ammonia at Refinery B were considered here in evaluating effectiveness of holding ponds in oil refinery waste stabilization. Refinery B had no pretreatment prior to the holding ponds, while Refinery A had an extensive pretreatment procedure. Conditions at the end of 10 days holding time at Refinery A were

similar in many ways to conditions at 37 days holding time at Refinery B.

1. Photosynthetic Production of Oxygen.

At certain times of the year there was no photosynthesis in the pond system at Refinery A (Figure 18). Photosynthesis occurred throughout the pond system during May, June, July and August. Oxygen production ceased at beginning of the system during September. Cessation of photosynthesis progressed through the pond system until by December there was no oxygen production in the entire system. Although no photosynthesis occurred during late December, January, February and early March, the holding pond system was not entirely anaerobic. Diffusion from the atmosphere provided a small amount of oxygen (Appendix Table I). In late March, photosynthesis occurred in the last five days holding time and by late May or early June, in the entire system.

At Refinery B, photosynthesis occurred throughout the year at 60 days holding time (Figure 19). Oxygen production by photosynthesis occurred in the last 45 days holding time from late March through September. Photosynthesis activity gradually disappeared through the pond system as winter approached, until by December, only effluent 60 days old supported algal photosynthesis.

Abrupt return of photosynthesis to the pond systems in late March (Figures 18 and 19) suggests that some limiting factor was present in winter. Three explanations for absence of algae in winter seem plausible.

1. Although the effluent became progressively less toxic with increased holding time, toxicity may have greater effect on algae as

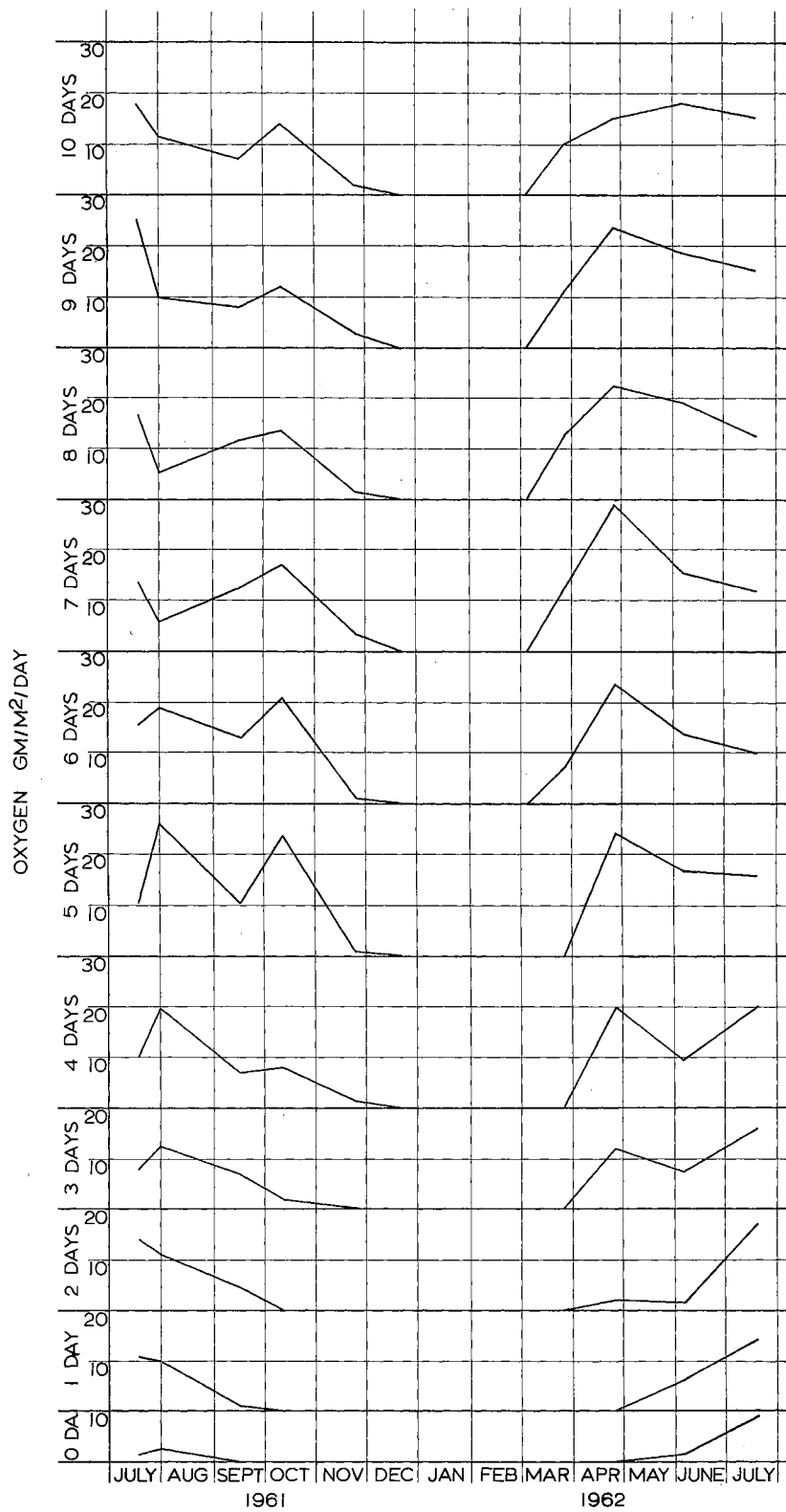


Figure 18: Annual course of photosynthesis at Refinery A for all stations during one year.

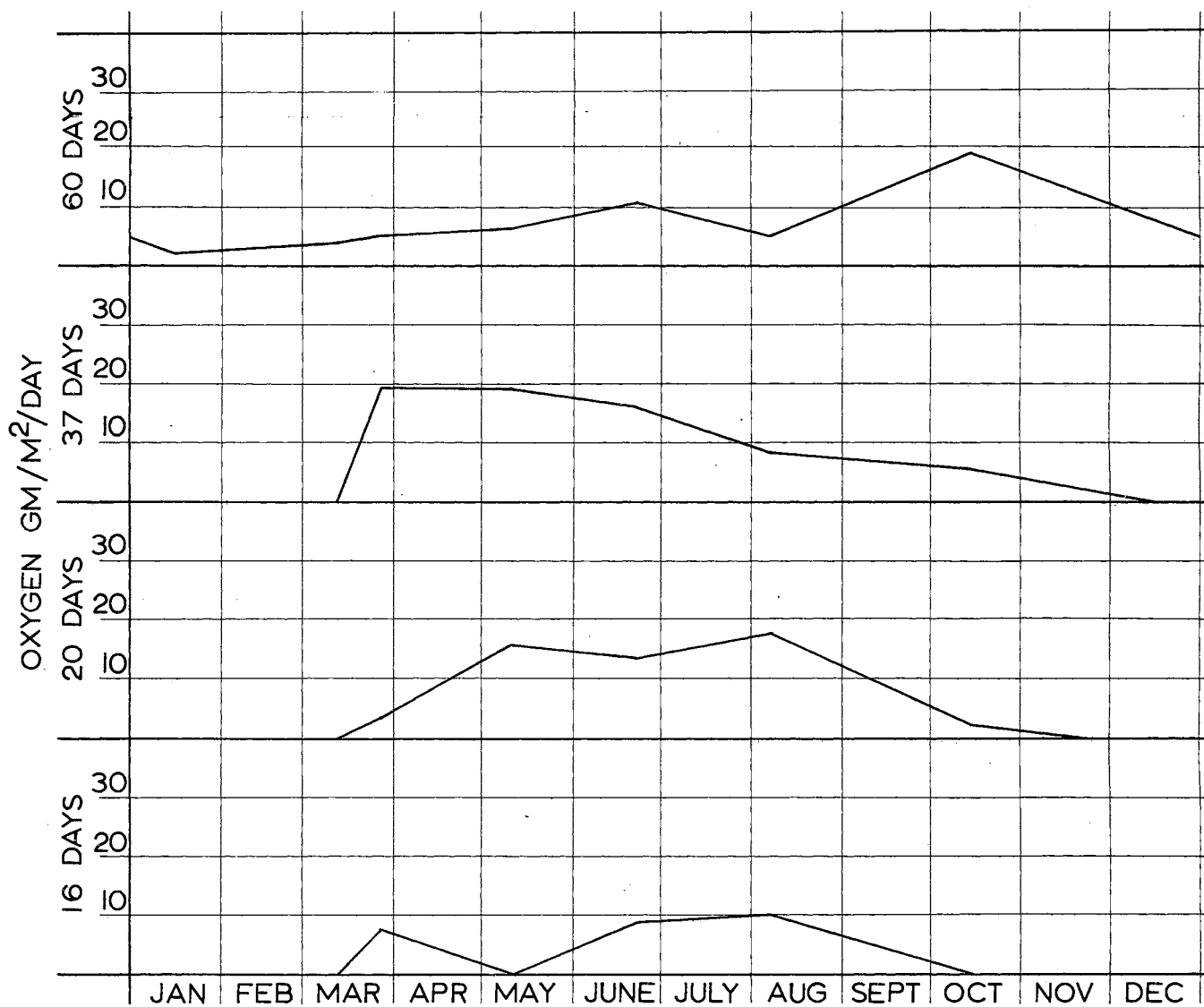


Figure 19: Annual course of photosynthesis at Refinery B for all stations during one year.



environmental conditions decline in the fall. Algae may be forced out of the system by toxicity as environmental conditions worsen. However, if holding time is sufficient, toxicity loses its effect even in winter at some point in the pond system. Presence of algal photosynthesis at Refinery B during winter indicates that sufficient holding time reduced toxicity below limiting levels.

2. Rate of decomposition of organic matter could be so slow that nutrients are not available to algae during winter. However, community respiration is only slightly less in winter than in summer (Figures 2 and 3) and nutrients from decomposition probably were not in short supply.

3. During winter, products of bacterial degradation may be different than during summer (Bartsch, 1961). Degradation-products in winter may be toxic to the algae or of such composition that algae cannot use them as a source of raw materials. In either case, algal populations would be reduced or eliminated and photosynthesis would be stopped.

## 2. Reduction of Phenol.

The holding pond system at Refinery A was more effective in reduction of phenol during summer than during winter (Figure 20). From October through early March phenol reduction was 61 to 85 percent. From late March through September, reduction was 95 to 99.9 percent.

Holding ponds at Refinery B were only slightly less effective for phenol reduction in winter than in summer (Figure 21). From December through March, there was 90 to 99 percent reduction. A period of 37 days holding time was only slightly less effective than 60 days. Twenty days holding time was more similar to the ten days at Refinery A.

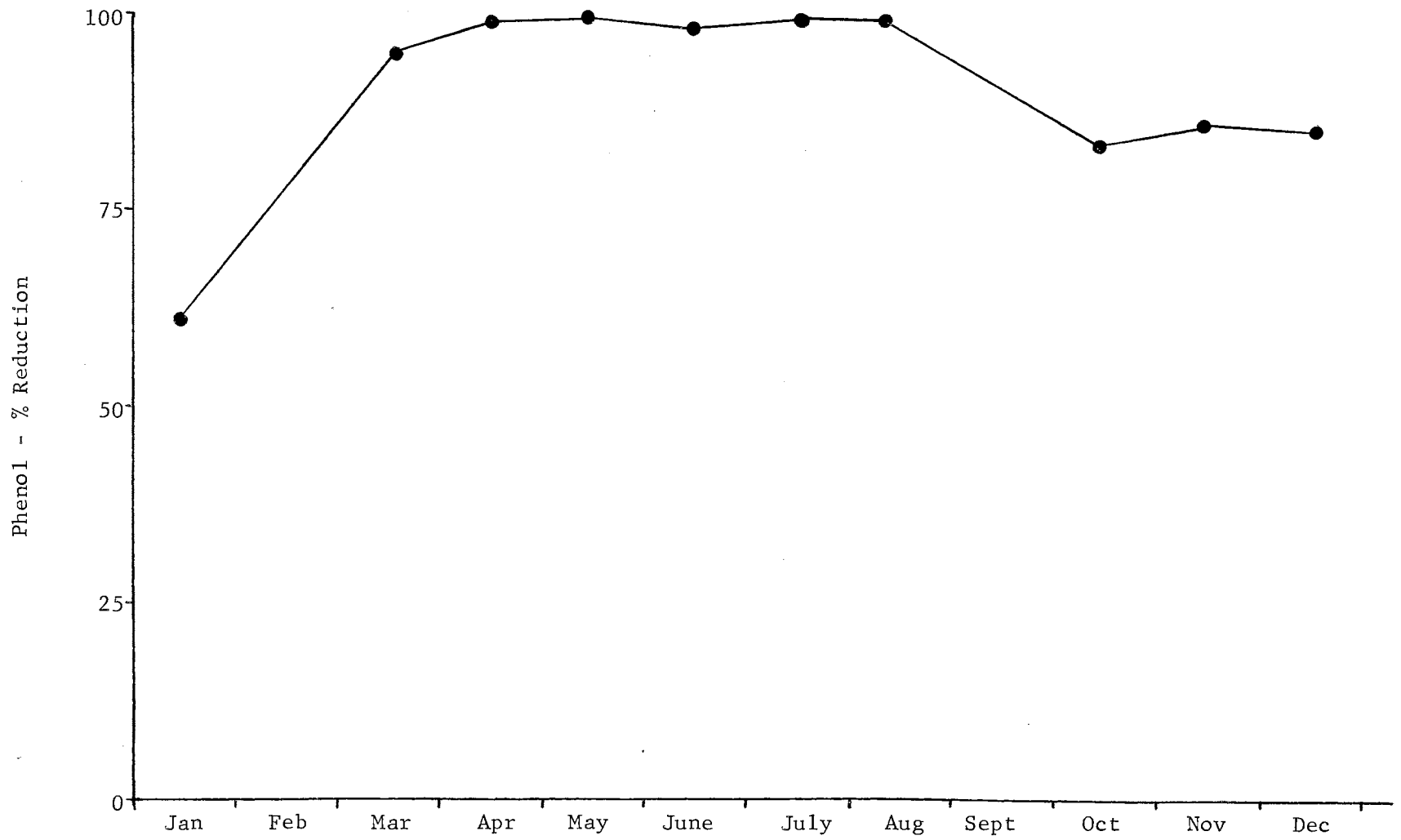


Figure 20: Reduction of phenol (0 to 10 days holding time) at Refinery A.

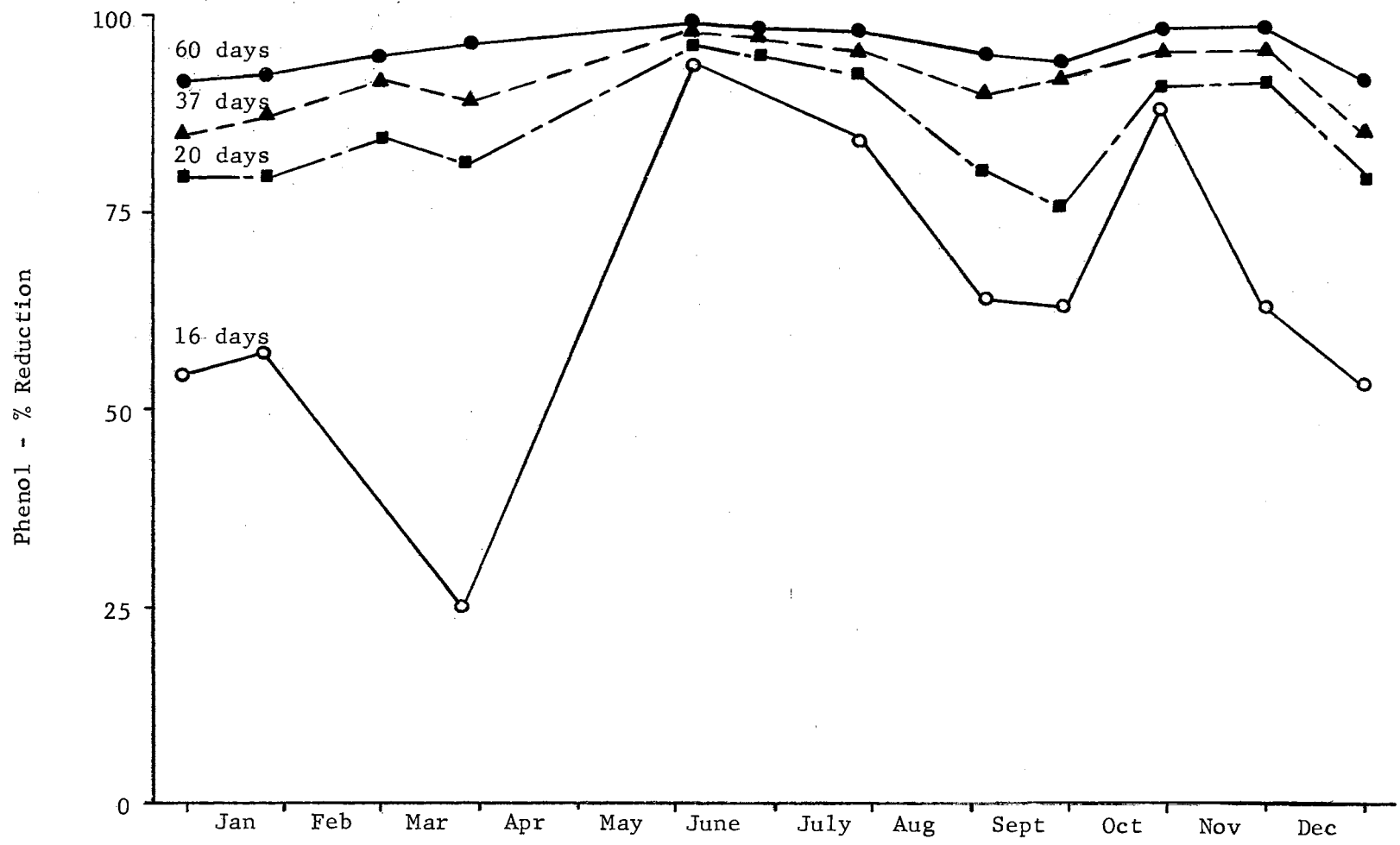


Figure 21: Reduction of phenol (0 to 16 days, 0 to 20 days, 0 to 37 days, and 0 to 60 days holding time) at Refinery B.

Reduction at 16 days holding time was rather erratic, depending on initial phenol load.

Longer holding time undoubtedly accounted for higher reduction during winter at Refinery B than at Refinery A. Since phenol reduction was approximately the same during summer at both refineries, ten days holding time was sufficient at that season. On the other hand, ten days holding time was not sufficient in winter.

### 3. Reduction of Biochemical Oxygen Demand.

Biochemical oxygen demand was determined at Refinery A from July through December and at Refinery B all year. Refinery A water was filtered to remove the effect of algae and B O D was determined for both filtered and unfiltered water. Since algal respiration and decomposition effects were probably removed by filtering, filtered B O D values were more representative of bacterial reduction of oxygen-demanding components of the effluent.

B O D reduction during winter at Refinery A was about 43 percent for unfiltered water and about 48 percent for filtered water (Figure 22). During summer, B O D reduction was about 60 to 63 percent for unfiltered water and about 80 to 90 percent for filtered water.

At Refinery B, B O D of unfiltered water was reduced about 45 to 57 percent during winter and about 76 to 96 percent during summer (Figure 23). Reduction possibly might have been higher had the algae been filtered from the water. High reduction values in May and September were the result of extraordinarily high initial B O D loads. Regardless of the initial load, B O D was usually reduced to the same final level. Effluent with an initially high B O D load would then have a larger percent reduction.

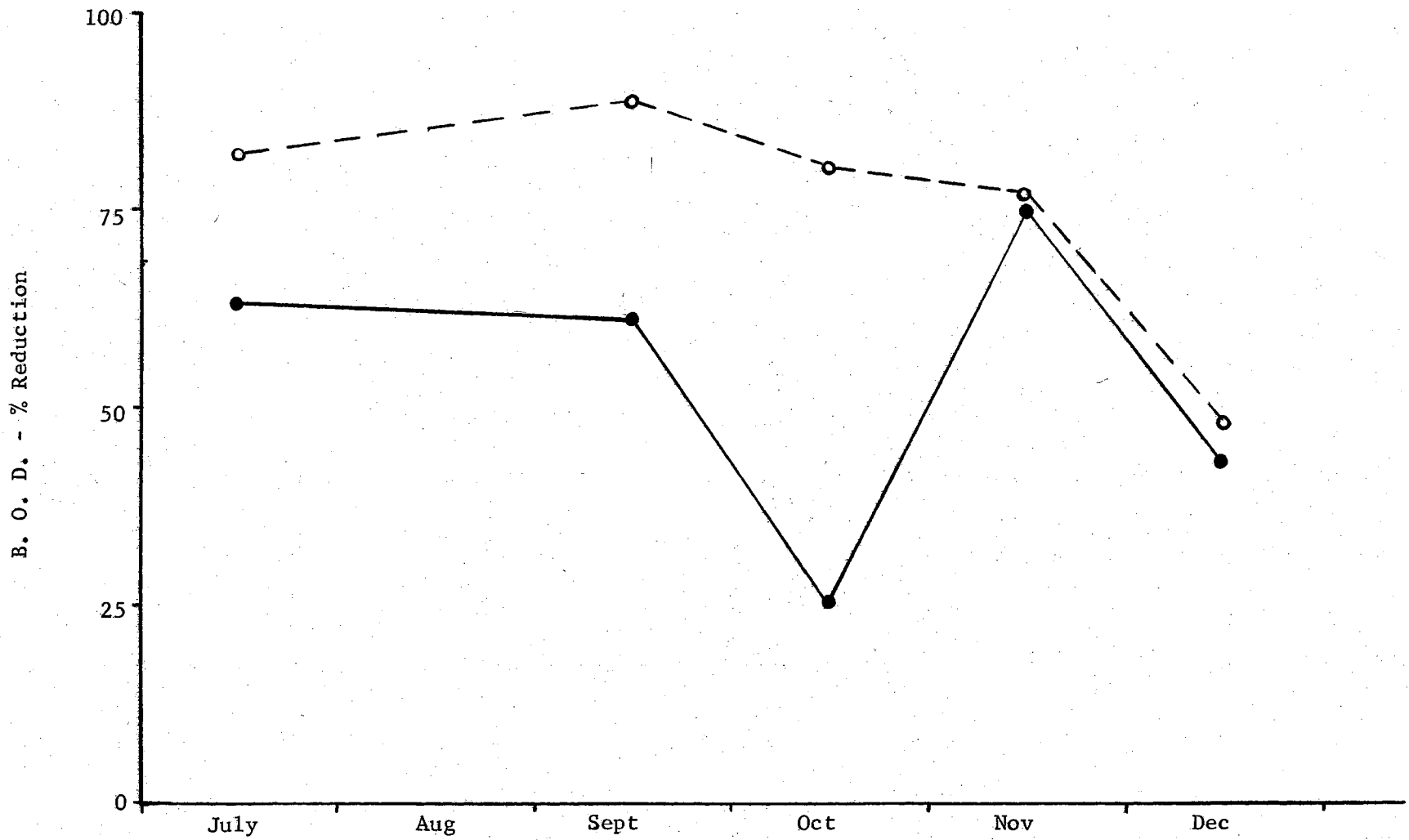


Figure 22: Reduction of biochemical oxygen demand (0 to 10 days holding time) at Refinery A.  
o = filtered samples. ● = unfiltered samples.

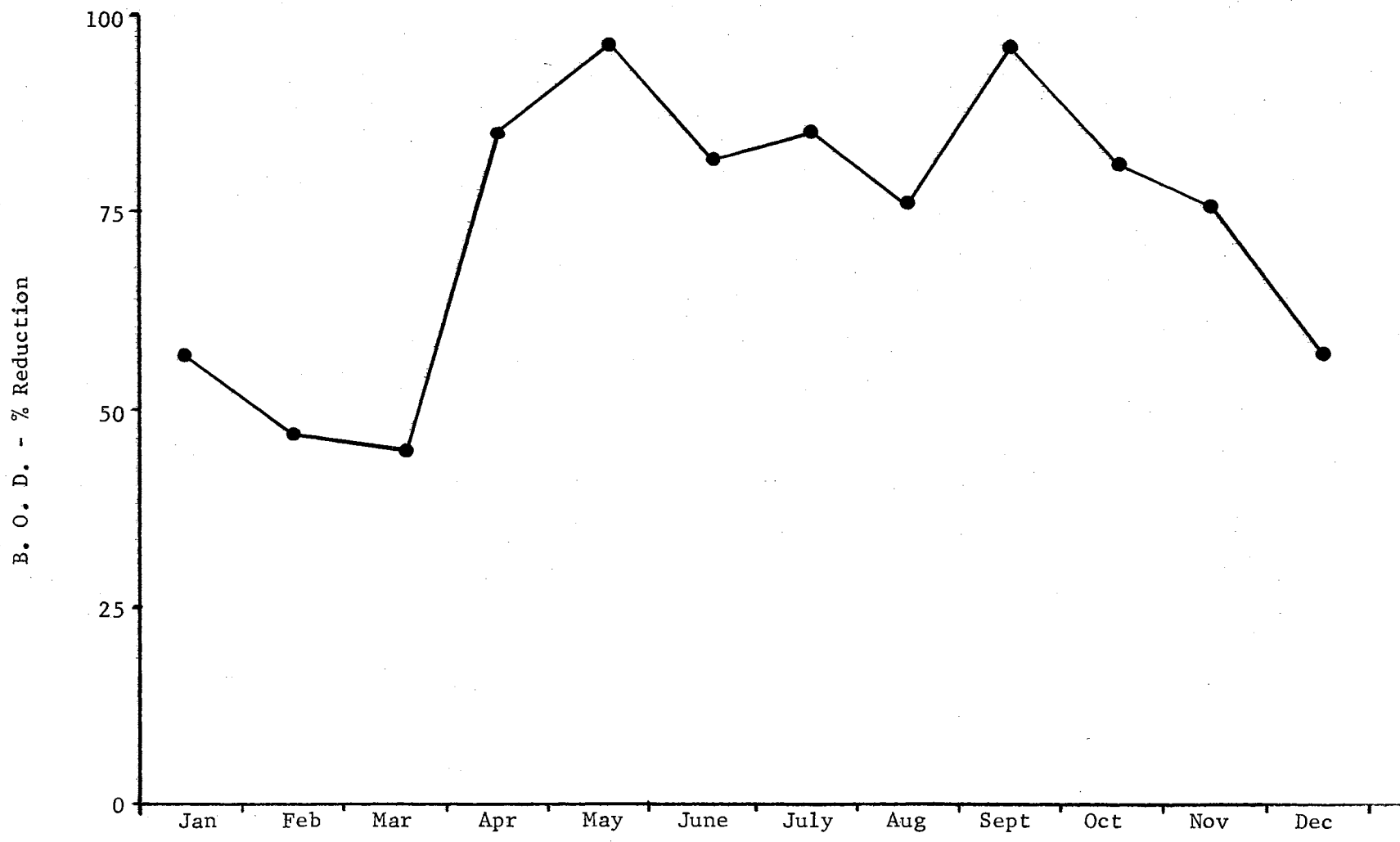


Figure 23: Reduction of biochemical oxygen demand (0 to 60 days holding time) at Refinery B.

#### 4. Reduction of Chemical Oxygen Demand.

Data for chemical oxygen demand were available for January through July at Refinery A, and for all year at Refinery B. During January and February at Refinery A, reduction of C O D was about 20 to 28 percent (Figure 24). From March through July reduction was about 28 to 36 percent. When algae were filtered from the sample prior to analysis, reduction was 40 to 56 percent in summer.

At Refinery B, reduction of C O D was 20 to 35 percent during December, January, February and March (Figure 25). Reduction during summer was 44 to 60 percent. Unfortunately, filtered samples were not available at Refinery B. In view of the difference between filtered and unfiltered samples at Refinery A during summer, reduction of C O D at Refinery B was probably higher than indicated in Figure 25.

#### 5. Reduction of Ammonia.

Effluent at Refinery A contained very small amounts of ammonia and no decrease in concentration occurred. At Refinery B, ammonia was decreased about 45 to 64 percent in winter and 69 to 95 percent in summer (Figure 26).

#### 6. Evaluation of Retention Time.

No oxygen production by photosynthesis occurred in the system with ten days holding time during the winter, while oxygen production occurred all year at 60 days holding time. Although the decrease in phenol concentration was about the same in summer at both refineries, a greater decrease occurred in the system with 60 days holding time than in the

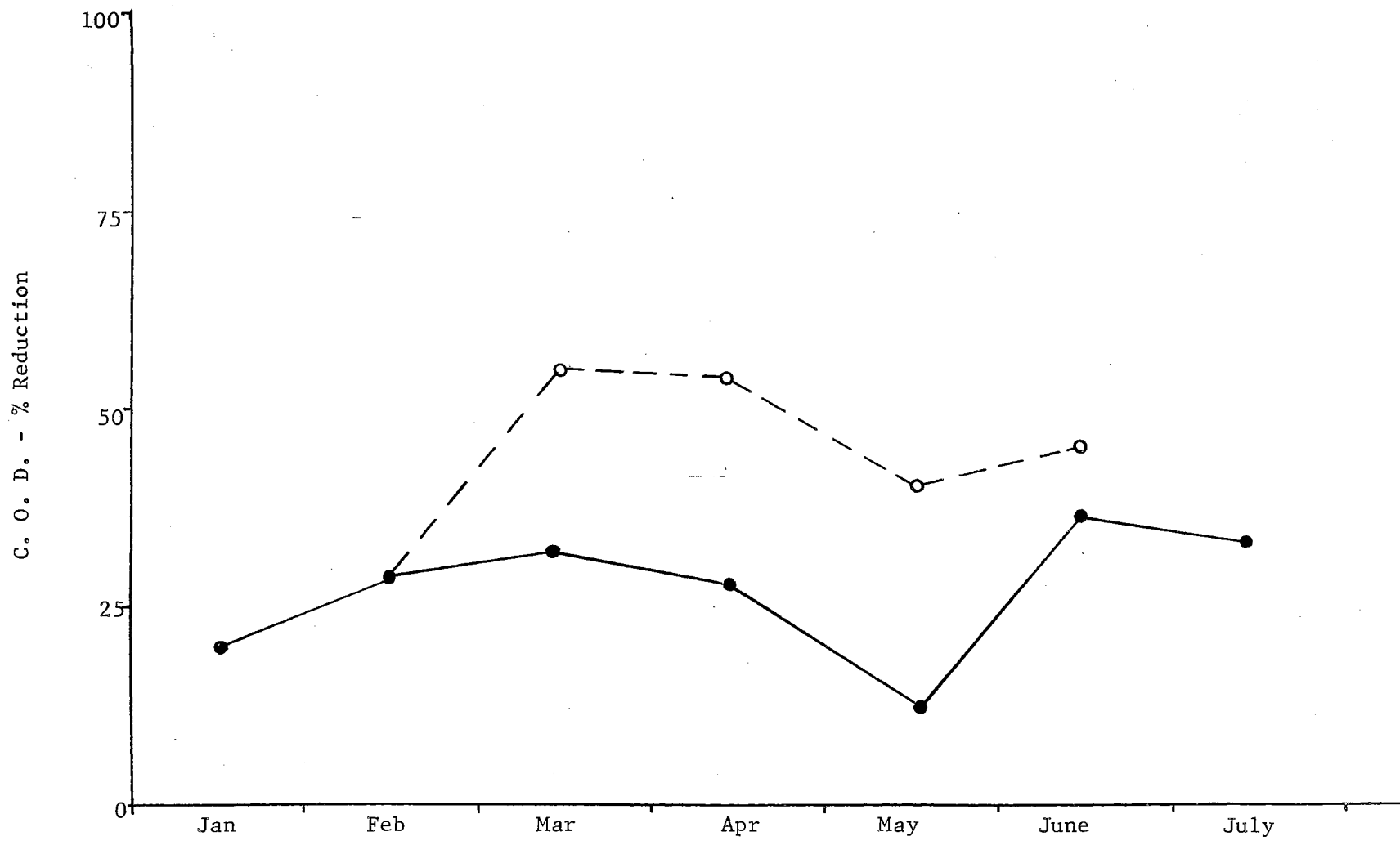


Figure 24: Reduction of chemical oxygen demand (0 to 10 days holding time) at Refinery A.  
 o = filtered samples. ● = unfiltered samples.



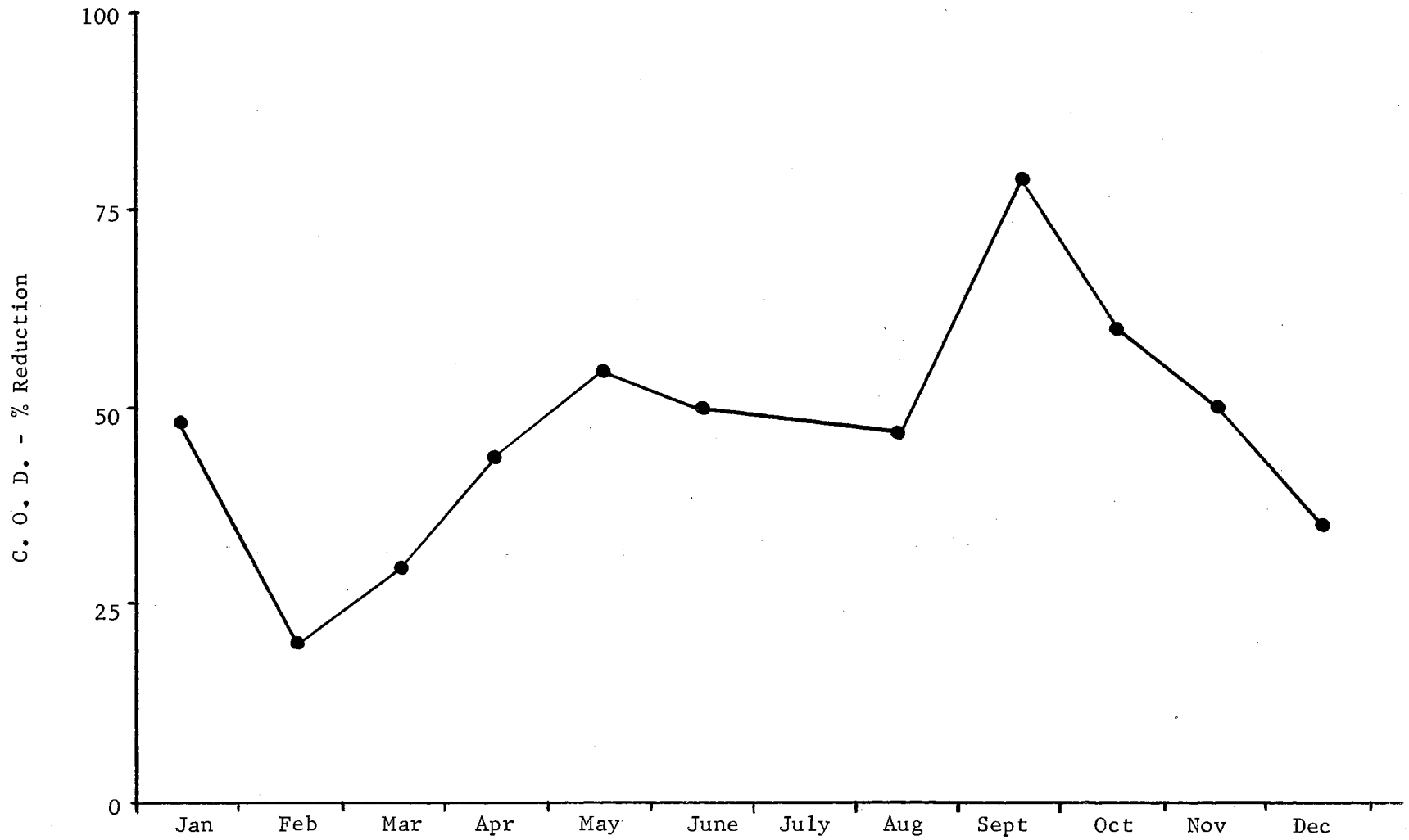


Figure 25: Reduction of chemical oxygen demand (0 to 60 days holding time) at Refinery B.

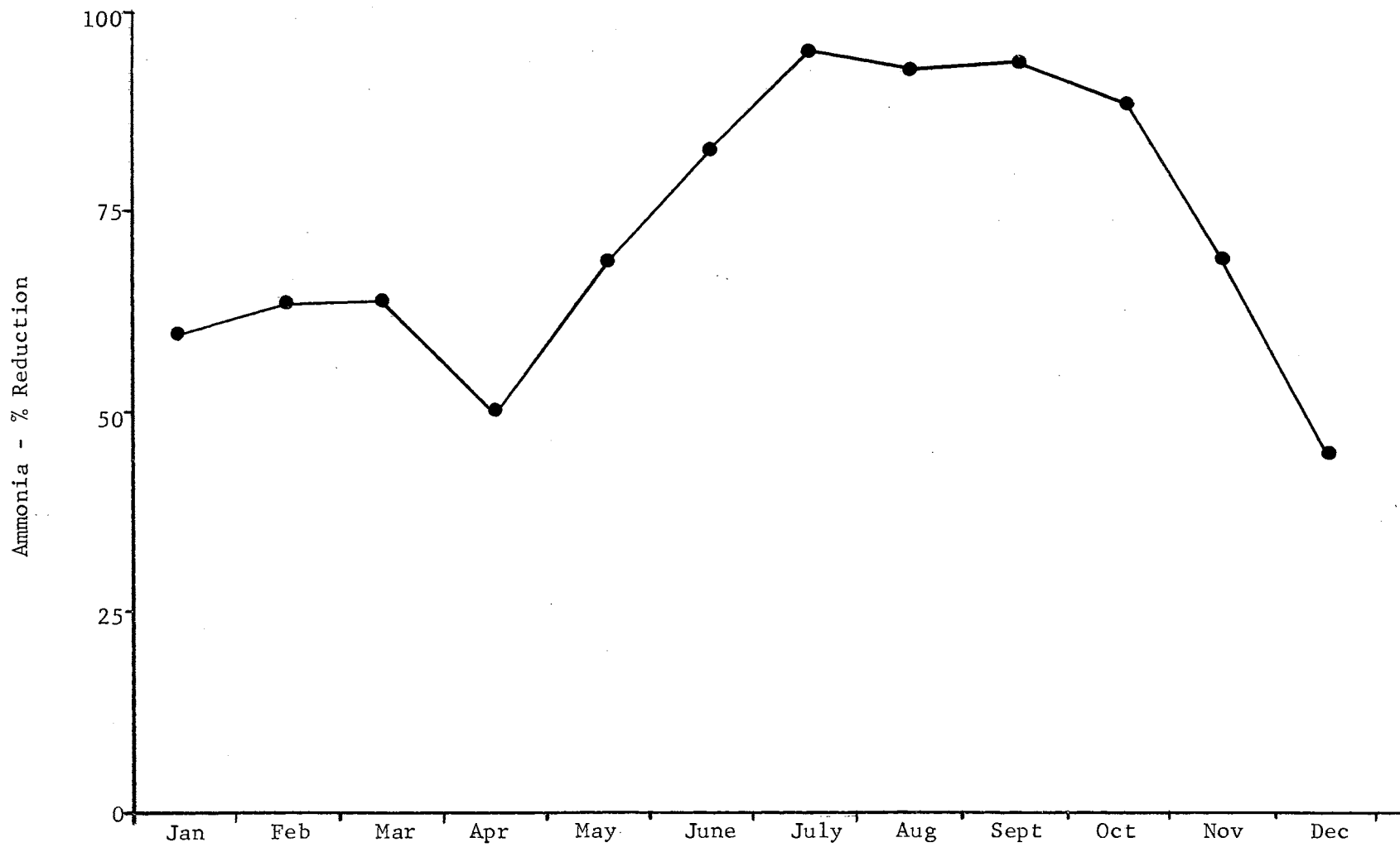


Figure 26: Reduction of ammonia (0 to 60 days holding time) at Refinery B.

system with ten days holding time in winter. Decrease of B O D and C O D during both summer and winter was greater with 60 days holding time than with ten days holding time. In terms of oxygen production and decrease in phenol, ten days holding time was sufficient in summer but not in winter. For decrease of B O D and C O D, ten days holding time was less effective than 60 days holding time during all seasons of the year.

Greater reduction of chemical components have been reported for longer holding time in oil refinery effluent holding ponds as well as sewage oxidation ponds. Dorris, et al. (1961) reported lower concentrations of phenol and ammonia after 60 days holding time than after 37 days holding time in two Oklahoma oil refinery effluent systems. Oswald, et al. (1957) found that B O D was more nearly satisfied when holding time was increased in sewage oxidation ponds.

## CHAPTER VI

### SUMMARY

1. The diurnal curve method was used to investigate basic properties of community metabolism in two oil refinery effluent holding pond systems during a one-year period. Photosynthetic productivity and community respiration, addition of oxygen from the atmosphere, effects of light and temperature, relationship of chlorophyll and suspended organic matter, and effectiveness of holding ponds in reduction of chemical components of the effluent, were studied.

2. Total community respiration ranged between 15.6 and 35.6  $\text{gm/m}^2/\text{day}$  during winter, 5.2 and 37.8  $\text{gm/m}^2/\text{day}$  during spring, 4.3 and 30.9  $\text{gm/m}^2/\text{day}$  during summer, and, 14.2 and 50.5  $\text{gm/m}^2/\text{day}$  during fall at Refinery A. At Refinery B, respiration ranged between 19.2 and 36.0  $\text{gm/m}^2/\text{day}$  during winter, 2.1 and 36.0  $\text{gm/m}^2/\text{day}$  during spring, 2.2 and 30.1  $\text{gm/m}^2/\text{day}$  during summer, and, 4.9 and 29.8  $\text{gm/m}^2/\text{day}$  during fall. In general, average community respiration was highest in late fall and lowest in early spring.

3. Measurable photosynthetic productivity did not occur during winter, ranged between zero and 29.2  $\text{gm/m}^2/\text{day}$  during spring, zero and 25.0  $\text{gm/m}^2/\text{day}$  during summer, and, zero and 21.3  $\text{gm/m}^2/\text{day}$  during fall, at Refinery A. At Refinery B, photosynthesis ranged between zero and 3.9  $\text{gm/m}^2/\text{day}$  during winter, zero and 19.2  $\text{gm/m}^2/\text{day}$  during spring, zero and 17.4  $\text{gm/m}^2/\text{day}$  during summer, and, zero and 19.3

gm/m<sup>2</sup>/day during fall. At Refinery B, with 60 days holding time, photosynthesis occurred in the last holding pond during the entire year, while at Refinery A, with ten days holding, no photosynthesis could be detected during winter in any holding pond. In general, photosynthetic productivity was higher in spring and fall than during summer, and lowest in winter.

4. Community metabolism in the oil refinery effluent holding ponds was higher than in most natural communities and lower than in sewage oxidation ponds. Presumably, inflow of nutrient-rich effluent provided raw material necessary for growth of algae and bacteria and photosynthetic activity of algae, which resulted in the relatively high community metabolism. Toxicity of the effluent probably prevented as high community metabolism as is possible in less toxic, but nevertheless nutrient-rich, sewage effluent.

5. Diffusion of oxygen from the atmosphere contributed to the satisfaction of oxygen demand of the community particularly during times of little or no photosynthesis.

6. Light saturation occurred on bright days. Cloudiness during the daylight period caused depressions in the normal diurnal oxygen curve.

7. Maximal efficiency of algae to convert solar energy to chemical energy was about 3.99 percent. Efficiency was greatest during fall and spring when sunlight was more optimal, and lowest in winter when sunlight was below optimal. Algae in oil refinery effluent are less efficient than algae in sewage communities or natural climax communities.

8. Direct effect of temperature upon bio-activity of the oil refinery effluent community was slight.

9. Productivity/respiration ratios ranged from zero to 4.5. The

community was moving toward a P/R ratio of about unity at the end of holding time.

10. Chlorophyll concentration at Refinery A ranged between zero and 0.100 mg/l during winter, 0.015 and 0.424 mg/l during spring, 0.035 and 0.937 mg/l during summer, and, zero and 0.253 gm/l during fall. Chlorophyll concentration was higher than in most natural communities and lower than in sewage communities.

11. Relationship between oxygen production and chlorophyll concentration was non-linear. As chlorophyll concentration increased, oxygen produced per gram of chlorophyll decreased, indicating presence of limiting factors.

12. Suspended organic matter ranged between 1.0 and 52.0 gm/m<sup>3</sup> at Refinery A. Relationship between suspended organic matter and chlorophyll was linear.

13. Refinery B, with 60 days holding time and little pretreatment, was more effective in reduction of chemical components of the effluent than Refinery A, with ten days holding time and extensive pretreatment.

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## APPENDIX

TABLE I  
COMMUNITY METABOLISM AT REFINERY A

Date	R	P	EZ	R	P	Diff Rate	Diff	P/R
	g			g				
	gm/m <sup>3</sup> /day		M	gm/m <sup>2</sup> /day		gm/m <sup>3</sup> /hr	gm/m <sup>2</sup> /day	
<u>Winter</u>								
0 days holding time								
12/21/61	24.0	0.0	1.15	27.6	0.0	1.0	+27.6	0.00
2/3/62	24.0	0.0	0.93	22.3	0.0	1.0	+22.3	0.00
3/3/62	48.0	0.0	0.67	32.0	0.0	2.0	+32.0	0.00
Average	32.0	0.00	0.92	27.3	0.0	1.3	+27.3	0.00
1 day holding time								
12/21/61	24.0	0.0	1.15	27.6	0.0	1.0	+27.6	0.00
2/3/62	24.0	0.0	0.84	20.2	0.0	1.0	+20.2	0.00
3/3/62	45.6	0.0	0.73	33.3	0.0	2.0	+33.3	0.00
Average	31.2	0.0	0.91	27.0	0.0	1.3	+27.0	0.00
2 days holding time								
12/21/61	24.0	0.0	1.15	27.6	0.0	1.0	+27.6	0.00
2/3/62	24.0	0.0	0.75	18.0	0.0	1.0	+18.0	0.00
3/3/62	37.9	0.0	0.79	30.0	0.0	2.0	+30.0	0.00
Average	28.6	0.0	0.90	25.2	0.0	1.3	+25.2	0.00
3 days holding time								
12/21/61	24.0	0.0	1.15	27.6	0.0	1.0	+27.6	0.00
2/3/62	24.0	0.0	0.65	15.6	0.0	1.0	+15.6	0.00
3/3/62	30.7	0.0	0.85	26.1	0.0	2.0	+26.1	0.00
Average	26.2	0.0	0.88	23.1	0.0	1.3	+23.1	0.00
4 days holding time								
12/21/61	22.8	0.0	1.19	27.1	0.0	1.0	+27.1	0.00
2/3/62	24.0	0.0	0.65	15.6	0.0	1.0	+15.6	0.00
3/3/62	27.4	0.0	0.86	23.5	0.0	2.0	+23.5	0.00
Average	24.7	0.0	0.90	22.1	0.0	1.3	+22.1	0.00
5 days holding time								
12/21/61	23.7	0.0	1.23	29.1	0.0	1.0	+29.1	0.00
2/3/62	24.0	0.0	0.65	15.6	0.0	1.0	+15.6	0.00
3/3/62	24.0	0.0	0.87	20.9	0.0	2.0	+20.9	0.00
Average	23.9	0.0	0.92	21.9	0.0	1.3	+21.9	0.00

R = Community Respiration

P = Gross photosynthesis

g

EZ = Euphotiz zone

Diff = Diffusion

P/R = Photosynthesis/community respiration

TABLE I (Cont.)

Date	R	P <sub>g</sub>	EZ	R	P <sub>g</sub>	Diff Rate	Diff	P/R
	gm/m <sup>3</sup> /day		M	gm/m <sup>2</sup> /day		gm/m <sup>3</sup> /hr	gm/m <sup>2</sup> /day	
6 days holding time								
12/21/61	21.8	0.0	1.28	28.0	0.0	1.0	+28.0	0.00
2/3/62	24.0	0.0	0.65	15.6	0.0	1.0	+15.6	0.00
3/3/62	25.0	0.0	0.87	21.7	0.0	2.0	+21.7	0.00
Average	23.6	0.0	0.93	21.8	0.0	1.3	+21.8	0.00
7 days holding time								
12/21/61	19.7	0.0	1.45	28.5	0.0	1.0	+28.5	0.00
2/3/62	24.0	0.0	0.87	20.3	0.0	1.0	+20.3	0.00
3/3/62	27.4	0.0	0.87	23.8	0.0	2.0	+23.8	0.00
Average	23.7	0.0	1.06	24.2	0.0	1.3	+24.2	0.00
8 days holding time								
12/21/61	20.5	0.0	1.62	33.2	0.0	1.0	+33.2	0.00
2/3/62	24.0	0.0	1.08	24.6	0.0	1.0	+24.6	0.00
3/3/62	30.5	0.0	0.87	26.5	0.0	2.0	+26.5	0.00
Average	25.0	0.0	1.19	28.1	0.0	1.3	+28.1	0.00
9 days holding time								
12/21/61	19.6	0.0	1.80	35.2	0.0	1.0	+35.2	0.00
2/3/62	24.0	0.0	1.30	29.6	0.0	1.0	+29.6	0.00
3/3/62	32.4	0.0	0.87	28.3	0.0	2.0	+28.3	0.00
Average	25.3	0.0	1.32	31.0	0.0	1.3	+31.0	0.00
10 days holding time								
12/21/61	19.8	0.0	1.80	35.6	0.0	1.0	+35.6	0.00
2/3/62	24.0	0.0	1.30	31.2	0.0	1.0	+31.2	0.00
3/3/62	33.2	0.0	0.87	28.9	0.0	2.0	+28.9	0.00
Average	25.7	0.0	1.32	31.9	0.0	1.3	+31.9	0.00
<u>Spring</u>								
0 days holding time								
3/26/62	26.4	0.0	0.85	22.4	0.0	1.1	+22.4	0.00
4/26/62	42.0	0.0	0.92	38.6	0.0	1.8	+38.6	0.00
Average	34.2	0.0	0.89	30.5	0.0	1.5	+30.5	0.00
1 day holding time								
3/26/62	26.4	0.0	0.75	20.3	0.0	1.1	+20.3	0.00
4/26/62	42.0	0.00	0.90	37.8	0.0	1.8	+37.8	0.00
Average	34.2	0.0	0.83	29.1	0.0	1.5	+29.1	0.00
2 days holding time								
3/26/62	26.4	0.0	0.65	17.2	0.0	1.1	+17.2	0.00
4/26/62	42.0	1.8	0.87	36.5	1.6	1.8	+34.9	0.04
Average	34.2	0.9	0.76	26.9	0.8	1.5	+26.1	0.03

TABLE I (Cont.)

Date	R	P <sub>g</sub>	EZ	R	P <sub>g</sub>	Diff Rate	Diff	P/R
	gm/m <sup>3</sup> /day			M	gm/m <sup>2</sup> /day		gm/m <sup>3</sup> /hr	gm/m <sup>2</sup> /day
3 days holding time								
3/26/62	26.4	0.0	0.56	14.8	0.0	1.1	+14.8	0.00
4/26/62	38.6	14.2	0.85	32.8	12.1	2.5	+20.7	0.37
Average	32.5	7.1	0.71	23.8	6.1	1.8	+17.7	0.26
4 days holding time								
3/26/62	26.4	0.0	0.69	18.7	0.0	1.1	+18.7	0.00
4/26/62	30.0	21.0	0.94	28.2	19.7	1.8	+ 8.5	0.70
Average	28.2	10.5	0.82	23.5	9.9	1.5	+13.6	0.42
5 days holding time								
3/26/62	26.4	0.0	0.82	21.7	0.0	1.1	+21.7	0.00
4/26/62	14.3	23.0	1.03	14.7	23.7	1.1	- 9.0	1.61
Average	20.4	11.5	0.93	18.2	11.8	1.1	+ 6.4	0.65
6 days holding time								
3/26/62	30.4	7.4	0.95	28.9	7.0	1.1	+21.9	0.24
4/26/62	4.7	20.9	1.13	5.3	23.6	1.3	-18.3	4.45
Average	17.6	14.2	1.04	17.1	15.3	1.2	+ 1.8	0.89
7 days holding time								
3/26/62	19.2	11.0	1.11	21.3	12.2	0.8	+ 9.1	0.57
4/26/62	4.7	22.3	1.31	6.2	29.2	3.0	-23.0	4.71
Average	12.0	16.7	1.21	13.8	20.7	1.9	- 6.9	1.50
8 days holding time								
3/26/62	12.0	9.9	1.27	15.2	12.6	1.0	+ 2.6	0.83
4/26/62	5.6	15.1	1.49	8.3	22.5	3.0	-14.2	2.71
Average	8.8	12.5	1.38	11.8	17.6	2.0	- 6.8	1.49
9 days holding time								
3/26/62	4.8	7.6	1.43	6.9	10.9	0.5	- 4.0	1.58
4/26/62	6.2	14.0	1.69	10.4	23.7	0.5	-13.3	2.28
Average	5.5	10.8	1.56	8.7	17.3	0.5	- 8.6	1.99
10 days holding time								
3/26/62	3.6	7.0	1.43	5.2	10.1	1.0	- 4.9	1.94
4/26/62	6.6	9.0	1.69	11.1	15.2	0.5	- 4.1	1.37
Average	5.1	8.0	1.56	8.2	12.7	0.8	- 4.5	1.55
<u>Summer</u>								
0 days holding time								
7/18/61	37.9	3.6	0.77	29.2	2.8	1.5	+26.4	0.10
9/16/61	28.8	0.0	0.50	14.4	0.0	1.2	+14.4	0.00
6/5/62	24.9	1.6	0.82	20.4	1.3	1.0	+19.1	0.06
7/19/62	45.8	15.2	0.59	27.0	9.0	1.5	+18.0	0.33
Average	34.4	5.1	0.67	22.8	3.3	1.3	+19.5	0.14

TABLE I (Cont.)

Date	R	P	EZ	R	P	Diff Rate	Diff	P/R
	g			g				
	gm/m <sup>3</sup> /day		M	gm/m <sup>2</sup> /day		gm/m <sup>3</sup> /hr	gm/m <sup>2</sup> /day	
1 day holding time								
7/18/61	43.0	16.6	0.72	30.9	12.0	1.7	+18.9	0.39
9/16/61	33.2	4.4	0.49	16.3	2.1	1.2	+14.2	0.13
6/5/62	29.7	7.2	0.88	26.1	6.3	1.0	+19.8	0.24
7/19/62	38.0	22.0	0.65	24.7	14.3	1.5	+10.4	0.58
Average	36.0	12.6	0.68	24.5	8.7	1.4	+15.8	0.36
2 days holding time								
7/18/61	28.3	22.5	0.63	17.8	14.2	1.6	+ 3.6	0.80
9/16/61	35.2	9.4	0.47	16.5	4.4	1.2	+12.1	0.27
6/5/62	23.7	1.8	0.94	22.3	1.7	1.0	+20.6	0.08
7/19/62	42.8	24.0	0.71	30.4	17.0	1.6	+13.4	0.56
Average	32.5	14.4	0.69	21.8	9.3	1.4	+12.5	0.43
3 days holding time								
7/18/61	16.1	13.4	0.56	9.0	7.5	1.0	+ 1.5	0.83
9/16/61	29.0	15.0	0.46	13.3	6.9	1.2	+ 6.4	0.52
6/5/62	14.0	7.5	1.00	14.0	7.5	0.3	+ 6.5	0.54
7/19/62	34.8	22.9	0.77	26.8	16.0	1.1	+10.8	0.60
Average	23.5	14.7	0.70	15.8	9.5	0.9	+ 6.3	0.60
4 days holding time								
7/18/61	15.4	16.9	0.58	8.9	9.8	1.3	- 0.9	1.10
9/16/61	15.2	14.3	0.49	7.4	7.0	1.2	+ 0.4	0.95
6/5/62	12.2	9.0	1.05	12.8	9.5	0.3	+ 3.3	0.75
7/19/62	38.6	28.8	0.70	27.0	20.2	1.0	+ 6.8	0.75
Average	20.4	17.3	0.71	14.0	11.6	1.0	+ 2.4	0.83
5 days holding time								
7/18/61	14.4	17.4	0.60	8.6	10.4	1.0	- 1.8	1.21
9/16/61	9.4	20.5	0.51	4.8	10.4	1.2	- 5.8	2.17
6/5/62	13.4	15.2	1.10	14.7	16.7	0.6	- 2.0	1.14
7/19/62	23.4	25.3	0.62	14.5	15.7	0.5	- 1.2	1.08
Average	15.2	19.6	0.71	10.7	13.3	0.8	- 2.6	1.24
6 days holding time								
7/18/61	18.7	24.8	0.62	11.6	15.4	1.4	- 3.8	1.33
9/16/61	9.4	24.3	0.54	5.1	13.1	1.2	- 8.0	2.57
6/5/62	9.0	12.0	1.15	10.4	13.8	0.6	- 3.4	1.33
7/19/62	18.2	18.2	0.54	9.8	9.8	0.3	0.0	1.00
Average	13.8	19.8	0.71	9.2	13.0	0.9	- 3.8	1.41
7 days holding time								
7/18/61	13.0	17.6	0.77	10.0	13.6	1.0	- 3.6	1.36
9/16/61	7.5	21.7	0.58	4.3	12.6	1.2	- 8.3	2.93
6/5/62	8.4	12.6	1.24	10.4	15.6	0.3	- 5.2	1.50
7/19/62	16.4	17.0	0.69	11.3	11.7	0.4	- 0.4	1.04
Average	11.3	17.2	0.82	9.0	13.4	0.7	- 4.4	1.49

TABLE I (Cont.)

Date	R	P <sub>g</sub>	EZ	R	P <sub>g</sub>	Diff Rate	Diff	P/R
	$\text{gm/m}^3/\text{day}$		M	$\text{gm/m}^2/\text{day}$		$\text{gm/m}^3/\text{hr}$	$\text{gm/m}^2/\text{day}$	
8 days holding time								
7/18/61	12.7	18.2	0.92	11.7	16.7	1.1	- 5.0	1.43
9/16/61	8.9	18.6	0.62	5.5	11.5	1.2	- 6.0	2.09
6/5/62	14.4	14.4	1.33	19.2	19.2	0.4	0.0	1.00
7/19/62	15.9	14.6	0.84	13.3	12.3	0.4	+ 1.0	0.92
Average	13.0	16.5	0.93	12.4	14.9	0.8	- 2.5	1.20
9 days holding time								
7/18/61	15.8	23.2	1.08	17.1	25.0	2.0	- 7.9	1.46
9/16/61	16.8	12.2	0.66	11.1	8.1	1.2	+ 3.0	0.73
6/5/62	13.1	13.1	1.43	18.8	18.8	0.3	+ 0.0	1.00
7/19/62	17.4	15.2	1.00	17.4	15.2	0.4	+ 2.2	0.87
Average	15.8	15.9	1.04	16.1	16.8	1.0	- 0.7	1.04
10 days holding time								
7/18/61	14.9	16.9	1.08	16.1	18.3	1.1	- 2.2	1.14
9/16/61	21.8	9.7	0.70	15.3	6.8	1.2	+ 8.5	0.44
6/5/62	12.8	12.6	1.43	18.3	18.0	0.3	+ 0.3	0.98
7/19/62	17.0	15.1	1.00	17.0	15.1	0.2	+ 1.9	0.89
Average	16.6	13.6	1.05	16.7	14.6	0.7	+ 2.1	0.87
<u>Fall</u>								
0 days holding time								
10/12/61	24.0	0.0	1.13	27.1	0.0	1.00	+27.1	0.0
11/24/61	36.0	0.0	1.18	42.5	0.0	1.50	+42.5	0.0
Average	30.0	0.0	1.16	34.8	0.0	1.25	+34.8	0.0
1 day holding time								
10/12/61	24.0	0.0	1.18	28.3	0.0	1.00	+28.3	0.0
11/24/61	36.0	0.0	1.21	43.6	0.0	1.50	+43.6	0.0
Average	30.0	0.0	1.20	36.0	0.0	1.25	+36.0	0.0
2 days holding time								
10/12/61	24.0	0.0	1.23	29.5	0.0	1.00	+29.5	0.0
11/24/61	36.0	0.0	1.24	44.6	0.0	1.50	+44.6	0.0
Average	30.0	0.0	1.24	37.1	0.0	1.25	+37.1	0.0
3 days holding time								
10/12/61	24.0	1.9	1.28	30.7	2.3	1.00	+28.4	0.07
11/24/61	36.0	0.0	1.28	46.1	0.0	1.50	+46.1	0.0
Average	30.0	1.0	1.28	38.4	1.2	1.25	+37.2	0.03
4 days holding time								
10/12/61	26.5	6.7	1.30	34.5	8.7	1.00	+25.8	0.25
11/24/61	37.0	1.2	1.36	50.3	1.6	1.50	+48.7	0.03
Average	31.8	4.0	1.33	42.4	5.2	1.25	+37.2	0.12



TABLE I (Cont.)

Date	R	P	EZ	R	P	Diff Rate	Diff	P/R
	$\text{gm/m}^3/\text{day}$	$\frac{\text{g}}{\text{g}}$	M	$\text{gm/m}^2/\text{day}$	$\frac{\text{g}}{\text{g}}$	$\text{gm/m}^3/\text{hr}$	$\text{gm/m}^2/\text{day}$	
5 days holding time								
10/12/61	26.0	17.8	1.31	34.0	23.3	1.00	+10.7	0.69
11/24/61	32.4	0.5	1.44	46.7	0.7	1.50	+46.0	0.01
Average	29.2	9.2	1.38	40.4	12.0	1.25	+28.4	0.30
6 days holding time								
10/12/61	20.4	16.0	1.33	27.1	21.3	1.00	+ 5.8	0.79
11/24/61	32.2	0.7	1.54	50.5	1.1	1.50	+49.4	0.02
Average	26.3	8.4	1.44	38.8	11.2	1.25	+27.6	0.29
7 days holding time								
10/12/61	12.4	12.8	1.30	16.1	16.6	1.00	- 0.5	1.03
11/24/61	30.7	2.2	1.63	50.0	3.7	1.50	+46.3	0.07
Average	21.6	7.5	1.47	33.1	10.2	1.25	+22.9	0.31
8 days holding time								
10/12/61	12.8	11.5	1.27	16.3	14.6	1.00	+ 1.7	0.90
11/24/61	27.3	0.8	1.72	46.9	1.4	1.50	+45.5	0.03
Average	20.1	6.2	1.50	31.6	8.0	1.25	+23.6	0.25
9 days holding time								
10/12/61	11.5	9.6	1.24	14.2	11.9	1.00	+ 2.3	0.84
11/24/61	26.1	1.6	1.80	47.0	2.9	1.50	+44.1	0.06
Average	18.8	5.6	1.52	30.6	7.4	1.25	+23.2	0.24
10 days holding time								
10/12/61	15.8	11.8	1.20	19.0	14.2	1.00	+ 4.8	0.75
11/24/61	26.3	0.9	1.80	47.4	1.7	1.50	+45.7	0.04
Average	21.1	6.4	1.50	33.2	8.0	1.25	+25.2	0.24

TABLE II  
COMMUNITY METABOLISM AT REFINERY B

Date	R	P	EZ	R	P	Diff Rate	Diff	P/R
	$\frac{g}{m^3/day}$			$\frac{g}{m^2/day}$		$\frac{g}{m^3/hr}$	$\frac{g}{m^2/day}$	
			M					
<u>Winter</u>								
0 days holding time								
1/15/60	36.0	0.0	0.75	27.0	0.0	1.5	+27.0	0.00
3/12/60	24.0	0.0	0.80	19.2	0.0	1.0	+19.2	0.00
Average	30.0	0.0	0.78	23.1	0.0	1.25	+23.1	0.00
16 days holding time								
1/15/60	36.0	0.0	0.90	32.4	0.0	1.5	+32.4	0.00
3/12/60	24.0	0.0	1.00	24.0	0.0	1.0	+24.0	0.00
Average	30.0	0.0	0.95	28.2	0.0	1.25	+28.2	0.00
20 days holding time								
1/15/60	24.0	0.0	1.00	24.0	0.0	1.0	+24.0	0.00
3/12/60	24.0	0.0	1.00	24.0	0.0	1.0	+24.0	0.00
Average	24.0	0.0	1.00	24.0	0.0	1.0	+24.0	0.00
37 days holding time								
1/15/60	30.0	0.0	1.20	36.0	0.0	1.25	+36.0	0.00
3/12/60	24.0	0.0	1.20	28.8	0.0	1.0	+28.8	0.00
Average	27.0	0.0	1.20	32.4	0.0	1.13	+32.4	0.00
60 days holding time								
1/15/60	16.0	1.4	1.50	24.0	2.1	1.5	+21.9	0.09
3/12/60	21.4	2.6	1.50	32.1	3.9	1.0	+28.2	0.12
Average	18.7	2.0	1.50	28.1	3.0	1.25	+25.0	0.11
<u>Spring</u>								
0 days holding time								
3/27/62	48.0	0.0	0.75	36.0	0.0	2.0	+36.0	0.00
5/10/60	24.0	0.0	0.75	18.0	0.0	1.0	+18.0	0.00
Average	36.0	0.0	0.75	27.0	0.0	1.5	+27.0	0.00
16 days holding time								
3/27/62	17.8	6.0	1.23	21.8	7.3	1.7	+14.5	0.33
5/10/60	24.0	0.0	0.75	18.0	0.0	1.0	+18.0	0.00
Average	20.9	3.0	0.99	19.9	3.7	1.4	+16.7	0.19
20 days holding time								
3/27/62	18.0	5.5	0.62	11.2	3.4	1.5	+ 7.8	0.30
5/10/60	29.2	19.6	0.80	23.4	15.7	1.0	+ 7.7	0.67
Average	23.6	12.6	0.71	17.3	9.6	1.25	+ 7.7	0.55

R = Community Respiration  
P = Gross photosynthesis  
EZ = Euphotic Zone

Diff = Diffusion  
P/R = Photosynthesis/community respiration

TABLE II (Cont.)

Date	R	P <sub>g</sub>	EZ	R	P <sub>g</sub>	Diff Rate	Diff	P/R
	gm/m <sup>3</sup> /day		M	gm/m <sup>2</sup> /day		gm/m <sup>3</sup> /hr	gm/m <sup>2</sup> /day	
37 days holding time								
3/27/62	2.3	10.0	0.92	2.1	9.2	2.0	- 7.1	4.38
5/10/60	26.8	19.2	1.00	26.8	19.2	1.0	+ 7.6	0.72
Average	14.6	14.6	0.96	14.5	14.2	1.5	+ 0.3	0.98
60 days holding time								
3/27/62	5.1	3.6	1.33	6.8	4.8	0.5	+ 2.0	0.71
5/10/60	3.4	4.0	1.50	5.1	6.0	0.9	- 0.9	1.18
Average	4.3	3.8	1.42	6.0	5.4	0.7	+ 0.6	0.90
<u>Summer</u>								
0 days holding time								
6/22/60	24.0	0.0	0.75	18.0	0.0	1.0	+18.0	0.00
8/7/61	24.0	0.0	0.50	12.0	0.0	1.0	+12.0	0.00
Average	24.0	0.0	0.63	15.0	0.0	1.0	+15.0	0.00
16 days holding time								
6/22/60	14.0	11.2	0.75	10.5	8.4	1.0	+ 2.1	0.80
8/7/61	24.6	18.2	0.54	14.3	9.8	0.5	+ 4.5	0.69
Average	19.3	14.7	0.65	12.4	9.1	0.75	+ 3.3	0.73
20 days holding time								
6/22/60	22.0	16.4	0.80	17.6	13.1	1.0	+ 4.5	0.74
8/7/61	27.4	28.1	0.62	17.0	17.4	0.3	- 0.4	1.02
Average	24.7	22.3	0.71	17.3	15.3	0.7	+ 2.0	0.88
37 days holding time								
6/22/60	21.6	16.0	1.00	21.6	16.0	1.0	+ 5.6	0.74
8/7/61	19.5	5.3	1.54	30.1	8.2	1.0	+21.9	0.27
Average	20.6	10.7	1.27	25.9	12.1	1.0	+13.8	0.47
60 days holding time								
6/22/60	13.2	7.2	1.50	19.8	10.8	1.0	+ 9.0	0.55
8/7/61	2.9	6.2	0.77	2.2	4.8	0.5	- 2.6	2.18
Average	8.1	6.7	1.14	11.0	7.8	0.75	+ 3.2	0.71
<u>Fall</u>								
0 days holding time								
10/13/61	28.8	0.0	0.60	17.2	0.0	1.2	+17.2	0.00
16 days holding time								
10/13/61	26.4	0.0	0.70	18.5	0.0	1.1	+18.5	0.00
20 days holding time								
10/13/61	27.0	3.4	0.72	19.4	2.5	1.0	+16.9	0.13

TABLE II (Cont.)

Date	R	P <sub>g</sub>	EZ	R	P <sub>g</sub>	Diff Rate	Diff	P/R
	gm/m <sup>3</sup> /day		M	gm/m <sup>2</sup> /day		gm/m <sup>3</sup> /hr	gm/m <sup>2</sup> /day	
	37 days holding time							
10/13/61	6.2	7.0	0.80	4.9	5.6	1.0	- 0.7	1.14
	60 days holding time							
10/13/61	29.8	19.3	1.00	29.8	19.3	1.1	10.5	0.65

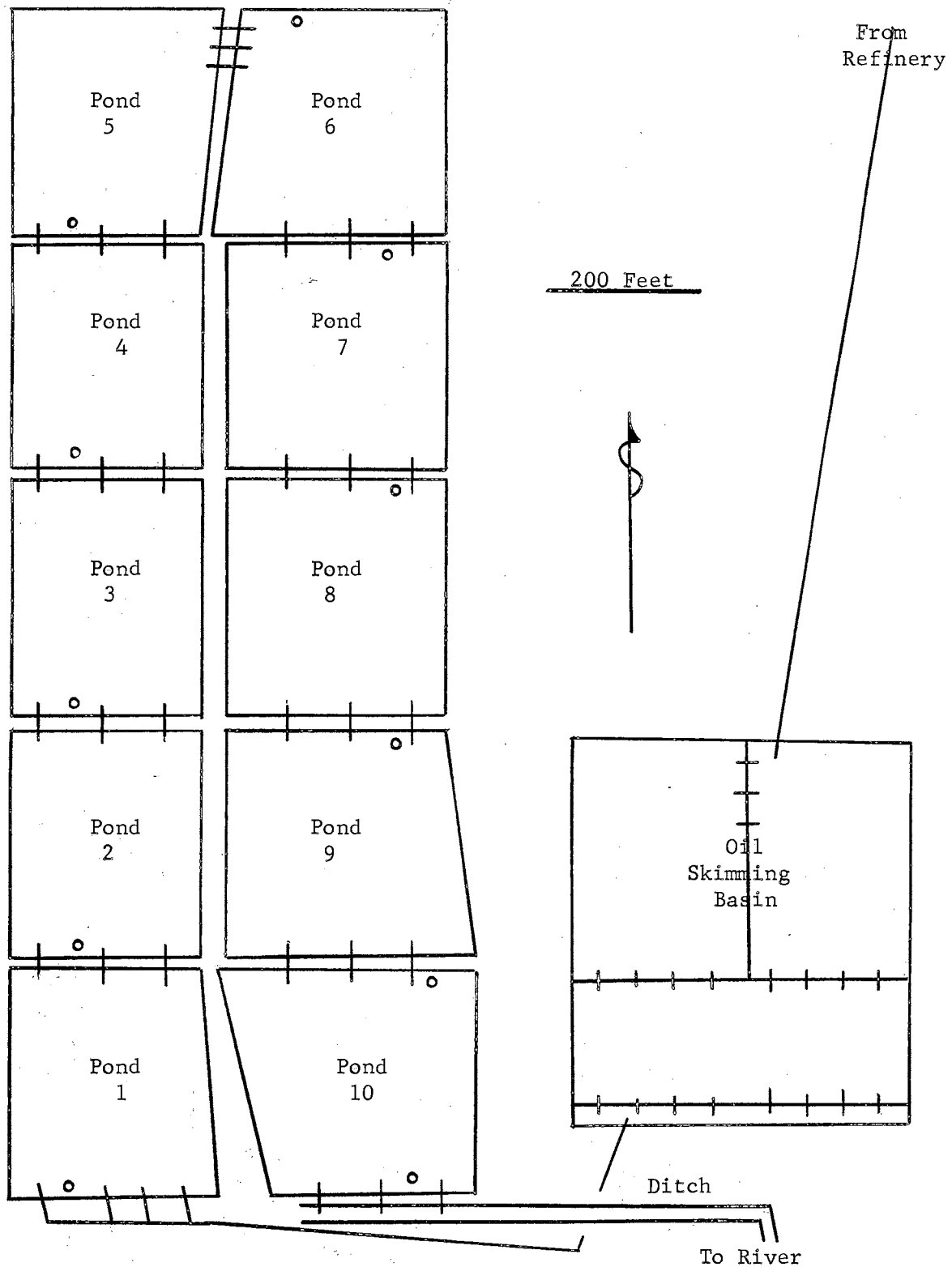


Figure 1: Diagram of the holding pond system at Refinery A. o = Sampling stations. - = Underwater pipe.

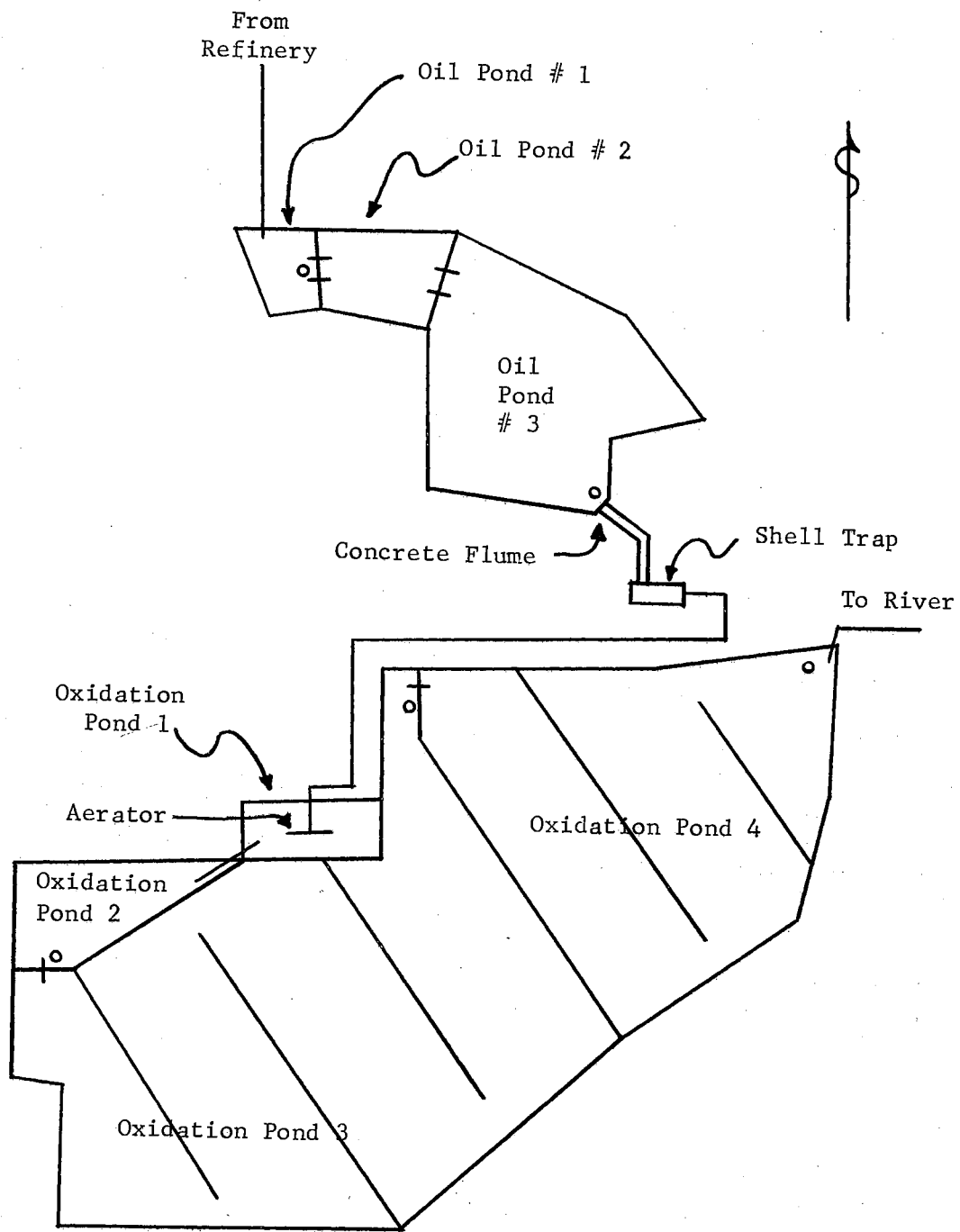


Figure 2: Diagram of the holding pond system at Refinery B. o = Sampling stations. - = Underwater pipe.

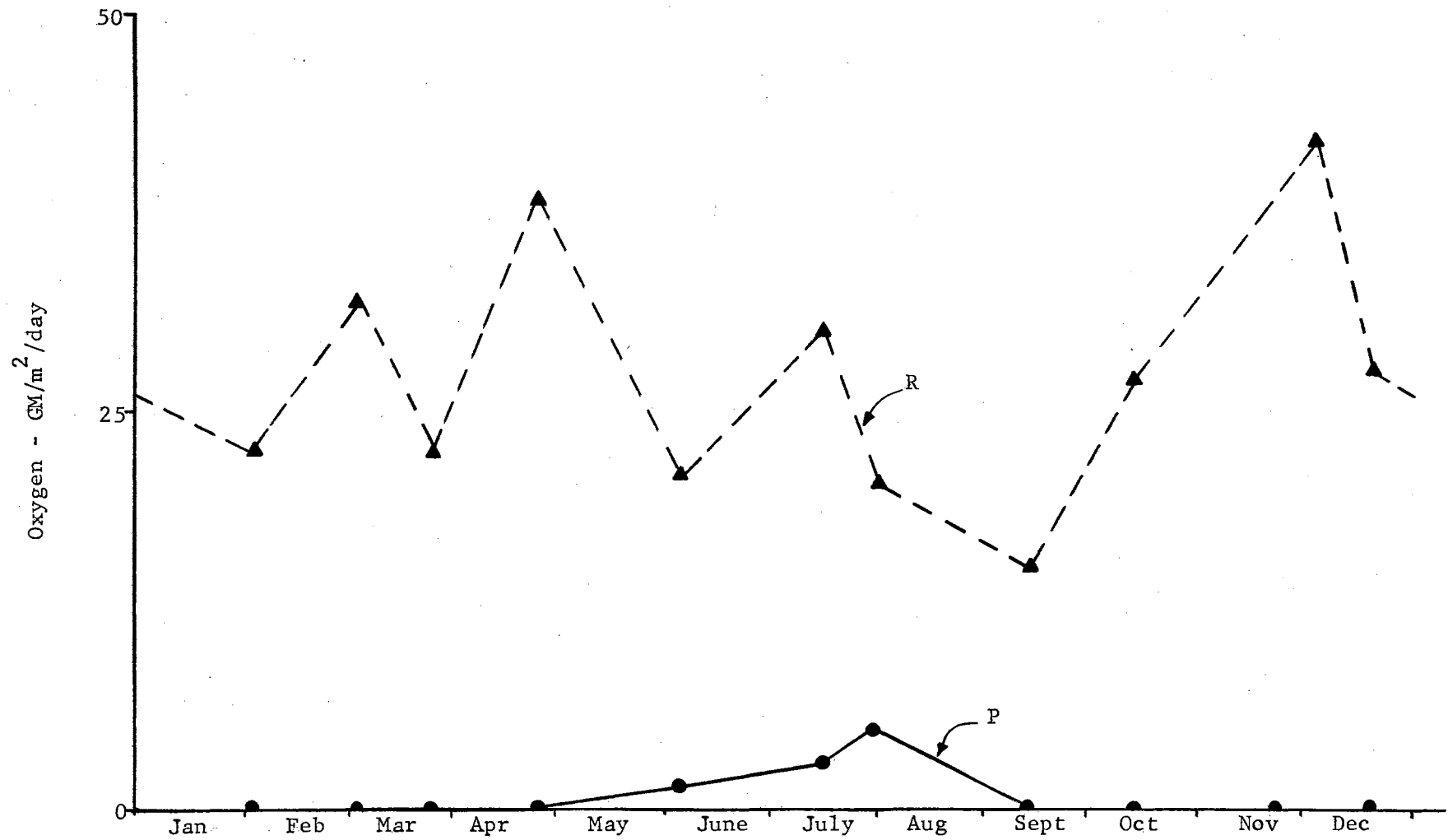


Figure 3: Annual course of productivity (P) and community respiration (R) for Refinery A at the beginning of the system.

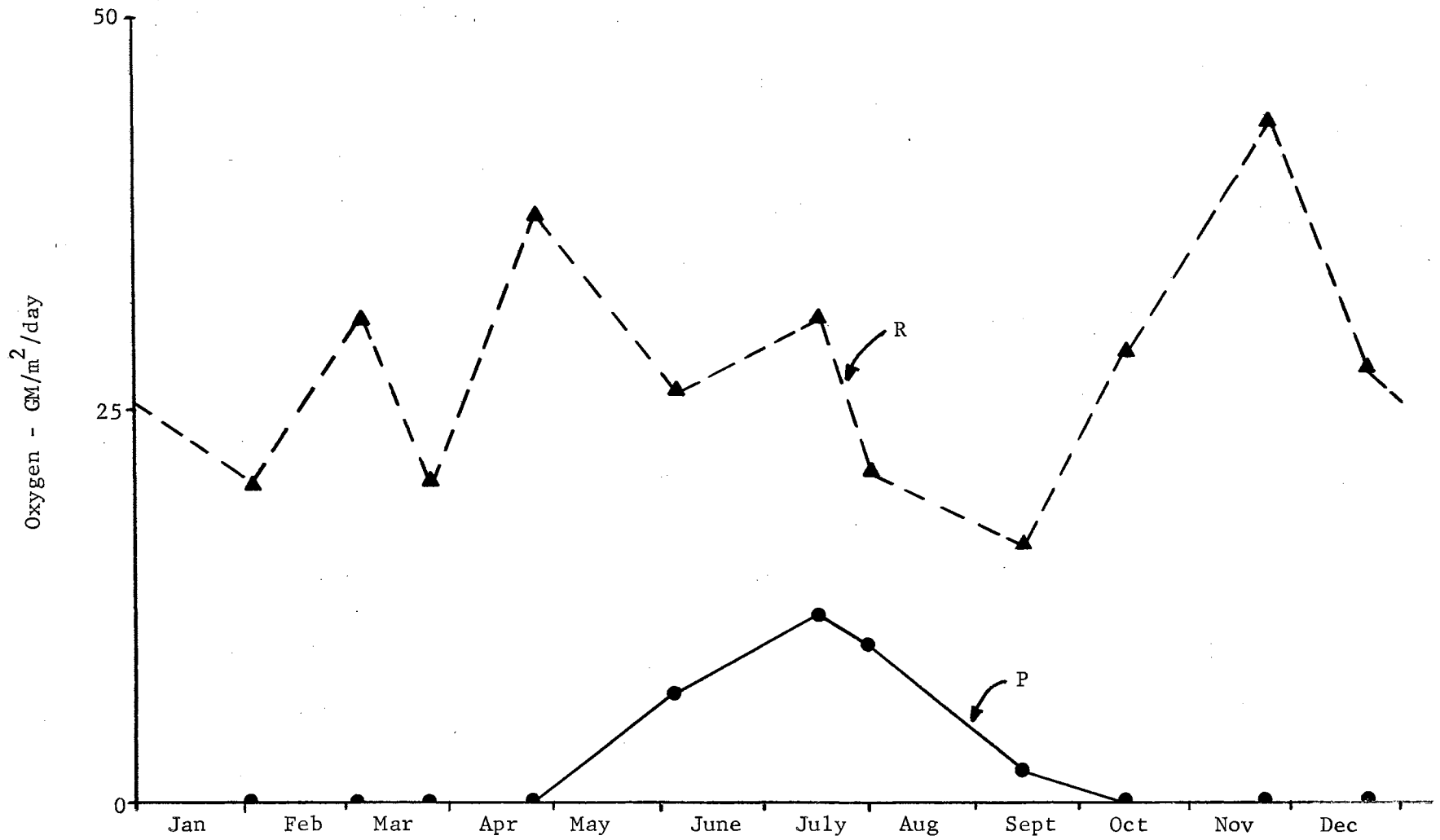


Figure 4: Annual course of productivity (P) and community respiration (R) for Refinery A at one day holding time.



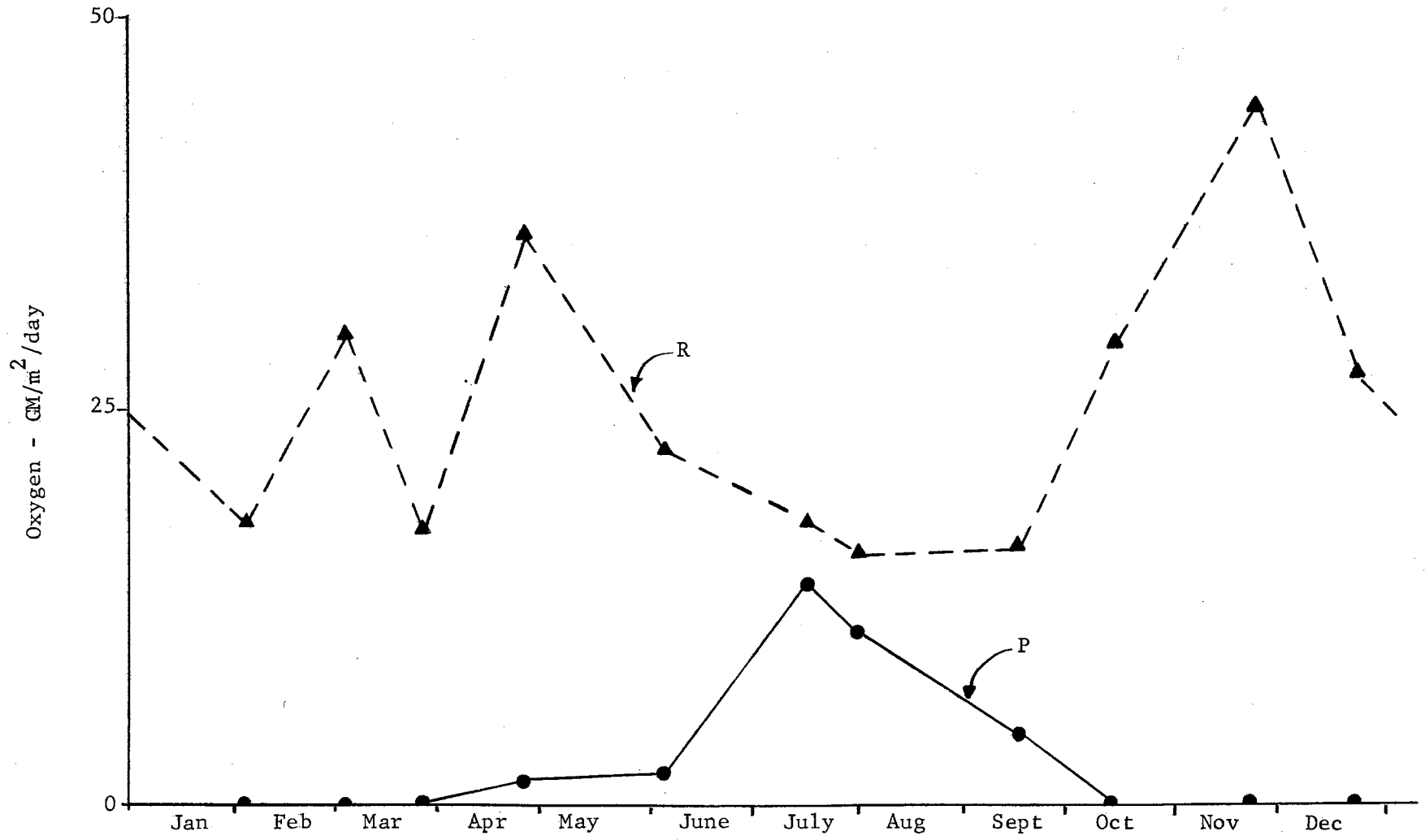


Figure 5: Annual course of productivity (P) and community respiration (R) for Refinery A at two days holding time.

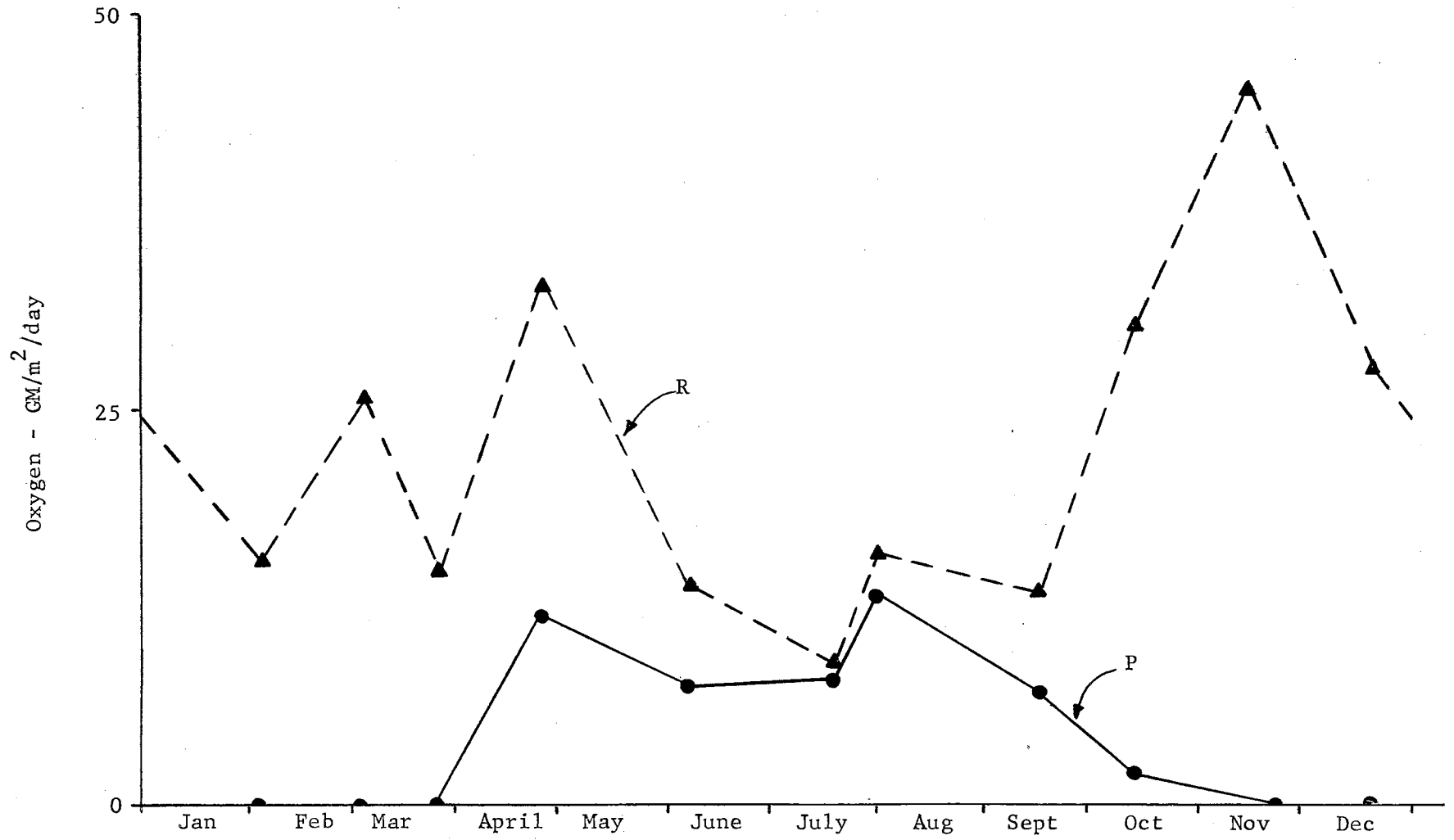


Figure 6: Annual course of productivity (P) and community respiration (R) for Refinery A at three days holding time.

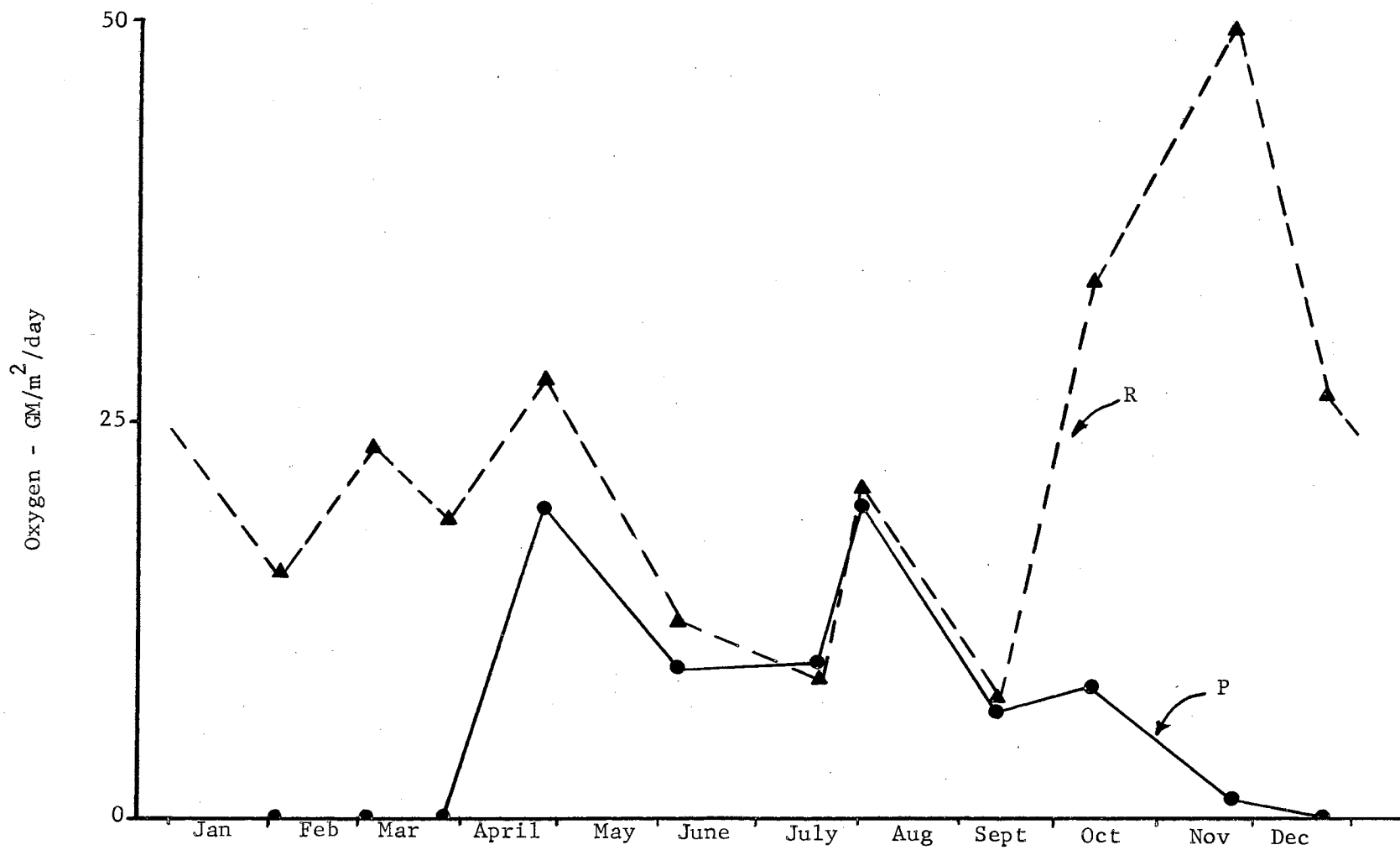


Figure 7: Annual course of productivity (P) and community respiration (R) for Refinery A at four days holding time.

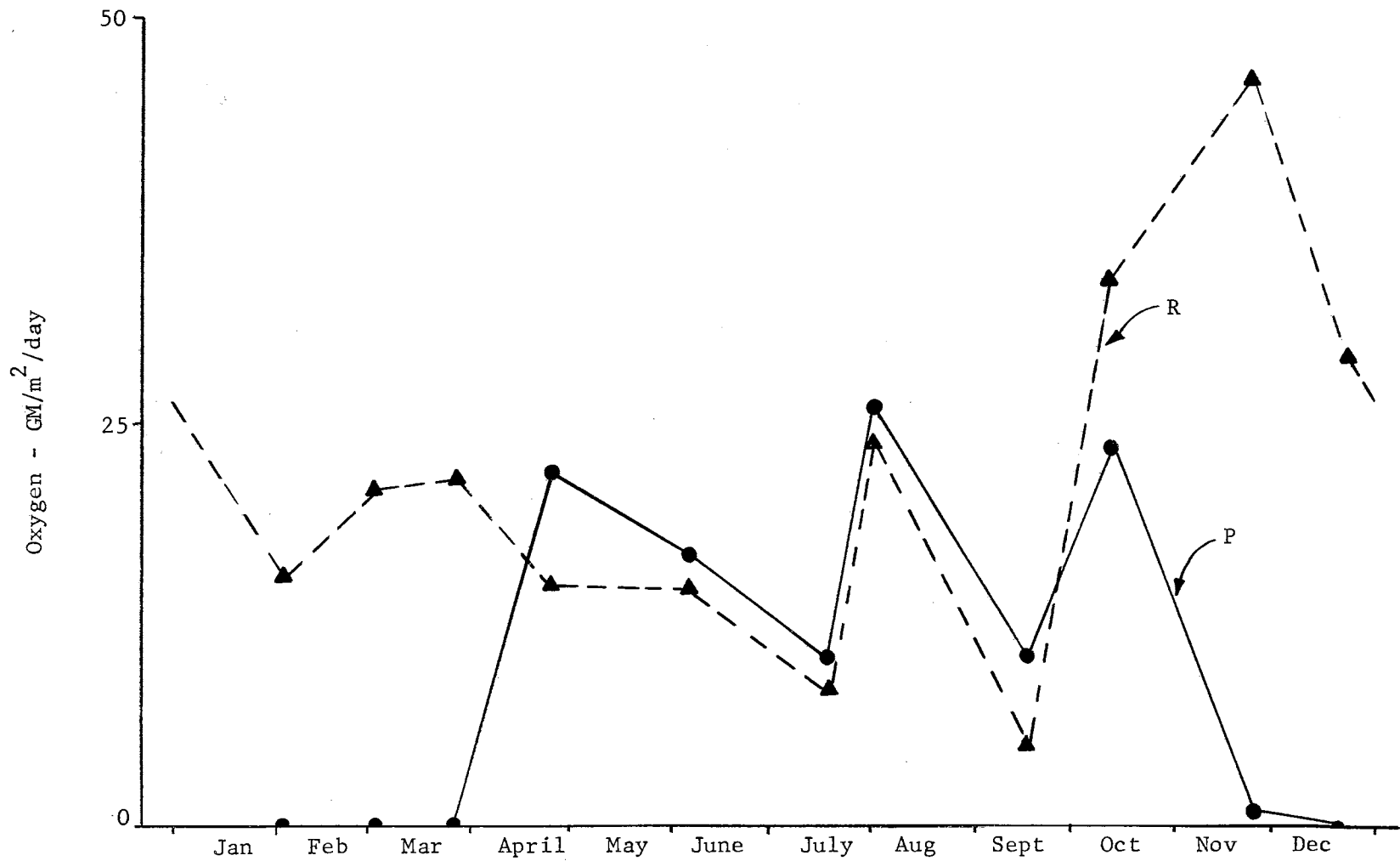


Figure 8: Annual course of productivity (P) and community respiration (R) for Refinery A at five days holding time.

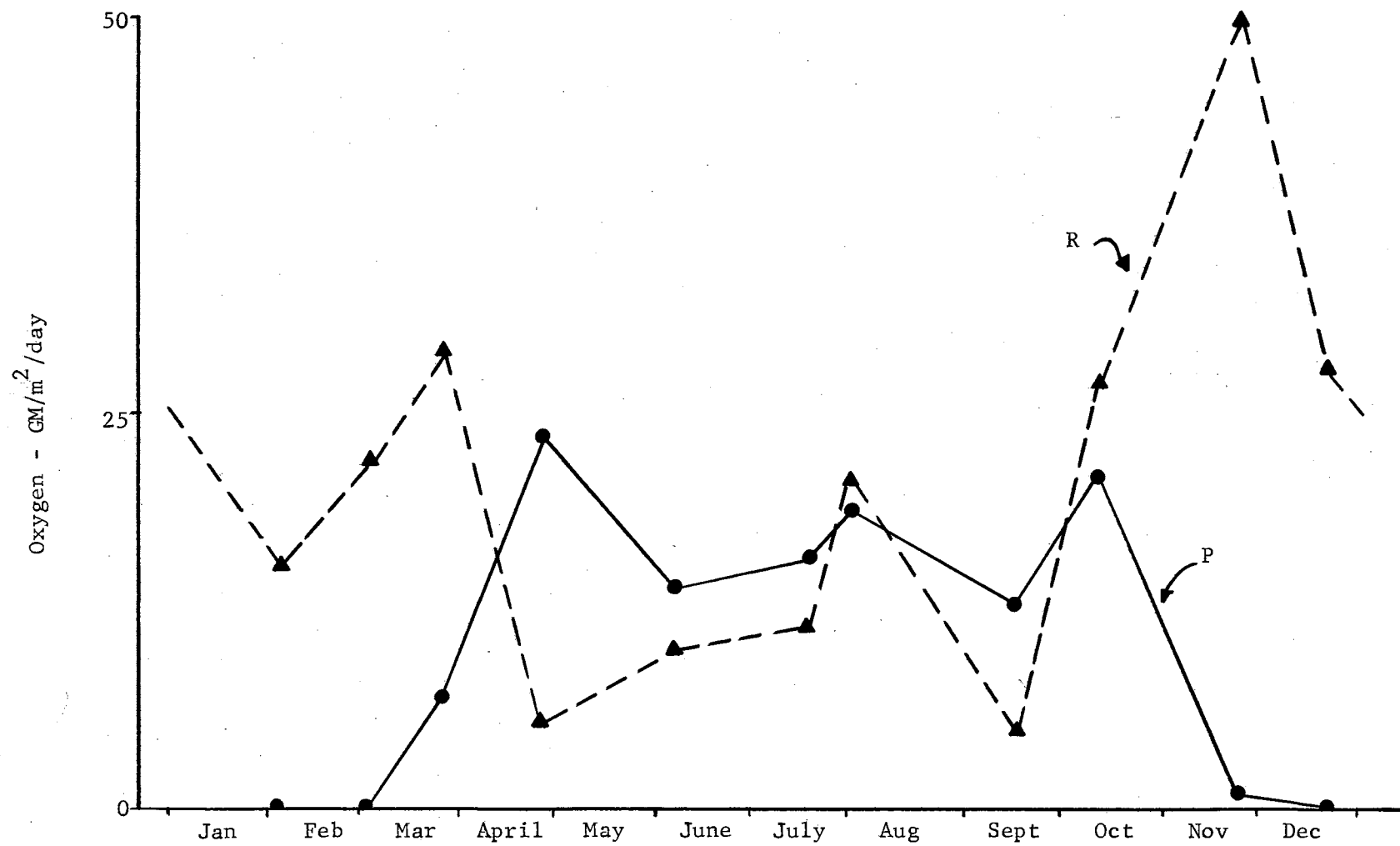


Figure 9: Annual course of productivity (P) and community respiration (R) for Refinery A at six days holding time.

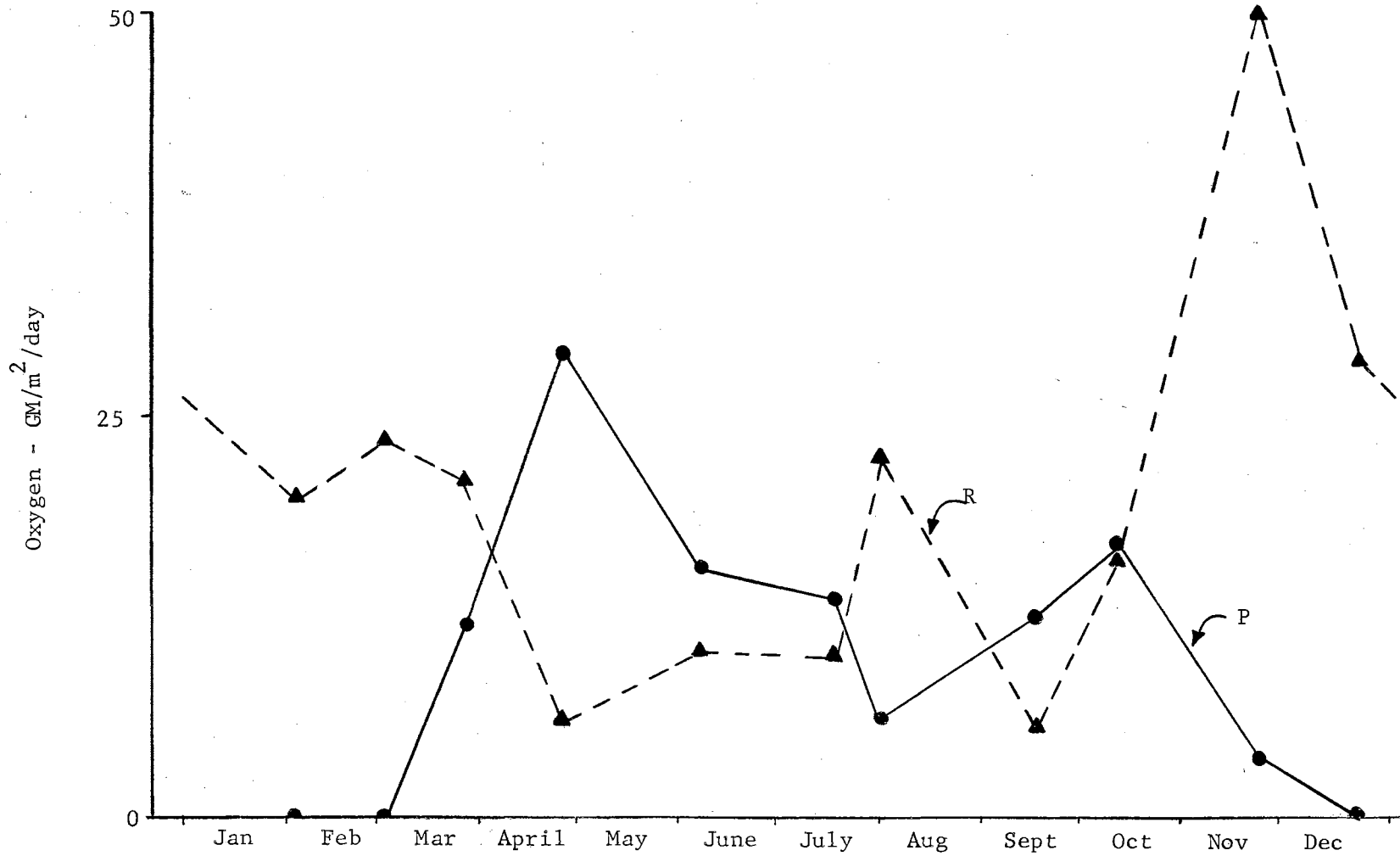


Figure 10: Annual course of productivity (P) and community respiration (R) for Refinery A at seven days holding time.

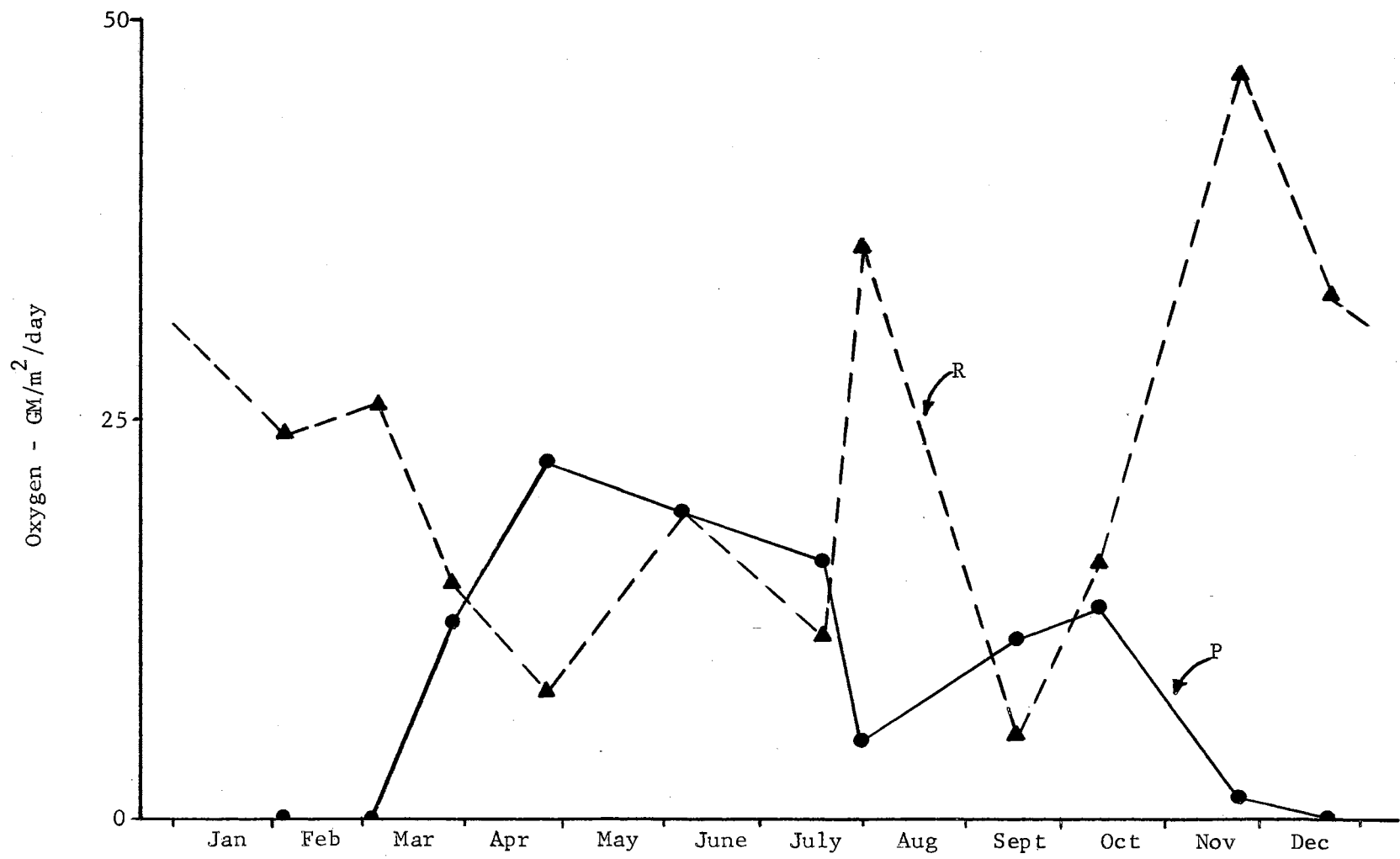


Figure 11: Annual course of productivity (P) and community respiration (R) for Refinery A at eight days holding time.

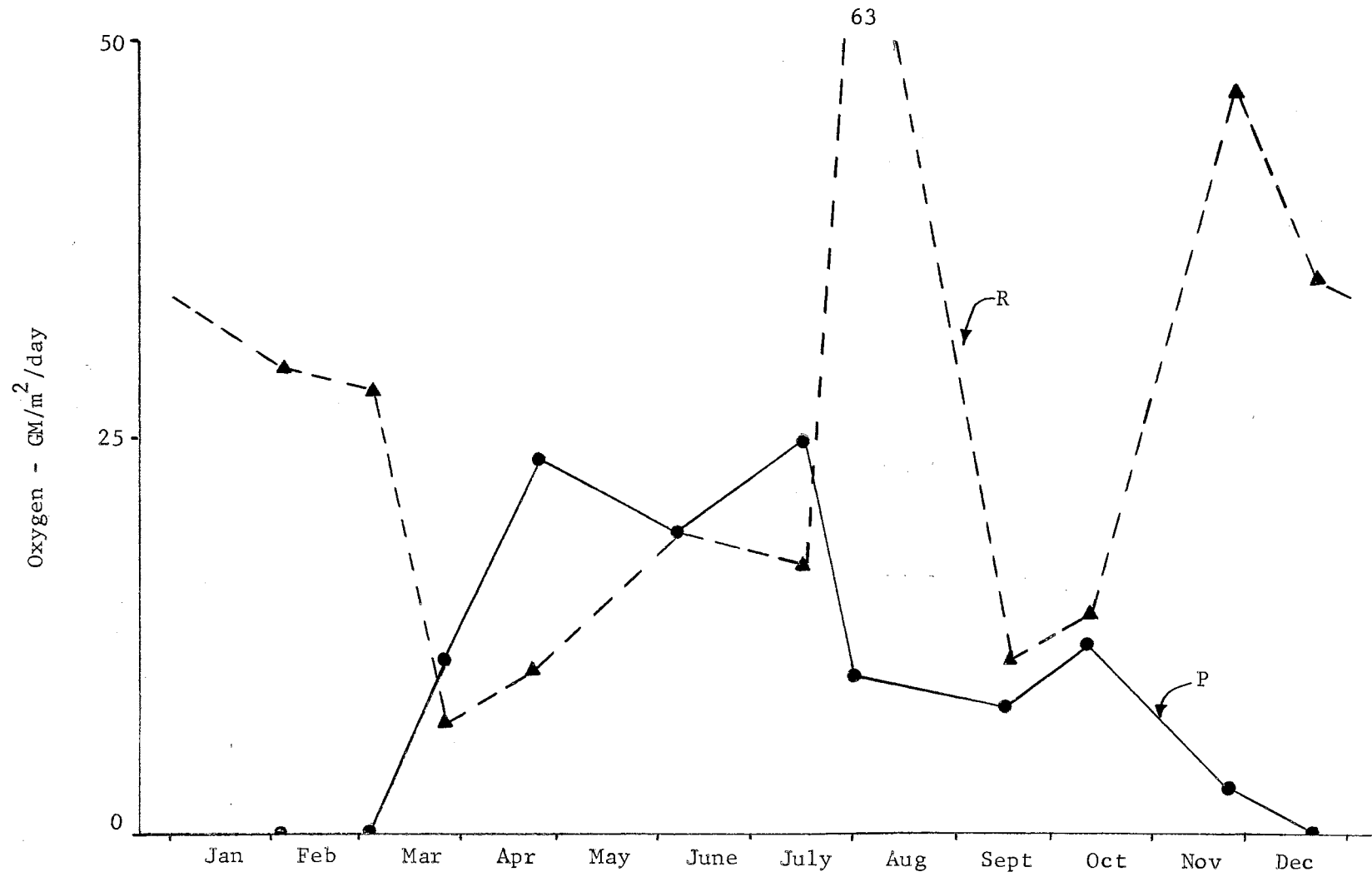


Figure 12: Annual course of productivity (P) and community respiration (R) for Refinery A at nine days holding time.



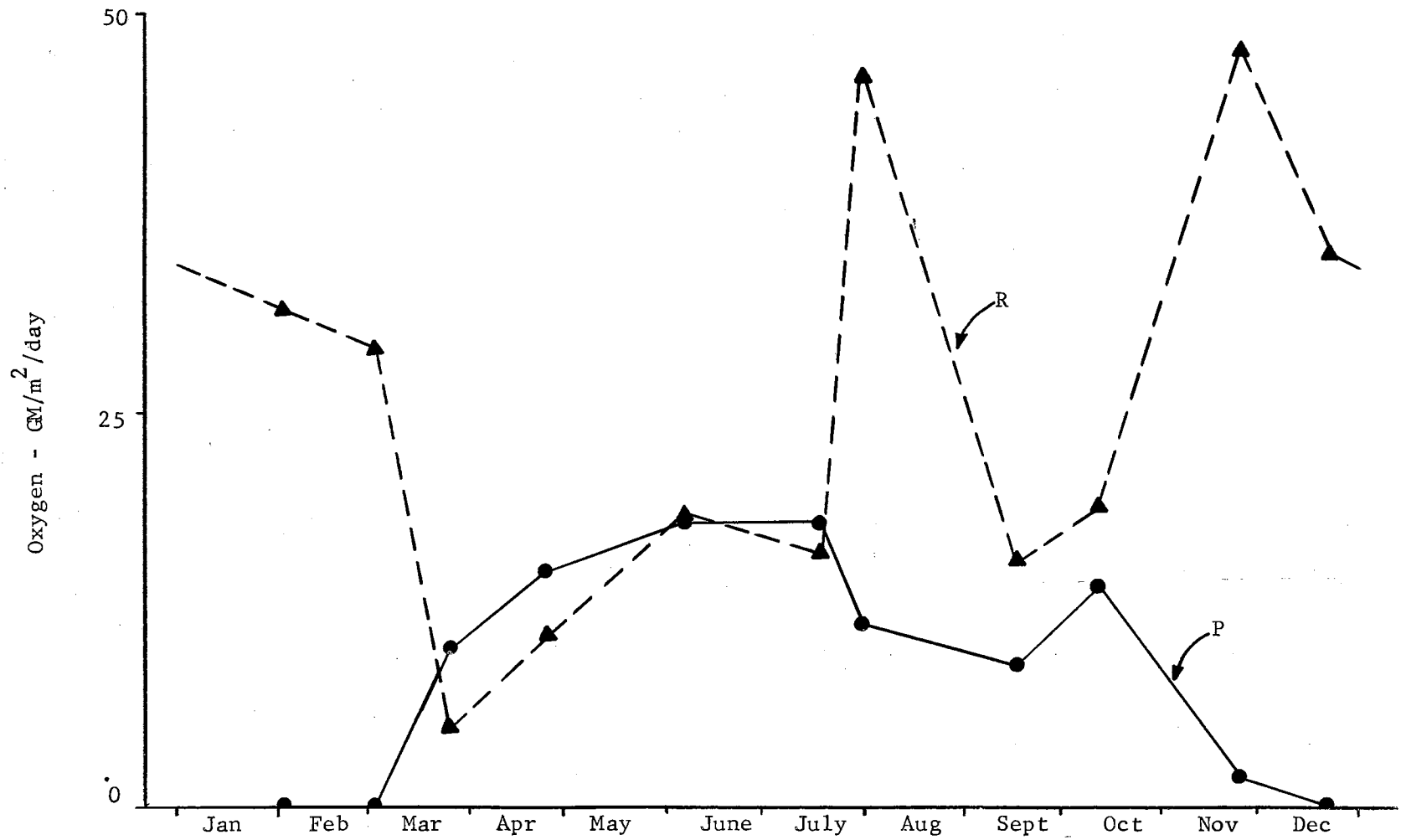


Figure 13: Annual course of productivity (P) and community respiration (R) for Refinery A at ten days holding time.

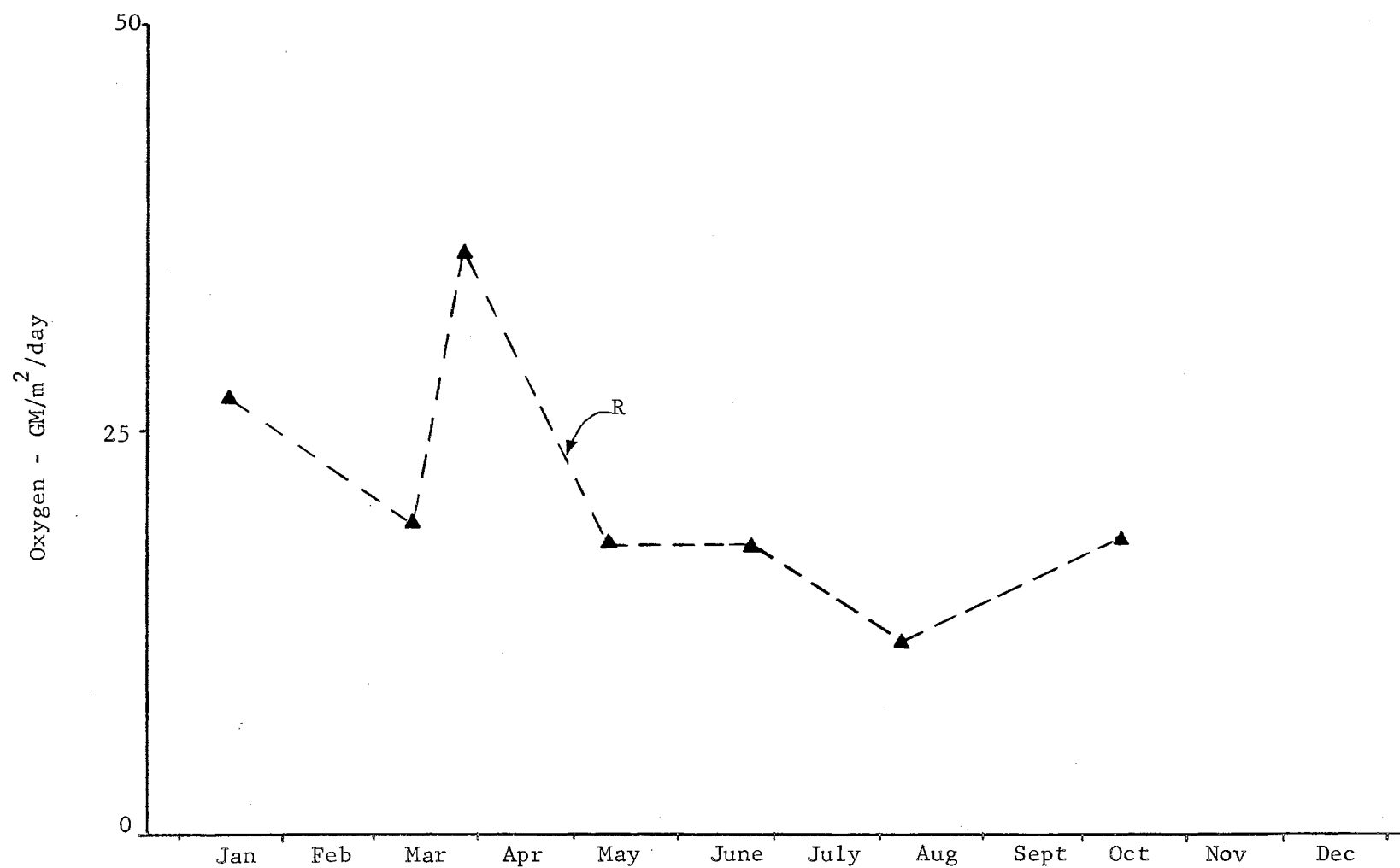


Figure 14: Annual course of productivity (P) and community respiration (R) for Refinery B at the beginning of the system.

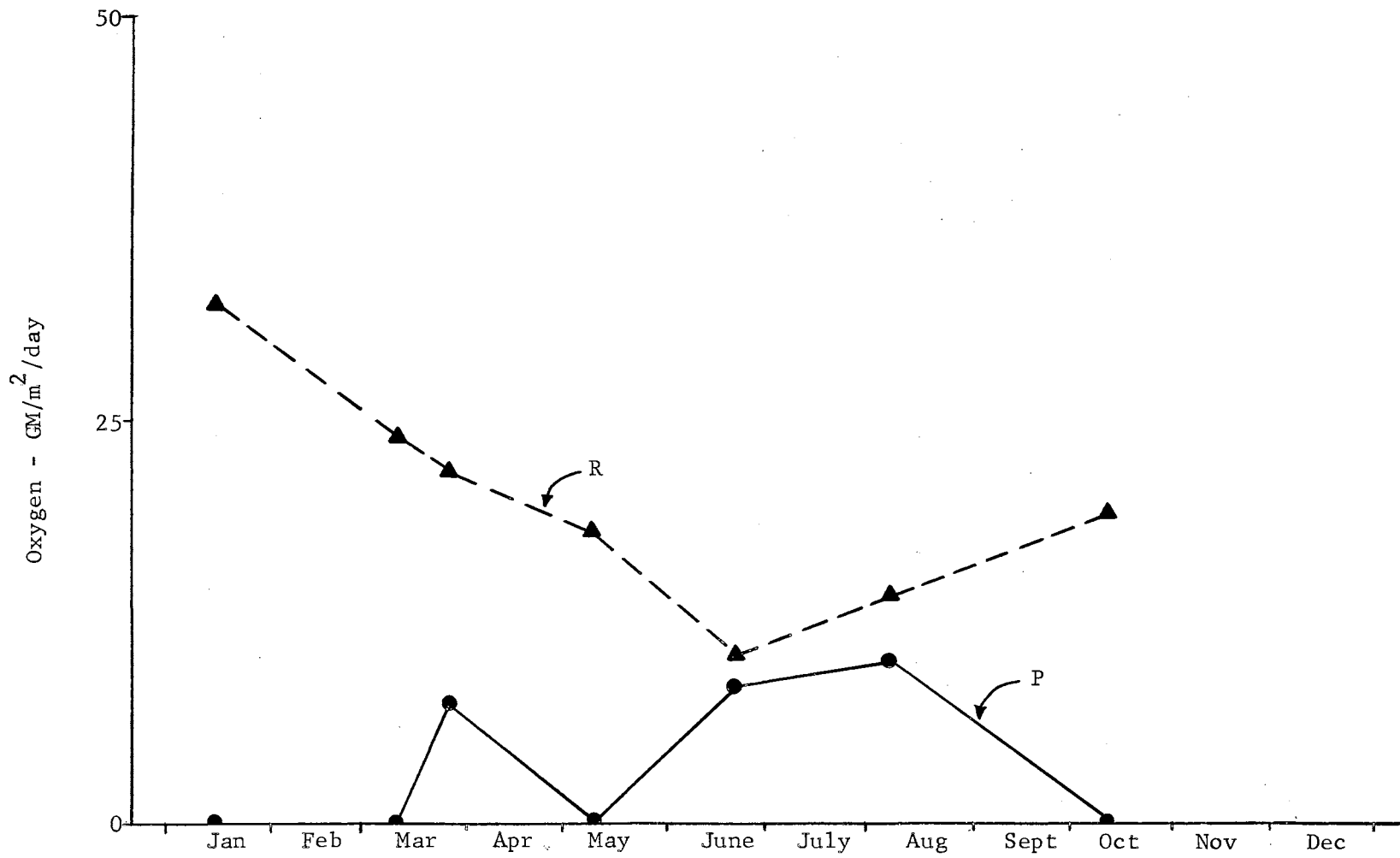


Figure 15: Annual course of productivity (P) and community respiration (R) for Refinery B at 16 days holding time.

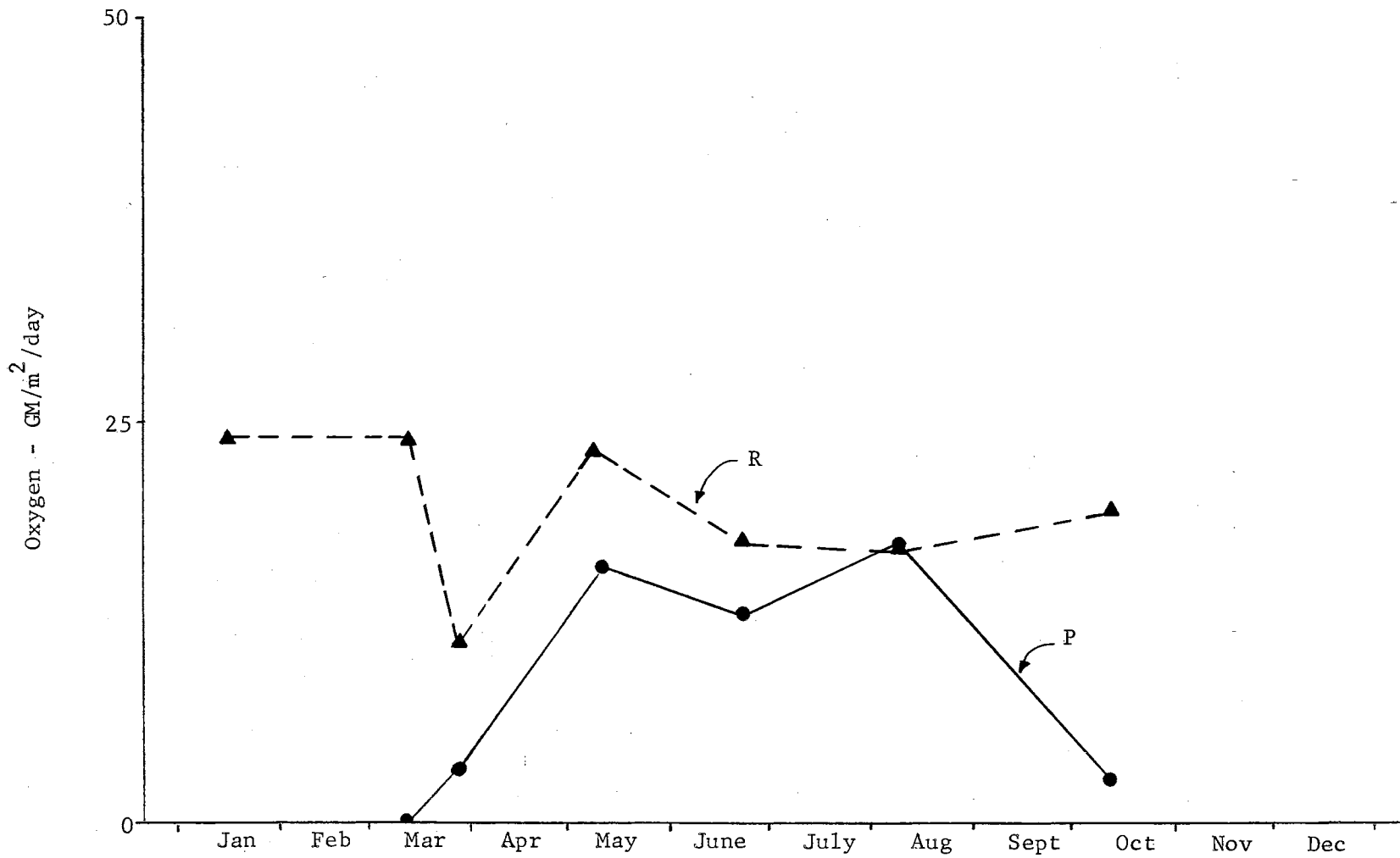


Figure 16: Annual course of productivity (P) and community respiration (R) for Refinery B at 20 days holding time.

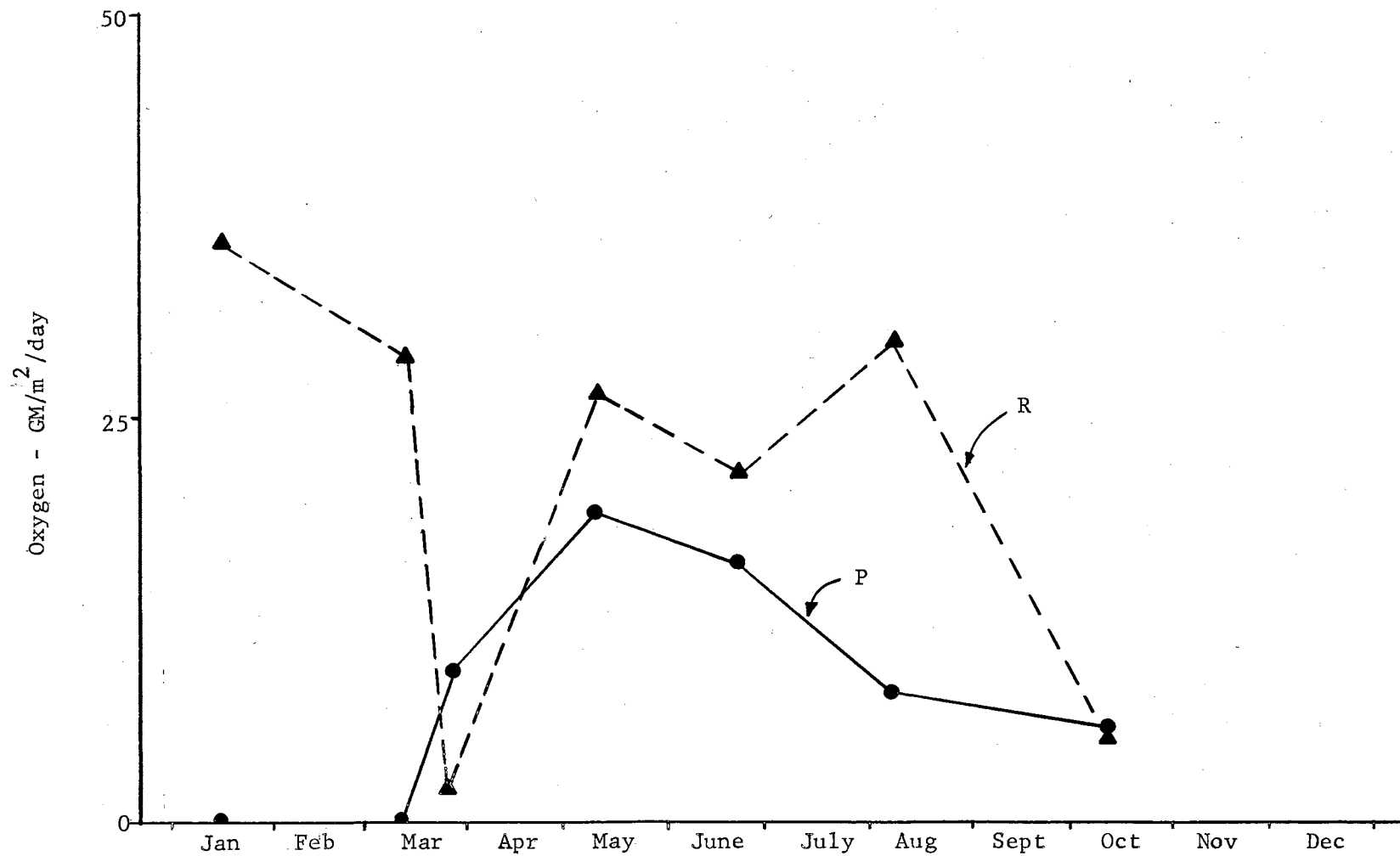


Figure 17: Annual course of productivity (P) and community respiration (R) for Refinery B at 37 days holding time.

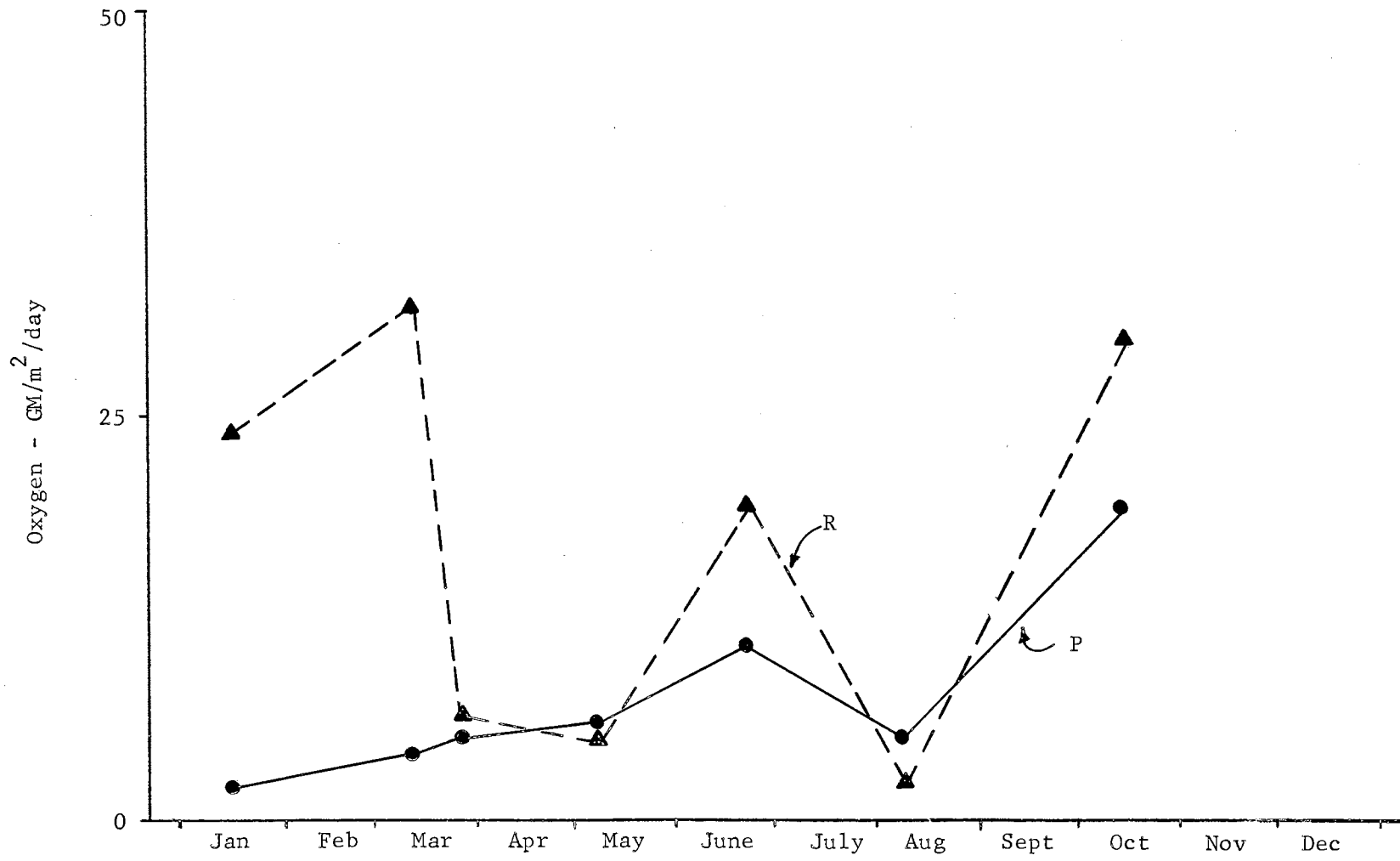


Figure 18: Annual course of productivity (P) and community respiration (R) for Refinery B at 60 days holding time.

VITA

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Doctor of Philosophy

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