

OXYGEN BALANCE IN A STREAM RECEIVING DOMESTIC  
AND OIL REFINERY EFFLUENTS

By

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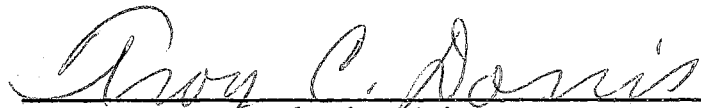
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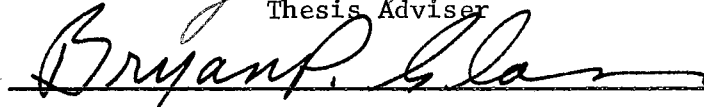
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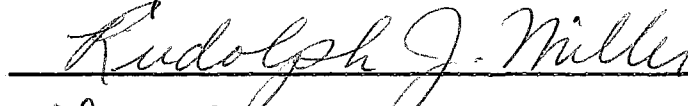
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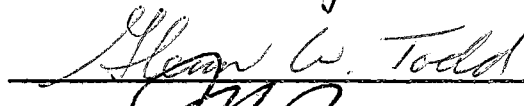
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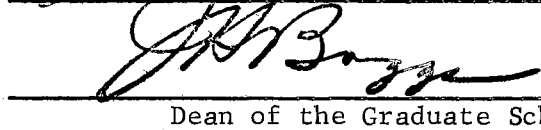
  
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## PREFACE

The objectives of the present study of the oxygen balance in a stream receiving domestic and oil refinery effluents were to investigate the physico-chemical and biological changes occurring in the stream and determine the magnitude of community metabolism in the oxygen "sag" zone.

Dr. Troy C. Dorris served as major adviser. Drs. Rudolph J. Miller, Bryan P. Glass, Frederick M. Baumgartner and Glen W. Todd served on the advisory committee and criticized the manuscript. Dr. B. J. Copeland of the Institute of Marine Sciences, University of Texas, gave advice on several occasions. Dr. Jerry L. Wilhm and Gene Dorris helped make field collections. The assistance of all these people is appreciated.

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## CHAPTER I

### INTRODUCTION

In a stream receiving oxygen demanding wastes, self purification depends upon water temperature, rate of flow and supply of oxygen. Oxygen demand is a result of respiration by aerobic bacteria, animals and plants and of chemical oxygen demand. Oxygen supply is dependent upon reaeration from the atmosphere and release of oxygen in photosynthesis by green plants. The relation between oxygen demand and oxygen supply at any time is the oxygen balance.

The amount and significance of oxygen contributed to water by photosynthesis has not been established. Many workers disregard photosynthesis when calculating the oxygen budget in streams, on the assumption that photosynthesis is relatively unimportant. However, photosynthesis may be a very significant source of oxygen, and if so, it must be accounted for in oxygen balance studies (Hull, 1960; Winberg and Sivko, 1962).

Photosynthetic oxygen production in water has been estimated by light and dark bottle methods. This procedure can account only for phytoplankton photosynthesis and respiration. Community metabolism, involves production and respiration of oxygen by the whole community. In the upstream-downstream procedure, based on diurnal changes of oxygen concentration (Odum, 1956), it is assumed that in a stretch of water



receiving no run off water, the change in oxygen concentration is dependent upon: (1) exchange of oxygen with the atmosphere in a direction which depends upon the degree of saturation of the water; (2) release of oxygen into the water as a result of photosynthesis; and (3) the uptake of oxygen from water as a result of respiration by aerobic bacteria, plants and animals and of chemical oxygen demand (Odum, 1956; Edwards and Owens, 1962).

Only a few investigators have used the diurnal rate of change method to study community metabolism of streams. The Neuse River System of North Carolina was studied by Hoskin (1959), a chalk stream in England by Edwards and Owens (1962) and a stream in the Southern Great Plains by Duffer (1965). Experiments on miniature streams have been conducted by Odum and Hoskin (1957), McIntire et al, (1964) and Copeland and Gloyna (1965). Most of the investigations were conducted in relatively unpolluted waters. Metabolism of polluted streams and bays has been investigated by Odum (1956) and Odum and Wilson (1962).

In the present study, the oxygen contributed by algae to the oxygen balance of a stream receiving domestic and oil refinery effluents was estimated by the diurnal rate of change method. Twenty-three diurnal analyses were made along a 97 km stretch of the stream from March 1963 to May 1964. Since the dissolved oxygen "sag" occurs at a significant point of minimum dissolved oxygen concentration, most of the metabolism analyses were made in the sag zone. Other physico-chemical and biological conditions were studied in relation to water quality.

## CHAPTER II

### DESCRIPTION OF THE STUDY AREA

#### General Description

Skeleton Creek originates in Garfield County, Oklahoma, 13 km northwest of Enid. The stream flows southeasterly for approximately 121 km and empties into Cimarron River in Logan County, 8 km north of Guthrie (Fig. 1). Stream elevation is 387 m at the origin and 277 m at the mouth. Average gradient is 1.1 m/km.

Skeleton Creek is a small prairie stream with high banks, shallow water and a shifting bottom of sand and silt. Stream width was normally 6 to 9 m along most of the stream course and widened to approximately 15 m near the mouth. Depth of water varied from 15 to 30 cm in riffles to over 1.5 m in deeper pools. Riffles were more abundant in the headwaters, and pools were more common in the middle and lower stretches. Low flow occurred throughout the greater part of the year. Spring and early summer rains produced rapidly fluctuating water levels. Flow was augmented by several tributaries including Boggy, Hackberry, Wolf, Ephraim, Otter and Bridge Creeks. Mean measured annual flow was 41.5 cu m/min at kilometer 97.

Several species of deciduous trees and shrubs lined the stream banks below kilometer 18. Elm, hackberry, cottonwood, chinquapin oak and post oak trees and plum, rough sumac, smooth sumac and rough leaf

dogwood shrubs were dominant. The channel was littered with logs and brush. There were no attached macrophytes but an occasional algal scum formed in front of log jams and in large quiet pools.

The Skeleton Creek basin lies in a mixed-grass association between mixed prairie and tall-grass savannah on undulating prairies dissected by wooded valleys. The watershed area is approximately 161,840 ha, of which approximately 80% is cultivated or open pasture.

The basin is located in Permian sandstone, clays and shales (Galloway, 1960). The upper basin is underlain by heavy red shales of the Lower Enid Formation. The red shales are commonly referred to as Permian "Red Beds" (Gray and Galloway, 1958).

Brown prairie soils with dense, heavy, clayey subsoils and prairie soils with both friable and heavy subsoils are prevalent (Fitzpatrick, Boatright and Rose, 1939). These soils developed under tall grass in clayey red beds. Heavy subsoils existing throughout north-central Oklahoma are favorable for production of small grains. Winter wheat is the major crop.

Rainfall averaged 76 cm/yr for the 61 year period through 1958; however, there were wide annual fluctuations (Galloway, 1960). Annual rainfall varied from 30.5 cm during 1936 to 132 cm for 1908. Monthly rainfall averaged 10.2 cm for May and June and about 2.5 cm for December, January and February.

Winters are fairly mild and characterized by numerous, short, cold periods with northerly winds. Temperature sometimes drops below freezing for short periods. Summers are warm and the temperature occasionally exceeds 40° C. Temperature varied from -31° C to 46° C and averaged 15° C

for the 61 year period through 1955 (Galloway, 1960). The sun shines approximately 70% of the time. The frost-free season averages 215 days, from about 30 March to 31 October (Fitzpatrick et al., 1939). Average wind velocity is 18 km/hr.

A number of oil wells were drilled in the basin between kilometers 8 and 50 during the present study. Older oil fields are located between kilometers 10 and 71.

Historically, Skeleton Creek drainage basin is located in what originally was called the Cherokee Strip in Indian Territory. The Chisholm Trail, a route for driving cattle from Oklahoma and Texas to the railroad at Wichita, Kansas, passed near the stream.

#### Sources of Waste Effluents

Several organic effluents entered Skeleton Creek. Approximately 340,650 liters/day of domestic sewage wastes from two small lagoons entered Skeleton Creek approximately 10 km north of the confluence of Skeleton Creek with Boggy Creek. Sewage effluents from Northeastern State Hospital entered the creek 3 km below the lagoons. Treatment facilities at the hospital consisted of an Imhoff tank, a trickling filter and a final settling basin. Discharge data were not available. Boggy Creek enters Skeleton Creek 6 km below the hospital and receives effluents from at least three sources. Sewage effluent from an Air Force Base entered Boggy Creek 16 km above its confluence with Skeleton Creek. Treatment facilities consisted of a trickling filter, a two-stage digester, sludge drying beds and a final stage settling tank. Average discharge in May 1964 was 700,225 liters/day. The Enid

municipal sewage effluent entered Boggy Creek about 1.6 km above the confluence with Skeleton Creek. Treatment included preaeration, primary settling, final aeration, activated sludge and sludge drying. Approximately 15 million liters of sewage were treated daily, of which 5.7 million liters were pumped to an oil refinery for cooling water. The remainder was discharged into Boggy Creek. Waste treatment processes at the oil refinery included a separator which removed free oil particles and acted as a settling basin for solids. Effluent from the separator flowed into a small lake where it was held for approximately 25 days. Effluent was pumped from the lake to a series of settling pits. Pit effluent was charged with carbon dioxide from an underwater burner to lower the pH, and passed through a series of five oxidation ponds. The final effluent of approximately 2.7 million liters/day entered Boggy Creek about 60 m above the Enid Sewage Plant outfall.

#### Sampling Stations

Eight study stations were selected on Skeleton Creek, numbered according to their distance in kilometers downstream from the confluence of Boggy Creek with Skeleton Creek. Station 6 was selected as the first station with a thorough mixing of Boggy Creek flow with that of Skeleton Creek. Wilhm (1965) studied macroinvertebrate populations at the same stations.

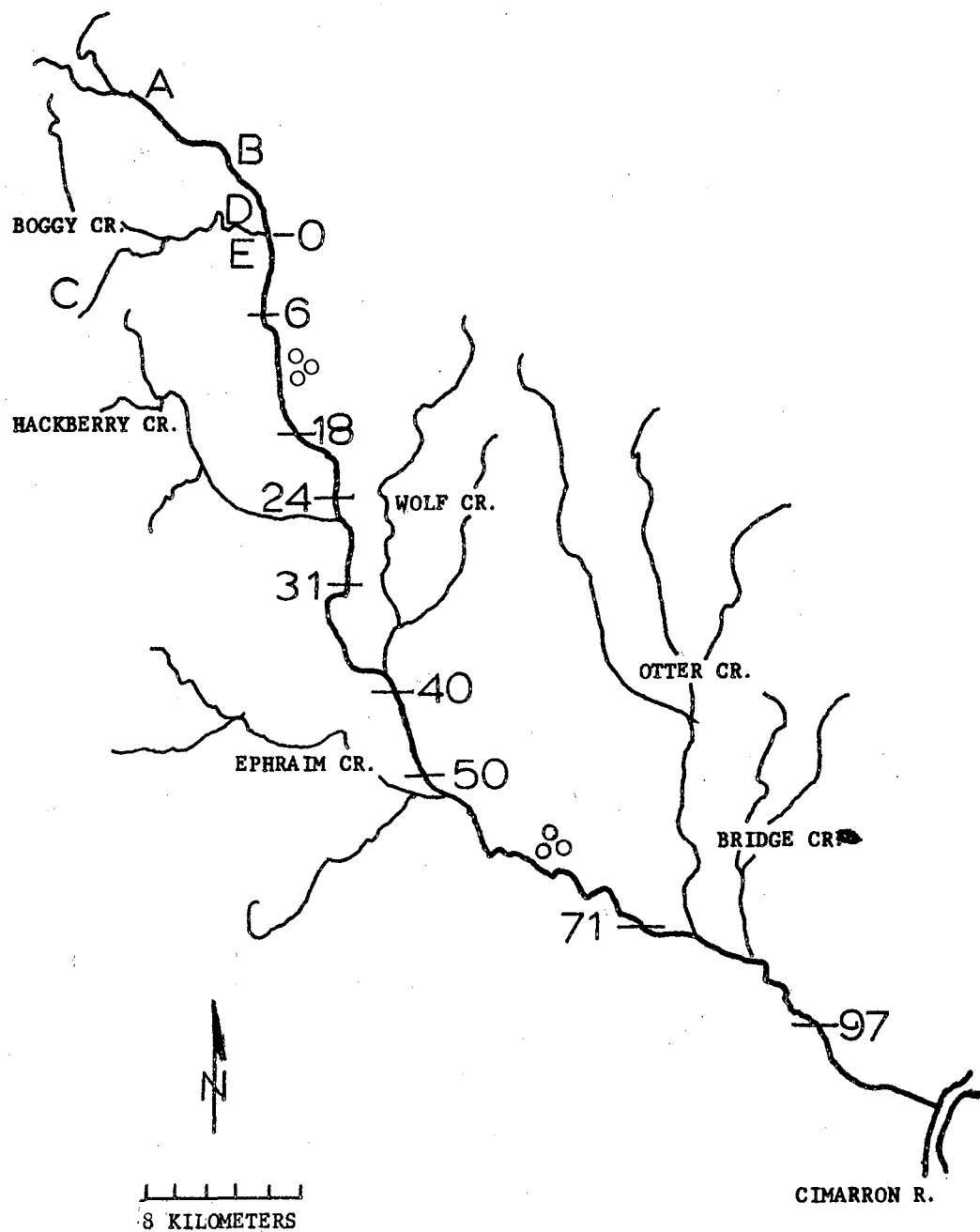


Fig. 1. Skeleton Creek and major tributaries. Sampling stations are indicated by distance in kilometers downstream from the confluence of Boggy and Skeleton Creeks. A = sewage lagoons, B = hospital outfall, C = air base outfall, D = oil refinery outfall, E = Enid sewage outfall,  $\circ\circ$  = oil wells.

## CHAPTER III

### MATERIALS AND METHODS

#### Physico-chemical

Water temperature was measured with a mercury thermometer. Concentration of hydrogen ions, expressed as pH, was determined with a Hellige pH Comparator. Conductivity measurements were made at 25 C with a Wheatstone Bridge. Turbidity, as measured with a Bausch and Lomb Spectronic 20 Colorimeter calibrated against a Jackson Turbidimeter, is expressed as "Turbidity Units," roughly equivalent to mg/liter.

Depth of light penetration was determined with a Gem submarine photometer. The euphotic zone was considered to be the depth at which light was 1% of surface intensity. In most cases the stream bottom was in the euphotic zone. Solar radiation was measured continuously with a pyrliimnometer at the Oklahoma State University Weather Station, and light intensity at the stream was measured with a Weston Illumination Meter.

Retention time of water between upstream and downstream stations was estimated by dividing volume by flow. Mean width and depth were obtained from cross-sectional measurements every 91 m between upstream and downstream stations. Total length was determined by summing the 91 m intervals. Flow was measured by a method described by Robins and Crawford (1954).

Methyl orange and phenolphthalein alkalinity were determined by titrating with N/50 sulphuric acid. Chemical oxygen demand, biochemical oxygen demand and chlorides were determined by methods outlined in Standard Methods for the Examination of Water and Wastewater (A.P.H.A., 1960).

Duplicate water samples for determination of dissolved oxygen concentration were fixed by the Alsterberg (Azide) modification of the Winkler method and titrated in the field. Oxygen saturation values were taken from Truesdale, Downing and Lowden (1955). Total residues were determined by evaporating 50 ml of water and weighing the residue. Fixed residue (total residue minus ashed weight) was calculated by ashing the residue at 600 C.

#### Biological Methods

A water sample of 600 ml was fixed with 10% formalin for species diversity counts, and 500 ml of the sample was centrifuged three times in a Foerst Plankton Centrifuge at 166 ml/min. Counts were made in a Palmer Cell at 430 X. Species diversity plots were made following the procedure described by Yount (1956).

Planktonic chlorophyll a analyses were made by filtering 100 ml of water through Millipore filters of 0.45  $\mu$  pore size. The residue was extracted in 10 ml of 90% acetone for 24 hr at 5 C and centrifuged. Optical density of the chlorophyll extract was determined at 665  $m\mu$  with a Bausch and Lomb Spectronic 20 Photoelectric Colorimeter. Planktonic chlorophyll a was determined from the equation: chlorophyll a in mg/l of 90% acetone =  $13.4 d_{665} \times \text{liters acetone/liters water}$  (Odum, McConnel and Abbott, 1958).



Benthic chlorophyll was determined from core samples. Chlorophyll was extracted with 20 ml of 90% acetone. Optical density of the chlorophyll extract was measured with a Beckman DU Spectrophotometer or a Bausch and Lomb Spectronic 20 Colorimeter. Optical density at 665 m $\mu$  was read with the spectrophotometer and concentration of chlorophyll a computed using the equation: chlorophyll a in g/m<sup>2</sup> of 90% acetone =  $13.4 d_{665} \times \text{liters acetone/core m}^2$ ; where  $d_{665}$  = optical density of acetone extract at 665 m $\mu$  and  $\text{core m}^2 = 0.000804$ . Optical density at 665 m $\mu$  was measured with a Spectronic 20 and converted to chlorophyll a concentration using a calibration curve (Fig. 2).

#### Measurement of Community Metabolism

Gross photosynthesis and respiration were measured from diurnal changes in concentration of dissolved oxygen between upstream and downstream stations (Odum, 1956; Edwards and Owens, 1962). Dissolved oxygen concentration was measured every two hours in daylight and every three hours in darkness at each station.

Oxygen concentration at two stations are shown in Fig. 3. The solid line in Fig. 3A represents the downstream station, and the dashed line, which has been moved to the right 270 min, represents the upstream station. The line shift corresponds to retention time of water between upstream and downstream stations. The difference in oxygen concentration between the curves represents the change in concentration which occurred in the water flowing between the two stations. Saturation values of dissolved oxygen for both stations were averaged and plotted in a single curve (Fig. 3B). Rate-of-change of oxygen concentration

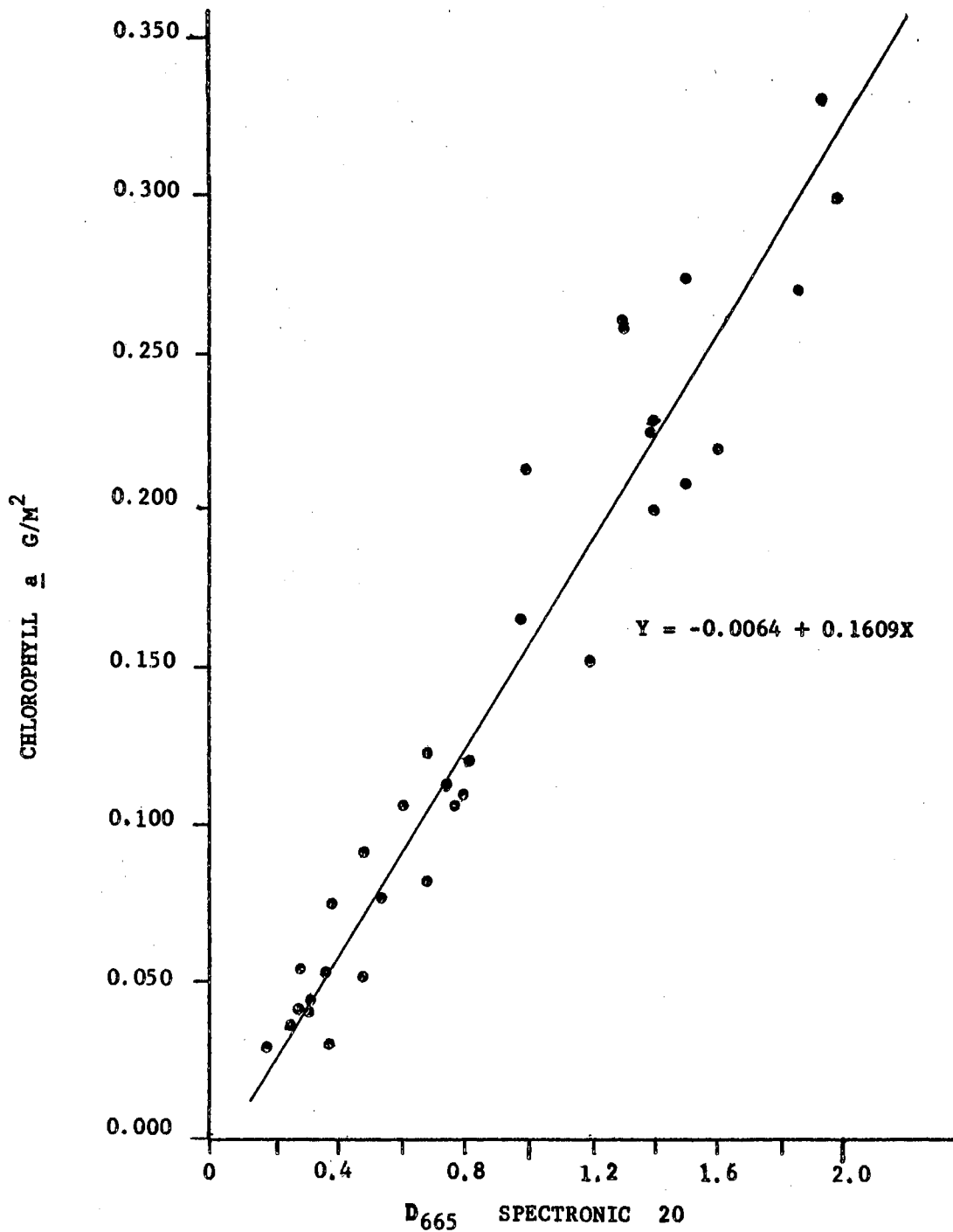
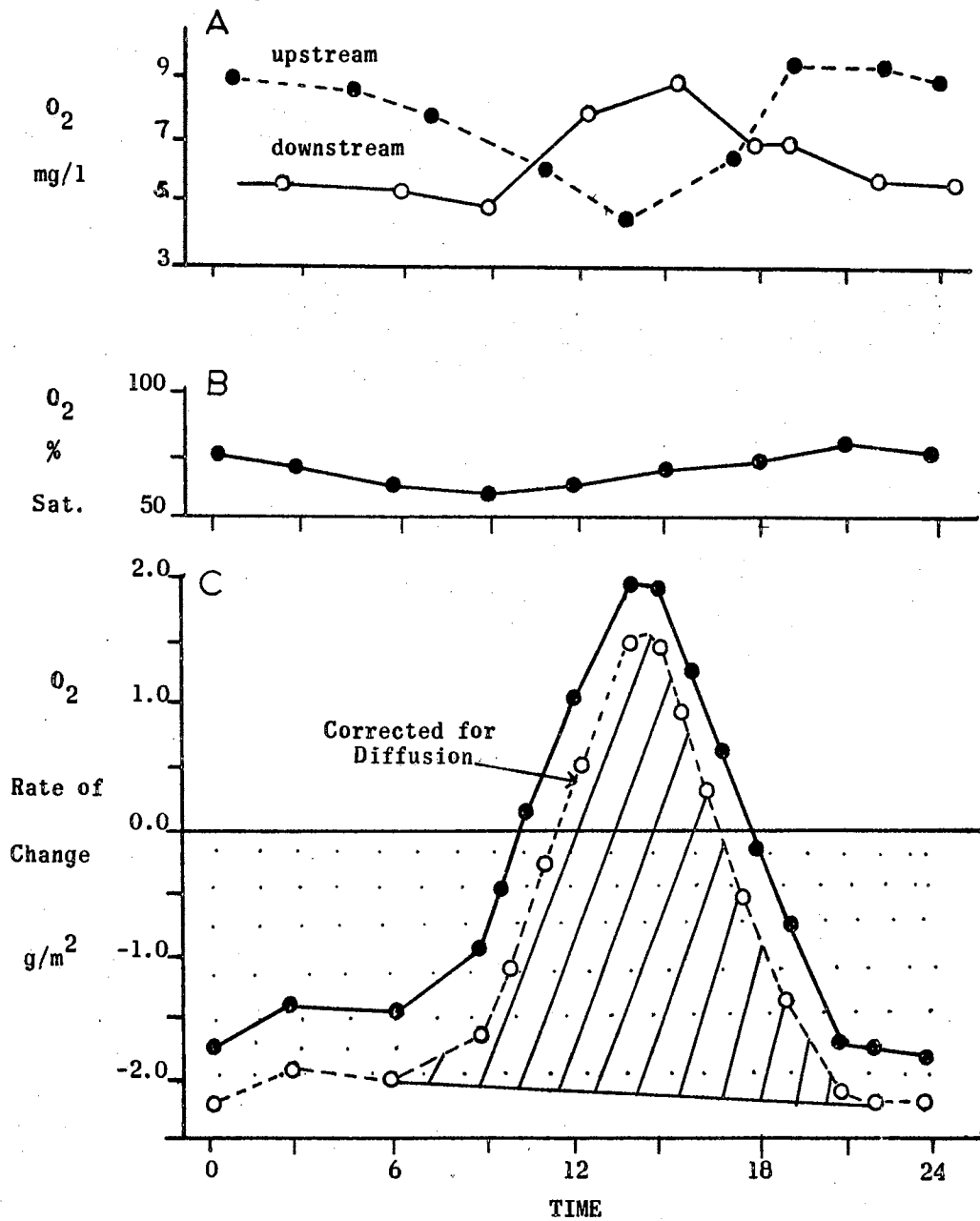


Fig. 2. Calibration curve for conversion of optical density measured colorimetrically to concentration of chlorophyll in the extract.

per unit area was determined as the product of the difference between upstream and downstream curves and the mean depth of the stream (Fig. 3C).

The rate of change curve was corrected for diffusion by the methods of Odum and Hoskin (1958). The exchange coefficient  $K$ , for Fig. 3C was  $2.0 \text{ g O}_2/\text{m}^2 \text{ hr}$  at 0% saturation. The saturation deficit at each period was multiplied by the diffusion coefficient  $K$ , and the produce subtracted from the original rate of change curve (solid line) to correct for diffusion gain (dashed lined).

The rate of community respiration was estimated by drawing a straight line on the corrected rate of change curve from the dawn point to the lowest point at night (Odum and Wilson, 1962; Copeland and Dorris, 1962). The amount of community respiration was calculated by measuring the area (stippled) between the respiration line and the zero rate of change line. Gross photosynthesis was computed by measuring the area (cross-hatched) between the respiration line and the area above the zero rate of change line.



Exchange coefficient  $K = 2.0 \text{ g } O_2/m^2 \text{ hr at } 0\% \text{ saturation.}$

Gross production =  $22.3 \text{ g } O_2/m^2 \text{ day.}$

Community respiration =  $44.6 \text{ g } O_2/m^2 \text{ day.}$

Fig. 3. Example of the upstream-downstream diurnal curve analysis for determination of community metabolism.

## CHAPTER IV

### ENVIRONMENTAL CONDITIONS

#### Physico-chemical Conditions

The data were assigned to cool or warm seasons on the basis of total monthly precipitation and mean water temperature. The cool season included December, January and February and the warm season included March through November. Mean measured seasonal physico-chemical conditions are shown in Tables I, II, III and Figures 4 to 16.

#### Precipitation

Mean precipitation was 10.2 cm/month for the warm season and 1.14 cm/month during the cool season (U. S. Weather Bureau Records, Enid). Precipitation varied from 0.28 cm during December to 24 cm in July (Table I). Rainfall exceeded 15.2 cm in May, June and July and was less than 2.54 cm in December, January and February. Rainfalls of 7.2 cm occurred 11 May, 10.1 cm 23 June, 16.5 cm 11 July and 5.6 cm 29 August. The longest period of minimum rainfall extended from 22 November to 30 January with 0.29 cm in December.

#### Water Temperature

The maximum water temperature occurred in July and the minimum in December. Ice covered the water at most stations in December. Mean water temperature was 22.4 C in the warm season and 3.3 C in the cool

season. Water temperature exceeded 15.6 C at all stations in the warm season and was 5.0 C or less in the cool season (Table I). Water temperature varied from 0 C in December at Station 97 to 35 C in July at Station 6. Diurnal water temperature ranged from 24 C to 34 C between 6:00 a.m. and 4:00 p.m. on 24 July at Station 6. The range at Station 50 was 26 C to 30 C at the same time. The greater range at Station 6 was attributed to low flow and warming of the bottom in the shallow, unshaded, clear water. Station 50 was situated in a shaded, sluggish area where current was low, riffles were scarce and pools were common.

#### Air Temperature

Mean air temperature was 28 C in the warm season and 9.1 C in the cool season (U. S. Weather Bureau Records, Enid). The maximum mean monthly air temperature occurred in August and the minimum in December (Table I). Air temperature varied from 17.2 C to 35.6 C in the warm season and from 5 C to 10 C in the cool season.

#### Solar Radiation

Mean solar radiation was 461 cal/cm<sup>2</sup> day in the warm season and 265 cal/cm<sup>2</sup> day in the cool season (Oklahoma State University Weather Station, Stillwater). Maximum mean solar intensity occurred in July and minimum in December (Table I). Radiation varied from 272 to 589 cal/cm<sup>2</sup> day in the warm season and from 218 to 307 cal/cm<sup>2</sup> day in the cool season.

TABLE I  
MEAN MONTHLY CONDITIONS

Month		Total ppt (cm)	Water Temp. (C)	Air Temp. (C)	Solar Rad. cal/cm <sup>2</sup> day
COOL SEASON					
Dec	63	0.28	0.8	5.0	218
Jan	64	0.14	4.2	12.2	270
Feb	64	0.18	5.0	10.0	307
WARM SEASON					
Mar	64	4.24	17.6	20.0	367
Apr	64	4.75	19.2	24.0	461
May	64	15.20	24.6	27.8	496
Jun	63	17.00	26.3	32.8	580
Jul	63	24.00	29.3	35.0	580
Aug	63	7.26	24.5	35.6	550
Sep	63	6.65	21.7	30.0	446
Oct	63	7.18	23.0	29.4	390
Nov	63	3.96	15.7	17.2	272

### Flow

Mean measured flow increased from 8.5 cu m/min at Station 6 to 55.25 cu m/min at Station 97 during the warm season (Fig. 4). Cool season flow increased from 7.27 cu m/min at Station 6 to 27.44 cu m/min at Station 97. Sample days were selected when stream flow was not altered by large rains. Daily flow was recorded at a gauging station at kilometer 76 (U.S.D.I., Water Resources Division, 1963, 1964). Daily flow was maximal at 10,302 cu m/min on 12 July following a rainfall of 16.5 cm at Enid on 11 July (Table II). On this occasion approximately one day was required for the water to flow 76 km to the gauging station. Flow exceeded 1700 cu m/min on several occasions in May, June and July following heavy rainfalls in the upper basin. Low rainfall and low flow occurred during the cool season.

TABLE II  
FLOW GAUGED AT KILOMETER 76

Month		Mean Flow (cu m/min)	Max. Flow (cu m/min)	Min. Flow (cu m/min)
COOL SEASON				
Dec	63	19.55	30.60	14.96
Jan	64	17.17	22.10	9.35
Feb	64	22.78	49.30	14.28
WARM SEASON				
Mar	64	19.20	57.80	13.94
Apr	64	34.00	365.50	7.99
May	64	*	7106.00	9.35
Jun	63	321.30	3961.00	3.40
Jul	63	1081.60	10302.00	7.48
Aug	63	46.07	249.90	11.56
Sep	63	110.16	1322.60	10.88
Oct	63	106.42	1453.50	7.14
Nov	63	24.65	105.40	12.58

\* No observation

The channel of Skeleton Creek is narrow, littered with logs and brush, and is inadequate to carry runoff from storms producing more than 5 cm of rainfall (Soil Conservation Service, Oklahoma City). The stream overflowed its banks at least six times during the present study.

Sewage and oil refinery effluents formed the major part of flow in the upper reaches of Skeleton Creek. Mean measured annual flow was 7.88 cu m/min at Station 6 (Table III). Flow increased downstream with influx from groundwater and tributaries.

Self-purification of streams depends on the time of passage of water, which may vary widely with conditions of the stream and the amount of water (Streeter, 1930). In the headwaters of Skeleton Creek the gradient was fairly steep and the water was shallow. Downstream the channel became deeper, log jams were common and large pools were



formed. Approximately 20 hr were required for water to flow from Station 6 to Station 24, whereas 40 hr were required for water to flow from Station 24 to Station 40 (Table III). Stream elevation dropped 27 m between Station 6 and Station 24, compared to a drop of only 9 m between Station 24 and Station 40 (Table III). The large increase of flow between Stations 50 and 97 was contributed by Ephraim, Otter and Bridge Creeks. Otter Creek is the largest tributary of Skeleton Creek and flowed most of the year. At times of measured flow approximately 8 days were required for water to traverse the 97 km stretch.

TABLE III  
CALCULATED STATION CHARACTERISTICS

Station	Discharge* (cu m/min)	Time of Flow From Km 0 (hr)	Elevation (m)
6	7.88	8	341
18	13.89	19	326
24	16.47	28	314
31	15.78	47	311
40	20.31	68	305
50	19.55	86	299
71	27.79	145	289
97	41.48	188	280

\* Means of monthly measurements

#### Turbidity

Skeleton Creek is bordered by croplands and pastures and the stream was usually turbid during the rainy season. Mean turbidity increased from 13 ppm at Station 6 to 175 ppm at Station 97 in the warm season (Fig. 5). During the cool season turbidity was highest at Station 18

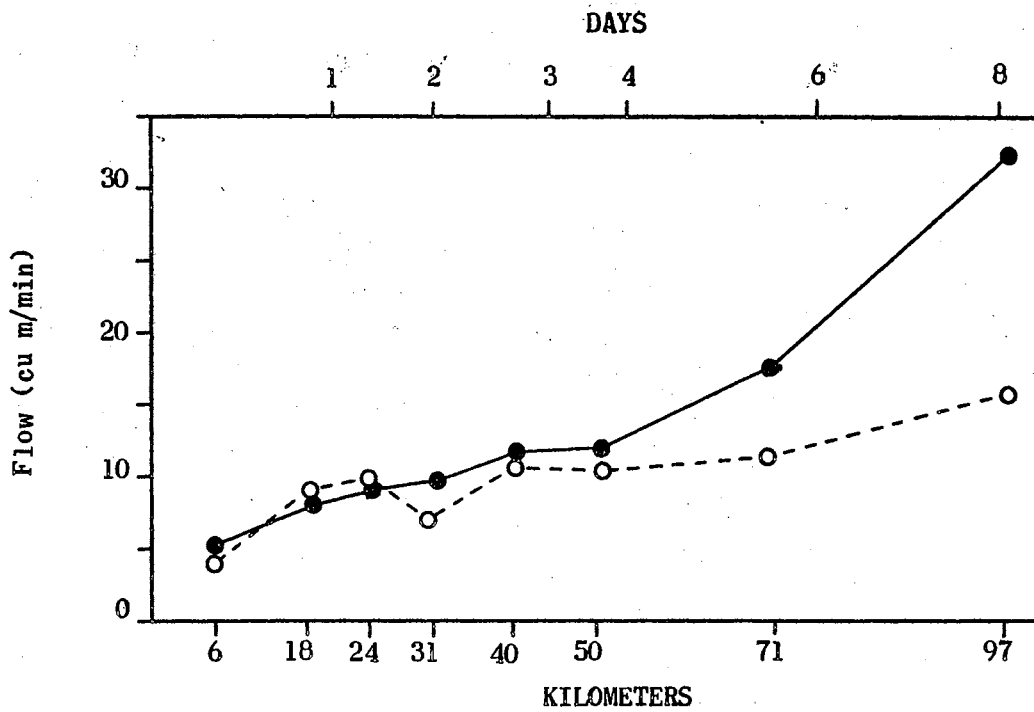


Fig. 4. Mean seasonal flow of Skeleton Creek. Cool season = (-O-), warm season = (-●-).

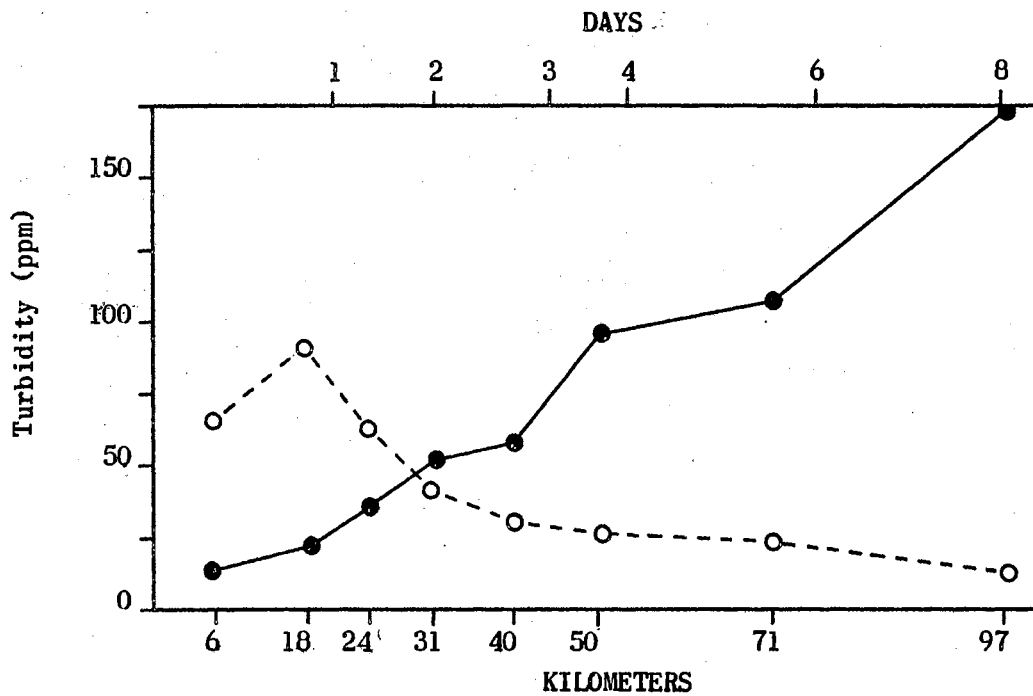


Fig. 5. Mean seasonal turbidity of Skeleton Creek. Cool season = (-O-), warm season = (-●-).

and lowest at Station 97. Turbidity increased from 62 ppm at Station 6 to 85 ppm at Station 18, then decreased downstream.

Turbidity was high between Stations 6 and 30 in the cool season. Clay particles did not appear to be the contributing factor, since the water had a gray color at all seasons. A high density of bacteria may have been the cause. Numbers of bacteria increase downstream from pollution outfalls and reach their greatest density at distances corresponding to 10 to 20 hr of flow (Streeter, 1930; Mohlman, 1933). Floating sludge, composed partially of algae, was observed between Stations 6 and 18 and was abundant in the cool season. Phillips (1965) found a large amount of light, flocculent matter drifting in the water at Station 18, sufficient to clog seines. Biochemical oxygen demand (BOD) was 18.2 ppm in the cool season compared to 9.0 ppm in the warm season. Greater BOD reduction in the warm season was accompanied by reduced color and turbidity. Biological growths attached to the stream bed extract organic matter and reduce turbidity (Velz and Gannon, 1962). During the winter months growths were not as abundant as during warm months in the headwater region.

Higher turbidity occurred in the warm season in middle and lower stretches with silt bottom, low current, inflow from tributaries and extensive cultivation of adjacent land. Turbidity decreased in the middle and lower stretches during the cool season at a time of low precipitation and little influx from tributaries.

### Alkalinity

Alkalinity was primarily due to bicarbonates. Phenolphthalein alkalinity was detected on only a few occasions. Mean methyl orange

alkalinity as  $\text{CaCO}_3$  equivalent ranged from 380 ppm at Station 71 to 353 ppm at Station 97 in the cool season (Fig. 6). Maximum alkalinity of 400 ppm occurred at Station 18, and the minimum of 325 ppm at Station 6. Mean warm season alkalinity ranged from 330 ppm at Station 50 to 270 ppm at Station 97, and a maximum of 445 ppm occurred in April at Station 24 and a minimum of 181 ppm occurred in August at Station 50. The decrease in alkalinity from Station 71 to Station 97 was influenced by the influx of water from Otter Creek.

#### pH

Mean pH ranged from 8.3 to 8.0 in the cool season (Fig. 7). A maximum of 8.4 was observed in January at Station 6 and a minimum of 7.9 in February at Station 40. The mean warm season range was 8.2 to 7.8 with a maximum of 8.6 in June at Station 6 and a minimum of 7.1 in July at Station 50. Minimum pH was observed at most stations in June, July and August, probably as a result of microbial release of carbon dioxide.

Seasonal pH was somewhat similar to dissolved oxygen concentration (DO) (compare Fig. 7 and Fig. 14). At the upper stations DO and pH were always highest. Since algae use carbon dioxide in photosynthesis, removal of carbon dioxide may have been responsible for the higher pH. Downstream, DO decreased, carbon dioxide increased and pH was lowered. The increase of pH at Station 40 during the warm season corresponded to an increase in photosynthetic productivity. Station 40 was the most productive station in the sag zone (Table VII). The pH decreased at Station 50 in the warm season, as did photosynthetic productivity. The

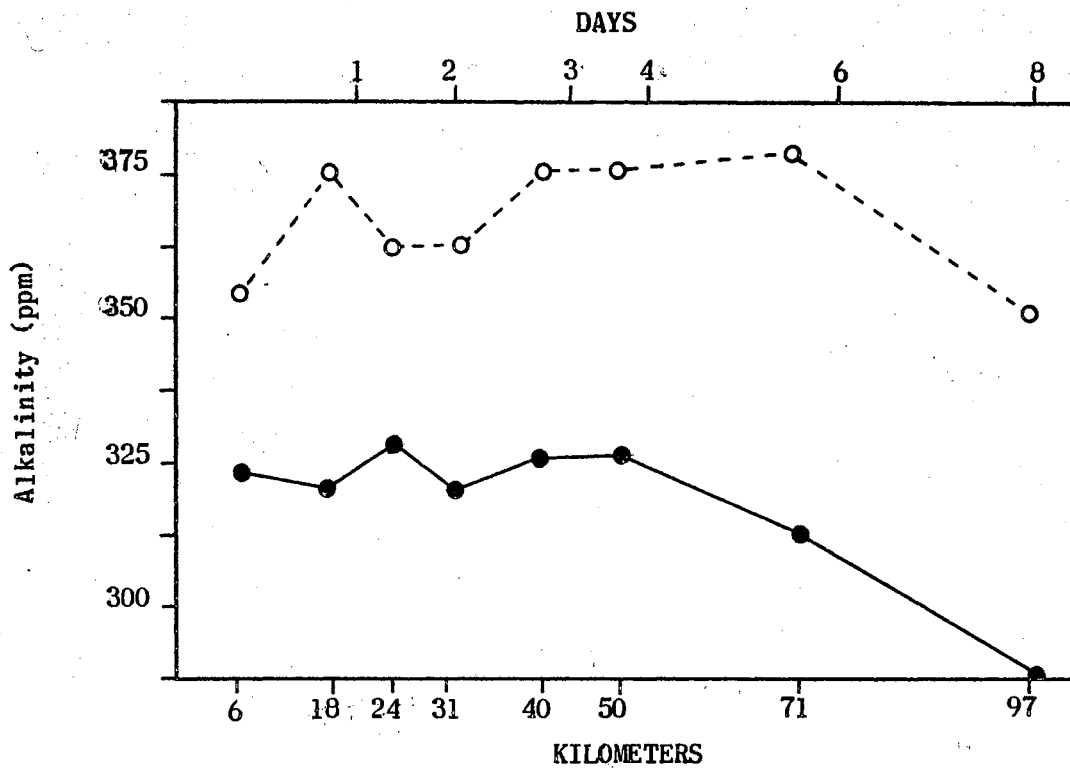


Fig. 6. Mean seasonal alkalinity of Skeleton Creek. Cool season = (-○-), warm season = (-●-).

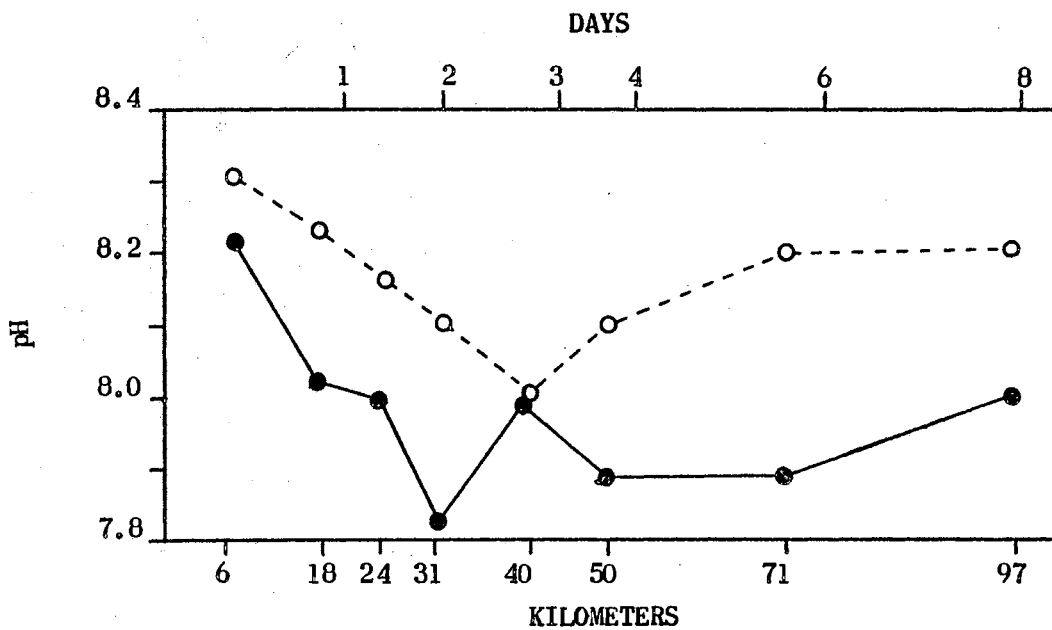


Fig. 7. Mean seasonal pH of Skeleton Creek. Cool season = (-○-), warm season = (-●-).

increase of DO in the lowest reaches was accompanied by an increase in pH.

### Conductivity

Mean conductivity ranged from 1650 to 2089 micromhos/cm in the cool season and from 1266 to 2053 micromhos/cm in the warm season (Fig. 8). Maximum conductivity of 2904 micromhos/cm occurred in November at Station 71, and minimum of 810 micromhos/cm in June at Station 97.

Conductivity increased between Station 6 and Station 18 in both seasons, and may have been the result of an influx of oil field brines. Conductivity decreased slightly in the middle stretch during the warm season when flow was augmented by precipitation. The increase observed at Station 71 was caused by oil field brines stored in earthen pits between Station 50 and Station 71. Such pits have been found to be pervious to salt water, and large quantities of salt water seep through the bottoms into subsurface formations and finally into local surface streams (Williams, 1940). The decrease in conductivity at Station 97 was attributed to an increase of dilution water from Otter and Bridge Creeks. During the warm season conductivity was lower at all stations because of an increase in stream flow.

### Chlorides

Chlorides were measured during the warm season (Fig. 9). Chlorides ranged from 132 ppm in June at Station 97 to 349 ppm in April at Station 71. Mean chloride concentration followed the same pattern as conductivity (compare Fig. 8 and Fig. 9). The increase at Stations 18 and 71 came from oil field brines and the decrease at Station 97 was attributed to dilution from tributaries.

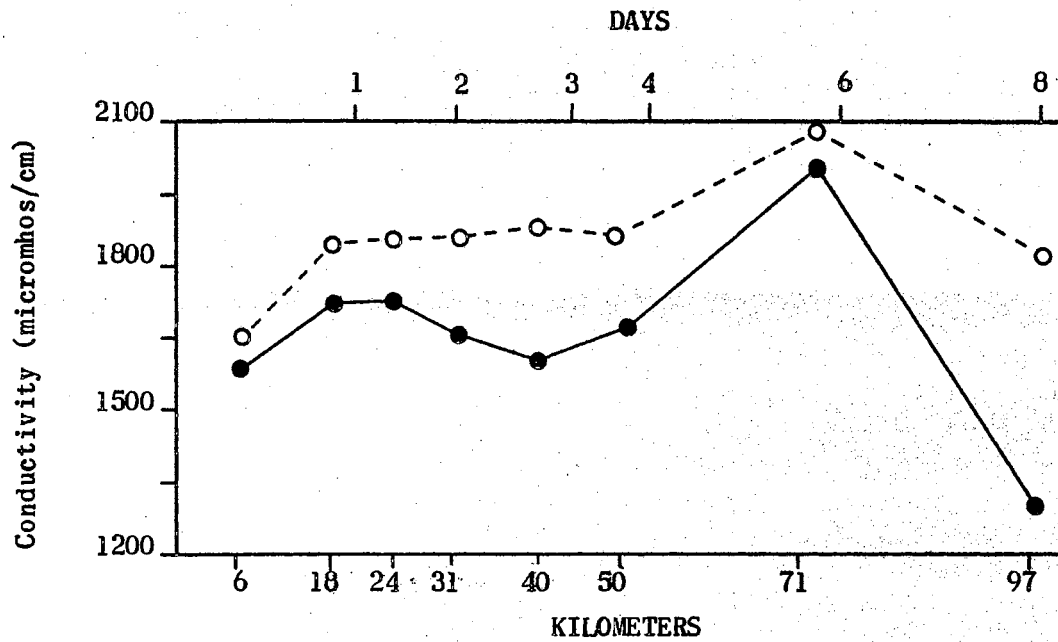


Fig. 8. Mean seasonal conductivity of Skeleton Creek.  
Cool season = (-O-), warm season = (-●-).

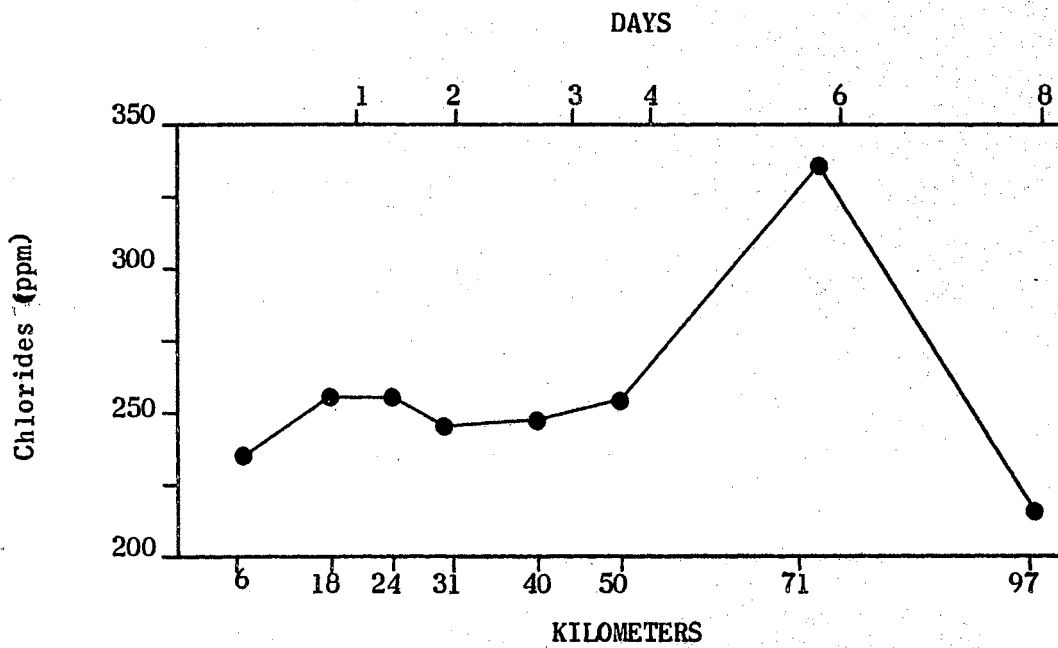


Fig. 9. Mean chloride concentration of Skeleton Creek.  
Warm season = (-●-).

### Biochemical Oxygen Demand

The 5-day biochemical oxygen demand (BOD) was determined once in January and six times between June and November. BOD decreased progressively from 21.0 ppm at Station 6 to 11.76 ppm at Station 97 in January (Fig. 10). Only 56% of the initial BOD was removed in the 91 km stretch. The warm season BOD decreased only slightly, from 10.61 ppm to 9.6 ppm. During the warm season most of the BOD was removed above Station 6, but during the winter the same reduction required 97 km of flow.

The BOD of sewage effluents was probably satisfied, for the most part, in the upper reaches, whereas the oil refinery effluent and other wastes imposed a BOD farther downstream. Sewage is well inoculated with bacteria and is adequately supplied with a wide range of compounds, so that it is broken down relatively fast (Hynes, 1963).

Some materials are poor bacterial foods, and being degraded very slowly, exert a lower oxygen demand for longer periods of time. Detergents released from sewage plants are degraded very slowly. Industrial wastes require specific organisms to degrade the large organic molecules and it may take several days before the specific requirements for growth of these organisms are met (Bollen, 1951). Almost any organic compound is susceptible to attack by some living organisms (Lackey, Calaway and Morgan, 1956). Organic mixtures which are attacked by the greatest variety of organisms usually are readily soluble, are approximately neutral and are short chain carbon compounds containing available phosphorous and nitrogen. As a substance deviates farther from these conditions, fewer kinds of organisms use it as a source of energy.

Other sources of oxygen demand were contributed by rubbish washed



into the stream and thrown off of bridges. Rubbish deposits on banks of streams are very important causes of pollution (Jaag, 1953). The Enid Municipal Refuse Dump was located near the banks of Skeleton Creek. During periods of precipitation, runoff from the dump could have added oxygen-demanding wastes to the stream. Cardboard boxes, tin cans, old clothing, dead animals and garbage were observed in the stream.

Natural pollution may occur from organic and inorganic materials washed or blown into streams from woods, fields, cultivated lands and country roads (Chase and Ferullo, 1958). Maple leaves may have an oxygen demand equivalent to 75% of their weight. Cellulose and lignin of plant matter exert slow BOD. Skeleton Creek is bordered with deciduous trees, and leaf fall undoubtedly increased the oxygen demand during the fall and winter.

#### Chemical Oxygen Demand

Mean chemical oxygen demand (COD) ranged from 135 ppm at Station 24 to 85 ppm at Station 97 in the cool season (Fig. 11). A maximum of 195 ppm was measured in December at Station 40 and the minimum of 53 ppm was observed in February at Station 50. The warm season COD ranged from a maximum of 125 ppm in June at Station 71 to 13 ppm in September at Station 50. Approximately 30% of the initial COD was satisfied in the 91 km stretch in both seasons.

During the winter months COD was always highest at Station 24, possibly because of influx of oil brines, but decaying algae may have contributed also. Higher precipitation in the warm season may have leached oil field brines into the stream at Station 71, to account for the high COD at that station.

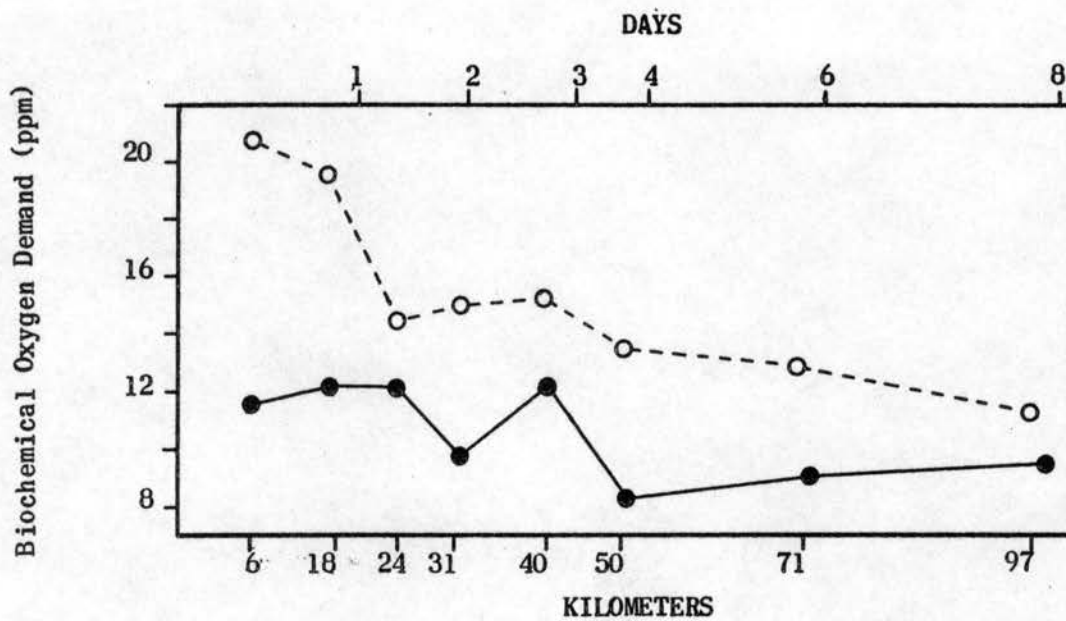


Fig. 10. Mean seasonal BOD of Skeleton Creek. Cool season = (-O-), warm season = (-●-).

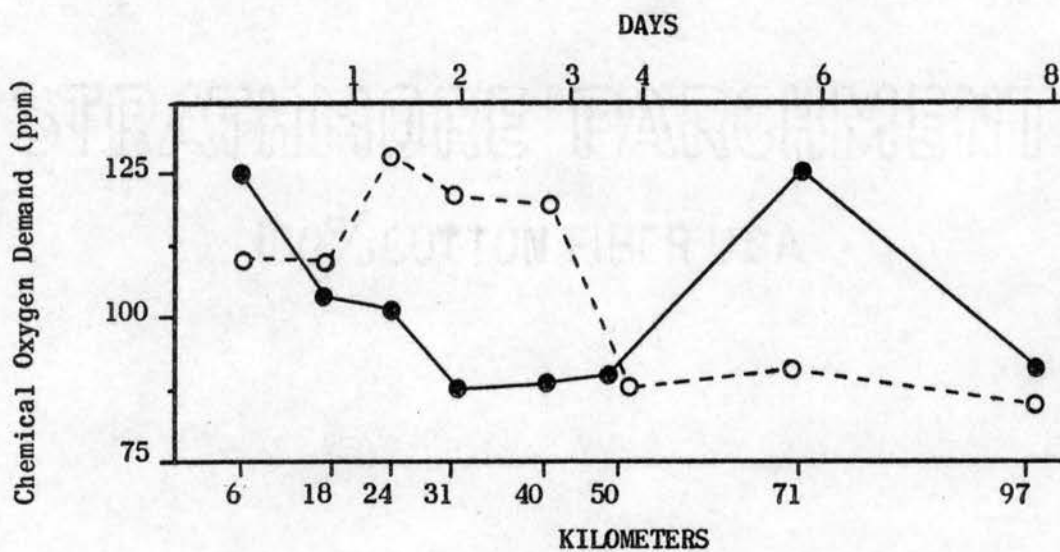


Fig. 11. Mean seasonal COD of Skeleton Creek. Cool season = (-O-), warm season = (-●-).

Silver sulphate was used as a catalyst in all tests and correction for chloride interference could not be determined. Very little difference is found in theoretical COD test results corrected for chlorides as compared with the test run with the catalyst, even at 400 ppm of chlorides (Gaudy and Ramanathan, 1964). Since all stations had chloride concentration below 350 ppm, it was assumed that there was no interference due to chlorides.

#### Total Residue

Total residue is partially composed of decomposed organic matter. The concentration varies as a result of decomposition processes. Total residue was higher at all stations during the cool season because of slower decomposition rates. Mean total residue ranged from 1040 to 1447 mg/liter in the cool season (Fig. 12). A maximum of 1582 mg/liter occurred in December at Station 71 with a minimum of 954 mg/liter in January at Station 6. Warm season total residue ranged from 939 to 1408 mg/liter with a maximum of 1900 mg/liter in April at Station 97 and a minimum of 708 mg/liter in August at Station 6.

The increase of total residue between Stations 6 and 24 was caused by an influx of oil brines and by the breaking loose of algal mats from the bottom of the stream bed. The decrease between Stations 24 and 50 was attributed to microbial action reducing organic matter and also suspended solids settling out in front of log jams in the sluggish area of the stream. Less microbial action occurred in the cold months. The increase observed at Station 71 was contributed by oil field brines. The decrease observed at Station 97 was caused by an increase of dilution water from tributaries.

### Fixed Residue

Fixed residue was higher at all stations in the warm season, probably because more photosynthetic production occurred in warmer water. Mean fixed residue ranged from 193 to 249 mg/liter in the cool season (Fig. 13). A maximum of 414 mg/liter was observed in February at Station 71 and the minimum of 98 mg/liter occurred in December at Station 97. Warm season mean values ranged from 237 to 323 mg/liter with a maximum of 500 mg/liter occurring in March at Station 71 and the minimum of 116 mg/liter in July at Station 97.

### Dissolved Oxygen

Dissolved oxygen concentration (DO) determined from daytime samples exhibited the sag curve frequently observed in streams below organic outfalls (Fig. 14). Stations were always sampled from the lower reaches to the upper reaches between 8:00 a.m. and 2:00 p.m. Mean DO was higher at all stations in the cool season than in the warm season. The cool season high was 21.0 ppm in February at Station 6 and the low was 3.9 ppm in February at Station 40. The warm season high was 16.6 ppm in August at Station 6 and the low was 0.2 ppm in May at Station 40.

Longitudinal variation in oxygen concentration was considerable. Algal growths were abundant at Station 6 and produced high DO by photosynthesis. Lower DO in the middle reach was accompanied by a decrease in benthic algae and an increase in turbidity and volume of water. Deoxygenation processes were probably maximal. The low point in DO occurred approximately 2 days (20 km) earlier in the warm season than in the cool season. As deoxygenation processes decrease an increase in oxygen occurs, accordingly DO increased at the two lower stations.

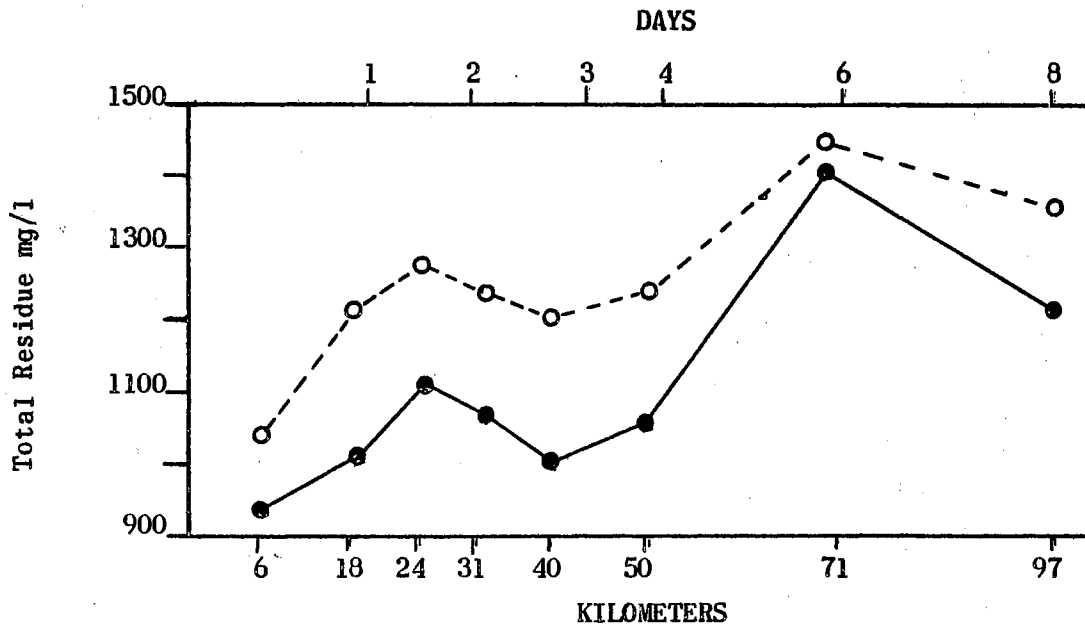


Fig. 12. Mean seasonal total residue of Skeleton Creek.  
Cool season = (-O-), warm season = (-●-).

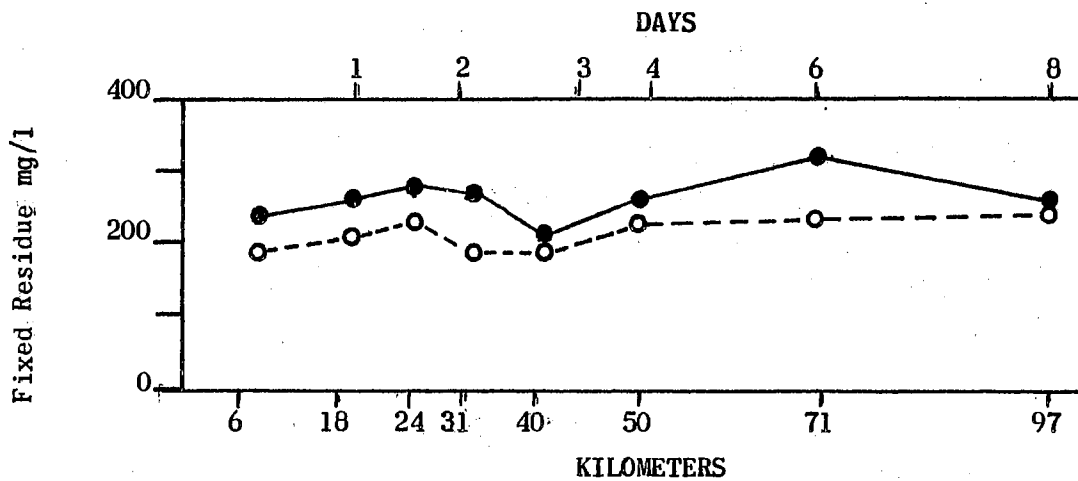


Fig. 13. Mean seasonal fixed residue of Skeleton Creek.  
Cool season = (-O-), warm season = (-●-).

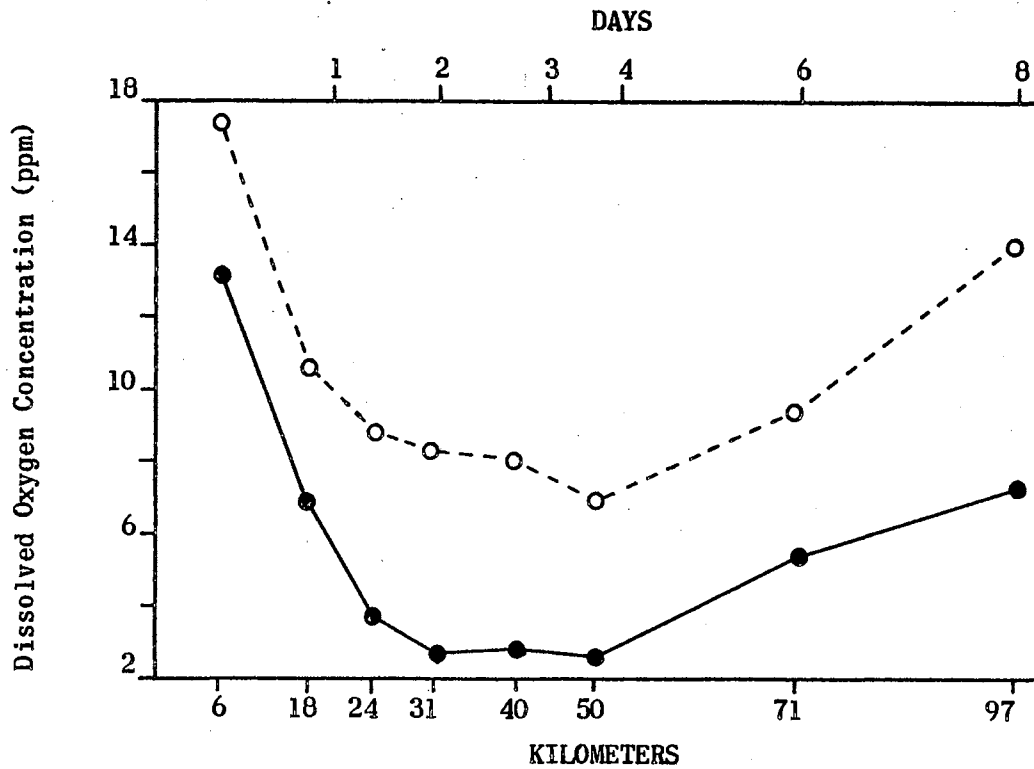


Fig. 14. Mean seasonal DO of Skeleton Creek. Cool season = (—○—), warm season = (—●—).

Daytime samples do not provide information on daily variation in DO. Samples taken around the clock measure diurnal variation of DO. Gameson and Griffith (1959) measured DO in a polluted river with an automatic recorder over a 6 month period. They found that samples taken at 10:00 a.m. and 3:00 p.m. did not satisfactorily represent the condition of the river, but that samples taken at 6:00 a.m. gave the best estimate of the lowest DO occurring in the river. Hoak and Bramer (1961) have shown that DO does not always fall to its lowest point early in the morning, but may fall to low values at other times when there is substantial pollution. They suggested collecting more samples at night.

During this study diurnal (diel) oxygen analyses were made at each station at least once, with most analyses between Stations 24 and 50. Diurnal variation of DO during the summer of 1963 at six stations along Skeleton Creek is presented in Fig. 15. The widest range in DO occurred at Station 6, ranging from 2.0 to 16.5 ppm at 23-225% saturation. During the sunlit hours algae produced more oxygen than the system could use and supersaturation occurred. At night the DO dropped off rapidly. Although oxygen demand was high, atmospheric reaeration furnished enough oxygen to keep the stream from becoming anoxic. The low in DO occurred at 1:00 a.m.

Less photosynthesis and high respiration occurred at Station 18. DO ranged from 2.25 to 8.50 ppm at 30-130% saturation. DO at Station 26 was the lowest ever measured in diurnal analyses, with a narrow range of 0.5 to 1.50 ppm at 6-9% saturation. This station was undoubtedly near the bottom of the sag curve. Little photosynthesis occurred and the oxygen demand was high.

DO increased and oxygen demand decreased downstream from Station 26. At Station 40 DO ranged from 1.7 to 4.5 ppm at 22-61% saturation. As the oxygen demand decreased reaeration processes became more effective and an increase in oxygen occurred. The diurnal range of DO at Station 50 was 2.25 to 6.40 ppm at 29-87% saturation. Diurnal variation in DO at Station 71 was considerable, and ranged from 6.5 to 18.60 ppm at 85-225% saturation. High photosynthetic production is common in the recovery zone of streams receiving effluents of high organic matter (Odum, 1956).

The position of the sag curve changed seasonally. In May, DO

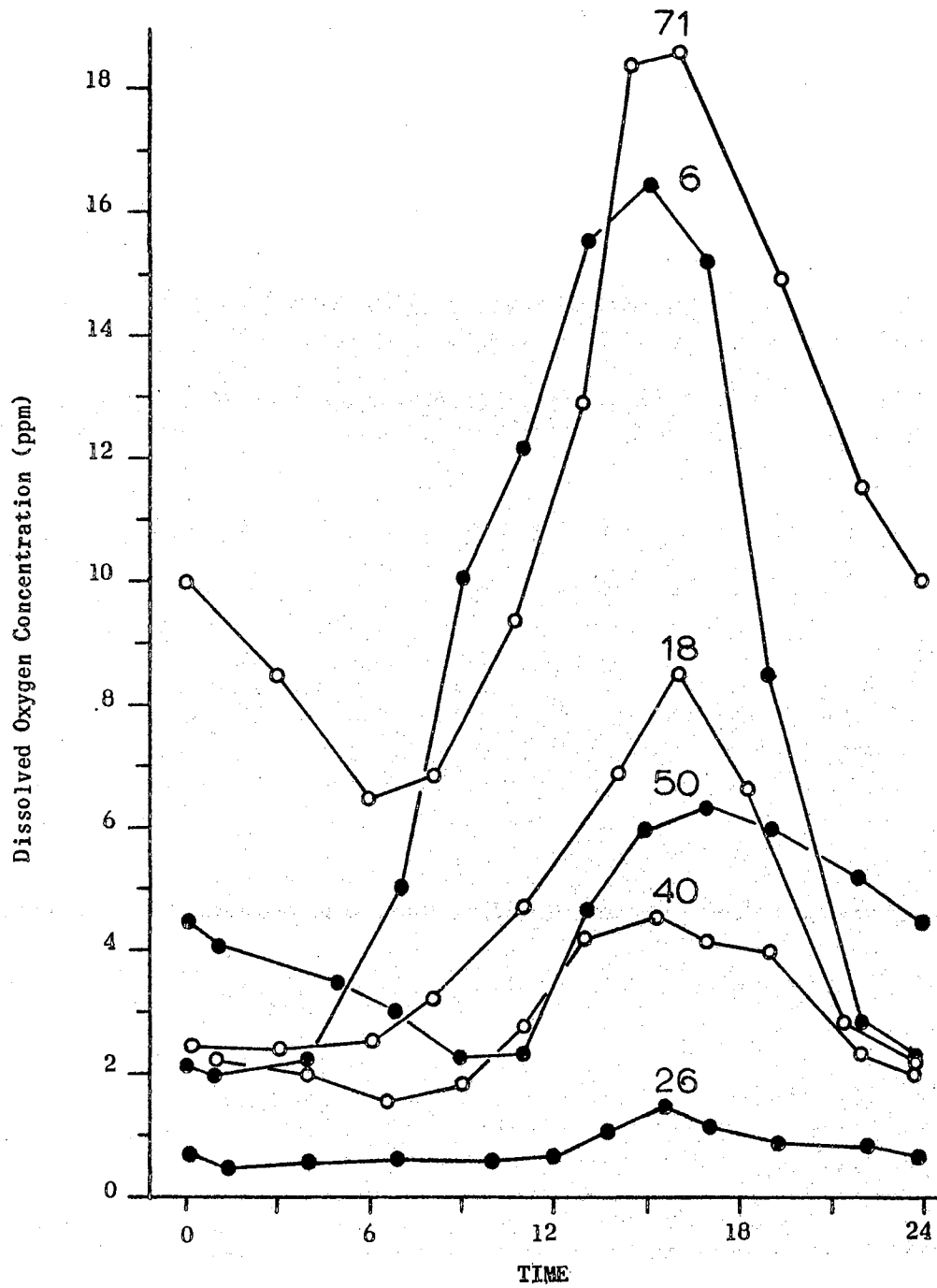


Fig. 15. Longitudinal and diurnal variation of DO along Skeleton Creek. Numbers indicate stations in kilometers downstream from the confluence of Boggy Creek with Skeleton Creek.



was higher at Station 26 than at Station 28 (Fig. 16 A), showing that an oxygen loss occurred between stations. At the same time DO was nearly the same at all hours at Station 36 and 39 indicating that the oxygen demand and the oxygen supply were about equal at both stations (Fig. 16 B). Stations 36 and 39 were near the bottom of the sag curve, since higher DO occurred at Station 48, ranging from 1.80 to 6.95 ppm on the same days.

In February, oxygen was lost in both stretches (Fig. 16 C-D), and the minimum DO must have occurred at some point further downstream. Stations below Station 39 were extremely difficult to sample during the winter months and no diurnal analyses were made. Daytime samples show that the minimum DO occurred at Station 50 during the cool season (Fig. 14).

The sag curve occupied at least three different stretches of the stream during the year. The low point occurred at Station 26 in June (Fig. 15), Station 39 in May and some place downstream from Station 39 in February.

## Biological Conditions

### Phytoplankton Population

Phytoplankters are absent or relatively few in numbers in some flowing waters, but many streams contain a true plankton population (Welch, 1952). Stream plankton organisms in Georgia do not become established until the stream is altered by dams (Scott, 1958). In four Oklahoma streams virtually no plankton was found, and light and dark bottles experiments showed no photosynthetic oxygen production (Hornuff, 1957). In Blue River, Oklahoma, Duffer (1965) found very

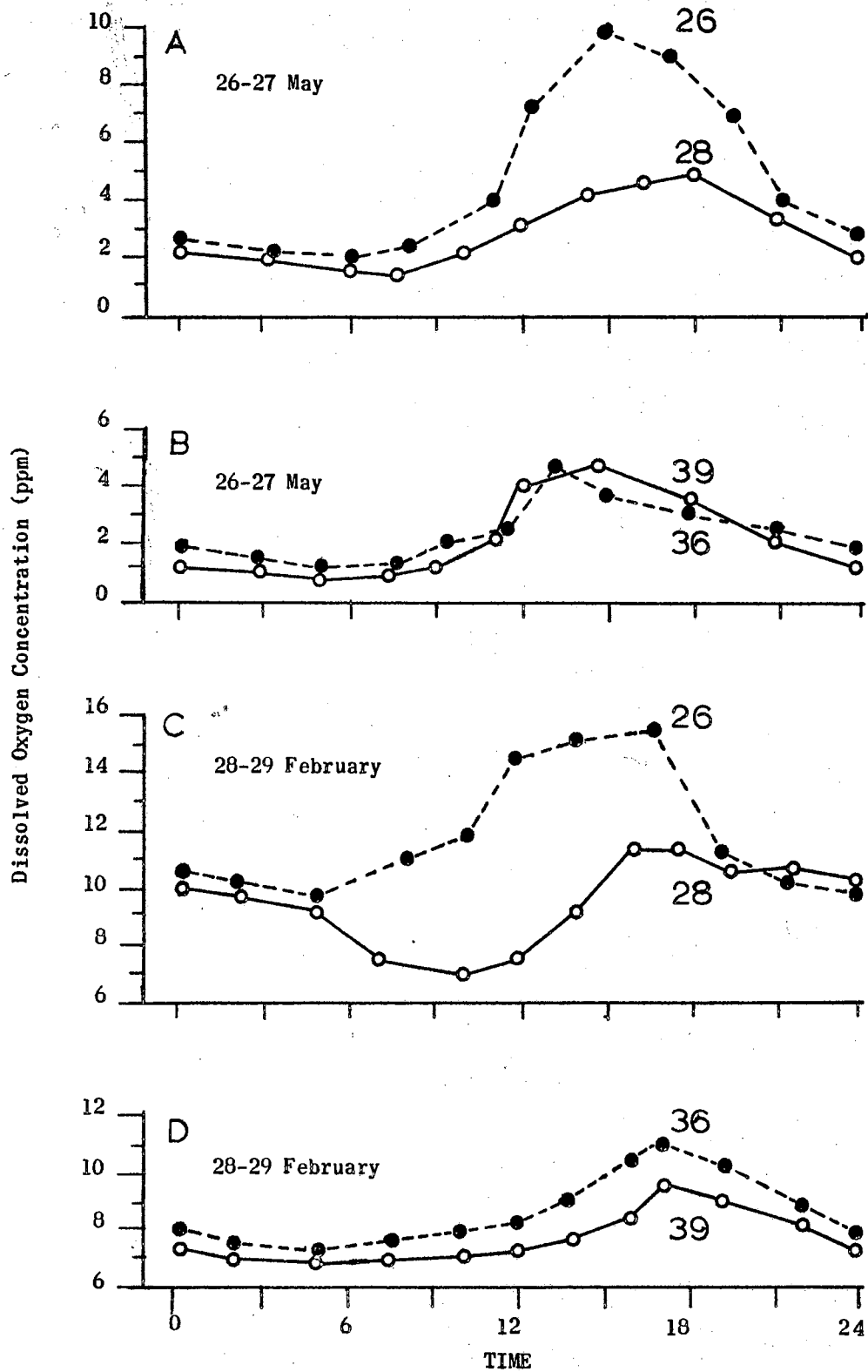


Fig. 16. Diurnal variation of DO at 4 stations on Skeleton Creek.

little suspended chlorophyll. Plankton is much less important in the stream economy than in lake ecosystems, but may supply an important source of food in the stream (Odum and Odum, 1962). The ratio of benthic algae to water volume is a significant factor in determining the amount of oxygen contributed by photosynthesis (Patrick, 1962). Phytoplankton can increase the algal ratio. Streams which receive organic wastes may be fertile and have fairly dense populations of plankton (Coker, 1954). In summer months in a polluted river dissolved oxygen contributed by plankton photosynthesis may be greater than atmospheric aeration (Knopp, 1962, quoted by Winberg and Sivko, 1962).

Phytoplankton populations of few species in large numbers were present in Skeleton Creek. Fifty-five species or distinct groups of microscopic organisms in five phytoplankton phyla were found. The phylum Chlorophyta included 14 genera (Table IV). There was one genus in Pyrrophyta, three genera in Euglenophyta, four genera in Chrysophyta and five genera Cyanophyta. Micro-cells of approximately 10 distinct forms consisted mainly of large bacterial cells and small blue green algal cells of uncertain identity.

Euglena, Navicula and Chlamydomonas were the dominant genera in most collections. Occasionally Anabaena, Ankistrodesmus and Chlorella were abundant. Euglena was generally the dominant genus in the first 48 km of stream and Navicula was dominant in the last 48 km. Micro-cells and Chlamydomonas occurred in most collections at all stations. In December, January and February blooms of Chlamydomonas and Euglena occurred between Stations 24 and 40. The water had a soupy, greenish appearance during this time.

TABLE IV

## PHYTOPLANKTON GENERA IDENTIFIED IN SKELETON CREEK

CHLOROPHYTA	PYRRHOPHYTA	CYANOPHYTA
<u>Chlamydomonas</u>	<u>Ceratium</u>	<u>Anabaena</u>
<u>Eudorina</u>		<u>Phormidium</u>
<u>Pandorina</u>	EUGLENOPHYTA	<u>Merismopedia</u>
<u>Palmella</u>	<u>Euglena</u>	<u>Gomphosphaeria</u>
<u>Stigeoclonium</u>	<u>Phacus</u>	<u>Oscillatoria</u>
<u>Pediastrum</u>	<u>Trachelomonas</u>	u-cells
<u>Ankistrodesmus</u>		
<u>Chlorella</u>	CHRYSOPHYTA	
<u>Tetraedron</u>	<u>Diatoma</u>	
<u>Micractinium</u>	<u>Asterionella</u>	
<u>Scenedesmus</u>	<u>Navicula</u>	
<u>Staurastrum</u>	<u>Fragilaria</u>	
<u>Actinastrum</u>		
<u>Phytoconis</u>		

In streams heavily polluted by sewage effluents, algae increase steadily downstream, and become very abundant where turbidity and settleable solids decrease and final mineralization takes place (Bartsch and Ingram, 1959). The algae to be expected include Microcystis, Anabaena, Euglena, Pandorina, Cladophora, Ankistrodesmus and Rhizoclonium. Only a limited number of algal genera occur in rivers and the same genera of algae tend to be dominant in all rivers (Palmer, 1961). The dominant genera in rivers include Chlorella, Chlamydomonas, Ankistrodesmus, Anacystis and Navicula. Most of the algae listed above were found in Skeleton Creek.

The 27 genera of algae reported in this study were considerably less than 97 genera reported in two streams in Ohio (Lackey, 1956). In a series of oil refinery holding ponds Minter (1964) found 18 genera and Oliver and Dorris (1964) reported 33 genera in paper mill waste holding ponds.

Variation of algal populations in polluted streams may be a measure of the degree of recovery from pollution (Bartsch and Ingram, 1959). Succession in algal genera has been shown in paper mill waste holding ponds (Oliver and Dorris, 1964). Water with the greatest organic load had fewer genera, but more individuals.

### Species Diversity

An index of species diversity of diatoms were used to characterize successional stages in a stream of constant temperature (Yount, 1956); and algal species were used in microcosms (Odum and Hoskin, 1957; Beyers, 1962). Butler (1964) found that algal diversity varied most with dissolved solids content of water in experimental microcosms. Phytoplankton diversity increased through a series of oil refinery holding ponds (Minter, 1964). The highest diversity is usually associated with the most stable conditions. An increase in nutrients lowers diversity in all levels of the aquatic food chain (Margalef, 1963).

A species diversity index may be obtained by plotting cumulative numbers of species against cumulative numbers of individuals on semilog graph paper (Fig. 17). All species need not be actually identified, but only separated into distinct groups (Odum and Hoskin, 1957). It is assumed that any species present in the sample would be represented at least once in a count of 1000 individuals, and a larger count would produce few, if any, new species.

Phytoplankton species diversity was determined on Skeleton Creek. In the cool season diversity was greatest at Stations 6 and 50 (Fig. 17) and least diverse at Station 31. Nutrients may not have been as abundant at Station 6 as at Station 31. Large populations of

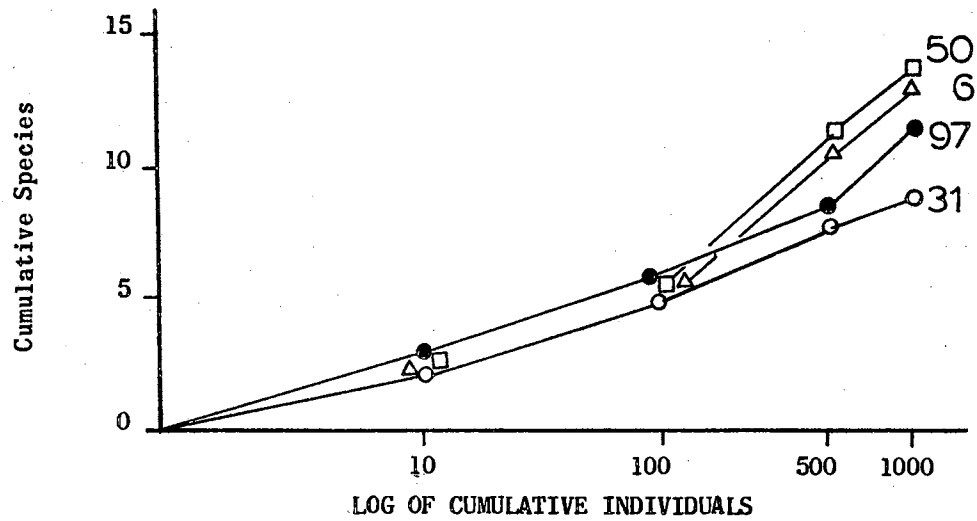


Fig. 17. Species diversity of phytoplankton at 4 stations along Skeleton Creek during the cool season. 6 = (△), 31 = (○), 50 = (□), 97 = (●).

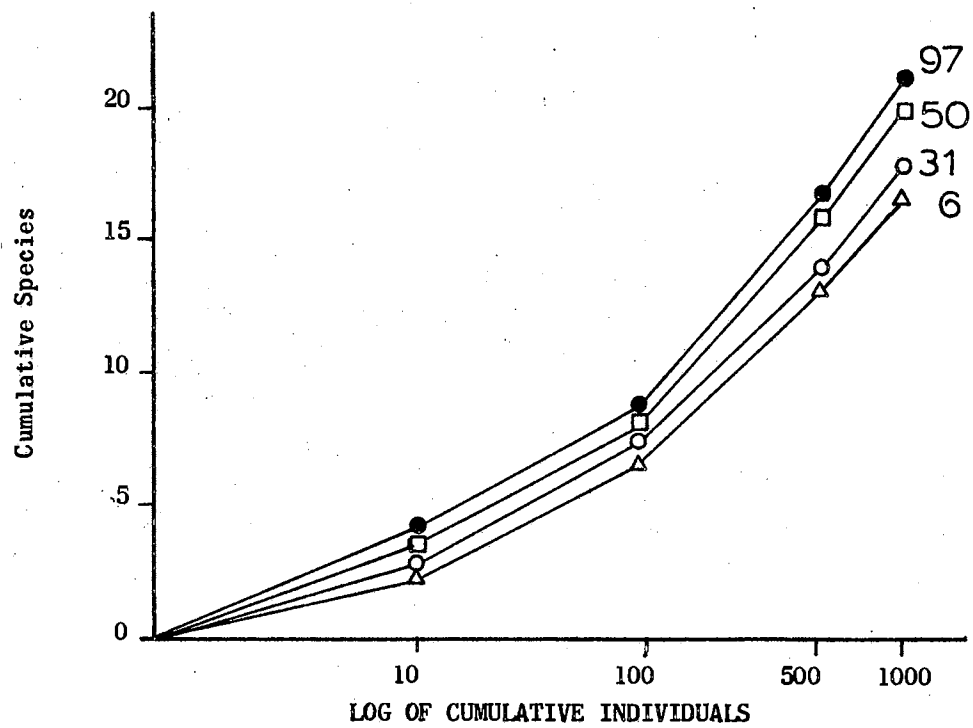


Fig. 18. Species diversity of phytoplankton at 4 stations along Skeleton Creek during the warm season. 6 = (△), 31 = (○), 50 = (□), 97 = (●).

Chlamydomonas, Navicula and Euglena were present at Station 31 during the winter months. Station 50 was probably below the area of maximum nutrients and five additional species found available niches. The decrease in diversity at Station 97 may have been caused by a secondary increase of nutrients. During the cool season more organic matter was present at Station 97 than during the warm season (Fig. 10).

In the warm season, species diversity increased progressively downstream as water quality improved (Fig. 18). More species were present at all stations in the warm season.

During the warm season, diversity of phytoplankton was considerably higher (Fig. 19). The low point in diversity occurred at Station 24. Diversity was highest at Station 71, in an area below an influx of oil field brines where reduced turbidity was observed on several occasions. Except for the unusual peak at Station 71 phytoplankton diversity was fairly uniform below Station 40. During the cool season, diversity was fairly constant throughout the stream.

Mean annual distribution of phytoplankton species did not follow the pattern demonstrated by fish and macroinvertebrate populations (Fig. 20). Fish species increased from 1 at Station 6 to 17 at Station 97 (Phillips, 1965). Macroinvertebrate species increased from 6 at Station 6 to 24 at Station 97 (Wilhm, 1965). Numbers of phytoplankton species remained essentially constant along the stream, ranging from about 15 in the upper reaches to about 18 in the lower reaches except at Station 71 where a maximum of 22 species occurred.

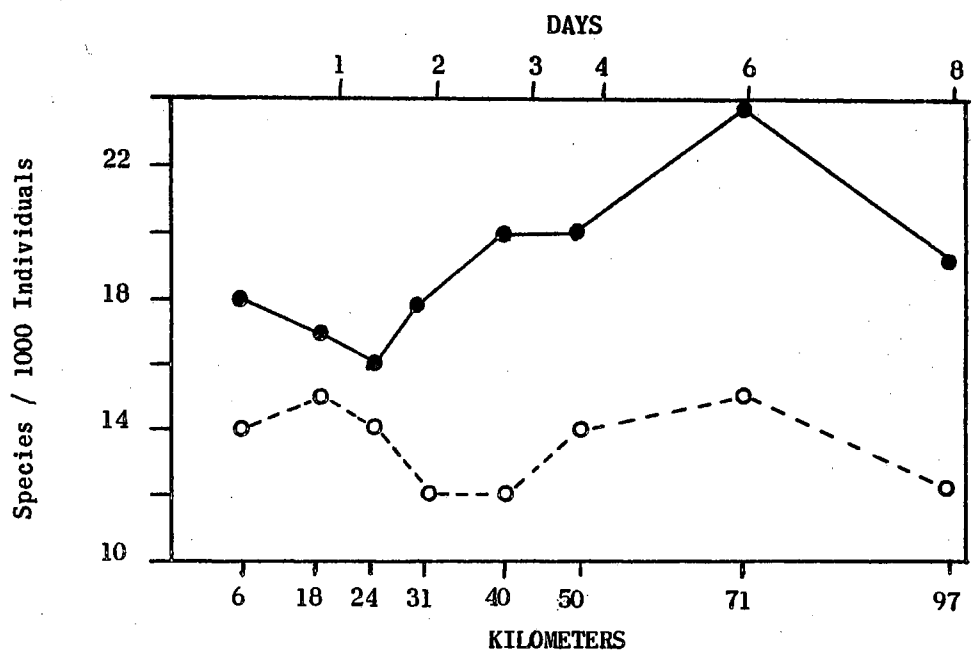


Fig. 19. Mean seasonal and longitudinal diversity of phytoplankton of Skeleton Creek. Cool season = (-O-), warm season = (-●-).

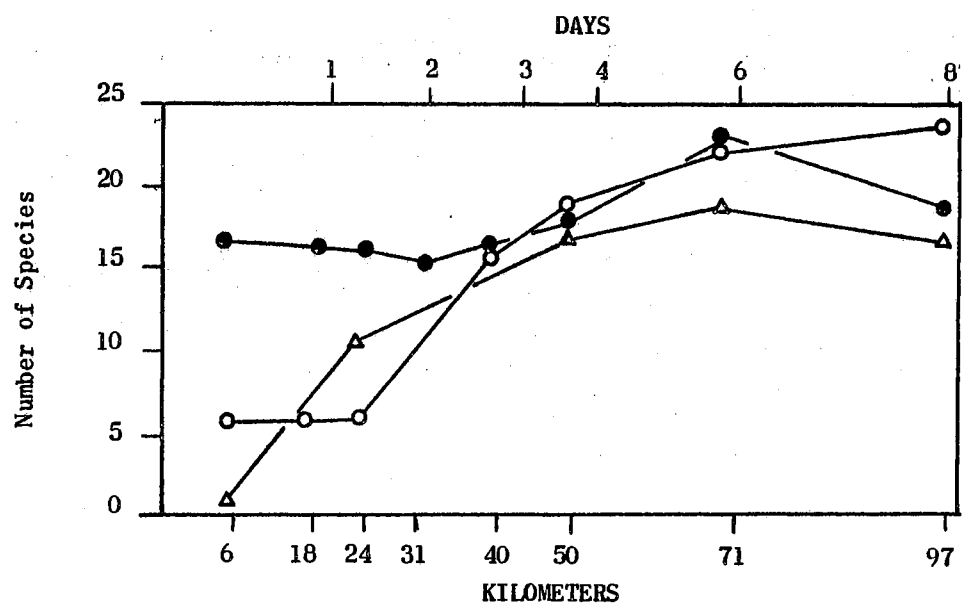


Fig. 20. Mean annual variation of species of Skeleton Creek. Macroinvertebrates = (-O-), fish = (-Δ-), phytoplankton = (-●-).



### Chlorophyll Distribution

The only primary producers in Skeleton Creek were benthic and phytoplankton algae. Benthic algae were the dominant chlorophyll producers during the warm season in the upper reaches where shallow water and a firm substratum for attachment existed (Fig. 21). Benthic algae decreased progressively downstream to a low at Station 31. Downstream from Station 31 benthic algae remained fairly uniform. Planktonic algae contributed more chlorophyll than benthic forms during the warm season between Stations 31 and 97 because of less current, deeper water, larger pools and reduced light intensity penetrating to the stream bed.

In the warm season mean benthic chlorophyll a ranged from 0.097 g/m<sup>2</sup> at Station 31 to 0.318 g/m<sup>2</sup> at Station 6 (Fig. 21). Minimum benthic chlorophyll a measured was 0.013 g/m<sup>2</sup> in June at Station 50 and maximum was 0.396 g/m<sup>2</sup> in April at Station 6.

Mean planktonic chlorophyll a ranged from 0.022 g/m<sup>2</sup> at Station 6 to 0.240 g/m<sup>2</sup> at Station 40. Minimum planktonic chlorophyll a measured was 0.008 g/m<sup>2</sup> in July at Station 6 and the maximum was 0.338 g/m<sup>2</sup> in July at Station 40.

Total mean chlorophyll a ranged from 0.190 g/m<sup>2</sup> at Station 31 to 0.388 g/m<sup>2</sup> at Station 50, in the warm season. More chlorophyll a was present at Stations 40 and 50 than at other stations. Although chlorophyll concentration was nearly the same at Stations 40 and 50, productivity was highest at Station 40 (Table VII). This may be attributed to greater turbidity at Station 50 on the days productivity measurements were made.

Planktonic chlorophyll concentration is higher in polluted than in unpolluted streams (Table V). Planktonic chlorophyll concentration in

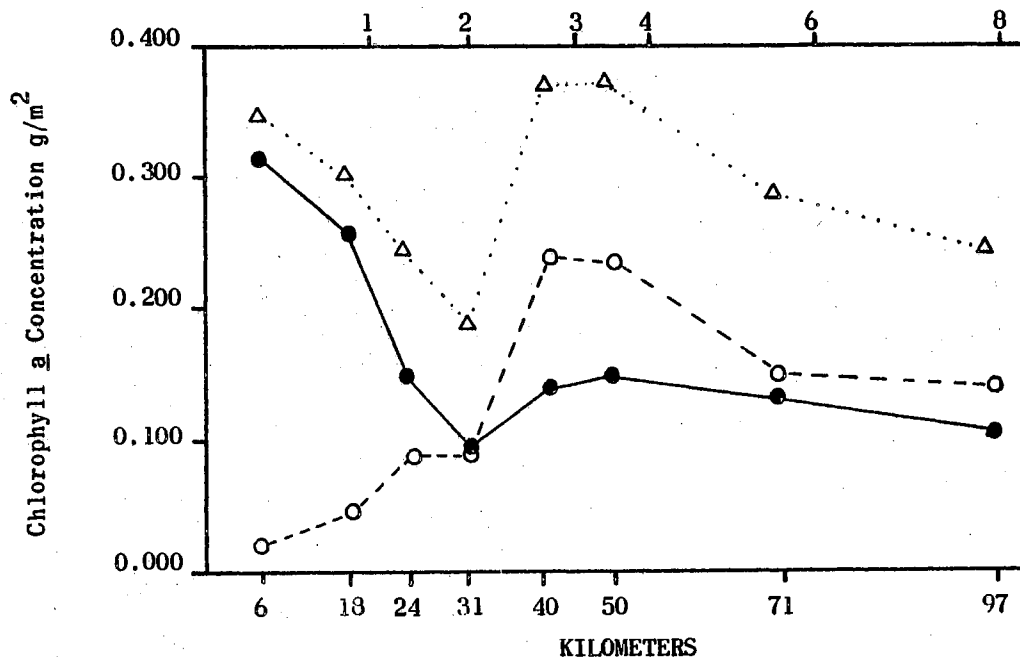


Fig. 21. Mean warm season chlorophyll *a* concentration of Skeleton Creek. Benthic = (—●—), planktonic = (---○---), total = (··Δ··).

Skeleton Creek was similar to concentrations found by Copeland (1963) in oil refinery holding ponds during spring (0.012 - 0.339 g/m<sup>2</sup>) and fall (0.000 - 0.202 g/m<sup>2</sup>).

Skeleton Creek benthic chlorophyll values are more comparable to benthic chlorophyll values from unpolluted streams (Table V). In Mission River, Texas, where primary producers were blue-green algal mats, benthic chlorophyll concentration was much higher than in Skeleton Creek.

TABLE V  
 CHLOROPHYLL a CONCENTRATION IN FLOWING WATERS

Source	Chlorophyll <u>a</u> g/m <sup>2</sup>
<u>Unpolluted</u>	
Granite substrate, Blue River, Okla., (Duffer, 1965)	
Plankton . . . . .	0.004
Benthic bryophytes and algae . . . . .	0.02 - 0.39
Canyon section of Logan River, Utah, (McConnell and Sigler, 1959)	
Benthic algae . . . . .	0.3
<u>Polluted</u>	
Blue-green algal mats, Mission River, Texas (Odum et al., 1958)	
Benthic . . . . .	2.5
River Svisloch, Ozero and Avtozavod, Russia (Winberg and Sivko, 1962)	
Plankton* . . . . .	0.039 - 0.154
Skeleton Creek, Oklahoma, 1963-64 (present study)	
Plankton . . . . .	0.022 - 0.24
Benthic . . . . .	0.097 - 0.318

\* Calculated from data presented assuming chlorophyll a was measured

## CHAPTER V

### OXYGEN BALANCE AND COMMUNITY METABOLISM

Oxygen production, consumption and reaeration determine the oxygen balance of a stream. In evaluating oxygen balance attention is usually given to the concentration of dissolved oxygen (generally measured in daylight hours) and the 5-day BOD test (Moens and Peeler, 1962). The conventional BOD test measures the amount of molecular oxygen required by aerobic bacteria to stabilize decomposable materials in solution and does not consider benthic demands. If photosynthesis is considered, it is frequently measured by the light and dark bottle method, which does not measure the metabolism of bottom forms. Bottom deposits have been found to exert an oxygen demand up to 50% of the total demand in laboratory tests (Oldaker, 1959). Benthic demands must be measured separately and the effects of benthic decomposition under actual stream conditions have been considered nearly impossible to determine (Phelps, 1944).

Oxygen measurement in situ provides a gauge of the metabolism of the whole community (Odum, 1960). The method is applicable to productive flowing systems (Pomeroy, 1961). Community metabolism includes all processes involved with production and consumption of oxygen by the community (Odum and Hoskin, 1958).

### Atmospheric Diffusion

The rate of uptake of oxygen from the atmosphere by water is proportional to the oxygen deficiency and to the area of the air-water interface (Gameson and Barrett, 1958). Oxygen absorption is usually greatest in fast flowing, shallow streams with rough bottoms. An increase in stream velocity, temperature or wind activity increases diffusion. Diffusion is greater when water is cooler than the atmosphere. Small streams follow air temperature more closely than large streams and are less affected by wave action (Welch, 1952). Gas exchange between water and air is affected by the presence of detergents (Hynes, 1963). Detergent components lower reaeration coefficients (Hanya and Hirayama, 1964). Foaming from detergents was noted on several occasions on Skeleton Creek as far downstream as Station 71. A small centrifugal pump was used to lift water from the stream to a garden near Station 25 and large piles of foam were formed in the process.

The diffusion coefficient (K), the rate of transfer of oxygen at 100% saturation deficit, was measured by the use of a clear plastic dome and a Scholander device modified for field use (Copeland and Duffer, 1964), or calculated by the equation of Odum and Hoskin (1958). The dome method did not function properly in cold weather because of flocculation of the pyrogallic solution in the Scholander apparatus. Measured summer K values ranged from 1.02 to 4.06 g O<sub>2</sub>/m<sup>2</sup> hr. Calculated K values ranged from 1.2 to 3.8 g O<sub>2</sub>/m<sup>2</sup> hr, with the highest values occurring in the shallow stretches.

Diffusion coefficients for use in metabolism studies have been determined for various types of water. Copeland (1963) calculated

diffusion rates of 0.3 to 3.0 g O<sub>2</sub>/m<sup>2</sup> hr for oil refinery effluent holding ponds. Odum and Hoskin (1958) reported values of 0.1 to 3.0 g O<sub>2</sub>/m<sup>2</sup> hr for still water with gentle circulation, and Duffer (1965) measured values with the plastic dome of 1.3 to 2.9 g O<sub>2</sub>/m<sup>2</sup> hr for Blue River.

Diffusion coefficients obtained from two nighttime measurements, one after sunset and the other before sunrise, frequently produced unrealistic values up to 60 or 70 g O<sub>2</sub>/m<sup>2</sup> hr. Gordon and Kelly (1962) criticized diffusion coefficients obtained from only two measurements and suggested calculating transfer coefficients over shorter periods of time during the night. The procedure was attempted in this study, but unrealistic values were obtained for most analyses.

Because of the difficulties of measurement, estimated exchange coefficients were used in calculations of respiration and photosynthesis in the present study. Estimates were based upon reach characteristics (Table VI), water temperature and measured and calculated K values. High banks and heavy cover of trees lining the stream prohibited most wind action and riffles were not common, so that turbulence was minimal. In the absence of accurate determinations at the time of metabolism analyses, assumed exchange coefficients have been used in other studies (Odum, 1957a; Edwards and Owens, 1962). Estimated K values ranged from 1.3 g O<sub>2</sub>/m<sup>2</sup> hr in the sluggish stretches of Skeleton Creek during winter to 3.7 g O<sub>2</sub>/m<sup>2</sup> hr in the faster flowing water in summer.

#### Community Metabolism

Certain carbohydrates and oxygen are products of photosynthesis. The rate at which algae produce carbohydrates is called primary

productivity. Assuming a photosynthetic quotient of one, one mole of oxygen is liberated or consumed for every mole of carbohydrate produced or respired. The measurement of oxygen production and respiration is an estimate of primary productivity.

TABLE VI  
MEAN ANNUAL REACH CHARACTERISTICS AND ESTIMATED EXCHANGE  
COEFFICIENTS FOR REACHES BETWEEN 26 and 50 KM

Reach	Depth (m)	Width (m)	Current (m/s)	Flow (cu m/min)	Exchange Coeffi- cient $\text{g O}_2/\text{m}^2 \text{ hr}$ at 0% Saturation
26.6-28.2	0.55	6.7	0.15	21.1	1.5 - 2.6
28.2-30.2	0.55	6.1	0.11	21.1	1.5 - 2.5
30.2-31.5	0.61	6.7	0.09	19.4	1.4 - 2.5
36.3-38.7	0.64	6.7	0.13	19.0	1.3 - 2.2
48.3-49.4	0.52	6.7	0.21	21.6	1.4 - 2.7

A stream is an import-export ecosystem in which the relative quantities of organic matter and raw materials influence the level of metabolism (Odum, 1960). Inflows of organic matter increase community respiration, whereas imports of mineralized materials stimulate photosynthetic production; therefore, the magnitude of photosynthesis and respiration provides a measure of water quality. Gross photosynthesis or respiration may amount to  $60 \text{ g O}_2/\text{m}^2 \text{ day}$  (Odum, 1960). Systems with large import of organic matter may have higher total respiratory metabolism than fertile photosynthetic systems. The polluted Lark River had a gross production of  $0.53 \text{ g O}_2/\text{m}^2 \text{ day}$  and respiration of  $53 \text{ g O}_2/\text{m}^2 \text{ day}$ . In the recovery zone of the sewage-laden White River, production was  $57 \text{ g O}_2/\text{m}^2 \text{ day}$  and respiration was  $18 \text{ g O}_2/\text{m}^2 \text{ day}$  (Table VIII).

The poorest conditions in a stream occur in the oxygen sag zone. This is the area of lowest DO and is of major importance in determining the amount of organic matter that can be assimilated by a stream. Many states regulate the amount of organic wastes that can be discharged into the stream by requiring that DO not fall below 5 ppm for any extended period. The oxygen balance in the sag zone may be significantly affected by photosynthetic oxygen production.

Five stretches in the oxygen sag zone of Skeleton Creek were analyzed periodically for a year (Table VII). In the following discussion stretches are identified by downstream station numbers. Stretches were selected for uniformity and availability. The time of flow between the upstream and downstream stations was limited to 7 hr with most stretches less than 5 hr. Stretch 49.4 had more riffles and was generally more turbid. Otherwise, the five stretches were very similar (Table VI).

Community respiration always exceeded photosynthetic oxygen production in the oxygen sag zone (Table VII). Mean community respiration decreased progressively downstream to Stretch 38.7. The same decrease occurred in concurrent analyses taken in May and December. Photosynthetic production varied only slightly and atmospheric diffusion supplied most of the oxygen for the system. At Stretch 38.7 respiration increased considerably, undoubtedly because of greater algal metabolism. Photosynthetic oxygen production was always higher at Stretch 38.7. The pH was generally a little higher in this stretch, as well as at Station 40, where a peak occurred during the warm season (Fig. 7). During the warm season, BOD (Fig. 10) and total chlorophyll concentration (Fig. 21) also peaked at Station 40. In May, when all stretches



TABLE VII

COMPARISON OF COMMUNITY RESPIRATION, PHOTOSYNTHETIC OXYGEN PRODUCTION  
AND ATMOSPHERIC DIFFUSION IN THE OXYGEN SAG ZONE OF SKELETON CREEK,  
G O<sub>2</sub>/M<sup>2</sup> DAY

Date	Stretch (km)	Community Respiration	Photosynthetic Oxygen Production	Atmospheric Diffusion
May 26-27	26.6-28.2	57.1	18.3	38.8
Jun 28-29		55.4	13.9	41.5
Dec 6-7		41.3	10.1	31.2
Feb 28-29		<u>31.2</u>	<u>6.1</u>	<u>25.1</u>
	Mean	46.2	12.1	34.2
Mar 22-23	28.2-30.2	44.6	22.3	22.3
May 26-27		43.4	21.3	22.1
Jun 19-20		17.8	5.5	12.3
Dec 6-7		<u>36.0</u>	<u>8.9</u>	<u>27.1</u>
	Mean	35.4	14.5	21.0
Mar 22-23	30.2-31.5	35.5	17.9	17.6
May 26-27		36.0	8.8	27.2
Jul 26-27		18.0	4.2	13.8
Dec 6-7		11.5	2.8	8.7
Jan 2-3		<u>12.0</u>	<u>9.6</u>	<u>2.4</u>
	Mean	22.6	8.7	13.9
May 26-27	36.3-38.7	44.6	28.4	16.2
Jul 6-7		41.3	29.4	11.9
Jul 26-27		30.2	16.1	14.1
Sep 27-28		35.3	23.6	11.7
Jan 2-3		24.2	13.5	10.7
Feb 28-29		<u>40.1</u>	<u>22.1</u>	<u>18.0</u>
	Mean	35.9	22.2	13.8
May 26-27	48.3-49.4	30.2	10.5	19.7
Jul 6-7		17.0	6.0	11.0
Sep 27-28		<u>35.3</u>	<u>15.0</u>	<u>20.3</u>
	Mean	27.5	10.5	17.0

were analyzed concurrently, Stretch 38.7 had the highest photosynthetic oxygen production. This was the only stretch in the sag zone in which photosynthesis provided more oxygen than atmospheric diffusion for community respiration.

The effect of flooding on community metabolism appeared in July at Stretch 38.7. A 16 cm rainfall on 11 July at Enid caused the stream to overflow its banks. Photosynthetic oxygen production and community respiration were higher on 5-6 July than on 26-27 July.

Although mean annual respiration appears higher at Stretch 49.4 than at Stretch 31.5, summer means, or the data taken on 26-27 May, show that Stretch 31.5 has higher respiration than Stretch 49.4. Photosynthetic oxygen production was approximately the same for both stretches.

The upstream-downstream procedure is a relatively new method for the analysis of community metabolism, and comparable data are not available for the oxygen sag zones of other streams. Most of the analyses of other polluted streams have been based on the single curve method.

Eight stretches of Skeleton Creek were analyzed during the summer of 1963 (Fig. 22). Photosynthetic oxygen production and respiration were high at Stretch 11.2. Gross photosynthesis was  $60.4 \text{ g O}_2/\text{m}^2 \text{ day}$  and respiration was  $81.5 \text{ g O}_2/\text{m}^2 \text{ day}$  on 19-20 June. These values are somewhat higher than are reported in the literature (Table VIII). High productivity occurred in shallow, clear water flowing over extensive algal growths attached to a shale bottom. Sewage effluents probably provided nutrients such as phosphates, nitrates and other growth-promoting substances (Lackey, 1958). In such a shallow section of the

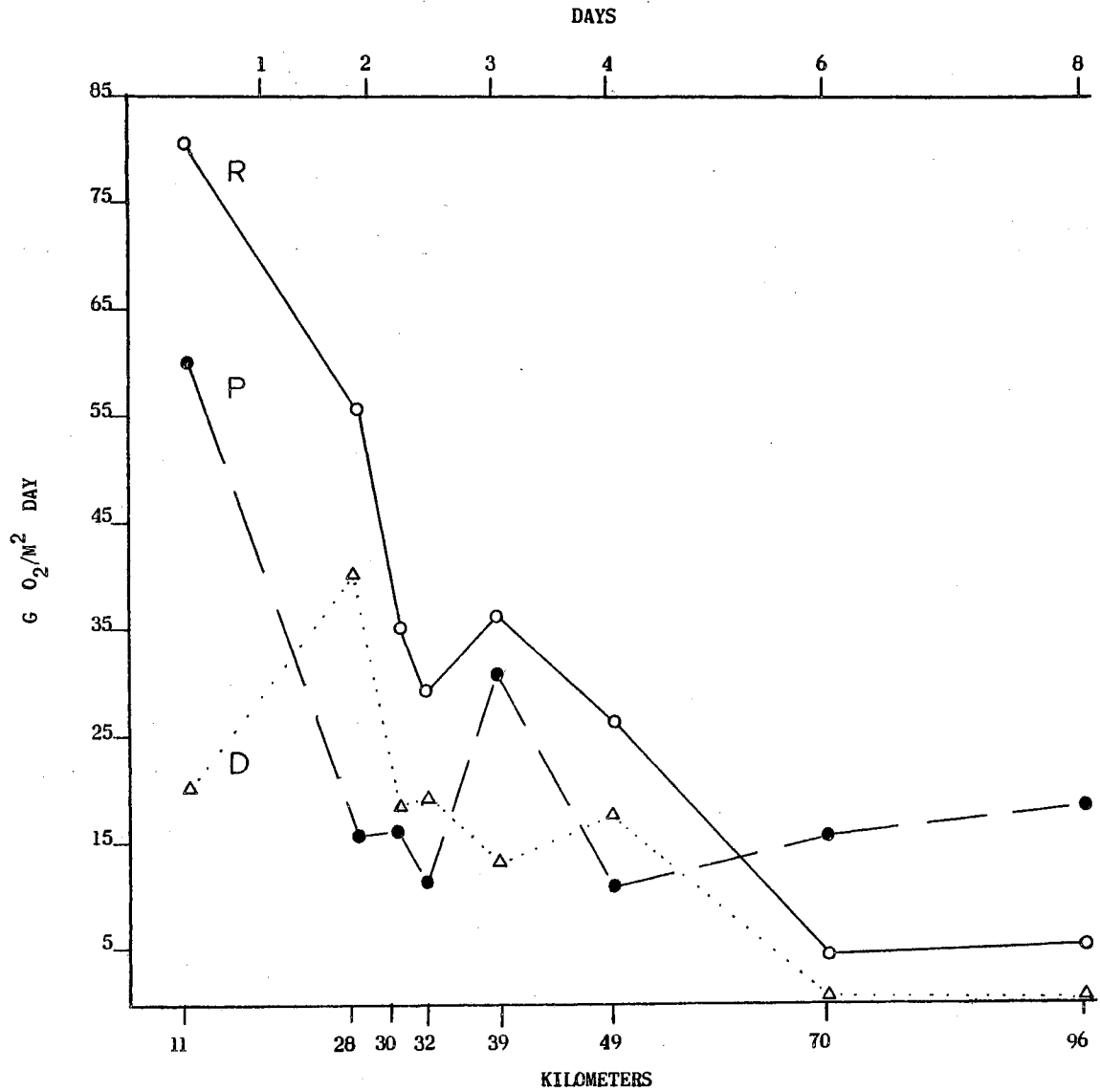


Fig. 22. Summer community metabolism and atmospheric diffusion in Skeleton Creek. Photosynthetic productivity = (—●—), community respiration = (—○—), atmospheric diffusion = (---△---).

stream, a large water surface to volume ratio permits assimilation of a large quantity of organic matter (Patrick, 1962). Since the water was supersaturated with oxygen during daylight hours, atmospheric diffusion was important only at night, preventing the stream from becoming anoxic. Reaeration coefficient for Stretch 11.2 was  $3.7 \text{ g O}_2/\text{m}^2 \text{ day}$ . Atmospheric diffusion furnished approximately  $20 \text{ g O}_2/\text{m}^2 \text{ day}$ . Diffusion up to  $30 \text{ g O}_2/\text{m}^2 \text{ day}$  has been reported for short stretches below pollution outfalls (Mahr, 1930). Respiration was high because of decomposition processes, but algal growths undoubtedly exercised a high oxygen demand.

As the water flowed downstream to Stretch 28.2 (approximately 2 days) respiration and photosynthesis decreased rapidly. Decline in photosynthesis was attributed to a reduction in nutrients and deeper, more turbid water. Chlorophyll concentration was lower at Station 31 than any other section of the stream (Fig. 21), and the lowest DO usually occurred there. Respiration of  $55 \text{ g O}_2/\text{m}^2 \text{ day}$  was satisfied mainly by diffusion. In the next two stretches a steady decline in respiration occurred, with very little change in photosynthetic oxygen production. Atmospheric diffusion and photosynthesis supplied about the same amount of oxygen.

At Stretch 38.7 (approximately 3 days) algae produced about  $30 \text{ g O}_2/\text{m}^2 \text{ day}$  compared to  $13 \text{ g O}_2/\text{m}^2 \text{ day}$  added by atmospheric diffusion. Respiration also increased at this point, and although it would seem that algal respiration might have accounted for much of the increase, the increase in respiration was much less than the increase in photosynthetic oxygen production. In this area in the stream mineralization

of degraded organic matter had occurred, and algal populations increased, especially phytoplankton. A definite improvement in environmental conditions occurred in this area. Fish and macroinvertebrate species increased markedly at this point and remained in larger numbers to the end of the stream (Fig. 20).

Productivity and respiration decreased and atmospheric diffusion increased at Stretch 49.4. Turbidity undoubtedly affected production, since the bottom of the stream was not in the euphotic zone in much of the reach. Respiration was still high, probably because of algal decay. At Stretch 69.6, after six days of flow, a slight increase in photosynthetic oxygen production occurred but there was a great decrease in respiration. For the first time photosynthetic oxygen production was greater than community respiration, and the water was supersaturated with oxygen most of the time. Atmospheric diffusion contributed very little oxygen to the system. The influx of oil brines between Stretches 49.4 and 69.6 may have had an eutrophicating effect since large algal populations were observed in this section of the stream.

Skeleton Creek demonstrated a recovery pattern similar to the sewage-polluted White River, Indiana (Fig. 23). Photosynthetic productivity exceeded respiration below 60 km in both streams. Productivity was greatest near the pollution source in Skeleton Creek, but was highest in the recovery zone in White River. Productivity was generally higher in White River. Respiration was fairly constant in White River, but in Skeleton Creek it varied from an initial high near the source of pollution, to a low in the lower stretches.

High productivity is not limited to polluted waters (Table VIII).

TABLE VIII  
COMPARISON OF COMMUNITY METABOLISM, G O<sub>2</sub>/M<sup>2</sup> DAY

Source	Gross Production	Community Respiration
<u>Unpolluted</u>		
Blue River, Granite Outcrop, Oklahoma (Duffer, 1965)		
Winter. . . . .	10.1	9.0
Summer. . . . .	48.0	19.9
Chalk Stream, England (Edwards and Owens, 1962) . . . . .	3.2 - 6.7	17.6 - 15.4
Neuse River, North Carolina (Hoskin, 1959). . . . .	0.3 - 9.8	0.7 - 21.5
Silver Springs, Florida (Odum, 1957b)		
Winter. . . . .	8.0	2.8
Spring. . . . .	35.0	5.0
<u>Polluted</u>		
Birs River, Switzerland (Schmassmann, 1951)*		
Spring. . . . .	50.0	18.0
River Lark, England (Butcher et al., 1930)*		
Fall. . . . .	0.53	53.0
Spring. . . . .	39.0	35.0
White River, Indiana (Denham, 1938)*		
Summer. . . . .	0.24 - 57.0	18.0 - 29.0
Skeleton Creek, Oklahoma		
Stretch 9.3-11.2		
Summer. . . . .	60.4	81.8
Stretch 26.6-28.2		
Summer. . . . .	13.9 - 18.3	55.4 - 57.1
Winter. . . . .	6.1 - 10.1	31.2 - 41.2
Stretch 30.2-31.5		
Summer. . . . .	4.2 - 8.8	18.0 - 36.0
Winter. . . . .	2.8 - 9.6	11.5 - 12.0
Stretch 36.3-38.7		
Summer. . . . .	16.1 - 29.4	30.2 - 44.6
Winter. . . . .	13.5 - 22.0	24.2 - 40.0
Stretch 69.3-69.6		
Summer. . . . .	15.5	4.9

\* Calculated by Odum (1956).

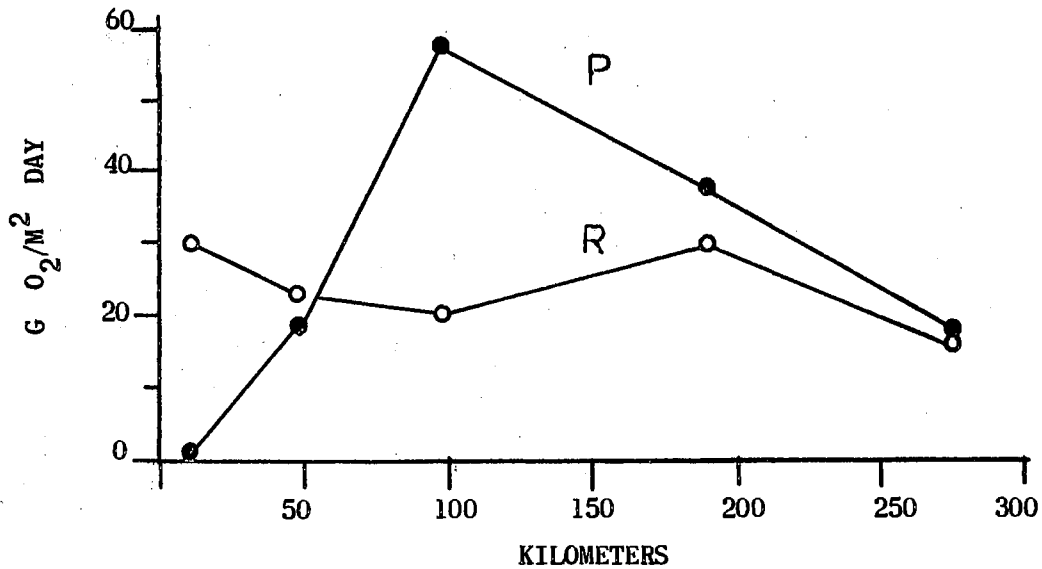


Fig. 23. Community metabolism in White River, Indiana July (Odum, 1956). Photosynthetic productivity = (—●—), community respiration = (—○—).

Duffer (1965) measured production of  $48 \text{ g O}_2/\text{m}^2$  day during the summer in Blue River and Odum (1957b) measured high primary productivity in the summer at Silver Springs, Florida. Although production can be high in unpolluted streams, respiration tends to be markedly lower than in polluted systems.

#### Productivity and Respiration Ratio - The P/R Ratio

The dimensionless ratio of productivity to respiration (P/R) provides an index by which flowing communities can be classified (Odum, 1956). When production equals respiration, with no accumulation of organic matter produced by photosynthesis or imported into the system, the community is in a steady-state condition. A P/R ratio greater than

one occurs in an autotrophic community in which productivity exceeds respiration and organic matter is accumulated in the form of plant biomass. A P/R ratio less than one indicates a heterotrophic community in which respiration exceeds productivity.

Low P/R ratios are characteristic of waters with a high oxygen demand. As the demand decreases the P/R ratio increases. In studies of the Moscow River, depression of P was found in waters polluted by industrial and sewage effluents, and increase of P and of the P/R ratio occurred according to the degree of self-purification (Kabanov, 1961).

The highest P/R ratios occurred in the two lower parts of Skeleton Creek (Table IX). High P/R ratios have been reported for the recovery zone of some streams (Odum, 1956). Birs River, Switzerland had a P/R ratio of 2.8 and White River, Indiana 3.2. In the recovery zone organic matter is accumulated faster than it is used, or in general, algal cells are produced faster than they die. Plant material is relatively stable and exerts less oxygen demand than organic wastes (Winberg, 1955).

The lowest P/R ratios in Skeleton Creek occurred in the oxygen sag zone, where productivity was low and respiration was high. Stretch 28.2 had a mean P/R ratio of 0.25, which was the lowest in the sag zone. Stretch 38.7 had a mean P/R ratio of 0.61, which was the highest in the sag zone. Mean P/R ratios increased from Stretch 28.2 to Stretch 36.7, indicating an improvement in water quality. P/R ratios were always lower at Stretch 49.4 than at Stretch 38.7, which may be attributed to lessened photosynthetic activity and increased respiration.



TABLE IX

## RATIO OF PHOTOSYNTHETIC PRODUCTIVITY TO RESPIRATION

Date	9.3-11.2	26.6-28.2	28.2-30.2	30.2-31.5	36.3-38.7	48.3-49.4	69.3-69.6	95.4-95.7
<u>1963</u>								
March 23			0.25	0.50				
June 19	0.73		0.31					
June 28		0.25						
July 6					0.71	0.35		
July 26				0.23	0.53			
Aug 12							3.17	3.62
Sept 27					0.67	0.43		
Dec 6		0.24	0.25	0.25				
<u>1964</u>								
Jan 2				0.80	0.56			
Feb 28		0.19			0.55			
May 26		<u>0.32</u>	<u>0.49</u>	<u>0.24</u>	<u>0.63</u>	<u>0.35</u>		
Mean	0.73	0.25	0.32	0.40	0.61	0.38	3.17	3.62

### Efficiency

Efficiency of algae in converting solar radiation energy to chemical energy was computed from gross photosynthesis and radiation data (Table X). Only 50% of total radiation was considered to be photosynthetically active (Edmondson, 1955; Ryther, 1956; Copeland, 1963; Butler, 1964). Efficiency values were obtained by the equation of Copeland (1963), assuming that 3500 calories are required to form (CH<sub>2</sub>O) equivalent to one gram of oxygen produced.

Efficiency ranged from 0.48 to 6.4% with a mean of 2.1%. Lowest efficiency occurred in July at Stretch 31.5, one week after a 15 cm rainfall which caused the stream to overflow the channel. Low efficiency, excluding flood conditions, was 0.58% at Stretch 30.2 in June. Highest efficiency and greatest productivity occurred in June at Stretch 11.2, where water was shallow and clear and algal growths were abundant. The high efficiency value is comparable to 6% at Eniwetok Atoll (Odum and Odum, 1955). Efficiencies (50% of total radiation) similar to Skeleton Creek occurred in Blue River (0.2 - 5.4%, Duffer, 1965), and Ivel River (2.0 - 4.4%, Edwards and Owens, 1962). Efficiencies up to 10% have been reported for sewage oxidation ponds (Oswald et al., 1957) and springs in Florida (Odum, 1957a).

Efficiencies were slightly higher between Stations 25 and 50 during summer months, when corrected for heavy shading. A similar efficiency change with shading was reported by Odum (1957b) at Silver Springs.

Algae in the sag zone were most efficient at Stretch 38.7, and least efficient at Stretch 49.4. Efficiency was highest at Stretch 38.7, probably because nutrients were available and the water was usually

TABLE X

## GROSS PHOTOSYNTHESIS, SOLAR RADIATION AND PHOTOSYNTHETIC EFFICIENCY

Date	Stretch (km)	Gross Photo- synthesis $G O_2/M^2$ Day	Total Solar Radiation Cal/Cm <sup>2</sup> Day	Photo- synthetic Efficiency %	
Jun	19-20	9.3-11.2	60.4	657	6.42
May	26-27	26.2-28.2	18.3	650	1.96
Jun	28-29		13.9	734	1.32
Dec	6-7		10.1	251	2.80
Feb	28-29		<u>6.1</u>	<u>365</u>	<u>1.16</u>
		Mean	12.1	500	1.81
Mar	22-23	28.2-30.2	22.3	520	2.98
May	26-27		21.3	650	2.30
Jun	19-20		5.5	657	0.58
Dec	6-7		<u>8.9</u>	<u>251</u>	<u>2.48</u>
		Mean	14.0	517	2.08
Mar	22-23	30.2-31.5	17.9	520	2.98
May	26-27		8.8	650	0.94
Jul	26-27		4.2	627	0.48
Dec	6-7		2.8	251	0.78
Jan	2-3		<u>9.6</u>	<u>277</u>	<u>2.42</u>
			8.7	465	1.48
May	26-27	36.3-38.7	28.4	650	3.06
Jul	6-7		29.4	711	2.88
Jul	26-27		16.1	627	1.80
Sep	27-28		23.6	518	3.18
Jan	2-3		13.5	277	3.40
Feb	28-29		<u>22.1</u>	<u>365</u>	<u>4.24</u>
		Mean	22.2	525	3.09
May	26-27	48.3-49.4	10.5	650	1.14
Jul	6-7		6.0	711	0.59
Sep	27-28		<u>15.0</u>	<u>518</u>	<u>2.02</u>
		Mean	10.5	626	1.25
Aug	12-13	69.3-69.6	15.5	529	2.04
Aug	12-13	95.4-95.7	18.5	529	2.44

less turbid. Flooding and high turbidity were limiting factors in productivity and photosynthetic efficiency in Skeleton Creek.

Chemical analyses on Skeleton Creek indicated that sources of pollution were entering the stream other than domestic and oil refinery effluents. At least two points along the stream were receiving oil field brines. Oxygen-consuming materials such as trash and leaf fall undoubtedly affected purification processes. Log jams along the stream increased retention time and were beneficial.

Macroinvertebrate and fish populations increased downstream with the addition of flow, improvement in water quality and higher minimum dissolved oxygen concentration. Oil field brines entering the stream in the lower reaches did not seem to affect these populations.

Photosynthetic oxygen production was an essential factor in Skeleton Creek. Photosynthesis provided most of the oxygen in the upper reaches, and diffusion was important during hours of darkness in keeping the stream from becoming anoxic. The large diurnal variation in oxygen concentration did not appear to be caused by a daily rhythm in the pollution load, since the flow did not vary over the 24 hr observation period. In the low part of the oxygen sag curve, photosynthesis supplied approximately 40% of the total oxygen for the system. The productive stretch in the sag zone was apparently very beneficial for stream life, since macroinvertebrates and fish species increased markedly in this area of the stream. In the lower reaches, photosynthesis supplied nearly all of the oxygen. Water quality had improved considerably after approximately 60 km of flow.

## CHAPTER VI

### SUMMARY

1. A small stream receiving domestic and oil refinery effluents was studied from March 1963 to July 1964. Physical, chemical and biological conditions were measured, with particular reference to the oxygen balance determined by the upstream-downstream oxygen curve method. Most diurnal analyses were conducted in the oxygen "sag" zone.

2. Stations on Skeleton Creek were numbered in kilometers below the confluence with Boggy Creek.

3. Data were assigned to cool or warm seasons on the basis of total monthly precipitation and mean water temperature. The cool season included December, January and February, and the warm season included March through November.

4. Mean measured seasonal flow and turbidity were lower in the cool season and alkalinity, pH, conductivity, BOD, COD, total residue and DO were higher in the cool season.

5. Diurnal and station variation of DO was considerable. The highest DO occurred in the upper and lower reaches and the lowest concentration in the middle of the stream.

6. The position of the sag curve changed seasonally. The sag curve occupied at least three different stretches of the stream during the study. The low point in the sag curve occurred at Station 26 in June, Station 39 in May and below Station 39 in February.

7. Twenty-seven genera of algae were identified in Skeleton Creek. Euglena, Navicula and Chlamydomonas were the dominant genera. Algal blooms of Euglena and Chlamydomonas were observed on several occasions.

8. Benthic chlorophyll a concentration was greater in the first 31 km of the stream, but planktonic chlorophyll a was higher downstream.

9. Estimated exchange coefficients were used in calculations of respiration and photosynthesis. Estimates were based upon reach characteristics, water temperature and measured and calculated K values. Estimated exchange coefficients ranged from 1.3-2.7 g O<sub>2</sub>/m<sup>2</sup> hr in the sag zone to 3.7 g O<sub>2</sub>/m<sup>2</sup> hr in the upper, shallow reaches.

10. Five stretches in the oxygen sag zone were analyzed for a year. Highest respiration occurred at Stretch 26.6-28.2 and lowest at Stretches 30.2-31.5 and 48.3-49.4. Highest productivity occurred at Stretch 36.3-38.7 ranging from 13.5 g O<sub>2</sub>/m<sup>2</sup> day in January to 29.4 g O<sub>2</sub>/m<sup>2</sup> day in July. This was the only stretch in the sag zone that supplied more oxygen by photosynthesis than by atmospheric diffusion for the system. Photosynthesis furnished approximately 40% of the total oxygen for the community demand in the sag zone.

11. The highest production measured was 60.4 g O<sub>2</sub>/m<sup>2</sup> day in the upper, shallow region of the stream. Respiration was also the highest in this region, amounting to 81.8 g O<sub>2</sub>/m<sup>2</sup> day.

12. Photosynthetic productivity exceeded community respiration in the lower reaches of the stream.

13. Ratio of productivity to respiration increased downstream in the sag zone, indicating an improvement in water quality. P/R ratios

increased from 0.25 in the sag zone to 3.6 in the lower reaches of Skeleton Creek.

14. Photosynthetic efficiency ranged from 0.48 to 6.4% with a mean of 2.1%. Highest efficiency and greatest productivity occurred in June at Stretch 9.3-11.2. Lowest efficiency occurred in the sag zone at Stretch 30.2-31.5, two weeks after flood conditions.

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