# DIURNAL VARIATIONS IN THE AMOUNT OF DISSOLVED OXYGEN, ALKALINITY, AND FREE AMMONIA IN CERTAIN FISH PONDS AT FAIRPORT, (IOWA). 

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## INTRODUCTION.

Some preliminary observations made during the summers of 1927 and 1928 (Wiebe, 1930) made it apparent that the changes in the amount of dissolved oxygen and the alkalinity that occur in a pond within a 24 -hour period are as large if not larger than the seasonal change where, for instance, the samples are taken regularly at 8 A. M. For this reason it was decided in 1929 to make a series of tests to determine the extent of the diurnal variations in dissolved oxygen, alkalinity, and in some instances ammonia nitrogen. Diurnal changes in the gaseous constituents of river water have been studied by Butcher et al. (1927-1928).

## RESULTS AND DISCUSSION.

The first series was made on a pond called D-10 that has an area of 3.54 acres, on June 6-7, 1929. The water had a depth of 7.5 at the place of sampling. A small amount of plankton was present in the pond. The sky was clear during the day. The results for this series are shown in Table I. This table shows that the variations in the absolute amount of dissolved oxygen were relatively small. The percent of saturation on the surface rose from $105.53 \%$ at $8 \mathrm{~A} . \mathrm{M}$. to $125.76 \%$ at $4 \mathrm{P} . \mathrm{M}$. It then decreased to $102.39 \%$ at 5 A . M. the next day. On the bottom the percent of saturation rose from $94.64 \%$ at 8 A. M. to $107.69 \%$ at 4 P. M. At 5 A. M. on June 7, it was down to $90.47 \%$. The variations in free ammonia nitrogen were very small. The water at the surface was alkaline to phenolphthalein throughout the entire test period. This means there was a deficiency in free $\mathrm{CO}_{2}$. This deficiency ranged from 2.26 p. p. m. to 5.65 p. p. m. On the bottom there was

[^0]some free $\mathrm{CO}_{2}$ at all times. This varied from a minimum of 1.13 p. p. m. to a maximum of 5.65 p. p. m.

Table I.
Table I Shows for D-10 Dissolved Oxygen, free $\mathrm{CO}_{2}$, and Ammonia Nitrogen in Parts per Million. Percentage of Saturation for Dissolved Oxygen are also Shown.

| Date | $\mathrm{O}_{2}$ |  | Percent Saturation |  | $\begin{gathered} \mathrm{NH}_{3} \\ \text { Top } \end{gathered}$ | $\qquad$ <br> Bottom | Free $\mathrm{CO}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Top | Bottom | Top | Bottom |  |  | Top | Bottom |
| 6-6-29 |  |  |  |  |  |  |  |  |
| 8 A. M. | 10.08 | 9.18 | 105.53 | 94.64 | . 054 | . 052 | $-2.26$ | 2.26 |
| 11 A. M | 10.80 | 9.72 | 108.67 | 98.94 | . 054 | . 050 | $-3.39$ | 2.26 |
| $2 \mathrm{P} . \mathrm{M}$. | 10.73 |  | 122.98 |  | . 052 | . 052 | $-5.65$ | 1.13 |
| 4 P . M. | 10.86 | 10.11 | 125.76 | 107.69 |  |  | $-5.65$ | 1.13 |
| $7 \mathrm{P} . \mathrm{M}$. | 10.56 | 9.93 | 120.00 | 105.00 |  |  | $-5.65$ | 2.26 |
| $10 \mathrm{P} . \mathrm{M}$. | 9.57 | 9.96 | 108.72 | 105.07 | . 052 | . 051 | -4.52 | 2.26 |
| 6-7-29 |  |  |  |  |  |  |  |  |
| $1 \mathrm{~A} . \mathrm{M}$ | 9.51 |  | 104.73 |  |  |  | -4.52 |  |
| $5 \mathrm{~A} . \mathrm{M}$. | 9.39 | 8.58 | 102.39 | 90.47 | . 050 | . 050 | -2.26 | 5.65 |

Table II.
Table II Shows for D-3 Value for Dissolved Oxygen, Phenolphthalein Alkalinity and Ammonia Nitrogen in Parts per Million. Percentage of Saturation for Dissolved Oxygen are also Shown.

| Date | Dissolved Oxygen |  | Percent Saturation |  | $\mathrm{NH}_{3}$ <br> Top | $\left\|\begin{array}{c} \begin{array}{c} \text { Nitro- } \\ \text { gen } \end{array} \\ \text { Bottom } \end{array}\right\|$ | Phenolphthalein Alk. |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Top | Bottom | Top | Bottom |  |  | Top | Bottom |
| 7-2-29 |  |  |  |  |  |  |  |  |
| $8 \mathrm{~A} . \mathrm{M}$. | 10.22 | 8.84 | 114.70 | 97.35 | . 052 | . 040 | 30.51 | 27.12 |
| $11 \mathrm{~A} . \mathrm{M}$. | 11.34 | 10.78 | 134.12 | 118.72 | . 028 | . 028 | 31.64 | 27.12 |
| 2 P. M | 11.52 | 12.64 | 142.74 | 150.83 | . 025 | . 025 | 31.64 | 39.55 |
| 5 P. M. | 11.90 | 14.87 | 151.68 | 189.90 | . 032 | . 032 | 33.90 | 37.29 |
| 8 P. M. | 11.15 | 13.76 | 131.87 | 167.39 | . 026 | . 028 | 31.64 | 33.9 |
| $12 \mathrm{P} . \mathrm{M}$. | 11.34 | 12.83 | 132.94 | 153.10 | . 032 | . 026 |  |  |
| 7-3-29 |  |  |  |  |  |  |  |  |
| $2 \mathrm{~A} . \mathrm{M}$. | 12.64 |  | 148.18 |  |  |  |  |  |
| 3:30 A. M. . | 12.64 | 11.15 | 145.62 | 128.45 | . 032 | . 032 |  |  |
| 5:30 A. M.. | 11.52 | 7.99 | 130.46 | 87.99 |  |  |  |  |
| 9:00 A. M. | 11.90 | 10.59 | 135.92 | 116.63 | . 027 | . 028 |  |  |

Table II gives the result for a series of determinations made on a pond called D-3 that has an area of approximately 0.9 acre and a depth of 5 feet at the sampling point. This series was run on July $2-3$, 1929. This pond had a good crop of Aphanizomenon at this time. It was approaching the state
of water bloom. The dissolved oxygen in the surface samples varied from 10.22 p. p. m. to 12.64 p. p. m. and the percent of saturation from $114.70 \%$ to $151.68 \%$. In the bottom samples the dissolved oxygen ranged from 8.84 p. p. m. at 8 A. M. July 2, to 14.87 p. p. m. at 5 P. M. At 5:30 the next morning it was down to 7.99 p. p. m. The percent of saturation ranged from $97.35 \%$ at 8 A . M. to $189.90 \%$ at 5 P. M. Then at $5: 30 \mathrm{~A}$. M.

Table III.
Table III Shows Values for C-2 and C-3 for Dissolved Oxygen, Phenolphthalein Alkalinity in Parts per Million. Percentages of Saturation for Dissolved Oxygen are also Shown.

| Date | Dissolved Oxygen |  | Phenolphthalein Alk. | Dissolved Oxygen |  | $\begin{aligned} & \text { Phenol- } \\ & \text { phthalein } \\ & \text { Alk. } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 8-16-29 |  |  |  |  |  |  |
| 8 A. M | 11.89 | 125.93 | 27.12 | 11.28 | 124.72 | 25.99 |
| $10 \mathrm{~A} . \mathrm{M}$. | 13.93 | 156.90 | 28.25 | 13.68 | 154.21 | 29.38 |
| 12 N . |  |  | 36.16 | 19.22 | 223.35 | 41.80 |
| $2 \mathrm{P} . \mathrm{M}$ | 20.18 | 240.81 | 44.07 | 21.98 | 262.29 | 44.07 |
| $3 \mathrm{P} . \mathrm{M}$ | 20.42 | 243.67 | 45.2 | 25.94 | 312.65 | 51.98 |
| $4 \mathrm{P} . \mathrm{M}$ | 21.74 | 259.42 | 45.2 | 24.85 | 297.67 | 57.63 |
| 6 P . M. | 19.70 | 233.76 | 48.59 | 24.25 | 289.37 | 61.02 |
| $8 \mathrm{P} . \mathrm{M}$. |  |  | 47.46 | 22.69 | 258.96 | 57.63 |
| 10 P. M. | 18.98 | 216.66 | 42.94 | 20.19 | 230.61 | 51.98 |
| 8-17-29 |  |  |  |  |  |  |
| $1 \mathrm{~A} . \mathrm{M}$ | 17.18 | 191.69 | 40.68 | 18.24 | 204.70 | 42.94 |
| $2 \mathrm{~A} . \mathrm{M}$. | 14.89 | 167.11 | 38.42 | 17.29 | 192.32 | 41.80 |
| $3 \mathrm{~A} . \mathrm{M}$. | 14.41 | 161.40 | 38.42 | 16.09 | 178.97 |  |
| 4 A . M. | 14.41 | 161.40 | 36.16 | 15.61 | 173.63 | 42.94 |
| 5 A. M. | 13.09 | 144.16 | 36.16 | 13.81 | 152.09 |  |
| $6 \mathrm{~A} . \mathrm{M}$. | 11.65 | 128.30 | 32.77 | 13.10 | 143.42 | 32.77 |
| $7 \mathrm{~A} . \mathrm{M}$. | 13.69 | 151.37 | 32.77 | 14.64 | 161.23 | 35.03 |
| $8 \mathrm{~A} . \mathrm{M}$. | 13.89 | 154.50 | 36.16 | 16.33 | 181.64 | 39.55 |

July 3, the percent saturation was down to $87.99 \%$. The ammonia nitrogen showed the largest change between 8 and 11 A. M. After that the changes were relatively small. Alkalinity determinations were made from 8 A . M. to 5 P . M. The water was always strongly alkaline to phenolphthalein, showing that a free $\mathrm{CO}_{2}$ deficiency existed. The changes in alkalinity were small in the surface samples. In the bottom samples the alkalinity varied from 27.12 p . p. m. at 8 A . M. to 39.55 p. p. m. at 5 P. M. At 8 P. M. it was down to 33.9 p. p. m.

The fact that greater variations in dissolved oxygen and alkalinity occurred in the bottom samples than in the surface
samples is accounted for by a peculiar habit of the alga, Aphanizomenon. This alga reacts negatively to strong sunlight. So on a clear day after the sun gets up fairly high in the sky this alga begins to move downward. During the night it migrates again into the upper strata. This is what happened on the day when this series of tests was run. This behavior of Aphanizomenon, I think, accounts also for the rise in the dissolved oxygen at the surface during the night.

Table III presents the results of a series of tests made on the waters of two small concrete ponds. These ponds, $\mathrm{C}-2$ and $\mathrm{C}-3$, each have an area of 378 square feet. The depth of the water is 14 inches at one end and 20 inches at the other. These ponds were in a state of water bloom consisting of a number of species of green and blue-green algæ. The algæ in these ponds were so thick that the transparency of the water was reduced to a few inches. Only surface samples were taken in this case. The percent of saturation in C-2 ranged from $125.93 \%$ at 8 A. M. August 16, 1929, to $259.42 \%$ at 4 P. M. on the same date. At 6 o'clock the next morning the percent of saturation was down to $128.30 \%$. In C-3 the percent of saturation of dissolved oxygen varied from $124.72 \%$ at $8 \mathrm{~A} . \mathrm{M}$. to $312.65 \%$ at $3 \mathrm{P} . \mathrm{M}$. on the same date. The following morning at 6 o'clock it was down to $143.42 \%$. The water in both ponds was strongly alkaline throughout the entire test period. This again shows the entire absence of free $\mathrm{CO}_{2}$. In C-2 the range in alkalinity was from 27.12 p. p. m. to 48.59 p. p. m. Then it decreased to 32.77 p. p. m. In C-3 the changes were from 25.99 p. p. m. to 61.02 p. p. m. and then to 32.77 p. p. m.

Table IV shows another set of determinations made on the ponds discussed in the preceding paragraph. In this case samples were taken from the bottom as well as from the surface. The condition of water-bloom still persisted. At 8 A . M. September 4, the percent of saturation with $\mathrm{O}_{2}$ amounted to $88.9 \%$ at the surface of C-2; at 4 P. M. this had risen to $267.90 \%$. The next day at 8 A. M. it stood at $52.34 \%$; at 4 P. M. it was up to $254.72 \%$. At 8 A. M. on September 6 , it was down to $114.45 \%$ again. The table shows that large changes in the percent of saturation also occurred in the bottom samples. The phenolphthalein alkalinity in the surface samples of C-2 ranged from 23.73 p. p. m. to 67.80 p. p. m. to 32.77 p. p. m. to 62.15 p. p. m. and finally to 45.2 p. p. m. Large changes

FIGURE 1.


Fig. 1. Variations in the percentage of saturation of dissolved oxygen. C and D indicate pond series; S stands for surface and B for bottom.
occurred also in the alkalinity of the bottom samples in C-2. The results for $\mathrm{C}-3$ are essentially similar to those for $\mathrm{C}-2$, i. e., the $\mathrm{O}_{2}$ and the alkalinity increased during the day and decreased during the night. The variations in the percentages of saturation with dissolved oxygen in D-10, D-3, and for the first two sets of experiments on the C-ponds are shown graphically in Fig. 1. The graphs were prepared by Mr. J. B. Southall.

Table IV.
Table 4 Shows Values for Dissolved Oxygen, Phenolphthalein Alkalinity in Parts per Million. Percentages of Saturation are also Shown.

| Date | Dissolved Oxygen |  | Percent Saturation |  | Phenolphthalein Alkalinity |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | C-2 | C-3 | C-2 | C-3 | C-2 | C-3 |
| 9-4-29 |  |  |  |  |  |  |
| 8 A. M. | 7.85 | 4.36 | 88.9 | 52.04 | 23.73 | 19.21 |
|  | 5.93 | 1.91 | 70.12 | 22.59 | 22.60 | 19.21 |
| 5 P. M. | 21.62 | 16.92 | 267.90 | 205.83 | 67.80 | 67.80 |
|  | 15.34 | 11.68 | 188.33 | 140.72 | 54.24 | 54.25 |
| 9-5-29 |  |  |  |  |  |  |
| 8 A. M. | 4.70 4.02 | 1.06 1.06 | 52.34 44.27 | 11.55 | 32.77 33.90 | 14.69 16.95 |
| $4 \mathrm{P} . \mathrm{M}$. | 21.11 | 17.62 | 254.72 | 204.76 | 62.15 | 54.24 |
|  | 19.88 | 7.66 | 229.03 | 86.74 | 64.41 | 39.55 |
|  |  |  |  |  |  |  |
| 8 A. M. | 11.34 | 5.06 | 120.44 | 54.11 | 45.2 | 19.21 |

[^1]Table V shows the results of some determinations made on C-3 on August 19, 1929. This table shows in addition to the dissolved oxygen and phenolphthalein alkalinity also the methyl orange alkalinity, pH and temperatures. The fact of particular interest here is that at $1 \mathrm{P} . \mathrm{M}$. the phenolphthalein alkalinity equalled one-half the methyl orange alkalinity, and at 4 P . M. the methyl orange alkalinity was less than twice the phenolphthalein alkalinity. This means that the algæ had used all the free $\mathrm{CO}_{2}$, all the bicarbonate $\mathrm{CO}_{2}$ and some of the $\mathrm{CO}_{2}$ of the normal carbonate. This means that the alkalinity was due to the normal carbonate and the hydroxide. It had previously been reported by Birge and Juday (1911) that certain algæ used as much as $83 \%$ of the half-bound $\mathrm{CO}_{2}$ and by Wiebe
(1930) that algæ used $92 \%$ of the half-bound $\mathrm{CO}_{2}$. That algæ can use all of the half-bound and some of the bound is in accord with the observation of Neresheimer and Ruttner (1929) that aquatic plants may withdraw small amounts of $\mathrm{CO}_{2}$ from normal carbonates.

Table V.
Table V Shows Dissolved Oxygen, Phenolphthalein Alkalinity, Methyl Orange Alkalinity in Parts per Million, Ph Values and Temperatures in Degrees C. for C-3 on August 19, 1929.

| Hour | $\mathrm{O}_{2}$ | Phenol- <br> phthalein <br> Alk. | M. O. <br> Alk. | Ph. | Temp. |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |
| 8:30 A. M..... | 12.01 | 40.68 | 138.99 | 9.3 | 20.75 |
| $1: 00 \mathrm{P} . \mathrm{M} \ldots \ldots$. | 18.25 | 68.93 | 137.86 | 9.5 | 27.5 |
| $4: 00 \mathrm{P} . \mathrm{M} . \ldots .$. | 27.63 | 76.84 | 137.86 | 9.5 | 27.5 |

## SUMMARY.

(1) The diurnal variations in dissolved oxygen, phenolphthalein alkalinity, and free ammonia nitrogen have been determined in several instances.
(2) Very marked changes in the actual amount of dissolved oxygen and phenolphthalein alkalinity were observed within a 24 -hour period.
(3) The extent of these variations are determined by the abundance of the algæ.
(4) It appears that the algae can utilize all the $\mathrm{CO}_{2}$ present as the bicarbonate as well as some of the $\mathrm{CO}_{2}$ of the normal carbonate.
(5) Table IV .suggests that the algae may become so abundant as to endanger fish life by depletion of the $\mathrm{O}_{2}$ during the night.

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[^1]:    Note.-In Table IV, the upper figures in each case refers to the surface sample. The lower figures has reference to a bottom sample.

