The Hydrogen Ion Concentration of Sea Water in its Relation to Photosynthetic Changes.

PART III.

By

W. R. G. Atkins, O.B.E., Sc.D., F.I.C.,

Head of the Department of General Physiology at the Plymouth Laboratory.

With Figures 1–4 in the Text.

INTRODUCTION.

THE present paper is a continuation of the work already published* under the above general title and should be considered in relation to the results previously recorded. The method of performing the measurements remained unchanged; xylenol blue was used to check the determinations made with cresol red in the more alkaline regions—namely, around pH 8·24. The water was tested immediately after being drawn, or within a few hours, unless otherwise stated in the tables.

The results obtained are tabulated for reference, but since the seasonal changes are in a general way similar to those of 1921–22 they have only been shown graphically in four figures, which are of interest as they illustrate the differences between the years and the variation of pH with depth.

Salinity determinations, made at the Government Chemist's Laboratory, were used to apply small corrections to the pH values of the L series where necessary, but since they are published as part of the International Hydrographic Investigations they are omitted here.

THE RELATION OF THE WATER OF PLYMOUTH SOUND TO THAT OF THE OPEN SEA THROUGHOUT THE YEAR.

In this series perhaps the most noticeable differences as compared with the previous year are the low pH values for March 12th, which extend right out to the Eddystone, L 5, instead of ceasing at the Breakwater,

* Journ. Mar. Biol. Assoc., Vol. XII, No. 4, pp. 717–771, 1922, and Vol. XIII, No. 1, pp. 93–118, 1923.

L 2. The samples of the 14th also show this, but to a much smaller degree ; while those of the 21st are normal.

The salinity determinations indicate that the effect was due to the great volume of fresh water coming down the rivers.

Unfortunately a complete series was not obtained in May, but photosynthetic activity must then have been very great, since the high values pH 8·23 were found at L 3 and L 4, both at the surface and at the bottom —namely, at 45 and 50 metres depth respectively. The E 1 depth series contains no such high values for these depths, but between Sardinia and Italy, Palitzsch records pH 8·23 at the surface and 8·21 at 100 metres.

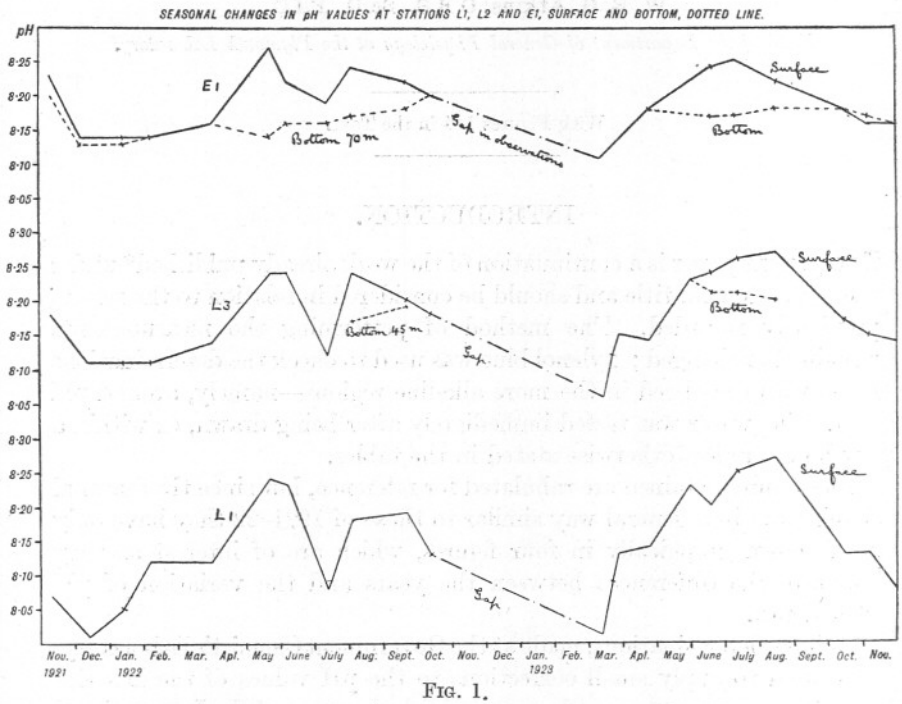

FIG. 1.

The July values for the L series are markedly different from those of the previous year. In 1922 the wet and stormy end of June caused the July pH values to be low, abnormally low it is probable, viz. pH 8·08 and pH 8·12 for L 1 and L 3, as compared with pH 8·25 and pH 8·26 respectively for 1923. This drop in July may be appreciated from a study of Fig. 1, which shows the pH values for L 1, L 3, and E 1 from November, 1921, to November, 1923, inclusive. Bottom values are shown by a dotted line. The water accordingly remained uniformly alkaline at the stations throughout the summer. The relation between this and the seasonal distribution of sunshine is shown in Fig. 4.

	March 12th.		March 14th.		March 21st.	March 28th.	
Station.	t °C.	pH	t °C.	pH	pH	t°C.	pH
L 1	8·7	8·01	8·6	7·98	8·09	9·6	8·13
L 2	8·8	8·01	8·8	8·09	8·09	9·4	8·13
L 3	9·1	—	9·0	8·09	8·12	9·25	8·15
L 4	9·1	8·01	9·1	8·08*	8·12	9·2	8·14
L 5	9·1	8·03	9·1	—	8·12	9·3	8·14
L 6	9·2	8·11	—	—	—	—	—
E 1	9·3	8·11	9·6	8·12	—	—	—

pH determined on 13th. * pH determined on 15th, rest on 16th.

	April 24th.		May 22nd.	May 31st.	June 19th.		July 10th & 12th.	
Station.	t °C.	pH	t °C.	pH	t °C.	pH	t °C.	pH
L 1	9·7	8·14	10·8	—	12·6	8·20	16·65	8·25
L 2	9·7	8·10	10·8	—	12·45	8·24	15·85	8·25
L 3	9·5	8·14	10·7	8·23†	12·35	8·24	16·7	8·26
L 4	9·7	8·13	10·4	8·23†	12·55	8·24	16·6	8·25
L 5	9·7	8·16	10·7	—	12·6	8·24	15·6	8·23
L 6	9·9	8·16	10·8	—	12·7	8·24	16·8	8·25
E 1	10·1	8·18	10·9	—	12·8	8·24	16·6	8·25

pH determined on 26th. † Same at bottom.

	August 15th.		Sept. 13th.	October.		November 7th.	
Station.	t °C.	pH	t °C.	t °C.	pH	t °C.	pH
L 1	15·4	8·27	14·8	13·0	8·13	11·0	8·13
L 2	14·5	8·26	14·6	12·8	8·14	11·3	8·14
L 3	16·3	8·27	14·4	13·1	8·17	12·1	—
L 4	16·7	8·26	15·1	13·3	8·17	12·1	8·17
L 5	16·2	8·26	14·7	13·6	8·17	12·0	—
L 6	17·0	8·22	14·6	13·6	8·18	11·9	—
E 1	16·7	8·22	15·0	13·0	8·18	12·1	8·16

pH determined on 9th.

	December 10th.		January 2nd, 1924.	
Station.	t °C.	pH	t °C.	pH
L 1	9·1	8·06	8·9	8·02
L 2	9·2	8·10	9·0	8·03
L 3	9·2	8·14	9·0	8·09
L 4	9·4	8·15	9·0	8·09
L 5	9·9	8·16	9·1	8·14
L 6	10·3	8·16	9·1	8·14
E 1	10·2	8·16	9·4	8·16

THE SEASONAL CHANGES IN THE HYDROGEN ION CONCENTRATION OF THE OPEN SEA AT VARIOUS STATIONS AND DEPTHS.

The monthly visits to E 1 were continued during 1923, but no pH values were determined for September or May. The depth series results are tabulated here and shown in Fig. 2.

When compared with 1922 the 1923 results are noticeable chiefly for the absence of the depression in July, as may be seen in Fig. 1. The results for November, 1921, which gave high values owing to the exceptionally sunny autumn, are also markedly above those for 1922 and 1923.

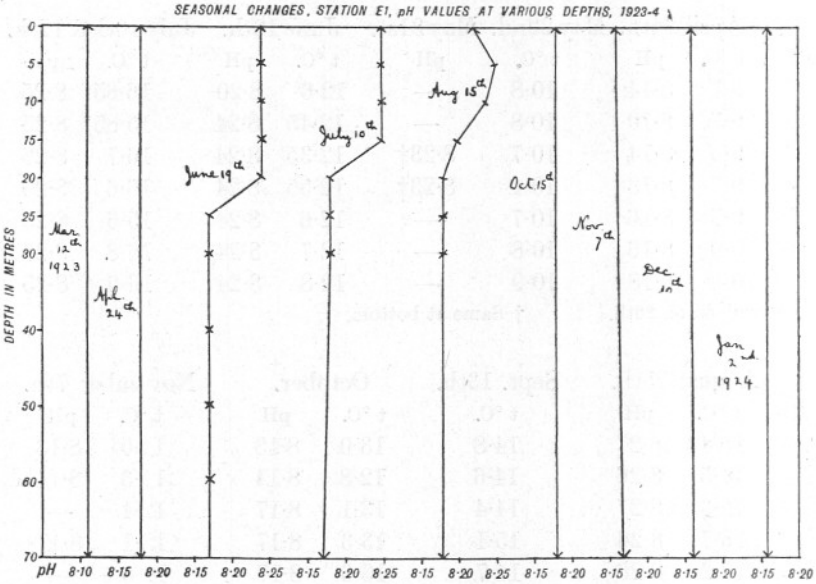

FIG. 2.

Furthermore, the 1922 maximum occurred in May, with a secondary one early in August; whereas in 1923, though June gave high values, the maximum was in July. No observations were made in May, however; but from the form of the depth series curves shown in Fig. 2 it is impossible to say whether the maximum had passed by June 19th. As in 1922, the bottom values at E 1 rose slightly during the summer to a maximum pH 8·18, at which on October 15th and April 24th the water column was uniform from top to bottom. In 1922 the October value was pH 8·20, which corresponds to a 3 per cent difference in hydroxyl ion concentration in favour of 1922.

As regards the question as to whether the July value was truly the maximum, it is of interest to note that the phosphate content at E 1

was a minimum in July, which points to the maximum algal development having occurred by that time. This does not necessarily indicate that July was also the true maximum for pH value, rather than May, but it lends support to that view.

As in 1922, the curves of the depth series, Fig. 2, are noticeably of different form during the summer months, when the more alkaline warm water is found nearest the surface, where it remains unmixed with the deeper and colder water until the autumn. This question of the mixing of the water is considered in a separate paper.

The pH values and temperatures are tabulated below, as are also similar results for stations E 2, E 3, N 1 and N 2. In Fig. 3 the pH depth series for these and E 1 is shown; the gradients at the different stations may be grouped according to position, those for the coastal stations E 3 and N 2 being nowhere steep; whereas those far from land, E 1, E 2, and N 1, are well marked.

E 1.	Mar. 12th, 1923.		April 24th.		June 19th.		July 10th.	
Depth in metres.	t °C.	pH	t °C.	pH	t °C.	pH	t °C.	pH
0	9·32	8·11	10·1	8·18	12·8	8·24	16·6	8·25
5	9·22	—	10·04	—	12·66	8·24	16·38	8·25
10	—	—	—	—	12·48	8·24	16·28	8·25
15	—	—	9·87	—	12·40	8·24	14·83	8·25
20	—	—	—	—	12·34	8·24	12·19	8·18
25	9·24	—	9·89	—	11·20	8·17	12·01	8·18
30	—	—	—	—	11·20	8·17	11·97	8·18
40	—	—	—	—	11·16	—	11·94	—
50	9·22	—	9·87	—	11·16	8·17	11·84	—
60	—	—	—	—	11·15	8·17	11·84	—
70	9·20	8·11	9·79	8·18	11·14	8·17	11·87	8·17

pH determined on 13th. pH determined on 26th.

E 1	Aug. 15th.		Sept. 13th.		Oct. 15th.		Nov. 7th.	
Depth.	t °C.	pH	t °C.	pH	t °C.	pH	t °C.	pH
0	16·75	8·22	15·0	—	13·0	8·18	12·15	8·16
5	16·52	8·25	14·98	—	13·48	—	12·34	—
10	16·28	8·24	14·32	—	13·36	—	—	—
15	12·96	8·20	13·59	—	13·38	—	—	—
20	12·70	8·18	13·33	—	13·46	—	—	—
25	12·50	8·18	13·30	—	13·43	—	12·33	—
30	12·50	8·18	13·25	—	13·35	—	—	—
40	12·50	—	13·25	—	13·35	—	—	—
50	12·46	—	13·25	—	13·35	—	—	—
60	—	—	—	—	—	—	—	—
70	12·46	8·18	13·25	—	13·40	8·18	12·32	8·17

pH determined on 9th.

E 1	Dec. 10th, 1923.		Jan. 2nd, 1824.	
Depth.	t °C.	pH	t °C.	pH
0	10·2	8·16	9·45	8·16
5	10·40	—	9·51	—
25	10·35	—	9·52	—
70	10·40	8·16	9·51	8·16
	pH determined on 11th.		pH determined on 3rd.	

E 2	March 14th, 1923.		April 24th.		July 10th.		Nov. 7th.	
Depth.	t °C.	pH	t °C.	pH	t °C.	pH	t °C.	pH
0	9·7	8·12	10·9	8·24	16·7	8·25	12·35	8·16
5	9·82	8·14	10·69	—	16·43	—	12·62	—
10	9·82	—	—	—	15·36	8·25	—	—
15	—	—	10·24	—	12·49	8·24	—	—
20	—	—	—	—	11·94	8·17	—	—
25	9·83	—	10·20	—	11·93	8·17	12·64	—
30	—	—	—		—	—	—	—
50	—	—	—	—	11·87	—	—	—
90	9·84	8·14	10·20	8·18	11·84	8·17	12·63	8·17
	pH determined on 15th.		pH determined on 26th.					

E 3	April 25th, 1923.		July 11th.		Nov. 8th.	
Depth.	t °C.	pH	t °C.	pH	t °C.	pH
0	10·3	8·19	14·43	8·24	11·15	8·16
5	—	—	13·93	—	11·85	—
10	—	—	13·69	8·23	—	—
15	—	—	12·33	8·22	—	—
20	—	—	12·19	—	—	—
25	—	—	12·14	8·19	11·85	—
50	—	—	11·81	—	—	—
75	—	—	11·59	—	—	—
100	10·39	8·19	11·57	8·17	11·85	8·17
	pH determined on 26th.					

N 1	July 11th.		Nov. 8th.	
Depth.	t °C.	pH	t °C.	pH
0	16·5	8·26	11·65	8·16
5	16·38	—	11·74	—
10	16·28	8·26	—	—
15	13·64	8·25	—	—
20	11·16	8·19	—	—
25	11·09	—	11·73	—
50	11·01	—	—	—
75	11·01	—	—	—
95	10·99	8·17	11·70	8·17
			pH determined on 9th.	

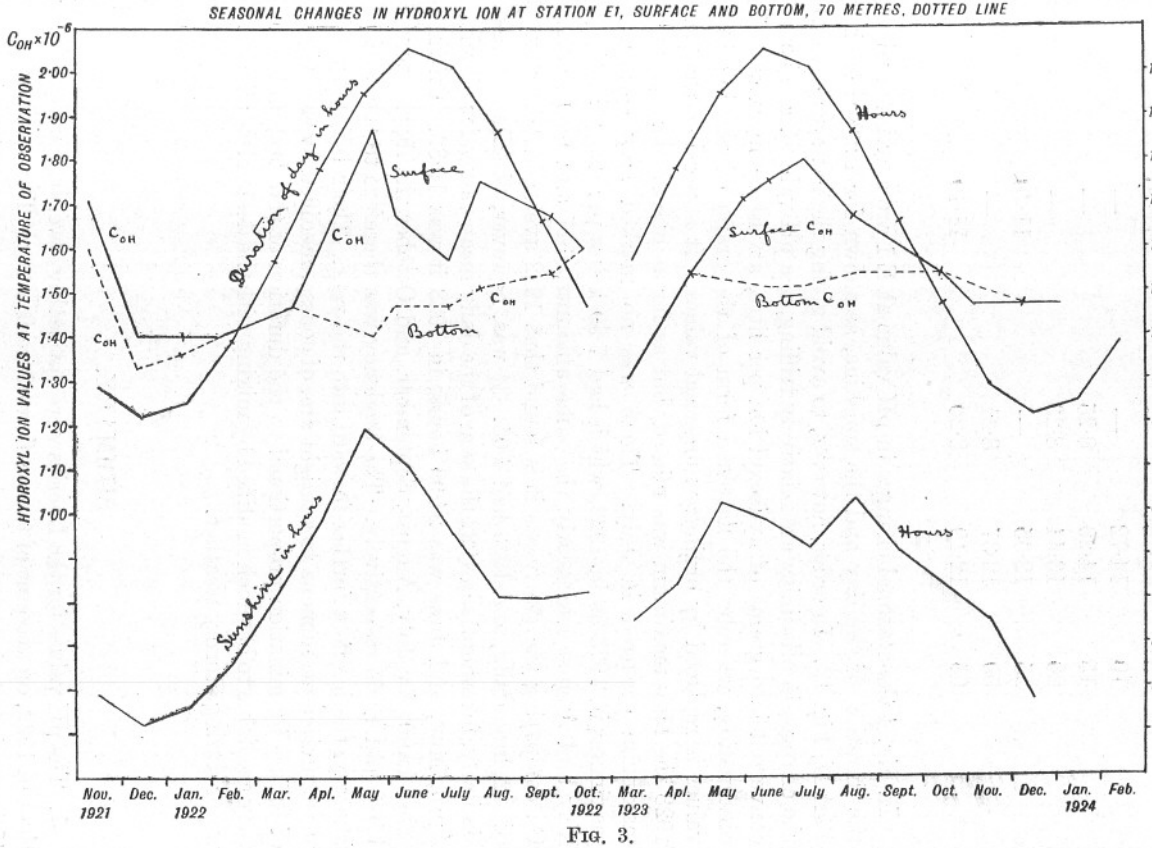
SEASONAL CHANGES IN HYDROXYL ION AT STATION E1, SURFACE AND BOTTOM, 70 METRES, DOTTED LINE
$C_{OH} \times 10^{-6}$
HYDROXYL ION VALUES AT TEMPERATURE OF OBSERVATION
2·00
1·90
1·80
1·70
1·60
1·50
1·40
1·30
1·20
1·10
1·00
Duration of day in hours
Surface
C_{OH}
Bottom
Sunshine in hours
Hours
Surface C_{OH}
Bottom C_{OH}
HOURS FROM SUNRISE TO SUNSET
HOURS OF SUNSHINE
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
Nov. 1921
Dec.
Jan. 1922
Feb.
Mar.
Apl.
May
June
July
Aug.
Sept.
Oct. 1922
Mar. 1923
Apl.
May
June
July
Aug.
Sept.
Oct.
Nov.
Dec.
Jan. 1924
Feb.

FIG. 3.

N 2	July 11th.		Nov. 8th.
Depth.	t °C.	pH	t °C.
0	14·7	8·24	11·65
5	14·78	—	11·70
10	14·72	—	—
15	14·29	8·25	—
20	13·44	8·23	—
25	12·35	—	11·70
50	12·37	8·21	—
65	12·19	8·20	11·70

In Fig. 4 the seasonal changes in pH value at E 1 are correlated with the duration of the day and the sunshine, as shown for 1922 alone in Part II, Fig. 12. In order, however, to avoid giving the impression that the changes in alkalinity are relatively trifling, the pH values have been converted into grams of hydroxyl ion per litre, at the temperature of observation, whereby the flattened form of the graph of the log $^1/_H$ values is replaced by ordinary numerical values. It is possible that in 1923 the May maximum was missed, but as far as observations go the maximum occurred in July. There was no marked May sunshine maximum in 1923 as in 1922, which had 7·90 hours per day; in 1923 May and August had nearly the same amounts, 6·17 and 6·30 hours. On comparing the two years it is found that 1922 averaged 4·12 hours of sunshine daily, and 1923 had 4·05. It was, however, distributed dissimilarly, for whereas in 1922 the sum of the daily mean values for March, April, May, and June was 24·90 hours, in 1923 it was 19·82. On the other hand, for July, August, September, and October the figures were 17·78 and 19·65 respectively. The tendency was therefore to throw the photosynthetic effect further forward into the year. The relationship of these surface phenomena to sunlight are, of course, modified by the effect of diffuse illumination proportional to the duration of the day, and also they are liable to be much modified by mixing with the deeper less alkaline water during stormy weather.

SUMMARY.

1. The pH values for the L series were noticeably lower in March, 1923, than in 1922, on account of the outflow of fresh water. The well-marked May maximum, followed by a depression in June and July, 1922, is not found in 1923, during the summer months of which the water increased in alkalinity until August, when it slowly decreased. This appears to be due to the absence of stormy and wet weather in June and July, 1923.

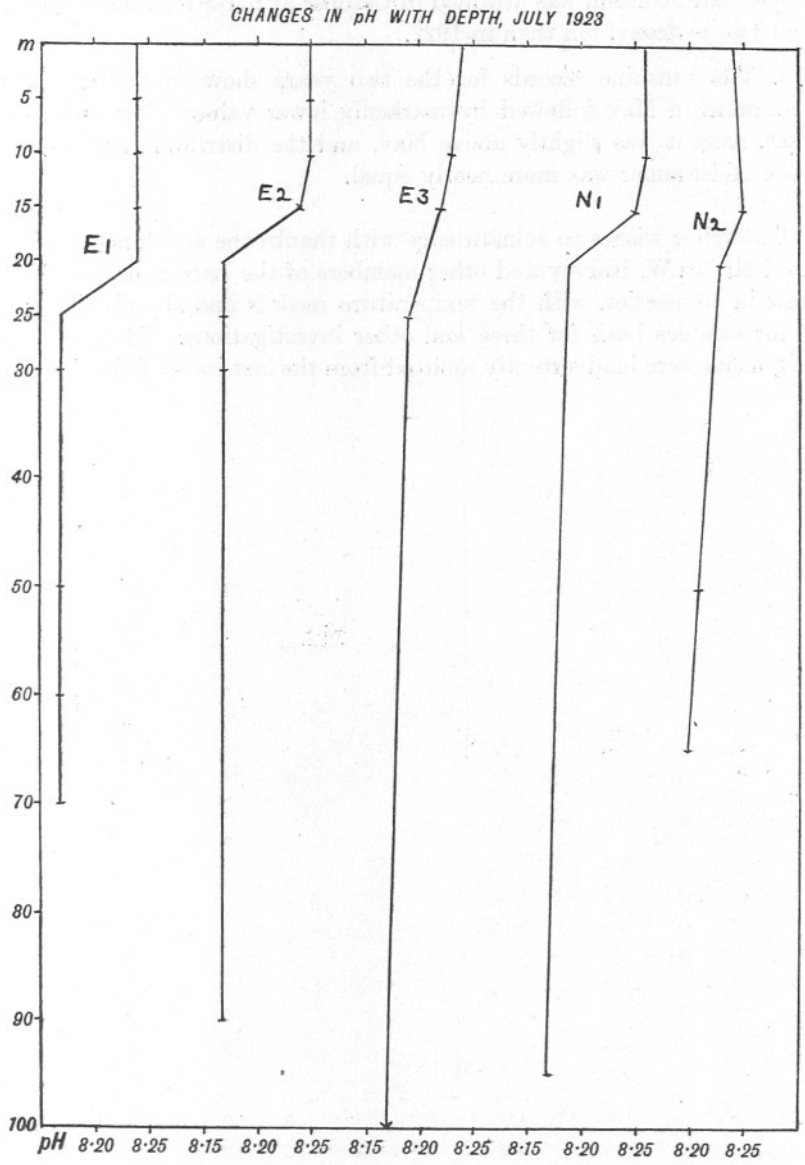
CHANGES IN pH WITH DEPTH, JULY 1923
m
5
10
15
20
25
30
40
50
60
70
80
90
100
E1
E2
E3
N1
N2
pH 8·20 8·25 8·15 8·20 8·25 8·15 8·20 8·25 8·15 8·20 8·25 8·20 8·25

FIG. 4.

2. The pH values for E 1 reached their maximum at the surface in July, but the bottom values were still low. These increased till uniformity of the water column was attained in October at pH 8·18, denoting 3 per cent less hydroxyl ion than in 1922.

3. The sunshine records for the two years show that 1922 had a maximum in May followed by markedly lower values after June. In 1923, August was slightly above May, and the distribution before and after midsummer was more nearly equal.

The writer wishes to acknowledge with thanks the assistance received from Mr. H. W. Harvey and other members of the Laboratory staff and crew in connection with the temperature records and the obtaining of water samples both for these and other investigations. Such acknowledgments were inadvertently omitted from the last issue of the Journal.