The Muds of the Clyde Sea Area.
1. Phosphate and Nitrogen Contents.

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With 5 Figures in the Text.

THE Clyde Sea Area is in many ways an ideal ground for the investigation of the nutrient salts in the bottom deposits. The different lochs present a range of depth of water of from 0 to 200 metres: some parts have strong tidal currents up to five knots, while others are practically unaffected by the tide: some lochs have also been affected by the dumping of sewage and harbour sludge, and the effect of these can be examined. Conditions may also be compared in muds ranging from the loch heads to the almost open sea conditions at Ailsa Craig.

The fact that the mud is as nearly homogeneous as any bottom deposit can well be, coupled with the taking of eight or ten cores from each station, ensures the representative sampling of any region. Also, since cores of up to forty centimetres in length can be taken, the vertical distribution of the components of the mud may be examined.

A series of investigations is being made on the chemical, physical and geological nature of these muds, and on the relation of these to the fauna. The present paper deals only with their phosphate content, and their organic content as represented by total nitrogen. The organic content has not been estimated directly, as there is no accurate method that is applicable, whereas the nitrogen can be determined with great accuracy; further, the nitrogen content is of importance in giving a link in the chain of the nitrogen cycle in the sea. The results are tabulated, and then discussed.

This is only a preliminary statement, and it is hoped later to trace a connection between more of the factors concerned. In dealing with such a very complex set of conditions, and before drawing conclusions, it is necessary to take a sufficient number of stations to give significant results, and one must not apply them to a single station as a test of their truth. Irregularities are frequent, such as those due to the interpolation of a layer of sand at some level, and similar causes, but neglecting these cases, it is possible to see a certain amount of correlation between some of the factors in the area.

The muds in general are soft for the top ten centimetres or more, but rarely so soft, even at the very surface, as to form a so-called " Pea Soup " layer ; they then become more clayey deeper down. The mud sampler, which is described in another paper (**3**), takes perfectly undisturbed samples, and shows that the surface of the mud is clearly marked off from the overlying water, with no contamination of the latter which would be clearly visible if present. It is not, however, the purpose of the present paper to discuss the physical character of the muds.

Although clear demarcation into layers is often present, no attempt has so far been made to analyse these natural layers separately. All samples taken are cut up on board the boat into five-centimetre lengths, and these are set aside in separate pots, to be taken back and dried as soon as possible. After drying at about 110° C. they are ground in an iron mortar and then passed through a 1 mm. sieve. They can then be stored in this condition in airtight jars until required.

Thirty-three stations have so far been worked, and their positions and depths are shown in the accompanying chart (Fig. 1). Wherever possible the stations have been those used by Marshall and Orr in their work on the plankton of the area (**1**).

Note on the Tides.

The chief points in the tidal streams, which vary greatly throughout the area, are given below. The figures refer to the maximum spring tides, and where two figures are quoted the first refers to the flood, and the second to the ebb tide. Up the Kilbrennan Sound (Arran Basin, west branch) the tide is about $2\frac{1}{2}$ knots, though greater in some shallows. In Loch Fyne the average tide is 2 knots, with an increase to $3\frac{1}{2}$ and $5\frac{1}{2}$ at the Otter Spit just north of St. 6, and $2\frac{1}{2}$ and 4 at the Minard Narrows : at St. 4 it has dropped to $1\frac{1}{4}$ and $1\frac{3}{4}$. The stream up the east coast of Arran is $1\frac{1}{2}$ knots, and the branch of this up the Inchmarnock Sound and West Kyle has a maximum of $2\frac{1}{2}$ knots. St. 7 has practically no tide, and there is very little in Loch Riddon (L. Ridun) : at the top of the East Kyle there is a tide of 3 knots, but Rothesay Bay and Loch Striven have very little indeed.

To the east of Cumbrae the tide is 2 knots, and to the west, $1\frac{1}{2}$ knots. In the Dunoon Basin it is about 1 knot, rising off Gourock to 2 knots (St. 20a.) The Holy Loch, and Lochs Long and Goil have very little tide, but in the mouth of the Gare Loch there is a peculiar swirl, and a tide of up to 5 knots.

These figures of course refer to the surface currents, little being known of the bottom currents which directly influence the muds themselves. Further details with regard to the area may be found in Mill's " Clyde Sea Area " (**2**).

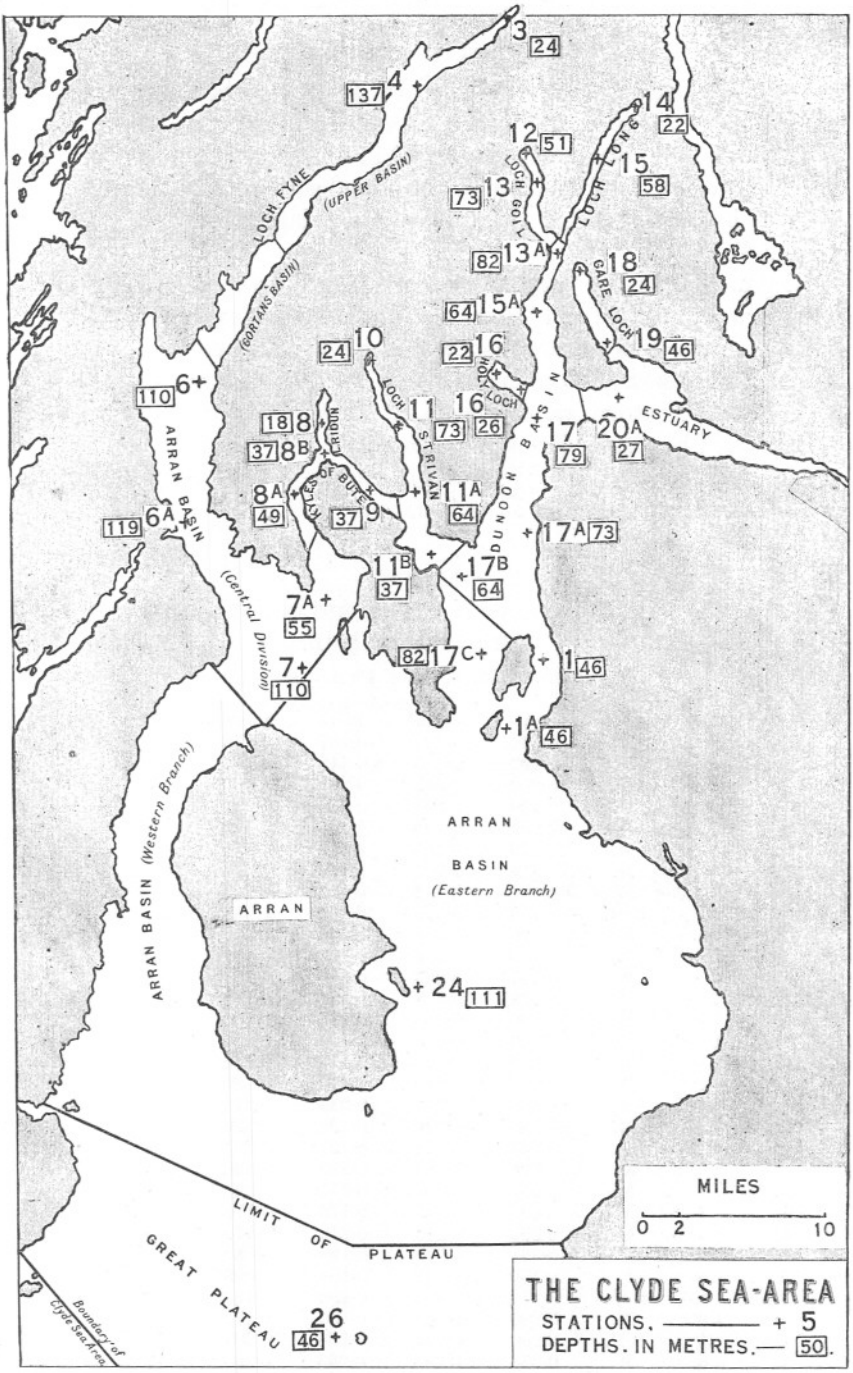
3 24
4 137
14 22
12 51
15 58
13 73
LOCH GOIL
LOCH LONG
13A 82
18 24
15A 64
GARE LOCH
19 46
10 24
16 22
16A
LOCH
11 16 73 26
17 79
20A 27
ESTUARY
6+ 110
18 8
37 8B
8A 49
CRIBOON
LOCH
STRIVAN
11A 64
DUNOON BASIN
9 37
17A 73
6A 119
11B 37
17B 64
7A+ 55
7+ 110
82 17C+
1 46
1A 46
ARRAN BASIN (Central Division)
ARRAN BASIN (Western Branch)
ARRAN
BASIN
(Eastern Branch)
ARRAN
24 111
LIMIT OF PLATEAU
GREAT PLATEAU
26 46
Boundary of Clyde Sea Area
MILES
0 2 10
THE CLYDE SEA-AREA
STATIONS. ——— + 5
DEPTHS. IN METRES.— 50.

FIG. 1.

Phosphate Content.

Since any extract of the mud is very highly coloured, no colorimetric method of estimation of phosphate can be used; the most suitable method has been found to be that used in soil analysis, viz., of precipitation as ammonium phospho-molybdate, and solution of this in standard sodium hydrate solution, the excess of the latter being then titrated (**3** and **4**).

20 gm. of the dried mud are extracted for 48 hours with hydrochloric acid, in a water-bath, and the extract after filtering is made up to 250 c.c. Four portions of 25 c.c. are then taken from this for analysis. It has not been found necessary to compare with a known standard at each estimation, but each extract was estimated, as stated, four times for the sake of accuracy. The results for each station, at depth intervals of 5 cm., are given in Table I, together with a note of the general type of the mud, and the depth of the water at each station.

TABLE I.

Phosphate Values expressed as Percentage by Weight of P_2O_5 in the Dried Mud.

M. = Mud. S.M. = Sandy Mud. S. = Sand.

Station.	Depth in Metres.	Type.	Depth in Mud in cm. 0–5.	5–10.	10–15.	15–20.	20–25.	25–30.
1	46	M.	0·244	0·195	0·187	0·175	—	—
1a	46	S.	0·152	0·145	0·142	0·142	—	—
3	24	S.M.	0·250	0·213	0·201	0·185	—	—
4	137	M.	0·270	0·220	0·240	0·216	—	—
6	110	M.	0·201	0·199	0·188	0·185	—	—
6a	119	M.	0·179	0·164	0·166	0·156	—	—
7	110	M.	0·214	0·177	0·180	0·169	—	—
7a	55	M.	0·169	0·156	0·142	0·149	—	—
8	18	S.M.	0·219	0·215	0·173	0·155	—	—
8a	49	M.	0·199	0·188	0·206	0·201	—	—
8b	37	M.	0·248	0·206	0·167	0·157	—	—
9	37	M.	0·237	0·203	0·229	0·201	—	—
10	24	M.	0·228	0·198	0·201	0·172	—	—
11	73	M.	0·226	0·206	0·220	0·204	—	—
11a	64	M.	0·266	0·188	0·219	0·216	—	—
11b	37	M.	0·219	0·178	0·177	0·185	0·170	0·175
12	51	M.	0·305	0·219	0·214	0·186	0·169	0·186
13	73	M.	0·406	0·219	0·239	0·211	0·207	0·203
13a	82	M.	0·284	0·266	0·230	0·226	0·236	0·200
14	22	M.	0·243	0·224	0·191	0·201	0·201	0·240
15	58	M.	0·328	0·321	0·289	0·266	0·299	0·253
15a	64	M.	0·241	0·209	0·261	0·228	—	—
16	22	M.	0·291	0·219	0·179	0·174	—	—
16a	26	M.	0·255	0·216	0·219	0·178	—	—
17	79	M.	0·267	0·228	0·198	0·087	—	—
17a	73	S.	0·149	0·142	0·109	0·099	—	—
17b	64	S.M.	0·215	0·187	0·209	0·183	0·182	0·197
17c	82	M.	0·200	0·181	0·181	0·172	0·156	0·152
18	24	S.M.	0·260	0·203	0·197	0·207	—	—
19	46	M.	0·364	0·298	0·263	0·284	—	—
20a	27	S.M.	0·168	0·189	0·185	0·141	—	—
24	111	M.	0·158	0·150	0·161	0·152	0·148	—
26	46	M.	0·117	0·101	0·129	0·119	—	—

Total Nitrogen Content.

As the various methods of organic content estimation are not of sufficient accuracy, whereas the total nitrogen can be estimated easily and very accurately, the latter estimation was chosen, and the ordinary Kjeldahl method used (**4**). Ten grammes of mud are taken for each estimation, and these are only duplicated when the results are suspected. The values found are given in Table II in the same form as those for the phosphates, the depths of water and types of mud being repeated for convenience.

TABLE II.

Nitrogen Values expressed as Percentage by Weight of N_2 in the Dried Mud.

M. = Mud. S.M. = Sandy Mud. S. = Sand.

Station.	Depth in Metres.	Type.	Depth in Mud in cm. 0–5	5–10	10–15	15–20	20–25	25–30
1	46	M.	0·189	0·170	0·165	0·181	—	—
1a	46	S.	0·099	0·101	0·097	0·083	—	—
3	24	S.M.	0·211	0·211	0·237	0·279	—	—
4	137	M.	0·304	0·279	0·232	0·209	—	—
6	110	M.	0·201	0·178	0·168	0·145	—	—
6a	119	M.	0·135	0·132	0·134	0·097	—	—
7	110	M.	0·183	0·167	0·162	0·161	—	—
7a	55	M.	0·089	0·083	0·074	0·074	—	—
8	18	S.M.	0·256	0·202	0·139	0·132	—	—
8a	49	M.	0·233	0·188	0·170	0·166	—	—
8b	37	M.	0·335	0·284	0·290	0·251	—	—
9	37	M.	0·219	0·201	0·195	0·194	—	—
10	24	M.	0·177	0·148	0·135	0·124	—	—
11	73	M.	0·238	0·237	0·211	0·204	—	—
11a	64	M.	0·262	0·245	0·223	0·211	—	—
11b	37	M.	0·137	0·153	0·132	0·146	0·114	0·114
12	51	M.	0·275	0·265	0·286	0·273	0·295	0·285
13	73	M.	0·379	0·291	0·267	0·237	0·260	0·250
13a	82	M.	0·257	0·198	0·167	0·211	0·242	0·210
14	22	M.	0·337	0·330	0·295	0·302	0·312	0·307
15	58	M.	0·268	0·271	0·231	0·172	0·216	0·188
15a	64	M.	0·242	0·208	0·206	0·202	—	—
16	22	M.	0·184	0·187	0·160	0·156	—	—
16a	26	M.	0·232	0·203	0·187	0·168	—	—
17	79	M.	0·208	0·255	0·221	0·212	—	—
17a	73	S.	0·069	0·051	0·043	0·041	—	—
17b	64	S.M.	0·229	0·204	0·205	0·178	0·180	0·177
17c	82	M.	0·195	0·201	0·176	0·174	0·167	0·160
18	24	S.M.	0·191	0·205	0·166	0·159	—	—
19	46	M.	0·221	0·285	0·158	0·163	—	—
20a	27	S.M.	0·208	0·123	0·150	0·099	—	—
24	111	M.	0·230	0·177	0·133	0·135	0·144	—
26	46	M.	0·119	0·116	0·111	0·102	—	—

Discussion of Results.

The results show that there is no general correlation of the depth of water with either the phosphate or nitrogen content of the mud in any layer, with the following exception. In the case of those shallow-water

stations less than forty metres, all the phosphate values lie close together, while covering a much wider range in the deeper stations. As in the case of most such linkages, the surface layers do not agree quite so well as the deeper layers where conditions seem to have become more stabilised. The distribution of P_2O_5 with depth of water for the 5–10 cm. layer, is shown in Figure 2, where the phosphate values for shallow

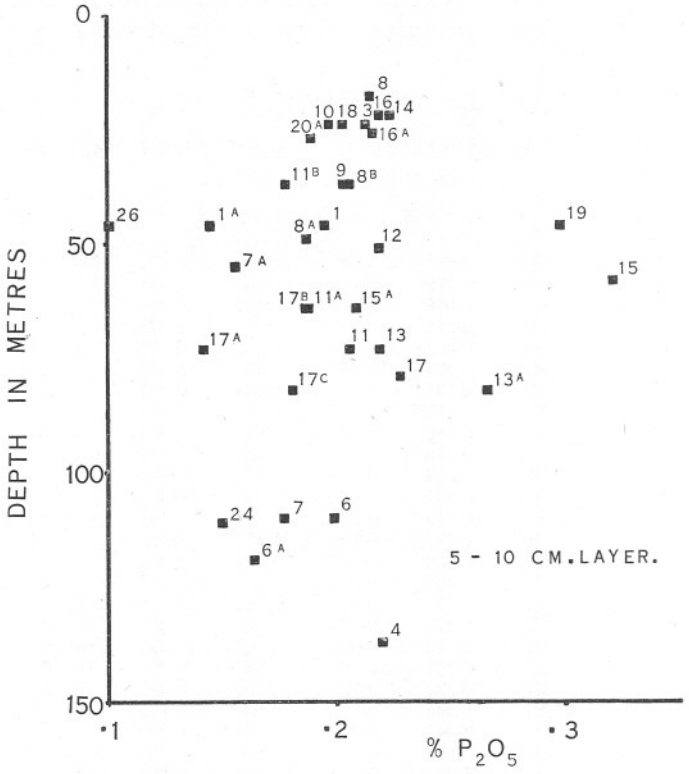

FIG. 2.—Graph showing the distribution of P_2O_5 with depth of water, in the 5–10 cm. layer throughout the area.

stations range only from 0·178% to 0·224%. In the case of the nitrogen content there does not seem to be such a correlation.

The distribution of phosphate with depth in the mud, throughout the area, is shown in Figure 3. The value falls with increasing depth in the mud in all but three stations in the whole area. These are St. 11b, 18 and 19, in all of which the value first drops and then rises again. The latter two stations are in the Gare Loch, which is a backwater into which much fine silt from the river is carried, forming a thick layer all over the bottom. (Mill, p. 646, **2.**)

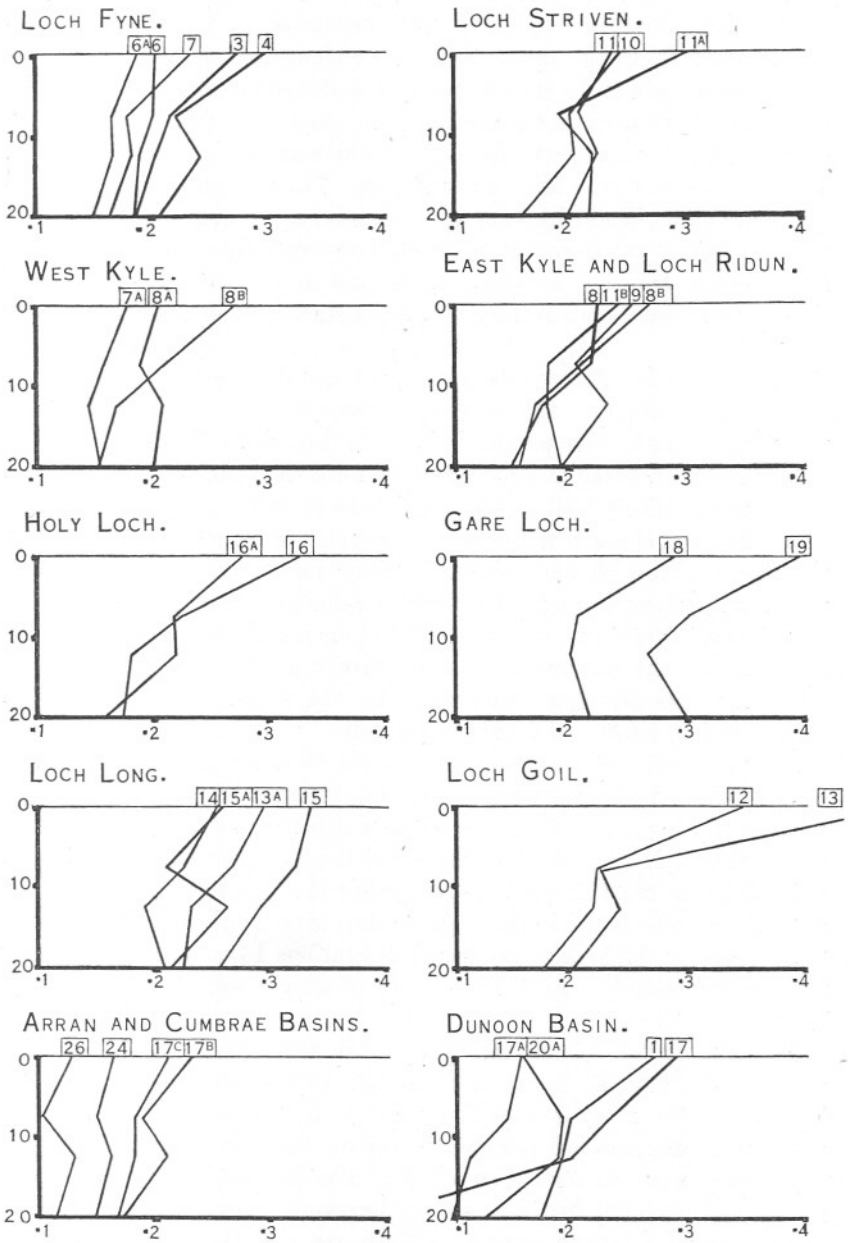

FIG. 3.—Distribution of phosphate with depth in the mud, in the main channels. Depth in cm. (ordinate) against % P_2O_5.

The most noticeable point, however, about the phosphate distribution, is the "Kink," or rise which so often occurs about the ten to fifteen-centimetre level in the mud. A kink, or change of slope of the curve, occurs in nineteen of the stations worked, and is so pronounced as to be an actual rise in thirteen of the stations : in some cases (St. 15a, 24, 26) it even rises higher than the surface values, which are usually far the highest. The significance of the kink is not known. The phosphate values themselves are high. While dropping low off shore, as at St. 26 by Ailsa Craig, they are lowest at sandy stations and those with a strong tide. Station 26, although showing a typical mud, and similar in appearance and texture to many found in the lochs, has a surface value for P_2O_5 of only 0·117%.

Where there is a heavy tidal action, the fine particles of the mud tend to be washed out ; also, the sediment in the water does not settle, and the phosphate value is correspondingly low. In these cases, the nitrogen value falls even lower, being in a more soluble form than the phosphate. This action of the tide is well shown in the case of Station 17a, which lies in 73 metres in a channel which shows typical mud at either end ; but in the centre of this channel, where for some reason the tide seems to be very strong, there is sand. The surface value here for phosphate is ·149 falling at the 15–20 cm. layer to 0·099, as against surface values of 0·267 and 0·244 for the stations above and below it in the same channel. The nitrogen values for these stations follow the same trend being, at the surface, 0·208, 0·069 and 0·188 respectively.

The phosphate values are highest in the Gare Loch and Lochs Long and Goil, the highest stations being 19, 15, and 13. The Gare Loch receives much rich silt from the river, which may account for the high values there. During the war there was sewage dumping at the mouth of Loch Long, but this would hardly affect the loch head. The cause is more likely to be found in the large streams entering these lochs, and this is born out by the high values found at Stations 16 and 16a in the Holy Loch, and 3 and 4 in Loch Fyne, both of which lochs are fed by large streams.

The distribution of the nitrogen in the muds is more erratic. Its variation with depth in the mud at the various stations is shown in Figure 4. The most outstanding point is the general fall of nitrogen value with increasing depth, which occurs in twenty-five stations, as against two with a rise, and six erratic. The fall in nitrogen with depth might be accounted for by a steady break-down of the organic nitrogenous compounds into nitrites and nitrates, and the removal of these by solution in the water.

Stations 18 and 19 are peculiar as regards nitrogen distribution, as they were for phosphates, and a type similar to them is found at St. 17,

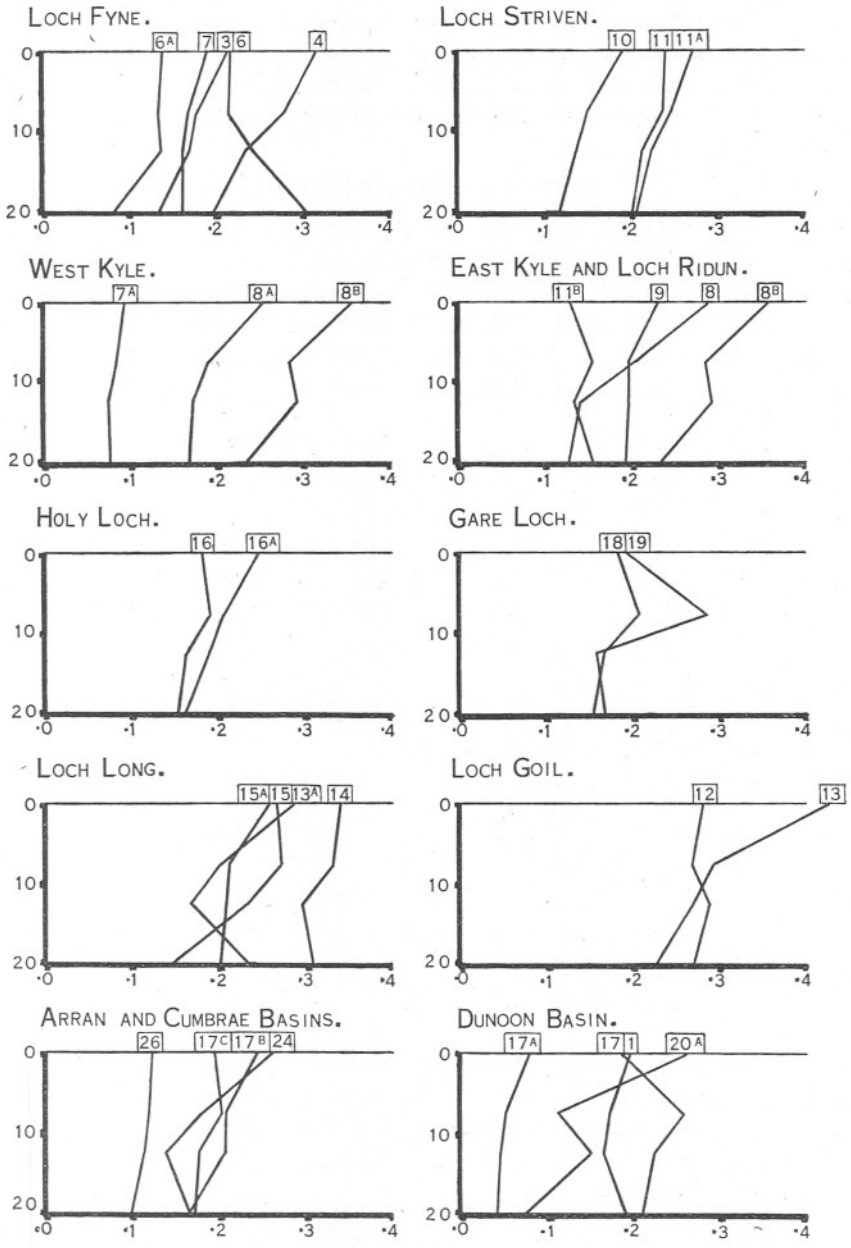

Fig. 4.—Distribution of nitrogen with depth in the mud, in the main channels. Depth in cm. (ordinate) against % N_2.

off Dunoon, where there is a fairly strong tide, though a typical mud. As is to be expected, the values are low in the sand at St. 17a, and in the sandy mud at St. 7a. They are very high at all depths at St. 14, and curiously they are also high at St. 8b where, though at the surface, at any rate, there is a strong tidal current, there is quite a typical mud.

Phosphate Nitrogen Ratio.

The ratio P_2O_5/N_2 also yields some interesting figures. There does not seem to be any constant relation of this ratio either to depth of water or depth in the mud, but in a chain of stations down any loch the ratio frequently varies similarly with depth in the mud, in successive stations. This variation, however, differs from one loch to another. Thus in Loch Long, the ratio tends to rise at first, and then fall again :—

	Depth in Mud.	Stations. 15	13a	15a
P_2O_5/N_2	0–5 cm.	1·22	1·10	1·00
	5–10 ,,	1·19	1·34	1·01
	10–15 ,,	1·21	1·38	1·26
	15–20 ,,	1·54	1·07	1·12
	20–25 ,,	1·38	0·97	—
	25–30 ,,	1·34	0·95	—

In Loch Striven, except the station at the loch head, the ratio tends to fall at first, and then to rise again

	Depth in Mud.	Stations. 10	11	11a	11b
P_2O_5/N_2	0–5 cm.	1·28	0·95	1·02	1·60
	5–10 ,,	1·34	0·87	0·77	1·16
	10–15 ,,	1·48	1·04	0·98	1·34
	15–20 ,,	1·38	0·99	1·02	1·27
	20–25 ,,	—	—	—	1·48
	25–30 ,,	—	—	—	1·54

The ratio is very high in the sandy Stations 7a and 17a, and also at St. 19 in the mouth of the Gare Loch, all of which stations have strong tides. It is lowest at St. 8b at the head of the Kyles, and then at St. 3 at Loch Fyne head, St. 12 at Loch Goil head, and St. 14 at Loch Long head.

Depth in Mud.	Stations. 7a	17a	19	8b	3	12	14
0–5 cm.	1·90	2·15	1·65	0·74	1·18	1·10	1·72
5–10 ,,	1·88	2·82	1·04	0·72	1·01	0·83	1·68
10–15 ,,	1·92	2·51	1·67	0·58	0·85	0·75	0·65
15–20 ,,	2·03	2·40	1·74	0·63	0·66	0·68	0·66

Figure 5 shows the nitrogen values in the 15–20 cm. layer, plotted against the corresponding P_2O_5 values. While, as is usual, the points are rather more scattered in the upper layers, with increase in depth they come more into line, and at this depth all but seven lie close to a straight line, as indicated by the two parallel lines in the figure. Certain stations lie outside these lines, and are discussed below. In the higher

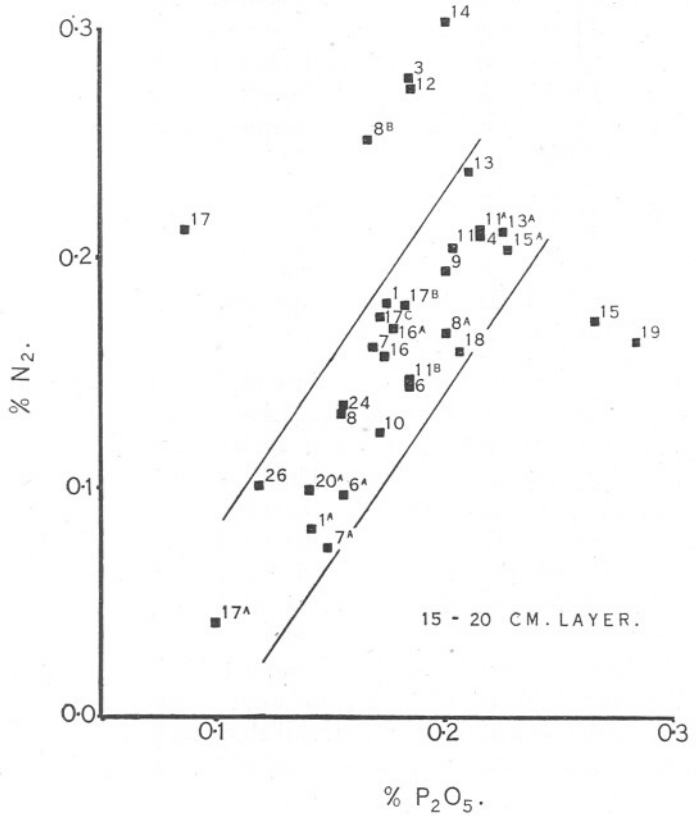

FIG. 5.—Percentage P_2O_5 against percentage N_2 in the 15–20 cm. layer throughout the area.

layers other stations also outlie, but come into line lower down. The extreme stations, too, are well in line, from the very low values in St. 17a, to the high values in the upper layers of Stations 13a, 15a and 19. The only stations which lie below the line in this figure are St. 15 in Loch Long, and St. 19 in the Gare Loch. In the layer five cm. higher, however, Stations 13a and 15a, both in Loch Long, also fall below the line, as well as St. 19. Stations 3, 12 and 14, which lie above the line, are all loch-head stations, near the entry of a large stream, and St. 8b and 17, which also

lie above, both have strong tides, though still remaining fairly normal muds.

Although subject to local irregularities, the successive stations down the various deep channels frequently conform to a typical pattern throughout the chain ; and this type is distinctive for each chain. We have already shown that some of the lochs have typical ratio distribution curves. Similarly the curves for the distribution of phosphates, and nitrogen, are often closely linked in the successive stations of a chain, and frequently grade in character from the head to the mouth of the loch. This agreement within the chains, and the difference between the chains, is well seen as far as phosphates are concerned, in the following groups of stations (Fig. 3).

St. 10, 11, 11a, 11b. In Loch Striven.
St. 18, 19. In the Gare Loch.
St. 12, 13. In Loch Goil.
St. 17b, 17c, 24, 26. In the Cumbrae and Arran Basins.
St. 14, 15, 13a, 15a. In Loch Long.

In the case of the last chain, it is interesting to note that the curves for the upper three stations of the loch have an unusual form, similar in them all, whilst the lowest station in the loch (15a) has attained the more normal type, with a pronounced kink. In this it comes more into series with Stations 12 and 13 in the adjoining Loch Goil, which, though abnormal, shows a distinct kink. Whilst the Loch Goil chain and the upper part of the Loch Long chain show an increase of phosphate towards the mouth, the chain which runs out to Ailsa Craig shows a marked fall seawards.

The nitrogren distribution shows a similar behaviour in some of the lochs (Fig. 4) though often masked by local irregularities. Thus the Gare Loch, Loch Goil and the Holy Loch all show typical curves throughout. Here again the seawards stations, 24 and 26, show a decided drop in nitrogen values.

Finally I wish to express my thanks to the members of the staff of the Millport Laboratory, who have assisted throughout the work.

SUMMARY.

1. The P_2O_5 and N_2 contents of the muds at 33 stations in the Clyde Sea Area, have been determined, at 5-cm. stages, down to 20, and sometimes 30 cm. below the mud surface.

2. In estimating, the phospho-molybdic method for phosphates, and the Kjeldahl method for total nitrogen, were used.

3. There is no general relation between P_2O_5 or N_2 values and the depth of water, with the following exception :—

4. The P_2O_5 values in depths of less than 40 metres all lie close together.

5. The P_2O_5 values fall off with increasing depth in the mud, but usually show a rise at the ten- to fifteen-centimetre level.

6. The nitrogen values usually fall with increasing depth in the mud.

7. Stations with strong tides, usually have low P_2O_5 and N_2 values.

8. A chain of stations down a deep channel holds more or less to the same type of distribution curve throughout; but the type of curve varies in the different chains and is distinctive of each.

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