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pH AND Eh ON ALDABRA ATOLL
1. COMPARISON OF MARINE AND FRESHWATER ENVIRONMENTS

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Abstract

An account is given of the range of pH and Eh in marine and freshwater aquatic sites on one atoll (Aldabra, Indian Ocean). There is a very wide range in values of pH and Eh for both marine and freshwater environments, the range for pH in general being wider in freshwater ones and Eh in marine ones. Photosynthetic microbial communities on lagoon sediments may be arranged in an approximate order of their association with sediments of particular Eh values. These are, from high to low: *Scytonema* sp., pennate diatoms, *Schizothrix* sp., *Microcoleus chthonoplastes, Hyella balani,* purple phototrophic bacteria.

Introduction

An atoll provides an excellent area for many types of ecological study. It has clearly defined geographical limits, most habitats are markedly influenced by the presence of limestone, and for microbial species, at least, it may be assumed that their long-term absence at one site but not another is seldom due to the lack of suitable inocula. Nevertheless there have been few accounts describing in any detail the variation occurring on a single atoll of key environmental parameters. The present study reports the general features of pH and Eh in aquatic sites on Aldabra Atoll, together with more detailed studies on conspicuous intertidal microbial communities.

The four islands of the Aldabra group (9° 24'S, 46° 20'E) are formed of coral reefs elevated 5 to 10 m above present sea-level. They are situated in an area of the Indian Ocean with a moderate rainfall (mean annual value of 940.6 mm: Stoddart & Mole, 1977). Farrow (1971a) reported that summer air shade maximum temperatures average 32°C at the research station (West Island), but that for much of the atoll, maxima are probably about 3°C lower. Winter minimum temperatures average 22°C. The lowest and highest shade temperatures recorded were 36.3°C and 19.5°C. In the lagoon mean values at spring tides may exceed local air shade temperatures by over 3°C, so very high temperatures may occur here in summer. For its large size (174 km^2), the lagoon is extremely shallow, averaging about 3 m and never exceeding 6 m (Farrow, 1971b). Tidally, the mean spring range of 2.74 m is far greater than the normal 0.5 m for truly oceanic atolls (Farrow & Brander, 1971). Further background information on geology, geography and ecology is given in the volume edited by Westoll & Stoddart (1971), while Braithwaite *et al.* (1973) have provided a detailed account of the geological history.

Some data on pH and Eh values found on Aldabra have already been reported. Trudgill (1972) found that the daytime oceanic water pH values off Aldabra, ranged from 8.1 to 8.3, and lagoon water values from 8.9 to 9.2. The lowest pH value for soil was 6.5. Observations on the pH values of freshwater pools on Aldabra have shown a range from 5.9 to 11.8 (Donaldson & Whitton, 1977; Whitton & Potts, 1977). Marked diurnal fluctuations are usual, with the very high values restricted to readings taken in the late afternoon. Whitton & Potts (1977) reported that in comparison with most values reported in the literature for freshwaters, small freshwater pools on Aldabra always had rather low values of Eh. These values were especially low in pools in *Casuarina* forest, where readings below +50 mV sometimes occurred. Distur-

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bance of anaerobic sediments in these pools, leads to the release of reducing substances, which have some stability in an otherwise oxygenated environment (Potts & Whitton, 1977a). Measurements of pH and Eh during acetylene reduction assays of lagoon communities of blue-green algae indicated that Eh tended to be more stable than pH during 60 minute incubations in a confined volume (Potts & Whitton, 1977b).

The use of Eh as an environmental parameter, and its major limitations, have been described in some detail by Stumm (1966) and Whitfield (1969, 1971, 1974). In a natural mixed system, such as a pool or lagoon sediment, conditions of equilibrium, thermodynamic reversibility and steady-state must be assumed to be lacking. The potential observed is purely an electrode response, dependent on the ratio of oxidized to reduced species, and not their absolute concentration. As such, the electrode response gives an indication of the activity of a system, and not its extent. However, all that is required is that clear differences in Eh (± 50 mV), should reflect changes in the 'redox' condition of the environment, and that electrodes should be as free as possible from 'artifacts', We therefore adopted Whitfield's more optimistic approach, the following factors playing a role in making this decision.

i) Preliminary surveys showed that a very wide range of Eh values occur on Aldabra, extreme values sometimes being separated from each other by only a short distance.

ii) It seemed possible that environmental combinations might occur which have previously been overlooked because of the diffidence of field workers in using Eh electrodes as an approximate indicator of environmental conditions.

iii) The lack of field data on Eh is probably responsible for the neglect of this parameter as a possible environmental factor influencing key processes in the physiology of aquatic plants. However Weller *et al.* (1975) have shown that photosynthesis of *Phormidium* sp. in the laboratory was stimulated by the addition of four out of the six low redox potential agents tested.

Methods

Measurement of pH and Eh

Measurements of pH and Eh were made simultaneously, using separate PYE UNICAM portable meters (model 293) with PYE UNICAM electrodes. Eh electrodes combined a platinum indicator electrode, and a silver/silver chloride reference system with relatively dilute (3 M KCl) reference solution. Eh electrodes were buffered initially using ferrocyanide/ferricyanide solution (ZoBell, 1946), as well as saturated solutions of quinhydrone (Ingold, 1966; Schneider, 1976). During periods of regular field use, the platinum electrode was immersed overnight in concentrated chlorine-free HNO_3, and then calibrated against quinhydrone buffers. Cleaning and buffering of the Eh electrode was made at frequent intervals during sampling, often after each reading; this cleaning being carried out by rubbing gently with fine silicon carbide paper (emery paper). A second electrode was kept for comparison with the first at important sites. Differences of up to 30 mV sometimes occurred between the two, even after the electrodes had been freshly calibrated. This value corresponds to the range of 30 mV found by ZoBell (1946) to occur sometimes in mud, even when the two electrodes agree within a few millivolts in buffer solution. Readings of pH were taken with pH glass electrodes (sinta plug membrane, 450 E_07), with a weak (1 M KCl) reference electrode to reduce 'suspension effects'. pH electrodes were buffered at the same time as Eh electrodes. Buffers were prepared at pH 4.0, 7.0 and 9.2 using 'soloid' buffer tablets (Burroughs Wellcome, U.K.) for field use, and checked carefully against Na_2HPO_4-NaH_2PO_4 buffers at pH 7.0 and 8.0 in the laboratory (Bower & Bates, 1955).

Measurements in water or mud were made by carefully immersing the separate pH and redox electrodes at adjacent positions. Obvious drift in Eh values had usually come to an end within 2-3 minutes of immersion. With the exception of measurements made at time intervals, most readings were repeated at least twice. Where small differences occurred between different readings at one position and time, the mean value is given. In the few cases where Eh values had not approached a plateau by the end of 5 minutes, the readings have been ignored.

Measurements of soil that was dry at the time of collection were made after mixing the soil in a bottle with an equal volume of distilled water, shaking gently, and then leaving the bottle to stand for five minutes. (This arbitrary technique was used only to assess whether a more detailed study of soils might provide useful clues to the pH and Eh characteristics of the small freshwater pools in their vicinity.)

Field Survey

Unless stated to the contrary, all field records were made between December 1974 and June 1975 (mostly in January), during daylight (mostly between 1000 and 1600 h).

The aquatic sites included in the general survey of pH and Eh were chosen to represent as wide a range of habitats and geographical regions as possible. The data for marine waters were collected while making various journeys outside and inside the lagoon, the measurements being taken at a depth of 50 mm in all cases except those of shallow pools. The data for the intertidal lagoon sediments include the results of 13 transects taken at different places round the lagoon; standard records were made at a depth of 10 mm below the surface of the sediment, and in some cases also at 40 mm.

Inland freshwater pools were studied from West Island (Île Picard and the Takamaka and Cinq Cases regions of South Island (Grande Terre). The system used for naming these pools has been described briefly by Donaldson & Whitton (1977), and more fully by Donaldson & Whitton (1975). Most were freshwater in composition, at least at the time of sampling, but T3 was markedly brackish (c. 18‰). Standard records were made at 10 mm below the surface of the water, immediately over the surface of the sediment and at either 100 mm below the surface of the sediment or at the deepest point if this was less than 100 mm. For the general survey summarized in Figs. 5-7 only one result has been included in most cases for each pool. However several results are given for the large pools T3 and CC9, since these showed marked differences according to position in the pool and on different days.

Data on soil were collected from only a few sites on West Island (= Île Picard) where deposits were deepest. No data at all were taken for the insides of rocks, since measurement of Eh here presents particular problems. It is however known that highly reducing conditions may occur inside dead coral (Pouradier *et al.,* 1967), and endolithic algae were abundant on the atoll, especially in marine habitats.

Results

1. Field Survey of Environment

The results of the general survey to find the range of pH and Eh (indicated by Pt electrodes) occurring in aquatic sites are illustrated by means of scatter diagrams (Figs. 1, 2, 5-7). For clarity, tentative conclusions and some discussion are included here. A marked diurnal cycle of pH resulting from changes in photosynthesis and respiration (Donaldson & Whitton, 1977) often occurred, especially in small pools. Since the majority of readings were taken in the afternoon, the pH values recorded were usually near their maximum.

Marine Waters

i) There is a wide range in both pH and Eh (6.4 to 9.5,-340 to ± 450 mV).

ii) In general, the lowest pH values are associated with mangrove creek waters, usually coloured brown.

iii) In general, the order of values for Eh of the various types of water is: ocean > shore water > main lagoon > mangrove creek. Many intertidal pools show such a marked variation through the day, that direct comparison with other types of site is difficult, but a mean value for the daily cycle would show many as intermediate between lagoon water and mangrove creek water.

Intertidal sediments

The results illustrated in Figs 2 and 4 are all for the lagoon. However all the measurements made for intertidal sediments on the seaward sides of the atoll fell within the limits shown for the lagoon. Fewer observations are shown for 40 mm than for 10 mm partly because the sediments often overlay rock at a depth less than 40 mm.

i) There is wide range in pH and Eh both at 10 mm and 40 mm depth (5.5 to 9.1, - 410 to + 300 mV; 4.1 to 8.35,-400 to + 179 mV).

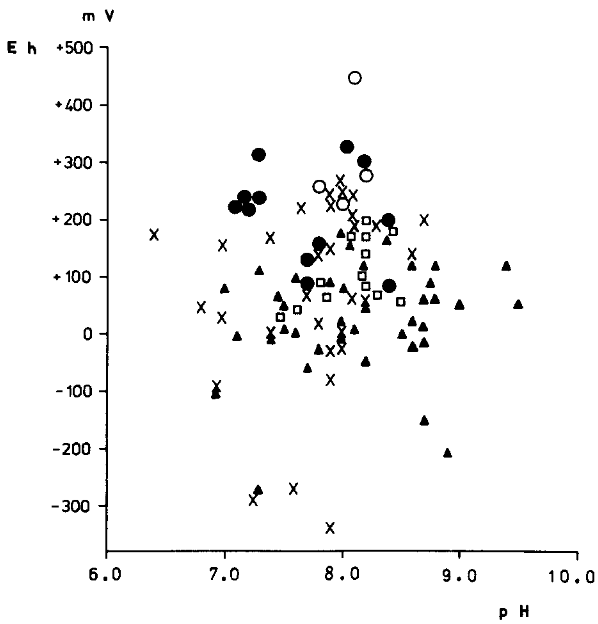

Fig. 1. pH-Eh values recorded during survey of marine waters.
o ± oceanic (ocean or channel into lagoon during inflowing tide)
□ shore (outside atoll); residual waters left at low tide
● main lagoon
▲ residual pools (in intertidal)
X creek waters

ii) In general, the values for both pH and Eh are lower in the sediment than in the water, and rather lower at 40 mm depth than at 10 mm depth.

iii) In general, whitish silts show considerably higher pH values than coloured silts; although the mean values of Eh are higher for whitish than coloured silts, the distinction is less clear than for pH, and some Eh values for whitish silts are very low.

iv) Sands are associated with a wide range of values of Eh, and a relatively wide range of pH, though with the latter not reaching such low values as the coloured silts. Among the probable reasons for the wide variation in values associated with sand is the fact that, at different locations, it is subject to marked differences in the amount of water draining slowly through it from mangrove forest.

Inland pool waters

i) There is a wide range of pH and Eh (6.0 to 10.2, -350 to + 268 mV: Fig. 5). However, if one of the values for the brackish pool T3 is omitted, the range of Eh is much less marked (-140 to + 268 mV). If the values for the (more or less) freshwater pools are compared with those for marine waters, it can be seen that there is a greater range of pH in the former, but a much smaller range of Eh. The contrast becomes even greater, if the pH results of Donaldson and Whitton (1977) are included in the comparison.

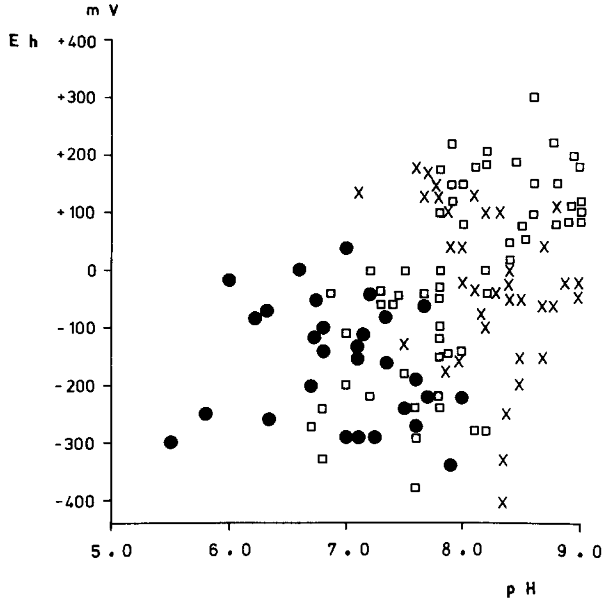

Fig. 2. Ph-Eh values recorded during survey of marine sediments, at 10 mm depth. (Colours refer to appearance at surface, and are not always the same at 10 mm depth.)
□ sands e.g. Fig. 3
X whitish silts
• coloured silts (mostly grey or red-brown)

Fig. 3. *Scytonema* sp. growing on a substratum of medium coarse sand near one of the minor lagoon passes (Passe Femme).

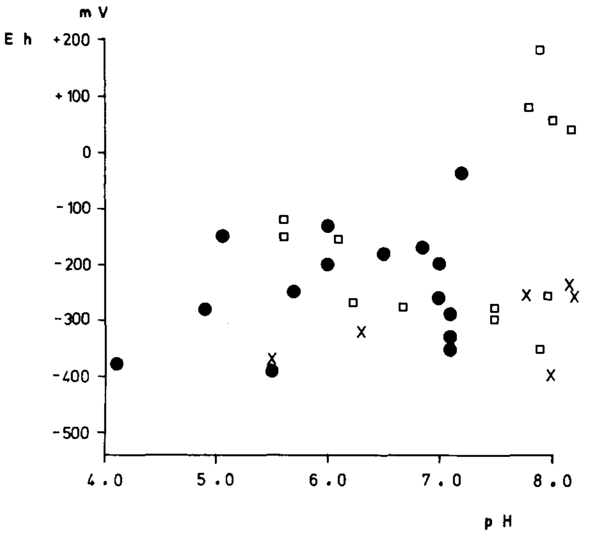

Fig. 4. pH-Eh values recorded during survey of marine sediments, at 40 mm depth. Symbols as for Fig. 2.

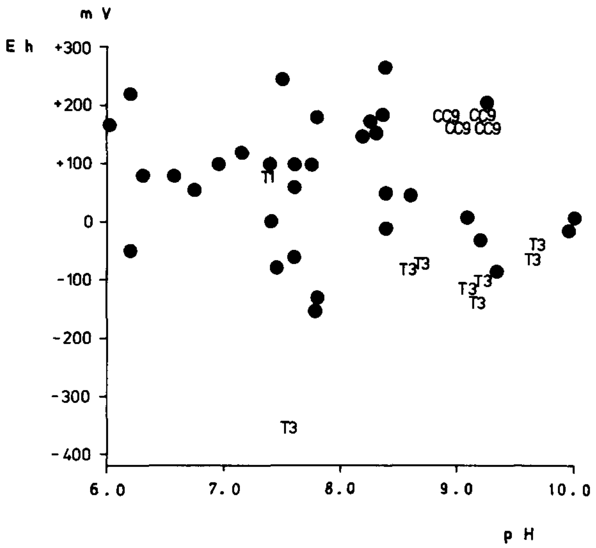

Fig. 5. pH-Eh values recorded during surveys of water in inland pools. Records for pools T1, T3 and CC9 shown individually; for details, see text.

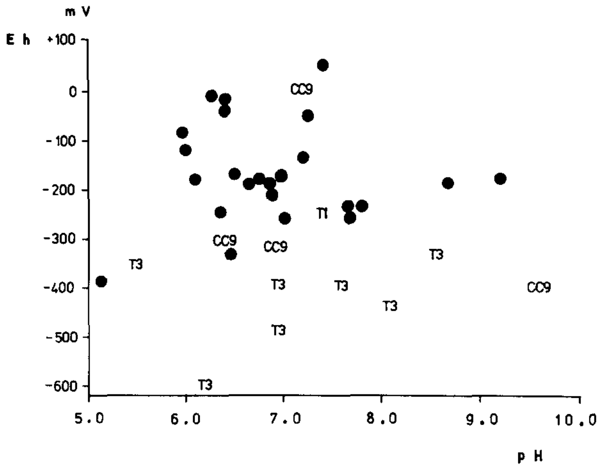

Fig. 6. pH-Eh values recorded during surveys of sediments in inland pools: taken at 10 mm depth.

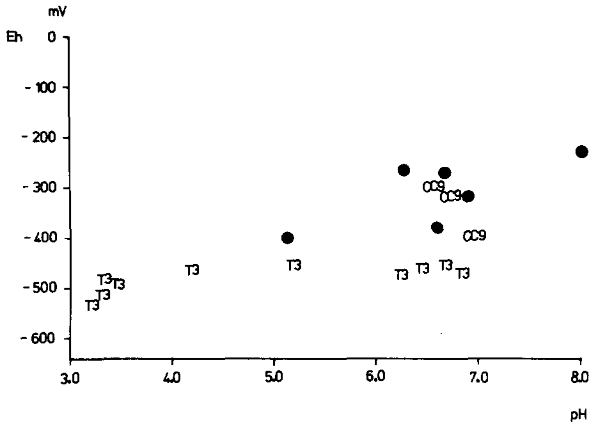

Fig. 7. pH-Eh values recorded during surveys of sediments in inland pools: taken at 100 mm depth.

Inland pool sediments

The sediments of T3 clearly differ so markedly from those of the other pools, that this pool is discussed separately.

i) There is a wide range in pH and Eh in the freshwater pools at 10 mm depth (5.15 to 9.6, - 400 to + 50 mV: Fig. 6). Among the few pools with sediments as deep as 100 mm, there is still a relatively wide range of pH values but not of Eh values (Fig. 7). The Eh values are mostly lower than those found by Viner (1975) for Lake George, Uganda, which were not normally below - 60 mV, and usually not below 0.0 mV. If the values for the freshwater pool sediments at 10 mm depth are compared with marine sediments at a similar depth, it can be seen that the range of pH and the lower limits of Eh are rather similar, but that the upper limits of Eh are not so high in the freshwater pools.

ii) The sediments of the brackish pool T3, which was sampled on three different days, and at different sites within the pool show a wide range in pH. In Fig. 7, values at 100 mm depth are shown from pH 3.25 to 6.85. In contrast, the values of Eh were uniformly very low.

Soil

Observations were made on soil only to find out whether the pattern of relatively low values for pH and Eh in some of the small pools inside the *Casuarina* forest was characteristic also of the soils there. The only obvious difference found was that a few samples from inside the forest showed a lower pH than found for any of the soils sampled just outside the forest (minimum pH values of 5.9 and 6.8, respectively).

2. Distribution of photosynthetic microorganisms in relation to pH and Eh

Certain microbial communities were both visually conspicuous and occurred at many sites on the intertidal lagoon sediments. A range of preliminary studies were carried out to ascertain to what extent the sediment associated with each community has clearly defined limits of pH and Eh. With the probes available, it was possible to obtain some indication of the immediate environment of the community only by extrapolating from the results of a large number of readings. However, the results shown in Fig. 8 clearly indicate that marked differences occur between some of the communities with respect to

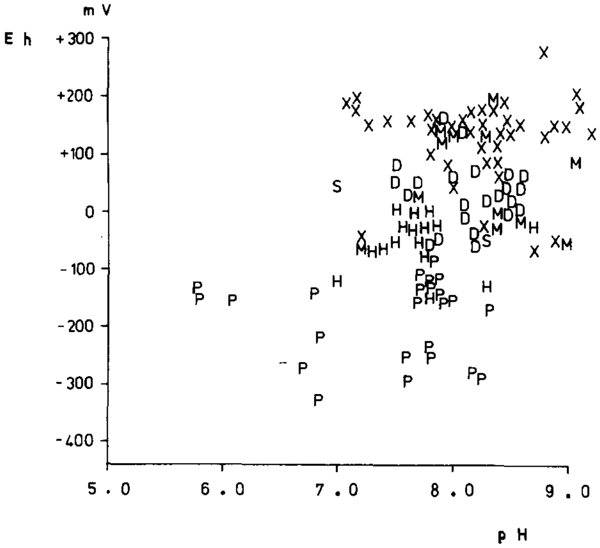

Fig. 8. Distribution of lagoon intertidal photosynthetic communities occurring on or near surface in relation to pH-Eh found in sediment at depth of 10 mm.
X *Scytonema* sp.
D pennate diatoms
S *Schizothrix* sp. dominated
M *Microcoleus chthonoplastes* dominated
H *Hyella balani*
P purple sulphur bacteria

the Eh values occurring at 10 mm depth at the same point. As the communities occur either on the surface of the sediment, or predominantly in a zone somewhere between 10 mm and the surface, the actual Eh values in the vicinity of the photosynthetic layer are likely to be higher. From these, it is possible to arrange the six communities shown in Fig. 8 in an approximate order of likelihood of being associated with a particular Eh range. This order is, from high to low: *Scytonema* sp. (Fig. 3), pennate diatoms, *Schizothrix* sp., *Microcoleus chthonoplastes* Thuret, *Hyella balani* Lehmann, purple phototrophic bacteria. The last two communities occur predominantly below the surface of the sediment. The first two and the last two communities all occur on the same medium coarse sand on West Island (Île Picard), so with these, at least, the characteristic Eh range is not merely because of correlated differences in particle size.

Discussion

It is clear that within the limits of a single atoll there can occur a very wide range of values for both pH and Eh. In comparison with the summary by Bass Becking *et al.* (1960) of the results then available for all environments, the most obvious omissions on the atoll are environments with an Eh above + 350 mV (if a single value of oceanic water is omitted) and environments with pH values below 3.25. The limits on Aldabra are extended considerably by the sediments on one brackish pool (T3), for which no parallel could be found anywhere else on the atoll; such a combination of very low pH and Eh appears to be exceptional among natural environment.

The range of environments is almost equally great in freshwater as in marine situations, with higher values of pH occurring in the former than ever occur in the latter, but with a narrower range of values of Eh in the former. The waters of Aldabra show Eh values which are low in comparison with most of those quoted in the literature. Using the values obtained by day (mostly afternoon), the majority of waters were found to have values less than + 200 mV, and about half of both marine and freshwater samples were less than + 100 mV. It seems probably that the main source of reducing materials in the lagoon is some component of the mangrove forest ecosystem. This is discussed further in the next paper. The possible reasons for the low values of Eh widespread in freshwater pools on Aldabra are discussed by Potts & Whitton (1977a).

Summary

An account is given of the range of pH and Eh in marine and freshwater aquatic sites on Aldabra Atoll, Indian Ocean, during the period November 1974 to June 1975. Although the values of pH and Eh are only the response of electrodes at particular sites, it is suggested that when taken together they do provide a semi-quantitative indication of the variation occurring on one atoll. There is a very wide range in values of pH and Eh for both marine and freshwater environments:

i) marine waters range from pH 6.4 to 9.5, and from Eh - 340 to + 450 mV.

ii) intertidal sediments at 40 mm depth range from pH 4.1 to 8.35 and Eh - 400 to + 179 mV.

iii) freshwaters range from pH 6.0 to 10.2 and Eh - 140 to + 268 mV.

iv) freshwater and brackish sediments at 100 mm depth range from pH 3.25 to 8.1 and Eh - 410 to - 240 mV.

It is possible to arrange some of the important photosynthetic microbial communities on lagoon sediments in an approximate order of their association with sediments of particular Eh values. These are, from high to low: *Scytonema* sp., pennate diatoms, *Schizothrix* sp., *Microcoleus chthonoplastes, Hyella balani,* purple phototrophic bacteria.

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