

Physico-chemical characteristics of a permanent Spanish hypersaline lake: La Salada de Chiprana (NE Spain)

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Abstract

La Salada de Chiprana Lake, located in the Ebro River basin, northeastern Spain, is the only permanent and deep water hypersaline ecosystem in all of western Europe. With a total surface of 31 ha and a maximum depth of 5.6 m, it has several basins bounded by elongated sandstone-bodies or *ribbons* which are paleochannels of Miocene age. Its salinity varied from 30 to 73 g l⁻¹ during the 1989 hydrological cycle and the most abundant ions were magnesium and sulphate. Depth-time distributions of major physico-chemical variables demonstrated that the lake was stratified in two distinctive layers during most of the year. The chemocline disappeared only in October, with the complete overturn of the water column. In the deep water, three conditions occurred which allowed development of green sulphur bacteria populations: (1) oxygen depletion, (2) presence of hydrogen sulphide and (3) presence of light. Benthic microbial mats covered the sediments of shallow shores of moderate slope.

Introduction

Hypersaline environments are known since Precambrian times. They present many environmental, social, economic and scientific values (Hammer, 1986; Williams, 1986). The present state of knowledge about the geochemistry and microbiology of the hypersaline systems is reviewed by Javor (1989).

Such ecosystems constitute a feature of the landscape of the arid and semiarid regions of Spain. The majority of saline lakes in Spain are shallow and ephemeral. These lakes have salinities ranging from 10 g l⁻¹ to 400 g l⁻¹ and depths of 0.05 to 0.70 m. They have mixed or sodium-chloride dominated ionic composition, and they show very high annual and interannual environ-

mental fluctuations (Montes & Martino, 1987; Comín & Alonso, 1988; Baltanas *et al.*, 1990).

In this context, La Salada de Chiprana Lake has great environmental value because it is a unique ecosystem in Western Europe. The basin of La Salada is a depression bounded by paleochannels (elongated sandstone-bodies), while all other Spanish saline lakes have basins of karstic, hydroecolic or tectonic origin. Its maximum depth is about 5.6 m, in contrast with the shallow character of other lakes. Because of this depth and of ground water inflow, La Salada is a permanent lake, showing very slight water level fluctuations. Its magnesium-sulphate dominated ionic composition also stands out from the sodium-chloride or mixed composition of other Iberian saline lakes.

The aim of this study is to describe the special

environmental characteristics of La Salada, the whole of which forms a suitable habitat for the development of two singular communities of phototrophic bacteria: planktonic green sulphur bacteria in the anoxic deeper water and benthic microbial mats which cover the flat sediments not deeper than 1.5 m.

Study area

La Salada ($41^{\circ} 14' W$, $0^{\circ} 10' N$) is located in the south-central region of the Ebro River basin in northeastern Spain (Fig. 1). The lake is at 150 m elevation, and about 3.5 km from the Ebro River which here is at 130 m.a.s.l.

The Ebro River basin has a semiarid climate with 330 mm of annual precipitation. Annual

mean temperature is $16^{\circ} C$. The high moisture deficit during the summer season is intensified by dry winds from the northwest.

The natural shrub vegetation of the region has been replaced in most areas by agricultural fields, an increasing proportion of which are irrigated.

The substrate of the La Salada area is characterized by Miocene fluvial sediments that present lithological formations known as *ribbons* which are very singular due to their size, extent and state of conservation in this region (Riba *et al.*, 1967). Ribbons are sinuous old river beds (paleochannels) that were filled with sand and fossilized when the basin was later a site of sediment deposition. Afterwards, erosion of softer surrounding material left these elongated sandstone bodies as emergent structures (Friend *et al.*, 1986). This type of landscape is referred to as 'inverted relief'.

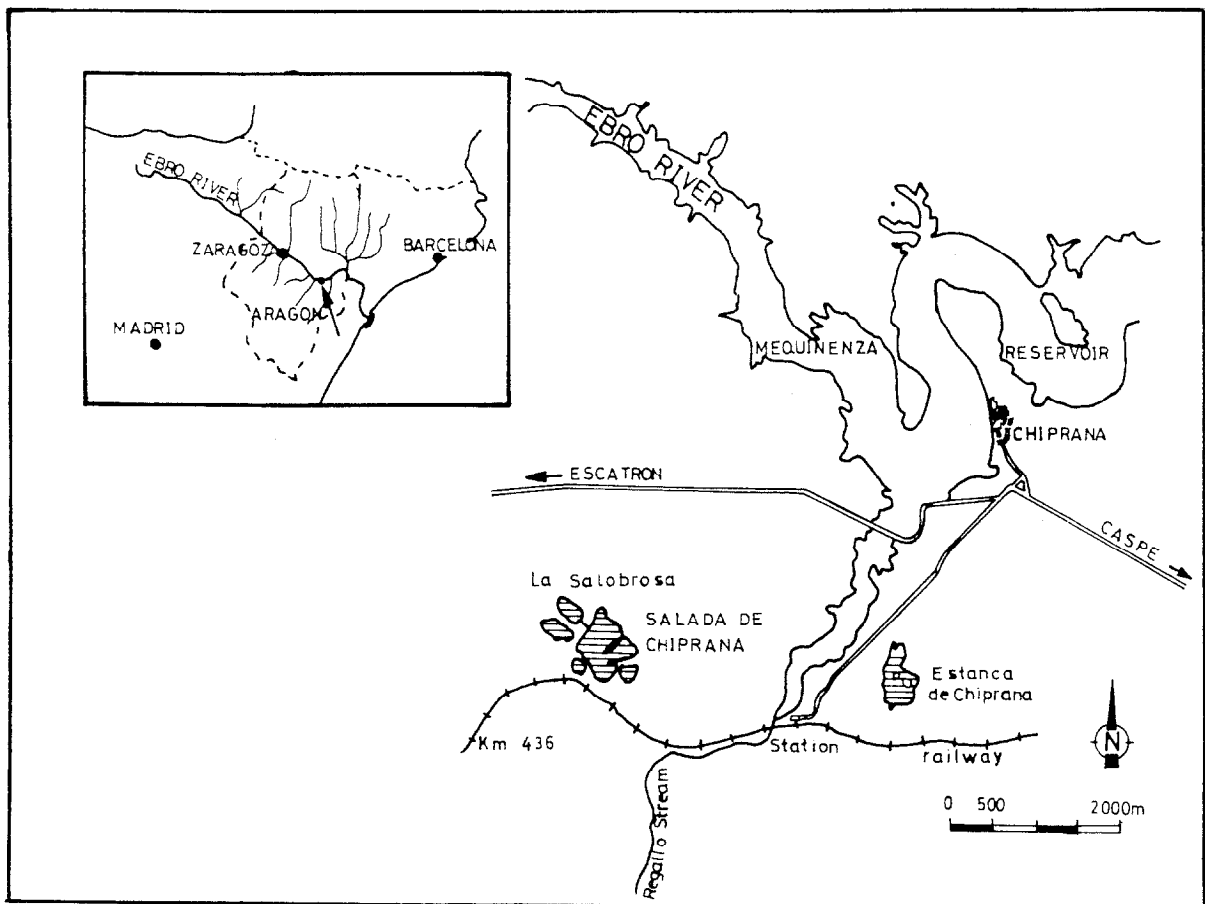


Fig. 1. Location of the study area.

The ribbons sometimes intersect, thereby delimiting depressions and playing an important role in the origin of some lakes in this area. In some cases, the ribbons can also act as conduits for ground water flow. Most of these depressions do not contain water because of the high moisture deficit of the region on the one hand, and losses by drainage on the other. Only those basins that receive ground water inflow ever contain temporary or permanent water bodies (Bernaldez, 1987). This probably explains the permanent nature of La Salada (Pueyo, 1978/79).

Apart from La Salada, three small former saline lakes exist in the Chiprana-Caspe region that are now freshwater (Fig. 1). The first one, Estanca de Chiprana (13.24 ha), is a deep and permanent freshwater lake as a result of receiving water from the Guadalupe river by a drainage canal. Adjacent to La Salada, the second one, Prado del Farol (1.51 ha) is very shallow, almost completely filled with sediments and covered by solid bed of reeds (*Phragmites australis* (Cav.) Trin.). The third one, La Salobrosa or Rocés Lake (2.8 ha), also receives by a drainage canal, freshwater rich in nutrients from agricultural lands and, in turns, drains through a canal into La Salada.

Methods

The depth-time distribution of major physico-chemical variables was studied during the 1989 hydrological cycle. Every month vertical profiles of temperature, conductivity, pH and redox potential were measured *in situ*, Secchi depth was determined, and water samples were taken for chemical analysis, at midday, at the sampling station located at one of the deepest points in the larger basin (Fig. 2). Samples were taken at different depths with the purpose of observing physical, chemical or biological gradients throughout the water column.

Conductivity at 25 °C and temperature were measured using an Instrand-10 compensating conductivity meter with a thermistor. The pH and redox potential were measured with a Crison-506

portable pH/redox meter equipped with a Metrohn platinum combination electrode. Because of the slight vertical variation in salinity and ionic proportions, it was considered unnecessary to determine separate temperature-conductivity adjustment curves for the different strata of the water column as Hall & Northcote (1986) recommend.

Dissolved major ion, nutrient (phosphate, nitrate and ammonia), oxygen, hydrogen sulphide and chlorophyll *a* concentrations were determined following the methodology proposed by A.P.H.A. (1985) with some modifications (Bernués *et al.*, 1990). Bacteriochlorophyll *a* concentration was calculated following Clayton (1966).

The percentage of error of chemical analysis was calculated as $[(\text{cations} - \text{anions}) / (\text{cations} + \text{anions})] \times 100$. All values of our analysis gave an error under 5–10 percent, which is considered admissible for saline waters (Custodio & Llamas, 1976). All absorbance values were obtained using a Hitachi U-2000 Spectrophotometer.

One sampling station for microbial mats was set up at 1 m depth off a sandy shoreline on the north side of the lake (Fig. 2).

Results and discussion

Basin morphometry and origin

La Salada de Chiprana lake is found on a landscape of 'inverted relief' as discussed earlier. The lake was formed when a Quaternary alluvial fan dammed the drainage into the Ebro river. This fact confirms the recent age of the lake.

This lake has several basins separated by ribbons which, above the water surface, are represented by narrow peninsulas and linear islands (Fig. 2). Its main morphometric parameters are given in Table 1. Its total surface is about 31.5 ha, of which 0.4 ha correspond to islands, giving an insulosity value of 1.3%. The bottom drops off very steeply in some areas and very gradually in others. The phytobenthos is composed of multi-

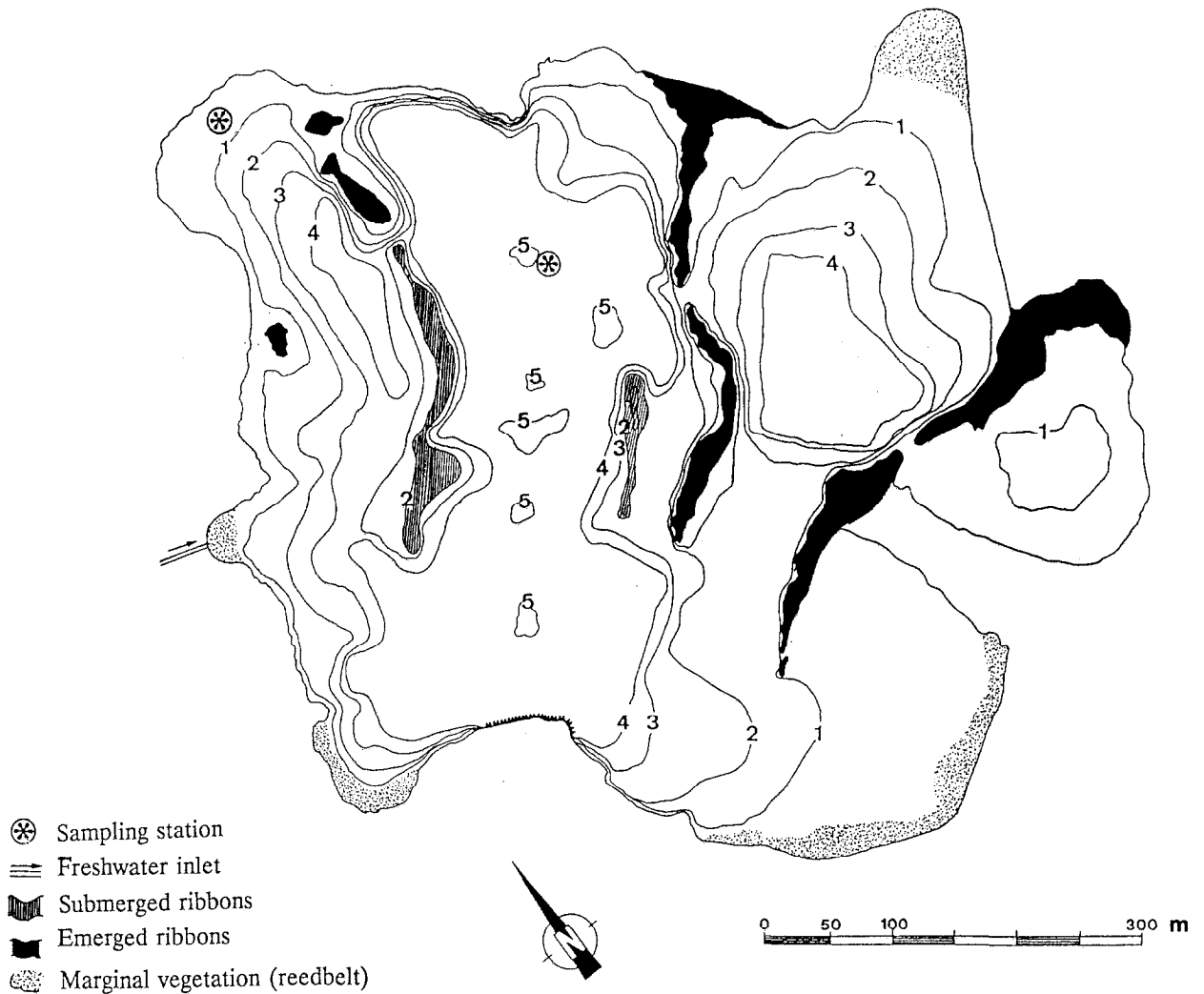


Fig. 2. Bathymetric map of La Salada de Chiprana Lake (May 1988), showing sampling stations (*) for vertical profiles and microbial mat communities.

laminated communities known as microbial mats which cover horizontal sediments not deeper than 1.5 m. Some stands of the submerged macrophyte *Ruppia maritima* L. var *maritima* are also present in these shallow areas. At greater depths, up to 3 m, sediments are covered by the charophyte *Lamprothamium papulosum* (Wallr.) J. Groves.

Maximum depths of 5.6 m occur in some areas of the central and largest basin. This basin is characterized by steep shorelines owing to the disposition of the ribbons, and a flat bottom con-

sisting of fine organically rich sediments up to 1 m thick in some areas. This morphometry play an important role in inhibiting the mixing of deep waters which are anoxic during most of the year.

Water regime

The original water regime of La Salada was characterized by the absence of outflows as well as by natural surface inflows (Reyes Prosper, 1915). Its

Table 1. Morphometric parameters of Salada de Chiprana Lake during the 1987/88 hydrological cycle. Parameter definitions follow Hakanson (1981).

Parameter	Value
Area (ha)	31.5
Volume (hm ³)	7.7
Maximum depth (m)	5.6
Mean depth (m)	2.3
Relative depth (m)	0.86
Shore development	1.89
Volume development	1.27
Mean slope (%)	3.4
Insulosity (%)	1.3
Bottom roughness	5.67
Shoreline length (m)	3750
Maximum length (m)	792
Maximum effective length (m)	792
Maximum width (m)	693
Maximum effective width (m)	523

permanence and slightly fluctuating level are related to ground water discharges. Main losses occur via evaporation and evapotranspiration. Precipitation is responsible for the small seasonal variations in water level and salinity. In 1989, the water level twice (in March and December) rose about 20 cm in response to the precipitation maxima in February and November (40 and 90 mm precipitation, monthly totals, respectively).

Nowadays, the water regime is altered by continuous freshwater input via a small canal coming from La Salobrosa lake. Several other canals in the vicinity of La Salada drain surrounding agricultural lands and supply water to La Salada intermittently from March to October, causing year to year fluctuations in water level and salinity. In May 1989, the salinity was about 64 g l⁻¹ while values of 84 g l⁻¹ (May 1987) and 76 g l⁻¹ (May 1988) have been obtained previously (Guertero *et al.*, 1991). These freshwater inflows, as well as the natural runoff, are difficult to quantify because of their irregularity and diffuseness.

Nevertheless, the potential of man's activities to reduce the salinity of La Salada is great, as demonstrated by the histories of the three small lakes near La Salada, mentioned earlier.

Mixing and stratification regime

This regime at La Salada was strongly under the influence of the hydrological factors and variations in salinity. Temperature was a factor of secondary importance.

Salinity

There was a strong stratification during most of the year, with surface salinity lower than deep salinity by more than 10 g l⁻¹. The steepest salinity gradient or chemocline was located at *ca.* 2 m in January, and gradually descended to about 4.5 m by August and September, when upper mixed layer had a salinity of 56 g l⁻¹ and was about 4 m thick (Fig. 5a). This gradient can be much more clearly appreciated in the depth-time distribution of conductivity (Fig. 5b). In October, strong winds caused mixing of the water column rendering it isosaline at *ca.* 53 g l⁻¹ and isothermal at *ca.* 19–20 °C. Salinity stratification was almost immediately reestablished by freshwater inflow and dilution of surface waters as a consequence of heavy rains in November.

Temperature

Thermal stratification was generally weak, being strongest in August when there was a 6 °C difference between surface and bottom waters (Fig. 5c). During midwinter, inverse stratification was present, with surface waters colder than deeper waters. Both phenomena mentioned above were possible in this shallow lake because of the stabilizing effect of the vertical salinity gradient. Seasonal temperature variation was greater in the surface oxic waters (7.1 °C to 24 °C) than in the deeper anoxic waters (11.8 °C to 21.4 °C).

Long term behavior: meromictic or holomictic?

One of the most interesting features of the lake is its apparent position at the holomictic/meromictic

boundary. It clearly was holomictic in 1989; but as the dynamic of the lake depends on the weather conditions, there may be years when the lake behaves like a meromictic one.

Precipitation and temperature data for 1989 and the previous twenty years (1969 through 1988) are represented in Fig. 3. These data were registered at Torre Los Baños (Chiprana) meteorological station, located at 177 m a.s.l. Monthly mean temperatures in 1989 were somewhat higher than the twenty-year average (1969 through 1988)

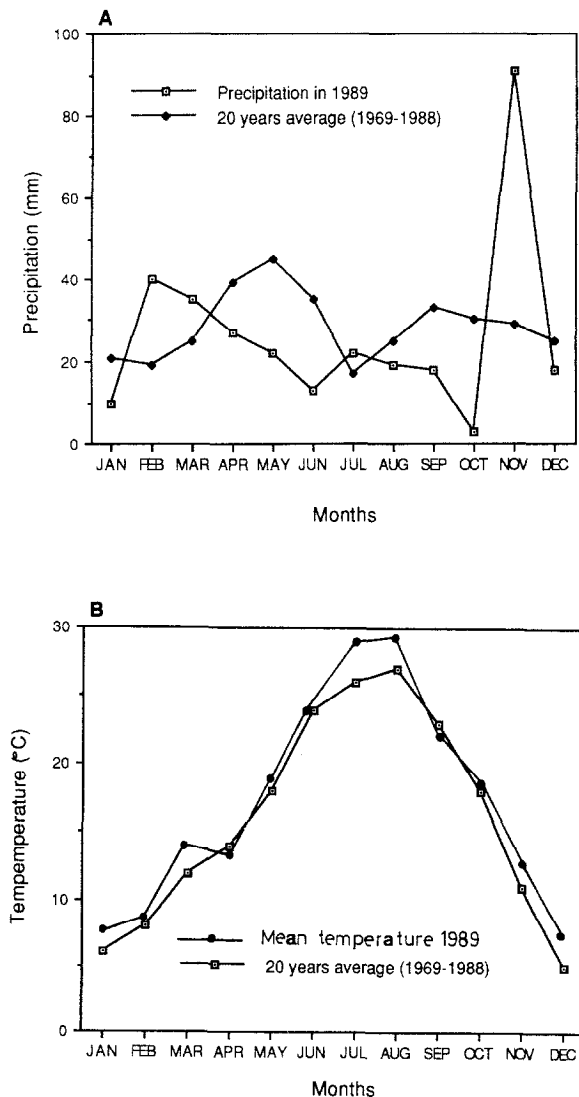


Fig. 3. Meteorological data for Torre Los Baños (Chiprana) meteorological station. A - Monthly Precipitation (mm). B - Mean monthly Temperatures (°C).

values, especially in mid-summer. From March to September of 1989, the chemocline was progressively displaced downward by wind-induced mixing. Because of higher than normal summer air temperatures, however, the rate of this downward displacement might have been slower than in cooler years. That is, meromixis or at least a delay of complete overturn may have been favored.

On the other hand, precipitation maxima in 1989 occurred earlier in spring (February) and later in autumn (November) than is typical, and total August-October rainfall was only about fifty percent of the twenty-year average for that period. This may have made it more likely that the water column would mix completely in 1989 than in a more typical year. If August-October precipitation in 1989 had been average or above average, the freshening of surface waters might have created a salinity gradient sufficient to have prevented complete mixing during that autumn. In previous years, when salinities were even higher (as noted earlier), it would have been even more likely for La Salada to have behaved as a meromictic lake if heavy rains occurred in early autumn.

Biological processes and water chemistry

Ionic composition

The ionic composition showed some variation with both depth and season. The most abundant ions were always magnesium and sulphate as a consequence of dissolution of evaporitic salts (gypsum, dolomite, carnallite) in the soil by the ground and pluvial waters that feed the lake. All samples taken in 1989 and during some years before (Pueyo 1978/79; Mingarro *et al.*, 1981) belong to SO₄-Cl-Mg-Na type of Eugster & Hardie's (1978) ionic series.

In March, calcium decreased throughout the water column, reflecting precipitation of calcium carbonate (Fig. 4a). As chlorophyll did not increase at this time, suggesting that photosynthetic activity did not either, it seems likely that calcium carbonate precipitation was caused by chemical

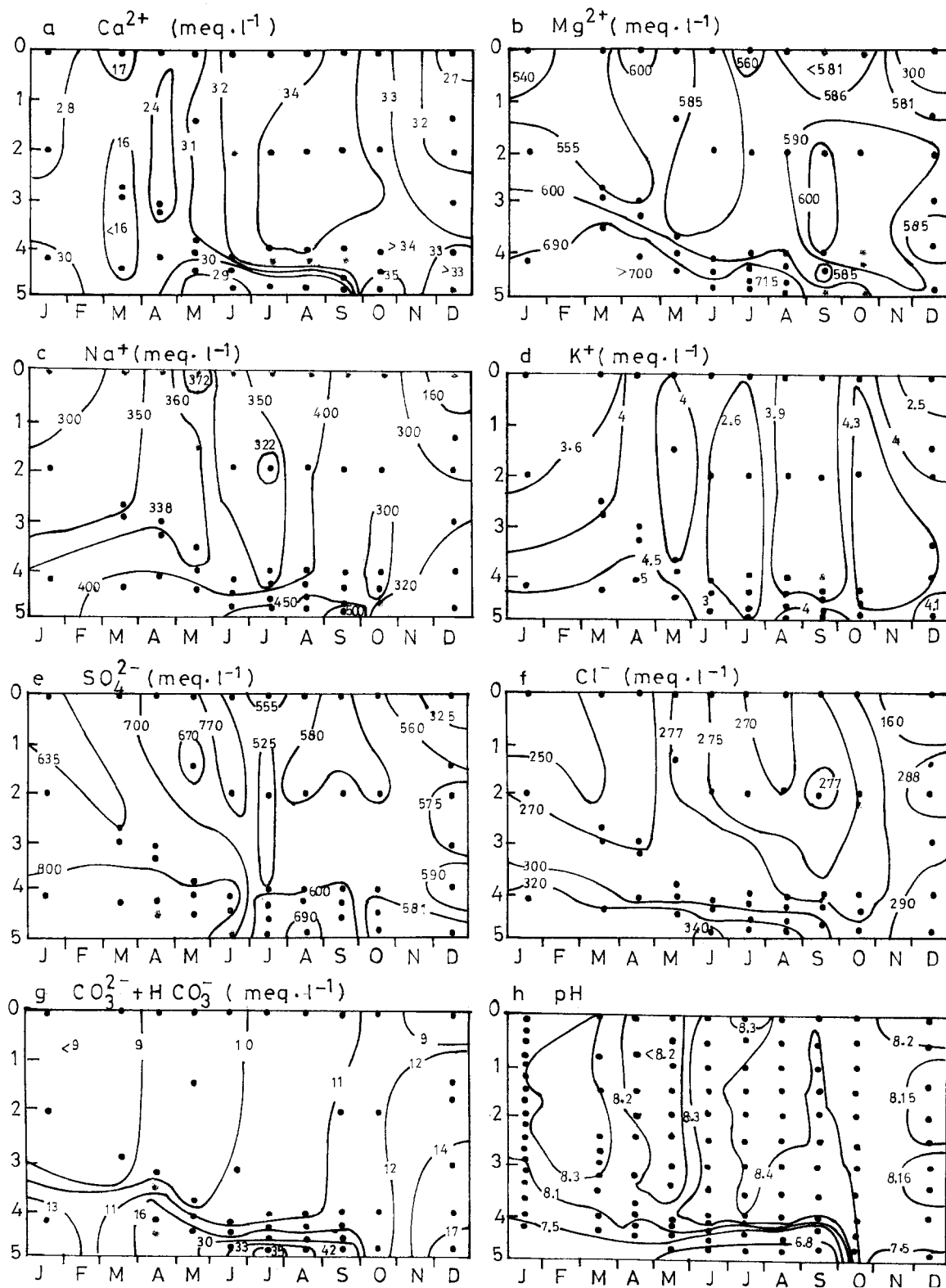


Fig. 4. Depth-time distribution of five major ions (meq l⁻¹) and pH in La Salada Lake during annual cycle 1989. a- Calcium, b- Magnesium, c- Sodium, d- Potassium, e- Sulphate, f- Chloride, g- Total alkalinity, h- pH.

processes. The rainfall (and runoff) maximum in February caused an increased input of clay and humic acids and these easily could have formed complex ions with calcium carbonate that would have precipitated at the basic pH of La Salada waters. The slight springtime temperature increase may also have favored calcium carbonate precipitation.

In summer, sulphate concentration tended to decrease slightly (Fig. 4e). Sulphate-reducing activity associated with organic matter decomposition at the higher temperatures of this period probably was responsible.

Total alkalinity was highly correlated with pH ($r = -0.94$, $N = 49$, $P = 0.0001$). In surface waters, alkalinity varied between 8.47 meq l^{-1} and 11.06 meq l^{-1} . In bottom waters, a maximum bicarbonate concentration of 42.49 meq l^{-1} coincided with a pH minimum at the end of summer (Fig. 4g, h). These variations reflected two processes. First, the higher water temperatures of summer season stimulated microbial production of CO_2 and a consequent lowering of the pH; and second, carbonate precipitated from surface waters during spring redissolved readily in these summertime low pH conditions.

Oxycline, nutrients and metabolic influences

The variables which best defined the chemical gradient of the water column were oxygen and hydrogen sulphide which presented complementary distributions (Fig. 5d, e). Bottom waters were anoxic during most of the hydrological cycle. Only in October, when mixing of the water column occurred due to strong winds, was oxygen detectable (up to 1.3 mg l^{-1}) in the deepest water.

There were several factors which led to this oxycline. One of them was the morphology of the basin which favours the isolation of the deep water and diminishes the stirring effect of wind. Another factor was the salinity gradient formed as a consequence of freshwater inflow from precipitation and runoff. Finally, the development of a temperature gradient also caused density differences that inhibited mixing. In the stagnant and

progressively anoxic deep water, sulphide accumulated. This was produced by the anaerobic respiration of sulphate-reducing bacteria and the decomposition of organic matter in the bottom sediments. Thus, it was not unusual that hydrogen sulphide levels as high as 220 mg l^{-1} were found near the bottom in late summer.

The reducing power of the deep water was indicated by a redox potential of -436 mV as well as by a decrease in pH values down to 7.5–6.8 (in contrast with pH values of 8.1–8.4 in oxic surface waters).

With regard to nutrients, phosphate-phosphorus concentration was very low ($0\text{--}0.7 \text{ } \mu\text{g at l}^{-1}$), even in anoxic waters, showed no detectable spatial or temporal patterns. Nitrate-nitrogen was only present in oxic waters and exhibited a maximum of $10\text{--}30 \text{ } \mu\text{g at l}^{-1}$ from January to April (Fig. 5f). This was associated with the rainfall and runoff maximum in February, which delivered nitrate from the surrounding agricultural fields. A nitrate minimum of $3.93 \text{ } \mu\text{g at l}^{-1}$ was recorded in May, coinciding with increasing chlorophyll *a* and bacteriochlorophyll *a* concentrations. The decrease in nitrate concentration with depth throughout the year probably was due to denitrification in the anoxic strata. Maximal ammonia concentrations were about $40 \text{ } \mu\text{g at l}^{-1}$ in surface waters, and up to $600 \text{ } \mu\text{g at l}^{-1}$ in the deep water in late summer near the end of the long period of stratification.

Planktonic photosynthetic organisms

Distribution, abundance and activity of planktonic photosynthetic organisms were inferred from pigment concentrations and Secchi disk measurements (Fig. 5g, h). The lake is highly eutrophic. In oxic waters chlorophyll *a* concentration varied from 1 to $30 \text{ } \mu\text{g l}^{-1}$, with a minimum in March and April and maxima were during summer. From January to May, the Secchi disk was visible only to 1.0–1.5 m when chlorophyll concentrations in the oxic surface waters were low. The clearest water occurred in May. In June, chlorophyll *a* concentrations begin to in-

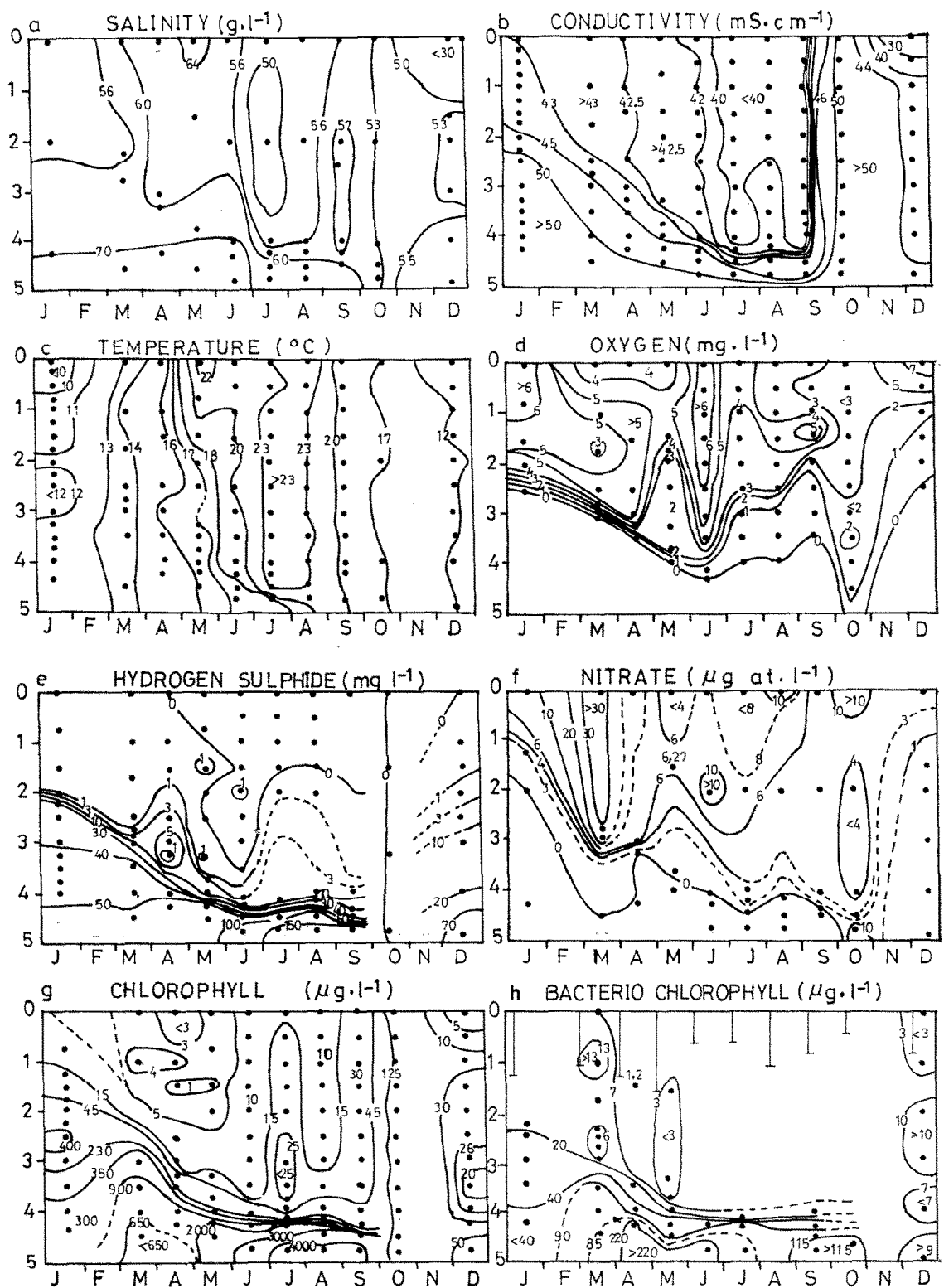
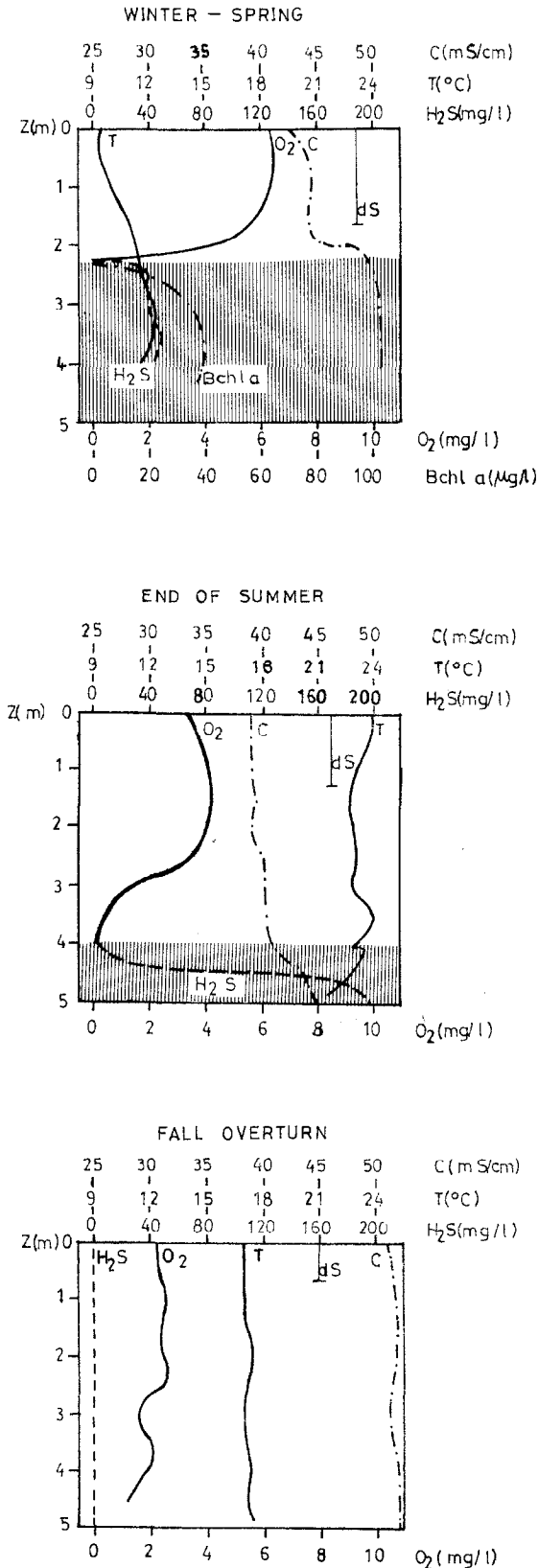


Fig. 5. Depth-time distribution of main limnological variables in La Salada lake during annual cycle 1989. a- Salinity (g l^{-1}), b- Conductivity at 25°C (mS cm^{-1}), c- Temperature ($^\circ\text{C}$), d- Oxygen (mg l^{-1}), e- Hydrogen sulphide (mg l^{-1}), f- Nitrate ($\mu\text{g at. l}^{-1}$), g- Chlorophyll *a* ($\mu\text{g l}^{-1}$), h- Bacteriochlorophyll *a* ($\mu\text{g l}^{-1}$) and Secchi disk depth (\perp).



crease, perhaps because of higher solar radiation and temperature. Algal blooms from July to October caused Secchi disk depth to decrease to a minimum. During the fall overturn, there was a large increase in chlorophyll *a* concentration, reflecting a plankton bloom perhaps stimulated by erosion of the chemocline and upward mixing of nutrients.

Chlorophyll *a* concentration apparently increased with depth at all times except during the period of mixing. Highest concentrations were at or below the oxic/anoxic interface, with a maximum of $4000 \mu\text{g l}^{-1}$ at the end of the summer. These high concentrations could not have corresponded to living algal populations because no algal cells were observed at these depths. Two explanations seem possible. (1) Chlorophyll *a* accumulated in anoxic waters where decomposition rates were low because of high salinity and absence of oxygen. (2) We overestimated chlorophyll *a* concentration because of the presence of bacteriochlorophyll *d*, which has a similar absorption maximum. Spectrophotometry may not provide an unequivocal method to distinguish and quantify these pigments. Spectrophotometric data must be confirmed by the chromatographic identification of the extracted bacteriochlorophylls as *Gloe et al.* (1975) recommend.

Depth-time distribution of bacteriochlorophyll *a* is shown in Fig. 5h. From April to June, bacteriochlorophyll *a* was found in small amounts in surface waters, but higher values, up to $220 \mu\text{g l}^{-1}$, were recorded in deeper water. In summer, bacteriochlorophyll *a* concentrations decreased to 85 or $100 \mu\text{g l}^{-1}$.

The presence of this pigment revealed anoxygenic phototrophs growing in the deep anaerobic water of Salada de Chiprana Lake. Absence of oxygen, presence of sulphide, and sufficient solar radiation permitted the development of green sulphur bacteria. Absorption spectra obtained for

Fig. 6. Seasonal variation of the structure of the water column of Salada de Chiprana Lake during annual cycle 1989. (T = temperature, C = conductivity, dS = Secchi disk depth). The shaded area shows the distribution of photosynthetic bacteria.

raw water samples indicated that the dominant bacterial population was the same throughout 1989. Biochemical and morphological characteristics of the isolated dominant population identified this species as *Chlorobium vibrioforme* Pelsh, possibly with some physiological adaptations to the environmental conditions of this lake (Guerrero *et al.*, 1991).

The seasonal variation of the structure of water column at La Salada is summarized in Fig. 6, where profiles of significant variables defining the depth gradient are represented. We have distinguished three periods:

- (a) In winter and spring, the oxygen-sulphide interface was located high in the water column,

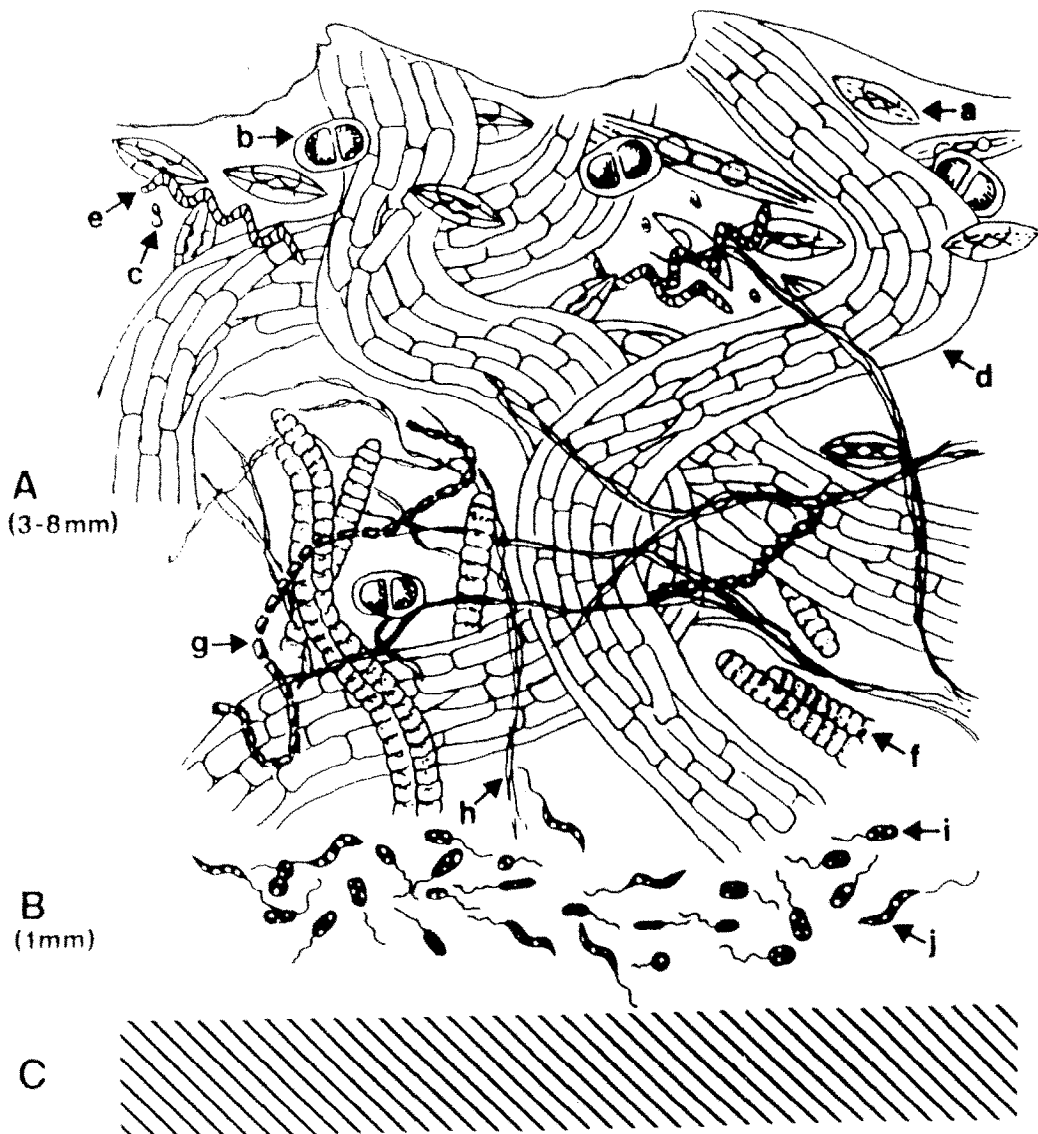


Fig. 7. Schematic drawing representation of vertical section through a summer microbial mat from Salada de Chiprana Lake showing the different constituent layers of the green and red layers. The letters on the drawing refer to the following: a, diatoms; b, *Gloeocapsa* sp.; c, *Synechococcus* sp.; d, *Microcoleus chthonoplastes*; e, *Spirulina* sp.; f, *Oscillatoria* spp.; g, *Pseudoanabaena* sp.; h, flexibacteria, i, *Chromatium* sp.; j, *Thiospirillum* sp.; A = green layer; B = red layer; C = black sediment.

- and solar radiation reached the anoxic layer.
- (b) At the end of summer, the chemocline was located nearer the bottom, and the anoxic water was confined to the last meter of the water column.
- (c) In autumn, complete oxygenation of the water column occurred because of strong winds. By December, if not earlier, strong stratification had been reestablished again.

During the first period (January to May), there was a large increase in *Chlorobium* density in bottom waters as the bacteriochlorophyll *a* indicate (Fig. 5h). Towards the end of the summer, light reduction in the deep water probably caused a decrease in this population. In autumn, oxygenation of bottom waters and elimination of sulphide would have been expected to cause a major decline in the *Chlorobium* population. High bacteriochlorophyll *a* levels at the bottom of the water column in October may have been due in part to non-metabolizing cells accumulated in this oxic and poorly lit region. In December, the distribution of the *Chlorobium* population had again expanded upward in concert with the thickening of the anoxic layer and perhaps aided by vertical mixing during the fall overturn.

Benthic microbial mats

The special physico-chemical characteristics of Chiprana Lake make it also suitable for the development of microbial mat communities. These benthic formations covered the sediments of shallow areas of moderate slope. The thickness and cohesion of this microbial formation was considerable and was due to the presence of a filamentous cyanobacterium *Microcoleus chthonoplastes* Thuret which was the principal component of the mats. The stratification of microbial populations was related to the gradient of oxygen, sulphide and light through the mat (Fig. 7). The surface layer was composed primarily of diatoms and unicellular cyanobacteria. Several green layers of filamentous cyanobacteria were present underneath. The deepest layer was red and constituted

by unicellular purple sulphur bacteria in contact with the black sediments, rich in sulphide produced by sulphate-reducing bacteria.

Conclusions

The extreme character of La Salada de Chiprana Lake causes a low species diversity and some unusual limnological and microbial features. These justify a rigorous protection of this ecosystem. A decrease of salinity, such as might result from the irrigation plans currently being considered for the surrounding agricultural area, could cause the disappearance of the microbial communities now present.

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