

Images of concentrations of dissolved sulphide in the sediment of a lake and implications for internal sulphur cycling

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ABSTRACT

The high-resolution mapping of dissolved sulphide in modern sediment of a permanently stratified (meromictic) lake is possible using a novel sulphide imaging technique (called a 'sulphur print'). The technique is simple, easy to use and can map a relatively large area (up to several dm²). *In situ* sulphur prints from anoxic fine-grained sediments are able to reveal internal structures in apparently homogeneous materials. Sulphur prints have been used to examine the formation and distribution of dissolved sulphide in the sediment and water column of the meromictic Lake Cadagno (southern Switzerland). The prints show clearly that a previously unknown laminar convective flow of sulphide-free porewater occurs across the sediment–water interface. Such convective flow out of the sediment must be accompanied by convective flow of sulphide- and sulphate-rich lake water into the sediment, and may be an important mechanism for the accumulation of sulphur in the sediment.

Keywords Anoxic lake sediment, convective flow, hydrogen sulphide imaging, sulphur cycle.

INTRODUCTION

Sulphur compounds in redox states from S²⁻ to S⁶⁺ dominate the chemistry of both the water column and the porewaters of stratified sulphur lakes and their sediments, but it is its most reduced form, sulphide S²⁻, that exhibits the greatest chemical and biochemical reactivity. However, the determination of dissolved sulphide (i.e. H₂S, HS⁻, S_x²⁻) in the water column or in the sediment by means of conventional sampling techniques (Sholkovitz, 1973; Emerson, 1976) allows only a poor spatial resolution and is hampered by outgassing of H₂S during sampling and losses resulting from oxidation. With porewater equilibrators, the vertical spatial resolution in sediments is improved down to a centimetre scale (Hesslein, 1976; Brandl & Hanselmann, 1991; Urban *et al.*, 1997), and almost down to a millimetre scale using different kinds of gel samplers (Davison *et al.*, 1991, 1994, 1997). With ion-selective electrode measurements, fine resolution to a micrometre scale has been achieved for sulphide in microbial mats (Kühl & Jørgensen,

1992) and deep sea sediments (Gundersen *et al.*, 1992) without the need for sampling. Outgassing and losses are minimized by continuous sulphide profiles in sediments with so-called 'dipstick' samplers (precursors of the gel samplers mentioned above), consisting of a polyacrylamide gel dosed with lead acetate (Reeburgh & Erickson, 1982).

The mapping area of the above techniques is limited and does not allow a continuous determination of the spatial variability in sulphide concentration of a large sediment or water column. Here, we propose a novel simple *in situ* technique, which images the distribution of dissolved sulphide in a sediment in two dimensions over an area of several dm², with an estimated resolution of less than 1 mm. This technique allows the depth of the sulphate-reducing zone, and its structure, to be evaluated quickly in anoxic sediments and gives new insights into the distribution of sulphate-reducing activity as well as the cycling of sulphur across the sediment–water boundary.

STUDY SITE

The meromictic Lake Cadagno (southern Switzerland) covers 0.27 km² in area and is 21 m deep (Fig. 1). This extraordinary sulphur-rich alpine lake lies at an altitude of 1923 m and is located in an area of crystalline rocks and dolostones containing gypsum and anhydrite (Losher, 1989). The lake is fed by surface water from a small drainage area (2 km²) encompassing mainly crystalline rocks, and by sublacustrine and mainly sulphate-rich springs originating from the subsurface dolostone area. From runoff data, the overall discharge of the sublacustrine springs is estimated to be of the order of a few litres per second. As a consequence, the lake is density stratified, with a surface water low in ionic strength and a saline anoxic bottom water. A chemocline is established at the interface of the two water bodies with a diverse community of bacteria, of which the phototrophic purple sulphur bacteria (Fischer *et al.*, 1996) are the most striking, because of their purple carotenoids (light-sensitive pigments; Boucherle & Züllig, 1983). These bacteria assimilate inorganic carbon at the expense of sulphide, which is subsequently oxidized to sulphur and sulphate. On the southern

shoulder of the lake basin (Fig. 1), dense areas of tall stoneworts (*Chara globularis varietas globularis*) locally accompanied by pondweeds (*Potamogeton alpinus*) occur at water depths down to 10 m.

Sediments in a short gravity core from 21 m water depth exhibit little sedimentological structure. The sediment is soft, black and fine-grained with silt, clay and biogenic detritus and intercalations of silty turbidites (Losher, 1989; Losher & Kelts, 1989). The sediments exhibit no bioturbation, and the sedimentation rate has been estimated to be 0.5 cm year⁻¹ (Birch *et al.*, 1996). Organic matter derived from the zone of primary production, especially from the zone of phototrophic bacteria, has been reported as being the most important input (Boucherle & Züllig, 1988; Losher, 1989; Birch *et al.*, 1996), and a fine lamina of red-brown flocs of sedimented phototrophic bacteria can usually be observed on the top of the core (Wagener *et al.*, 1990). The carotenoids from these phototrophic bacteria reach concentrations of up to 0.25% in the sediment (Boucherle & Züllig, 1988). The total sulphur content attains values of up to 4% (dry weight) in the upper 10 cm of the sediment (Losher & Kelts, 1989;

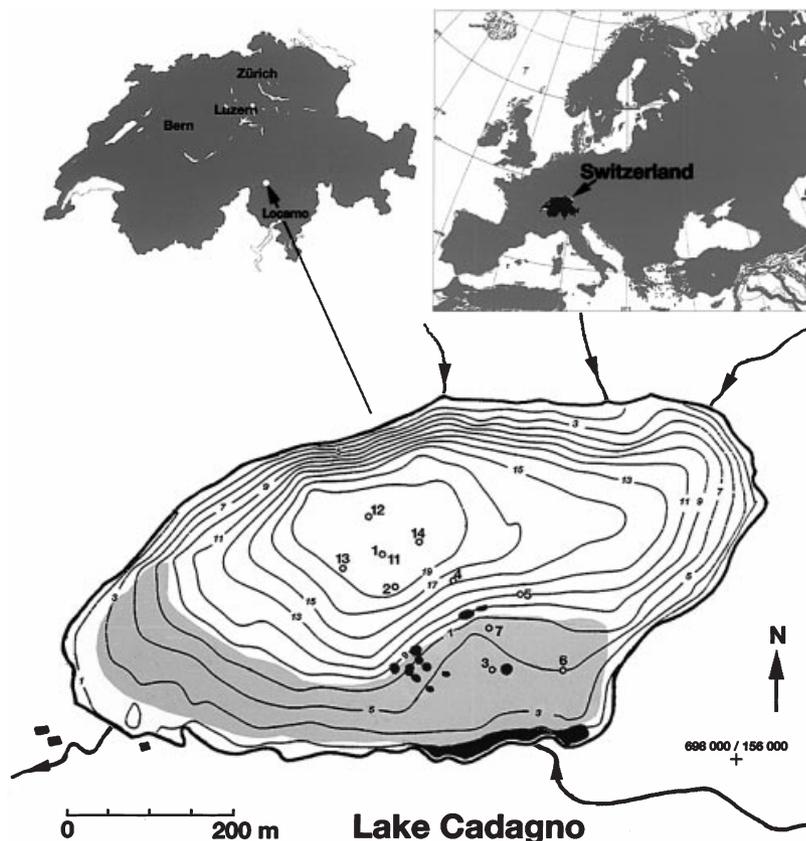


Fig. 1. Bathymetric map of Lake Cadagno (southern Switzerland 1921 m), with the positions of sampling sites for sulphur prints. Depth contours are drawn every other metre. Light grey, stoneworts; dark grey, pondweeds; black, subsurface springs.

Putschew *et al.*, 1995). Organic carbon decreases from a maximum of 17% (dry weight) at the surface to 2% at a depth of 30–40 cm, although the fraction of organic S-compounds declines less rapidly (Loshner, 1989; Putschew *et al.*, 1996). The occurrence of dissimilatory sulphate reduction by sulphate-reducing bacteria was confirmed through radiotracer ($^{35}\text{SO}_4^{2-}$) studies of the core. Average sulphate reduction rates of $35 \text{ nmol cm}^{-3} \text{ h}^{-1}$ occurred at the sediment surface and of $4.7\text{--}0.7 \text{ nmol cm}^{-3} \text{ h}^{-1}$ at 1.2–8.5 cm sediment depth. Sulphate in the sediment is completely converted to sulphide, as indicated by stable isotope analyses (Loshner, 1989).

METHODS

Sulphide has a strong tendency to form highly insoluble compounds with heavy metals. The emulsion layer of common photographic paper contains silver, which produces a brown precipitate when immersed in a sulphide solution. The reaction $2 \text{ Ag}^+ + \text{S}^{2-} \rightarrow \text{Ag}_2\text{S}$ is well known in photography ('sepia toning'; 'sulphur print'). The tone of the Ag_2S precipitate varies from light to dark brown depending on the concentration of sulphide in the solution, the temperature and the immersion time, but must also be dependent on the concentration of silver halide and the diffusive properties of the emulsion layer of the paper. Within certain limits, the tone of the Ag_2S precipitate is assumed to be proportional to the sulphide concentration in the solution and to the immersion time of the photographic paper for a particular brand of paper and a given temperature. This property can be used to estimate semi-quantitatively the concentration of dissolved sulphide.

Silver is quite selective for sulphide, as outlined by Cooper & Saltzman (1987) and references therein. Anions (Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^-), heavy metals (Ni^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+}), various organic compounds (ethanol, acetone, acetamide) and organic sulphur compounds (mercaptoethanol, dimethyl sulphide, methane thiol, carbon disulphide) do not interfere with silver nitrate-impregnated filters. Only carbonyl sulphide was found to react with silver nitrate. A humic acid suspension of 2%, which is an unrealistically high level for a lake sediment, produced some golden brown precipitate on photographic paper when immersed, probably by a chelation reaction or by transfer of electrons from the humics to the Ag^+ , similar to the reduction of Fe(III) by humic

substances (Lovley *et al.*, 1996). Amino acids with sulphhydryl (cysteine and methionine), dimethyl sulphide, sulphate, carbonate and phosphate produced no reactions on photographic papers.

Resin-coated photographic paper (Multigrade IV RC de Luxe; Ilford) was used in this study. A sulphide profile of the water in Lake Cadagno was obtained by immersing a 20-m-long and 4-cm-wide narrow strip in the water body for 30 min after sunset to avoid exposure to light. For sediments, special equipment has been designed that allows the sediment to be profiled in the daytime. A strip of photographic paper, half a metre long, is fixed cylindrically around a stainless steel tube (4 cm diameter) and inserted into an outer tube to prevent exposure to light during preparation and also in the upper few metres of the lake (Fig. 2). Immersion time in the sediment was 15 min. To obtain stable prints, the paper was treated with a fixing agent as used in



Fig. 2. Photograph of the experimental set up for obtaining sulphur prints from the sediment. (a) Stainless steel tube (4 cm diameter) with PVC foil cover; (b) outer PVC tube with lids to avoid exposure to light; (c) PVC tube for fixation process of the photographic paper. The lengths of the PVC tubes are $\approx 1 \text{ m}$.

photography (1 M sodium thiosulphate), washed with water and air dried. For the semi-quantitative evaluation of the sulphur prints, a set of calibration prints was prepared by immersing papers for various times in solutions of Na_2S and at approximately the same temperature (10°C) as in the field. The product of sulphide concentration and immersion time was found to be constant for concentrations up to 4 mM. The calibration prints served to estimate semi-quantitatively the sulphide concentration in the water and sediment visually. Aqueous solutions of Na_2S are very alkaline, and the main dissolved sulphide species is therefore HS^- (Sigg & Stumm, 1994), whereas the lake's pH lies around 7–7.5, and the dissolved species are H_2S and HS^- . However, as the diffusion coefficients for H_2S and HS^- are very similar in water (Li & Gregory, 1974; Weast, 1986) and are probably also similar in the emulsion layer of the photographic paper, the pH difference between the calibration solution of Na_2S and the lake water is considered to be unimportant, i.e. the calibration prints made by immersing photographic papers in a Na_2S solution can be compared quantitatively with sulphur prints from the sediments and water column.

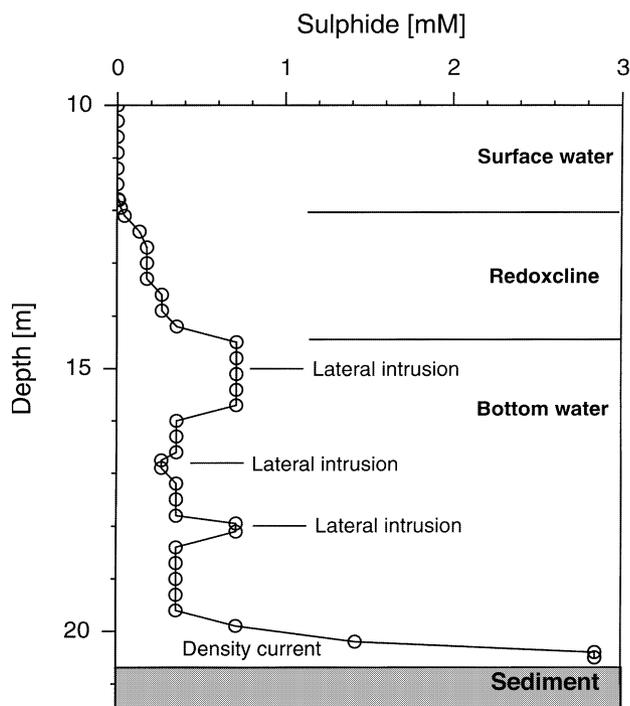


Fig. 3. Continuous depth profile of sulphide from the water column of Lake Cadagno at site 1 as estimated from sulphur prints in October 1997.

RESULTS AND DISCUSSION

The sulphide concentration in the water column near the centre of the lake, as revealed by a continuous sulphur print, shows three peaks at 15 m, 18 m and 20 m water depth (Fig. 3); the last peak on the print, with a concentration of 2.8 mM, suggests a diffusion of sulphide from the sediment into the water body (Birch *et al.*, 1996). The sulphur prints from the sediment, however, show a different picture. The overall solute sulphide

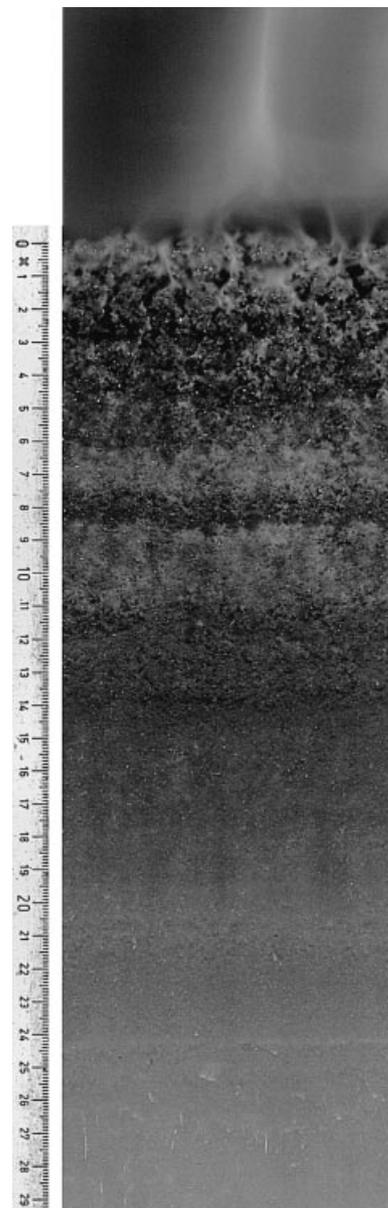


Fig. 4. Sulphur print (black-and-white copy) from the sediment of Lake Cadagno at 21 m water depth at site 12 (see Fig. 1) in October 1997, showing the different layers in the sediment.

content in the sediment at 21 m water depth has a maximum at a sediment depth of a few centimetres (Fig. 4) and decreases downwards to practically zero at a depth of 40–50 cm. The sulphide-rich zone extends over the top 15 cm. The thin layer (0.2–0.3 cm thick) on top of the sediment, which is sulphide free, apparently consists of phototrophic bacteria settled from the water column (see above and Wagener *et al.*, 1990). Below the sediment–water interface and to 6 cm sediment depth, numerous dark and irregular spots, indicating sulphide concentrations of at least 4 mM, represent accumulations of sulphate-reducing bacteria. This heterogeneity in sulphide concentration probably results from the irregular distribution of biologically available organic carbon, which is oxidized by the sulphate-reducing bacteria. The bright white spots on the print are caused by mica particles.

A remarkable phenomenon on the sulphur prints is the laminar flow of sulphide-free water

through the numerous veinlets (draining channels) in the sediment and across the sediment boundary layer into the sulphide-rich bottom water (Fig. 5A and B). This flow must have lasted throughout the whole exposure time (15 min) of the photographic paper in the sediment and can hardly have been influenced by the rapid penetration of the tube into the sediment. The driving force for such a vertical flow must be a density difference between sulphide-free porewater and sulphide-rich bottom water resulting from a salinity gradient. Such a convective upward flow must necessarily be counterbalanced by a downward flow of heavy fluid, i.e. of bottom water rich in both sulphide and sulphate, into the sediment. Upward flows of sulphide-free and probably also sulphate-free water (as all sulphate is converted to sulphide; Losher, 1989) are visible on all prints at the sediment–water interface from the bottom of the lake. This sediment therefore acts as a sulphur sink. The sediment on the slope of the

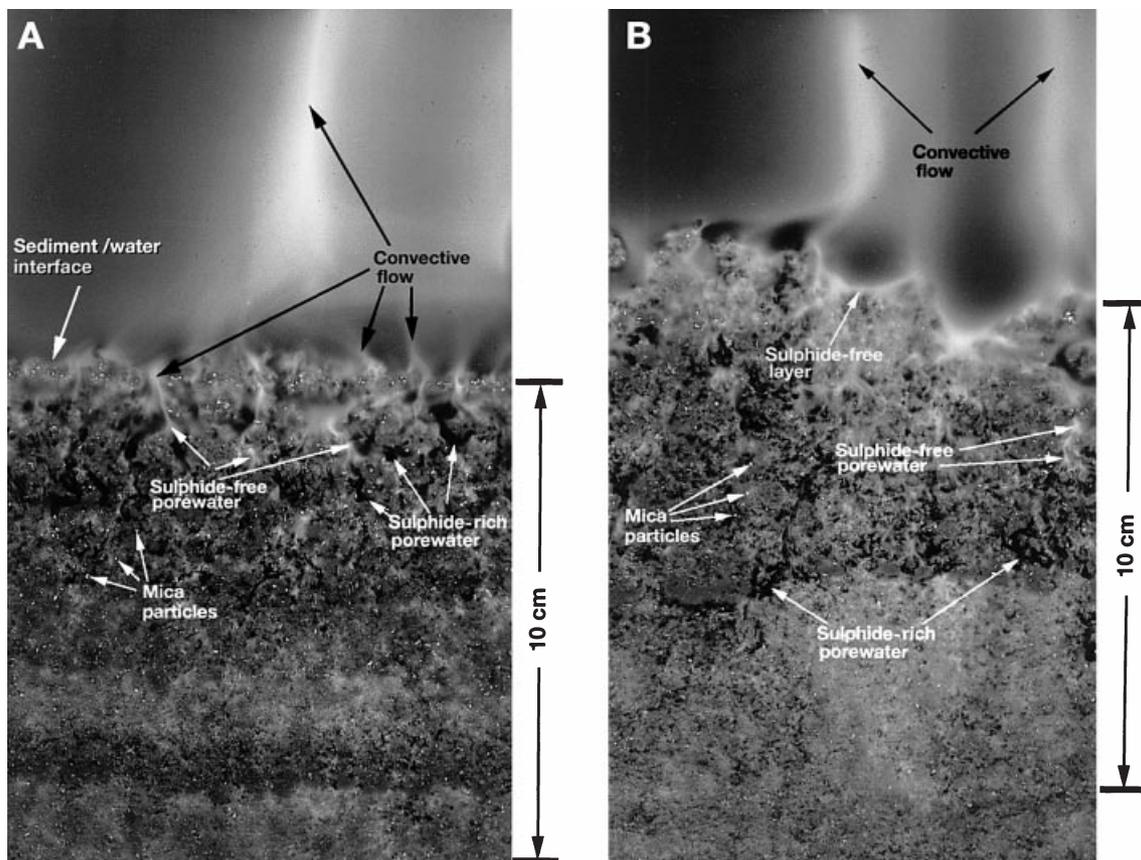


Fig. 5. Details of sulphur prints (black-and-white copy) from the sediment of Lake Cadagno at 21 m water depth at sites 12 (A) and 13 (B) in October 1997, showing pores containing both sulphide-free and sulphide-rich water and demonstrating vertical laminar convective flows of sulphide-free porewater out of the sediment. The numerous dark spots between 0 and 6 cm sediment depth are precipitates of Ag_2S formed from locally produced hydrogen sulphide by sulphate-reducing bacteria.

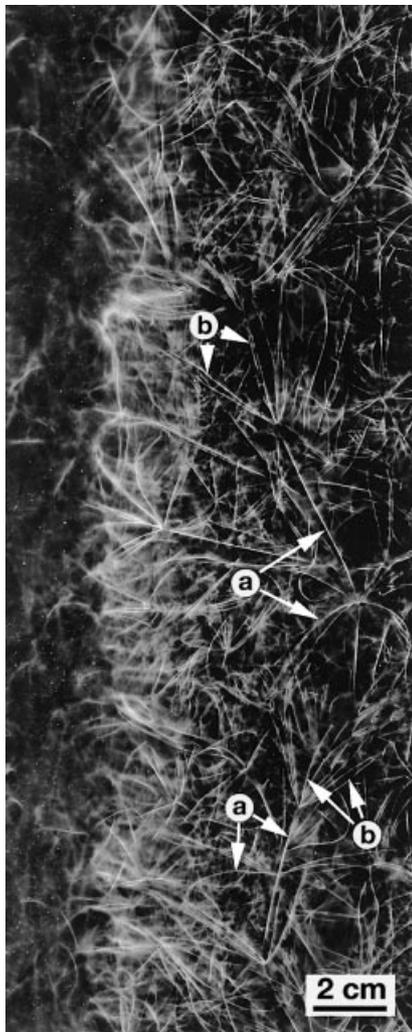


Fig. 6. Sulphur print (black-and-white copy) from the characean meadow on the southern shoulder in the shallow water of Lake Cadagno at site 6 (see Fig. 1) in October 1997. A filigrane structure is built up by (a) the main axes and (b) branches and branchlets of the green alga *Chara globularis varietas globularis*. The interstitial waters in the meadow have a sulphide concentration of more than 4 mM.

lake basin (Fig. 1, site 4) contrasts sharply with the sediment on the lake bottom. It is fine-grained without any visible lamination and homogeneous except for some sulphidic spots. The sulphide concentration here is relatively low (530 μM) and is similar to the value in the lake water at that depth. In the region of the stonewort on the lake shoulder (Fig. 1), all prints exhibit a thick interweave of stoneworts in sulphidic water with sulphide concentrations higher than 4 mM (Fig. 6). The interstitial water in these dense stands of stoneworts represents a large reservoir of highly concentrated sulphide formed by the microbial *in situ* reduction of sulphates discharged by sublacustrine springs. Microbial sulphate reduction may be stimulated by the release of organic compounds, as has been shown for marine seagrass (Isaksen & Finster, 1996). Stoneworts are reported to accumulate sulphate and produce several sulphur-bearing compounds (Ruiters *et al.*, 1994).

The distribution of sulphide in the lake water and in the sediments and the convective flows across the sediment–water interface suggest a sulphide circulation in Lake Cadagno (Fig. 7), which is dominated by sulphide-rich density currents (Fig. 3). The current system is initiated by the input of spring water rich in sulphate into the lake (Fig. 1); sulphide and sulphate are transported from the stoneworts area by density flows to the basin floor and by horizontal intrusions into the bottom water, as indicated by the sulphide profile in the water column (Fig. 3). In the redoxcline, the sulphide is oxidized to sulphate by the population of phototrophic bacteria, which diffuses into the surface water and finally leaves the lake at the outlet. At the bottom, sulphide and sulphate are transported convectively into the sediment, where the sulphate is reduced to sulphide, which is completely precip-

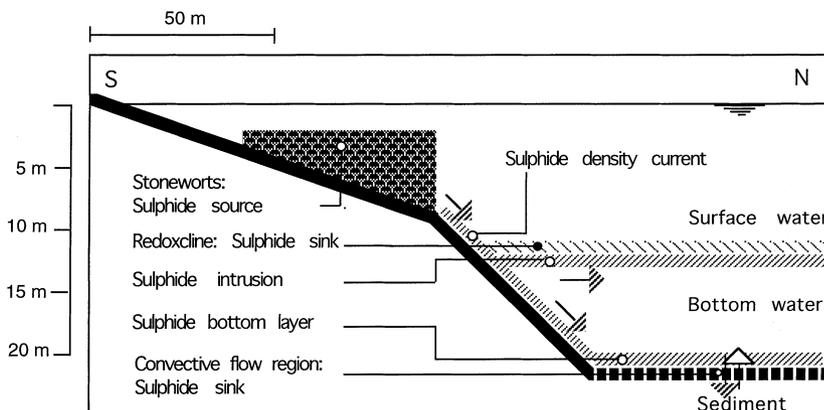


Fig. 7. Model of sulphide circulation in Lake Cadagno. Upward-pointing arrow in the bottom sediment, convective flow of sulphide-free (and probably sulphate-free) water; downward-pointing arrow in the bottom sediment, flow of sulphide-rich water across the sediment–water interface.

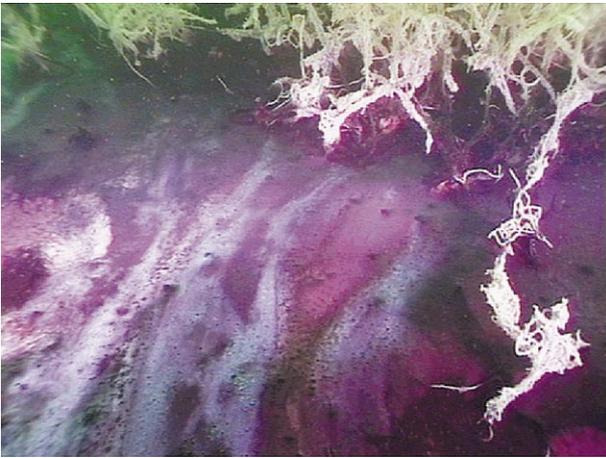


Fig. 8. View of stonewort meadow in Lake Cadagno at 8 m water depth (September 1997). Saline water is flowing on the bottom downslope towards the observer. Phototrophic bacteria, feeding on sulphide, form purple mats in the foreground. The white areas are sulphur formed from sulphide having reacted with oxygen produced by the plants. An area of approximately 1 m × 0.5 m is shown.

itated in the uppermost 50 cm as either FeS or FeS₂ (Losher, 1989; Birch *et al.*, 1996), or is incorporated into organosulphur compounds (Putschew *et al.*, 1996; Fritz & Bachofen, 1998). Such a sulphide circulation model for Lake Cadagno (Fig. 7) is substantiated by subaquatic photographs taken by divers, which show small density currents originating in the stonewort fields and flowing down in small channels towards the basin floor (Fig. 8). The model explains the strong sulphur accumulation of up to 4% in the anoxic sediments of Lake Cadagno (Losher & Kelts, 1989), similar to accumulations in marine deposits, although the levels of sulphate in the water column in the lake are much lower than in their marine counterparts (Berner, 1982).

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