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Sulfate-reduction process in sediments of Lake Kinneret, Israel

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Abstract

Monomictic Lake Kinneret is stratified during summer and autumn, resulting in a hypolimnion rich in H_2S (3-7 mg l^{-1}). In winter and spring every year a bloom of dinoflagallate *Peridinium gatunense* produces an average biomass of 150000 ton wet weight. Part of this biomass sinks to the hypolimnion and sediments where it is decomposed and mineralized, with some of the mineralization due to the activity of sulfate-reducing bacteria (SRB). The sulfate-reduction potential of the upper sediment layer at the deepest part of the lake (42 m) was measured. The activity of the enzyme arylsulfatase was also monitored. Rates of sulfate-reduction ranged from a minimum of 12 nmoles SO_4^{2-} reduced cm^{-3} day^{-1} in December before lake overturn to a maximum of 1673 nmoles SO_4^{2-} reduced cm^{-3} day^{-1} in July during stratification. These rates are considerably higher than those recorded from other freshwater lakes in the world and are probably limited more by the availability of organic matter than by sulfate concentrations.

Introduction

The sulfate reducing bacteria are strict anaerobes and derive oxygen from sulfate for the oxidation of either organic matter or hydrogen. Sulphate reduction is one of the most important processes in the anaerobic decomposition of organic matter (Jorgensen, 1977, 1978; Smith & Klug, 1981a; Skyring, 1987; Capone & Kiene, 1988). The sulfate reducing bacteria play a key role in the mineralization processes in marine sediments. Significant sulfate-reduction rates have also been reported for fresh water sediments, despite low sulfate concentrations in the pore water (Smith & Klug, 1981b; King & Klug, 1982; Ingvorsen *et al.*, 1981; Hordijk *et al.*, 1985; Capone & Kiene, 1988; Landers & Mitchell, 1988; Dunnette 1989). This finding suggests that sulfate reducing bacteria in freshwater have acquired high affinity sulfate uptake systems to cope with the low sulfate concentrations (Smith & Klug, 1981a; Ingvorsen & Jorgensen, 1984).

One of the factors controlling the rate of sulfate-reduction is the availability of organic substrates, resulting from decomposing material in the water. Westrich & Berner (1984) found that sulfate-reduction was linearly related to the amount of planktonic carbon. Other factors such as SO_4^{2-} availability, favourable redox potential, temperature and pH all create a suitable biotope for sulfate reducing bacteria (Westrich & Berner, 1984, 1988; Canfield, 1989).

In this study sulfate-reduction rates in the upper sediments of Lake Kinneret are presented.

Site description

Lake Kinneret is a freshwater, warm monomictic lake located in the northern part of the Afro-Syrian Rift Valley. The annual bloom of the dinoflagellate *Peridinium gatunense* (Pyrrophyta) dominates phytoplankton biomass between February and the end of May. Total *Peridinium* biomass in the lake reaches 150000 ton wet weight a year. The lake is thermally stratified from May–December developing an anoxic hypolimnion rich in H_2S (3–7 mg l^{-1}). Mixing occurs between December–January resulting in a homogenous, oxygenated water column. Epilimnion temperatures range between 15 and 26 °C during mixing and stratification, respectively. The *in situ* temperature of the hypolimnion does not vary during the whole year and is approximately 15 °C–16 °C.

Experimental details

Sampling

Four sediment cores were taken at Station A (the central station in the lake) at maximum depth (42 m) with a Tessenow gravity sampler (Tessenow *et al.*, 1977). Cores were transferred to the laboratory within 30 minutes and processed for sulfate-reduction rates, pore water sulfate concentrations, pH and pH_2S. One core was left at *in situ* temperatures overnight and assayed for arylsulfatase activity as described below.

Sulfate reduction

Sulfate reduction was assayed by the method of Jorgensen (1978). The upper water layer was removed from the core and the sediment subcored with a 50 ml hypodermic syringe. Holes were drilled laterally (diameter 0.1 cm) in the subcore and 50 µl (~5 µCi) of diluted (1:10) carrier free $Na_2^{35}SO_4$ (Amersham, specific activity 64 mCi $mmol^{-1}$) injected directly into the sediment at 0.3 cm intervals to 2.4 cm depth. The subcores were incubated anaerobically under an atmosphere of N_2 at the *in situ* sediment temperature. After 1 hour the subcores were sliced, put into flasks and the sulfide was fixed by the addition of 5 ml of 5% zinc acetate. The flasks were connected to a closed apparatus and flushed with N_2. Acid volatile sulfide (FeS + free H_2S) was separated from the sediment by the additions of 20 ml of deoxygenated 6N HCl. The H_2S regenerated was collected in two traps containing 3–5 ml of 5% zinc acetate. After 20 minutes of flushing, 15 ml of scintillation liquid (Insta-gel II Packard) were added to each vial and radioactivity counted in a liquid scintillation counter (Kontron). Distilled water (25 ml) was added to the remaining sediment slurry and 1 ml supernatant of each sample was counted for the remaining $^{35}SO_4^{2-}$. Controls of sediment treated with formaldehyde or autoclaved gave little or no sulfate-reduction activity.

Sulfate in pore water

Pore water for sulfate analyses of the respective slices was extracted into a test tube containing 0.2 g of zinc acetate and left overnight at 4 °C. The water was filtered through GF/C filters to remove precipitates of zinc and sulfate was determined turbidometrically according to Standard Methods (APHA, 1985).

pH, pH_2S

These were measured in the sediment cores with Ingold mini electrodes inserted into the sediment core.

Arylsulfatase activity

Arylsulfatase activity was assayed by measuring the hydrolysis of p-nitrophenyl sulfate (PNPS) using the methodology described by Tabatabai & Bremner (1970) and King & Klug (1980).

Results

Sulfate and H_2S in the hypolimnion

There are strong seasonal variations in sulfate and sulfide concentrations in the hypolimnion of Lake Kinneret. Levels of sulfate range from 0.5 mM during the mixing period (February) dropping to 0.2 mM at stratification in the lake (December). This decrease in sulfate concentration corresponds stoichiometrically to the increase in sulfide concentration (from 0 to 0.28 mM) during the same period, suggesting that sulfate-reduction in the hypolimnion is occurring.

Sulfate, H_2S and pH in the sediments

The distribution of SO_4^{2-} in the profoundal sediments at Station A (42 m) ranged between 430 μM in the first 0.3 cm layer (February) to 50 μM at 2.1 cm depth (April) (Fig. 1). In December 1987 and March 1989 no SO_4^{2-} was detected deeper than 1.5 cm (data not shown). During July, SO_4^{2-} concentrations were 250–280 μM throughout the 2.4 cm depth. Sulfate concentrations were higher during the mixing period in the overlying water and in the first few millimetres of the sediment ($\sim$500 μM).

H_2S

No H_2S was observed during the mixing period (February and April) in the overlying water, but concentrations increased gradually during the stratified period. The concentrations of free H_2S in the pore water varied seasonally (Fig. 2). In winter (February) there was almost no H_2S in the upper sediments, whereas in spring and summer

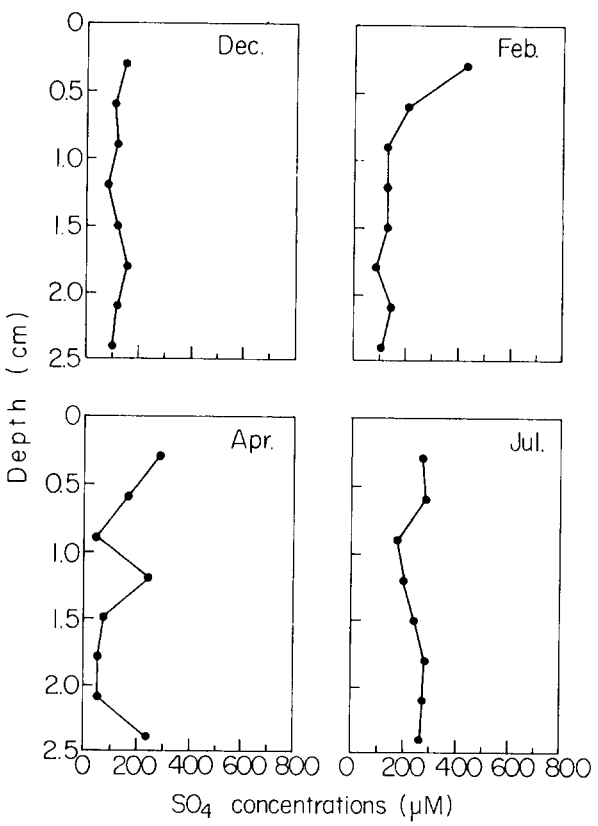

Fig. 1. Sulphate concentrations in Lake Kinneret sediments (μM).

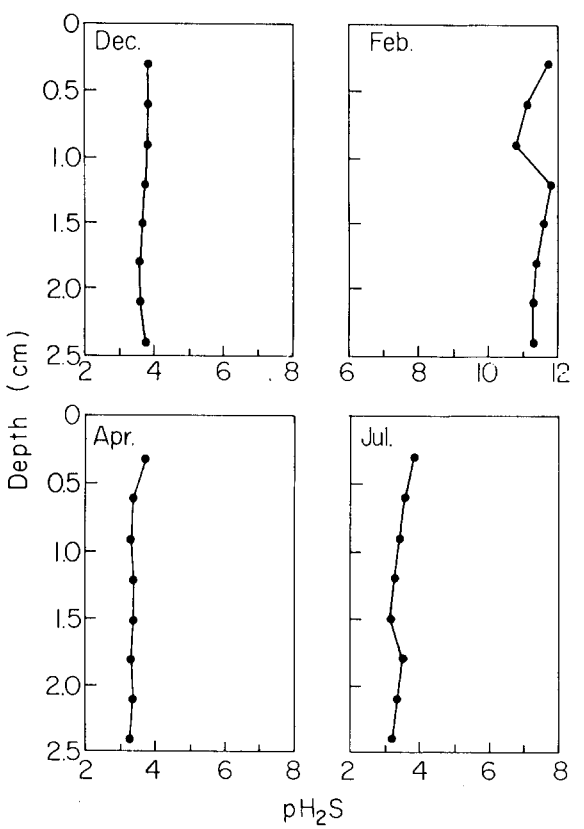

Fig. 2. pH_2S values in Lake Kinneret sediments.

concentrations of H_2S increased to 400 μM and 700 μM in April and July, respectively. In December, before overturn, the H_2S values in the sediment ranged between 100–200 μM (Fig. 2).

pH

pH decreased with depth and ranged between 7.45 (February) at the depth of 0.3 cm to 7.05 at 2.4 cm depth during the stratified period (July and December). There was no seasonal variation in the annual sediment pH values.

Sulfate reduction rates

The rate of sulfate-reduction varied seasonally (Fig. 3). In December, before overturn, sulfate-reduction rates were low with a minimum of 12 nmol SO_4^{2-} reduced cm^{-3} day^{-1} at the depth of 2.4 cm. In February, when mixing occurs and oxygen may diffuse into the upper layers of the sediment higher sulfate-reduction rates were seen at 2.4 cm depth, reaching rates of 366 nmol SO_4^{2-} reduced cm^{-3} day^{-1}. During the summer (July) the rates increased further, reaching a maximum of 1673 nmoles SO_4^{2-} reduced cm^{-3} day^{-1} in the upper few millimetres with another peak of sulfate-reduction, (800 nmoles SO_4^{2-} reduced cm^{-3} day^{-1}) at 2 cm depth.

Arylsulfatase activity

The activity of arylsulfatase varied with both depth and season (Fig. 4). Maximum activity was detected in July at 0.6 cm depth (670 nmol g^{-1} (w.w.) h^{-1}) at 2.4 cm depth. The lower arylsulfatase activity in the surface sediment in February

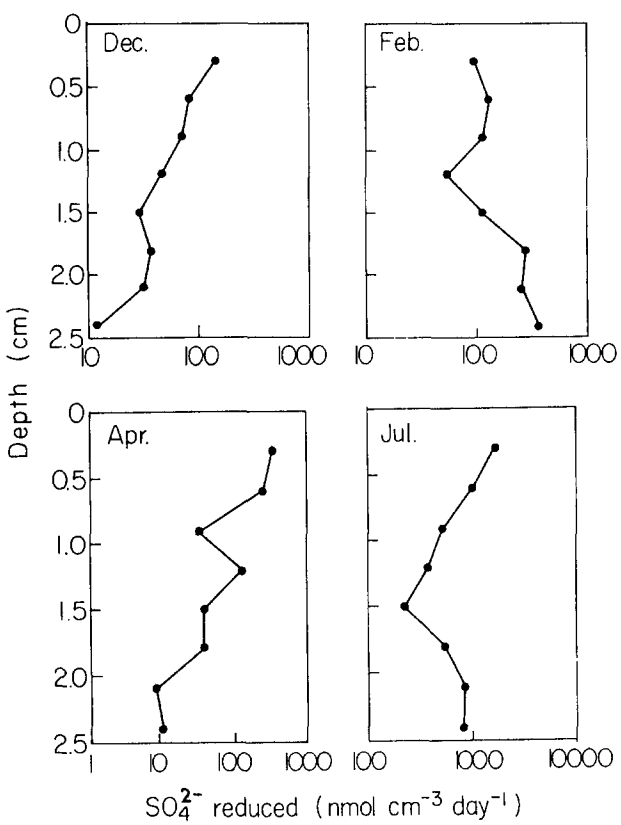

Fig. 3. Sulfate reduction potential in Lake Kinneret sediments (nmol cm^{-3} day^{-1}).

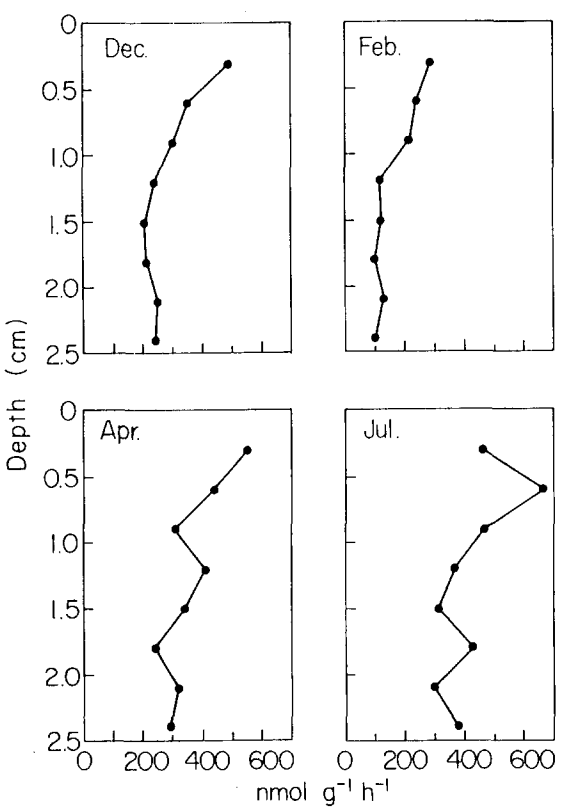

Fig. 4. Arylsulfatase activity in Lake Kinneret sediments (PNP nmol g^{-1} h^{-1}).

may be correlated to the relatively higher SO_4^{2-} (434 μM at 0.3 cm) and low H_2S concentrations available which would inhibit the microbial production of sulfates (Jarvis & Lang, 1987). High arylsulfatase activity was found during the stratified period because of low SO_4^{2-} concentrations in December and the high availability of organosulfate-ester substrates in July probably resulting from the decay of the *Peridinium* bloom.

Discussion

At Station A, the deepest (42 m) station in the lake, anaerobic conditions prevail during nine months of the year, with increasing H_2S and decreasing SO_4^{2-} concentrations in the hypolimnion during the stratified periods (Serruya, 1978). Both the high level of H_2S produced in the hypolimnion and the black sediments suggests that sulfate-reduction in Lake Kinneret is ecologically important. The highest SO_4^{2-} concentrations in the upper sediment layer were observed during the mixing period (Fig. 1) caused by turbulence, the diffusion of oxygen into the first few millimetres and bioturbation of the surface by the transitory dwellers, e.g. *Leydigia* sp. (Cladocera) some copepods and chironomids, which appear during oxygenated conditions (Serruya, 1978). It seems that in the upper sediments (2.5 cm), SO_4^{2-} concentrations were not the limiting factor for sulfate-reduction during most of the year (except December – before overturn). The sulfate reducing bacteria in freshwater sediments have acquired high affinity (low K_m) uptake system for sulfate in order to cope with low SO_4^{2-} levels and sulfate-reduction was independent of the sulfate concentrations down to 0.1 mM SO_4^{2-} (Smith & Klug, 1981a; Ingvorsen & Jorgensen, 1984; Ingvorsen *et al.*, 1981; Capone & Kiene, 1988).

The sulfate-reduction rates in Lake Kinneret varied seasonally but were not correlated to the *in situ* temperature of the hypolimnion and sediments (which do not change during the year) in contrast to other sites (Ingvorsen *et al.*, 1981; Westerman & Ahring, 1987; Westrich & Berner, 1988; King, 1988).

One of the factors affecting sulfate-reduction is the availability of organic matter which would serve as potential electron donors to the sulfate-reducers (Skyring, 1987; Westrich & Berner, 1984). Primary production in Lake Kinneret during the mixing period is high (2000 mg C m^{-2}) with a biomass of ~ 150 g m^{-2} consisting mainly of the dinoflagettate *Peridinium gatunense* (Berman & Pollingher, 1974), but during some years (e.g. 1988 and to some extent 1989) a bloom of *Melosira* sp. (diatom) appeared (27 g m^{-2}). At the beginning of the summer, degradation and decomposition of phytoplankton occurs and fresh detritus is continually supplied to the hypolimnion and sediments. The depth of Lake Kinneret hypolimnion at Station A is 20 to 42 m. Usually when depth increases, more sedimenting organic material will be degraded in the water column and less primary production will reach the bottom (Capone & Kiene, 1988). The relative fraction of organic matter reaching the sediments would be dependent on the shapes of the isotherms and the time of the algal bloom. An early bloom of *Peridinium* and a long mixing period would increase the amount of organic matter reaching the sediments (Serruya *et al.*, 1974). Recent studies using sediment traps at 26 m showed greater number of *Peridinium* cells and theca, which are rich in carbon-compounds and fatty materials and are available for fermenters and sulfate reducers. The most prominent effect was seen with *Melosira* (high cell density and high sinking rate), which reached the sediment surface quickly during 1988.

The availability of organic matter resulted in high microbial metabolism, depletion of oxygen, development of negative redox potential and a reducing environment in the sediment (Serruya *et al.*, 1974; Staudinger, 1989). These interrelated factors may explain the high sulfate-reduction rates which occurred in July (1673 nmol SO_4^{2-} reduced cm^{-3} day^{-1}). The primary mechanisms triggering the event was the availability of fresh organic material and concentrations of SO_4^{2-}. The same phenomena were reported for Big Soda Lake, Nevada (Smith & Oremland, 1987) and a salt marsh in South Carolina (King, 1988). In other lakes (e.g. Lake Vechten, the Netherlands)

the sulfate reducing activities were correlated with seasonal fluctuations of sulfate with a peak during the winter (Hordijk *et al.*, 1985). The lowest sulfate-reduction rates were observed in December as a result of low organic load (small algae-chlorophyta in the epilimnion) and low sulfate which might be the limiting factor in the sulfate-reduction process. During winter and mixing period (February, Fig. 3) sulfate-reduction rates were low, limited by the supply of organic matter. In April–May the thermocline develops and H_2S production begins. The coexistence of H_2S and O_2 enables the development of *Beggiatoa* mats supplying the sediments with another source of organic matter.

An additional possibility for partly supplying the sulfate demands of sulfate reducing bacteria might be the activity of arylsulfatases that occur in Lake Kinneret sediments (Fig. 4). Since sulfate esters might appear in significant quantities in freshwater sediments the enzyme provides a mechanism for the maintenance of sulfate-reducing bacteria when inputs of sulfate are low (Cooper, 1972; King & Klug, 1980; Landers & Mitchell, 1988; Jarvis & Lang, 1987).

We did not check sulfate-reduction potential in the hypolimnion of Lake Kinneret, but in the long stratification period no oxygen and in some years no nitrate enables sulfate-reduction to occur. The good stoichiometric correlation between the decrease in sulfate and increase in sulfide in the hypolimnion implied that sulfide concentration is a good estimator of the reduction process in hypolimnion. The hypolimnion of Lake Kinneret is not sulfate-limited so sulfate-reduction would probably be limited by the availability of organic matter (Serruya, 1980). As reported by others, 50% or more of the primary productivity may be decomposed in the anoxic water column of the hypolimnion (Smith & Oremland, 1987; Canfield, 1989).

Our sulfate-reduction rates were based on the acid distillation technique which might underestimate sulfate-reduction rates because of the incomplete recovery of all the reduced sulfur compounds. Nevertheless, Lake Kinneret sulfate-reduction rates are higher than those reported for other lakes (King & Klug, 1982) and close to the rates found for Lake Mendota and for coastal surface sediment (Ingvorsen *et al.*, 1981; Jorgensen, 1977).

The high rates may be partly explained by the geological history of Lake Kinneret. Saline water aquifers underlie the Kinneret Basin from which the water penetrate to the lake as mineral springs and by the constant flux of saline water entering the Kinneret through the lake bottom (Mazor, 1978; Stiller, 1974).

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