

## Microbially — related redox changes in a subtropical lake

### 1. *In situ* monitoring of the annual redox cycle

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**Abstract.** Using a recently developed *in situ* multiprobe the redox development in the water column of warm-monomictic Lake Kinneret was investigated during three annual cycles. During the time when sulfide release into the meta- and hypolimnion is initiated, our measurements show a linear relationship, close to the thermodynamic function, between the platinum electrode potential and the amount of sulfide produced by the sulfate reducing bacteria. A change of this relationship during summer stratification coincides with the bloom of the phototrophic sulfur bacterium *Chlorobium phaeobacteroides*.

## Introduction

Since the early applications of redox measurements in natural environments (Gillespie 1920), there has been a persistent controversy concerning the usefulness of redox data measured in natural waters. The deviation of aquatic systems from thermodynamic equilibria, the unspecific performance of commonly used platinum — or gold redox sensors, and the wide variability of redox measurements within a single redox system are major arguments against the employment of redox as a characteristic hydrochemical parameter (Stumm 1966, 1978, 1984; Whitfield 1974; Baas-Becking et al. 1960).

As such, redox sensors are commonly used operationally, e.g. to delimit the redoxcline in stratified lakes (e.g. Sorokin 1970; Serruya 1972) or to follow the transition from aerobiosis to anaerobiosis in bioreactors (Kjaergaard 1970; Wimpenny & Necklen 1971; Jakob 1974; Wimpenny 1984). In some sulfide enriched systems, however, quantitative dependencies of the measured potentials to the amount of sulfide present were reported in interstitial waters of sediments (Berner 1963; Whitfield 1969) or in

mineral springs (Boulegue & Michard 1979). These findings suggest that in the case of the  $\text{H}_2\text{O}$ - $\text{H}_2\text{S}$  system redox measurements can be a useful tool to describe redox dynamics.

One intention of the present study was to describe the evolution of the  $\text{H}_2\text{O}$ - $\text{H}_2\text{S}$  system in the meta- and hypolimnion of Lake Kinneret by means of redox measurements and to evaluate the extent to which measured redox values can be related to prevailing hydrochemical conditions. This venture was stimulated by a recently developed multi-probe for *in situ* determination of  $p_e$  (see below), pH, and  $p\text{H}_2\text{S}$  values that can be operated in the presence of sulfide, irrespective of the prevailing temperature and hydrostatic pressure (Eckert et al. 1990a).

Furthermore, we wished to investigate to what extent the measured redox values are influenced by microbiological processes of sulfate reduction and phototrophic sulfide oxidation.

### The $p_e$ redox concept

When measuring redox values, the redox concept, upon which the interpretation of the data is based, should be defined. In the classical thermodynamic way (e.g. Sillen 1967; Stumm & Morgan 1981), a redox system is described in terms of the redox potential (Eh) or the redox intensity ( $p\varepsilon$ ) with:

$$Eh = Eh^0 + \frac{2.3 \cdot R \cdot T}{n \cdot F} \log \frac{a_{\text{ox}}}{a_{\text{red}}}, \quad (1)$$

and:

$$p\varepsilon = \frac{F}{2.3 \cdot R \cdot T} Eh = p\varepsilon^0 + \frac{1}{n} \log \frac{a_{\text{ox}}}{a_{\text{red}}}, \quad (2)$$

where  $R$  = gas constant,  $T$  = temperature [°K],  $F$  = Faraday constant,  $n$  = number of electrons transferred,  $a_{\text{red,ox}}$  = activities of reactants,  $p\varepsilon^0 = 1/n \log K$  with  $K$  = equilibrium constant of redox reaction,  $Eh^0 = G^0/nF$ , with  $G^0$  = standard Gibbs free energy of reaction.

Because Eh and  $p\varepsilon$  are defined for equilibrium conditions and natural systems deviate from thermodynamic equilibrium measured redox data should be interpreted following an operationally defined redox concept (Whitfield 1969, 1972; Frevert 1979, 1984; Hostettler 1984). Here we follow the sensor specific  $p_e$ -redox concept as introduced by Galster

(1975) and operationally defined by Frevert (1979, 1984) as:

$$pe \equiv \log \left( \sum_i \{e^-\}_i \right)_{\text{platinum}} \quad (3)$$

where  $e_i$  is the electroactive component  $i$  in the test solution. According to this concept an equilibrium exists between the platinum sensor and the investigated aquatic system leading to an electrode reading representative for the sum of all electron exchange reactions. It is the intention of this concept to access mixed potential readings from aquatic systems as obtained with a platinum sensor that is calibrated against a suitable reference electrode by looking at the electron exchange kinetics at the sensor surface without implying equilibrium conditions within the respective test solution. Two conditions are necessary to apply this concept:

1.  $pe$  and  $pH$  data have to be measured precisely and *in situ*
2. all electroactive processes that generate the measured electrode potential must be identified including the prevailing microbial processes.

## Materials and methods

### *Study area*

Lake Kinneret ( $12 \times 22$  km,  $168$  km<sup>2</sup>) is a warm monomictic lake  $209$  m below mean sea level in the northern part of the Afro-Syrian rift valley at  $32^\circ\text{N}$  latitude (Serruya 1978). Maximum and average depths are  $42$  m and  $24$  m, respectively. The water quality of Lake Kinneret is influenced by the carbonate- and nitrate-rich Jordan waters and numerous saline upwellings along the western shore (Serruya 1978). A prominent biological event during the annual lake cycle is the spring bloom of the dinoflagellate *Peridinium gatunense* (Berman & Pollinger 1974). In summer, when hydrogen sulfide reaches the photic zone, a metalimnetic bloom of the brown phototrophic sulfur bacterium *Chlorobium phaeobacteroides* develops lasting from July until September (Eckert et al. 1990b).

### *In situ measurements*

The custom made multi-probe used with this study for the *in situ* measurement of  $pe$ ,  $pH$  and  $pH_2S$  values has been introduced by Eckert et

al. (1990a). The main advantage of this probe is that the liquid-junction-type reference cell typically used as the reference electrode for the pH and pe working electrodes has been replaced by a sodium glass electrode. This strategy guarantees highly reproducible readings, provided that the sodium ion activity is constant in the water column, as found in Lake Kinneret ( $[Na^+] \approx 120 \text{ mg/l}$  (Serruya 1978)). The built-in  $pH_2S$  cell consists of a glass/ $Ag_2S$  electrode combination (Ingold) developed by Frevert & Galster (1978). A five channel amplifier (impedance  $10^{13} \Omega$ ), is fitted into the stainless steel housing of the probe to insure maximum signal stability.

Weekly measurements of pe, pH,  $pH_2S$ , dissolved oxygen (DO) and temperature were taken from March 1986 until January 1989 in the water column at 1 m intervals (at 10 cm intervals in steep gradients) at station A, the central, maximum depth station (Fig. 1) used for lake monitoring during the past 24 years. Due to the central location of this station daily changes in the stratification pattern that might be caused by internal seiches are minor (Serruya 1978). Electrode outputs (pe, pH,  $pH_2S$ ) were read on an on-board mV meter (WTW). DO and temperature were measured using a DO-T sensor (Orbisphere Laboratories, Switzerland) attached to the probes' housing.

The pH and pe sensors were calibrated in pH-adjusted (7.00 and 5.00) lake water saturated with chinhydrone ( $pe_{20^\circ C, pH 7.00} = 5.09$ ,  $pe_{20^\circ C, pH 5.00} = 7.09$ ). The  $pH_2S$  electrode was calibrated using the silver iodine method (Peiffer & Frevert 1987). DO concentrations and hydrogen sulfide activities were measured beginning July 1986.

In order to obtain a comparison of pe values measured under variable pH conditions all pe data from oxic waters were standardized to pH 7.00 using the relationship:

$$pe_7 = pH - 7.00 + pe \quad (4)$$

as derived from the standard-hydrogen-electrode (Frevert 1979). The empirical function:

$$pe_7 = pe + 0.59 - 300 \cdot e^{-0.89 \cdot pH} \quad (5)$$

developed by Eckert (1993) was applied for sulfide rich Kinneret water.

Total sulfide concentrations  $[S(-II)]$  were calculated for dilute Kinneret water and  $pH \leq 9.0$  from the measured  $pH_2S$ , temperature and pH values using the relationship:

$$[S(-II)] = 10^{-pH_2S} \cdot \frac{1 + 10^{-pK_1}}{10^{-pH}} \quad (6)$$

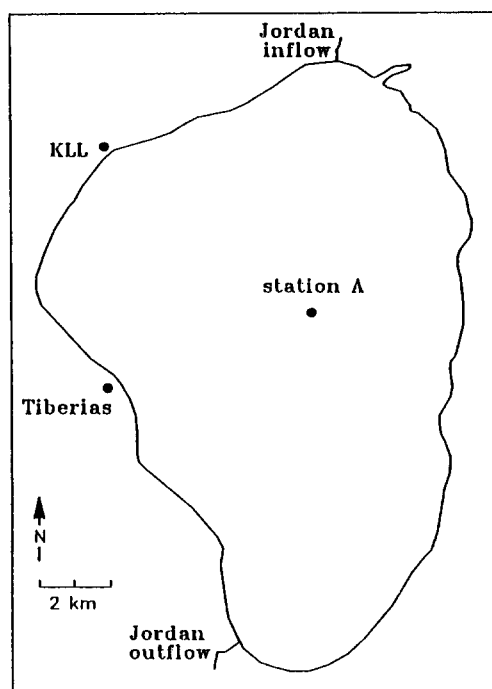


Fig. 1. Schematic diagram of Lake Kinneret showing sampling site.

where the  $pK_1$  (first protolysis constant of the  $H_2S-HS^- - S^{2-}$  system) =  $3.122 + 1132/T$ , temperature in degrees K (Broderius & Smith 1977).

## Results and discussion

During the three annual lake cycles  $pe_7$  values ranged between 10 and  $-2.5$  in the oxic and anoxic zone, respectively (Fig. 2). The three years showed similar vertical distributions during summer months (J, A, S, O) and during the overturn (December), while anaerobic conditions developed in the hypolimnion at different times in each year (the beginning of April in 1986, the end of May in 1987, and in the middle of May in 1988).

Our results suggest a division of the redox cycle into four stages generally coincident with the typical stages of mixis in a monomictic lake (mixis, stratification, amixis, destratification).

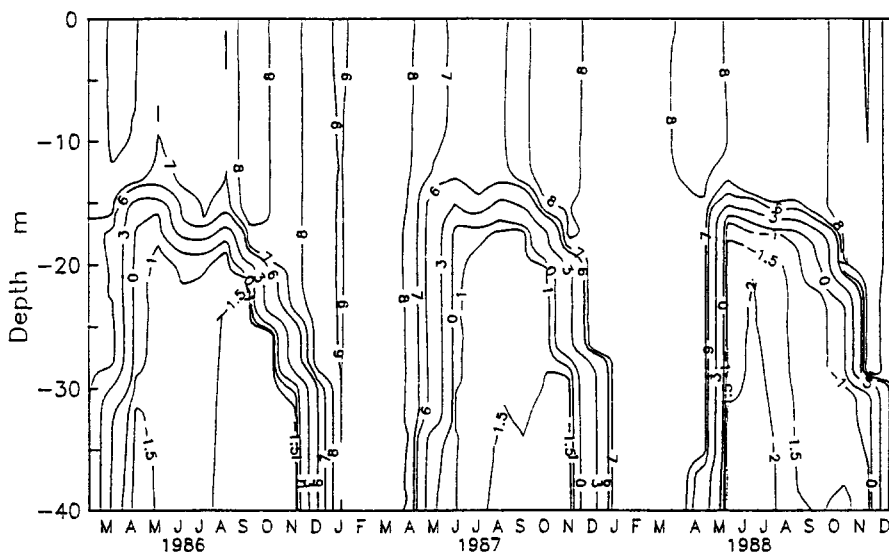


Fig. 2. Isopleth diagram showing  $pe_7$  as a function of depth for the years 1986–1988.

### Mixis

Complete mixing of the water column lasted generally from early January until March or April (Fig. 3). Although we have shown profiles from a single date in January, 1987, the linearity of the vertical profiles in Fig. 3 with  $T = 15.7^\circ\text{C}$ ,  $\text{DO} = 8$  ppm and  $\text{pH} 8.0$  is characteristic for the period of mixis and the values correspond to those expected for a carbonate-buffered freshwater system in equilibrium with the atmosphere. The redox values are positive throughout the water column ( $pe_7 = 8.9$ ).

### Stratification

The warming of the surface waters in spring initiated differentiation of the water column into the epi-, meta- and hypolimnion as characterized by a profile sequence in May and June, 1987 (Fig. 4). The prolonged temperature gradient from 0 ( $25^\circ\text{C}$ ) to 34 m ( $15^\circ\text{C}$ ) in Fig. 4a does not allow yet for a clear location of the metalimnion. This profile was taken during a bloom of *Peridinium* as indicated by the elevated oxygen (15 mg/l) and pH (9.5) levels near the surface. While the first 4 m are oversaturated with oxygen (170% at 1 m, 105% at 4 m), on-going respiration diminishes the oxygen content in water layers that are excluded from atmospheric gas exchange. The result is a gradual vertical decline in  $\text{O}_2$  and pH value, both

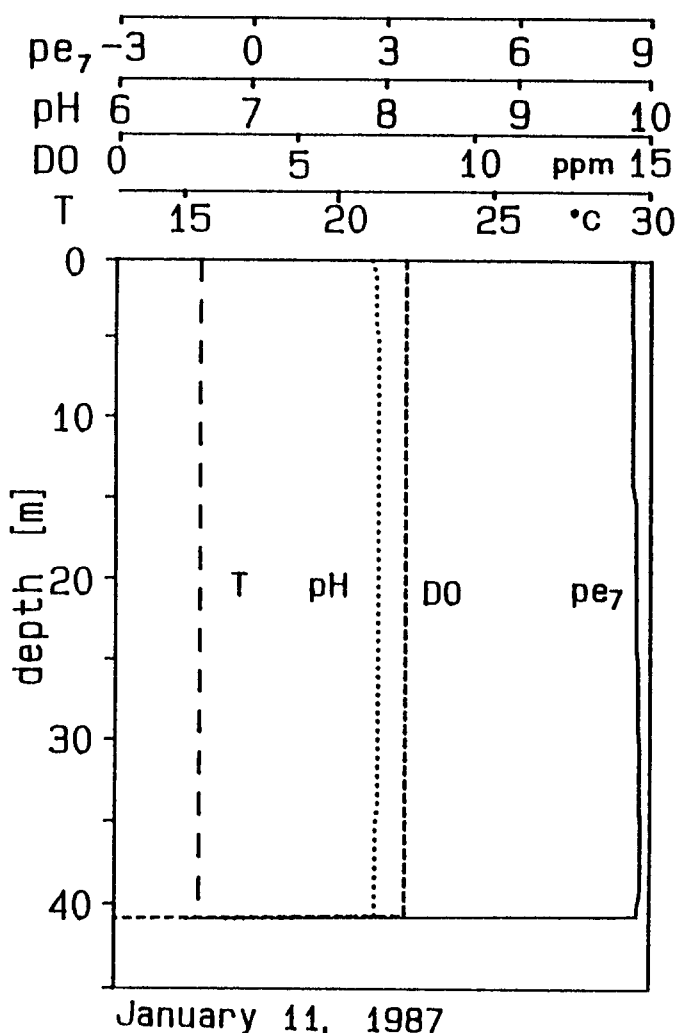


Fig. 3. Representative profile of  $pe_7$ , pH, DO and temperature during mixis. Data shown are from 11 Jan 1987.

of which follow the temperature profile from 5 m downward. From 34 m temperature becomes constant (15 °C) while  $O_2$  drops suddenly from 4 to  $\leq 1$  mg/l, and pH drops by 0.2 units.  $pe_7$  was relatively constant throughout the water column during this early phase of stratification.

As stratification proceeds, T, DO and pH profiles showed a more pronounced metalimnion (Fig. 4b). Concurrent with the depleting  $O_2$  at 34 m a sharp redoxcline coupled with increased  $pS_{tot}$  resulted as aerobic respiration was replaced by anaerobic respiration. In the upper hypo-

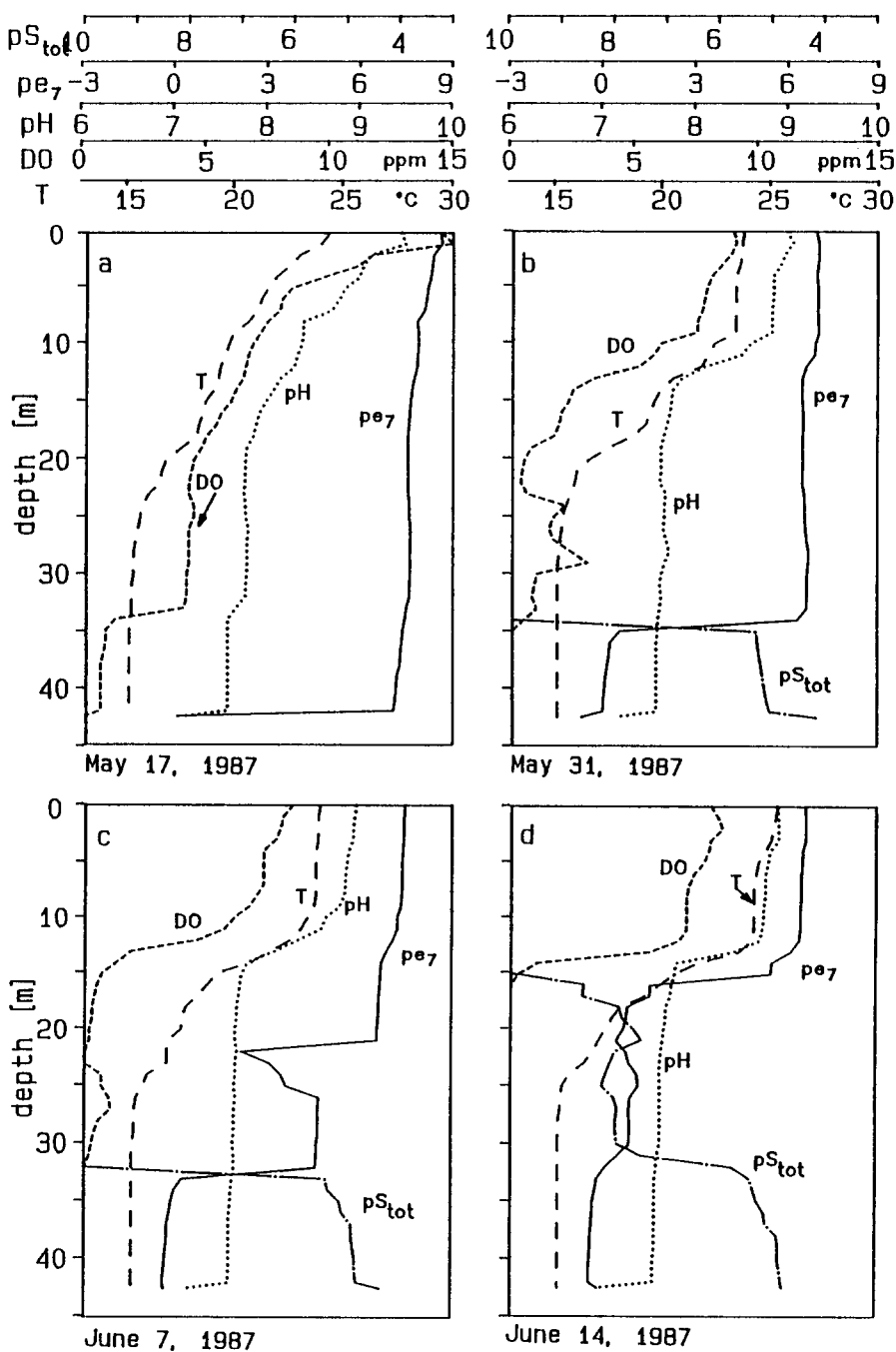


Fig. 4. Representative profiles of  $pS_{tot}$ ,  $pe_7$ , pH, DO and temperature during the stratification period 1987.



limnion (22 m) an oxygen minimum (0.5 ppm) developed, overlaying a zone of higher DO with three oxygen peaks (25 m, 1.5 ppm; 29 m, 4 ppm; 33 m, 1 ppm). This phenomenon is similar to previously reported metalimnetic oxygen minima (Ohle 1951; Shapiro 1960). Wetzel (1981, pp. 166) explains this event by enhanced oxygen consumption following the accumulation of organic detritus when entering colder (denser) water layers. In Lake Kinneret the phenomenon of two hypolimnetic respiration centers seems to be an annual event. It was measured initially in spring 1983 by Eckert & Frevert (1984) using an *in situ* DO device and was confirmed by the present study.

The depletion of oxygen at 23 m by June 7 (Fig. 4c) yielded a second redoxcline ( $2.5 \leq pe_7 \leq 7.0$ ). One week later (Fig. 4d) the residual oxygen peak between 23 and 33 m dissipated leading to an anoxic hypolimnion with elevated sulfide levels below 15 m. The zone of the previous oxygen peak is still reflected by the fluctuations of the total sulfide and redox profiles between 15 and 25 m. The process of stratification is completed within a month (Fig. 4) and characterized by a distinct redoxcline and a sulfuretum (i.e. a sulfide containing zone dominated by the microbial processes of sulfate reduction and sulfide oxidation (Baas-Becking 1925)).

The development of the redoxcline in 1988 is presented in Fig. 5. As in the previous year, oxygen was depleted first in the upper and lower zones of the hypolimnion (Fig. 5a). In this figure, two thermoclines are present: one at a depth of 9 m and a second at 16 m. Both thermoclines display profound decreases in oxygen content and pH value. The  $pe_7$  profile remained nearly unchanged until a depth of 35 m from where values started to decrease towards the bottom. A redoxcline formed at 35 m, below which sulfide accumulated (Fig. 5b). This redoxcline was separated from the oxycline at 15 m by a 20 m thick zone free of oxygen and sulfide where  $pe_7$  values decreased about 1 unit. Five days later (Fig. 5c) the picture changes with hydrogen sulfide emerging in the hypolimnion in three distinct peaks at 21 m, 27 m and below 31 m. These sulfide peaks were reflected in a reversed pattern, by the redox profile. Note that the first  $pe_7$  drop at 15 m from 8.0 to 3 was not related to the development of sulfide. A  $pe_7$  of 3 is within the redox range found empirically for the redox couple  $NO_2^-/NO_3^-$  (Frevert 1983). Because of the transitory character of this state, a designation of the measured redox data to the process of nitrate reduction can only be hypothetical.

The antagonistic trend of the sulfide and redox profiles was repeated in Fig. 5d where the continuous release of sulfide 'smoothed-out' the previous triple peak. Hydrogen sulfide was detected below the thermocline and formed two peaks in the upper ( $\approx 20$  m) and lower ( $\leq 35$  m) hypolimnion.

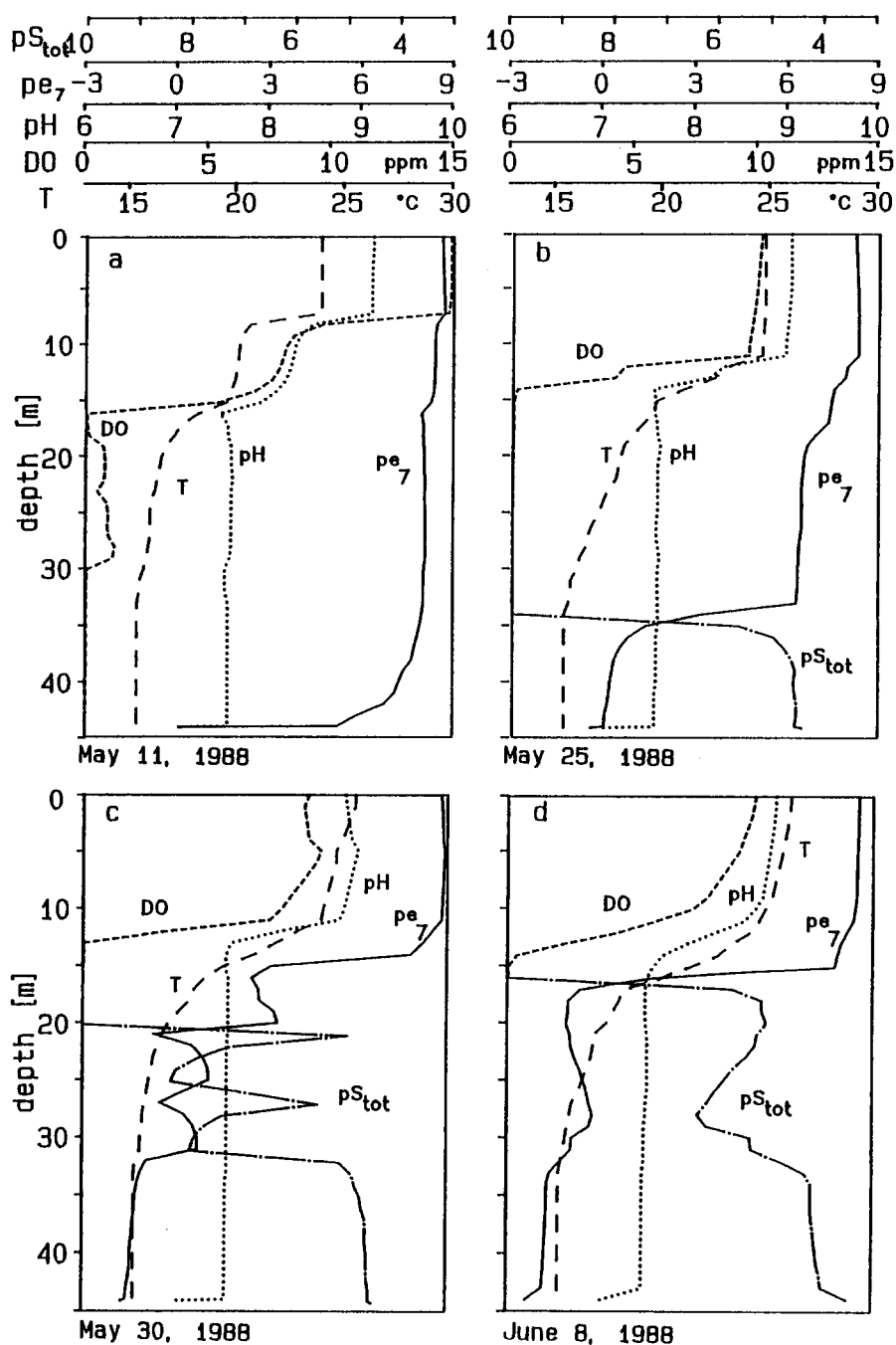


Fig. 5. Representative profiles of  $pS_{tot}$ ,  $pe_7$ , pH, DO and temperature during the stratification period 1988.

The shape of the  $pe$  and  $pS_{tot}$  profiles in Figs. 4 and 5 (most obvious in Fig. 5c) indicates a quantitative response of the platinum electrode to the amount of sulfide present. Such an electrode response would correspond to previous findings from anaerobic sediments (Berner 1963; Whitfield 1969) and from sulfide rich mineral springs (Boulegue & Michard 1979) where the potential of the employed redox sensor was linearly related to  $pH_2S$  following the theoretical relationship:

$$pe = 2.4 - pH + 0.5 \cdot pH_2S. \quad (7)$$

The corresponding plot of meta- and hypolimnetic  $pe_7$  values obtained with this study against the  $pH_2S$  displays a similar linear response with a slightly more positive slope (Fig. 6).

### *Amixis*

The advancement of sulfide into the metalimnion and, consequently, into the range of light penetration is the principal ecological stimulator for the growth of phototrophic sulfur bacteria (e.g. Pfennig 1967). As a result, an

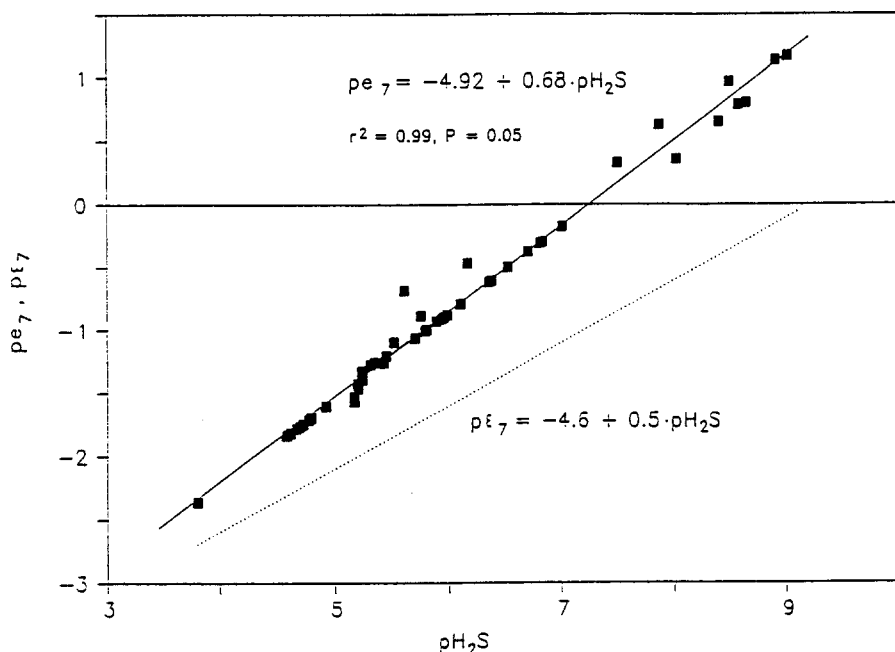


Fig. 6.  $pe_7$ - $pH_2S$  plot of meta- and hypolimnetic data during the stratification: ■  $pe_7$  values during stratification, .....  $p\epsilon_7$  function.

annual mass development of the brown phototrophic sulfur bacterium *Chlorobium phaeobacteroides* emerges in the metalimnion of Lake Kinneret from July until September (Bergstein et al. 1979; Eckert et al. 1990b).

The establishment of the sulfuretum marks the end of the stratification process and the beginning of stable amixis which lasted generally from July through December. The profiles of 29 October 1988 (Fig. 7) are typical to the period for all three years. Epilimnetic pH was uniformly 8.7 and oxygen concentrations near saturation depending on water temperatures that reached maximum values ( $\approx 30^\circ\text{C}$ ) in August.

The hypolimnion was characterized by pH 7.5 and temperatures around  $15.5^\circ\text{C}$ . Sulfate reduction and phototrophic sulfide oxidation are the dominant microbial processes in the metalimnion, with total sulfide concentration near  $100\ \mu\text{M}$  until October, rising to  $300\ \mu\text{M}$  by the beginning of November. Figure 8 shows the redox and sulfide changes at the depth with the highest *Chlorobium* biomass throughout the time period of the phototrophic bacterial bloom. Both parameters followed the fluctuation of the bloom that appeared in two peaks (July and September) and lasted until the end of October (Eckert et al. 1990b). The comparison of the  $\text{pe}_7\text{-pH}_2\text{S}$  relationship in Fig. 7 with the one obtained in the upper 5 m of the metalimnion during the *Chlorobium* bloom (Fig. 9) shows that during the two peaks of the bloom in July and September two distinct linear functions evolved both having a slope of 1.0.

### *Destratification*

From September the cooling of the epilimnion initiated sinking processes of the thermocline (destratification). During the three lake cycles investigated, we observed a stepwise sinking behavior where large drops occurred following storm events rather than gradual cooling of the surface water. Figure 10 is characteristic for this time period with epilimnetic temperature, pH, D.O. and pe conditions similar to those of the time of mixis (Fig. 3). The redox conditions within the shrinking hypolimnion remained the same as during the summer stratification.

### **General discussion and conclusions**

The goal of our research was to collect a detailed set of *in situ* redox data from the water column of Lake Kinneret and to relate those data to the prevailing hydrochemical and microbial conditions.

The aerobic respiration that is the cause for the parallel decline of

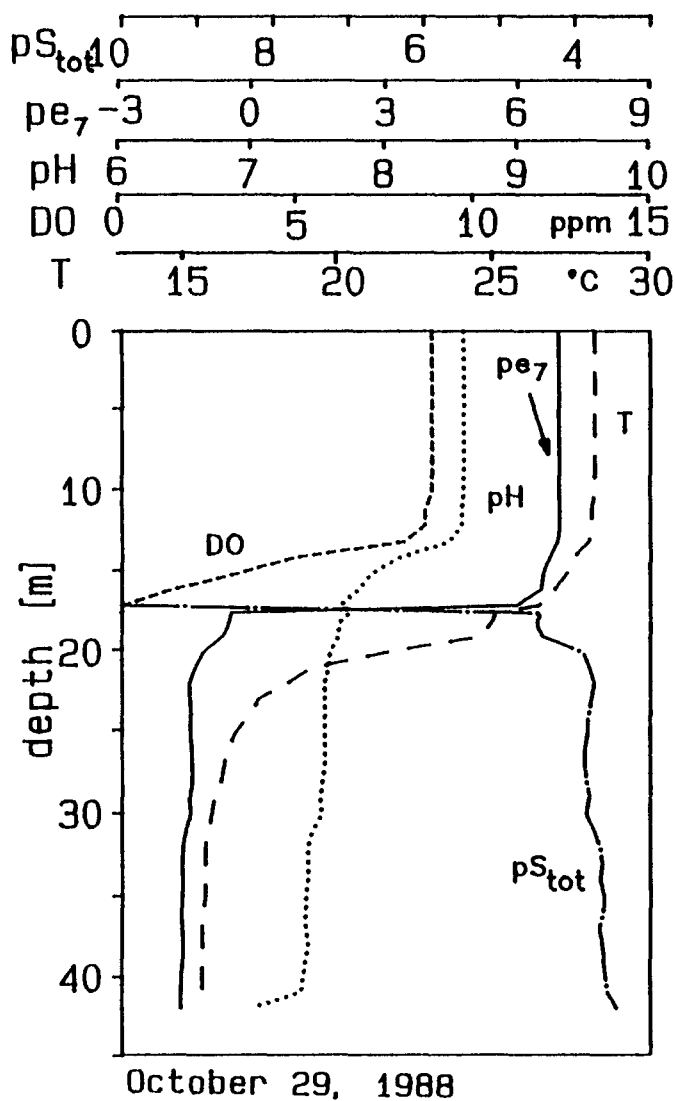


Fig. 7. Representative profile of  $pS_{tot}$ ,  $pe_7$ , pH, DO and temperature during amixis. Data from 29 Oct 1988.

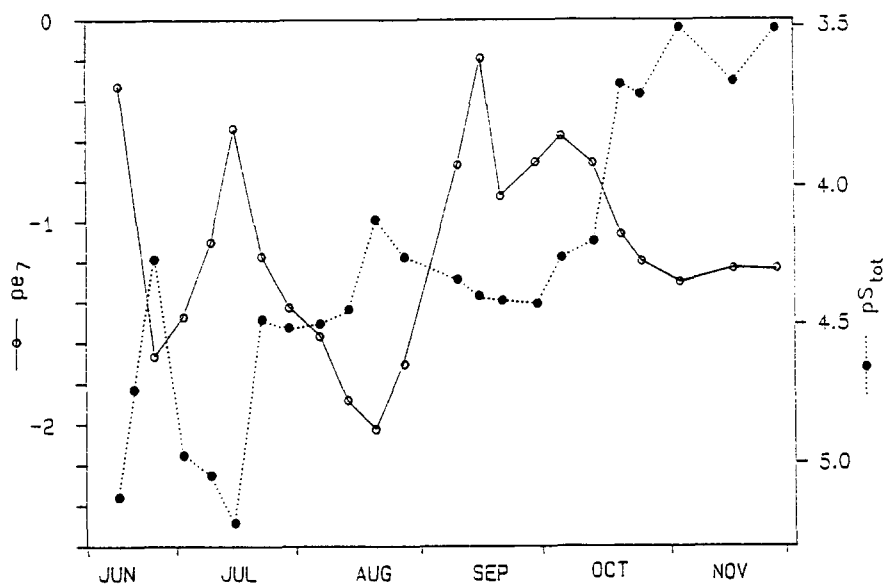


Fig. 8. Total sulfide (●) and redox (○) development in the metalimnion during the *Chlorobium* bloom of 1988.

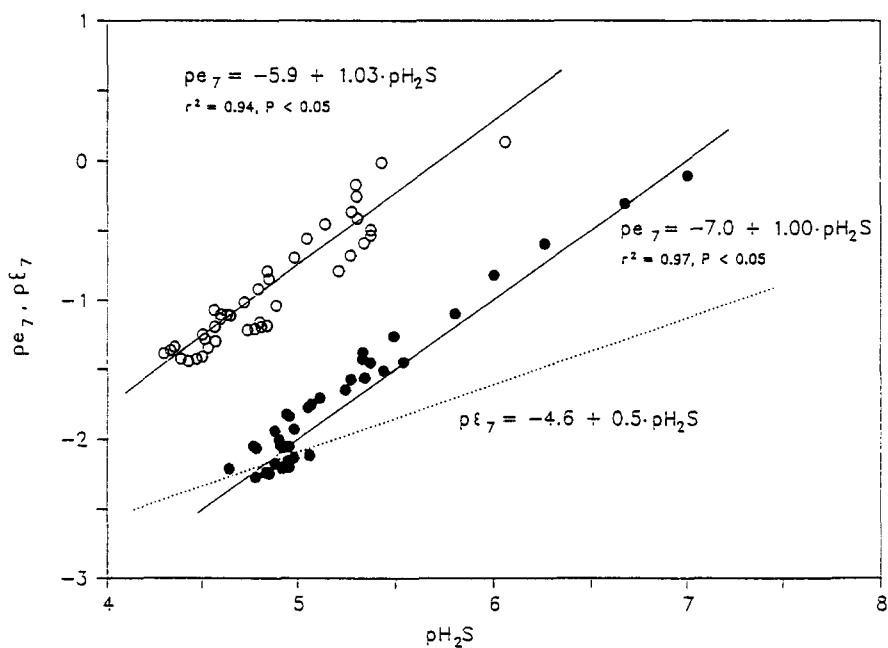


Fig. 9.  $pe_7$ - $pH_2S$  plot of metalimnetic data during the *Chlorobium* bloom: ●  $pe_7$  values during Jul 1988, ○  $pe_7$  values during Oct 1988; .....  $pe_7$  function.

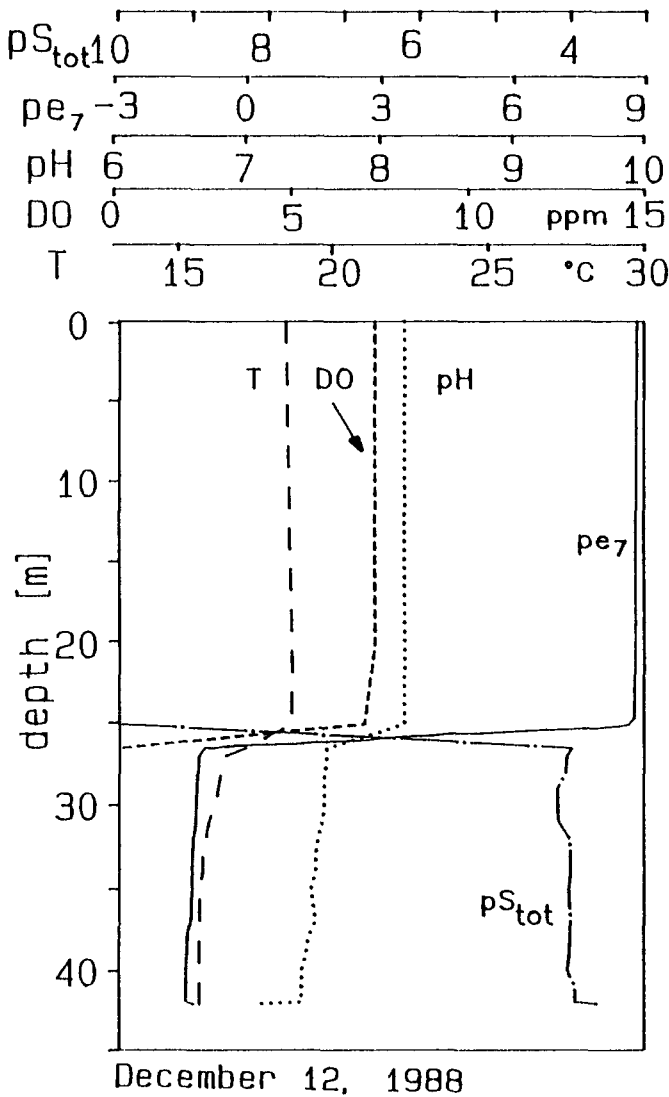


Fig. 10. Representative profile of  $pS_{tot}$ ,  $pe_7$ , pH, DO and temperature during destratification. Data from 12 Dec 1988.

oxygen and pH when stratifications starts did not measurably effect the redox conditions.  $pe_7$  values remained positive between 7 and 9 as long as traces of oxygen were present. The fact that platinum electrode potentials from natural aquatic systems do not correspond to the prevailing oxygen concentration has repeatedly been used as an argument against the applica-

tion of redox measurements in natural systems (Harrison 1973; Whitfield 1974). The reason for this electrode performance is the low electron exchange density of oxygen at the platinum surface (Bockris & Huq 1970; Stumm & Morgan 1984). Only in pure water and with an extremely long response time, a linear relationship between the platinum electrode potential and the concentration of dissolved oxygen is measurable (Schuldiner et al. 1966). Because of the slow kinetic of dissolved oxygen, mixed potentials from aerobic systems are dominated by traces of reductants rather than by the actual oxygen concentration.

The main prerequisite for a redox change is a microbial shift to different electron acceptors after the depletion of oxygen. During the three annual cycles investigated this anaerobiosis started in the deeper hypolimnion displaying a second peak of enhanced oxygen uptake in the upper hypolimnion.

By far the strongest impact on the redox conditions resulted from the release of sulfide and our results demonstrate for the first time a quantitative response of a redox sensor within the meta- and hypolimnion of a stratified lake. The possible influence of phototrophic bacteria on the  $pe/pH_2S$  relationships found with this studies was investigated in a related study (Eckert 1993) by stimulating the metalimnetic conditions present in Lake Kinneret.

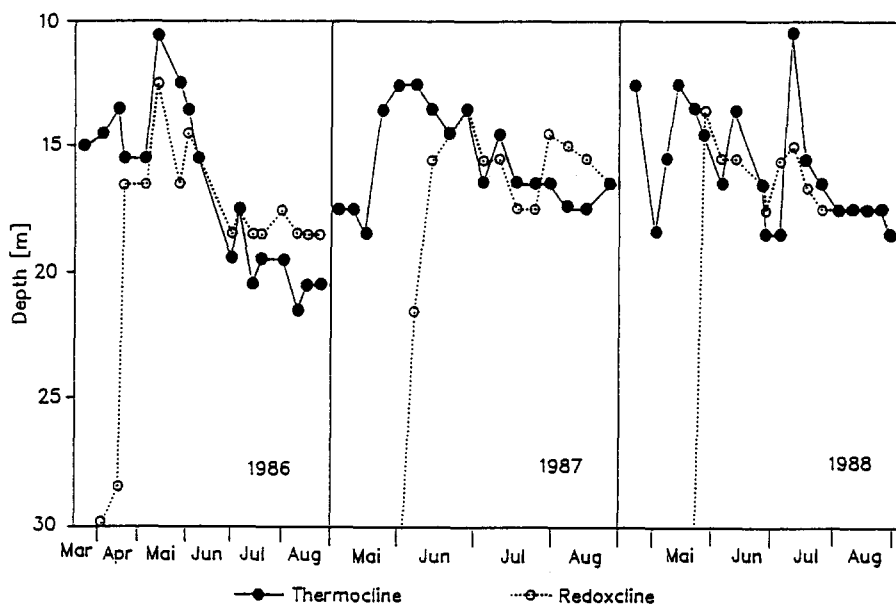


Fig. 11. Thermocline and redoxcline development in Lake Kinneret during the years 1986–1988.



In general, high-resolution *in situ* measurements of redox and related parameters allow for a clear definition of the oxic and anoxic water layers. The advantage of this concept becomes obvious when comparing the time changes of the depth of the redoxcline with that of the thermocline ( $\Delta T_{\max} \cdot \text{m}^{-1}$ ), respectively (Fig. 11). There is in most stages a discrepancy between both 'clines' which in practice can cause an over- or underestimation of the anaerobic water mass when relying only on the determination of the thermocline.

We have shown further an example of more than operational use of redox measurements by relating the measured values to the predominating bacteria.

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