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## THE REDOX POTENTIALS IN SMALL OLIGO AND MEROMICTIC LAKES

JOHANNES KJENSMO

Department of Limnology,  
University of Oslo, Blindern, Norway

The redox potentials of lake water have been the subject of several investigations (Kusnetzow 1935, Pearsall & Mortimer 1939, Hutchinson, Deevey & Wollock 1939, Deevey 1941, Allgeier, Hafford & Juday 1941, Mortimer 1941-42). The ecological significance of the redox potentials is stressed in several of these works. The work of Mortimer (1941-42) also shows the importance of the seasonal variations in redox potentials for the liberation from the sediments of different important nutrients.

At present very little is known about the redox potential of the deep water in meromictic lakes. Allgeier, Hafford & Juday (1941) recorded vertical distribution of redox potential in one meromictic lake, Lake Mary, Wisconsin. The redox potential of the monimolimnion of Lake Mary varied from  $E_h = 0.140$  volts at 8 m to  $E_h = 0.075$  volts at 20.5 m. Hutchinson (1957) assumes it probable that other, but by no means all, meromictic lakes will be found to show a similar phenomenon.

In the present paper the vertical distribution of redox potential of the water of three meromictic and one oligomictic lake is described.

### METHODS

The measurements of redox potentials were carried out in the laboratory by means of a Radiometer pH meter and a bright platinum electrode. The water

intended for measurement of redox potential was tapped in stoppered glass bottles in the field. The sampling procedure was the same as the procedure employed when tapping water for oxygen analyses. Special care was taken to avoid introduction of oxygen, or in other words, to avoid changes in the redox conditions. The electrodes were dipped into the bottles during the potential measurements. The platinum electrode was carefully rinsed with nitric acid before the measurements.

The methods employed for the different chemical analyses given were the same as those given in Kjensmo (1967a).

### LAKES INVESTIGATED

The three meromictic lakes investigated, Svinsjøen, Skjennungen, and Store Aaklungen, were previously described by Kjensmo (1967b, 1968). Svinsjøen is a productive lake with waters relatively rich in electrolytes. The  $\kappa_{18}$  of the mixolimnion is *ca.* 135. Skjennungen and Store Aaklungen are fundamentally oligotrophic soft water lakes with  $\kappa_{18}$  of *ca.* 25-30 units in their mixolimnia. Store Aaklungen is an oligohumic lake and Skjennungen is mesohumic. A feature which the three lakes have in common is a very high iron content in their monimolimnia. The fourth lake investigated, Lake Villbergtjern, is situated south of Lake Mjøsa in eastern Norway. The basin of Villbergtjern is a kettle formed when previously buried ice melted in the glacio-fluvial deposits in the area. Villbergtjern is a small lake with a maximum depth of 16 m. During the spring 1967 a full circulation was lacking, and the lake appeared oligomictic but it could also have been meromictic. The specific conductivity of the epilimnetic water amounted to 10  $\kappa_{18}$ -units. Thus, Lake Villbergtjern is extremely poor in electrolytes, and, further, the lake is unproductive.

### RESULTS

The redox potentials of the waters from 0.5 m depth of the various lakes ranged from  $E_h = 0.491$  to  $E_h \cong 0.565$  volts. The corresponding  $E_7$  values are 0.474 to 0.530 volts. The bottom waters, i. e. the waters *ca.* 0.5 m above the mud surface, showed potentials in the range 0.030 to 0.069 volts when measured as  $E_h$ .

Figures 1 to 4 show the results obtained on the different lakes. The distribu-

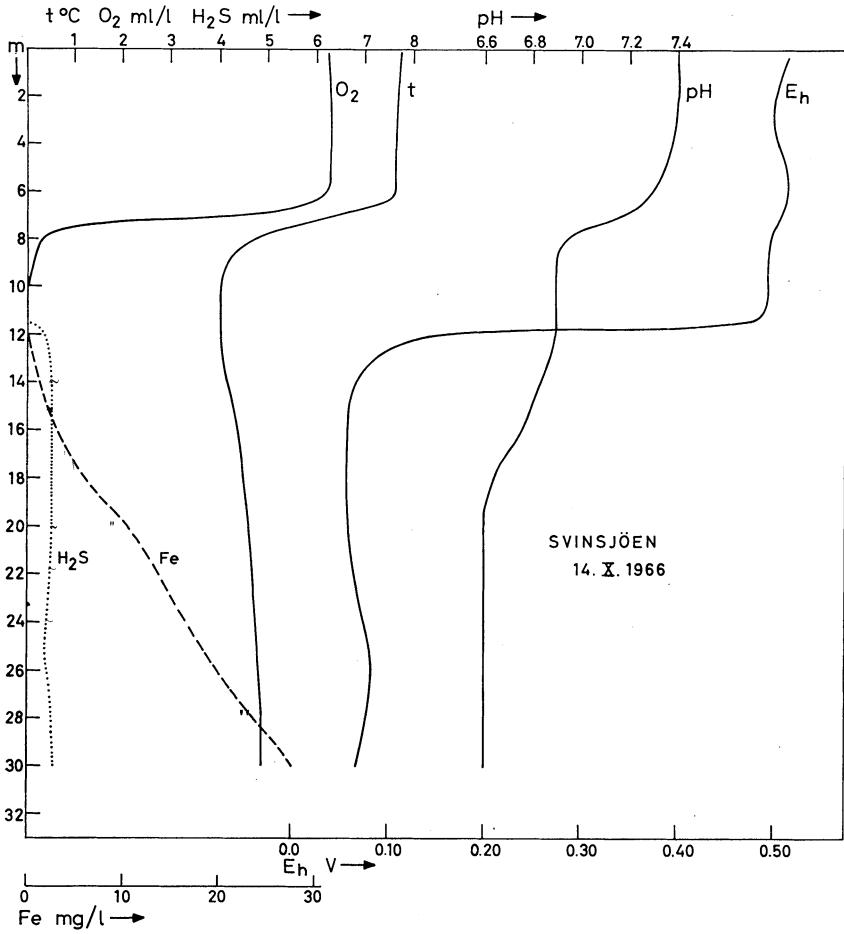


Fig. 1. Svinsjöen. Vertical distribution of temperature, oxygen, hydrogen sulphide, pH, total iron, and redox potential  $E_h$ .

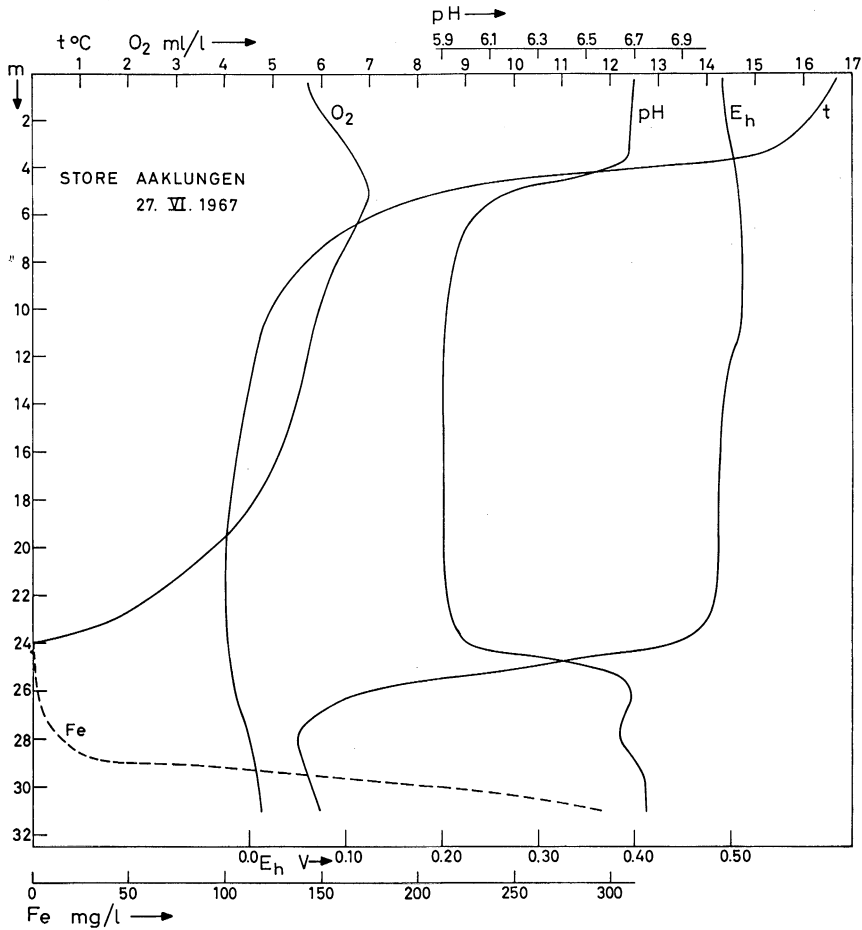
tion of temperature, oxygen, hydrogen sulphide, pH, and total iron are plotted in the diagrams also. The redox potentials are depicted as  $E_h$  in the diagrams since oxygen potentials are not involved in the redox system of the deep waters of the lakes.

In Lake Svinsjöen (Fig. 1) relatively small variations occurred in redox potentials down to *ca.* 11 m depth. Between 11 and 12 m depth a sharp fall in the

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potential was recorded. The range in  $E_h$  in the 15 to 30 m water layer was from 0.060 to 0.082 volts. The 12-15 m water layer in Svinsjøen represented the chemocline region of the lake. Oxygen could be traced downwards to *ca.* 10 m depth on the day of observation. Among the reducing agents present in the monimolimnion, ferrous iron is undoubtedly of great importance. Traces of hydrogen sulphide were also present in the monimolimnion.

In Lake Store Aaklungen (Fig. 2) the monimolimnion stretches downwards



*Fig. 2.*  
Store Aaklungen. Vertical distribution of temperature, oxygen, pH, total iron, and redox potential  $E_h$ .

from *ca.* 26 m depth. In the uppermost 22 m of the mixolimnion the redox potential  $E_h$  showed variations in the range 0.488 to 0.512 volts. The highest value was recorded at 10 m depth. At 24 m depth oxygen was undetectable by analysis, and the potential at that depth was 0.445 volts. Downwards from 24 m a very sharp fall in the potential was observed and it reached a minimum of 0.050 volts at 28 m. Further downwards a slight increase occurred. At 31 m depth,  $E_h$  of 0.069 volt was recorded. The monimolimnion of Store Aaklungen contained enormous amounts of iron. At 31 m depth a total iron content of 295 mg per litre was found on the day of observation. In such an environment it seems probable that the most important system involved in determining the redox potential is the ferrous-ferric system.

Lake Skjennungen (Fig. 3) is also an iron-meromictic lake, and the iron content amounted to 20 mg Fe per litre at 16 m depth on the day of observation. The redox potential of the monimolimnetic water varied between  $E_h$  of 0.307 volts at 10 m depth to 0.058 volts at 16 m depth. In this case also the ferrous-ferric system must be expected to be a determinative factor for the greatness of the potential.

In the uppermost 6 m water layer of the mixolimnion the redox potential

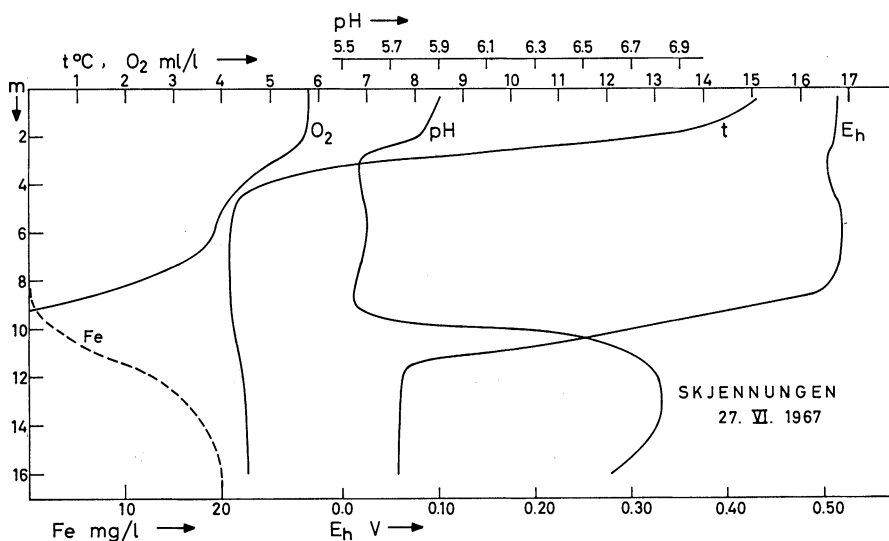


Fig. 3.

Skjennungen. Vertical distribution of temperature, oxygen, pH, total iron, and redox potential  $E_h$ .

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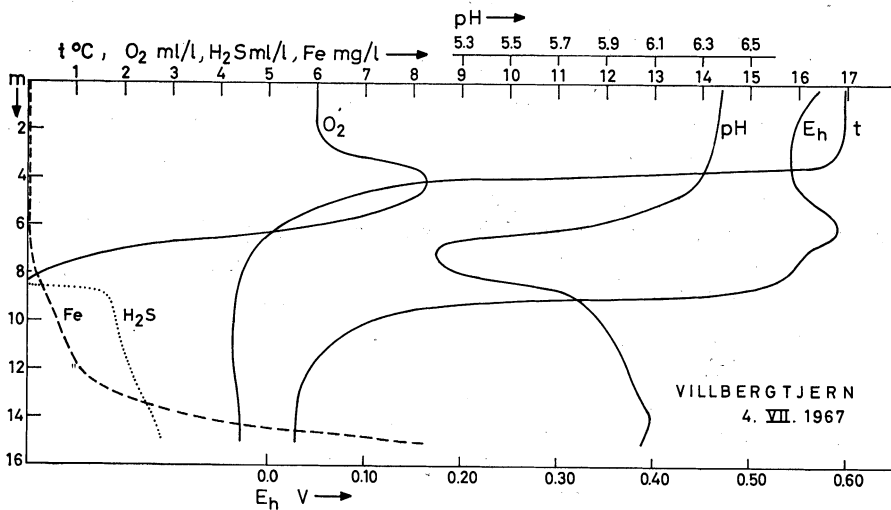
showed small variations; the range in  $E_h$  observed was from 0.503 to 0.519 volts.

At 9 m depth an oxygen content of 0.48 ml per litre was recorded, and the redox potential at the same depth was 0.443 volt.

As was the case for Store Aaklungen, no hydrogen sulphide could be traced in the monimolimnion of Lake Skjennungen.

As stated above, it is highly probable that Lake Villbergtjern is an oligo-mictic lake. The lake may, however, even be meromictic, but more research is necessary in order to decide its circulation pattern with certainty.

At 8 m depth in Villbergtjern (Fig. 4) an oxygen content of 0.33 ml per litre was recorded. The redox potential  $E_h$  at this depth amounted to 0.536 volts. From 8 to 10 m depth a very sharp fall was observed, and very low potentials were recorded for the deep waters. Thus,  $E_h$  values of 0.030 volts were measured at 14 and 15 m depths. In Lake Villbergtjern also, accumulating of iron occurred in the deep water. At 15 m depth the total iron content amounted to 8.3 mg per litre. The total content of hydrogen sulphide at 15 m (i. e. molecular free  $H_2S$  and  $H_2S$  bound to soluble sulphides) amounted to 2.95 ml per litre. The deep water also smelled strongly of  $H_2S$ .



*Fig. 4.*

Villbergtjern. Vertical distribution of temperature, oxygen, hydrogen sulphide, pH, total iron, and redox potential  $E_h$ .

Relatively high  $E_h$  values were recorded for the uppermost 7 m water layer; the total range was 0.544 to 0.580 volts. The highest value was observed at 6 m depth, where a relatively marked maximum occurred.

### CONCLUSION

The redox potentials measured with a platinum electrode dipped in well-oxygenated natural waters may be regarded as irreversible oxygen potentials. For comparisons with other observations it is convenient to correct the measured potentials at different pH to pH 7. This correction can be done by addition of 0.058 (pH - 7) volts (Hutchinson 1957).

In Table 1, the redox potentials at pH 7, i. e.  $E_7$ , are given for the well-oxygenated water layers of the four investigated lakes.

As far as redox potential is concerned the present lakes divide into two groups. Thus Svinsjøen and Villbergtjern are characterized by higher redox potentials in their uppermost waters than Skjennungen and Store Aaklungen. In the uppermost 6 m water layer of Svinsjøen,  $E_7$  values from 0.532 to 0.535 volts were recorded. In Villbergtjern the range in  $E_7$  for the uppermost 6 m water layer was from 0.511 to 0.542 volts. The total range in  $E_7$  for the uppermost 6 m layer in Skjennungen was 0.438 -0.450 volts and the range in  $E_7$  for the uppermost 10 m layer of Store Aaklungen was 0.449-0.474 volts.

The lower potentials observed in Skjennungen and Store Aaklungen may be due to the presence of reducing organic substances. The two lakes are typical coniferous forest lakes, and their catchment areas are relatively rich in *Sphagnum* bogs. Organic reducing substances may, accordingly, be supplied to the lakes from the bogs. Müller (1939) assumed an organic compound as a reducing agent present in the water pressed from a *Sphagnum* bog. Visser (1964) found the redox potentials ( $E_7$ ) of humic acids extracted from a tropical *Sphagnum* peat deposit to lie between 0.32 and 0.38 volts. It therefore seems plausible that drainage from bogs may introduce reducing matter which also influences the oxygen potential.

The very small influence of the oxygen concentration on the oxygen potential is clearly demonstrated by the present investigation. In all four lakes the greatest fall in  $E_h$  was recorded at depths well below the depths at which oxygen was analytically detectable.

Characteristic for the lakes are high contents of iron in their deep waters. In the three meromictic lakes the maxima in total iron were: Svinsjøen, 27.5 mg Fe per litre; Skjennungen, 20 mg Fe per litre; and Store Aaklungen, 295 mg

Table 1.  
Dissolved oxygen and redox potentials  $E_T$  in Svinsjøen, Store Aaklungen, Skjennungen, and Villbergjtjern

Svinsjøen			Store Aaklungen			Skjennungen			Villbergjtjern		
Depth (m)	O <sub>2</sub> (ml/l)	E <sub>T</sub> (V)	Depth (m)	O <sub>2</sub> (ml/l)	E <sub>T</sub> (V)	Depth (m)	O <sub>2</sub> (ml/l)	E <sub>T</sub> (V)	Depth (m)	O <sub>2</sub> (ml/l)	E <sub>T</sub> (V)
0.5	6.24	0.535	0.5	5.73	0.474	0.5	5.79	0.450	0.5	6.00	0.542
3	6.24	0.532	5	6.97	0.462	2	5.70	0.441	2	6.07	0.521
6	6.27	0.532	10	5.95	0.449	3	5.08	0.422	4	8.27	0.528
7	4.68	0.519	15	5.37	0.427	6	3.87	0.438	6	5.84	0.511
			20	3.71	0.425						



Fe per litre. In such environments the ferrous-ferric system must be assumed to be of greatest importance among the factors involved in the total oxidation-reduction system. Except for one value at 25 m depth in Svinsjøen, where  $E_h$  0.082 volts was recorded, the range in  $E_h$  for the waters containing high iron contents in the three meromictic lakes was 0.050-0.069 volts.

The deep water of Lake Villbergtjern also contained high amounts of iron. At 15 m depth the total iron content amounted to 8.3 mg Fe per litre. The redox potential  $E_h$  at 14 and 15 m depth was 0.030 volts, which was the lowest value recorded in the investigated lakes. In the case of Villbergtjern also, the ferrous-ferric system must be expected to be an important factor governing the redox potential of the deep water. Considerable amounts of free hydrogen sulphide were present in the deep waters, a fact which was confirmed by a strong smell of hydrogen sulphide arising from this water. Hydrogen sulphide may have been the additional factor responsible for the lower potentials of this water as compared with the potentials of the deep waters of the three meromictic lakes. Experiments of Hayes, Reid & Cameron (1958) show that hydrogen sulphide has a direct effect on the redox potential. In the three meromictic lakes there was no smell of hydrogen sulphide from the deep waters. The traces of hydrogen sulphide found by analyses of the water of Svinsjøen (see Fig. 1) were probably derived from soluble sulphides included by the method of analysis employed. With the high iron contents at the pH of the monimolimnetic waters of the meromictic lakes, free hydrogen sulphide should not be expected.

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