

## EXPERIMENTAL STUDY OF THE DEPENDENCE OF THE DISTRIBUTION OF SULPHATES IN THE LAKE SEDIMENT CORE ON THE OXYGEN SUPPLY

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**Abstract.** Regularities of the distribution of sulphates in water/sediment systems in lakes were studied using an experimental device constructed for this purpose. The device enables to follow the variation of sulphate distribution and redox conditions.

**Key words:** Eh, sulphate, pore water, lacustrine sediments.

### INTRODUCTION

Increasing human impact on inland water bodies has substantially changed their ecosystems, causing a permanent trend toward increasing trophicity (Varvas, 1994). The state and dynamics of a lake's ecosystem are determined to a large extent by processes at the water/sediment interface. Special attention in the studies of the behaviour of chemical compounds in the water/sediment interface has been paid to the elements whose valence and migration ability are directly dependent on the oxygen supply. As a result, the basic research carried out by Balistrieri et al. (1992), Davison et al. (1982), and De Vitre et al. (1988) has made it possible to show Fe and Mn dynamics in a seasonally anoxic lake and to evaluate the numerical parameters.

Establishing the cycling of chemical elements able to form different transitional compounds like sulphur is more complex. However, the accumulation of sulphur often plays an important role in the worsening of the state of an ecosystem, especially in the regions with high sulphur emissions. Sulphate is the most common form of inorganic sulphur in oxygen-rich water (Andrea, 1990; Mitchell et al., 1984). Sulphur can accumulate as a result of the deposition of particulate matter or be derived by immobilization of soluble forms, predominantly sulphate, from water. Soluble forms are greatly responsible for the accumulation of sulphur in sediments subject to anoxia. Soluble sulphate in the sediment can be transformed through biotic activity to sulphide, which can form a range of precipitates such as FeS, Fe<sub>3</sub>S<sub>4</sub>, FeS<sub>2</sub>.

The problems concerning the biogeochemical cycling of sulphur and its role in the regulation of ecosystems have been discussed widely in recent scientific papers (Dornblaser et al., 1994; Giblin et al., 1990; Turk et al., 1993; Vile & Wieder, 1993).

Monitoring of the lakes and studies of sediment cores have showed that the seasonal changes in the sulphate content depend on the oxygen supply and consumption (Carignan & Tessier, 1988; Mattson & Likens, 1993; Urban et al., 1994) and are also related to the changes in the redox potential (Eh) values. In theory, the microbially mediated redox reactions in closed systems containing oxidizable organic matter such as surficial sediments, occur in the order of thermodynamic probability of each reaction (Froelich et al., 1979). Thus, during the oxidation of organic matter, the energetically more favourable oxidants are consumed first. After the utilization of oxygen and nitrate, Fe(III) and sulphate reduction should occur in close proximity. Organic carbon fermentation is also favoured under similar redox conditions. Sulphate is used as the electron acceptor at the Eh values between +115 mV and -450 mV. However, for initiating the process, Eh must decrease below -95 mV (Mitchell et al., 1984). Vertical distribution of sulphate reduction and methanogenesis have been modelled for freshwater lake sediments. Lovley & Klug (1986) showed that sulphate reduction became limited under insufficient sulphate supply when sulphate concentration in pore water decreased below 30  $\mu\text{M}$  and methanogenesis became predominant.

The main determinants of Eh in sedimentary environment are photosynthesis, respiration, and reactions associated with oxidation or reduction of iron and sulphur (Langmuir, 1971). Since oxidation and reduction processes are practically irreversible in natural environments, the observed Eh values represent a mixed potential resulting from several redox reactions (Langmuir, 1971; Lindberg & Runnells, 1984; Stumm & Morgan, 1981). Therefore, the Eh measurements should be considered only as a descriptive tool for the characterization of the degree of sediment stagnation. As long as the conditions in water are not close to anoxia, the Eh values will remain positive and fairly high. When oxygen concentration approaches zero and anoxic conditions appear, the Eh values will decrease. No free oxygen is detectable when Eh values in either sediment or water fall below 100 mV (Hargrave, 1972). Eh may also provide a sensitive measure of the thickness of the oxidized surface layer and probability of the occurrence of redox reactions.

These problems are crucial in Estonia because of a high content of sulphates in the atmospheric precipitation. Huge amounts of alkaline and sulphate-rich emissions from oil-shale-fired power plants increase the content of sulphate in the atmospheric precipitation near the plants to 30  $\text{mg} \cdot \text{l}^{-1}$  (Roots & Saare, 1995), whereas in several lakes which are used as natural reservoirs for sulphate-rich mining waters the sulphate content is as high as 300  $\text{mg} \cdot \text{l}^{-1}$  (Varvas, 1994).

The aim of the present study was to establish the distribution regularities of sulphate in the water/sediment column and to estimate the sulphate transformation pathway and its correlation with Eh values using a special experimental device. The study of the regularities of the biogeochemical cycling of compounds in the water/sediment system is complicated because of the spatial variability of the sediment composition, mechanical and biological redistribution of sediments, etc. In order to eliminate the effect of these factors, we investigated the regularities of the distribution of sulphates in the water column and pore water in the cores taken from Lake Harku under laboratory conditions.

## METHODS

The experiments were performed with cores taken from Lake Harku. Lake Harku is a shallow (max. depth 2.5 m) lake, with an area of 1.64  $\text{km}^2$ , situated at the western border of Tallinn. This is a hypereutro-



phic lake with a long water residence time. The water in the lake is well mixed during the summer season and oxygen is present in the entire water column. The oxygen content is remarkably high even in winter. The pH of water is 9.0—9.2 in winter, and 7.2 in summer (Mäemets, 1977). The upper 20 cm part of the sediment, consisting of greyish-brown organic-rich gyttja, has formed during the last 40—50 years as shown by  $^{210}\text{Pb}$  studies (M. Varvas, pers. comm.).

Different approaches have been developed for getting representative samples from pore waters of soft sediments (Andersson, 1985; Carignan, 1984; Carignan et al., 1985). A special device for the study of the distribution parameters of sulphate and Eh values in the vertical column of lake water and sediments was constructed by Englo Ltd, Tallinn. The device consists of a transparent tube with holes in walls for the insertion of electrodes and taking samples from water, sediments, or pore water (Fig. 1). The tube with closed holes was equipped with extension rods and used as a piston corer in routine sediment sampling. Immediately after sampling both ends of the tube were closed vacuum tightly and the tube (about 1/3 water and 2/3 sediment) was carefully transported to the laboratory in vertical position.

In the laboratory the Pt electrodes were placed into selected holes for Eh measurements. The column was moved by piston (Fig. 1), if necessary, so that one electrode can fix the Eh value immediately under the sediment surface. Eh was measured once a day. A calomel electrode (in 3M KCl solution) served as the reference one. The Eh value in the testing solution (1/300 M  $\text{K}_3\text{Fe}(\text{CN})_6$ , 1/300 M  $\text{K}_4\text{Fe}(\text{CN})_6$ , 0.1 M KCl) was +223 mV. The samples of water above the sediment and pore water from the sediment were taken with a syringe through the selected holes. Filters were placed between the injector and the syringe in order to avoid the contamination of the samples by sediment particles. Aliquots were withdrawn slowly to minimize the mixing of water in the tube. The concentration of sulphate in the samples was determined on an ion chromatograph AVK-II designed and produced by the Special Design Office of the Estonian Academy of Sciences. The minimum detectable quantity was  $0.2 \text{ mg} \cdot \text{l}^{-1}$ ; the standard deviation was 1.5%.

To follow the influence of seasonal changes (chemical, microbiological, etc.) the cores for laboratory experiments were taken in April, June, and October.

The cores were hermetically closed in an experimental tube and left in the lab at 20°C in dark. For the study of the impact of oxygen on sulphate transmission, the water in the tube was saturated with air (during 3 hours after 5 days of sampling in the April experiment and during 3 days after 2 weeks of sampling in the June experiment). After saturation the tube was again closed hermetically.

For the analyses of the bulk sediment matter a core was taken from the upper part of the sediment on 15 June using a Livingstone-Vallentyne piston corer equipped with extension rods. From the core 2-cm subsamples were taken and the water content, as well as Fe, S, and organic content, was measured.

## RESULTS

### Sediments

The analysed part of the sediments from Lake Harku was typical greyish-brown gyttja with a soft uppermost layer. A layer of black gyttja at a depth of 0—10 cm indicates the presence of iron sulphide. The content of water in the sediment decreased from 96.1% near the interface to 90.3% at a depth of 18 cm.

Chemical data (Table 1) showed a small increase in the organic matter content in the core from a depth of 10–12 cm towards the surface. The contents of Fe and S have a slight maximum at depths from 12 cm to 6 cm. The annual sedimentation rate in the lake was less than 1 mm in the second half of the last century, whereas in the 1950s and 1960s it was 3–4 mm and reached its maximum in the late 1980s when more than 10 mm of sediment was annually accumulated (M. Varvas, pers. comm.).

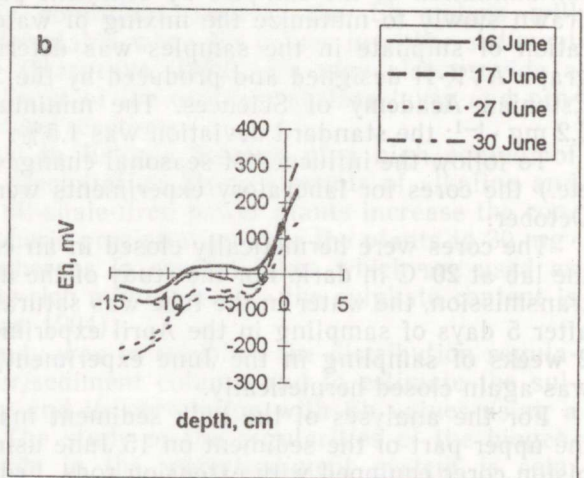
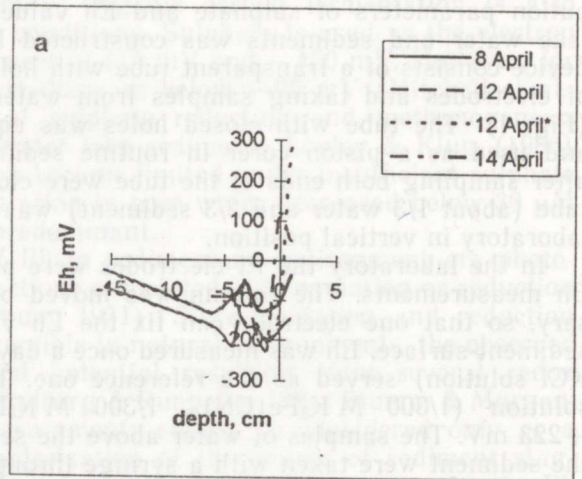
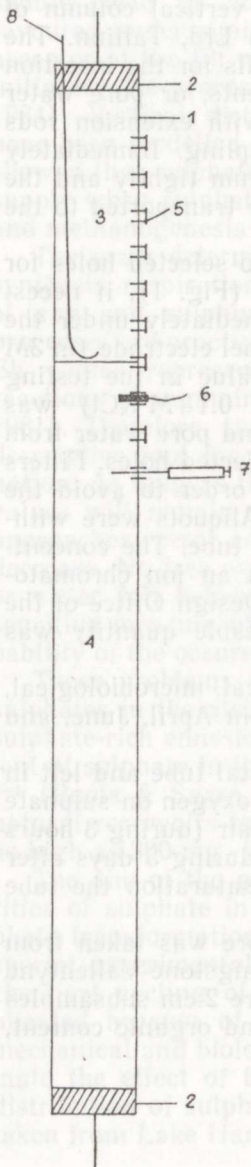


Fig. 2. Temporal changes of Eh values in water and sediment cores taken on 7 April (a) and 15 June (b). The water in the tube was saturated with air on 12 April and 28–30 June.

Fig. 1. Device for the study of processes in lake water and sediment. 1, transparent tube; 2, vacuum tight rods; 3, water; 4, sediment; 5, closed holes; 6, Eh electrode; 7, syringe for sampling; 8, tube for inserting oxygen.



Table 1

Data of chemical analysis of sediment from Lake Harku

Depth, cm	Dry weight (dw), %	Org. matter, % dw	Fe, % dw	S, % dw
0-2	3.89	39.50	1.56	1.92
2-4	5.32	37.54	1.62	1.72
4-6	6.26	37.84	1.66	1.96
6-8	6.60	35.64	1.80	1.96
8-10	7.04	33.96	1.78	2.04
10-12	8.47	30.70	1.78	1.88
12-14	9.31	30.94	1.64	1.80
14-16	9.50	32.64	1.66	1.64
16-18	9.72	33.34	1.52	1.40
18-20	9.33	33.74	1.42	1.04

Table 2

Temporal changes in Eh values (mV) in water (+) and sediments (-) in cores taken on 7 April (a) and 15 June (b). \* Data during aeration of the water (during three hours on 12 April and three days on 28-30 June)

a

Date	Depth, cm								
	+2.5	-0.1	-1.0	-2.0	-3.0	-4.0	-6.0	-16.0	-28.0
7.04	+079	-068	-067			-074			
8.04	-037	-103	-124	-123	-058	-090	-092		+054
11.04	-120	-129	-204	-133	-088	-083	-128	-001	+002
12.04	-145	-178	-209	-171	-168	-104	-137	-024	-025
12.04*	+283	-153	-201	-160	-160	-103	-134	-026	-048
14.04	+048	+111	-225	-190	-049	-216	-166	-070	-046
15.04	-023	+074	-223	-199	-041	-234	-156	-076	-144
18.04	-076	-231	-232	-213	-193	-233	-186	-215	-202
20.04	-075	-240	-233	-223	-192	-238	-188	-239	-261

b

Date	Depth, cm				
	+2.5	-1.5	-8.0	-10.0	-14.0
16.06	+233	+027	+015	-051	-037
17.06	+229	-023	-008	-081	-068
20.06	+245	-031	+012	-111	-100
21.06	+248	-005	-005	-107	-121
22.06	+174	-003	-008	-116	-132
27.06	+144	-041	-058	-176	-214
28.06*	+167	-049	-064	-180	-224
29.06*	+317	-045	-072	-193	-235
30.06*	+307	-044	-086	-199	-248
1.07	+278	-047	-094	-201	-248

### Experiment in April

Immediately after the sampling the Eh values in the core taken on 7 April 1994 were slightly negative (Table 2a, Fig. 2 a). The minimum Eh value was estimated at a depth of 1 cm in the sediment; further, the Eh values had a tendency to increase with depth. The negative Eh values in a tightly closed system fell continuously, whilst the shape of the corresponding Eh curves remained the same. During the aeration on the 6th day of the experiment the Eh values in the bulk water phase increased rapidly up to +283 mV. The Eh value in the sediment near the surface (0.1 cm) increased by 25 mV, whereas it remained unchanged in deeper layers of the sediment. After aeration, when the tube was closed hermetically, changes in the Eh values were more remarkable in bulk water and immediately below the sediment surface. The Eh value in water decreased by 300 mV during three days. In the upper 0.1 cm layer of the sediment the Eh value increased by 260 mV during two days and then dropped 350 mV during the following three days.

The data on the sulphate content in the water and sediments and their temporal changes are presented in Table 3a and Fig. 3a. The sulphate concentrations in the water and pore water near the water/sediment inter-

Table 3

Temporal changes in  $\text{SO}_4^{-2}$  concentration ( $\text{mg} \cdot \text{l}^{-1}$ ) in water (+) and sediment (-) in cores taken on 7 April (a), 15 June (b), and 17 October (c). \* Data after aeration of water (three hours on 12 April and three days on 28–30 June)

a

Date	Depth, cm								
	+11.5	+0.5	-0.5	-1.5	-2.5	-4.5	-5.5	-8.5	-14.5
8.04		32.0	34.2	25.6	16.6	11.8		11.2	7.0
12.04	65.8	60.4	60.5	33.8	24.3	15.1		17.2	7.5
14.04*	65.7	68.6	61.3	32.4	24.7	22.1	19.7	31.0	12.6
20.04		68.6				1.3	9.4		10.0

b

Date	Depth, cm									
	+7.0	+3.0	+1.0	-1.0	-2.0	-3.0	-4.0	-5.0	-9.0	-11.0
15.06	50.9	47.0	47.9	41.3	36.0	19.4	13.3	9.6	11.4	4.5
16.06	43.5	48.2	41.6	18.1						
17.06	44.6	45.8	39.5	10.6	9.3	1.3				
27.06	48.6	46.4	33.3	14.4	1.0	1.0				
30.06*	50.3	49.3	47.9	38.1	3.1	1.1				
17.08	39.8	38.8	39.0	6.5	1.9	1.8				

c

Date	Depth, cm								
	+34.0	+32.0	+2.0	+0	-2.0	-4.0	-6.0	-8.0	-10.0
17.10	64.2			66.5		50.4	43.4		
18.10	64.9		64.7	57.4	41.3	34.2	30.5	26.8	
20.10		65.3	50.9	38.0	5.6	7.0	2.5	1.8	9.6



face were  $30\text{--}35\text{ mg}\cdot\text{l}^{-1}$  and then decreased continuously up to the deepest analysed layers at a depth of 14.5 cm of sediment. During the first six days of the experiment the sulphate concentration in the upper layers increased about twofold; the increase was remarkable up to a depth of 14 cm. The aeration did not affect significantly the sulphate concentration in the water and in the sediment to a depth of 2.5 cm. In deeper layers a remarkable increase in the sulphate concentration was observed.

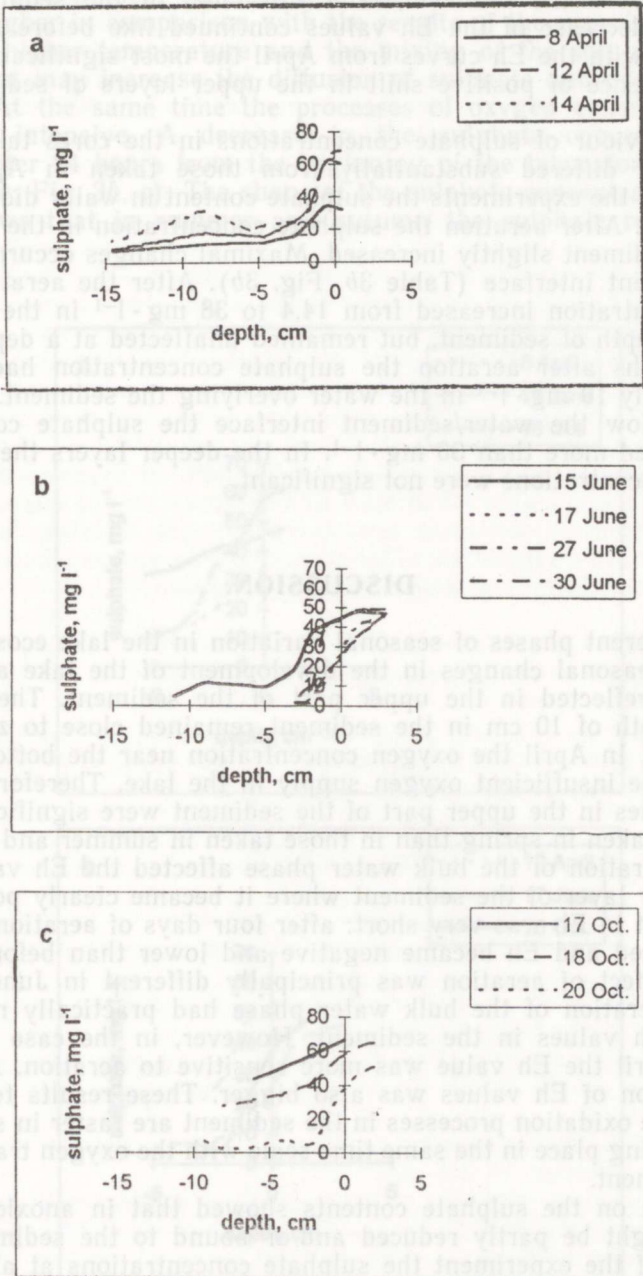


Fig. 3. Temporal changes in sulphate concentrations in the water and pore water in sediment cores taken on 7 April (a), 15 June (b), and 17 October (c). The water in the tube was saturated with air on 12 April and 28–30 June.

### Experiments in June and October

Owing to the higher content of oxygen in the water column and in pore water the Eh values of the core taken in June were higher than those taken in April up to a depth of 6–8 cm (Table 2b, Fig. 2b). During 12 days the negative values of the Eh were rather stable and then began to fall, essentially at depths of 10–14 cm in sediment. The effect of aeration was less pronounced being reflected mainly in an increase in the Eh value above the sediment/water interface. In the sediments below 1.5 cm the decrease of the Eh values continued like before aeration. In comparison with the Eh curves from April the most significant difference was the absence of positive shift in the upper layers of sediments after aeration.

The behaviour of sulphate concentrations in the cores taken in June and October differed substantially from those taken in April. In the beginning of the experiments the sulphate content in water did not change significantly. After aeration the sulphate concentration in the water overlying the sediment slightly increased. Maximal changes occurred near the water/sediment interface (Table 3b, Fig. 3b). After the aeration the sulphate concentration increased from 14.4 to 38 mg · l<sup>-1</sup> in the pore water at a 1 cm depth of sediment, but remained unaffected at a depth of 3 cm. In 1.5 months after aeration the sulphate concentration had decreased approximately 10 mg · l<sup>-1</sup> in the water overlying the sediment. At a depth of 1 cm below the water/sediment interface the sulphate concentration had decreased more than 30 mg · l<sup>-1</sup>. In the deeper layers the changes in sulphate concentrations were not significant.

## DISCUSSION

Two different phases of seasonal variation in the lake ecosystem were observed. Seasonal changes in the development of the lake are substantially well reflected in the upper part of the sediment. The Eh values below a depth of 10 cm in the sediment remained close to zero in both experiments. In April the oxygen concentration near the bottom was low reflecting the insufficient oxygen supply in the lake. Therefore the negative Eh values in the upper part of the sediment were significantly lower in the core taken in spring than in those taken in summer and autumn. In April the aeration of the bulk water phase affected the Eh value only in a thin upper layer of the sediment where it became clearly positive. This positive shift in Eh was very short: after four days of aeration all oxygen was consumed and Eh became negative and lower than before the aeration. The effect of aeration was principally different in June (Fig. 2b) when the aeration of the bulk water phase had practically no influence upon the Eh values in the sediment. However, in the case of the core taken in April the Eh value was more sensitive to aeration. As a result, the dispersion of Eh values was also bigger. These results tend to indicate that the oxidation processes in the sediment are faster in summer and they are taking place in the same time scale with the oxygen transportation to the sediment.

The data on the sulphate contents showed that in anoxic conditions sulphate might be partly reduced and/or bound to the sediment. In the beginning of the experiment the sulphate concentrations at all depths of water as well as in pore water were smaller in April than in June. Considering the data in literature (Lovley & Klug, 1986) it can be suggested that the concentration of sulphate was sufficient to initiate the bacterial reduction of sulphate in lake water (sulphate concentration was more than 30 mM). The increase in sulphate concentration in the April experi-



ment may be caused by desorption of sulphate and/or hydrolysis of sulphate esters. The importance of the oxidation of reduced sulphur compounds in both aerobic and anaerobic sediments was pointed out by several authors (Dornblaser et al., 1994; Urban et al., 1994). After two weeks from the beginning of the experiment the concentration of sulphate decreased in the sediment core. This might result from the reduction of sulphate or its sorption.

In June and October the sulphate concentrations in the sediment profile were higher in comparison with the results of the experiment made in April. The higher temperature and the mixing of the soft upper part of the sediment may increase the diffusion of sulphate and oxygen into the sediment. At the same time the processes of oxygen consumption were also more intensive. A decrease in the sulphate concentration was observed after 24 hours from the beginning of the laboratory experiment (Table 3b, c; Fig. 3b, c). The shape of the sulphate concentration curve in Fig. 4 shows that in summer and autumn the sulphate reduction was

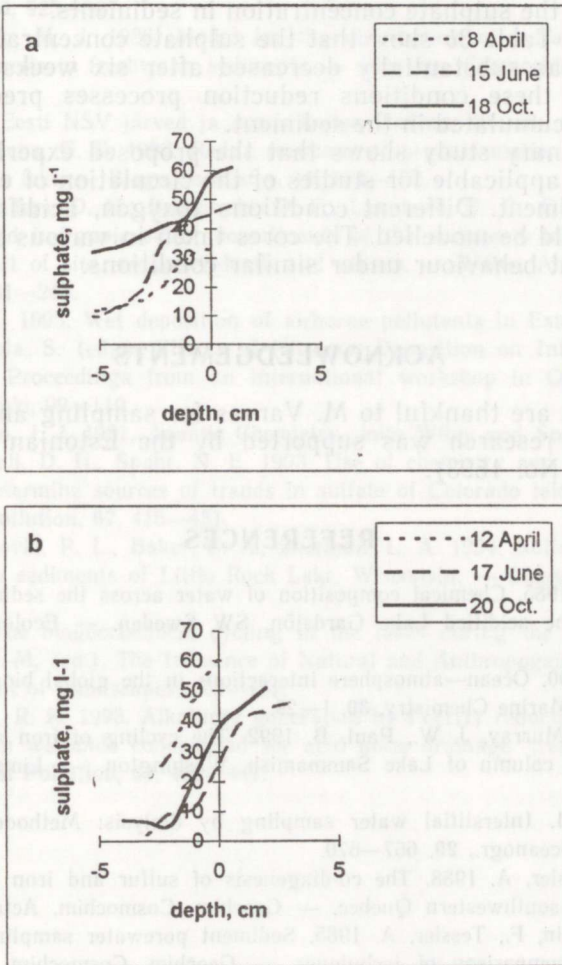


Fig. 4. Temporal changes in sulphate concentrations in the cores: a, on the second day (in April and October) and on the first day (in June) after sampling; b, after keeping the core hermetically closed in laboratory.

much faster than in spring. The data show important differences in the transformation of sulphur in cores taken during different seasonal stages of the development of the lake ecosystem.

The effect of aeration on the sulphate content was also different. In the April experiment a remarkable increase in the sulphate concentration in pore water up to a depth of 14 cm below the water/sediment interface occurred after two days of aeration. This could suggest that a large amount of sulphur was in reduced form and oxygen diffusion into the sediment was sufficient for sulphur oxidation. After the oxygen was consumed (on the sixth day) sulphate was again reduced. It should be noted that only minimal changes were observed in the first 3 cm below the interface. Unlike in April, aeration increased the sulphate concentration in June to a depth of only 1 cm below the interface; no significant change was observed deeper in the sediment. It could mean that in spite of similar conditions in laboratory, there were different forms of sulphur in the sediment depending on the season when the core was taken.

The comparisons of the sulphate concentration curves after aeration (30 June) and on the first day of the experiment (15 June) in Fig. 3*b* show that beside the oxygen content in the water there were other factors which regulate the sulphate concentration in sediments.

The data in Table 3*b* show that the sulphate concentration in the bulk water phase was substantially decreased after six weeks air-tight incubation. Under these conditions reduction processes predominated and sulphur was accumulated in the sediment.

Our preliminary study shows that the proposed experimental method and device are applicable for studies of the circulation of elements in lake water and sediment. Different conditions (oxygen, acidification, temperature, etc.) could be modelled. The cores taken in various seasons demonstrated different behaviour under similar conditions.

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