Modelling the hydrochemical status of small stratified Lake Verevi (Estonia)

Henno Starast[a*], Tõnu Möls[a], Katrin Ott[b], Aini Lindpere[a],
and Marina Haldna[a]

[a] Võrtsjärv Limnological Centre, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Riia 181, 51014 Tartu, Estonia
[b] Võrtsjärv Limnological Centre, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, 61101 Rannu, Tartumaa, Estonia; katrin.ott@emu.ee

Abstract. A survey is given of the vertical distribution and seasonal changes of the chemical composition of water in Lake Verevi. The majority of data consist of 166 to 1011 measurements per parameter from 1984–2001. Statistical analysis was performed with the SAS system, Release 8.1, using a 64-parameter linear model with independent factors 'sampling year', 'sampling day within the year', and 'sampling depth'. The depth intervals where the chemical composition of water changed significantly, confidence limits, and predicted mean values were estimated using specific contrasts tailored for the General Linear Models (GLM) procedure of the SAS program package. The hydrochemical state of the lake in summer, autumn, and winter is characterized on the basis of 18 parameters. Stratification is the strongest in summer when water temperature, dissolved oxygen, oxygen saturation, and pH decrease towards the bottom. At the same time, alkalinity, the sum of Ca and Mg, conductivity, Si, COD_{Cr}, and COD_{Mn} increase in the same direction. The most significant increase towards the bottom was shown by total P, PO_4^{3-}, total N, and NH_4^+. The concentrations of SO_4^{2-}, Cl^-, NO_2^-, and NO_3^- show relatively constant values from surface to bottom. In autumn, at the time of convective mixing, differences in the water composition from surface to bottom persist but become less pronounced. According to chemical composition, the water in L. Verevi is stratified all the year round.

Key words: Lake Verevi, water chemical composition, lake stratification, seasonal changes, regression model.

INTRODUCTION

Lake Verevi is a small but relatively deep lake in southern Estonia. The lake is thermally sharply stratified and strong gradients of chemical composition occur

---

during summer (Ott & Kõiv, 2005). It was studied extensively over a long period between 1929 and 2001. The first published chemical research about L. Verevi describes the chemical composition of lake water in 1929 (Riikoja, 1940). Mäemets (1977) provided further hydrochemical data about the lake in 1957. A research team of the Institute of Zoology and Botany at the Võrtsjärv Limnological Station studied the lake in 1984–1989. Results of this study were published in the monograph *Verevi järve seisund* (State of Lake Verevi) in 1991 (Timm, 1991). The same team continued hydrochemical studies to 2001 focusing on major ions, total soluble solids, organic matter, biogenic elements, dissolved oxygen, water temperature, and pH, as well as conductivity and transparency of water. Part of these chemical data were used in several articles in the monographic issue *Lake Verevi, Estonia – A Highly Stratified Hypertrophic Lake* (Ott & Kõiv, 2005).

The present paper aims to complement previous L. Verevi studies with a more detailed analysis of the vertical distribution of the chemical composition of water in the lake. We discuss 18 limnological parameters measured in the years 1984–2001. Seasonal variation in the chemical composition of water was established by observations carried out during summer, autumn, and winter. The study presents a statistically sound analysis of both published and new data available for L. Verevi. The mathematical approach for describing changes in the chemical composition of lake water is also new.

MATERIAL AND METHODS

Field observations and the chemical analyses of water were carried out in 1984–2001. No sampling was performed in 1987 and 1997. In most years the sampling was carried out only once in summer from 0.5 m below the surface. Detailed seasonal and vertical investigations were conducted in 1991, 1993, and 2000–2001. The majority of data consist of 166 to 1011 measurements per parameter. Altogether 18 water parameters were studied: water temperature, dissolved oxygen (O_2), oxygen saturation ($O_2\%$), water pH, alkalinity (HCO_3^-), sulphate ion (SO_4^{2-}), chloride ion (Cl^-), sum of calcium and magnesium ions ($Ca^{2+} + Mg^{2+}$), conductivity (EC), total phosphorus (TP), ortophosphate ion (PO_4^{3-}), total nitrogen (TN), nitrate ion (NO_3^-), nitrite ion (NO_2^-), ammonium ion (NH_4^+), silicon (Si), and chemical oxygen demand (COD_{Cr} and COD_{Mn}).

The main methods of chemical analysis used since 1984 have not been changed. Water temperature and O_2 concentration were measured with a thermooximeter. Oxygen saturation for different water temperatures was calculated according to Hellat et al. (1986). The pH of water was measured with a pH-meter. The concentrations of HCO_3^- and Cl^- were determined titrimetrically and mercuri-metrically, respectively (Gubachek & Artamoshkina, 1977). $Ca^{2+} + Mg^{2+}$ was determined complexometrically using Na_2EDTA (Alekin, 1959). EC was measured with a JENWAY Model 4150 Conductivity Meter (Fall, 1996). The

content of TP was determined after persulphate oxidation as PO_4^{3-}. The content of PO_4^{3-} was determined with the molybdene blue method (Reports…, 1977). NO_3^- was reduced to NO_2^-. Sulphanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride were used for the determination of NO_2^- (Koroleff, 1982). The content of TN was determined after persulphate oxidation as NO_2^-. Since 1995 TN was determined after persulphate digestion as NO_3^-. The content of NO_3^- was measured using second-derivative UV spectroscopy (Crumpton et al., 1992). The concentrations of NH_4^+ and Si were determined with indophenol blue and silico-molybdic blue method, respectively (Hansen & Koroleff, 1999). Chemical analyses of different fractions of organic matter by means of dichromate and permanganate oxidizability were performed titrimetrically using standard methods recommended by Alekin (1959).

For statistical analyses water variables, except for pH and water temperature, were $\log_2$ transformed to normalize their residual distribution with respect to the used statistical model. Zero values were replaced by small non-zero values fitted individually for each variable. Thus, all the calculated means, except for pH and temperature, are geometric means. Before the analysis, data values deviating from the value predicted by the model more than by 2.7 in Student's scale were dropped. This filtering eliminated 0–1% of the data values, depending on the variable.

Statistical analysis was based on a 64-parameter linear model using the SAS/STAT software, Release 8.1. The main working procedure was the general linear models procedure GLM. Independent variables (factors) were sampling year (1984–2001), sampling day within the year, and sampling depth (0–9 m). Regression function for the depth-dependence was modelled as a linear combination of five Gaussian density curves all having standard deviation $\sigma = 3$ and mean values −2, 1, 4, 7, and 10. This method is described in detail in Möls (2005). Due to the multiple interaction terms in the model, the depth function depends on the year and day. For details of the model see Appendix 1.

After estimating its parameters from the data, the model was used as a big formula (regression function). It served for calculating the values of water variables for different times and depths. Graphs illustrating how the water variable depends on depth were calculated immediately from this formula. The related statistical procedure GLM provided also confidence limits for graphs. These limits characterize how precise the predicted (estimated) value is: the real mean value of the modelled variable lies between these limits with a probability of 95%. In addition, using derivatives of the regression function as estimable contrasts, the depth intervals where the change of the variable was statistically significant were established. The underlying statistical method is described in detail in Möls (2005).

To find the mean value of a water variable for a given depth interval, this interval was subdivided into 10-cm layers and for each layer the mean value was calculated from the model. After that all these partial means were averaged.

RESULTS

Table 1 presents the mean values of limnological parameters in the upper water layer (0–3 m), in the middle layer (3–6 m), in the lower layer (6–9 m), and in the whole water column (0–9 m) in different seasons. The mean composition of lake water in summer is characterized by the status on the 200th day of the year (19 July 2000). The autumn status is calculated for the 320th day (16 November 2000), and for winter the means are estimated for the 60th day (1 March 2001).

The water temperature varied from 0.1 to 25.8 °C in 1984–2001. The mean temperature ranged from 13.4 °C in summer to 3.2 °C in winter. Lake water showed thermal stratification all the year round (see Figs 1–3). The strongest stratification occurred in summer when temperature decreased significantly in the depth interval from 1.4 to 7.2 m. The mean temperature ranged from 20.5 °C in the upper layer (0–3 m) to 6 °C in the lower layer (6–9 m). Towards the autumn, water is cooling down, especially in the upper 3 m layer. On 16 November the mean temperature in this layer was the same as in the deepest 1 m layer (4.6°). As calculated for 16 November 2000, the temperature of the water column was more uniform than five or more days earlier or later. Therefore, the mean composition of lake water in autumn is characterized by the status on 16 November; after that the winter stratification will develop. Cooling of water continues in the upper 4 m layer. By 6 December the water in this layer had cooled down to 0 °C. In the lower isothermal layer (6–9 m) the temperature had risen to 6 °C by this time due to heat release in the oxidation of organic matter. The temperature of this deep layer decreases during the winter. By 1 March 2001, water temperature had decreased below 4 °C in the whole water column. At that time a stratification characteristic of winter is still observed in the lake: temperature increases
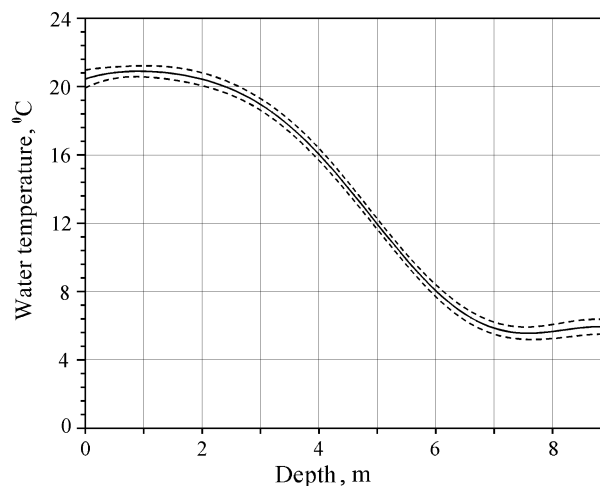

Fig. 1. Thermal stratification of L. Verevi referenced to 19 July 2000.
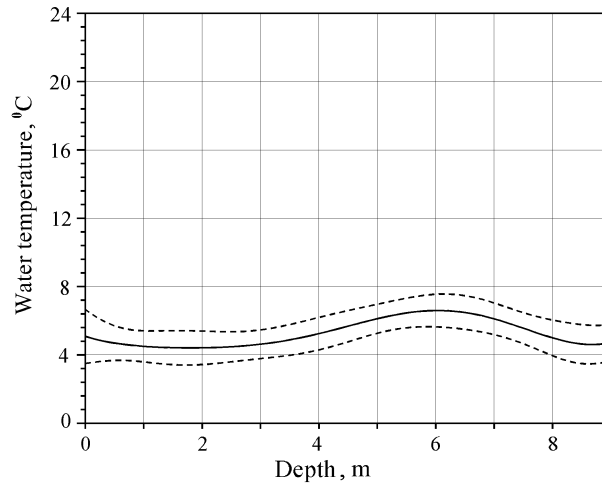
Fig. 2. Thermal stratification of L. Verevi referenced to 16 November 2000.
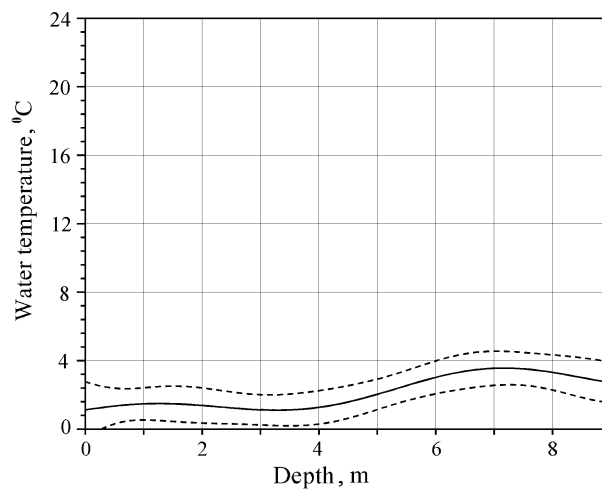

Fig. 3. Thermal stratification of L. Verevi referenced to 1 March 2001.

towards bottom. The mean temperatures of the 3-m upper, middle, and lower water layers were 1.3, 1.8, and 3.3 °C, respectively. Therefore, the mean composition of lake water in winter can be characterized by the status on 1 March. In the second half of April, after the melting of the ice, the summer stratification starts to develop.

The water pH fluctuated from 6.30 to 9.12 in 1984–2001 decreasing towards the bottom ($P < 0.0001$). The near-bottom water was slightly acidic. The surface water was slightly alkaline or at times strongly alkaline in summer. The pH stratification was most strongly expressed in summer (see Fig. 4). A pH maximum
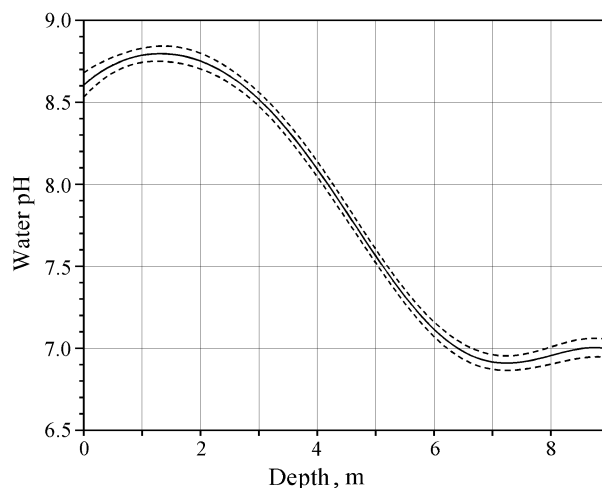
Fig. 4. Stratification of water pH in L. Verevi referenced to 19 July 2000.

was established at a depth of 1 m. Further, from 1.6 m to 7 m, the pH diminished sharply. The mean pH value was at maximum (8.72) in the upper water layer, and at minimum (6.97) in the lower water layer. In autumn, the water pH was lower than in summer, the mean pH being in the upper layer 7.81 and in the lower layer 7.21. Between 0 and 4.6 m the pH values were relatively constant but from 4.8 m to the bottom the pH showed a sharp decrease. In winter a pH minimum of the water column was registered. The vertical decline of the pH was significant between 1.8 and 4.4 and 7.8 and 8.8 m. The mean pH of the upper water layer was 7.6 and of the lower water layer 7.10. The dynamics of the pH showed seasonal variation, decreasing from summer towards winter ($P < 0.0001$). These changes were the most pronounced in the upper water layer (Table 1).

The concentration of O_2 in water varied from 0 to 23.3 mg L^{-1}; the relative content varied between 0% and 217% in 1984–2001. The oxygen regime in the lake is poor. In summer there occurred a strong stratification of the O_2 content (see Fig. 5) and O_2%. The vertical distributions of O_2 and O_2% were quite similar. A relatively high and uniform content of O_2 was registered in the epilimnion up to 2.4 m. Fast oxygen consumption started already from 2.6 m. At a depth of 6 m, O_2 was practically absent and the water was anaerobic. At the same time the mean O_2 content was the highest, 10.6 mg L^{-1} (113%), in the upper water layer. In the middle water layer the mean O_2 was negligible (1.5 mg L^{-1}; 17%). In the deeper water the O_2 content diminished to zero. In autumn the oxygen loss was not so substantial as in summer. The O_2 content was quite even down to 5 m but from 5.2 m (O_2% from 4.6 m) it decreased sharply (see Fig. 6). The mean O_2 content in the upper layer was 9.3 mg L^{-1} (68%), in the middle layer 7.8 mg L^{-1} (61%), and in the lower layer 0.8 mg L^{-1} (9%). In winter, under the ice, oxygen deficit was observed already in surface water: the mean O_2

92

Table 1. Mean values of water parameters calculated from the basic model for different layers and reference times. All means are geometric except for pH and water temperature. The reference times are: Su – 19 July 2000, Au – 16 November 2000, Wi – 1 March 2001. For geometric means, the upper and lower standard confidence limits are Mean × SE and Mean/SE, respectively. For pH and water temperature the confidence limits are Mean + SE and Mean – SE

| Parameter	Season	0–3 m		3–6 m		6–9 m		0–9 m	
		Mean	SE	Mean	SE	Mean	SE	Mean	SE
Water temperature, °C	Su	20.45	0.14	13.8	0.14	6.05	0.15	13.45	0.10
	Au	4.56	0.37	5.66	0.37	5.54	0.37	5.25	0.23
	Wi	1.34	0.39	1.77	0.39	3.28	0.41	2.13	0.24
O_2, mg L^{-1}	Su	10.87	1.05	1.51	1.06	0.03	1.06	0.76	1.04
	Au	8.96	1.17	7.71	1.17	0.92	1.17	4.02	1.10
	Wi	1.74	1.24	1.33	1.31	0.04	1.24	0.47	1.16
O_2 %	Su	113	1.05	17.0	1.05	0.49	1.05	9.89	1.03
	Au	68.4	1.15	61.3	1.14	8.91	1.15	33.6	1.09
	Wi	19.7	1.21	5.71	1.20	1.30	1.18	5.28	1.12
pH	Su	8.72	0.02	7.82	0.02	6.97	0.02	7.83	0.01
	Au	7.81	0.04	7.79	0.05	7.21	0.05	7.60	0.03
	Wi	7.6	0.05	7.41	0.05	7.10	0.05	7.37	0.03
HCO_3^-, meq L^{-1}	Su	3.57	1.01	4.79	1.01	6.83	1.01	4.89	1.01
	Au	4.00	1.06	3.91	1.04	7.37	1.07	4.85	1.04
	Wi	4.78	1.11	3.82	1.09	4.98	1.11	4.49	1.07
SO_4^{2-}, meq L^{-1}	Su	0.56	1.02	0.56	1.01	0.56	1.03	0.56	1.01
	Au	0.53	1.07	0.53	1.04	0.63	1.11	0.56	1.09
	Wi	0.82	1.18	0.55	1.11	0.64	1.13	0.66	1.10
Cl^-, meq L^{-1}	Su	0.73	1.03	0.83	1.02	1.13	1.04	0.88	1.02
	Au	0.78	1.12	0.77	1.07	1.14	1.09	0.88	1.06
	Wi	0.50	1.22	0.61	1.16	0.68	1.18	0.59	1.14
$Ca^{2+} + Mg^{2+}$, meq L^{-1}	Su	4.3	1.01	5.14	1.01	6.42	1.01	5.21	1.00
	Au	4.79	1.03	4.63	1.02	7.20	1.03	5.41	1.02
	Wi	4.83	1.10	6.74	1.13	7.54	1.27	6.27	1.13
Conductivity, $\mu S\, cm^{-1}$	Su	475	1.00	550	1.01	746	1.00	579	1.00
	Au	504	1.01	487	1.01	692	1.01	553	1.01
	Wi	538	1.01	551	1.01	638	1.01	574	1.01
Total P, mgP m^{-3}	Su	35.4	1.07	124	1.07	1171	1.11	172	1.05
	Au	38.2	1.46	56.6	1.26	1423	1.34	144	1.23
	Wi	127	1.93	67.3	1.66	227	1.80	123	1.57
PO_4^{3-}, mgP m^{-3}	Su	1.58	1.16	8.51	1.15	1100	1.24	24.2	1.11
Total N, mgN m^{-3}	Su	852	1.06	1643	1.05	9780	1.09	2380	1.04
	Au	934	1.33	1186	1.19	15000	1.25	2530	1.17
	Wi	1008	1.66	1402	1.47	1285	1.56	1221	1.41
NO_3^-, mgN m^{-3}	Su	1.09	1.04	1.12	1.04	1.04	1.05	1.08	1.03
NO_2^-, mgN m^{-3}	Su	0.98	1.06	0.95	1.05	1.14	1.08	1.02	1.04
NH_4^+, mgN m^{-3}	Su	1.00	1.42	9.35	1.34	5780	1.68	37.3	1.28
Si, mg m^{-3}	Su	455	1.12	1991	1.10	7380	1.21	1880	1.08
COD_{Cr}, mgO L^{-1}	Su	29.4	1.02	35.1	1.02	43.5	1.03	35.5	1.01
	Au	18.9	1.12	21.3	1.07	41.5	1.09	25.5	1.06
	Wi	53.0	1.27	29.3	1.17	25.0	1.20	33.8	1.16
COD_{Mn}, mgO L^{-1}	Su	10.1	1.02	12.0	1.02	16.3	1.03	12.5	1.01
	Au	7.32	1.13	8.25	1.08	24.3	1.10	11.3	1.07
	Wi	10.7	1.27	8.11	1.18	7.85	1.20	8.8	1.16
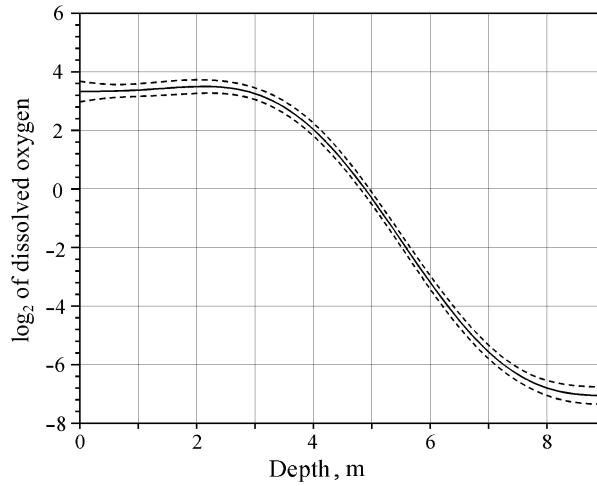
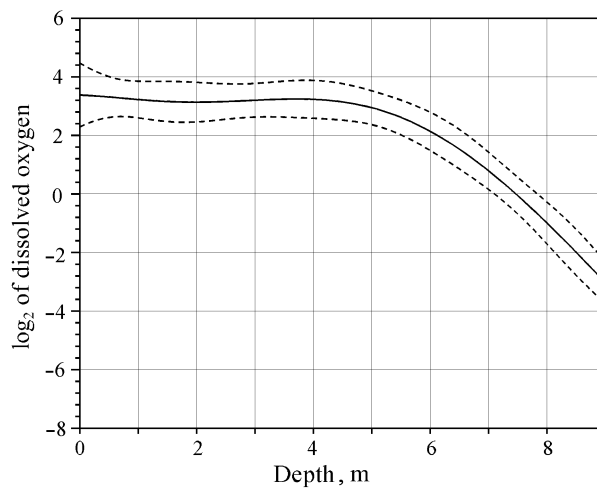**Fig. 5.** Vertical distribution of dissolved oxygen in L. Verevi referenced to 19 July 2000.

Fig. 6. Vertical distribution of dissolved oxygen in L. Verevi referenced to 16 November 2000.

in the upper water layer (0–3 m) was 1.1 mg L^{-1} (20%) only (see Fig. 7). The concentration of oxygen exhibits a very distinct seasonal cycle. A strong thermal stratification develops in summer. With the onset of stratification, O_2 in the hypolimnion is rapidly utilized in the oxidation of organic matter. The cooling period starts with a slow convective erosion of stratification and a subsequent deepening of the thermocline. The vertical gradient of O_2 during the period of convective mixing is the consequence of higher consumption in the deeper layers compared with the supply by vertical transport.
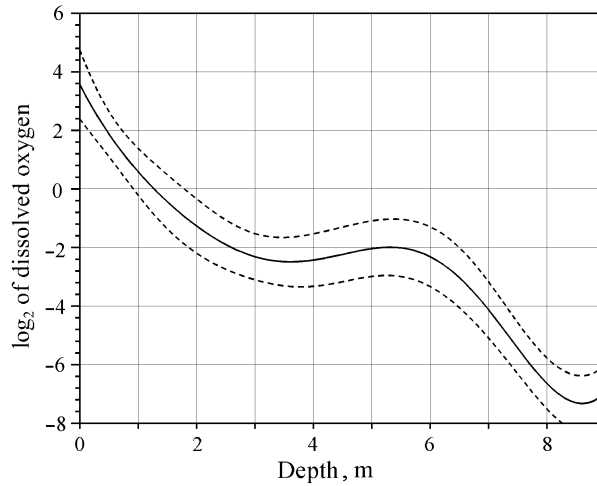
Fig. 7. Vertical distribution of dissolved oxygen in L. Verevi referenced to 1 March 2001.

The concentration of HCO_3^- varied in quite a broad range, between 2.80 and 8.25 meq L^{-1}, in 1984–2001. It was tested statistically that the HCO_3^- content increased $(P < 0.0001)$ towards the lake bottom. In summer, stratification was clear and strong (see Fig. 8). From surface down to 1.2 m, the HCO_3^- content was constant. Deeper, between 1.4 and 6.8 m, it increased a great deal, approximately twofold. At the same time, the mean content of HCO_3^- in the upper water layer was 3.57, in the middle layer 4.79, and in the lower layer 6.83. meq L^{-1}. In autumn and winter HCO_3^- underwent undulating changes from surface to bottom. In autumn HCO_3^- was constant down to 1.6 m. From 1.8 to 3.2 m it showed a decrease. The most long lasting and sharpest increase compared with summer occurred in the deeper layer, between 4 and 6.6 m. In winter a weak decrease in HCO_3^- was noted between 4 and 4.6 m. A long-term increase in HCO_3^- occurred from 6.4 to 8.6 m. Compared with the data for summer and autumn, the differences in the HCO_3^- content between different water layers decreased in winter. Statistically, no regular seasonal changes were detected in the HCO_3^- content. The mean HCO_3^- concentration in the water column varied relatively little, between 4.49 and 4.89 meq L^{-1} (Table 1).

The concentration of SO_4^{2-} varied between 0.21 and 2.91 meq L^{-1} in 1988–2001. There occurred no stratification in the SO_4^{2-} content. In summer the vertical distribution of the SO_4^{2-} content was even. The mean SO_4^{2-} content of different water layers varied between 0.56 and 0.57 meq L^{-1}. In autumn the SO_4^{2-} content increased while in winter it decreased slightly from surface to bottom. In winter the highest mean value of SO_4^{2-} (0.84 meq L^{-1}) was recorded in the upper water layer. The mean SO_4^{2-} content in the water column was the same in summer and autumn, but slightly higher in winter (0.66 meq L^{-1}, Table 1).
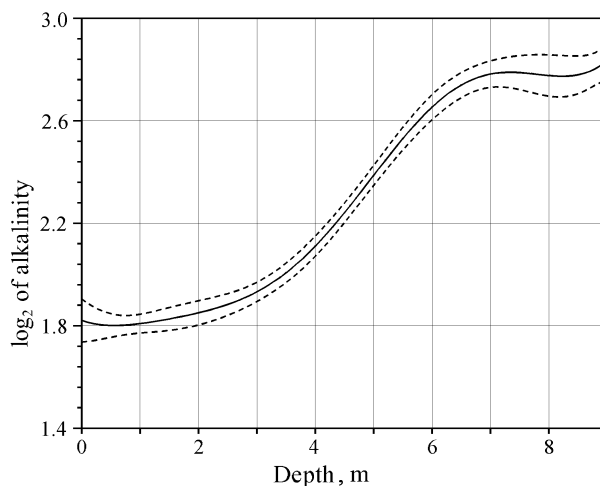
95

Fig. 8. Stratification of alkalinity in L. Verevi referenced to 19 July 2000.

The concentration of Cl^- varied between 0.21 and 1.79 meq L^{-1} in 1984–2001, increasing towards the bottom ($P < 0.0001$). The Cl^- content was slightly but significantly stratified. In summer Cl^- increased from 0.6 to 1 m and from 4 to 6.6 m. The mean Cl^- content in the upper layer was 0.73, in the middle layer 0.83, and in the lower layer 1.14 meq L^{-1}. In autumn the Cl^- content was constant from surface water to a depth of 6 m. Further, between 6.2 and 6.6 m, Cl^- showed an increase. The mean Cl^- content in the water column was the same as in summer. In winter a decrease in Cl^- took place from 0.2 to 1 m, while an increase was recorded at 2.2–3.4 and 7.2–8.2 m. Regardless of these increases, in winter the content of Cl^- was lower in all water layers compared with summer and autumn (Table 1). The Cl^- content revealed no regular seasonal changes ($P > 0.03$).

The concentration of $Ca^{2+} + Mg^{2+}$ varied between 3.10 and 7.10 meq L^{-1} in 1991–2001, increasing towards the bottom ($P < 0.0001$). The stratification was well expressed in different seasons. In summer a long-term significant increase in $Ca^{2+} + Mg^{2+}$ occurred from 2.6 to 6.4 m. Close to the bottom, at 7.7–8 m, the content decreased slightly. In the upper water layer the mean content of $Ca^{2+} + Mg^{2+}$ was 4.29 meq L^{-1}. In the lower layer it was higher, 6.42 meq L^{-1}. In autumn the content of $Ca^{2+} + Mg^{2+}$ was higher compared with summer. The vertical curve had a wavy form. The first significant rise was registered at 1.2 m, the second, a larger one, between 5.2 and 7.6 m. Between 2.6 and 3.8 m the content of ions decreased. In winter, the $Ca^{2+} + Mg^{2+}$ content in water was the highest (Table 1). The vertical distribution was the most uniform, however, between 2.2 and 3.6 m and a slight but significant increase was observed there. Statistically, no regular seasonal variation was detected in the $Ca^{2+} + Mg^{2+}$ concentration ($P > 0.8$).

96

Conductivity (EC) varied between 368 and 1050 μS cm^{-1} in 1996–2001. It increased towards the bottom ($P < 0.0001$). Seasonal changes in the stratification of EC were very clearly expressed. In summer, EC decreased slightly but significantly in the epilimnion, down to 2 m. The sharpest and the most long-term increase in EC was registered in the metalimnion, from 2.6 to 7.6 m. A mean EC minimum (476 μS cm^{-1}) was registered in the upper water layer and a mean EC maximum (746 μS cm^{-1}) in the lower layer. In autumn the stratification of EC was as strong as in summer. Between 1.8 and 2.8 m, a slight decrease in EC was obvious. The largest increase in EC occurred in autumn deeper than in summer, between 4.8 and 8.8 m. In the upper layer the mean EC was higher (504 μS cm^{-1}) in autumn than in summer (476 μS cm^{-1}); in the lower layer it was lower (692 μS cm^{-1}) in autumn than in summer (746 μS cm^{-1}). In winter EC was constant down to 5 m, and showed slightly but significantly higher values at 5.2–9 m. The mean EC was higher in the upper water layer and lower in the lower layer than in summer and autumn (Table 1).

The concentration of TP varied in a broad range, from 20 to 2900 mgP m^{-3} in 1984–2001. The water was extremely rich in TP in anaerobic conditions, in the lower water layer. The vertical distribution of the TP content varied seasonally. In summer the stratification was the strongest (see Fig. 9). The TP concentration increased from surface to bottom in an undulating mode. A slight but significant increase was revealed down to 1.2 m, while a sharp continuing increase occurred between 3.2 and 6.8 m, followed by a slight decrease between 7.6 and 8 m. The mean TP content was the lowest (35 mgP m^{-3}) in the upper water layer, higher in the middle layer (124 mgP m^{-3}), and very high in the lower layer (1170 mgP m^{-3}). In autumn, the TP content in the upper water layer had slightly risen. The metalimnion
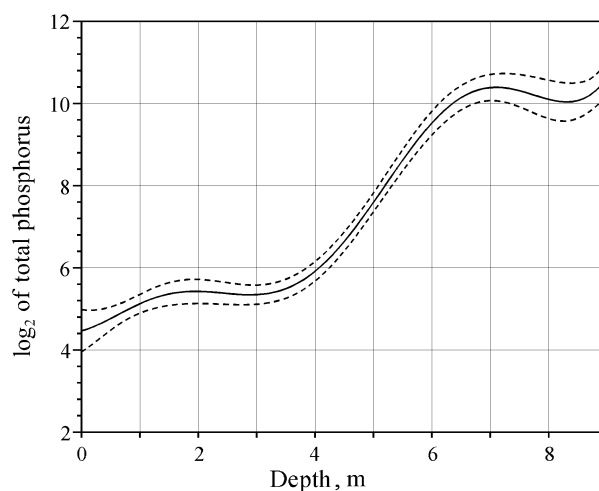

Fig. 9. Vertical distribution of total phosphorus in L. Verevi referenced to 19 July 2000.

had shifted deeper and a considerable increase in TP was recorded at a depth of 4–7 m. In winter the TP content increased in the upper water layer and decreased in the lower layer, while anaerobic hypolimnetic water with a high TP content had mixed with the water of the upper layer. In winter an extremely high TP concentration was registered in the upper layer (127 mgP m^{-3}, Table 1). Proceeding from the classification of Estonian small lakes, based on TP concentration, the state of L. Verevi is close to hypertrophic. The mean content of TP for hyper-trophic small lakes at a depth of 0–1 m is 56–171 mgP m^{-3} (Milius et al., 1991).

The concentration of PO_4^{3-} varied from 0 to 2900 mgP m^{-3}, i.e. in an almost the same range as TP in 1991–2001. The vertical distribution of PO_4^{3-} and TP was quite similar. In summer a slight increase in PO_4^{3-} was observed down to 1.4 m. Deeper, in the metalimnion at 3.2–6.6 m, PO_4^{3-} showed a sharp increase. A weak decrease followed in the hypolimnion between 7.8 and 8.2 m. The mean content of PO_4^{3-} was the lowest (1.45 mgP m^{-3}) in the upper water layer. A considerably higher value of PO_4^{3-} was registered in the middle layer (7 mgP m^{-3}) and a very high value (1060 mgP m^{-3}) in the lower layer. By autumn the PO_4^{3-} content had increased in the upper two water layers. In the hypolimnion, the PO_4^{3-} content was also high (Table 1). By winter the difference in PO_4^{3-} concentrations between different water layers had decreased and the PO_4^{3-} content was higher in the upper layer and lower in the lower layer compared with summer and autumn (Table 1).

The concentration of TN varied in a broad range, from 400 to 19 000 mgN m^{-3} in 1984–2001, increasing towards the bottom ($P < 0.0001$). The stratification of TN proceeded in an undulating mode (see Fig. 10). In summer the TN content increased down to 1.2 m, and decreased between 2.2 and 2.6 m. Further, from
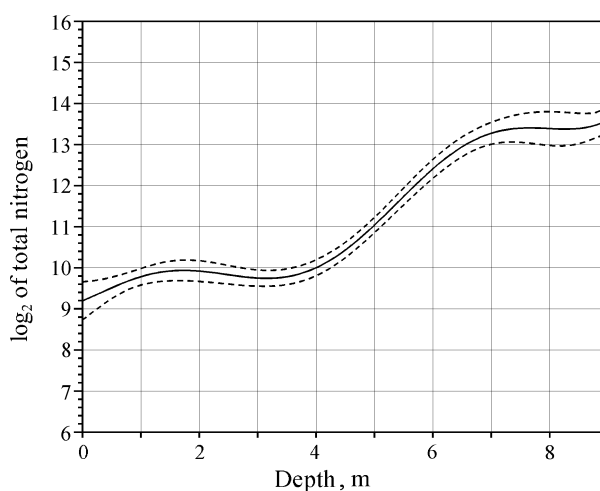

Fig. 10. Vertical distribution of total nitrogen in L. Verevi referenced to 19 July 2000.

3.6 m to 7 m, a significant continuous increase in TN was evident. At the same time, the mean TN content in the upper water layer was 852 mgN m^{-3}, in the middle layer 1643 mgN m^{-3}, and in the lower layer 9780 mgN m^{-3}. In autumn a short decrease in TN in the epilimnion was registered at 1.8–2.4 m. A long-term sharp increase proceeded deeper compared with summer, to 4–6.8 m. In winter a sharp increase in TN was registered deeper than 8 m. In winter the TN content was higher in the upper water layer and lower in the lower layer compared with summer and autumn (Table 1).

The content of NO_3^- varied in a very large range, from 0 to 2700 mgN m^{-3} in 1991–2001. No NO_3^- is found in anaerobic water that contains hydrogen sulphide. In summer 2000 aerobic water contained a few milligrams of nitrate-N per cubic metre, in autumn up to 15 mgN m^{-3}. The NO_3^- content increased sharply in winter. In late winter 2001 (29 March) the concentration of NO_3^- was 1000 mgN m^{-3} under the ice at a depth of 0.5 m. The NO_3^- concentration decreased sharply from surface to bottom. On this date the content of NO_3^- at a depth of 8 m was 4 mgN m^{-3}.

The content of NO_2^- varied from 0 to 125 mgN m^{-3} in 1998–2001. In summer NO_2^- is absent from anaerobic water and sometimes from aerobic water. Its mean content in summer was 1 mgN m^{-3}. In autumn the NO_2^- content in aerobic water increased up to a few milligrams per cubic metre, while it was absent from anaerobic water. In winter anaerobic water may exceptionally contain NO_2^-. For example, on 29 March 2001 the NO_2^- content was the highest (53 mgN m^{-3}) in the anaerobic middle water layer. At the same time, the content in surface water was 13 mgN m^{-3}. In spring the NO_2^- concentration decreases in the upper water layer, increases in the middle layer, and is absent from near-bottom anaerobic water. In 2001, three weeks after the melting of the ice, NO_2^- had disappeared from the water of the upper layer. In the middle layer NO_2^- showed an increasing trend during two weeks after the melting of the ice, attained a maximum value (131 mgN m^{-3} on 30 April), and disappeared thereafter from water within two weeks.

The content of NH_4^+ varied within very large limits, between 0 and 10 100 mgN m^{-3} in 1996–2001. Its concentration increased significantly towards the bottom ($P < 0.0001$). The mean content of NH_4^+ in the upper water layer was 1 mgN m^{-3} in summer. The concentration increased very sharply from aerobic water to anaerobic water, which contains hydrogen sulphide. In the lower anaerobic water layer the mean content of NH_4^+ was 5780 mgN m^{-3} in summer. In autumn, during the period of convective mixing, the NH_4^+ content increased in near-surface aerobic water but its level there was much lower compared to near-bottom anaerobic water. Such distribution of NH_4^+ persisted until the melting of the ice. Further on, the NH_4^+ content in the illuminated water layer decreased to a few milligrams of ammonium-N per cubic metre.

The concentration of Si varied within a broad range, from 0 to 10 800 mgSi m^{-3} in 2000–2001. Towards the bottom, Si showed increasing concentrations

($P < 0.0001$). The stratification of Si proceeded in an undulating mode. In summer a significant sharp increase in the Si content occurred between 2.7 and 6.2 m. The lowest mean concentration of Si (455 mgSi m^{-3}) was registered in the upper water layer (Table 1). In autumn a significant short-term increase in Si took place deeper (between 5.8 and 6.6 m). The Si content of the upper water layers was higher in autumn than in summer.

Both COD_{Cr} and COD_{Mn} varied in a broad range, from 17 to 65 mgO L^{-1} and from 7.3 to 28 mgO L^{-1}, respectively, in 1984–2001. In summer and autumn the content of organic substances increased towards the bottom. The stratifications of COD_{Cr} and COD_{Mn} (see Fig. 11) were quite similar. In summer, there was a long significant increase in COD_{Cr} and in COD_{Mn} between 3.4 and 6.2 m. The mean value of COD_{Cr} in the upper water layer was 29 mgO L^{-1}, in the middle layer 35 mgO L^{-1}, and significantly higher in the lower layer of water, 44 mgO L^{-1}. The mean COD_{Mn} values in the upper and middle layers were roughly equal, 10 and 12 mgO L^{-1}, respectively. In the lower water layer COD_{Mn} showed higher values, the mean value being 16 mgO L^{-1}. In autumn the vertical distributions of COD_{Cr} and COD_{Mn} proceeded in a wavy mode. The mean of COD_{Cr} was low in the upper layer (19 mgO L^{-1}) and high (42 mgO L^{-1}) in the lower layer. The mean COD_{Mn} was low (7–8 mgO L^{-1}) in the middle and upper layers. Very high COD_{Mn} values were recorded in the lower layer (24 mgO L^{-1}). In winter, owing to the mixing of water, COD_{Cr} as well as COD_{Mn} had increased in the upper layer and decreased in the lower layer with COD_{Cr} being very high in the upper layer of water. The mean COD_{Mn} of different layers varied in a small range, from 8 to 11 mgO L^{-1} (Table 1).
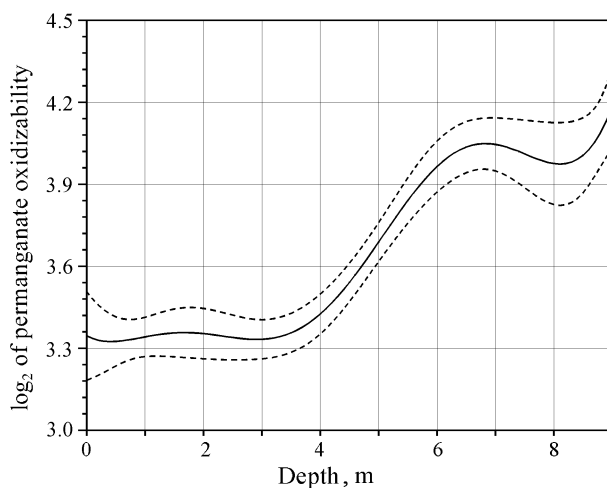

Fig. 11. Vertical distribution of permanganate oxidizability in L. Verevi referenced to 19 July 2000.

DISCUSSION

Stratification of water temperature

In L. Verevi the thermal stratification of water is the strongest in summer. According to Mäemets et al. (1991), complete mixing of water in spring takes commonly place in April. In 2000 and 2001, a stratification that is typical for summer developed in April. On 16 April water temperature in the lake was quite uniform being 4.4 °C at the surface and 3.8 °C at the bottom at a depth of 9 m. On 24 April 2001 the water temperature near the surface (16.4 °C) was 12.1 °C higher than at the bottom at a depth of 9.5 m (4.3 °C). On the basis of the measurements it can be hypothesized that temperature in the water column was also uniform in the first half of April.

The thermal stratification that developed in the second half of April lasted until November. When in May the thermocline was located at a depth of 3–6.5 m then with the cooling of water in autumn it had fallen to a depth of 6.5–8.5 m by 16 October 2000. Mäemets et al. (1991) suppose that in autumn the complete mixing of water occurs in October. On 23 October 2000 a weak thermal stratification was registered in the lake. The temperature gradient from 7 to 8 m was 1.4 °C. Water temperatures calculated for 27 October and 6, 11, and 16 November 2000 show that lake water was thermally not completely mixed. On 16 November the temperature in the water column was more uniform than earlier. The temperatures of the near-surface 3-m water layer and of the near-bottom 1-m layer were similar (4.6°). The temperature of the medium water layer was higher. It is not clear if water was completely mixed in the second half of November. On 4 December water was completely mixed to a depth of 8.5 m. In winter the water in the surface layer cools down and a reversed thermal stratification develops, which is weaker than the summer stratification. In winter 2001 the thermocline was located at a depth of 0–1.5 m. In this layer the water temperature was lower (2.1–3.5 °C) than at the bottom (3.7–4.0 °C).

In 2000 and 2001 the lake was thermally stratified from the second half of April to mid-November and from December to late March. A complete stratification of the lake either did not take place, or it occurred in the first half of April or in the second half of November.

Dissolved oxygen and pH

According to O_2, O_2%, and pH the lake is stratified all the year round. After the melting of the ice, summer stratification starts to set in before the water is completely mixed. For example, in spring 2001, three days after the melting of the ice, water was mixed to a depth of 5 m; O_2, O_2%, and pH were practically constant. At a depth of 8–9 m water was anaerobic like in winter. In spring 2000, nine days after the melting of the ice, the water temperature was 4 °C in the hypolimnion but 16 °C in the epilimnion. A metalimnic maximum of O_2 and pH

occurred as a result of photosynthesis, while in the hypolimnion the water was anaerobic. Occurrence of a metalimnic maximum of O_2 and pH in L. Verevi was common in spring and in the first half of summer until late July. At that time, water temperature started to fall at a larger or the same depth as O_2 and pH. In autumn, when water is cooling down, the thermocline drops deeper compared with the metalimnion of O_2 and pH. There are not yet data that would confirm the complete mixing of water from surface to bottom. According to the available data, the composition of water and its temperature from surface to bottom were the most uniform in early December. Yet even then the values of O_2 and pH were much lower at a depth of 8.5–9.5 m than above this layer. During winter pH and, especially, O_2 decreased in the whole water column. For example, on 29 March 2001 the water was anaerobic only to a depth of 2 m.

Major ions and EC

Lake Verevi is a hard-water lake. The ionic composition of water is dominated by hydrogen carbonate and $Ca^{2+} + Mg^{2+}$ ions. In summer the mean alkalinity (HCO_3^-) in the upper (0–3 m) layer of water was 3.57 meq L^{-1}. In comparison with other Estonian lakes, the content of mineral substances is relatively high. The content of mineral substances dissolved in water is characterized by major ions (HCO_3^-, SO_4^{2-}, Cl^-, $Ca^{2+} + Mg^{2+}$) and EC. In comparison with the variation of the concentration of gases or biogenic elements, the concentration of mineral substances varied both in the water column and seasonally to a smaller degree. The SO_4^{2-} concentration is practically constant in the water column and in different seasons. Changes in the Cl^- level are insignificant compared with changes in HCO_3^- and $Ca^{2+} + Mg^{2+}$. The values of major ions (except for SO_4^{2-}) and EC increase towards the bottom and are at maximum in the lower water layer. The lowest values of all above-mentioned parameters were observed in the upper water layer in summer. In autumn the values of these parameters increased in the upper water layer and decreased in the middle layer. This was caused by the mixing of near-surface water, poor in mineral substances, with the water of the lower layer containing more mineral substances. In winter the values of all parameters were the highest in the lower water layer, which is enriched with substances dissolved in mud.

Biogenic elements

The content of biogenic elements in Lake Verevi varied in a broad range both in the water column and in different seasons. The concentrations of TP, PO_4^{3-}, TN, NH_4^+, and Si depended significantly on depth ($P < 0.0001$). In summer NO_2^- and NO_3^- were almost absent from surface to bottom. In the upper water layer the concentrations of PO_4^{3-} and NH_4^+ were low at that time too. In the epilimnion the mineral compounds of phosphorus and nitrogen are utilized in

photosynthesis for protein synthesis. In anaerobic conditions, bacterial nitrification of NH_4^+ to NO_3^- and NO_2^- ceases and the adsorptive capacity of the anoxic bottom sediments is greatly reduced, which may cause a marked release of NH_4^+ from the sediments (Wetzel, 1983). At the same time NH_4^+ is generated also by heterotrophic bacterial decomposition of organic matter settled into the anoxic hypolimnion.

In summer the stratification of biogenic elements was the strongest. The stratification of TP, PO_4^{3-}, TP, NH_4^+, and Si proceeds from the epilimnion, where the concentrations are the lowest, to the hypolimnion, where the concentrations are the highest. The values of these parameters increased statistically significantly in the metalimnion. In summer and autumn, PO_4^{3-} accounted for the largest share of TP in the hypolimnion. In summer the concentrations of NO_3^- and NO_2^- were uniform and very low from surface to bottom (Table 1). These compounds were often absent from the hypolimnion. In autumn all biogenic elements were strati-fied. Compared with summer, the concentrations of TP, PO_4^{3-}, TN, NH_4^+, and Si had increased in the upper 3-m layer and decreased in the middle 3-m layer during the period of convective mixing. The concentrations of NO_2^- and NO_3^- had increased in the whole aerobic layer. In the anaerobic layer, these compounds were lacking as before. Like in summer and autumn, all biogenic elements were stratified in winter. Compared with autumn, in winter the concentrations of TP, PO_4^{3-}, TN, NO_3^-, NO_2^-, and Si increased even more in the surface layer (0–4.5 m). In winter NO_3^- showed the largest increase, especially in aerobic conditions but also in anaerobic water.

Organic matter

The main product of organic matter in L. Verevi is phytoplankton. In summer the mean value of COD_{Cr} in the upper water layer was 29 mgO L^{-1} and in the lower layer 44 mgO L^{-1}. At the same time the mean COD_{Mn} was 10 mgO L^{-1} and 16 mgO L^{-1}, respectively. According to the COD_{Cr} and COD_{Mn} scale for Estonian small lakes (Simm, 1975), both the total concentration of organic matter and its chemically easily oxidizable fraction in the upper water layer can be estimated as average ($35 > COD_{Cr} > 25$ mgO L^{-1}; $15 > COD_{Mn} > 10$ mgO L^{-1}). These values were high in the lower water layer ($COD_{Cr} > 35$ mgO L^{-1}; $COD_{Mn} > 15$ mgO L^{-1}). In the composition of the lake's organic matter the hardly oxidizable fraction was prevalent, because COD_{Mn} made up less than 50% of COD_{Cr} both in the upper (34%) and the lower layer (36%).

THE BASIC LINEAR STATISTICAL MODEL FOR LAKE VEREVI, EXPRESSED IN SAS PROGRAMMING LANGUAGE

MODEL water_ variables = m
y yy yyy d yd yyd yyyd dd ydd yydd ddd yddd dddd
h1 yh1 yyh1 yyyh1 dh1 ydh1 yydh1 ddh1 yddh1 dddh1
h2 yh2 yyh2 yyyh2 dh2 ydh2 yydh2 ddh2 yddh2 dddh2
h3 yh3 yyh3 yyyh3 dh3 ydh3 yydh3 ddh3 yddh3 dddh3
h4 yh4 yyh4 yyyh4 dh4 ydh4 yydh4 ddh4 yddh4 dddh4
h5 yh5 yyh5 yyyh5 dh5 ydh5 yydh5 ddh5 yddh5 dddh5
/ NOINT SS3

Here y is sampling year, d is sampling day, and h1–h5 are values of the five normal densities calculated from sampling depth. For example,

$$h3 = \exp\left(-\left(\text{sampling depth} - \mu_3\right)^2 \big/ 2\sigma^2\right),$$

where $\sigma = 3$ and $\mu_3 = 4$. The mean values $\mu_1, \ldots, \mu_5$ were taken –2, 1, 4, 6, and 8, correspondingly. The intercept of the model is implicitly presented by parameter m. This specific form of the model is convenient for calculating derivatives of the regression function when estimating the change points of the depth-dependence curve.

REFERENCES

Alekin, O. A. 1959. Methods for investigation of physical and chemical properties of water. In *Vital Functions of Fresh Water in the Soviet Union*, vol. 4(2) (Pavlovski, E. N. & Zhadin, V. I., eds), pp. 213–300. Izdatel′stvo Akademii Nauk SSSR, Moskva–Leningrad (in Russian).

Crumpton, W. G., Isenhart, T. M. & Mitchell, P. D. 1992. Nitrate and organic N analyses with second-derivative spectroscopy. *Limnol. Oceanogr.*, **37**(4), 907–913.

Fall, M. J. 1996. *JENWAY Model 4150 Conductivity Meter Manual*. Jenway Ltd., Dunmow, Essex.

Gubachek, Z. & Artamoshkina, F. M. (eds) 1977. *Standardized Methods for the Investigation of Water Quality*. Moskva (in Russian).

Hansen, H. P. & Koroleff, F. 1999. Determination of nutrients. In *Methods of Seawater Analysis* (Grasshoff, K., Kremling, K. & Ehrhardt, M., eds), pp. 159–226 . WILEY-VCH, Weinheim.

Hellat, K., Mashirin, A., Mei, L. & Tenno, T. 1986. Metrological guaranteeing of devices for measuring oxygen in the water. *Acta Comment. Univ. Tartu.*, **757**, 184–193 (in Russian).

Koroleff, F. 1982. Total and organic nitrogen. In *Methods of Seawater Analysis* (Grasshoff, K., ed.), pp. 162–168. Verlag Chemie.

Mäemets, A. 1977. *Eesti NSV järved ja nende kaitse*. Valgus, Tallinn.

Mäemets, A., Ott, K. & Parts, M. 1991. Hüdrokeemia. In *Verevi järve seisund* (Timm, H., ed.), pp. 44–68. Tartu.

Milius, A., Saan, T., Starast, H. & Lindpere, A. 1991. Total phosphorus in Estonian lakes. *Proc. Estonian Acad. Sci. Ecol.*, **1**, 122–130.

Möls, T. 2005. *Lineaarsed statistilised meetodid Eesti mageveekogude vee ja elustiku analüüsimiseks*. Eesti Looduseuurijate Seltsi Kirjastus, Tartu.

Ott, I. & Kõiv, T. (eds) 2005. *Lake Verevi, Estonia – A Highly Stratified Hypertrophic Lake*. Springer, Netherlands.

Reports of the Baltic Intercalibration Workshop. 1977. Kiel.

Riikoja, H. 1940. Zur Kenntnis einiger Seen Ost-Eestis, insbesondere ihrer Wasserchemie. In *Tartu Ülikooli Loodusuurijate Seltsi Aruanded*, **46** (Lepik, E., ed.), pp. 168–329. Tartu Ülikooli juures oleva Loodusuurijate Seltsi Kirjastus.

Simm, H. 1975. *Eesti pinnavete hüdrokeemia*. Valgus, Tallinn.

Timm, H. (ed.) 1991. *Verevi järve seisund*. Estonian Academy Publishers, Tartu.

Wetzel, R. G. 1983. *Limnology*. Saunders College Publishing.

Verevi järve hüdrokeemilise seisundi modelleerimine

Henno Starast, Tõnu Möls, Katrin Ott, Aini Lindpere ja Marina Haldna

Aastatel 1984–2001 määrati Verevi järve vee keemiline koostis nii vertikaalselt kui ka sesoonselt. Järve hüdrokeemilist seisundit iseloomustati suvel, sügisel ja talvel 18 parameetri – temperatuuri ($t°$), lahustunud hapniku (O_2), hapnikuga küllastumuse ($O_2\%$), vee pH, aluselisuse (HCO_3^-), sulfaatiooni (SO_4^{2-}), kloriidiooni (Cl^-), kaltsium- ning magneesiumiooni summa ($Ca^{2+} + Mg^{2+}$), elektrijuhtivuse (EC), üldfosfori (TP), ortofosfaatiooni (PO_4^{3-}), üldlämmastiku (TN), nitraatiooni (NO_3^-), nitritiooni (NO_2^-), ammooniumiooni (NH_4^+), räni (Si), dikromaatse oksüdeeritavuse (COD_{Cr}) ja permanganaatse oksüdeeritavuse (COD_{Mn}) – järgi. Andmebaas sisaldab 166–1011 mõõtmist parameetri kohta. Vee koostise sõltuvust vaatlusaastast, vaatluspäevast ja vaatluse sügavusest järvel uuriti 64-parameetrise kovariatsioonanalüüsi mudeliga, mis sobitati andmetega statistilise andmetöötluspaketi SAS abil. Kihistumine järves oli tugevaim suvel, kui vee $t°$, O_2, $O_2\%$ ja pH vähenesid vees põhjakihtide suunas. Samal ajal suurenesid samas suunas HCO_3^-, $Ca^{2+} + Mg^{2+}$, EC, Si, COD_{Cr} ja COD_{Mn}, eelmistest olulisemalt TP, PO_4^{3-}, TN ja NH_4^+. Pinnast põhjani jäid SO_4^{2-}, Cl^-, NO_3^- ja NO_2^- kontsentratsioonid suhteliselt konstantseks. Sügisel, vee konvektiivse segunemise ajal olid erinevused veekihtide keemilises koostises väikesed. Aastaringselt on vesi järves kihistunud.