

ASSESSMENT OF THE SEDIMENT CHEMICAL QUALITY IN SALMONID LAKES IN LATVIA

Maruta Jankēvica¹, Jānis Šīre², Ilga Kokorīte³, Māris Kļaviņš⁴

^{1,2,3,4} Faculty of Geography and Earth Sciences, University of Latvia, Rīga, Latvia,
maruta.jankevica@gmail.com

ABSTRACT

Freshwater ecosystems have changed significantly due to human activities, leading to accumulation of excessive nutrients, thus increasing primary productivity in many lakes and causing structural changes in food web.

Studies on lake sediment composition can provide valuable information about character of lake development and thus can be used to study long-term natural and anthropogenic impacts on lakes and their catchment. The aim of this study is not only to evaluate concentrations of phosphorus, nitrogen and heavy metals in 18 salmonid lake ecosystems in Latvia and possible anthropogenic pressures, but also to estimate the possible impacts of the land use as well.

The studied lakes are mesotrophic and eutrophic. During the summer and winter seasons hypoxic conditions can be observed in most of the studied lakes. Lake sediments can be characterized as rich in organic matter; loss-on-ignition (550°C) can exceed 45%. Total phosphorus concentrations in upper part of sediments vary from 300 till 2400 mgP kg⁻¹ with the highest concentrations attributed to areas with direct human impact (e.g., municipal effluents and historically accumulated pollution from intensive farming practices during the Soviet-period). Phosphorus speciation analyses reveal that up to 25% of extractable P is found in reducible form, which can be released in water column under hypoxic environmental conditions. Relatively inert HCl-extractable P fraction comprises the largest part of total phosphorus concentration in sediments (up to 44%). Concentrations of heavy metals in sediments of studied lakes are very low to low (Cu, Zn, Cd, Pb) or medium high (Ni and Cr) according to the criteria of Swedish EPA.

Key words: nutrients, nutrient speciation forms, heavy metals, lake sediments

INTRODUCTION

Human activities during last centuries have changed freshwater ecosystems leading to accumulation of pollutants, especially nutrients but also persistent pollutants, thus supporting increased primary productivity in

many lakes, structural changes in food webs and deterioration of quality of water bodies (Wetzel, 2001). The lake sediments can act as a sink of pollutants, thus studies of sediments (especially sediment profiles) can provide valuable information on how the ecosystem has changed and needed environmental protection measures.

In early 1990'ies, dramatic reduction in industrial and agricultural activities had taken place due to socio-economic and political crisis in the territory of former Soviet Union. For example, fertilizer and manure use has fallen by five times and the number of livestock has decreased by around three times (Stålnacke, 1996; Klavins et al., 2002), and it is assumed that these changes have reduced loading of nutrients to the surface water (Stålnacke, 1996). Subsequently, the recent socio-economic recovery has increased anthropogenic pressure, but still it is lower than during the Soviet period (Agriculture Census, 2008). Regarding reduction of anthropogenic impact to the environment, historical pollution accumulated in lake sediments may threaten ecological quality of lake. Some studies (Phillips et al., 2005; Jeppesen et al., 2007) are reporting the lake recovery due to nutrient reductions, however, eutrophication and bad ecological quality of lake ecosystems remain to be a problem despite to the implemented measures for reduction of nutrient loadings (Leeben et al., 2008; Bjerring et al., 2008). Impact of internal phosphorus loading from lake sediments is also mentioned among factors that inhibit recovery of lake ecosystems (Phillips et al., 2005; Lake et al., 2011), as pollutants accumulated in lake sediments can be slowly released and are able to influence lake ecosystem in a long run.

The aim of this study was to evaluate concentrations of nutrients and heavy metals in lake sediments and possible anthropogenic impacts on Latvian water bodies.

MATERIALS AND METHODS

Site description

All studied lakes are located in SE part of Latvia – in Latgale (Figure 1). This region is characterized by a hilly relief. In Latvia, there are 2256 lakes having an area of >1 ha and almost a half of them is located in Latgale. The surficial geology has been formed by

Quaternary glacial sediments and by recent exogenous processes. All of the studied lakes are of glacial origin. Many lakes (e.g., Rāznas, Ežezers, Sīvers) were formed in local depressions after melting of buried ice blocks. The deepest lakes, e.g., lakes Drīdzis, Bešons, Lejas, Dubuļu are situated in subglacial depressions. The most widely distributed parent soil materials are moraine loam and sands. More than a half of the soils are humic podsols. Eroded soils are also widespread in the catchments of studied lakes, as most of the lakes are located in Latgale Upland.

Most of the studied lakes are classified as deep (mean depth >9 m) or medium deep (5 – 9 m) (Table 1). Only Lake Ārdavs is medium shallow lake (Klavins et al., 2002). Due to morphometric properties most of the studied lakes are dimictic. The studied lakes represent slightly and moderately eutrophic lakes (Poikāne, 2009). According to the national water quality Regulation No. 118 (2002), the studied lakes are categorized as priority salmonid fish lakes. It means that measures to improve water quality, in order to ensure favorable living conditions for the salmonid fish population, should be implemented. 18 out of the 26 Latvian salmonid lakes were chosen for the study. Their main morphometric values are summarized in Table 1.

Field work

Sediment samples from profundal zone of 18 lakes (25 sampling stations) were collected using a stainless steel Eckman sediment sampler (20x20 cm) in July, 2010 and August, 2011. Additional sediment samples from lakes Rāznas, Drīdzis and Sventes were taken in November of 2010 and March of 2011. Sediment samples were transferred to acid-rinsed polypropylene buckets to be transported to the laboratory.

Water samples were taken from depth of 0.5 m and hypolimnion using Ruthner type batometr for general water chemistry. Concentration of

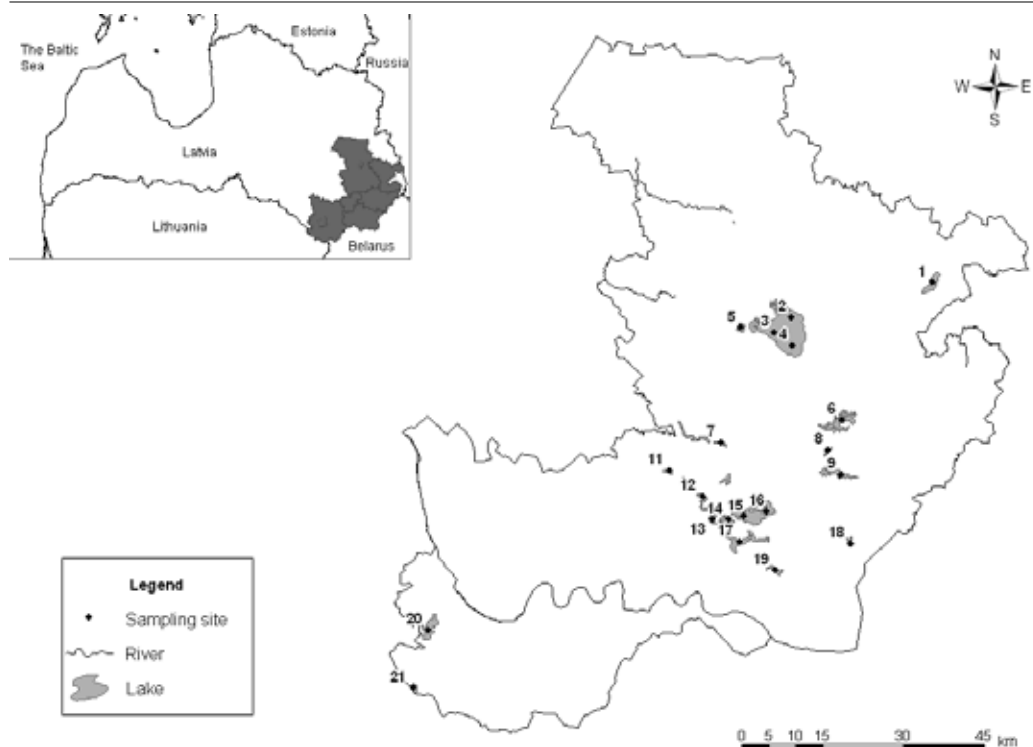


Figure 1. Location of sampling sites (names of the studied lakes are given in Table 1).

dissolved oxygen, conductivity, pH and water temperature were measured in situ by using portable probe HACH Q40d.

Laboratory analyses

Sediment samples were air dried and homogenized by using a mortar. Sediment aliquots for loss-on-ignition (LOI) analysis at first were oven-dried at 105°C for 24 h, and then 1 g of sample was taken for analysis of content of organic matter and carbonates as described by Heiri et al. (2001). First, 1 g of dried sample was heated in a muffle furnace at 550°C for 4 h and reweighed to determine content of organic matter. Afterwards, the sample was heated at 950°C for 2 h and reweighed to determine content of carbonates.

Granulometric composition was analyzed as follows:

To analyze sand particles (size > 0.063 mm), 50 g of sediment sample was sieved and washed through a 0.05 mm sieve until dust and clay particles were washed out. The sample was then dried on a hot plate, cooled and sieved through a 0.063 mm sieve, the residue being weighed. Sand particle content in percentage was calculated using formula:

$$X = \text{residue (g)} * 2$$

To analyze clay particles (diameter < 0.02 mm), 15 g of sample was weighted in 200 ml Erlenmeyer flask, mixed with 4 ml of 0.1 M NaOH and 150-200 ml of distilled water and shaken for 1 hour. The sample was then boiled on a hot plate for 1 hour, cooled and poured into 1 liter cylinder and diluted with distilled water to 1 liter mark. The sample was then dispersed for 1 min and exact time needed for sedimentation was recorded. The temperature was monitored and maintained constant during

Table 1.

Characteristics of the studied lakes and location of the sampling sites.

No.	Lake	Geographical coordinates		Lake area, km ²	Mean (max) depth, m	Lake volume, million m ³	Catchment area, km ²
		N	E				
14	Ārdavs	56°00' 626"	27°14' 553"	2.24	4.6 (14.0)	10.3	48.4
12	Cārmins	56°03' 201"	27°11' 097"	2.218	9.1(31.0)	20.2	210
11	Bešons	56°05' 864"	27°05' 419"	0.642	6.8 (22.7)	4.4	34.5
9	Dagdas	56°05' 148"	27°35' 486"	4.841	5.2 (19.2)	25.17	176.2
17	Drīdzis 1	55°58' 950"	27°16' 406"	7.532	12.8 (65.1)	94.7	33.5
	Drīdzis 2	55°58' 843"	27°16' 396"				
	Drīdzis 3	55°57' 827"	27°15' 770"				
	Drīdzis 4	55°58' 645"	27°21' 094"				
	Drīdzis 5	55°58' 982"	27°18' 827"				
7	Dubuļu	56°08' 617"	27°14' 054"	0.724	11.8 (30.0)	8.5	17.7
6	Ežezers	56°10' 730"	27°38' 741"	9.879	6.4 (21.0)	61.0	120
8	Galšūns	56°06' 730"	27°33' 410"	0.653	5.6 (14.8)	3.7	129.6
10	Jazinka	56°05' 047"	27°07' 582"	2.639	8.1 (33.0)	21.4	17.3
21	Laucesas	55°46' 930"	26°32' 179"	1.91	5.4 (15.5)	10.3	320
13	Lejas	56°01' 040"	27°12' 141"	1.774	8.2 (34.0)	14.6	210
18	L.Gusens	55°57' 786"	27°36' 650"	1.205	9.3 (38.0)	11.2	8.1
1	Nirzas	56°24' 091"	27°55' 075"	5.516	8.2 (21.0)	45.5	24.7
4	Rāzna 5	56°19' 467"	27°23' 354"	57.564	7.0 (17.0)	405.0	221
3	Rāzna 7	56°17' 253"	27°29' 370"				
2	Rāzna 11	56°20' 766"	27°26' 296"				
15	Sīvers R	56°01' 596"	27°17' 375"	18.74	6.3 (24.5)	106.8	84
16	Sīvers A	56°01' 525"	27°12' 625"				
19	Stirnu	55°55' 276"	27°23' 948"	1.494	7.7 (25.8)	11.5	18.2
20	Sventes	55°50' 655"	26°20' 961"	7.348	7.8 (38.0)	57.3	18
5	Zosnas	56°19' 925"	27°19' 627"	1.565	6.0 (15.4)	9.4	54.4

the sedimentation. Using granulometric tables, precise time after which in 7 cm depth a sample must be taken with a pipette, was established. The sample was then poured on a previously weighed metal plate, placed on a hotplate dish to evaporate the water, and weighed. Percentage of clay particles was calculated using the following formula:

$$X = \frac{\text{weight of the plate (g)} * 1000}{\text{weight of the sample (g)} * \text{sample taken (ml)}} * 100$$

Dust particles (diameter 0.02 mm – 0.063 mm) were calculated using the formula (Soils. Methods of laboratory .., 1982):

$$X = 100 - (X = 100 - (\text{amount of sand particles (\%)} + \text{amount of clay particles (\%)))$$

Once the fraction percentages were known, the granulometric composition group by the FAO classification was determined (Kārkliņš, 2008).

Total P in sediments was determined by ashing sample at 550°C for 3 h and following extraction with 0.5 M HCl. Inorganic P was analyzed in extracts following ascorbic acid method (APHA, 2005). Sequential extraction was carried out following the modified method by Psenner et al. (1984) (Table 2). Residual P was calculated as a difference between total P and the sum of extracted P fractions. Residual P includes also organic phosphorus fraction.

Analysis of the forms of nitrogen (NH_4^+ , NO_3^- , NO_2^-) was performed by mixing 1 g of the dry sample with 25 ml of 1M KCl solution and shaking it for 24 h. Nitrogen compounds in the extract were determined using the same methods as for water analysis (Tan, 2005).

For analysis of metals, 1 gram of sediment sample was digested with 50 % HNO_3 and 30 % H_2O_2 on a hot plate at $70 \pm 5^\circ\text{C}$ (Csuros & Csuros, 2002). Content of Fe, Cr, Mn Co, Ni, Cu, Zn, Cd and Pb were determined by flame atomic absorption spectrophotometer PerkinElmer Instruments AAnalyst 200. Every extraction batch included blank sample and reference material ISE 1998.3-921 (Wageningen Evaluating Programmes for Analytical Laboratories) to control the quality of measurements. The average recovery varied

from 82 % for Zn to 99 % for Cr (mean recovery for nine metals was 93 %).

Concentration of P-PO_4^{3-} in water was analyzed following ascorbic acid method (APHA, 2005), N-NO_3^- using diazotisation of gentisic acid after reduction of nitrates with cadmium, colour spectrophotometrically at wavelength 455 nm in the Pt/Co scale (HACH, 1992).

Software IBM SPSS Statistics 19 was used for data statistical treatment.

RESULTS

Water chemical composition at 0.5 m depth in vegetation season is presented in Table 3. Nutrient concentrations in studied lakes were low: N-NO_3^- ranged from 0.1 – 0.3 mg l^{-1} ; N-NH_4^+ - from 0.03 – 0.51, but those of P-PO_4^{3-} often were even below detection limit. Conductivity values ranged from 187 – 366 $\mu\text{S cm}^{-1}$. pH of lake water in vegetation season was alkaline (pH 7.89 – 9.61).

Granulometric composition was analyzed in 24 sediment samples. Dusty loam and heavy loam groups were dominating (7 samples in each group), followed by 5 dust, 3 sandy loam and 2 sand samples.

Composition of studied sediments is presented in Table 4. LOI analysis revealed that fraction of mineral matter was dominating (49.8 - 93.6%) in the sediments of studied lakes. Content of

Table 2.
Sequential extraction procedure (modified method after Psenner et al., 1984).

Step	Reagents	Extraction time	Fractions extracted
I	1 M NH_4Cl	4 h	$\text{NH}_4\text{Cl-P}$ - porewater P, loosely adsorbed P
II	0.11 M NaHCO_3 0.11 M $\text{Na}_2\text{S}_2\text{O}_4$	1 h	BD-P – redox sensitive P (P associated with Fe and Mn hydroxides)
III	1 M NaOH	16 h	NaOH-P – P associated with metal (Fe, Al) oxides; hydrolyzed organic P
IV	0.5 M HCl	17 h	HCl-P – carbonate-bound and apatite P

organic matter (OM) comprised 4.3 - 46.2%, but that of carbonate matter (CM) varied in range 1.2 - 10.2%.

The highest concentration of all studied metals had Ca (6060 – 61665 mg kg⁻¹ d.w.) and Fe (7900 – 38980 mg kg⁻¹ d.w.). Mg and K were also found in high concentrations 3600 – 1100 mg kg⁻¹ d.w. and 980 – 4600 mg kg⁻¹ d.w., respectively, as well as Mn 126 – 2150 mg kg⁻¹ d.w. (not shown in the table). Order of heavy metals according to their concentration was Zn > Pb ≥ Cr > Ni > Cu > Cd.

Concentrations of total P in studied lakes varied between 340 – 2360 mg kg⁻¹ d.w. (Table 4). Considerable variation of sedimentary

phosphorus was observed also within the lake, for example, variation of P concentration between sampling stations in Lake Drīdzis was 2.6 times, but that in Lake Rāzna – almost 4 times.

Inorganic phosphorus speciation forms were analyzed for 14 sampling stations in 10 lakes (Figure 2). Concentrations of easily extractable NH₄Cl-P were in range 0.05 – 8.17 mg kg⁻¹ d.w., with the lowest concentration found at station Lake Drīdzis 3, but the highest – in Lake Dagdas. Content of NH₄Cl-P accounted less than 0.35% of total P. Concentrations of reducible P species (BD-P) varied from 3.2 to 361.3 mg kg⁻¹ d.w. that represents 0.9 – 15.6% of total P content. The lowest absolute

Table 3.
Water chemical composition at 0.5 m depth.

Lake	N-NO ₃ ⁻ mg l ⁻¹	Color Pt-Co	N-NH ₄ ⁺ mg l ⁻¹	P-PO ₄ ³⁻ mg l ⁻¹	Conductivity μS cm ⁻¹	pH
Ārdavs	0.20	21	0.03	<i>b.d.</i>	224	8.48
Bešons	0.30	41	0.06	<i>b.d.</i>	259	8.88
Cārmans	0.20	28	0.29	0.005	298	8.54
Dagdas	0.20	34	0.28	0.005	345	8.38
Drīdzis 1	0.30	13	0.51	0.012	275	7.89
Drīdzis 2	0.20	23	0.03	<i>b.d.</i>	234	8.96
Drīdzis 3	0.30	17	0.47	0.010	279	8.06
Drīdzis 4	0.10	16	0.16	0.006	282	8.57
Drīdzis 5	0.20	25	0.03	<i>b.d.</i>	234	8.90
Dubuļu	0.10	20	0.25	0.005	366	8.37
Ežezers	0.30	38	0.06	<i>b.d.</i>	265	8.82
Galšūns	0.30	35	0.05	<i>b.d.</i>	276	8.35
L. Gusens	0.30	33	0.47	0.004	312	8.72
Laucesa	0.30	59	0.32	0.006	362	9.61
Lejas	0.30	35	0.05	<i>b.d.</i>	228	8.89
Nirzas	0.15	23	0.03	<i>b.d.</i>	250	8.90
Rāzna 5	0.15	15	0.13	0.004	226	8.75
Rāzna 7	0.20	12	0.49	0.017	230	8.10
Rāzna 11	0.10	17	0.16	0.005	227	8.80
Sīvers A	0.20	28	0.04	<i>b.d.</i>	199	8.90
Sīvers R	0.20	26	0.04	<i>b.d.</i>	203	8.85
Stirnu	0.20	23	0.11	0.005	283	8.96
Svente	0.20	14	0.07	<i>b.d.</i>	218	9.07
Zosna	0.30	36	0.09	<i>b.d.</i>	303	8.62

and relative values for BD-P were found at station Lake Drīdzis 1, but highest – in Lake Stirnu. Content of inorganic P extracted in NaOH (NaOH-P) varied from 9.5 mg kg⁻¹ (Lake Drīdzis 1) to 477 mg kg⁻¹ (Lake Dagdas). Relative values of NaOH-P varied from 1.5% at station Lake Rāzna 7 to 20.2% in Lake Dagdas. Concentrations of HCl-P were from 81.9 mg kg⁻¹ at station Lake Drīdzis 1 to 894.0 mg kg⁻¹ in Lake Rāzna 7. Relative content of HCl-P were in range from 23.2% (Lake Stirnu) to 44.0% (Lake Drīdzis 3). Proportion of residual P was high, ranging from 39.8% (Lake Drīdzis 3) to 72.2% (Lake Drīdzis 1).

Statistical analysis of sediments revealed several links between the sediment characteristics (Table 5). 12 correlations were found with a confidence level of 90% ($\alpha = 0.1$), 14 correlations with a confidence level of 95% ($\alpha = 0.05$) and 11 relationships with a very high confidence level of 99% ($\alpha = 0.01$).

DISCUSSION

According to the sediment quality criteria set by Swedish EPA (2000) concentrations of Zn, Cd and Pb can be regarded as very low, Zn as low, but concentrations of Cr and Ni as low or moderate. Concentrations of studied metals in lake sediments are attributed to natural factors such as geochemical properties of bedrock and soil (Klavins et al., 2002), as the studied lakes do not have significant pollution sources from industrial activities.

Total P concentration in sediments varied highly (from 341 till 2361 mg kg⁻¹) with the lowest values specific for mesotrophic or slightly eutrophic lakes, but the higher values are characteristic of eutrophic and hypertrophic lakes (Xiang & Zhou, 2011; Kaiserli et al., 2002). There exists statistically significant ($p < 0.05$) correlation between content of total phosphorus, its labile forms and concentrations of nitrogen compounds (Table 5). This possibly indicates on similar

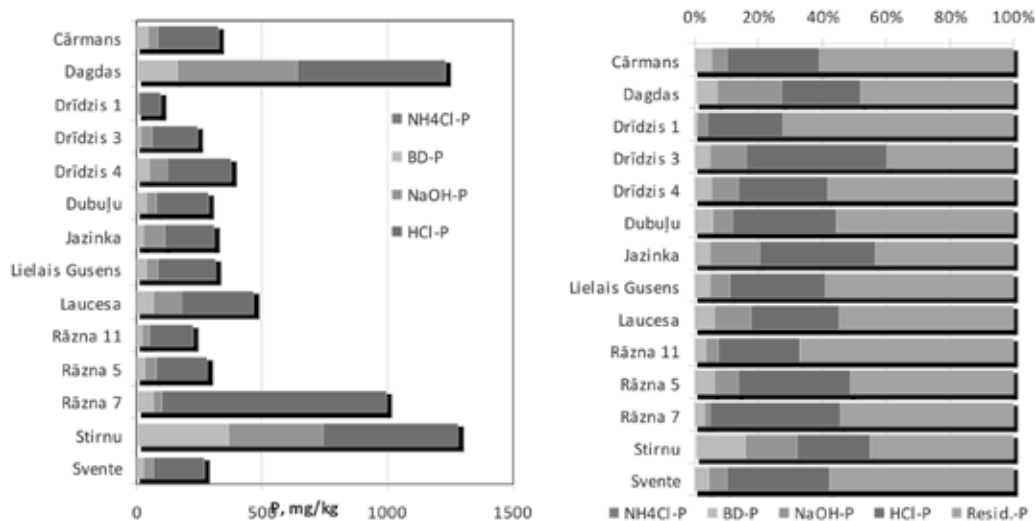


Figure 2. Distribution of phosphorus forms in the sediment samples from studied lakes (left – absolute values, right - percentages).

Table 4.
Composition of the studied lake sediments.

Lake	OM,%	CM,%	Mineral matter, %	tot-P, mg kg ⁻¹	Ca, mg kg ⁻¹	Fe, mg kg ⁻¹	Cr, mg kg ⁻¹	Mn, mg kg ⁻¹	Co, mg kg ⁻¹	Ni, mg kg ⁻¹	Cu, mg kg ⁻¹	Zn, mg kg ⁻¹	Cd, mg kg ⁻¹	Pb, mg kg ⁻¹
Ārdavs	39.6	1.68	58.7	554.1	9069	10573	26.3	176	7.2	20.5	19.6	70	0.12	23.59
Bešons	18.7	2.33	79.0	753.4	10274	23315	38.2	328	11.8	26.5	22.6	103	0.35	30.67
Cārmans	15.1	1.66	83.2	837.3	7139	19070	41.5	396	10.0	24.9	21.1	100	0.59	31.28
Dagdas	23.7	7.11	69.2	2361.2	54208	20684	23.4	1733	6.4	16.0	16.9	68	0.31	20.91
Dīrdzis 1	17.2	3.56	79.3	340.6	1179	2627	7.7	49	1.4	4.1	2.7	16	<0.07	3.06
Dīrdzis 2	11.1	2.02	86.9	608.1	6120	22408	31.1	450	12.3	26.1	23.1	75	0.31	21.23
Dīrdzis 3	22.4	2.23	75.4	398.0	4229	18672	30.4	228	8.5	23.0	17.6	68	0.28	18.03
Dīrdzis 4	11.2	1.80	87.0	894.7	9118	22492	35.9	600	11.1	23.5	18.9	85	0.42	25.47
Dīrdzis 5	4.4	1.99	93.6	368.2	9997	7908	12.1	126	4.7	8.5	8.2	28	<0.03	9.24
Dubuļu	19.9	6.12	74.0	641.3	53469	23036	18.6	359	5.2	12.4	11.8	52	0.39	24.41
Ežezers	29.8	3.05	67.1	601.4	23179	24205	33.9	399	9.3	24.0	24.5	116	0.58	35.25
Galšūns	20.8	3.92	75.3	1601.5	27580	38981	23.5	1904	9.0	16.0	22.1	88	0.22	28.85
Jazinka	12.1	5.04	82.9	543.3	5296	15610	22.0	220	7.8	19.5	18.3	89	0.84	41.92
L.Gusens	16.1	1.24	82.7	769.7	7698	12349	33.3	274	7.9	16.9	15.0	79	0.66	30.04
Laucesas	18.8	10.24	71.0	1029.9	61665	18679	27.7	481	7.1	19.1	18.6	79	0.26	18.07
Lejas	12.5	1.78	85.8	766.9	6061	17384	27.4	288	9.7	19.9	19.0	76	0.06	15.44
Nirza	19.8	2.17	78.0	763.6	11581	22883	25.2	384	9.8	18.5	22.8	85	0.40	24.86
Razna 7	18.0	2.81	79.2	2178.7	2874	1108	<0.4	93	0.2	0.5	0.6	3	0.13	2.04
Razna 11	24.7	2.06	73.2	785.9	12623	26416	23.5	683	7.2	18.2	19.5	102	0.79	50.13
Razna 5	23.8	2.85	73.3	571.8	14272	19598	16.4	593	6.9	14.4	17.0	85	0.81	41.24
Sivers-A	19.0	2.09	79.0	648.7	7816	23793	47.1	410	11.8	31.5	23.5	81	0.08	22.56
Sivers-R	35.0	1.57	63.5	500.0	11143	10861	20.0	246	6.6	16.1	19.0	64	0.57	24.81
Stirnu	23.3	5.97	70.8	2324.0	45248	20691	25.8	2153	7.7	19.6	23.4	78	0.51	27.50
Sventes	17.9	2.40	79.7	630.1	9061	23489	42.3	367	9.3	28.9	18.4	78	0.33	28.89
Zosna	46.2	3.99	49.8	780.5	28356	16121	15.6	1035	7.1	11.5	10.7	128	0.33	13.06

Table 5.
 Pearson's correlation coefficients (r) between the physico-chemical parameters characterizing lake sediments (n – number of observations;
 in bold significant correlations \wedge - \wedge $\alpha < 0.1$ *, $\alpha < 0.05$; **- $\alpha < 0.01$).

Parameter	Granulo- metric content, %	OM, %	CM, %	Tot-P, mg kg ⁻¹	N-NH ₄ ⁺ , mg kg ⁻¹	N-NO ₃ ⁻ , mg kg ⁻¹	NH ₄ Cl-P, %	BD- P, %	NaOH-P, %	HCl-P, %	Residual-P, %	Ca, mg kg ⁻¹
OV, %	0.349 n=16											
CM ₃ , %	0.234 n=16	0.092 n=25										
Tot-P, mg kg ⁻¹	0.146 n=16	0.083 n=25	0.445*									
N-NH ₄ ⁺ , mg kg ⁻¹	0.454\wedge n=16	0.385\wedge n=25	0.723** n=25	0.403* n=25								
N-NO ₃ ⁻ , mg kg ⁻¹	0.291 n=16	0.151 n=25	0.666** n=25	0.529** n=25	0.616** n=25							
NH ₄ Cl-P, %	0.322 n=14	0.437 n=14	0.465\wedge n=14	0.868** n=14	0.362 n=14	0.711** n=14						
BD-P, %	0.602* n=14	0.379 n=14	0.407 n=14	0.582* n=14	0.648** n=14	0.470\wedge n=14	0.585* n=14					
NaOH-P, %	0.650* n=14	0.361 n=14	0.605* n=14	0.450 n=14	0.541* n=14	0.671** n=14	0.686** n=14	0.619* n=14				
HCl-P, %	-0.296 n=14	-0.331 n=14	-0.424 n=14	-0.347 n=14	-0.516\wedge n=14	-0.189 n=14	-0.466\wedge n=14	-0.393 n=14	-0.396 n=14			
Residual-P, %	-0.399 n=14	-0.089 n=14	-0.179 n=14	-0.215 n=14	-0.142 n=14	-0.466\wedge n=14	-0.268 n=14	-0.443 n=14	-0.554* n=14	0.496\wedge n=14		
Ca, mg kg ⁻¹	0.369\wedge n=22	0.251 n=22	0.870** n=22	0.492* n=22	0.579** n=22	0.504* n=22	0.403 n=14	0.542* n=14	0.521* n=14	-0.361 n=14	-0.222 n=14	
Fe, mg kg ⁻¹	0.113 n=22	0.103 n=22	0.140 n=22	0.127 n=22	-0.024 n=22	-0.095 n=22	0.191 n=14	0.430\wedge n=14	0.432\wedge n=14	-0.309 n=14	-0.168 n=14	0.371\wedge n=22

sources of both phosphorus and nitrogen compounds.

Despite to high phosphorus content found in sediments, P-PO₄³⁻ concentration in lake waters at 0.5 m layer was very low, often below detection limit (Table 3). In hypolimnion P-PO₄³⁻ concentrations were slightly higher; exceptions were lakes Laucesa, Dagda and Stirnu with 0.019, 0.069 and 0.099 mg l⁻¹ P-PO₄³⁻, respectively. Most of the studied lakes in summer are thermally stratified, nutrient flows from hypolimnion to upper layers are limited. Besides, studied lakes naturally have high calcium concentrations in water (20 – 52 mg l⁻¹), which can favour phosphorus binding and co-precipitation with calcite, under alkaline conditions (Dittrich & Koschel, 2002). Co-precipitation of phosphorus with calcite decreases concentrations of dissolved phosphorus in epilimnion, as the sediment acts as a sink of phosphorus (Kaiserli et al., 2002; De Vicente et al., 2006). In such lakes, only measurements of phosphate concentration in water cannot give reliable information on the quality of lake ecosystems and the estimation of both total nutrient concentrations and their speciation forms in sediments is essential for predicting internal nutrient cycling in water bodies (Xiang & Zhou, 2011; Kaiserli et al., 2002).

Analysis of phosphorus speciation forms revealed that HCl-P comprised 42.1 – 89.7% of inorganic P concentrations or 23.2 – 44.0% of the total sedimentary P in the studied lakes, that corresponds to the results found mainly in eutrophic and calcareous lakes (Kaiserli et al., 2002; De Vicente et al., 2006). NaOH-P was the second most abundant form of inorganic phosphorus comprising 3.31 – 38.67% of inorganic P. This phosphorus form can be considered as a potentially bio-available under certain circumstances, e.g., alkaline sediments or prevailing anoxic conditions, as the NaOH solution extracts not only inorganic phosphorus bound to metal oxides and hydroxides, but can hydrolyze some fraction

of organic P (Rydin, 2000; Golterman, 2001). Reducible phosphorus form (BD-P) comprised slightly smaller part of inorganic P (3.37 – 28.2%), but loosely adsorbed P comprised less than 1% of inorganic P. Regarding high content of organic matter in lake sediments (Table 4), substantial amount of residual P possibly can be comprised by organic P. Due to microbial degradation organic P is a potential source of dissolved reactive phosphorus to the lake, especially, in anoxic conditions, thus promoting eutrophication (Rydin, 2000; Ahlgren et al., 2011).

Table 5 shows, from the forms of nitrogen analyzed, ammonium nitrogen formed a statistically significant ($\alpha < 0.1$) relationship with both the granulometric composition and organic matter content in sediments, confirming that decomposition of organic matter is one of the sources of nitrogen in sediments. Since the ammonium ion is positively charged, it has a tendency to bind to the negatively charged colloids (Klaviņš & Cimdiņš, 2004). This explains the close relationship between the ammonium and the dust particle content in sediments.

Relationship between the ammonium, Tot-P and BD-P content has also been found, suggesting a possible common source of nutrients. BD-P and ammonia nitrogen are forming during anaerobic conditions, which possibly determines this relationship.

Ammonium nitrogen forms a positive correlation with nitrate nitrogen, suggesting common sources of these elements. Amounts of nitrate nitrogen are dependent on almost all the sediment characterizing parameters except granulometric composition, organic matter content and HCl-P. This is due to biochemical processes ongoing in the lake and the sediment layer, as well as common sources of supply. The amount of Tot-P is closely related to the amount of carbonates and calcium, which are attributed to the fact that a large part of the dissolved inorganic

phosphorus in sediments bound with calcium carbonate. A similar statistically significant correlation has been found in the lakes of Estonia (Kapanen, 2008).

To avoid autocorrelation, during the assessment of the relationships between forms of phosphorus and other parameters, the distribution percentages were taken into account. Therefore, the total phosphorus is no longer correlating with residual forms of phosphorus.

Hierarchical cluster analysis was used to group studied lakes according to nutrient concentrations, percentage of phosphorus forms (as % of tot-P), percentage of granulometric fractions, content of carbonates and organic matter (%) in sediments (Figure 3).

Two main lake groups can be distinguished by using sediment characterization parameters (Figure 3). One group contains 12 study sites, but the second consists of two – Dagda and Stirnu lakes, containing elevated concentrations of nutrients, fine granulometric composition and medium organic matter content, compared to the other lakes. The first group of studied lakes can be divided into several subgroups. Most dissimilar from the rest of the group is point 7 in Lake Rāzna, where high concentrations of nutrients and coarse granulometry are observed. It should be noted that in Lake Dagda and Lake Rāzna 7 pollution accumulated from point sources has been observed. Similarly high concentrations of nutrients in Lake Stirnu point to anthropogenic discharges.

Lake Dagda has the highest nutrient concentrations in sediments, mainly due to

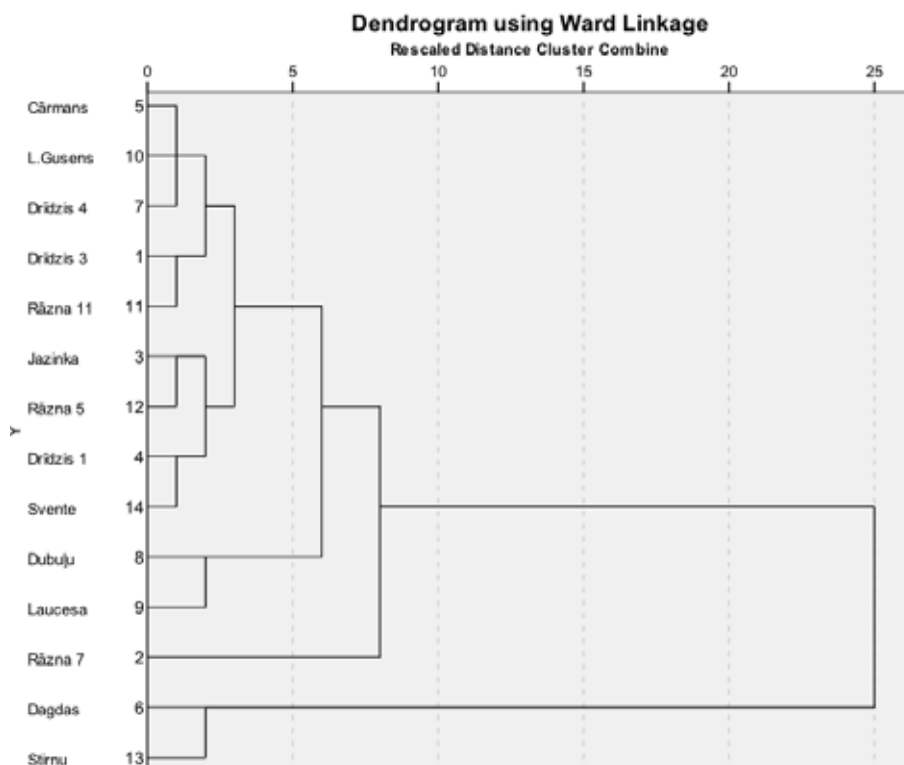


Figure 3. Hierarchical clustering of lake sediments according to nutrient concentrations, phosphorus speciation forms (as the percentage of total P). Ward's method, squared Euclidean distance and z-transformation used for analysis.

discharge of untreated or partially treated municipal wastewater for many decades. According to Compilation of statistical data (2012), after reconstruction of wastewater treatment plant average annual load of total phosphorus by municipal wastewater was estimated to be 0.5 tons (time period 2000 – 2011 average).

In the upper part of the Figure 3 five study sites have been grouped (lakes Cārmans, Lielais Gusens, Drīdzis 3 and 4, Rāzna 11), where the lowest concentrations of nutrients and organic matter have been detected. Generally the study sites are classified by the increase of nutrient concentrations – in lakes Cārmans and Lielais Gusens - the lowest, but in lakes Dagda and Stirnu – the highest.

Lakes with the highest total P concentration – Lake Dagdas and Lake Stirnu – have also the highest proportion of biologically available phosphorus forms that can adversely affect ecological quality of the lakes suffering from frequent hypoxic conditions during summer and winter. Earlier studies done by Kļaviņš and Briede (1995) show higher proportions of mobile phosphorus fractions in the lakes with direct human impact. However, sampling station Lake Rāzna 7 also has high concentration of total P (2178.7 mg kg⁻¹), but the most part (89.7%) of extractable inorganic phosphorus is found in its inert form (as a residual P and P bound to carbonates). The differences in distribution of phosphorus forms can be attributed to the physical and chemical properties of lake sediments and allochthonous suspended matter, concentrations of dissolved oxygen in hypolimnion, intensity of biological processes in benthic zone (De Vicente et al., 2006; Mitchell et al., 2005; Spears et al., 2006).

CONCLUSIONS

Studies on lake sediment composition can be used to evaluate long-term natural and anthropogenic impacts on lakes and their catch-

ment as well as to evaluate potential ecological risks to the lake ecosystems. Concentrations of heavy metals in the studied lakes were at the background level. Order of heavy metals according to their concentration was Zn > Pb ≥ Cr > Ni > Cu > Cd. Total phosphorus concentrations varied greatly (340 – 2360 mg kg⁻¹ d.w.). Phosphorus speciation forms according to their concentrations can be ordered: residual P > HCl-P > NaOH-P > BD-P > NH₄Cl-P, indicating that the large part of sedimentary phosphorus is found in its inert form, however, organic phosphorus (part of residual P and NaOH-P) due to bacterial mineralization can be a potential source of dissolved reactive phosphorus to the lake. Increased proportion of labile phosphorus is characteristic for disturbed lakes.

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