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# MULTI-YEAR INVESTIGATIONS OF ORGANIC MATTER IN THE WATERS OF LAKE STARODWORSKIE, AFTER PHOSPHORUS INACTIVATION

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# WIELOLETNIE OBSERWACJE ZMIAN ZAWARTOŚCI SUBSTANCJI ORGANICZNYCH W WODACH JEZIORA STARODWORSKIEGO PO INAKTY WACJI FOSFORU

Obserwacje prowadzono na niewielkim (6 ha), lecz głębokim (23,3 m) Jeziorze Starodworskim w Olsztynie. W latach 1994 i 1995, w dwóch etapach, przeprowadzono zabieg inaktywacji fosforu w użyciem siarczanu glinu. Po około trzyletnim okresie utrzymywania się korzystnych zmian wywołanych tym działaniem, badania przeprowadzone w latach 1997-2004 wykazały tendencję wzrostową zawartości wszystkich analizowanych wskaźników materii organicznej. W powierzchniowej warstwie wód dominowała materia allochtoniczna (BOD/COD<sub>Mn</sub> ok. 0,5) i istniały sprzyjające warunki do rozwoju zakwitów sinicowych (niski stosunek N/P). Stwierdzono wysoce istotne korelacje DOC i COD<sub>Mn</sub> oraz POC i COD<sub>Mn</sub> (odpowiednio: r = 0,696, r = 0,637, p  $\leq$  0,01). Korelacje między BOD i chlorofilem a (r = 0,4317, p  $\leq$  0,05) oraz między POC a stężeniem chlorofilu a, BOD i DOC (odpowiednio: r = 0,4622, r = 0,5100, r = 0,5000,  $p \le 0,01$ ) sugerują, że źródłem materii organicznej w powierzchniowej warstwie wód jeziora Starodworskiego był nie tylko fitoplankton, ale ważną rolę odgrywała również produkcja wtórna oraz tempo i kierunek przemian martwej materii organicznej. Stężenia BOD, COD<sub>Mn</sub> i fosforu organicznego wzrastały wraz z głębokością, co było szczególnie widoczne w wodach poniżej 15 m. Jednocześnie stwierdzano niewielką, bądź zerową ilość azotu organicznego, o czym decydowały występujące tam warunki beztlenowe. W okresie badawczym zaobserwowano wzrost udziału POC w stosunku do DOC - wyraźnie zaznaczony na głębokości 1 i 5 m oraz bardziej łagodny w głębszych partiach wód jeziora.

#### Summary

The investigations regarded a small (6 ha) but deep (23.3 m) Lake Starodworskie, located in Olsztyn. In 1994 and 1995 the lake experienced a two-phase phosphorus inactivation with aluminium sulphate. The favorable effects of the treatment were observed for approximately three years. The examinations of 1997–2004 revealed a tendency to increase all observed indexes of organic matter. The surface water was dominated by the allochthonous matter (biochemical oxygen demand (BOD)/chemical oxygen demand ( $COD_{Mn}$ )  $\approx$  0.5) and the conditions were favorable for blue-green algae blooms (low N/P ratio). The correlations between dissolved organic carbon (DOC) and  $COD_{Mn}$ , alike between particulate organic carbon (POC) and  $COD_{Mn}$ , were significant (r = 0.696 and r = 0.637, respectively, p  $\leq$  0.01). The correlations

between BOD and chlorophyll a content (r = 0.4317,  $p \le 0.05$ ), POC and chlorophyll a, and BOD and DOC (r = 0.4622, r = 0.5100, r = 0.5000, respectively,  $p \le 0.01$ ) indicate that not only the phytoplankton was a source of organic matter in the surface water layer of Lake Starodworskie but that an important role was played also by primary production and the rate as well as direction of the dead organic matter transformations. Concentrations of BOD,  $COD_{Mn}$ , and organic phosphorus increased along with the depth which was especially evident in the water below 15 m. Simultaneously, due to the anaerobic conditions, organic nitrogen was low or close to zero. The study also revealed that the ratio between POC and DOC increased, especially at 1 m and 5 m depths, and that deeper down the increase was smaller.

#### INTRODUCTION

Eutrophication is a natural effect of lakes ageing and at the same time, a threat to water quality. In most cases, it is phosphorus that determines trophic condition of lakes and phytoplankton abundance. Sporadically, nitrogen and – only incidentally – carbon play this role [11]. The reason is the quantitative ratio between these elements, however, important is not only the constant concentration of the available forms of each nutritive element but also the overall availability of the provided forms and their circulation rate. As a result of enhanced primary production the near bottom water is oxygen-deficient during summer stagnation and so-called internal loading begins [12, 20].

Internal loading can be suspended or at least slowed down through application of restoration measures. The purpose of such action is to decrease the content of the nutritive elements, particularly phosphorus, circulating in the system through reduction of primary production and trophic condition improvement.

Lake Starodworskie in Olsztyn was also restored. To improve the water quality and trophic condition phosphorus inactivation was carried out twice (in 1994 and 1995) with the use of aluminium sulphate. The resulting positive changes were observed for approximately three years.

The goal of this study was to seek tendencies regarding changes in the selected organic matter indexes and to find the reasons for the lake's trophic condition impairment in subsequent years.

## MATERIAL AND METHOD

Lake Starodworskie is a small (6 ha) but deep (23 m) municipal reservoir, located in the south-western Olsztyn. The lake has no natural inflows and is regarded as a reservoir with no economic value. The main morphometric parameters are shown in Table 1. The drainage basin is small (0.24 km<sup>2</sup>) and experiences fast changes in the development, displayed mainly by new constructions rising near the lake's edges.

Parameter	Value	
Water surface area (ha)	6.0	
Maximum depth (m)	23.3	
Mean depth (m)	9.0	
Relative depth	0.095	
Maximum length (m)	345	
Maximum width (m)	312	
Volume (tys. m <sup>3</sup> )	540	

Table 1. Selected morphometric	parameters of Lake	Starodworskie	according to	Paschalski [24],
	changed by Lossow	v ct al. [17]		

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The favorable (i.e. close) location of the University of Warmia and Mazury was the reason for carrying out a few various restoration experiments on Lake Starodworskie [6, 13–16], one of them being the phosphorus inactivation with aluminium sulphate, applied in 1994 and 1995, for the first time in Poland [30, 33].

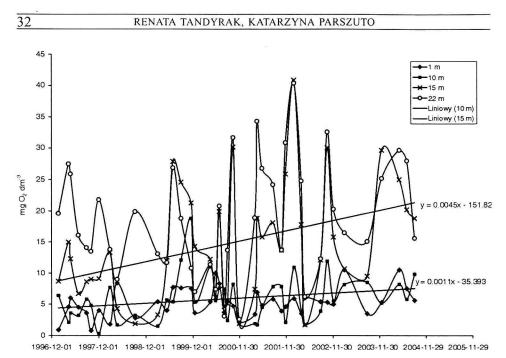
Water for the physico-chemical analyses was sampled from 1997 to 2004, usually in two-month intervals, from one sampling post over the deepest spot in the lake, from the depths of 1, 5, 10, 15, 20, and 22 m. This paper presents the results of the laboratory examinations of organic matter according to the methods obligatory for surface waters examinations [28].

The content of organic matter was determined (indirectly) as  $BOD_5$  and  $COD_{Mn}$ . Organic phosphorus (P org.) was calculated as a difference between total and mineral phosphorus. Mineral phosphorus was measured by colorimetry with ammonium molybdate and tin(II) chloride, as reducer. Total phosphorus was marked in a similar way, however, after prior mineralization with  $H_2SO_4$  and ammonium pershulphate. Organic nitrogen (N org.) was calculated as a difference between Kjeldahl-N and ammonium nitrogen, the latter determined by distillation or with the use of a Merck 118 spectrophotometer. Concentration of chlorophyll a in the water at 1 m depth was determined by colorimetry after preparation on a Whatman GF/C glass fiber filter and extraction with acetone (665 and 750 nm).

Concentration of total (non volatile) organic carbon (TOC) and dissolved organic carbon (DOC) – after filtration on a Whatman 0.45  $\mu$ m membrane filter – was determined with a Shimadzu TOC 5000 analyzer, after acidification to pH 2 and CO<sub>2</sub> removal. POC (particulate organic carbon) was calculated as a difference between TOC and DOC.

#### RESULTS

**BOD:** During the survey, the content of easily degradable organic matter (BOD<sub> $\epsilon$ </sub>) in the surface water varied in the broad range of 0.8-10.5 mg O<sub>2</sub> dm<sup>-3</sup>. The lowest mean annual concentrations were observed in 1997 and 1998 (3.92 and 4.33 mg O, dm-3, respectively) while next year, in the 5-m thick surface layer, the concentrations of BOD increased by approximately 50% (Tab. 2). The mean annual values detected at 5 m depth were lower than observed in the surface water and varied from 1.6 mg O, dm<sup>-3</sup> in 1998 to 4.93 mg O, dm<sup>-3</sup> in 2003. Higher concentrations and simultaneously the highest oscillations of this parameter were observed in deeper waters, especially at 10 and 15 m depths (Fig. 1). The mean values varied from 3.30 (1997) to 8.0 mg O, dm<sup>-3</sup> (1999 and 2004), and from 10.12 mg  $O_2$  dm<sup>-3</sup> at the beginning of the study to 17.23 mg O<sub>2</sub> dm<sup>-3</sup> in 1999. Similar values were measured in the following years, except for 2000 when the average amount of organic matter decreased. The tendency curves, describing the changes of the autochthonous matter content in Lake Starodworskie, show the tendency towards growth, especially with regard to the 15-m depth water layer. The deepest water layers (20 and 22 m depths) were characterized by the highest BOD values which was indirectly illustrated by the content of organic matter. Initially, the BOD went down from 18.69 (1997) to 10.68 mg  $O_2$  dm<sup>-3</sup> (2000) but then increased to 24.44 mg O, dm<sup>-3</sup> and similar values were observed until the end of the study.





 $COD_{Mn}$ : The mean value of this parameter, describing the content of allochthonous matter, ranged from 11.32 mg O<sub>2</sub> dm<sup>-3</sup> at 1 m depth in 1999 to 22.45 mg O<sub>2</sub> dm<sup>-3</sup> in the near bottom water in 1997 (Tab. 2). The vertical distribution of  $COD_{Mn}$  was analogous to that of the BOD. The highest  $COD_{Mn}$  oscillations were observed in the surface layer; the mean values in the following years changed from 11.32 (1999) to 18 mg O<sub>2</sub> dm<sup>-3</sup> (2000 and 2004). The water layer at 5 m depth contained less organic matter than the surface layer and the mean  $COD_{Mn}$  values oscillated in the narrow range of 11.92–14.42 mg O<sub>2</sub> dm<sup>-3</sup>. Only in the beginning of the study  $COD_{Mn}$  reached the maximal value of 18.5 mg O<sub>2</sub> dm<sup>-3</sup>. The variability of the  $COD_{Mn}$  values in other layers of Lake Starodworskie was small; usually, the values increased along with the depth. The maximum mean value 22.45 mg O<sub>2</sub> dm<sup>-3</sup> was noted in 1997; in the following years the concentrations were lower.

**Organic carbon:** From the beginning of the study until 2000 the mean content of **POC** in the surface water increased three times (from 1.61 to 4.77 mg C dm<sup>-3</sup>) and remained practically unchanged until the end of 2004 (Tab. 2). The increase in deep water was much smaller. At 10 and 15 m depths, the mean concentration varied between 0.94 mg C dm<sup>-3</sup> in 1997 and 2.09 mg C dm<sup>-3</sup> in 2001, and did not change considerably until the end of the study. Similar tendency was observed at 20–22 m depths. In the initial phase (until 1999) there were no important changes of the mean POC concentrations (1.31–1.53 mg C dm<sup>-3</sup>). In 2002, the mean POC concentration doubled, i.e., reached 2.77 mg C dm<sup>-3</sup> and remained at this level till the end of 2004. The variations of **DOC** were higher only in surface water. The lowest mean DOC concentration was detected in 1999 (7.73 mg C dm<sup>-3</sup>) while the highest in 2000 (10.56 mg C dm<sup>-3</sup>). The other water layers were characteristic of low DOC variability; the mean annual values ranged from 7.03 to 8.03 mg C dm<sup>-3</sup>. Only at the beginning of the study in the deep water DOC reached the maximum value of 9.89 mg C dm<sup>-3</sup>.

**Organic phosphorus:** Over recent years a growth tendency can be observed in the Lake Starodworskie waters, regarding both the mineral and the organic form of phosphorus (Fig. 2).

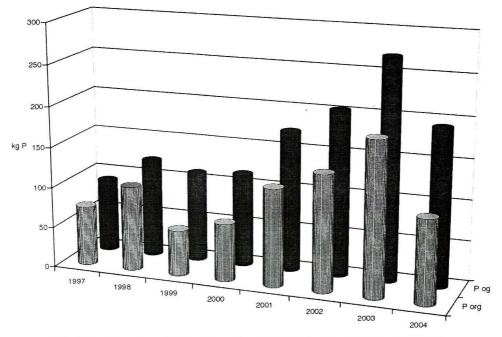
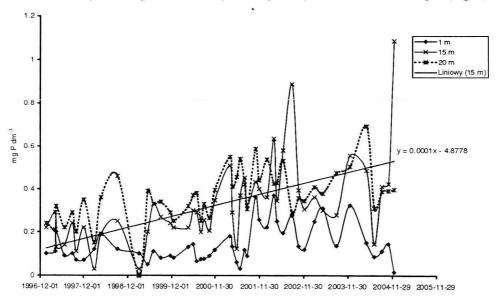


Fig. 2. Mean content of total and organic phosphorus in Lake Starodworskie waters

Organic phosphorus dominated in the water to 5 m depth, or even deeper in the winter and early spring, and comprised from 84.6 to 100% of the total phosphorus. Simultaneously, the same water layer contained from 32 to 60% (March 1999) of the organic phosphorus in the whole lake. In the following years of the study phosphorus increased considerably below 10 m depth. The growth tendency was especially clear below 15 m depth (Fig. 3)





where the mean concentrations varied in the range of 0.16 mg P·dm<sup>-3</sup> (1998) - 0.52 mg P·dm<sup>-3</sup> (2002) (Tab. 2). The near bottom water was characteristic of the highest mean concentrations of organic phosphorus, varying in a narrow range of 0.26 - 0.47 mg P dm<sup>-3</sup>.

**Organic nitrogen:** Organic nitrogen also revealed the tendency towards increase in the subsequent years. The increase was the most evident in water above 15 m depth (Fig. 4). With regard to the vertical distribution, the organic form in shallow waters contributed more to total nitrogen and decreased as the depth increased. The biggest differences and reduction of concentration were observed usually between 5 and 10 m depths; sporadically between 10 and 15 m depths. The maximum concentration of organic nitrogen was detected in 2003: in the surface layer in February (4.63 mg N·dm<sup>-3</sup>) and in the near bottom water in May (7.84 mg N·dm<sup>-3</sup>).

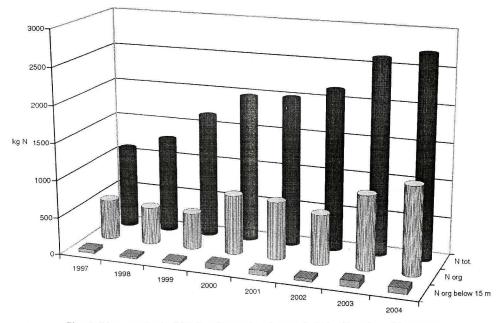


Fig. 4. Mean content of total and organic nitrogen in Lake Starodworskie waters

**Chlorophyll a:** Likewise, chlorophyll a revealed a tendency towards concentration growth in the surface water (Fig. 5). In the peak of the summer stagnation concentrations of the dye varied between 3.34 (1997) and 36.22 mg·m<sup>-3</sup> (2003) and were lower than in the cooler seasons. The highest values were measured usually in the autumn and early spring and the maximal concentration, i.e., 155.43 mg·m<sup>-3</sup> was detected in February 2003.

				years 1	997-2004			
	Depth [m]	BOD [mg O₂·dm <sup>-3</sup> ]	COD <sub>Mn</sub> [mg O₂·dm <sup>-3</sup> ]	POC [mg C·dm <sup>-3</sup> ]	DOC [mg C⋅dm <sup>-3</sup> ]	POC/DOC [%]	N org. [mg N·dm <sup>-3</sup> ]	P org. [mg P·dm <sup>-3</sup> ]
1997-	1	3.92 0.80 - 6.00	15.44 13.60 - 17.20	1.61 0.30 - 5.30	8.22 6.50 - 10.30	19.59	0.88 0.48 - 1.05	0.11 0.07 - 0.20
	5	2.77	18.56	2.18	7.66 6.60 - 9.60	28.46	0.91 0.62 - 1.10	0.13 0.07 - 0.21
	10	1.90 - 4.20 3.30	15.20 - 27.70 16.94	0.40 - 4.10 0.94	7.85	11.97	0.66	0.12
		0.30 - 5.80 10.12	11.00 - 20.00 18.82	0.00 - 2.50	6.00 - 12.90 7.44	17.34	<u>0.11 - 1.96</u> 1.93	0.02 - 0.26 0.19
	15	6.70 - 12.30 18.69	15.70 - 22.40 22.45	0.00 - 2.40	6.70 - 8.00 9.89	111101101	0.01 - 4.47 0.83	0.11 - 0.29 0.26
	20 - 22	13.50 - 27.50	20.20 - 24.50	0.00 - 3.60	7.30 - 12.20	13.25	0.00 - 2.02	0.14 - 0.36
	1	4.33 1.80 - 8.40	13.20 10.70 - 15.00	2.55 0.90 - 5.20	7.54 6.20 - 9.00	33.82	1.20 0.68 - 2.10	0.14 0.12 - 0.19
	5	1.60 1.00 - 2.40	13.97 10.70 - 17.30	3.24 0.70 - 6.50	7.29 6.30 - 8.40	44.44	0.96 0.74 - 1.28	0.22 0.17 - 0.27
8661	10	4.20 1.70 - 7.70	12.80 10.40 - 14.90	1.19 0.70 - 2.00	6.73 6.20 - 7.30	28.23	0.79 0.47 - 1.12	0.18 0.13 - 0.28
1	15	6.50	17.53	1.30	7.04	18.47	0.63 0.15 - 0.90	0.16 0.03 - 0.25
	20 - 22	1.90 - 13.30 11.00	<u>17.40 - 17.60</u> 21.06	0.90 - 2.10 1.47	6.60 - 7.70 8.28	17.75	0.44	0.33
Н		3.40 - 19.90 5.97	19.20 - 23.20 11.32	0.50 - 2.40 2.37	6.60 - 9.40 7.73		0.00 - 1.31 0.91	0.15 - 0.46 0.09
	1	3.60 - 7.70	9.10 - 13.40 11.92	1.20 - 5.10 2.73	7.00 - 8.70 7.52	30.66	0.09 - 1.82	0.05 - 0.11 0.10
	5	4.02 2.00 - 7.80	7.80 - 14.60	1.00 - 4.90	6.90 -8.20	36.30	0.34 - 1.77	0.09 - 0.11
666	10	8.13 1.50 - 18.80	13.92 9.30 - 17.60	1.28 0.80 - 1.90	7.20 6.40 - 8.60	17.78	0.72 0.11 - 2.21	0.12 0.06 - 0.16
-	15	17.23 3.30 - 27.90	16.88 14.40 - 18.60	1.25 0.70 - 1.60	7.12 6.70 - 7.60	17.56	0.55 0.11 - 1.23	0.22 0.03 - 0.33
	20 - 22	14.02 7.00 - 26.90	18.12 16.50 - 21.10	1.53 0.40 - 2.10	7.39 6.40 - 8.70	20.70	1.05 0.51 - 2.52	0.27 0.00 - 0.39
_	1	5.72	18.18	4.77	10.56	45.17	1.58	0.09
		2.10 - 10.00 2.97	21.90 - 13.30 13.20	2.20 - 7.40 2.35	8.45 - 12.00 8.08	28.96	1.09 - 2.33 1.62	0.07 - 0.14 0.09
	5	1.90 - 4.20 5.52	10.20 - 16.00 13.12	2.00 - 2.80 1.2	7.10 - 10.45 7.71		1.15 - 1.90 0.64	0.05 - 0.15 0.09
2000	10	1.90 - 8.20	11.40 - 14.10	1.00 - 1.50	6.50 - 9.50	15.56	0.20 - 1.23	0.05 - 0.16
	15	11.30 1.90 - 30.20	18.57 17.60 - 20.00	1.47 0.86 - 2.16	7.94 6.60 - 10.40	18.51	1.40 0.59 - 2.68	0.27 0.20 - 0.35
	20 - 22	10.68 2.10 - 32.70	19.61 18.70 - 20.30	2.23 1.45 - 2.93	7.76 6.70 - 10.40	28.74	0.77 0.00 - 2.02	0.33 0.20 - 0.46
	1	4.90 3.40 - 6.90	14.33 12.00 - 17.2	3.75 2.63 - 4.80	8.24 7.00 - 10.52	45.51	1.59 0.98 - 2.52	0.15 0.03 - 0.36
	5	4.45 1.50 - 8.20	13.10 9.12 - 15.20	3.40 1.98 - 4.92	7.58 6.75 - 9.70	44.85	1.63 0.46 - 3.92	0.17 0.06 - 0.42
2001	10	4.30	12.65 9.60 - 15.20	2.08 1.46 - 2.75	7.15 6.33 - 9.00	29.23	0.84 0.17 - 1.91	0.22 0.09 - 0.62
20	15	16.62	17.63	2.09	7.26	28.79	1.68	0.36
	20 - 22	7.40 - 25.90 24.52	16.00 - 19.20 19.59	1.57 - 2.80 2.53	6.58 - 9.20 7.56	33.73	0.22 - 5.99 0.87	0.12 - 0.51 0.47
_		13.70 - 34.30 5.04	17.60 - 21.30 16.82	1.75 - 3.90 5.06	6.65 - 9.40 9.54		0.00 - 2.77	0.31 - 0.59
	1	3.50 - 6.00	8.20 - 21.30	3.11 - 8.37	7.07 - 13.13	52.31	0.78 - 2.58	0.12 - 0.37
	5	3.92 1.70 - 7.90	12.57 9.10 - 16.50	2.77 2.13 - 3.45	7.95 6.84 - 10.69	34.84	1.59 0.67 - 2.49	0.22 0.12 - 0.37
2002	10	6.23 3.60 - 11.90	12.03 9.10 - 14.10	2.01 1.46 - 2.73	7.34 6.74 - 8.03	27.38	1.02 0.20 - 2.35	0.23 0.12 - 0.59
3	15	15.50 1.70 - 30.10	16.93 14.40 - 20.00	2.03 1.70 - 2.31	7.52 7.05 - 7.94	26.99	1.08 0.36 - 1.82	0.52 0.31 - 0.89
	20 - 22	19.22 3.70 - 32.60	18.03 14.40 - 21.90	2.77 2.30 - 3.35	7.90 7.30 - 8.80	35.06	1.19 0.11 - 2.30	0.42 0.29 - 0.67
	1	7.19 3.50 - 10.50	18.93	4.99	9.61	51.93	2.60 0.35 - 4.36	0.25
	5	4.93	15.70 - 20.60 15.87	3.52 - 6.54 2.61	7.30 - 13.72 8.63	30.24	1.28	0.14 - 0.32 0.20
33		4.00 - 6.10 7.29	12.00 - 19.30 16.00	1.77 - 3.15 2.11	7.64 - 9.94 7.89		0.49 - 2.33 1.60	0.00 - 0.30 0.27
2 003	10	5.20 - 8.50 16.63	15.20 - 16.50 16.00	1.40 - 3.35 2.36	7.68 - 8.08 7.39	26.74	0.25 - 3.76	0.00 - 0.62
	15	9.50 - 29.70	13.40 - 17.80	1.25 - 3.75	6.09 - 8.65	31.94	0.56 - 4.10	0.00 - 0.56
	20 - 22	17.74 7.15 - 29.70	17.95 16.30 - 18.90	2.58 1.88 - 3.34	8.11 6.57 - 9.30	31.81	2.72 0.64 - 7.84	0.40 0.00 - 0.57
2004	1	6.75 3.30 - 10.50	18.07 16.32-20.64	4.84 2.44 - 9.46	9.72 6.86 - 11.59	49.79	2.50 1.84 - 3.04	0.10 0.02 - 0.15
	5	4.23 3.00 - 5.80	14.42 12.60 - 16.80	2.28 1.37 - 3.35	7.72 6.91 - 8.73	29.53	2.56 1.43 - 3.98	0.13 0.00 - 0.23
	10	8.08 5.00 - 9.80	14.91 12.80 - 17.92	2.00 1.52 - 2.96	7.26 6.64 - 7.61	27.55	1.88 0.67 - 4.34	0.13 0.00 - 0.25
	15	18.43	17.47	1.75	7.03	24.89	1.87	0.30
	20 - 22	8.00 - 25.00 24.44	16.00 - 20.32 18.42	1.49 - 2.05 2.24	5.79 - 7.77 7.42		1.04 - 3.58 1.42	0.04 - 0.49 0.37
	20.22	15.00-31.00	17.40 - 20.48	1.28 - 2.84	6.01 - 8.40	30.19	0.61 - 3.95	0.16 - 0.64

Table 2. The range and mean values of parameters measured in Lake Starodworskie waters over the years 1997–2004

\*- POC and DOC on the basis of results received by Zimińska and Wójtowicz [36]

\*\*- POC and DOC on the basis of results received by Stanecka [29]

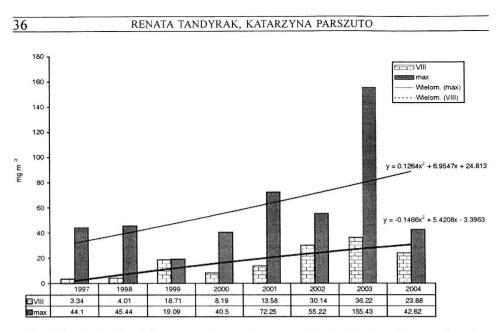


Fig. 5. Trends of chlorophyll a changes (maximum values and September) in surface water layer in Lake Starodworskie waters

### DISCUSSION

The dynamics of the water mass in Lake Starodworskie is limited. Paschalski [24] classified the lake as bradymictic, however recently water mixing in the lake is more meromictic. Below 13 m depth (unpublished data), the water is practically not mixed and oxygen-deficient.

In 1994 and 1995 (two phases), the lake was treated with aluminium sulphate in order to inactivate phosphorus. The direct effect of the treatment was a considerable reduction of the mineral phosphorus concentration in the water and inhibition in the bottom deposits [31, 33]. Additionally, the aluminium hydroxide produced in hydrolysis, precipitated the organic matter [32]. In effect, the water visibility improved and the organic matter parameters (BOD and  $COD_{MP}$ ) decreased, as well as the chlorophyll a content.

The positive effects of the inactivation were evident for only three years after the second phase of the experiment [33]. The current research indicates constant growth of all organic matter indexes in the lake.

The overall biological and hydro-geochemical processes in lakes are affected by the type and amount, as well as relationships, dynamics, conditions, and ecological effects of the organic matter transformations [21].

Organic matter in lake can be imported from the drainage basin or produced directly in the water (primary production) which is displayed by the chlorophyll a concentration. In the lake discussed there is a strict relation between the mineral phosphorus circulating in the spring and the primary production in the summer stagnation [32]. Reduction of phosphates from the surface water which occurred right after the restoration experiment considerably limited the primary production [31].

As far as the eutrophication abatement is concerned, not only the quantity of nutritive elements in the water is important but most of all the relationships between them [18]. In Lake Starodworskie, the N/P ratio for the whole water volume was contained in the range

10–21 (13.3 on the average). The value was similar in the productive layer, although with bigger oscillations. Sporadically, in the summer stagnation periods, the ratio was extremely high and exceeded 30. Low values indicate limited occurrence of the ecologically valuable phytoplankton species and the conditions for blue-green algae blooms [15, 26]. It is therefore required to increase the N/P ratio above 29 [35].

Surface waters receive phosphorus with so-called specific external load or, in anaerobic and aerobic conditions, by internal loading from the bottom sediments. As in Lake Starodworskie epilimnion covers approximately 33% of the total bottom area, the role of this bottom's section must not be neglected with respect to phosphorus release Boström and Petterson [1] share the opinion that phosphorus is released from the active bottom surface directly to the trophogenic layer.

In reductive conditions, the amounts transported from the bottom sediments to water are many times higher [5, 27]. In the past years, the concentration of phosphates constantly increased in the deepest layers (unpublished data), nonetheless the mictic type of the lake prevented transport to the epilimnion and supplementation of the primary production.

The calculations by Lossow et al. [17], according to Vollenweider criteria, indicate current external loading to the lake with the basic nutrients exceeding the permissible loads and, to a smaller degree, the load described as hazardous. The permissible loads calculated for Lake Starodworskie equal 1.5 g N m<sup>-2</sup> year and 0.093 g P m<sup>-2</sup> year while the hazardous amount to 3 g N m<sup>-2</sup> year and 0.186 g P m<sup>-2</sup> year, respectively. The loads currently imported to the lake from the drainage basin are 3.2 g N m<sup>-2</sup> year and 0.227 g P m<sup>-2</sup> year. Nonetheless, it may be assumed that even small violation of the critical loads will result in an increase of all the discussed parameters' values.

Although carbon content almost never determines the trophic condition of a lake, nor stimulates algal blooms, it is the element that builds all organic compounds. Therefore, it seems justified to seek relations between organic carbon forms and other organic matter indexes.

The relationship between the easily degradable and resistant to degradation organic matter (BOD/COD<sub>Mn</sub>), only sporadically higher than 0.5, indicates the dominance of allochthonous matter in the water above 10 m depth. Such dominance is in turn the evidence for the input of organic substance from the drainage basin in dissolved and particulate forms, as shown by the correlation coefficients: between DOC and COD<sub>Mn</sub> (r = 0.696,  $p \le 0.01$ ), and POC and COD<sub>Mn</sub> (r = 0.637,  $p \le 0.01$ ). The study revealed an important role of the organic nitrogen (correlation between N org. and COD<sub>Mn</sub> r = 0.4726,  $p \le 0.01$ ) and lack of correlation with the organic phosphorus. Górniak's study [8] revealed the influence of DOC and dissolved humic substance (DHS) on the concentration of some ions, important for the water fertility (orthophosphates, total phosphorus, ammonium ions, nitrites).

The correlation coefficients also point out the relationship between the organic nitrogen and POC in the shallow water (r = 0.6406,  $p \le 0.01$ ). Similar relationship for organic phosphorus was not found.

It should be mentioned that the development in the close vicinity of the lake underwent large transformations: new buildings of the university were raised on the western side; an estate of detached houses was located near the lake. Lossow et al. [17] reported that among the major threats to the lake is the fifty-year old slope, extremely vulnerable to erosion and constantly damaged by horses from a horse riding centre. They called attention to the alarming need to protect this slope.

In the water of Lake Starodworskie a relationship was found between the amount of the easily degradable autochthonous organic matter (BOD) and the chlorophyll a content  $(r = 0.4317, p \le 0.05)$  and significant correlations between POC and chlorophyll a  $(r = 0.4622, p \le 0.05)$  $p \le 0.01$ ), POC and BOD (r = 0.5100,  $p \le 0.01$ ), and POC and DOC (r = 0.5000,  $p \le 0.01$ ). Therefore, assumingly, not only the phytoplankton is the source of organic matter in the lake's surface water but also the secondary production and the rate and direction of transformations of the dead organic matter. Vulnerability of lakes and water reservoirs to eutrophication is determined not only by the quantity of mineral nutrients and organic matter imported from the drainage basin but also by the rate of autochthonous matter utilization by the aquatic bacteria assemblages. The fast rate of decomposition and utilization of the organic matter performed by the heterotrophic bacteria leads to its mineralization, preventing first of all excessive accumulation of particulate and dissolved organic matter in the water and in the bottom sediments [4]. The high primary production is accompanied by an increase of the amount of simple organic compounds excreted by algal cells, as indicated by the positive correlation between BOD and chlorophyll a content. Tranvik et al. [34] found out that dissolved organic matter (DOM) produced in a lake with high primary production can be transformed into forms resistant to biological degradation.

Intensity of organic matter circulation in lake depends on water mixing [25]. In the discussed lake production dominates in the shallow water (1 and 5 m depths). Shallow (1–2 m) epilimnion, large thermal gradient (to  $8.8^{\circ}$ C/m in September 2001), relatively low temperatures (5.2–5.4°C) and de-oxygenation of the water mass in the meromictic Lake Starodworskie, stimulated POC sedimentation and accumulation of the compounds resistant to degradation (COD<sub>Mo</sub> and DOC).

The evidence that production in Lake Starodworskie increased during the study period was the increase of the POC contribution in relation to DOC (Tab. 2), clearly observable at 1 and 5 m depths (to 52.31% on the average in 2002 vs. 19.59% in 1997) and lower in the deeper water (to 35.06% on the average in 2002 vs. 13.25% in 1997). Parszuto and Grochowska [23] reported that in Lake Długie, for many years restored by artificial aeration [7, 9], the mean value of the POC/DOC ratio did not exceed 20% whereas in Lake Kortowskie the POC/DOC ratio, except for the autochthonous organic matter, was greatly affected by the allochthonous organic matter imported with the inflows [22].

The content of organic substance (BOD,  $COD_{Mn}$ , POC) in the deeper waters of Lake Starodworskie increased along with the depth. The apparent increase of the concentrations to 15 m depth resulted possibly from the meromixis in the lake. The monimolimnion water is characterized by elevated density [3] which slows down sedimentation of organic matter.

The correlations determined in the deepest water (20 and 22 m depths) between POC and organic phosphorus (r = 0.31,  $p \le 0.05$ ), and between POC and BOD (r = 0.34,  $p \le 0.01$ ), indicate that suspended organic matter is an important source of the easily degradable organic compounds and nutritive elements in the monimolimnion.

The increased concentration of organic phosphorus below 15 m depth and the simultaneous lower per cent contribution to total phosphorus may be the effect of the inactivation performed in the 1990s.

Reductive conditions in the near bottom water are regarded as the main factor controlling phosphorus release from the bottom sediments [19]. Constant reductive conditions in deep water stimulate release of phosphates from the few cm thick layers of the sediments deposited on the coagulant. Despite the ongoing increase of phosphates concentration in the near bottom water (Fig. 3), it remains lower than before the restoration experiment [31].

Mineralization of the organic matter in the bottom sediments is the reason for ammonium nitrogen production. The process is favored by low (or zero, as in the discussed lake) oxygen content [2, 10]. Therefore, organic nitrogen in the water below 15 m depth comprised only a minor part of the organic nitrogen (6.5–8.9% on the average) in the whole lake (Fig. 4).

### CONCLUSIONS

The content of chlorophyll a, reflecting the primary production, has revealed a growth trend, alike the BOD content. The increase of this parameter's value observed in the deeper water layers was caused by the sedimentation of organic matter which while decomposed in the anaerobic hypolimnion produced high amounts of ammonium nitrogen. This form of nitrogen dominated in the total nitrogen underneath the 15<sup>th</sup> meter. At the same time, the prevailing form of the total phosphorus was organic which may indicate inhibition of the so-called internal loading.

Constant increase of all examined parameters was caused by the enhanced primary production and the input of organic substances and nutrients from the drainage basin (in quantities slightly higher than the critical values). In order to diminish this input it is necessary to implement some protective measures, concerning especially the nearby slope at the horse riding centre.

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