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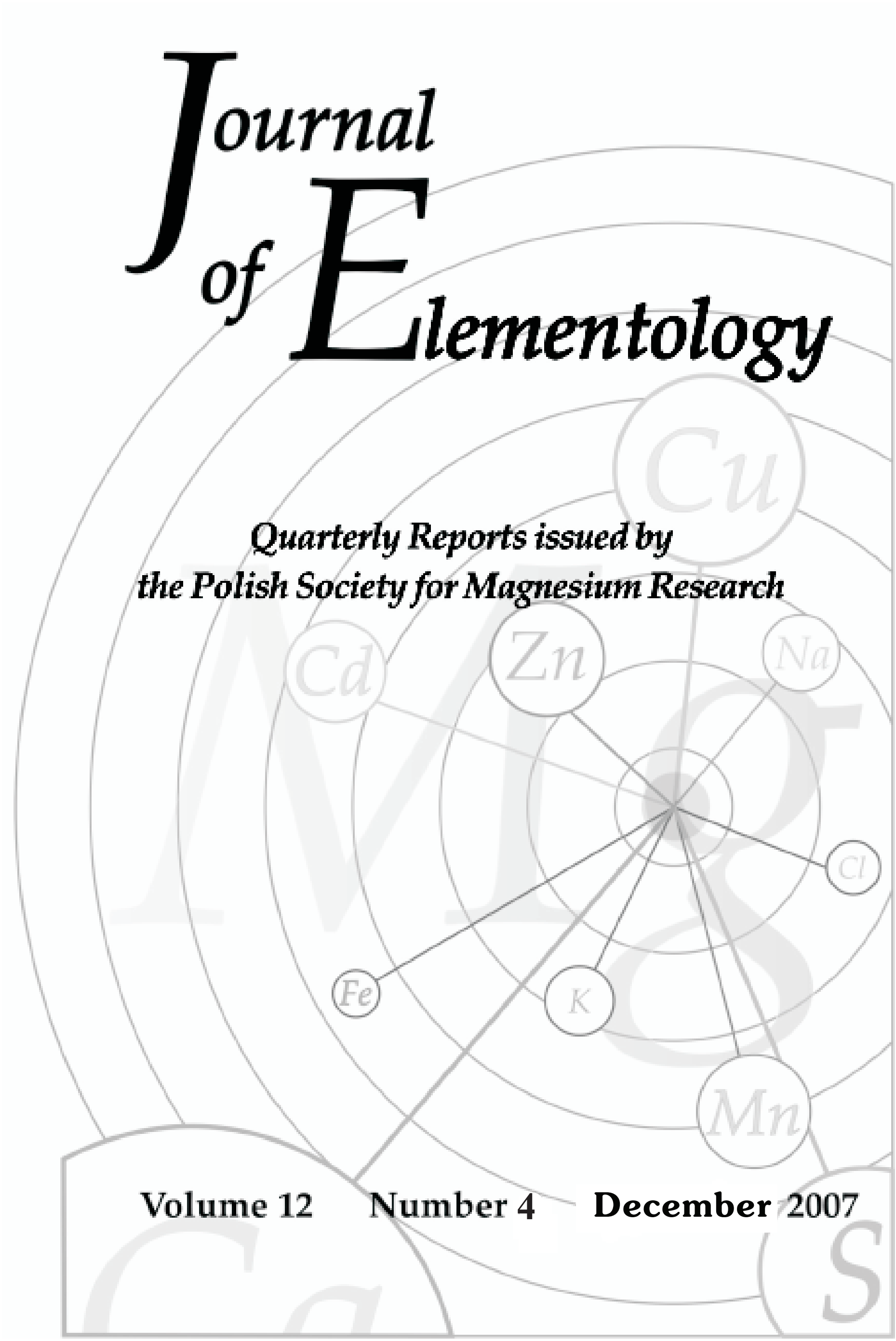

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Original papers

CONTENT OF SOME NUTRIENTS IN NEW BLACK OAT STRAINS

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Abstract

The nutritive benefits of oats for both human consumption and animal feeding stimulate scientifically based breeding efforts to obtain new varieties, including brown oat grain (black oat).It is a fodder the cereal is used chiefly for racehorses. The objective of the present research was to compare the contents of the selected nutrients, i.e. crude protein, crude fat, composition of fatty acids and minerals in grain of three black oat strains: CHD 28/75/01, CHD 28/ /33/02 and CHD 2909/01 with reference to two oat standard varieties (Bohun and Deresz), commonly grown in Poland. The three new black oat strains showed varied crude protein levels and a slightly lower crude fat content compared to the oat standard varieties Bohun and Deresz. The black oat strain CHD 28/75/01 exhibited the highest percentage of unsaturated fatty acids (UFA) and monounsaturated fatty acids (MUFA) versus the other strains and varieties. This oat strain grain is also characterized by a substantially higher content of magnesium, phosphorus, zinc, copper and iron than the other strains and varieties investigated.

Key words: oat, crude protein, crude fat, fatty acids, mineral elements.

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ZAWARTOŚĆ WYBRANYCH SKŁADNIKÓW POKARMOWYCH W NOWYCH RODACH OWSA CZARNEGO.

Abstrakt

Zalety żywieniowe owsa, zarówno dla ludzi, jak i zwierząt, są bodźcem do prac hodowlanych nad nowymi odmianami, w tym owsa czarnego o brunatnej barwie ziarniaków. Jest to zboże paszowe, stosowane głównie do skarmiania koni wyścigowych. Celem pracy było porównanie zawartości wybranych składników pokarmowych, tj.**:** białka ogólnego, tłuszczu surowego, składu kwasów tłuszczowych oraz elementów mineralnych, w ziarnie trzech rodów owsa czarnego: CHD 28/75/01, CHD 28/33/02 i CHD 2909/01 w odniesieniu do dwu odmian wzorcowych owsa (Bohun i Deresz) powszechnie uprawianego w Polsce. U 3 nowych rodów owsa czarnego stwierdzono zróżnicowany poziom białka ogólnego oraz nieznacznie obniżony poziom tłuszczu surowego w stosunku do owsa odmian wzorcowych Bohun i Deresz. Nawiększy udział procentowy nienasyconych kwasów tłuszczowych (UFA) i jednonienasyconych kwasów tłuszczowych (MUFA), w porównaniu z pozostałymi rodami i odmianami, wykazano u rodu CHD 28/75/01. W ziarnie tego rodu stwierdzono również wyższą zawartość magnezu, fosforu, cynku, miedzi i żelaza w porównaniu z pozostałymi testowanymi rodami i odmianami.

Słowa kluczowe: owies, białko ogólne, tłuszcz surowy , kwasy tłuszczowe, składniki mineralne.

INTRODUCTION

Recently, there has been an increasing worldwide interest in oat, stimulated by the beneficial nutritive value of this cereal for humans and animals. The foods produced from oat grain show hypocholesterolemic activity due to the presence of water-soluble dietary fibre containing beta-glucan fraction. These polysaccharides are capable of binding cholesterol and bile acids in the digestive system (NEWMAN et al. 1992, WURSCH, PI-SUNYER 1997, GĄSIOROWSKI 2003). The chemical composition of oat grain is similar to that of other cereals, yet it is far richer in protein and fat. The content of exogenous amino acids is higher than in other cereals so the biological value of oat protein is also markedly higher. Beside proteins, fat substances constitute a major component of oat which shapes its physiological, nutritional and processing characteristics. Oat grain fat is rich in unsaturated fatty acids, which make up 80% of all the fatty acids (GĄSIOROWSKI, URBANOWICZ 1992, OZCAN et al. 2006, BANAŚ et al. 2007).

Compared to other cereals, oat grain is low in saccharides, like starch (average 53%) and cellulose, but it is abundant in soluble fibre fractions, which prove vital in maintaining the beneficial microflora of the intestines, stimulating generation of probiotic bacteria of milk fermentation and inhibiting development of pathogens (KOLANOWSKI 1998, GAJEWSKA et al. 2002).

Comparison of the content of minerals in oat grain and other cereals indicates that oat is far more abundant in Ca, Fe, Zn and Mn. Consequently, oat grain is recognized as an excellent source of dietary minerals for humans and animals. The content of minerals in hulled oat grain is considerably higher than in dehulled grain. However, although the qualities of oat prove to be beneficial, the cultivation area of this cereal systematically decreases all over the world. Currently, oat grain is mainly used as fodder for animals and only as little as 5% of the total crop yield is utilized by the food industry. The breeders make efforts to market new varieties of black oat. Black oat is very popular, especially as a staple constituent of a diet for racehorses. Moreover, it is a major nutritional supplement of grain feed given to animals taking part in races, as it enhances their performance as a short- and medium-term energy supplement, essential during competitions.

The present research compared the content of basic nutrients in three black oat strains and two standard varieties commonly grown in Poland. The qualitative evaluation included crude protein, crude fat, fatty acid composition and mineral content.

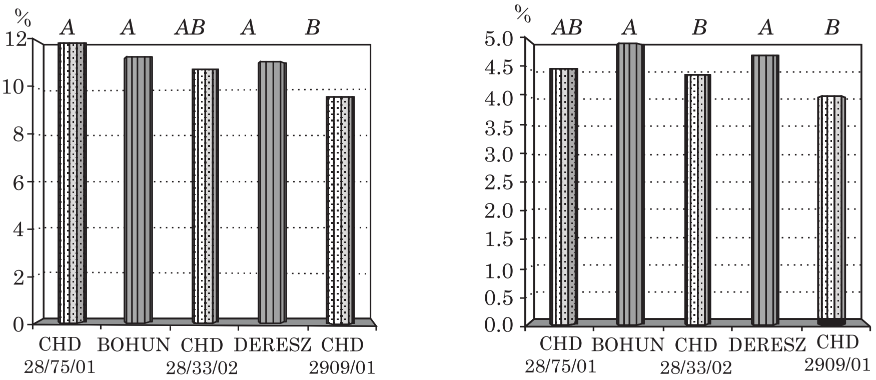
MATERIAL AND METHODS

The experimental material embraced two yellow-grain oats varieties, Deresz and Bohun, of average hull content. These two varieties served as reference for three black oat strains: CHD 28/75/01, CHD 28/33/02 and CHD 2909/01, which were obtained from the Breeding Station DANKO in Choryń. Black oat is a fodder cereal, used chiefly as a component of the equine diet.

For analytical examinations, we used oatmeal produced by thorough grinding in a laboratory mill. In the test material, crude protein in grain samples was determined according to Kjeldahl method using a Kiel-Foss apparatus whereas crude fat content was assessed according to the Soxhlet method, on Soxtec MT-6 apparatus. The minerals were analyzed using AAS method on a UNICAM 939 apparatus, after wet mineralization of oatmeal in a mixture of $HClO_4$ and HNO_3 (5:1 ratio). Percentage of fatty acids in oat grain triglycerides was determined by the gas chromatography method, after their esterification process (methyl ester form).The results were analyzed statistically using Statistica program version 5 and a single factor analysis of variance ANOVA test at significance levels of 0.01 and 0.05.

RESULTS AND DISCUSSION

Figure 1 presents the crude protein content in the strains and varieties of oat. In oat grain, the protein content usually ranges from 11 up to 15% (BARTNIKOWSKA et al. 2000). Owing to an elevated lysine content, the



crude protein – białko ogólne

crude fat – tłuszcz surowy

A,B – significantly different values ($p \le 0.01$)
A,B – różnice istotne ($p \le 0.01$)

Fig. 1. Content of crude protein (%) and crude fat (%) in ground grain of oat strains and cultivars

Rys. 1. Zawartość białka ogólnego (%) i tłuszczu surowego (%) w śrucie owsianej badanych rodów i odmian

proteins in oat have the highest biological value among the cereals (Särkijärvi, Saastamoinen 2006). Another advantage of oat proteins is their good digestibility (Pedo et al. 1999, Frątczak et al. 2003). Compared to some other cereal species, negative correlation between grain yield and protein content proved weak (Bartnikowska et al. 2000). Oat grain of CDH 28/75/01 strain was characterized by a higher crude protein (11.91%±0.85) level than Deresz and Bohun varieties. The protein concentration in this strain was similar to that reported by Pisulewska et al. (1997) for naked oat grown on light soil. The lowest crude protein content was determined in oat grain from CDH 2909/01 strain (9.580% ± 0.080). There was no statistically significant difference in the protein level between the standard varieties Bohun and Deresz. In agricultural practice, this parameter can be strongly modified through different levels of nitrogen fertilization, while the technological treatment of oat grain dehulling increases protein content.

The present research revealed that the highest crude fat content was in oat grain of Bohun and Deresz varieties (Fig. 1). Bohun variety, according to the BS DANKO, proves to be high in fat, with an average 5.7% fat content. The analysis performed on this variety showed that its fat content, 4.94%±0.05, was the highest among all the oat samples. The lowest crude fat content was detected in oat grain of CHD 2909/01 strain (4.00%±0.07). All the new black oat strains contained less crude fat than Bohun and Deresz varieties.

Table 1 presents fatty acid percentage in triglycerides of the oat strains and varieties studied. Among the cereals, oat appears to be the most valuable cereal product due to the elevated content of unsaturated fatty acids (UFA) compared to saturated fatty acids (SFA). Our study showed that the highest unsaturated fatty acid level (83.17%) was in CHD 28/75/01oat strain. The other oat samples, except Bohun (80.33%), had similar UFA proportion (over 81%). In a human organism, the fatty acid desaturation can proceed exclusively between the C9 and C10 carbon atom, therefore the polyunsaturated fatty acids (PUFA), i.e. linoleic and linolenic acid, must be consumed from the dietary sources. In this aspect, the most beneficial was grain of CDH 2909/01 strain, which contained 43.80% of PUFA, while the lowest PUFA proportion was observed in the black oat strain CDH 28/75/01 (39.88%). These results were similar to those reported by Kamińska (2003). Currently, a growing physiological role is attributed to the monounsaturated fatty acids (MUFA), which are known to promote atherosclerosis prevention. The highest percentage of MUFA (43.29%) was established in CDH 28/75/81 black oat strain, whereas the lowest one – in CDH 2909/01 (37.60%). Among the fatty acids composing the dietary fat, the most frequent appears to be double bond cis configuration, although in some foods fatty acids may occur in a trans isomer form. The loose their biological value and become an energy source only. In all the oat varieties investigated, the presence of trans isomer was confirmed referring to C18:1. However, in each case similar quantities trans isomer fatty acids were obtained (approximately 1% of all the fatty acids).

Table 1
Tabela 1

Fatty acids content (%) in grain of different oat cultivar and strains
Udział kwasów tłuszczowych (%) w ziarnie różnych odmian i rodów owsa

Fatty acids Kwasy tłuszczowe (%)	Oat cultivar and strains – Odmiany i rody owsa				
	CHD 28/75/01	Bohun	CHD 28/33/02	Deresz	CHD 2909/01
14:0	0.17	0.22	0.25	0.27	0.26
16:0	14.50	17.04	16.93	16.74	16.70
16:1	0.23	0.21	0.19	0.24	0.22
18:0	1.05	1.53	0.92	1.13	1.06
18:1c	40.56	37.37	38.87	39.17	35.44
18:1t	1.28	1.00	1.03	0.97	1.01
18:2c	38.06	38.78	38.44	38.82	42.12
18:3c	1.82	1.56	1.47	1.66	1.68
20:0	0.17	-	0.14	0.13	0.14
20:1	1.22	0.78	1.26	0.80	0.93
22:2	0.00	0.63	0.29	0.00	0.00
Other – Inne	0.94	0.88	0.21	0.07	0.44
SFA	15.89	18.79	18.24	18.27	18.16
UFA	83.17	80.33	81.55	81.66	81.4
MUFA	43.29	39.36	41.35	41.18	37.60
PUFA	39.88	40.97	40.20	40.48	43.80

Black oat grain differed from the standard varieties by a higher ash content (Tab. 2). A similar relationship was found by GAMBUŚ et al. (2006) who recorded a 3.35% ash content in yellow hull oat, and 3.66% in black hull oat. The highest percentages of available ash in oat strains were found in CHD 28/75/01 (2.528%±0.019) and CHD 2909/01 (2.502%±0.016), while cv. Bohun variety was the poorest in ash (2.159% ± 0.034). These results are slightly higher than those concerning ash content in oat grain established by SKIBNIEWSKA et al. (2002) – 2.05%.

The highest potassium level was in black oat strains CDH 2909/01 (0.423% ± 0.016) and CDH 28/33/02 (0.378% ± 0.081). CDH 28/75/01 strain contained less potassium (0.331% ± 0.032) compared to the standard varieties, although the difference between CHD 28/75/01 and CHD 28/33/02 versus the standard varieties was not statistically significant. GAMBUŚ et al. (2006) found that the potassium level in flour produced from black hull oat reached 0.292%, while in flour of yellow hull oat it was 0.324%. SOUCI et al. (2000) reported a higher range of this element content in oat grain, i.e. 0.338 – – 0.387%, but it was still under the level reported for black oat strain CHD 2909/01.

A significantly higher phosphorus level, compared to the other samples, was determined for CHD 28/75/01 strain (0.388% ± 0.004) and Bohun variety (0.362% ± 0.009); this was even higher than quoted by Souci et al. (2000), where it varied from 0.332 up to 0.352%. In the study by GAMBUŚ et al., (2006), the phosphorus content was 0.411% in black oat grain and 0.361% in yellow grain oat. The difference in phosphorus between the standard varieties and CHD 28/33/02 and CHD 2909/01 strains was not statistically significant at p?0.05.

Magnesium in the oat strains differed from that in the standard varieties. Grain of CHD 28/75/01 and CHD 2909/01 strains proved richer in this element than the standard varieties. The highest magnesium level was determined in the strains CHD 28/75/01 (0.117% ± 0.014) and CHD 29090/01 (0.114% ± 0.019). These values were close to those reported by SKIBNIEWSKA et al. (2002), GAMBUŚ et al. (2006) and SOUCI et al. (2000).

The content of calcium in the oat samples ranged from 0.001 up to 0.015% and its highest contents was determined in CHD 28/33/02 and CHD 2909/01 strains as well as Deresz variety, whereas CHD 28/75/01 strain and Bohun variety contained significantly less Ca. However, the range of the calcium values for the strains and varieties studied was markedly lower compared to the results given by SOUCI et al. (2000) and SKIBNIEWSKA et al. (2002).

As for manganese, two statistically homogeneous groups at $p \leq 0.01$ were determined: strains CHD 28/75/01 and CHD 2909/01 with a higher manganese content and the remianing samples with a lower manganese level. Likewise, the study by GAMBUŚ et al. (2006) showed higher manganese content in black oat.

Table 2
Tabela 2

Content of mineral nutrient components in grain of oat strains and cultivars
Zawartość składników mineralnych w ziarnie rodów i odmian owsa

Oat Owies	K	P	Mg	Ca	Mn	Fe	Zn	Cu	Ash % d.w. Popiół % s.m.
	% d.w. – % s.m.				mg•kg^{-1}d.w. – mg•kg^{-1}s.m.				
CHD 28/75/01	$0.331^{b}\pm0.032$	$0.388^{a}\pm0.004$	$0.117^{a}\pm0.015$	$0.001^{B}\pm0.000$	$49.1^{A}\pm5.0$	$48.9^{A}\pm6.8$	$41.7^{A}\pm6.0$	$5.5^{A}\pm0.2$	$2{,}528^{A}\pm0.019$
Bohun	$0.326^{b}\pm0.028$	$0.362^{ab}\pm0.009$	$0.104^{ab}\pm0.001$	$0.009^{B}\pm0.001$	$36.3^{B}\pm1.1$	$43.0^{A}\pm6.0$	$38.0^{A}\pm0.4$	$5.2^{A}\pm0.6$	$2.159^{B}\pm0.034$
CHD 28/33/02	$0.378^{ab}\pm0.081$	$0.3402^{b}\pm0.005$	$0.083^{b}\pm0.012$	$0.015^{A}\pm0.003$	$34.1^{B}\pm3.0$	$31.5^{B}\pm0.5$	$24.6^{B}\pm2.3$	$2.8^{B}\pm0.1$	$2.437^{A}\pm0.022$
Deresz	$0.355^{ab}\pm0.015$	$0.345^{b}\pm0.005$	$0.089^{b}\pm0.014$	$0.013^{AB}\pm0.001$	$32.0^{B}\pm2.6$	$44.9^{A}\pm2.8$	$23.6^{B}\pm7.1$	$3.4^{B}\pm0.3$	$2.274^{B}\pm0.000$
CHD 2909/01	$0.423^{a}\pm0.016$	$0.320^{b}\pm0.002$	0,114a±0.016	$0.014^{AB}\pm0.002$	$58.2^{A}\pm8.6$	$29.7B\pm1.5$	$24.6^{B}\pm3.6$	$3.3^{B}\pm0.6$	$2.502^{A}\pm0.016$

A, B – statistically significant differences at $p \leq 0.01$ – różnice istotne statystycznie gdy $p \leq 0{,}01$
a, b – statistically significant differences at $p \leq 0.05$ – różnice istotne statystycznie gdy $p \leq 0{,}05$

The iron content in grain oat appeared to be the highest in CHD 28/75/ /01 strain and the standard varieties. The strains CHD 28/33/02 and CHD 2909/01 contained significantly less Fe. This is in contrast to GAMBUŚ et al. (2006), who found more iron in black oat compared to yellow hull oat.

Among the oat samples under investigation, CHD 28/75/01 strain and Bohun variety proved to be most abundant in zinc and copper. The other samples were shown to contain zinc below the values presented by SOUCI et al. (2000) and SKIBNIEWSKA et al. (2002). However, the oat grain copper content in all the samples investigated was within the limits reported by SOUCI et al.(2000), i.e. 23 – 0.7 mg·100 g^{-1}.

The present research revealed that CHD 28/75/01 strain had the highest level of phosphorus, magnesium, iron, zinc and copper in oat grain but its potassium content was the lowest. Among the strains and varieties examined, oat grain of CHD 28/33/02 strain showed the highest calcium level, although it was the poorest in magnesium, manganese, zinc and copper. The strain CHD 2909/01 was shown to contain more potassium and manganese but less phosphorus and iron than the other strains.

CONCLUSIONS

1. The new black oat strains showed differentiated levels of crude protein and a slightly lower crude fat content compared to the oat standard varieties: Bohun and Deresz.

2. The black oat strain CHD 28/75/01 had the highest content of unsaturated fatty acids (UFA) and monounsaturated fatty acids (MUFA) compared to the other strains and varieties.

3. Black oat grain of CHD 28/75/01 strain had a substantially higher content of magnesium, phosphorus, zinc, copper, manganese and iron than the other strains and varieties investigated.

REFERENCES

ŃMAN P. 1987. *The variation in chemical composition in Swedish oats*. Acta Agric. Scand., 37: 347-352.

BANAŚ A., DĘBSKI H., BANAŚ W., HENEEN W.K., DAHLQVIST A., BAFOR M., GP.O., MARTTILA S., EKMAN A., CARLSSON A.S., STYMNE S. 2007. *Lipids in grain tissues of oat (Avena sativa): differences in content, time of deposition, and fatty acid composition.* J. Exp.Bot. 11 (in press) PMID: 17586606.

BARTNIKOWSKA E., LANGE E., RAKOWSKA M. 2000. *Ziarno owsa – niedoceniane źródło składników odżywczych i biologicznie czynnych* Cz. I. *Ogólna charakterystyka owsa. Białka, tłuszcze.* Biul. IHAR, 215: 209-222.

FRĄTCZAK M., RUTKOWSKI A., JÓZEFIAK D. 2003. *Apparent digestibility of nutrients, amino acids and metabolizable energy of seven cereal species in studies on growing guinea fowls (Numida meleagris L.).* Ann. Anim. Sci. Suppl., 2: 255-258.

Gajewska J., Fabijańska M., Garbolińska M. 2002. *Microbiological studies of feed and faeces of fatteners fed mixtures containing naked oat and permutite*. Acta Microbiol. Pol., 51(1): 63-69.

Gambuś H., Gambuś F., Pisulewska E. 2006. *Całoziarnowa mąka owsiana jako źródło składników dietetycznych w chlebach pszennych.* Biul. IHAR, 239: 259-267.

Gąsiorowski W. 2003. *Wartość żywieniowa owsa*. Prz. Zboż.-Młyn., 3: 26-28.

Gąsiorowski H., Urbanowicz M. 1992. *Owies roślina XXI wieku.* Prz. Zboż.-Młyn., 4, 2-3.

Kamińska B.Z. 2003. *The effect of various grains in grower diet on broiler performance and dietetic value of carcass*. Ann. Anim. Sci., Suppl., 2: 185-188.

Kolanowski W. 1998. *Zastosowanie błonnika pokarmowego w produkcji żywności.* Żywność, Żywienie Zdrowie., 4: 412-414.

Makarska E., Rachoń L., Michalak M., Szumiło G. 2006. *Zawartość makroskładników i β-glukanów w oplewionych i nagoziarnistych odmianach jęczmienia i owsa w przypadku zróżnicowanej ochrony chemicznej.* J. Elementol., 11(2),165-174.

Newman R.K., Klopfenstein C., Newman C., Guritno N., Hoter P. 1992. *Comparison of the cholesterol lowering properties of barley, oat bran and wheat red in chicken and rats.* Cereal Chem., 69: 240-244.

Ozcan M.M., Ozcan G., Topal A. 2006. *Characteristics of grains and oils of four different oats (Avena sativa L.) cultivars growing in Turkey.* Int. J. Food Sci. Nutr., 57(5-6): 345-352.

Pedo I., Sgarbieri V.C., Gutkoski L.C. 1999. *Protein evaluation of four oat (Avena Sativa L.) cultivars adapted for cultivation in the south Brazil.* Plant Foods for Human Nutrition, 53: 297- 304.

Pisulewska E., Kołodziejczyk M., Witkowicz R. 1997. *Porównanie składu chemicznego ziarna owsa oplewionego i nagoziarnistego uprawianych w różnych warunkach siedliska.* Acta Agr. Silv. ser. Agr., 35: 99-106.

Särkijärvi S., Saastamoinen M. 2006. *Feeding value of various processed oat grains in equine diets.* Livestock Sci., 100: 3-9.

Souci S.W., Fachmann W., Kraut H. 2000. *Food composition and nutrition tables.* Sci. Publ., Studgard.

Skibniewska K.A., Kozirok W., Fornal Ł., Markiewicz K. 2002. *In vitro availability of minerals from oat products.* J. Sci. Food Agric., 82: 1676-1681.

Wursch P., Pi-Sunyer F.X. 1997. *The role of viscous soluble fiber in the metabolic control of diabetes. A review with special emphasis on cereal rich in â-glucan.* Diabetes Care, 20: 1774-1780.

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POSSIBILITIES OF REDUCING ENVIRONMENTAL POLLUTION WITH NITROGEN AND PHOSPHORUS AS PART OF AN AGRI-ENVIRONMENTAL PROGRAMME

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Abstract

Data from the Central Statistical Office and from the literature of the subject have been used to present the hazards for the natural environment, created by nitrogen and phosphorus compounds. The issue concerns inland waters and the Baltic Sea. The existing hazards are controlled by rational fertilisation, the appropriate structure of cultivation and biochemical barriers. Following Poland's accession to the European Union, an effective instrument has been obtained in the form of an agri-environmental programme, especially the packages: „water and soil protection" and „establishing buffer zones", which can result in reducing the infiltration of biogenes to the environment. The data from the Agency of Agriculture Restructuring and Modernisation and the research conducted by the authors in the Warmia and Mazury and the West Pomerania Provinces have confirmed the large interest of farmers in the „water and soil protection" package. The clearly observed lack of interest in the „buffer zones" package necessitates corrections, mainly by increasing financial subsidies for farmers.

Key words: nitrogen, phosphorus, infiltration to the environment, agri-environmental programme, „soil and water protection" and „buffer zone creation" packages.

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MOŻLIWOŚCI OGRANICZENIA ZANIECZYSZCZEŃ ŚRODOWISKA AZOTEM I FOSFOREM W RAMACH PROGRAMU ROLNOŚRODOWISKOWEGO

Abstract

Na podstawie literatury oraz danych Głównego Urzędu Statystycznego przedstawiono zagrożenie środowiska przyrodniczego związkami azotu i fosforu. Dotyczy to zarówno wód śródlądowych, jak i Morza Bałtyckiego. Ograniczaniu występujących zagrożeń sprzyja racjonalna gospodarka nawozowa, właściwa struktura upraw oraz bariery biogeochemiczne. Po wstąpieniu Polski do Unii Europejskiej uzyskano skuteczny instrument w postaci programu rolnośrodowiskowego, a zwłaszcza pakietów „ochrona gleb i wód" oraz „tworzenie stref buforowych", mogący redukować przenikania biogenów do środowiska. Materiały Agencji Restrukturyzacji i Modernizacji Rolnictwa oraz badania własne przeprowadzone w województwach warmińsko-mazurskim i zachodniopomorskim, potwierdziły duże zainteresowanie rolników pakietem „ochrona gleb i wód". Wyraźny brak zainteresowania pakietem „strefy buforowe" wymaga korekty, polegającej zwłaszcza na zwiększeniu dotacji finansowych przeznaczonych dla rolników.

Słowa kluczowe: azot, fosfor, przenikanie do środowiska, program rolnośrodowiskowy, pakiety „ochrona gleb i wód" i „tworzenie stref buforowych".

INTRODUCTION

Intensive agriculture adversely affects the natural environment, especially the quality of surface and underground waters. The biogenic elements, unused in the course of agricultural production, especially nitrogen and phosphorus, cause the degradation of aquatic ecosystems. A significant factor in the north of Poland is the pollution of the Baltic Sea by biogenes carried by rivers from agricultural areas.

An important system solution to reduce water pollution, mainly with nitrogen and phosphorus, may be provided by the agri-environmental programme, which is one of the forms of subsidising farmers by the European Union. The program consists in voluntary actions taken by farmers, aimed at promoting such systems of agricultural production which comply with the requirements of environment production (*Plan Rozwoju … 2003*).

This study analyses the manner of operation of the agri-environmental programme in Poland, in particular the packages which comprise it – soil and water protection as well as buffer zones creation in terms of possibilities of restriction of water pollution with nitrogen and phosphorus.

MATERIALS AND METHODS

Data from the Central Statistical Office and from the literature of the subject have been used to present the hazards to the natural environment created by nitrogen and phosphorus compounds, which concerns the Baltic Sea.

Then, based on an analysis of documents of the Agency of Agriculture Restructuring and Modernisation, The Ministry of Agriculture and Rural Development and studies conducted in two provinces in the northern part of Poland – the Province of Warmia and Mazury and the Province of West Pomerania – the current and potential use of specific packages (soil and water protection as well as the creation of buffer zones) of the agri-environmental programme in order to restrict the adverse effect of biogens on the natural environment has been shown. Field studies conducted in the years 2005–2007 on a group of 750 beneficiaries have provided data on the execution of the programme by farmers.

RESULTS AND DISCUSSION

Agriculture is one of the most important sources of environment pollution. This regards both area pollution (agriculturally utilised land) and point pollution (farms with their immediate surroundings) (Koc 1994, Sapek 2006).

According to Smoroń (1998), it is extremely difficult to determine the exact load of nitrogen and phosphorus which infiltrate into waters as a result of agricultural activity, as it depends on a number of factors. These include: the structure of land use, amount of fertilisers and the manner of their use, intensity and manner of farm animals breeding, etc. Hence, the load of nitrogen and phosphorus which infiltrate into water, and then to the Baltic Sea, can be a good measure of the amount of pollution of the environment by both elements.

The data shown in Fig. 1 show that despite a clear decrease in the load of nitrogen carried to the Baltic Sea, the hazard is still present. Utilisation of nitrogen used in agricultural production is better in plant production – it ranges from 40% to 90% – than in animal production, where it is lower than 20%. Poor utilisation of nitrogen in animal production is caused mainly by an improper method of animal nutrition, and the main source of nitrogen losses is an improper method of storing dung (Sapek, Sapek 2001).

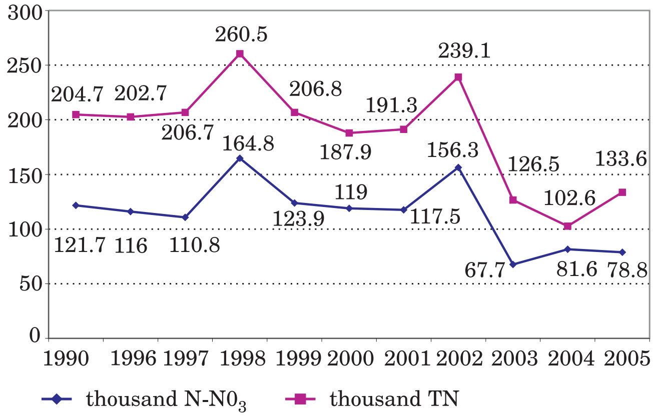

Fig. 1. The load of nitrogen carried to the Baltic Sea from the area of Poland
Source: Environment protection. Statistical information and analyses 2006. GUS Warszawa

The case of phosphorus is similar (Fig. 2). It is widely believed not to be harmful to humans or animals; however, when accumulating in the environment, it increases its fertility, i.e. it causes its eutrophication. As Sapek (2002) reports, only one-tenth of the phosphorus introduced to the food chain with fertilisers, ends up in consumed food; the remaining part is accumulated or dispersed in the environment

There are several methods of restricting the outflow of nitrogen and phosphorus to the environment. Among them there are rational fertilisation and correct storage of fertilisers, especially organic ones. Of great importance is also the creation of natural barriers which prevent infiltration of N and P compounds into surface and underground waters. This paper focuses on the latter.

According to Roman (1995), the major ways of restricting the process of washing biogens out to waters include, as long as possible, the period when soil remains under plant cover. This was confirmed by Sapek (1997), who claims that it is necessary to create conditions to encourage farmers to introduce catch crops or intercrops in the area endangered with pollution of underground waters with nitrates. The plants used as catch crops and intercrops take up a lot of nitrogen and phosphorus. For example, 1 tonne of rye cultivated as green crop takes up about 4.9 kg of N and 0.7 kg of P, and 1 tonne of oats cultivated as green crop – ca 3.7 kg of N and 0.5 kg of P.

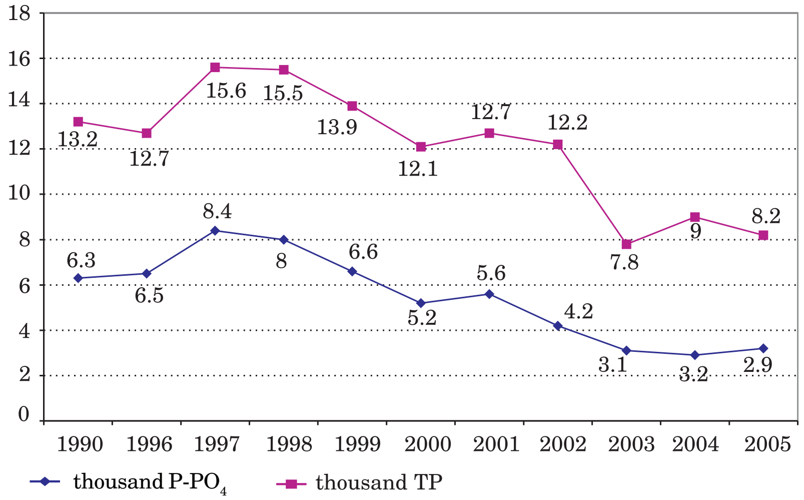

Fig. 2. The load of phosphorus carried to the Baltic Sea from Poland

Source: Environment protection. Statistical information and analyses 2001 and 2006. GUS Warszawa

An important factor in restricting the amount of nitrogen and phosphorus which infiltrate into water is the creation of biogeochemical barriers which help control migration of chemical substances from fields to waters [Zajączkowski 2000, Drupka 2003, Golinowska 2004]. An example of this was shown in the study by Koc and Solarski (2006), which indicates that the concentration of $N\text{-}NO_3$ in drainage ditches is significantly reduced owing to biological absorption of nitrogen, mainly by vegetation growing in the ditches.

Koc (1999) studied the process of biogen accumulation in zones surrounding small water reservoirs and found that one hectare of waterside vegetation can accumulate material which inflows from 40 ha of the drainage area and protects 1 ha of the reservoir from eutrophication. Biogen accumulation depends on the type of vegetation and the zone width. The study found that a 20-metre wide zone of turf surrounding a water reservoir accumulates 250 kg nitrogen and 40 kg of phosphorus per hectare. Thickets absorb 79 kg^{-1} ha of N and 12 kg^{-1} ha of P, whereas rushes – 37 kg^{-1} ha and 6 kg^{-1} ha, respectively.

In practical terms, developing and conducting such protective actions encounter numerous obstacles. Therefore, the agri-environmental programme can be a helpful instrument in executing such actions (Latacz-Lohamann, Hodge, 2003, Glebe 2006). In Poland it concerns two packages which comprise it: „water and soil protection” and „buffer zones creation”.

The first agri-environmental programme in Poland was developed as part of the Plan of Rural Area Development for the years 2004–2006 at the Ministry of Agriculture and Rural Development. Farmers who conduct agricultural production on an area of at least 1 hectare can participate in the national agri-environmental programme. An additional obligation is to apply the principles contained in the Code of Good Agricultural Practice, especially in the part concerning the restriction of nitrogen and phosphorus outflow. Implementation of the programme in Poland is planned in two phases (years 2004-2006 and 2007-2013).

The „soil and water protection" consists of the following variants: supplementary crops, winter catch crops and stubble intercrop (*Krajowy program rolnośrodowiskowy*…2004).

For „buffer zones", the environmental plan provides for creating sodded strips, whose main purpose is to reduce the contamination of water in w courses. 2- or 5-metre wide buffer zones will be established along water courses and small water reservoirs on soil of low intensity use. 5-metre wide zones will be established on arable land and meadows of high intensity use – along the water courses running through them and small water reservoirs or valuable habitats situated within them, e.g. peat bogs (*Krajowy program rolnośrodowiskowy*…2004).

An analysis of data provided by the Agency of Agriculture Restructuring and Modernisation has shown that the „soil and water protection" package, which is of great importance in terms of environment protection, attracted the greatest interest. In the years 2004–2006 farmers filed 54,504 applications, 51 185 of which have been positively verified. However, it is a cause of certain concern that so few potential beneficiaries of the agri-environmental programme are interested in the „buffer zones" package. In the years 2004–2006 only 122 applications were filed around the country, 80 of which were positively verified.

According to the data provided by the Agency of Agriculture Restructuring and Modernisation, soil and water protection attracted the greatest interest in the Provinces of Pomerania and Lublin. Surprisingly, actions related to the package were the least frequent (excluding the Province of Silesia) in the Province of Warmia and Mazury and in the Province of Subcarpathia. These are the provinces where so-called „Naturally Sensitive Areas" were established and the agri-environmental programme appeared as a pilot programme before Poland's accession to the European Union (*Programy rolnośrodowiskowe w Europie Środkowo-Wschodniej*…2000).

Studies concerning the interest of farmers in the agri-environmental programme have been conducted in the Province of West Pomerania and the Province of Warmia and Mazury. The provinces were ranked 11th and 14th, respectively, in terms of the number of applications for the „soil and water protection" package. Actions related to the soil and water protection were taken by the relatively greatest number of farmers – 49.2% (47.2% in West Pomerania and 51.2% in Warmia and Mazury). No interest was recorded in creating buffer zones.

It was found in the study that the choice of the „soil and water protection package was usually caused by good financial conditions and by the fact that most farmers had grown catch crops and intercrops earlier.

In the „buffer zones" package, which requires excluding considerable areas from agricultural use and in which additional work has to be done, the financial resources which accompany the programme have proved insufficient. Given the threat caused by the outflow of nitrogen and phosphorus compounds from fields to waters, a correction of the package is necessary.

CONCLUSIONS

1. As the data provided here show, agricultural production in Poland is a cause of deterioration of the natural environment. This concerns in particular water pollution by nitrogen and phosphorus compounds. Contamination of water by such substances poses a threat to the quality of the Baltic Sea waters.

2. An analysis of the available materials has shown the need to reduce the threat discussed above. The most important actions include the rational use of fertilisers, maintaining the appropriate structure of cultivations as well as creating and maintaining geochemical barriers. However, such actions encounter numerous obstacles.

3. Following Poland's accession to the European Union, the agri-environmental programme, especially the packages: „water and soil protection" and „establishing buffer zones", is an effective instrument which can help control infiltration of biogens to the environment.

4. An analysis of documentation provided by the Agency of Agriculture Restructuring and Modernisation and the studies conducted in the Province of Warmia and Mazury and the Province of West Pomerania have confirmed the national tendency which indicates a high interest in the „soil and water protection" package". However, the other package, „buffer zone creation", which is also important for the discussed issue, did not attract much interest on the national level or in either of the two provinces. Therefore, a correction of the package is necessary, mainly by increasing the amount of financial subsidies for farmers.

REFERENCES

DRUPKA S. 2003. *Obszary trwałej zieleni – nowa forma strukturalna w obszarach wiejskich*. Woda-Środowisko-Obszary Wiejskie. IMUZ Falenty. 3 (2) 8: 11-30.

GLEBE T. 2006. *The inveronmental Imact of European Forming: How Legistimate Are Agri-environmental Payment.* Rev. Agric. Econ., 29 (1): 87-102.

GOLINOWSKA M. 2004. *Wdrażanie Dobrych Praktyk Ochrony Roślin w rolnictwie* W: *Ekologiczne aspekty gospodarki przestrzennej*. Fundacja Ekonomistów Ochrony Środowiska i Gospodarki Wodnej w Olsztynie, s. 226-233.

KOC J. 1999. *Problemy ochrony wód na obiektach wielkoobszarowych specjalnego przeznaczenia (wojskowych).* W: *Inżynieria środowiska w eksploatacji terenów wojskowych*. Mat. XIII Międz. Konf. Nauk.-Tech. WAT, DMW RP, GUNB, Jurata, s. 237-244.

KOC J., 1994. *Zagrożenia środowiska rolniczego, rodzaje, źródła, rozmiary i skutki*. ODR, Olsztyn.

KOC J., SOLARSKI K. 2006. *Wpływ systemów melioracyjnych na wymywanie związków azotu i fosforu ze zlewni użytkowanych rolniczo.* Woda-Środowisko-Obszary Wiejskie. IMUZ, Falenty, 6. (1) 195-205.

Krajowy program rolnośrodowiskowy. W. *Plan rozwoju obszarów wiejskich dla Polski,* lipiec 2004: http://www.minrol.gov.pl

LATACZ-LOHMANN U., HODGE I. 2003. *European agri-environmental policy for the 21st century.* Austr. J. Agric. Res. Econom., 47(1): 123-139.

Ochrona środowiska. Informacje i opracowania statystyczne 2001. GUS Warszawa.

Ochrona środowiska. Informacje i opracowania statystyczne 2006. GUS Warszawa.

Plan rozwoju Obszarów Wiejskich 2003. Projekt – podstawowe informacje. Dokument Ministerstwa Rolnictwa i Rozwoju Wsi, Warszawa.

Programy rolnośrodowiskowe w Europie Środkowo-Wschodniej na przykładzie zielonych płuc Polski w latach 1997–1999. Report końcowy. Opracował: Zenon Dederko – Fundacja IUCN Polska, współpraca: J. Tyburski Uniwersytet Warmińsko-Mazurski, Peter Veen I Herman Van Den Bijtel Veen Ecology, Holandia, Gerwin Verschuur Avalon Foundation, Holandia, Warszawa, listopad 2000, s. 19-23.

ROMAN M. 1995. O*chrona wód przed zanieczyszczeniami pochodzenia rolniczego.* W: *Zanieczyszczenia pochodzące z rolnictwa*. Program UNEP/WHO. Warszawa, s. 8-23.

SAPEK A. 1997. *Dlaczego realizowany jest projekt BAAP.* W: *Udział Programu BAAP w ograniczaniu zanieczyszczeń wód ze źródeł rolniczych w przyjaznej środowisku gminie Ciechocin.* Przysiek, s. 11-32.

SAPEK A. 2002. *Rozpraszanie fosforu do środowiska – mechanizmy i skutki.* W: *Cele i sposoby ograniczania rozpraszania składników nawozowych z gospodarstwa rolnego do środowiska.* Zesz. Edukacyjne IMUZ, 7: 9-24.

SAPEK A., SAPEK B. 2001. *Agenda 21 dla regionu Morza Bałtyckiego – zrównoważony rozwój rolnictwa w Polsce.* Zesz. Edukacyjne IMUZ, Wyd., ss. 24.

SAPEK B. 2006. *Jakość gleby i wody gruntowej z zagrody jako wskaźnik punktowych źródeł rolniczych zanieczyszczeń na obszarach wiejskich.* Woda-Środowisko-Obszary Wiejskie. IMUZ Falenty., 6. (1): 349-366.

SMOROŃ S. 1998. *Przenikanie substancji biogennych ze źródeł rolniczych do środowiska – czynnik eutrofizacji wód powierzchniowych.* Zesz. Edukacyjne, IMUZ, 5: 57-70.

WAWRZYNIAK B. M., WOJTASIK B, 2007. *Analiza przebiegu i realizacji programów rolnośrodowiskowych w latach 2004-2006.* Acta Sci. Pol. Oeconom., 6 (1): 71-78.

ZAJĄCZKOWSKI K. 2000. *Rola zadrzewień w kształtowaniu przyrodniczych warunków rolniczej przestrzeni produkcyjnej oraz akumulacji węgla z atmosfery*. Zesz. Edukacyjne IMUZ, 6: 72-84.

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CHANGES IN MERCURY CONTENT IN WATERS OF THE NAREW RIVER AND SOME OF ITS TRIBUTARIES

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Abstract

Although some small amounts of mercury in surface water come from natural environment, much higher quantities originate from anthropogenic sources, including industry and agriculture. Mercury readily accumulates in bottom sediments, from which it can return to water, which can be a serious cause of mercury pollution even after other mercury sources are removed from a river's drainage basin. Concentration of mercury was examined in river waters flowing from basins characterised by different land use and population density. Samples of water were collected from two right tributaries of the Narew River, called the Pisa and the Biebrza, and at six sites in the middle section of the main river. The areas drained by these three rivers lie within the ecosystem known as the Green Lungs of Poland. It was found that the average mercury concentration in the waters of the Narew and its tributaries ranged between 0.3 and 0.9 µg dm^{-3}, being only slightly higher than the concentrations typical of unpolluted territories. The highest mercury content occurred in spring and in the waters from agricultural-forested basins with large towns. Changes in the mercury outflow were associated with accumulation of household pollutants downstream, atmospheric conditions as well as the content of organic matter and suspended solids in the river waters. Low concentration of mineral suspension and organic substance carried by the Pisa River significantly depressed the mercury content in the water of this river. In the Biebrza River, the concentration of both organic and mineral substance was directly proportional to the content of mercury.

Key words: agricultural basin, river water, mercury, concentration, load.

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ZMIANY ZAWARTOŚCI RTĘCI W WODACH NARWI I WYBRANYCH JEJ DOPŁYWÓW

Abstrakt

Niewielkie ilości rtęci w wodach powierzchniowych pochodzą ze źródeł przyrodniczych. Wielokrotnie więcej tego metalu pochodzi ze źródeł antropogenicznych, w tym z przemysłu i rolnictwa. Rtęć łatwo gromadzi się w osadach, skąd może powracać do wód, co może stać się istotnym jej źródłem po usunięciu zagrożeń w zlewni. Badano zawartość rtęci w wodach rzecznych odpływających ze zlewni o zróżnicowanym użytkowaniu i zaludnieniu. Próbki wody pobrano z dwóch prawostronnych dopływów Narwi, tj.: Pisy i Biebrzy, oraz w sześciu punktach środkowego odcinka rzeki głównej. Tereny odwadniane przez badane cieki położone są w zasięgu ekosystemu „zielonych płuc” Polski. Stwierdzono, że średnie stężenie rtęci w wodach Narwi i jej dopływów mieściło się w granicach od 0,3 do 0,9 µg dm^{-3} i były niewiele wyższe od stężeń charakterystycznych dla obszarów niezanieczyszczonych. Najwyższe stężenie rtęci wykazano wiosną w wodach ze zlewni rolniczo-leśnych z dużymi ośrodkami miejskimi. Średni roczny odpływ rtęci wyniósł 0,3–3,3 g z 1 ha, średnio ok. 1 g z 1 ha zlewni. Na różnice w odpływie rtęci miały wpływ kumulacja zanieczyszczeń bytowych z biegiem rzeki, warunki atmosferyczne oraz zawartość materii organicznej i zawiesin w wodach rzecznych. Niska zawartość zawiesiny mineralnej i substancji organicznej w wodach Narwi nie wpływała istotnie na stężenia Hg. Stwierdzono, że mineralna część substancji niesionych wodami Pisy miała istotny wpływ na obniżenie stężenia rtęci w wodzie tej rzeki. W wodach Biebrzy zarówno stężenia substancji organicznych, jak i mineralnych wykazywały wprost proporcjonalną zależność w stosunku do zawartości rtęci.

Słowa kluczowe: agricultural basins, river water, mercury, concentrations, load.

INTRODUCTION

Regular environmental monitoring is a basic measure which enables us to determine the causes and their quantitative and qualitative contribution to pollution. As a result, it can imply possible preventive actions to stop degradation of natural resources. Water ecosystems largely contribute to influx of pollutants. Content of harmful substances in river ecosystems is shaped, either directly or indirectly, under the effect of natural conditions and man-made factors (HERMANOWICZ et al. 1999). Dispersion of elements in a river channel depends on hydrodynamic processes, the river's hydrological regime as well as physical and chemical parameters, which, on a global scale, are differentiated primarily by climatic conditions (GRABIŃSKA et al. 2005a, JAIN et al. 2005). Other than natural factors contributing to pollution of surface waters with heavy metals are intensive farming practice, increasing urbanisation and growth of industry (ADAMIEC, HELIOS-RYBICKA 2002).

The content of mercury in the waters of the Narew could be conditioned by the agricultural use of its basin (surface influx) and atmospheric depositions. Mercury compounds are found in minerals fertilisers, pesticides and waste products used in agriculture (FALENICKA-JABŁOŃSKA 1991). The quality of water in the Narew River is also affected by household sewage and wastewater from larger human settlements (Białystok, Bielsk

Podlaski, Łapy, Łomża, Ostrołęka, Różan) as well as wastewater from agricultural, food processing, construction material industries and power plants located in the river's catchment basin (Skorbiłowicz 2005).

This article deals with concentrations of mercury in river waters depending on the atmospheric conditions and land use. The analysis of Hg content fluctuations is a preliminary step towards studying changes in the Hg concentration in bottom sediments. Negative effect of mercury accumulated in sediments on living organisms can occur also when the Hg concentration in the water above is within the water purity standards. Elements retained in bottom sediments can be a secondary source of pollution, which threatens not only a given water ecosystem but also the nearby land ecosystems (Bojakowska 2001). By knowing the volume of Hg outflow, we should be able to predict the ecological state of the whole ecosystem, which belongs to the extraglacial lowland belt and the Green Lungs of Poland. This knowledge can also help to plan and implement a sustainable development concept for the whole basin of the Narew River. Mercury, like cadmium and lead, is useless and often harmful to water plants and animals. In man, mercury causes neurological disorders (Hermanowicz et al. 1999). Another reason why our study seemed worthwhile was the fact that waters from the Narew River are used by Warsaw agglomeration (Zegrzyński reservoir).

MATERIAL AND METHODS

The results presented in this paper comprise seven years (1997–2003). The study involved the middle part of the Narew at six gauging sections, with one site, in Strękowa Góra (262 km from the river mouth) being treated as a representative point for the partial catchment basin of the Narew. The sampling site in Różan (117 km from the river mouth) served as a closing point for the area distinguished for the research project. Comparative analysis was performed for the two main tributary rivers of the Narew, the Pisa and the Biebrza, at the mouth profiles.

The natural conditions and varied effects of man's economic activities within the drainage basin of the three rivers have been discussed in the paper published by Grabińska et al. (2005b). Detailed description of field work (hydrometric measurements) and data processing (statistical processing and graphic presentation of the results) can be found in Grabinska et al. (2006).

The results concerning the mercury content in river waters are part of the physicochemical determinations performed on samples of water collected in the basin. Water samples were obtained four times a year: in spring (April), summer (July), autumn (October) and winter (January) from the river current. Water sampling and mercury determinations relied on the methods presented by HERMANOWICZ et al. (1999).

RESULTS

The literature claims that the migration rate of trace elements from water solution to sediments in a river channel depends on physicochemical properties of river waters, proportion between the suspension mass and mass of water as well as presence of fine-grain deposits (clay and silt), which are highly sorptive (MILLER 1997). The results of our analyses suggest that the Narew and its two tributary rivers, compared to other Polish rivers (the Vistula and the Bug) carried very small amounts of suspended solids (an annual average of 37.8 thousand tonnes). GRADZIŃSKI et al. (2000) emphasise that the load in the Narew River is dominated by sandy material (medium and coarse-grain), the river waters are rich in organic suspension, and the amount of mineral suspension (i.e. silt and clay) is small. Increasing quantities of heavy metals transported by the Narew can be attributed to small amounts of clastic material (small sorptive properties) carried by the river waters and the presence of organic matter. Humus compounds, common in soils, marshes, peatbogs and wetlands, and such types of land are present in the Biebrza River valley and the upper Narew drainage basin, shape the distribution of heavy metals in water environment in the form of dissolved organic complexes (HERMANOWICZ et al. 1999).

The highest concentration of mercury was determined in the waters of the Biebrza and Pisa (Table 1). The ranges of mercury concentration in the Biebrza and Pisa remained on approximately the same level, but were wider in the Narew (the longitudinal profile).

As regards the land use, less mercury was determined in waters flowing from the forested- agricultural basin (the upper Narew), which, in terms of mercury content, were classified as water purity class I (very good) than from the agricultural-forested basins, where the waters belonged to water purity class II (good).

According to the seasons of the year (Table 2), the highest average Hg concentration occurred in summer (0.7 $\mu g \cdot dm^{-3}$) and the lowest one – in winter (0.4 $\mu g \cdot dm^{-3}$). Particularly high levels of mercury (3-fold higher) in summer were determined in the Biebrza compared to the other two rivers. Elevated concentrations of mercury in summer could be attributed to the surface influx of pollutants (e.g. plant protection chemicals) caused by rains. The content of mercury in each season of the year in the waters of the Narew was much more variable than in the waters of the Biebrza and Pisa, which is due to the contribution of different sources of pollution.

Table 1
Tabela 1

Effect of land use in the drainage are on average mercury concentration in waters of the three rivers ($\mu g \cdot dm^{-3}$)
Wpływ zagospodarowania zlewni na średnie stężenia rtęci w wodach badanych rzek ($\mu g \cdot dm^{-3}$)

Land use Użytkowanie zlewni	Basin/gauging point in a longitudinal profile of the Narew Zlewnia/ punkt pomiarowy w profilu podłużnym Narwi	Year – Rok							Average Średnia
		1997	1998	1999	2000	2001	2002	2003	
Agricultural and forested Rolniczo-leśne	Biebrza/mouth Biebrzy/ujście	0.3	0.4	1.5	0.9	0.4	0.5	0.5	0.7
	Pisa/mouth Pisy/ujście	0.3	0.4	1.5	0.8	0.4	0.5	0.6	0.7
Forested and agricultural Leśno-rolnicze	upper Narew górnej Narwi (262 km rzeki)	0.3	0.5	0.5	0.4	0.3	0.5	0.6	0.4
Agricultural and forested Rolniczo-leśne	Narwi/Wizna (246 km rzeki)	0.8	0.5	0.8	0.4	0.3	0.5	0.8	0.5
	Narwi/Piątnica (204 km rzeki)	0.3	0.3	0.9	0.3	0.3	0.5	0.7	0.5
	Narwi/Nowogród (181 km rzeki)	0.4	0.5	0.6	0.4	0.3	0.5	0.5	0.5
	Narwi/Ostrołęka (147 km rzeki)	0.5	0.6	0.9	0.7	0.4	0.4	0.9	0.6
	Narwi/Różan (117 km rzeki)	0.5	0.6	1.0	0.6	0.6	0.3	0.9	0.7
Average – Średnia		0.4	0.5	1.0	0.6	0.4	0.5	0.7	

Different loads of mercury transported by the Narew in its longitudinal profile (Fig. 1) could prove that the source of this element is anthropogenic. Our study showed that the highest levels of mercury were in the waters of the Narew collected at the last gauging section (in Różan). This could have been a result of the increasing accumulation of mercury in the river water downstream, caused by the influx of household sewage and wastewater from treatment plants in the towns located on the Narew (i.e. Łomża, Nowogrów, Ostrołęka and Różan) and from some smaller towns and villages, situated in the river valley, which lack proper wastewater management systems.

Table 2
Tabela 2

Comparison of seasonal concentrations of mercury in waters of the three rivers ($\mu g \cdot dm^{-3}$)
Porównanie sezonowych stężeń rtęci w wodach badanych rzek ($\mu g \cdot dm^{-3}$)

Land use Użytkowanie zlewni	Basin/gauging point in a longitudinal profile of the Narew Zlewnia/ punkt pomiarowy w profilu podłużnym Narwi	Spring Wiosna	Summer Lato	Autumn Jesień	Winter Zima	Average Średnia
Agricultural and forested Rolniczo-leśne	Biebrza/mouth Biebrzy/ujście	0.4	1.5	0.4	0.3	0.7
	Pisy/ujście	0.6	0.4	1.0	0.5	0.6
Forested and agricultural Leśno-rolnicze	upper Narew górnej Narwi (262 km rzeki)	0.4	0.4	0.5	0.4	0.4
Agricultural and forested Rolniczo-leśne	Narwi/Wizna (246 km rzeki)	0.7	0.5	0.6	0.3	0.5
	Narwi/Piątnica (204 km rzeki)	0.6	0.5	0.4	0.3	0.4
	Narwi/Nowogród (181 km rzeki)	0.5	0.4	0.5	0.4	0.4
	Narwi/Ostrołęka (147 km rzeki)	0.5	0.5	0.6	0.6	0.6
	Narwi/Różan (117 km rzeki)	0.6	0.6	0.6	0.7	0.6
Average – Ś rednia		0.5	0.7	0.6	0.4	

The mean outflow of mercury (Table 3) in the upper Narew (Strękowa Góra) was 0.7 $g \cdot ha^{-1}$, rising to 1.0 $g \cdot ha^{-1}$ in Różan. The average annual load of mercury transported by the water of the Biebrza was slightly higher than that determined for the Pisa. The fact that loads of mercury transported by the Biebrza and Pisa were similar could be explained by similarities in the land use between both drainage areas.

The distribution of Hg concentrations (Table 1) and outflow (Table 3) was not uniform in the years, as it depended on the volume of flow, which was a product of time-related variability in atmospheric precipitation, on the basis of which unit outflows were computed (GRABIŃSKA et al. 2005b). In 1999, which was a wet year (KACZOROWSKA 1962), the outflow was 17% higher than the average unit outflow for the whole time period (1997–2003), Increased concentrations of mercury in the waters of all the three rivers in this wet year exceeded those in years characterised by typical

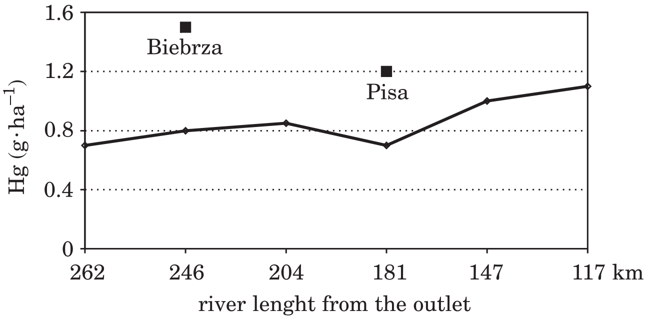

Fig. 1. Changes in the mean annual load of mercury in a longitudinal profile of the Narew river ($g \cdot ha^{-1}$). The tributary river Biebrza – 248.5 km of the Narew's course; the Pisa – 181 km

Rys. 1. Zmiany średniego rocznego ładunku rtęci w profilu podłużnym rzeki Narwi ($g \cdot ha^{-1}$). Dopływ Biebrzy – 248,5 km biegu Narwi; Pisy – 181 km

Table 3
Tabela 3

Effect of land use in the drainage basin on the outflow of mercury with waters of the three rivers ($g \cdot ha^{-3}$)

Wpływ zagospodarowania zlewni na odpływ rtęci z wodami badanych rzek ($g \cdot ha^{-3}$)

Land use Użytkowanie zlewni	Basin Zlewnia	Year – Rok							Average Średnia
		1997	1998	1999	2000	2001	2002	2003	
Agricultural and forested Rolniczo-leśne	Biebrza/mouth Biebrzy/ujście	0.3	0.6	3.3	1.2	0.5	1.1	1.0	1.5
	Pisy/ujście	0.4	0.7	2.9	1.3	0.5	0.9	1.0	1.2
Forested and agricultural Leśno-rolnicze	upper Narew górnej Narwi (262 km rzeki)	0.4	0.7	1.1	0.5	0.4	0.7	0.9	0.7
Agricultural and forested Rolniczo-leśne	Narwi/Wizna	1.1	0.6	1.1	0.5	0.4	0.7	1.1	0.8
	Narwi/Piątnica	0.5	0.5	1.4	0.5	0.5	0.8	1.0	0.8
	Narwi/Nowogród	0.6	0.8	0.9	0.7	0.5	0.8	0.8	0.7
	Narwi/Ostrołęka	0.8	1.0	1.4	1.1	0.6	0.6	1.4	1.0
	Narwi/Różan	0.8	1.0	1.6	1.0	0.9	0.5	1.4	1.1
Average – Średnia		0.6	0.7	2.0	0.9	0.5	0.8	1.1	

rainfalls, and the average Hg load computed for 1999 was 50% higher relative the value obtained for the whole experiment.

No elevated Hg concentrations or outflows were observed in the upper Narew, where the largest urban settlement (Białystok) in the whole basin is located.

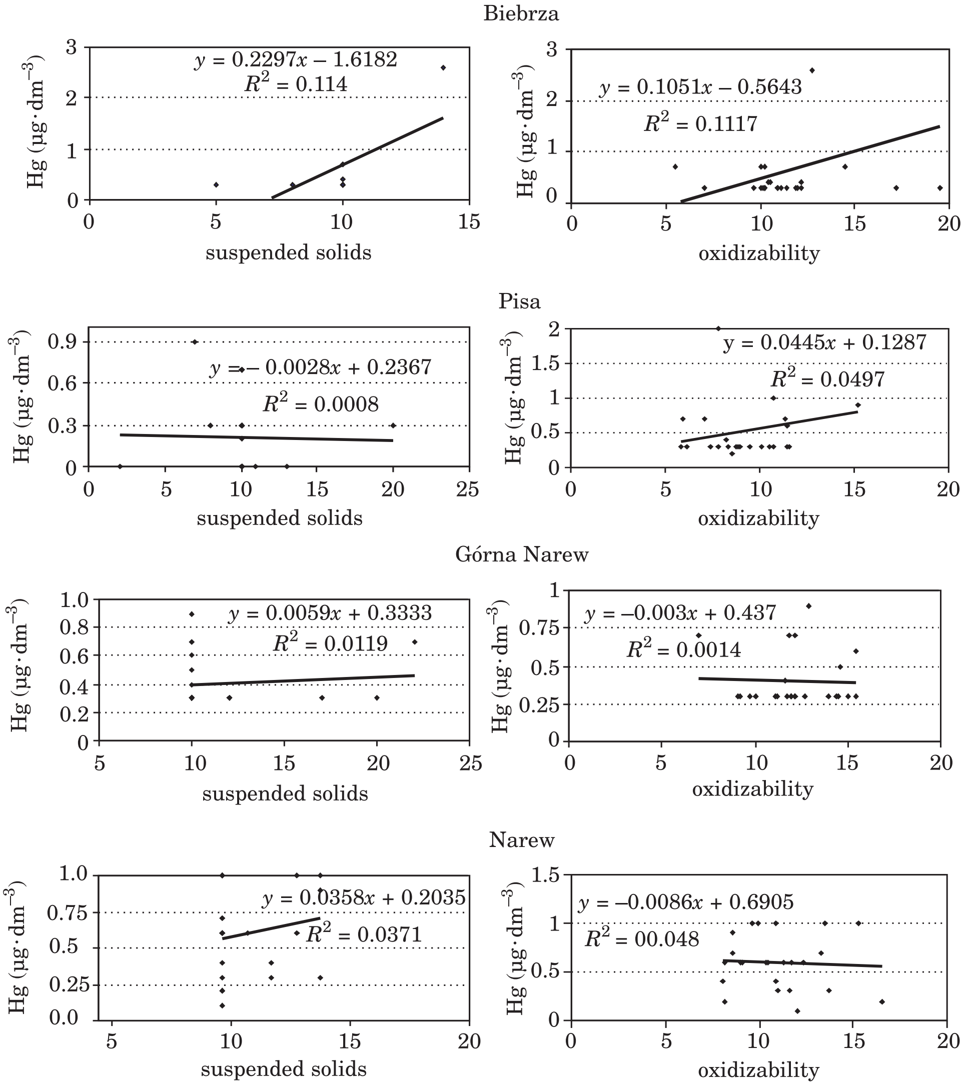

Fig. 2. Correlation between the content of suspended solids and oxidizability (µg·dm^{-3}) and concentrations of mercury in waters of the three rivers

Rys. 2. Zależność między zawartością zawiesin i utlenialności (µg·dm^{-3}) a stężeniami rtęci w badanych wodach rzecznych

Changes in the content of total suspended solids and organic matter versus Hg concentrations in the river waters are shown in Figure 2. Concentrations of the heavy metals in the Biebrza waters turned out to be directionally proportional in terms to oxidizability. In the waters of the Narew, Hg concentrations showed no correlation with the content of organic matter, whereas in the Pisa River they were directly proportionally correlated with the oxidizability value (concentration of easily decomposable substances). Reversely proportional correlation occurred between concentrations of mercury and contribution of matter suspended in the waters of the Pisa. Likewise, the concentrations of Hg were directly proportionally correlated with the amount of organic matter in the waters of the Biebrza River, which were classified as belonging to the poorest water quality class among the three rivers (GRABIŃSKA et al. 2005b). The analyses suggest that the mineral part of the substances transported by the Narew River did not have any influence on retaining mercury in the river. The suspended and organic material carried by the Biebrza River seemed to produce a much stronger effect.

In the waters of the tributary rivers, increase in the concentration of mercury corresponded to a highly significant (α<0.01) increase in the value of expected cadmium concentrations (Table 4). Negative, highly significant correlation was found between Hg and Ni in the Biebrza River. Positive, significant correlations were determined for Hg and Cu, Cd, Pb and Ni in the waters of the Narew. As regards the remaining elements, increased concentrations of mercury were accompanied by significant decrease in expected concentrations of sulphates.

The results indicate that the waters of the Narew and its two tributary rivers contained small quantities of mercury compared to other major Polish rivers (ŚWIDERSKA-BRÓZ 1987). However, the Hg concentrations

Table 4
Tabela 4

Coefficients of linear correlation (r) between mercury concentrations and chosen properties of water in investigated river
Współczynniki korelacji prostej (r) między stężeniami rtęci oraz niektórymi cechami badanych wód rzecznych

Basin Zlewnia	Zn	Cu	Cd	Pb	Ni	SO_4^{-2}	PO_4^{-3}	Ca
Biebrza	-0.080	-0.043	0.408*	0.005	-0.992***	-0.447*	0.256	0.185
Pisa	-0.038	-0.086	0.802***	-0.198	-0.066	0.197	-0.086	0.132
Górna Narew	-0.117	-0.164	-0.191	-0.158	-0.131	-0.224	-0.236	-0.294
Narew	-0.117	0.328*	0.391*	0.492**	0.415*	-0.185	-0.043	0.010

*r – significant at level α=0.05; **α=0.01; ***α=0.001;
n=24; sample size

determined in the course of the study were slightly higher than the value regarded as natural in river waters (Kabata-Pendias, Pendias 1993). The statistical analyses confirmed that the presence of towns or large villages and, in consequence, influx of household sewage and wastewater, results in increased loads of mercury transported in a river down its flow. The distribution of mercury loads in river waters was affected by particular meteorological and hydrological conditions prevailing in the years and seasons of the year during our experiment. The concentration of mercury in the Narew River did not depend significantly on its content of organic matter and mineral substances. This dependence was stronger in the case of the Biebrza and Pisa.

CONCLUSIONS

1. Waters transported down the Narew River and two of its tributaries contained slightly higher mercury concentrations than typical of unpolluted environment. Differences in the hg content were conditions by atmospheric factors and accumulation of household pollutants downstream.

2. In a wet year (1999), the unit outflow of water increased by 17% and the load of mercury went up by 50% compared to an average water outflow and mercury concentration in 1997-2003.

3. Waters drained from a forested-agricultural catchment area (the upper Narew) contained 57% less mercury than those flowing from agricultural-forested drainage areas (the Biebrza and the Pisa). The mean annual load of mercury carried away with the waters of the Narew River was increasing down the river stream, as a result of increasing loads of household pollutants from point sources of pollution (wastewater treatment plants) and surface flows from farmland.

4. Concentration of organic matter and mineral suspension in the waters of the Narew did not affect significantly the concentration of mercury. Stronger dependence between these two factors was found in the case of the Biebrza River.

5. Statistical analyses revealed highly significant positive correlation between mercury concentrations and expected concentrations of cadmium as well as highly significant but negative correlation between nickel concentrations in the waters of the Biebrza and Pisa. In the waters of the Narew, increased Hg concentrations corresponded to a significant increase in the values of expected concentrations of Cu, Cd, Pb and Ni, which may confirm the fact that all these metals originate from a similar source and circulate in a similar way. On the other hand, increased concentrations of sulphates were accompanied by significantly depressed levels of mercury.

REFERENCES

ADAMIEC E., HELIOS-RYBICKA E. 2002. *Distribution of pollutants in the Odra river system. Part IV. Heavy metal distribution in water of the upper and middle Odra River, 1998-2000.* Pol. J. Environ. Stud., 11(6): 669-673.

BOJAKOWSKA I. 2001. *Kryteria oceny zanieczyszczenia osadów wodnyc*h. Prz. Geol., 49(3): 213-218.

FALENCKA-JABŁOŃSKA M. 1991. *Zagrożenia środowiska przyrodniczego w Polsce a rolnictwo i gospodarka żywnościowa.* Narodowy Fundusz Ochrony Środ. i Gosp. Wod. Warszawa, 18-23.

GRABIŃSKA B., KOC J., SZYMCZYK S. 2005a. *Effect of natural factors and land use on the content of lead in river water of the Narew River and some of its tributaries.* J. Elementol., 10(3/2): 701-710.

GRABIŃSKA B., KOC J., GLIŃSKA-LEWCZUK K. 2005b. *Effect of land use on the river water pollution as exemplified by the Narew River and its tributaries.* Part I. *Oxygen indicators.* Zesz. Probl. Post. Nauk Rol., 503: 101-110.

GRABIŃSKA B., KOC J., SZYMCZYK S. 2006. *Fluctuations in concentration of zinc in river waters depending on environmental conditions and type of use of a river basin: A case study of the narew river and some of its tributaries.* Pol. J. Environ. Stud., 15(2a): 78-82.

GRADZIŃSKI R., BARYŁA J., DANOWSKI W., DOKTOR M., GMUR D., GRADZIŃSKI M., KĘDZIOR A., PASZKOWSKI M., SOJA R., ZIELIŃSKI T., ŻUREK S. 2000. *Anastomosing system of the upper Narew river, NE Poland.* Ann. Soc. Geolog. Pol., 70: 219-229.

HERMANOWICZ W., DOJLIDO J., DOŻAŃSKA W., KOZIOROWSKI B., ZERBE J. 1999. *Fizyczno-chemiczne badanie wody i ścieków.* Arkady, Warszawa, 205-208.

JAIN C. K., SINGHAL D. C., SHARMA M. K. 2005. *Metal pollution assessment of sediment and water in the River Hindon, India*. Environmental Monitoring and Assessment, 105(1/3): 193-207.

KABATA-PENDIAS A., PENDIAS H. 1993. *Biogeochemia pierwiastków śladowych*. PWN, Warszawa.

KACZOROWSKA Z. 1962. *Opady w Polsce w przekroju wieloletnim*. Inst. Geogr. PAN, Prz. Geogr., 33.

LIWSKI S., MATYJASIK Z., LITWIŃSKI J. 1991. *Heavy metals in water, soil and plants of the Ner river valley.* Zesz. Nauk. AR im. H. Kołątaja w Krakowie, Sesja Nauk,. 249(28/2): 103-117.

MILLER J., R. 1997. *The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites.* J. Geochem. Explor., 58: 101-118.

SKORBIŁOWICZ E. 2005. *Oddziaływanie punktowych źródeł zanieczyszczeń na zawartość ołowiu, kadmu i cynku w osadach dennych wybranych rzek województwa podlaskiego.* J. Elementol., 10(2): 385-393.

ŚWIDERSKA-BRÓZ M. 1987. *Wpływ działalności człowieka na zanieczyszczenie wód powierzchniowych metalami ciężkimi.* Gosp. Wod., 5: 114-116.

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THE TOXIC EFFECT OF ALUMINIUM AND ITS SUPPOSABLE MECHANISM IN *DROSOPHILA*

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Abstract

During the early epoch of biological evolution, aluminium was not available for the primitive organisms because of the low solubility of aluminium compounds. This can explain why aluminium is toxic for the present-day living organisms. We studied the toxic effect of aluminium by feeding *Drosophila melanogaster* adults for 24 hrs. with a 1% sugar solution containing different concentrations of aluminium sulphate. The effect of magnesium chloride was also tested in combination with aluminium. After 24 hrs. we calculated the survival rate, and solubilised the flies in concentrated nitric acid in a microwave oven. The Al, Na, Mg and Zn content of the solubilised flies was measured with the ICP-AES method. We found no change in the Zn content while the Al and Mg content changed according to the treatment, and the Na content decreased significantly (20-30%) in all the cases. We suppose that the flies were mainly killed by the elevated sodium efflux resulting in a decreased intracellular pH. The cause of the elevated Na efflux could be the increased rigidity of the cell membrane caused by the aluminium. We discuss the experimental results and the supposable mechanism of toxicity.

Key words: Aluminium, magnesium, sodium, *Drosophila*, membrane rigidity.

INTRODUCTION

According to Matsumoto (1980) and Butnaru (1996), the aluminium caused chromosome abnormalities (non-disjunction, chromosome breakage and rearrangement) which could have a deleterious effect in the offspring.

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The aluminium can inhibit the activity of some mitochondrial enzymes like hexokinase (LAI 1984). MITANI (1992) found that the Al caused a 25-60% increase of calcium concentration in certain cells of the central nervous system resulting in cell death. Aluminium can interfere with the energy production by inhibiting the ATPases (SIEGEL-HAUG 1983).

With respect to these deleterious effects, we studied the lethal effect of aluminium and its possible mechanism of action on adult *Drosophila melanogaster*.

MATERIALS AND METHODS

Adult flies of the Canton S wild type stock were used for the experiments. The flies were fed with 1% sugar solution containing different concentrations of aluminium sulphate, magnesium chloride and their combinations, as follows:

$Al_2(SO_4)_3$:	10 mM, 50 mM, 100 mM, 250 mM, 500 mM
$MgCl_2$:	100 mM, 250 mM, 500 mM
$Al_2(SO_4)_3 + MgCl_2$:	50 mM Al + 100 mM Mg

Twenty ml plastic vials were filled with the sugar solution and closed with wetted cotton plugs so that no air bubbles were trapped under the plugs. In this way, the plugs never dry out and the flies can continuously feed on them. The vials were put into 500 ml milk bottles closed with cotton plugs. 200 flies were weighed and added to each bottle. The treatments were made in three parallels each. After 24 hrs. we calculated the survival rate, pooled the flies of the three parallels and solubilised them (living and dead together) in cc.nitric acid in a microwave oven. The concentrations of Al, Mg, Na and Zn were determined with a Jobin Yvon 24 sequential atomic emission spectrometer (ICP-AES).

RESULTS AND DISCUSSION

Table 1 shows the effect on the survival and element content of feeding the flies with the different solutions. As it revealed, the different treatments had no effect on the Zn content of the flies, while the Al and Mg values changed according to the experimental conditions. Both the Al and the Mg treatments significantly decreased the Na content, although to different extents.

Table 1

Survival and the element contents of adult *Drosophila* after treatment with Mg and Al for 24 hours

Treatment, mM		Number of flies		Element content in flies, mg kg^{-1}			
$Al_2(SO_4)^3$	Mg SO_4	alive±SD	survival % ± SD	Al	Na	Mg	Zn
0	0	199 ± 2.0	100 ± 0.5	163	850	260	35.4
10	0	194 ± 4.0	97 ± 2.0	201	790	256	35.2
50	0	176 ± 9.5	88 ± 2	355	600	262	34.2
100	0	160 ± 7.5	80 ± 3.8	534	600	187	33.9
250	0	56 ± 15.0	28 ± 7.5	980	520	136	34.8
500	0	0	0	998	480	102	33.8
0	100	196 ± 4.4	98 ± 2.2	47	760	705	34.7
0	250	56 ± 14.9	28 ± 7.5	13	600	945	34.9
0	500	0	0	15	580	1089	35.2
50	100	166 ± 13.2	83 ± 6.6	430	619	310	34.6

The experimental results show that feeding with elevated concentrations of aluminium significantly increased the death rate of adult *Drosophila* already within a few hours. The intoxication with aluminium resulted in not only an increase of the Al content but a significant decrease of the Na content of the flies as well. Therefore, we think that the mechanism of the toxicity lies in these two effects. The treatment with Mg strongly reduced the Al content and, similarly to the treatment with Al, decreased the Na content albeit to a lesser extent. At higher concentrations (250–500 mM), the Mg strongly increased the death rate either.

Structural integrity and normal permeability of the cell membrane are of vital importance for its normal functioning and cell viability. The aluminium exerts a deleterious effect on both the cell membrane and important enzyme functions.

Already a low level (25 µM) of aluminium increased the rigidity of the cell membrane (DELERS 1986). In addition, in the presence of Al, the ion channels remained open for a longer time (DELHAIZE-RYAN 1995) which can result in the increased Na efflux (BITTAR et al. 1992). Because of the high Na efflux, the Na^+/H^+ balance is shifted leading to a decreased intracellular pH and an increased frequency of cell death (POYSSEGUR et al. 1984) We also found that treating the flies with aluminium decreased their Na content which offers a possible explanation for its toxicity. This is in parallel with the observation of HAVAS-LIKENS (1985) that in *Daphnia* the decrease of Na content is accompanied by their increased mortality.

Another possible factor in the mechanism of aluminium toxicity is the decreased activity of ATPase. According to Siegel and Haug (1983), the Al binds to calmodulin, possibly causes the loss of the α-helix structure (Kiss 1996), and changes the protein conformation. This would result in the loss of enzyme activity and can contribute to the increased mortality.

In the presence of aluminium, the blood platelets aggregate at a higher rate (Neaiva et al. 1997): at 20 µM Al the rate of aggregation is 4%, at 50 µM it is 43% and at 100 µM it reaches 83%. The aggregation of proteins can further increase the death rate of *Drosophila*.

As Table 1 shows, the elevated Mg concentration above 100 mM can drastically increase the mortality. We also found that at higher Mg concentration the amount of Na in the flies decreased, probably due to the higher Na efflux which can result in the decrease of cytoplasmic pH in the cells. This is in line with the observation of Günzel et al. (1996) that at higher Mg concentrations the Na efflux was increased.

The combined effect of Al and Mg (50 mM Al + 100 mM Mg, see Tab. 1) was not really additive. This can be explained by the antagonism of their biological effects (Balla and Kiss 1996).

In summary, we think that the decreased intracellular pH caused by the higher Na efflux, the lowered level of energy production due to the inactivation of ATPase, as well as the unfavorable changes in general protein conformation are important factors in the mechanism of aluminium toxicity.

REFERENCES

Balla Á.,Kiss A.S. 1996. *Magnesium in Biology and Pediatrics* (In Hungarian). Pro Print Publisher, Csikszereda, Romania

Beaugé L., Rojas H.,DiPolo B. 1983. *In squid axons intracellular Mg is essential for ADP-dependent Na-efflux in the absence and presence of strophantidin.* Biochim. Biophys. Acta 728: 463-466.

Bittar E.E., Xiang Z., Hunag Y.P. 1992. *Citrate as an Al chelator and positive effect of the sodium efflux in single barnacle muscle fibers.* Biochim. Biophys. Acta, 1108: 210-214.

Butnaru G. 1996. *Aluminium and Drosophila melanogaster life cycle. Metal Elements in environment, biology and medicine*. 2nd Intern. Symp. Timisoara (Romania), 7. sc.

Delers M., Servais J.P., Wulfert E. 1986. *Neurotoxic cations induced membrane rigidification and membrane fusion at micromolar concentration.* Biochim. Biophys. Acta, 855: 271-276.

Delhaize E., Ryan P.R. 1995. *Aluminium toxicity and tolerance in plants.* Plant Physiol., 107: 315-321.

Günzel D., Müller A., Hintz K., Schule W.R. 1996. *Investigations on the intracellular free Mg in retzius neurones and glia cells of the leech Hirudo medicinalis*. Magnes. Res., 9: 67-68.

Havas M., Likens G.E. 1985. *Changes in ^{22}Na influx and outflux in Daphina magna as function of elevated Al concentrations in soft water at low pH.* Proc. Natl. Acad. Sci. USA, 82: 7345-7349.

KISS T. 1996. *Interaction of Al with biomolecules* (in Hungarian). In: *A kémia újabb eredményei*. Csákvári, B.: 82. Akadémiai Kiadó, Budapest, 37-42.

LAI J.C.K., BLASS J.P. 1984. *Inhibition of brain glycolysis by aluminium*. Neurochem., 42: 438-446.

MATSUMOTO H., MORIMURA S. 1980. *Repressed template activity of chromatin of pea roots treated with aluminium.* Plant Cell Physiol., 21: 951-959.

MITANI K. 1992. *Relationship load, especially amyotrophic lateral sclerosis, and magnesium status.* Magnes. Res., 5: 203-213.

NEAIVA T.J.C., FRIES D.M., MONTEIRO H.P., D'AMICO E.A., CHAMONE D.A.F. 1997. *Aluminium induced lipid peroxidation and aggregation of human blood platelets.* Brasil J. Med. Biol. Res., 30: 599-604.

POUYSSEGUR J., SARDET C., FRANCNI A., L'ALLEMAIN G., PARIS S. 1984. *A specific mutation abolishing* Na^+/H^+ *antiport activity in Hamster fibroblasts precludes growth at neutral and acidic pH.* Proc. Natl. Acad. Sci. USA, 81: 4833-4837.

SIEGEL N., HAUG A. 1983. *Aluminium interaction with calmodulin.* Biochim. Biophys. Acta, 744: 36-45.

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MODIFICATIONS OF PHYSICO-CHEMICAL SOIL PROPERTIES FOLLOWING APPLICATION OF SEWAGE SLUDGE AS SOIL AMENDMENT

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Abstract

The results of a pot experiment on soil application of sewage sludge samples (at the rate of 200 g DM · pot^{-1}) from 19 sewage treatment plants localized in region of the Green Lungs of Poland in three areas: the Great Masurian Lakes, Iława Ostróda Lake District and Łyna River Basin, are discussed in the paper. The sewage treatment plants had different capacities, received different shares of industrial sewage water and used different technologies of sewage sludge dewatering. In the pot experiment the following five vegetable crops were grown (without winter break): root celery, lettuce, small radish, Swiss chard and spinach. Before planting the first plant (celery) and after harvesting the last plant in the rotation (spinach), physical and chemical properties of the soil were studied in order to determine if the amendment of soil with sewage sludge could pose any environmental risk to the growth of vegetable crops. It was found that most of the applied samples of sewage sludge did not produce adverse effects on the determined parameters. In many cases, the content of organic carbon increased soil retention properties were improved under the effect of sewage sludge. Sewage sludge form Zalewo, because of its high content of chromium, was implied as being hazardous for growing plants, as it could result in soil and plant contamination. When sewage sludge from Olsztyn, Olsztynek and Spychowo was applied to soil, zinc contamination occurred.

Key words: sewage sludge, water treatment plants in east-northern Poland, soil properties, trace metals.

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ZMIANY FIZYKOCHEMICZNYCH WŁAŚCIWOŚCI GLEBY W NASTĘPSTWIE ROLNICZEGO STOSOWANIA OSADÓW ŚCIEKOWYCH

Abstrakt

W pracy przedstawiono wyniki doświadczenia wazonowego z zastosowaniem osadów ściekowych, w jednakowej dawce 200 g s.m.$\cdot$wazon^{-1}, pobranych z 19 oczyszczalni ścieków zlokalizowanych na obszarze tzw. Zielonych Płuc Polski w trzech regionach geograficznych: Wielkich Jezior Mazurskich, Pojezierza Ostródzko-Iławskiego i zlewni rzeki Łyny. Oczyszczalnie różniły się wielkością, udziałem przemysłowych ścieków i technologią odwadniania osadów, z czego wynikały różnice w składzie chemicznym tych odpadów organicznych. W doświadczeniu uprawiano kolejno po sobie (bez przerwy zimowej) pięć roślin warzywnych, jak: seler korzeniowy, sałata, rzodkiewka, burak liściowy i szpinak. Przed założeniem doświadczenia i po zbiorze każdej rośliny badano podstawowe właściwości fizyczne i chemiczne gleby w celu określenia, czy nawożenie osadami ściekowymi może powodować zagrożenie skażenia środowiska glebowego w warunkach uprawy roślin warzywnych. Wykazano, że w większości przypadków zastosowanie osadów ściekowych nie wpłynęło ujemnie na badane parametry gleby. Zawartość węgla organicznego pod wpływem nawożenia osadami w wielu przypadkach wzrosła i nastąpiła poprawa właściwości retencyjnych gleb. Stosowanie osadów ściekowych z Zalewa – ze względu na wysoką zawartość chromu – może spowodować zagrożenie dla środowiska glebowego. W przypadku stosowania doglebowego osadów ze Spychowa, Olsztyna i Olsztynka stwierdzono w glebach ponadnormatywne stężenie cynku.

Słowa kluczowe: : osady ściekowe, oczyszczalnie w północno-wschodniej Polsce, właściwości gleby, metale ciężkie.

INTRODUCTION

Difficulties in sustainable management of sewage sludge in Poland have lead to a series of studies concentrated on presenting available options. Because the European Council recommends recycling as the most desirable solution for management of growing amounts of sewage sludge, this option has been studied most extensively (FILIPEK-MAZUR, GONDEK 2001, JACKOWSKA AND PIOTROWSKI 1995, MAĆKOWIAK 2001, SIUTA 1999).

It has been concluded that, as sewage sludge contains nutrients in the proportions that can satisfy demands of many crops, it can be treated as high value organic amendment. On the other hand, sewage sludge can contain many undesirable and harmful substances such as trace metals, polycyclic organic hydrocarbons, polychlorinated chemicals like PCBs, PCDDs/PCDFs and AOX (BERNACKA, PAWŁOWSKA 2000). These pollutants usually pass intact through the sewage treatment processes and can be accumulated in soil environment after soil application of sewage sludge, which might lead to their transfer to a food chain (BECK et al. 1996, PARKPAIN et al. 2000).

Therefore, it must be stressed that sewage sludge to be applied in agriculture should meet detailed criteria stated by legal regulations. Studies on sewage sludge agricultural utilization in the region of north-eastern Poland, where tourism and agriturism are becoming an important branch of economy, are essential. Besides, the society demands that an environmentally safe alternative for sewage sludge utilization be found. Another factor that must be taken into account is that deposition of sludge on landfills will be banned in 2010 and at present Poland lacks mature technology of sludge incineration. There are many water treatment plants in Poland that have just started operation or gone through modernization, so the amount of sludge they generate is expected to increase considerably in the nearest future. Therefore, finding a sustainable solution for management of growing amounts of sewage sludge is highly desirable.

The study presented in this paper aimed to evaluate the risk of agricultural utilization of sewage sludge originating from north-eastern Poland by performing a model experiment on a pot trial scale.

MATERIAL AND METHODS

Samples of sewage sludge were taken from 19 water treatment plants localized in north-eastern Poland. The treated wastewater from those plants is discharged surface water bodies (lakes and rivers) in the area known as the Green Lungs of Poland, hardly polluted and characterised by high and unique environmental values.

The wastewater treatment plants were divided accordingly:

- ten plants were localized in the Great Masurian Lakes region: Giżycko, Kętrzyn, Mikołajki, Mrągowo, Orzysz, Piecki, Pisz, Ryn, Spychowo and Węgorzewo
- six plants were localized in the Łyna River Basin: Bartoszyce, Biskupiec, Dobre Miasto, Lidzbark Warmiński, Olsztyn and Olsztynek
- three plants were localized in Ostróda and Iława Lake District: Iława, Ostróda and Zalewo.

All the wastewater treatment plants purify sewage waters from relatively small towns (the average population less than 40.000) except the treatment plant in Olsztyn, which receives sewage and wastewater from the regional capital town with a population of 170.000 (Table 1).

Nearly all the wastewater treatment plants treated mainly municipal sewage waters, including a small percentage of industrial effluents (from 0 to 30%), mainly form the dairy, meat or vegetable processing industries. In Mrągowo, 95% of sewage waters came from the dairy industry and in Zalewo – 80% of effluents were from a tannery plant, in which $FeSO_4$ was applied for immobilization of chromium ions.

Differences in technologies for the drying of sewage sludge determine the content of dry matter. Among the nineteen plants we examined, two methods prevailed: filtration press or lagoons. In two plants, Mikołajki and Węgorzewo, reed biofilters were established. The content of dry matter in sewage sludge samples ranged from 10.6% ((Mrągowo) to 33.3% (Biskupiec) – Table. 1.

Basic physical and chemical parameters of soil used in the pot model experiment are given in Tables 2 and 3. Soil reaction was acid and the humus content was very low. The soil was very rich in available phosphorus but poor in potassium and magnesium. None of the trace metals we determined exceeded the permissible levels for agricultural soils (KABATA-PENDIAS, PENDIAS 1999).

The model pot trial was conducted in a greenhouses owned of the University of Warmia and Mazury. The soil samples were placed Kick-Brauckmann plastic pots of the capacity of 10 kg of a growing medium.

The experiment was performed in four replicates and samples of sewage sludge taken from the nineteen sewage treatment plants were applied at the rate of 200 g DM pot^{-1}. Pots without sludge were treated as control.

Before planting the first experimental plant (root celery) mineral nutrients were applied once at the following rates:

- N – 0.35 g · pot^{-1} as $CO(NH_2)_2$,
- P – 0.25 g · pot^{-1} as KH_2PO_4,
- K – 1.54 g · pot^{-1} as K_2SO_4 and KH_2PO_4.

Then the following plants were grown in the this sequence:

- root celery (3 plants · pot^{-1}),
- lettuce cv. Justyna (3 plants · pot^{-1}),
- small radish cv. Agata (5 plants · pot^{-1}),
- Swiss chard cv. Lukullus (5 plants · pot^{-1}),
- spinach cv. Asta (9 plants · pot^{-1}).

The plants selected for the experiment belong to fast growing and high yielding vegetables. During the plant growth, soil humidity was maintained at 60% of water capacity.

In the nineteen wastewater treatment plants, representative samples of sewage sludge were taken and pretreated for laboratory analyses. Samples were air dried at of 22°C and then grounded in a pestle and mortar then with a laboratory mill. The following analyses were performed:

- dry matter content determination,
- pH in H_2O and 1M KCl,
- electroconductivity,
- content of organic carbon by Tiurin method.

In order to determine the trace metals, such as Cd, Pb, Cr, Ni, Cu, Zn, soil samples were digested in a mixture of concentrated acids: HNO_3

Table 1

Characteristics of origin and content of dry matter of sewage sludge samples

Sewage treatment plant	Amount of sewage waters ($m^3 \cdot day^{-1}$)	Kind of effluents	Branch of industry	Per cent of industrial effluents	Method of sludge dewatering	Dry matter (%)	Population $\times 10^3$
Great Masurian Lakes							
Giżycko	7000	municipal/ industrial	dairy	13	press	15.2	25
Kętrzyn	12000	municipal/ industrial	machine, electrical	25	press	14.0	27
Mikołajki	800	municipal/ industrial	food processing	10	press	15.3	8
Mrągowo	1200	municipal/ industrial	dairy	95	lagoon	10.6	0.35
Orzysz	1000	municipal	-	0	press	19.1	4
Piecki	500	municipal	-	0	lagoon	11.5	3.3
Pisz	3000	municipal/ industrial	wood processing	5	lagoon	18.8	20
Ryn	360	municipal	-	0	lagoon	17.1	3
Spychowo	136	municipal	-	0	lagoon	24.3	1.6
Węgorzewo	2270	municipal/ industrial	dairy, meat processing	15	press	11.5	13
Ostróda and Iława Lake District							
Iława	5800	municipal/ industrial	meat processing, machine	10	lagoon	22.2	32
Ostróda	14 000	municipal/ industrial	dairy, meat processing	30	lagoon	20.6	35
Zalewo	122	municipal/ industrial	tannery	80	membrane press	24.3	2
Łyna River Basin							
Bartoszyce	4790	municipal/ industrial	diary	13	press	14.3	28
Biskupiec	2600	municipal/ industrial	food processing	10	lagoon	33.3	11
Dobre Miasto	1500	municipal/ industrial	dairy, machine	12	press	27.4	11
Lidzbark W.	630	municipal	–	0	lagoon	21.4	18
Olsztyn	50000	municipal/ industrial	food processing, rubber	15	lagoon	17.1	165
Olsztynek	500	municipal/ industrial	food processing	30	lagoon	27.5	7

Table 2

Basic physical and chemical parameters of soil sampled before establishing the pot experiment

pH in 1 M KCl	Humus (%)	Hh	S	CEC	V (%)	P_2O_5	K_2O	Mg
		(cmol(+) · kg^{-1} soil)				(mg · 100 g^{-1} soil)		
5.46	0.55	0.97	6.75	7.22	87.00	21.4	5.5	2.1

Table 3

Content of trace metals in soil before establishing the experiment

Total form (mg·kg^{-1})					
Cd	Pb	Cr	Ni	Cu	Zn
0.01	7.86	3.21	1.91	1.77	21.95

and $HClO_4$ (3:1 ration) and the digested samples underwent AAS analyses.

The soil was sampled from each pot at 02–0 cm depth after harvesting each of the tested plants. The soil samples were mixed to form one sample per treatment and then representative samples were taken for the following analyses:

- pH in 1M KCl ;
- hydrolytical acidity (Hh) – by Kappen method;
- basic cations (S) – by Kappen method;
- total sorption capacity (CEC) was calculated;
- electroconductivity;
- content of organic carbon by Tiurin method;
- content of ash and organic matter after ignition at 550°C;
- content of the total form of the following trace metals Cd, Pb, Cr, Ni, Cu, Zn by AAS after digestion of soil in a mixture of HNO_3 and $HClO_4$ (2:1 ratio).

All the results were subjected to ANOVA tests and significance of differences was tested by t-test at $P < 0.05$ or $P < 0.01$.

RESULTS

Most of the sewage sludge sampled from the sewage treatment plants showed neutral or slightly acid reaction, except Zalewo, where basic reaction was observed. It can be concluded that in each case sludge was treated with lime (Table 4). Content of organic carbon in the analysed samples ranged from 20.0 (Olsztyn) to 35.7% (Piecki). Despite this range of values, the mean percentages of the organic carbon content in all the areas analysed were nearly identical. Presence of high concentration of organic mat-

Table 4

Chemical and physical properties of samples of sewage sludge taken from 19 sewage treatment plants

Sewage treatment plant	pH in 1M KCl	Organic carbon (%)	Electroconductivity (µS · cm^{-1})	C:N ratio
Giżycko	6.74	24.2	3012	5.6
Kętrzyn	6.69	24.7	3433	4.7
Mikołajki	6.62	27.3	1566	6.8
Mrągowo	7.02	20.8	2891	4.7
Orzysz	6.40	30.0	1145	6.3
Piecki	6.48	35.7	958	11.6
Pisz	6.63	24.8	1687	5.5
Ryn	6.09	25.8	1596	6.7
Spychowo	6.39	29.5	1807	7.6
Węgorzewo	6.53	26.9	2891	6.0
Mean values	6.56	27.0	2099	6.3
Iława	6.76	27.9	731	6.1
Ostróda	6.14	25.5	1867	6.4
Zalewo	8.06	22.4	2407	8.2
Mean values	6.99	25.3	1669	6.7
Bartoszyce	6.87	26.2	2439	6.4
Biskupiec	6.56	30.6	1684	5.2
Dobre Miasto	6.64	30.5	1867	5.8
Lidzbark W.	6.77	20.2	2620	4.6
Olsztyn	6.55	20.0	904	9.8
Olsztynek	6.17	24.6	1747	7.3
Mean values	6.59	25.4	1877	6.1
LSD$_{0.05}$	n.s.	n.s.	n.s.	–

ter in sewage sludge indicates its high value as organic amendment. The organic matter content in the samples of sludge examined varied within a wide range: from 74.5 (Piecki) to 37.5% (Ostróda). In general, samples of sludge from smaller treatment plants had more organic matter than that from bigger plants, although the differences between the four areas set out for the study were within the experimental error.

Analysing the value of C:N ratio it is worth mentioning that the values of this parameter indicated biological stability of organic matter in most of the samples of sewage sludge. Piecki wasterwater treatment plant differed in this respect as the C:N ratio in its sludge was higher than 10. Sludge salinity can be determined by its electroconductivity, which in our study ranged between 903 and 3433 $\mu S \cdot cm^{-1}$. High salinity of sewage sludge can depress its value as soil amendment and pose environmental problems because of the leaching of some ions to groundwater.

Table 5 presents concentrations of the trace metals in the samples of sewage sludge. The average concentration cadmium, which was 2.34 mg $Cd \cdot kg^{-1}$, appeared to be lower than the maximum permissible level for sludge for agricultural applications (10 mg $Cd \cdot kg^{-1}$). This was true even for the sludge from Ostróda, in which as much as 4.89 $Cd \cdot kg^{-1}$ was found. The same results were obtained for lead, copper and nickel, which occurred in the concentrations lower than permissible levels. The content of zinc in sludge from Spychowo plant was slightly higher than the permissible value (2542 vs. 2500 mg $Zn \cdot kg^{-1}$) while the level of chromium in sludge from Zalewo was 17-fold higher than the level allowed for agricultural application of sludge. The latter finding was attributed to the fact that the sludge in Zalewo originated mainly from a tannery plant, in which chromium salts has been used extensively for many years.

The basic parameters of the sewage sludge samples, presented in Tables 4 and 5, indicated that these organic wastes may be used unconditionally in agriculture and in soil reclamation except sludge from Zalewo due to its contamination with chromium.

As is shown in Table 6, most of the sludge samples had quite good influence on soil acidity during the course of the experiment because after harvesting the last test plant (spinach) the soil treated with the sewage sludge from Mrągowo, Piecki, Zalewo, Dobre Miasta and Lidzbark Warmiński was basic in reaction. It is well known that maintaining higher soil pH can prevent transfer of most of trace metals to plant tissues.

One of the environmental targets of organic waste utilization in agriculture is to enrich soil with stable organic matter. The sewage sludge samples we analysed, when added to soil raised its content of organic carbon. The content of organic carbon in soil determined after harvest of the first tested plant was considerably higher comparing to the untreated control (Table 7). The highest organic carbon content increase was observed after application of sludge from Spychowo.

Table 5

Content of trace metals in samples of sewage sludge taken from 19 sewage treatment plants digested in a mixture of HNO_3 and $HClO_4$ (mg · kg^{-1})

Sewage treatment plant	Cd	Pb	Cu	Zn	Ni	Cr
Great Masurian Lakes						
Giżycko	2.50	28.1	200.7	1560	29.6	61.9
Kętrzyn	1.34	17.5	100.8	655	27.0	52.9
Mikołajki	2.09	22.	92.1	1280	27.1	56.5
Mrągowo	0.79	20.1	25.4	363	7.7	19.1
Orzysz	2.50	25.1	96.8	1200	21.1	44.3
Piecki	2.83	24.3	80.8	1715	14.9	40.6
Pisz	2.12	53.3	90.3	1182	26.2	160.5
Ryn	2.89	27.8	110.1	1810	36.1	87.2
Spychowo	4.08	28.6	115.8	2542	20.0	39.3
Węgorzewo	1.89	32.0	91.7	1317	30.0	134.0
Mean values	2.30	27.9	100.4	1363	24.0	69.6
Ostróda and Iława Lakel District						
Iława	3.06	43.4	118.8	1288	35.9	137.2
Ostróda	4.89	42.4	258.4	1985	49.6	112.8
Zalewo	0.03	2.6	12.6	120	31.0	8748.6
Mean values	2.66	29.5	129.9	1131	38.8	2999.6
Łyna River Basin						
Bartoszyce	1.93	23.4	95.0	1243	30.5	74.6
Biskupiec	2.00	17.7	124.0	1173	30.3	73.1
Dobre Miasto	2.15	24.5	140.6	1535	23.3	67.5
Lidzbark W.	0.80	24.2	31.6	417	21.7	71.6
Olsztyn	3.53	33.4	229.3	2175	38.8	90.6
Olsztynek	3.01	44.2	106.3	1493	36.0	94.6
Mean values	2.24	27.9	121.1	1339	30.1	78.6
$LSD_{0.05}$	n.s.	n.s.	n.s.	n.s.	10.1	n.s.

SE – standard error
$LSD_{0.05}$ – for each area
n.i. – non-significant differences

After harvesting the last tested plant (spinach), owing to the accumulation of organic residues from five vegetable crops, the content of organic carbon was higher for each treatment, including the control, and the beneficial effects of sewage sludge treatments were still visible.

Table 6

Effects of application of sewage sludge on some physicochemical properties of soil (samples taken after spinach harvest)

Sewage treatment plant	pH in 1 M KCl	Organic carbon (%)	Electro conductivity ($\mu S \cdot cm^{-1}$)	CEC ($cmol(+) \cdot kg^{-1}$)
Control	7.18	1.04	38.4	11.4
Great Masurian Lakes				
Giżycko	7.14	1.29	170.4	15.5
Kętrzyn	6.91	1.19	56.3	13.9
Mikołajki	7.11	1.29	46.1	16.0
Mrągowo	7.44	1.11	66.5	19.1
Orzysz	6.91	1.29	40.9	15.8
Piecki	7.38	1.37	81.9	16.5
Pisz	7.08	1.29	37.0	15.2
Ryn	6.98	1.22	87.0	12.1
Spychowo	7.07	1.36	110.0	14.2
Węgorzewo	7.13	1.15	87.0	14.4
Mean value	7.12	1.26	78.3	15.3
Ostróda and Iława Lake District				
Iława	7.30	1.24	41.0	18.0
Ostróda	7.17	1.29	28.2	16.9
Zalewo	7.58	1.11	614.2	18.3
Mean value	7.35	1.21	227.8	17.7
Łyna River Basin				
Bartoszyce	7.04	1.31	51.0	15.8
Biskupiec	7.03	1.39	76.8	15.5
Dobre Miasto	7.33	1.32	51.2	15.3
Lidzbark W.	7.54	1.28	89.6	20.2
Olsztyn	7.09	1.21	64.0	15.7
Olsztynek	7.20	1.34	76.8	14.2
Mean value	7.21	1.31	68.2	16.1

The same trend could be found for CEC values. For this parameter, the highest increase was found in the treatment with sludge from Lidzbark Warmiński versus the control (20.24 and 11.44 cmol(+) · kg^{-1}, respectively). The increase of CEC caused by sewage sludge application can be regarded as an advantage of organic waste utilization. More impor-

Table 7

Effects of application of sewage sludge on some physicochemical properties of soil (samples taken after harvest of root celery)

Sewage treatment plant	pH in 1 M KCl	Organic carbon (%)	Electro conductivity (µS · cm^{-1})	CEC (cmol(+) · kg^{-1})
Control	6.30	0.42	1120	8.2
Great Masurian Lakes				
Giżycko	5.78	0.81	2126	10.7
Kętrzyn	6.28	0.85	1137	12.6
Mikołajki	6.11	0.63	1713	11.6
Mrągowo	7.15	0.65	1230	16.2
Orzysz	6.25	0.77	1093	10.8
Piecki	7.19	0.77	1184	12.7
Pisz	6.38	0.65	1335	11.1
Ryn	6.38	0.79	1163	10.7
Spychowo	6.67	0.92	151	13.8
Węgorzewo	6.06	0.80	2030	10.2
Mean value	6.43	0.76	1397	12.0
Ostróda and Iława Lake District				
Iława	6.95	1.10	1150	15.1
Ostróda	6.66	0.84	1094	12.5
Zalewo	7.50	0.58	2021	16.2
Mean value	7.04	0.84	1422	14.6
Łyna River Basin				
Bartoszyce	6.66	0.73	1132	12.8
Biskupiec	6.70	0.68	1136	12.1
Dobre Miasto	6.54	0.80	1410	10.4
Lidzbark W.	7.19	0.71	1172	16.0
Olsztyn	6.70	0.79	1150	11.4
Olsztynek	6.39	0.76	1120	10.6
Mean value	6.61	0.77	1142	12.2

tantly, this effect was seen during the whole experiment. When soil was amended with sludge from Ryn or Kętrzyn, this increase was small. Berkvist et al. (2003) showed that effects of sewage sludge application were durable and consisted of improvement of soil retention properties.

It is worth mentioning that high values of soil conductivity noticed after the last harvest (spinach) were considerably reduced comparing to the samples tested after harvesting the first rotation plant (root celery). High values of soil conductivity observed after the first harvest seem to have resulted from the application of mineral fertilizers rather than from sewage sludge amendment, which was suggested by a similar pattern of the decrease in conductivity in the control (Tables 6 and 7).

When considering the content of cadmium in soil, one should remember that Kabata-Pendias and Pendias (1999) reported a limit for agricultural soil of 1-8 mg $Cd \cdot kg^{-1}$. As can be seen from the data in Tables 8 and 9, the values of cadmium in soil, irrespective of the sludge treatment, were lower 10-fold and over than the limit. Berkvist et al. (2003) concluded that sewage sludge applications did not pose a serious risk of Cd accumulation in soil.

The same relationships were seen for lead content in soil, as sewage sludge treatments increased the Pb content in soil from 5.40 to 10.54 mg $Pb \cdot kg^{-1}$ whereas the legally permissible lead level in agricultural soil is set at 40 mg $Pb \cdot kg^{-1}$.

Because the tannery plant in Zalewo used chromium compounds, the content of this metal in soil during the whole experiment was above the permissible level of 50 mg $Cr \cdot kg^{-1}$, but in the other sludge treatments this level was higher than 7.29 mg $Cr \cdot kg^{-1}$ of the soil sampled after the first or the last harvests.

The nickel content in agricultural soils according to the Polish norms should not be exceed 20 mg $Ni \cdot kg^{-1}$. In the experimental treatments, the level of this metal was considerably lower and the modifications of its content were very small in the course of the experiment. In some earlier studies conducted by Mazur et al. (1997), elevated concentrations of nickel were found in sewage sludge from tanneries.

Sewage sludge samples appeared to be a source of copper for vegetable plants and the concentration of this trace metal in soil during our the experiment never exceeded the limit value of 25 mg $Cu \cdot kg^{-1}$. In one case, i.e. sludge from Zalewo wastewater treatment plant, it was lower than for the control. Regarding copper, sewage sludge can be considered as a source of this micronutrient for growing vegetable plants. Haneklaus et al. (1999) noticed that agricultural application of sewage sludge from different sewage treatment plants in north-eastern Poland increased the level of copper in soil and in plant tissues. Gambuś et al. (1996) found high variability of chemical composition of sewage sludge from sewage treatment plants in southern Poland and different effects of application of this waste on soil properties.

Table 8

Effects of application of sewage sludge on content of some trace metals in the soil (sampled after root celery harvest)

Sewage treatment plant	Trace metal (mg · kg^{-1})					
	Cd	Pb	Cr	Ni	Cu	Zn
Control	0.03	5.40	5.29	2.96	2.39	35.4
Great Masurian Lakes						
Giżycko	0.07	6.36	3.96	2.59	4.11	43.1
Kętrzyn	0.74	6.69	3.26	2.87	3.33	56.4
Mikołajki	0.07	6.61	7.22	3.66	4.50	61.5
Mrągowo	0.04	6.90	6.64	3.34	4.08	57.4
Orzysz	0.03	8.91	3.79	3.18	3.66	64.1
Piecki	0.06	8.18	3.58	3.00	3.11	78.2
Pisz	0.09	8.65	7.97	3.63	4.81	66.8
Ryn	0.07	9.55	4.27	2.45	4.18	74.0
Spychowo	0.13	8.51	4.61	3.24	5.15	90.1
Węgorzewo	0.05	8.45	6.74	3.45	4.11	62.4
Mean value	0.13	7.88	5.20	3.14	4.10	65.4
Ostróda and Iława Lake District						
Iława	0.10	10.63	4.51	2.97	6.91	66.0
Ostróda	0.09	9.95	3.82	3.47	7.53	76.2
Zalewo	0.05	3.71	210.50	2.55	1.71	43.0
Mean value	0.08	8.10	72.94	2.99	5.38	61.6
Łyna River Basin						
Bartoszyce	0.06	8.73	4.16	3.06	4.22	67.0
Biskupiec	0.07	9.29	4.85	3.67	5.27	60.4
Dobre Miasto	0.05	7.95	3.07	2.81	4.30	75.6
Lidzbark W.	0.02	7.75	2.85	2.42	2.06	61.5
Olsztyn	0.06	10.54	7.96	3.90	8.79	97.7
Olsztynek	0.06	8.79	4.22	9.31	9.98	108.1
Mean value	0.05	8.84	4.52	4.20	5.77	78.4

A different pattern was found for zinc, whose permissible content in agricultural soil is set at 80 mg Zn·kg^{-1}, because in three treatments (Spychowo, Olsztyn and Olsztynek) the soil analysed after harvesting the first plant and in one treatment (Olsztyn), in which soil was sampled

Table 9

Effects of application of sewage sludge on content of some trace metals in the soil (sampled after spinach harvest)

Sewage treatment plant	Trace metal (mg · kg^{-1})					
	Cd	Pb	Cr	Ni	Cu	Zn
Control	0.02	5.86	3.76	3.64	3.78	25.8
Great Masurian Lakes						
Giżycko	0.05	4.20	4.17	3.27	5.27	32.6
Kętrzyn	0.14	6.75	3.84	4.10	5.66	47.3
Mikołajki	0.06	7.44	5.10	4.16	5.58	54.8
Mrągowo	0.03	6.65	6.22	3.14	3.78	61.1
Orzysz	0.17	7.46	4.50	5.52	5.33	60.6
Piecki	0.07	6.86	3.49	4.13	4.56	54.6
Pisz	0.13	8.05	4.86	3.54	4.95	66.8
Ryn	0.06	7.01	2.95	3.27	5.12	68.3
Spychowo	0.36	7.16	3.58	3.46	5.50	54.1
Węgorzewo	0.65	8.64	5.47	3.56	5.49	49.1
Mean value	0.17	7.02	4.42	3.81	5.12	54.9
Ostróda and Iława Lake District						
Iława	0.07	7.35	3.11	4.07	5.35	78.5
Ostróda	0.05	8.05	3.06	4.26	7.47	65.9
Zalewo	0.04	5.25	227.78	3.22	2.93	24.5
Mean value	0.05	6.88	77.98	3.85	5.25	56.3
Łyna River Basin						
Bartoszyce	0.06	13.24	3.17	3.81	5.36	49.7
Biskupiec	0.11	6.74	3.10	3.59	5.14	55.7
Dobre Miasto	0.06	11.19	5.65	3.51	6.50	48.7
Lidzbark W.	0.05	7.62	3.74	4.00	4.07	28.9
Olsztyn	0.07	7.85	7.29	3.52	8.43	89.0
Olsztynek	0.11	7.78	4.98	4.07	5.81	64.7
Mean value	0.08	9.07	4.65	3.75	5.88	56.1

after the harvest of the last plant in rotation, this limit value was exceeded. It is worth noticing that KABATA-PENDIAS and PENDIAS (1999) set this norm at a higher level, i.e. 150-400 mg Zn·kg^{-1} and this value was not exceeded in the experiment. BARAN et al. (1996) found that sewage sludge application resulted in increased Pb and Zn content in soil and the content of lead in maize was four-fold higher than in the control.

Generally, if sewage sludge from Zalewo is excluded from agricultural use, the method of soil application of sewage sludge can be acceptable, even if the soil is used for growing vegetable crops, in terms of the status of soil chemical properties and contamination with trace metals is concerned. MAZUR et al. (1997) studied effects of sewage sludge from tanneries and they found that there is a risk of contamination of soil environment.

Environmental threats associated with soil application of sewage sludge from wastewater treatment plants which treat municipal waters can be considered as negligible. Further studies have to be performed concerning effects of sewage sludge application on accumulation of persistent organic pollutants and transfer to a food chain because in some papers such risk has been implied.

REFERENCES

BARAN S., FLIS-BUJAK M., KWIECIEŃ J., ŻUKOWSKA G., PIETRASIK W., ZALESKI P. 1996. *Zawartość Pb i Zn w glebie i kukurydzy uprawianej na glebie lekkiej użyźnionej osadem ściekowym i wermikompostem wytworzonym z tego osadu.* Zesz. Probl. Post. Nauk Rol., 437: 45-51.

BECK A. J., JOHNSON D.L., JONES K.C. 1996. *The form and bioavailability of non-ionic organic chemicals in sewage sludge-amended agricultural soils.* Sci. Total Environ., 185: 125-149.

BERNACKA J., PAWŁOWSKA L. 2000. *Substancje potencjalnie toksyczne w osadach z komunalnych oczyszczalni ścieków.* IOŚ, Warszawa.

BERKVIST P., JARVIS N., BERGGEREN D., CALGREN K. 2003. *Long term effects of sewage sludge applications on soil properties, cadmium availability and distribution in arable soil.* Agricult., Ecosystems Environ., 97: 167-179.

FILIPEK-MAZUR B., GONDEK K. 2001. *Wpływ składowania osadów z oczyszczania ścieków garbarskich na zawartość i przemieszczanie metali ciężkich w profilu glebowym.* Inż. Ekol., 3: 83-89.

GAMBUŚ F., GORLACH E., GRABOWSKI M., WIECZOREK J. 1996. *Porównanie zawartości metali ciężkich w osadach ściekowych z oczyszczalni województwa krakowskiego.* Zesz. Probl. Post. Nauk Rol., 437: 175-180.

HANEKLAUS S., HARMS H., SCHNUG E., KLASA A., NOWAK G. A. 1999c. *Akumulacja żelaza, manganu, miedzi oraz cynku w roślinach i glebie w warunkach rolniczej utylizacji osadów ściekowych z północno-wschodniej Polski i wybranych aglomeracji miejskich*. Cz. III. *Akumulacja miedzi i cynku w roślinach.* Inż. Ochr. Środ., 2 (2): 153-160.

JACKOWSKA I., PIOTROWSKI J. 1995. *Osady pościekowe źródłem metali ciężkich w środowisku glebowym.* Zesz. Probl. Post. Nauk Roln., 418: 578-582.

KABATA-PENDIAS A., PENDIAS H. 1999. *Biogeochemia pierwiastków śladowych.* PWN, Warszawa.

MAĆKOWIAK Cz. 2001. *Wartość nawozowa osadów ściekowych.* Inż. Ekolog., 3, 135-145.

MAZUR K., FILIPEK-MAZUR B., KOPEĆ M., GONDEK K., ROŚCISZEWSKA M. 1997. *Cadmium and nickel in compost and vermicompost of sewage sludge from tanneries and effect on their contents in plants*. Zesz. Probl. Post. Nauk Rol., 448a, 243-248.

PARKPAIN P., SREESAI S., DELAUNE D.R. 2000. *Bioavailability of heavy metals in sewage sludge-amended Thai soils.* Water, Air Soil Pollution., 122: 163-182.

Rozporządzenie Ministra Ochrony Środowiska, Zasobów Naturalnych i Leśnictwa z dnia 11 sierpnia 1999 r., w sprawie warunków jakie muszą być spełnione przy wykorzystywaniu osadów ściekowych na cele nieprzemysłowe. Dz. U. 72. 813 z dnia 31 sierpnia 1999 r.

SIUTA J. 1999. *Sposoby przyrodniczego użytkowania osadów ściekowych.* Mat. Konf. *Przyrodnicze użytkowanie osadów ściekowych*. Świnoujście 9-11.06.1999, 7-19

J. Elementol. 2007, 12(4): 303–315

INFLUENCE OF HYDROGEOLOGICAL CONDITIONS ON FLUORINE CONCENTRATIONS IN UNDERGROUND WATER INTENDED FOR CONSUMPTION

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Abstract

This study presents the results of an analysis of factors which affect fluorine concentrations in deep water drawn for consumption. The analysis covered two water intakes in Tczew (northern Poland) consisting of 19 wells which supply water from Cretaceous (4), Tertiary (10), and Tertiary and Quaternary (5) horizons. Fluoride concentrations ranged from 0.3 to 2.8 $mg \cdot dm^{-3}$ with the Maximum Allowable Concentration of 1.5 $mg \cdot dm^{-3}$. The allowable qualitative standards were exceeded in 38% of the investigated samples. It was found that fluorine concentrations were most profoundly affected by the water-bearing horizon (the highest concentration levels were observed in water drawn from Cretaceous horizons) and well depth. As a general trend, fluorine concentrations increase with depth, but the analysis of water drawn from the same horizon indicates that bottom-layer water may be characterised by a significantly lower fluoride content. The highest fluorine concentrations were reported in water drawn from Cretaceous water-bearing horizons to a depth of 150 m. The mixing of water from various water-bearing horizons proved to be a sufficient measure to obtain water of satisfactory quality with the optimum fluoride concentration.

Key words: fluorine, underground water, hydrogeological conditions, water of satisfactory quality.

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WPŁYW WARUNKÓW HYDROLOGICZNYCH NA STĘŻENIE FLUORU W WODACH GŁĘBINOWYCH POBIERANYCH DO CELÓW KONSUMPCYJNYCH

Abstrakt

W pracy przedstawiono wyniki analizy czynników mających wpływ na stężenia fluoru w wodach głębinowych pobieranych do celów konsumpcyjnych. Badaniami objęto dwa ujęcia wody w Tczewie (płnocna Polska), na które składało się 19 otworów eksploatacyjnych ujmujących wodę z piętra kredy (4), trzeciorzędu (10) i wód trzeciorzędowo-czwartorzędowych (5). Stężenie fluorków mieściło się w granicach od 0,3 do 2,8 mg·dm^{-3} (najwyższe dopuszczalne stężenie do spożycia (NDS) to 1,5 mg·dm^{-3}). Wykazano, że 38% badanych prób przekraczało normę jakości. Stwierdzono, że istotny wpływ na stężenie fluoru ma warstwa wodonośna (najwyższe stężenie w wodach z utworów kredowych) oraz głębokość studni. Pomimo ogólnego trendu wzrostu stężeń F z głębokością, analiza wód pobieranych z tego samego pietra wykazała istotnie niższe wartości stężeń fluorków w wodach czerpanych z warstw spągowych. Najwyższe stężenia fluoru stwierdzono w wodach pobieranych z poziomów wodonośnych kredy do głębokości 150 m. Mieszanie wód pochodzących z różnych warstw wodonośnych okazało się wystarczającym zabiegiem dla uzyskania wody dobrej jakości, o optymalnym stężeniu fluorków.

Słowa kluczowe: fluor, wody głębinowe, warunki hydrologiczne, woda dobrej jakości.

INTRODUCTION

Fluorine is a relatively popular element in underground water layers, and its concentrations often significantly exceed the content of other micronutrients. The main source of fluorine enrichment in underground water are minerals which release fluorine in the weathering process: fluoroapatite $Ca_2(PO_4)_3F$, fluorite CaF_2 and cryolite Na_2AlF_6. Fluorine-bearing mineral zones usually contribute to abnormally high fluorine concentrations in underground water. The processes which are responsible for the chemical composition of underground water should also be analysed in view of fluorine's inhibited ability to migrate in a hard water environment (with a high calcium content).

Fluorine concentrations in crude water usually do not exceed 1.5 mg·dm^{-3}, but in deep underground layers in areas rich in fluoride minerals, they may reach 10 mg·dm^{-3}. Extensive fluoride anomalies are observed in Cretaceous water-bearing horizons, but solely of hydrogencarbonate and alkaline type, where the fluorine-containing minerals are dissolved at a very high rate (JACKOWSKA, BOJANOWSKA 2007).

The allowable fluorine concentration in potable water is 1.5 mg·dm^{-3} (Resolution of 2007, WHO 1998). Subject to climate, the optimum fluoride content of water ranges from 0.7 to 1.2 mg·dm^{-3} (INDULSKI 1980). Concentrations in excess of the above level carry the risk of dental fluorisis, and significantly exceeded fluoride levels pose the threat of skeletal fluorisis. WHO has classified inorganic fluorides into Group 3 carcinogens which are not classifiable as to their carcinogenicity to humans. Fluoride is added to potable water to prevent dental decay.

The threat posed by fluorides in potable water is largely determined by environmental factors (KABATA-PENDIAS, PENDIAS 1999, KOC et al. 2006). Domestic standards concerning fluoride concentrations should be set in view of climatic conditions (PASIUK-BRONIKOWSKA 1999) as well as the quantities of water consumption and fluoride uptake from other sources (such as air and food). In areas marked by high natural fluoride levels, the recommended allowable values may be difficult to observe, mainly due to the complexity of the process of removing excess fluoride from water (KOC et al. 2005).

The aim of this study was to determine the extent to which the geological conditions that accompany the process of drawing water for consumption determine the usable properties of water and its available treatment options.

MATERIALS AND METHODS

Research area and object. The study covered underground water intakes in Tczew: „Park" and „Motława". The geological and hydrogeological background was determined based on the reports developed by the Geological Study and Research Office in Gdańsk. Water samples from two intakes were analysed between 1994 and 2004: from the „Motława" intake where 11 wells are operated, including 10 wells drawing water from the Tertiary water-bearing horizon at a depth of 93-101.5 m and one well drawing water from the Cretaceous horizon at a depth of 150 m (Fig. 1). The wells of the „Park" intake draw water from the Quaternary and Tertiary horizon (5 wells) at a depth of 92–101 m and from the Cretaceous horizon (3 wells) at a depth of 150–180 m (Fig. 2).

Hydrogeological background of the research area. The oldest deposits determined in the hydrogeological structure of the investigated area consist of Cretaceous marl and limestone to a depth of 150 m (not bored through) with a thickness of more than 50 m. The Cretaceous horizon was determined only in the roof layer where water is supplied via limestone and marl fissure deposits. Fissure water of the Cretaceous horizon is supplied solely through infiltration from the Tertiary water-bearing horizon (possibly also from Cretaceous sand layers situated below). Two water-bearing horizons were determined in the Cretaceous layer: a shallower horizon which supplies the „Motława" intake in Tczew at a depth of 150 m, and a deeper horizon which supplies the „Park" intake at 180 m. The oldest deposits determined in the „Park" intake are Cretaceous fine-grained sand deposits with

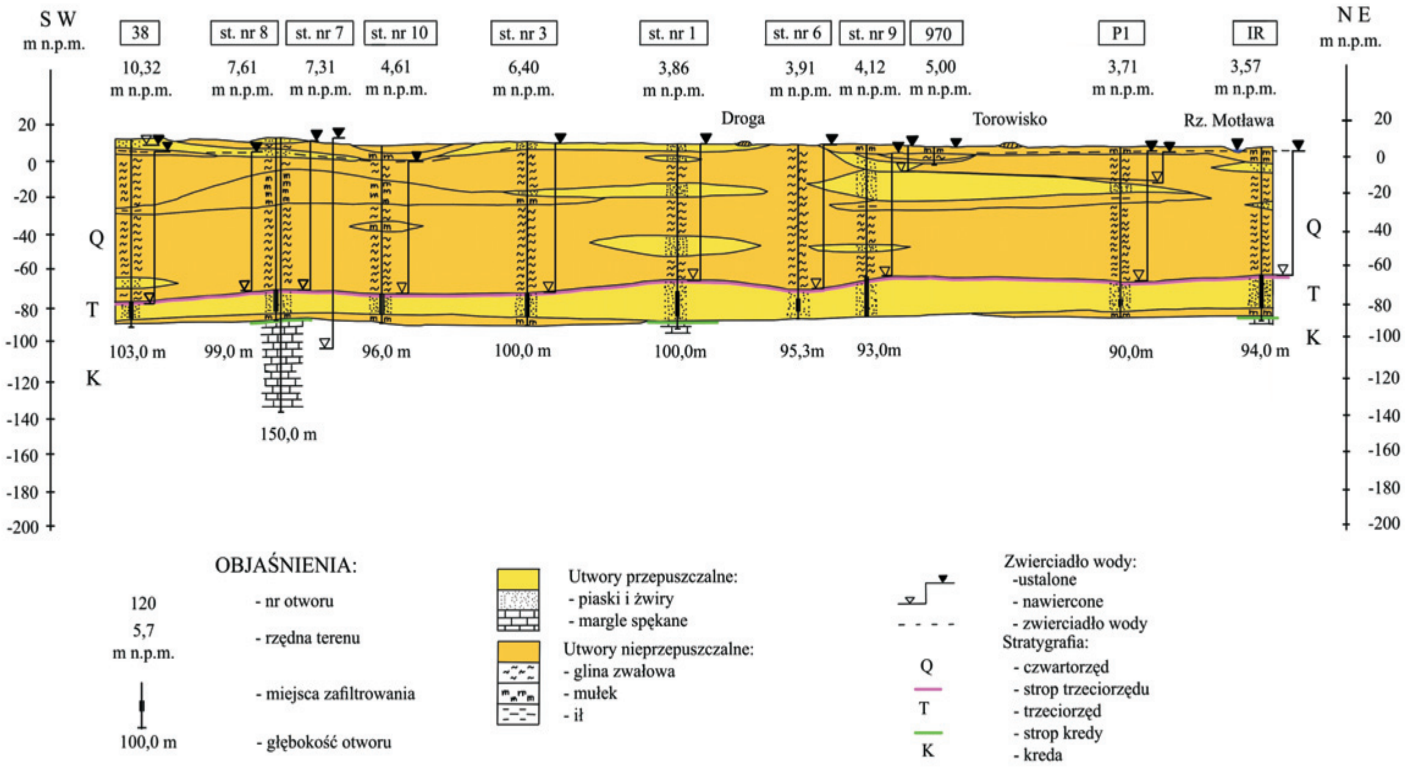
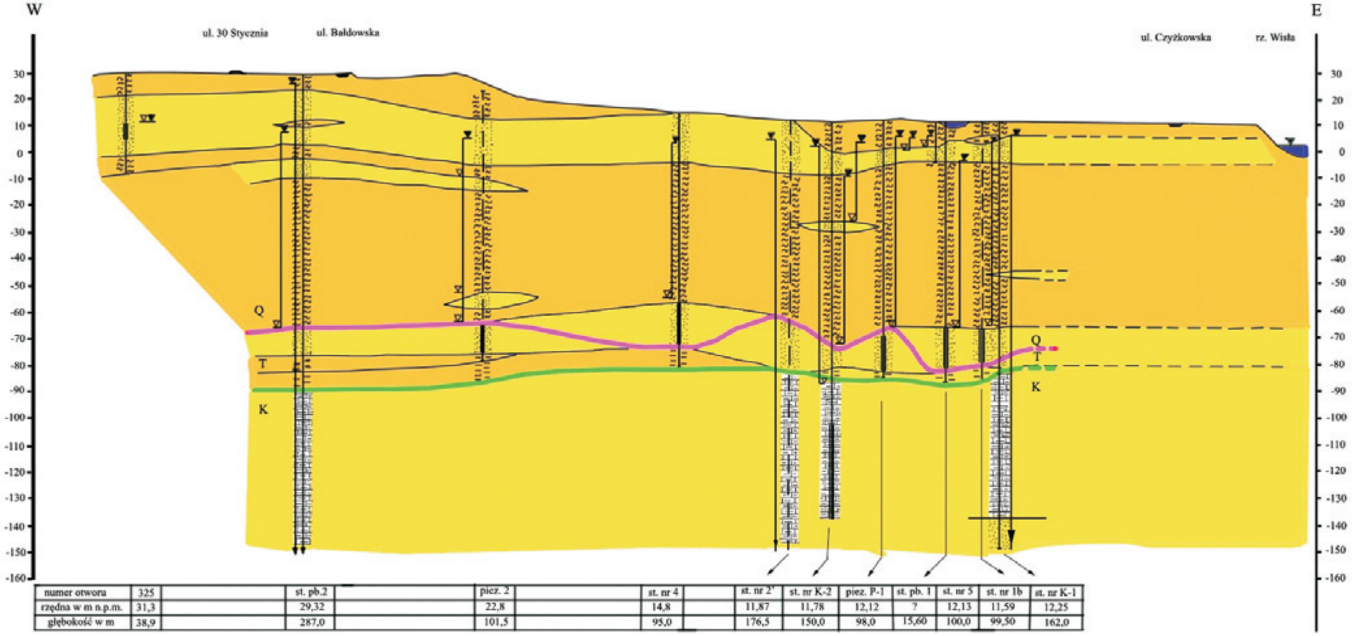


Fig. 1. Hydrogeological crossection of deep wells at the ,"Motława" in Tczew (acc. to water quality impact assessment)
Rys. 1. Przekrój hydrogeologiczny studni głębinowych w ujęciu ,"Motława" w Tczewie (wg Operatu wodnoprawnego)



numer otworu	325	st. pb.2	piez. 2	st. nr 4	st. nr 2'	st. nr K-2	piez. P-1	st. pb. 1	st. nr 5	st. nr 1b	st. nr K-1
rzędna w m n.p.m.	31,3	29,32	22,8	14,8	11,87	11,78	12,12	?	12,13	11,59	12,25
głębokość w m	38,9	287,0	101,5	95,0	176,5	150,0	98,0	15,60	100,0	99,50	162,0

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Fig. 2. Hydrogeological crossection of deep wells at the ,"Park" in Tczew (acc. to Water uality impact assessment, 2005)

Rys. 2. Przekrój hydrogeologiczny studni głębinowych w ujęciu ,"Park" w Tczewie
(wg Operatu wodnoprawnego 2005

a roof level at around 200 m above sea level and thickness of more than 55 m (not bored through). They are covered by a marl layer, which is a frequently fissured deposit, with a thickness of 113.5 m.

The Tertiary profile begins with Oligocene clays and loams with glauconite and phosphorites with a thickness of up to several meters. They are covered by a layer of fine-grained to coarse-grained quartz sand with a thickness of 8.5 to 19.0 m. The top sand layer may date back to the Quaternary period. Sand layers are infrequently covered by carbonaceous silts. The oldest Quaternary deposits are fluvioglacial sand layers of the Middle Poland glaciation which are connected with the Tertiary sand layers situated below. The stratigraphic boundary of the Quaternary and Tertiary profile is uncertain – it is found in a sandy layer where the division of soil profiles into horizons is difficult to perform. It is covered by a boulder clay formation of the Wűrm glaciation (probably of the Middle Poland glaciation in the bottom layer), divided by at least two fluvioglacial sand and gravel layers. Holocene sands and silts are found locally in areas of land subsidence.

The Tertiary water-bearing horizon consists of fine-grained to coarse-grained sand, partially mixed with gravel. In the roof profile, sand layers are silted and contain carbonaceous substances. In the bottom profile, sand layers are silted and contain glauconite. It is estimated that the roof part of this layer may date back to the Quaternary period. The thickness of the Tertiary water-bearing horizon ranges from 8.5 to 19.0 m. The Tertiary profile is supplied by lateral input and infiltration. The natural process of water outflow from the Tertiary water-bearing horizon took place from the upland to the north, in the direction of the Motława river valley. Since then, the filtration balance has been disturbed by well operation. The initial water table, determined during local surveys before the launching of the „Motława" intake, had been found on ground surface. In consequence of well operation, the water table has been lowered and, subject to the quantity of water uptake, is presently found at a depth of 2.2 to 5.4 m.

The oldest Quaternary formations are fluvioglacial sand layers of the Middle Poland glaciation, connected with the Tertiary sand profiles found below. They are covered by a boulder clay formation of the Wűrm glaciation, divided by at least two fluvioglacial sand and gravel layers. Holocene sands and silts are found locally in areas of land subsidence. The Quaternary profile comprises up to four water-bearing horizons. They consist mostly of non-continuous lenses inside boulder clay formations, where the youngest lens fills the Motława river valley. Lenses consist of differently-grained sand layers, ranging from fine- to coarse-grained sand, with locally occurring sand and gravel layers as well as gravel layers. The detritus interbedding has a thickness of several to 26 m. Quaternary water-bearing horizons are supplied mainly by lateral input from the upland and, to a lesser degree, by infiltration from the Tertiary layer and direct infiltration of precipitation water, meltwater and surface water.

The water-bearing horizon of the shared Quaternary and Tertiary profile used by the „Park" intake in Tczew comprises from fine- to coarse-grained sand layers as well as sand mixed with gravel. In the roof profile, sand layers are silted and contain carbonaceous substances. In the bottom profile, sand layers are silted and contain glauconite. The thickness of the water-bearing horizon ranges from 12 to 19 m. The filtration coefficient is 0.13 to 0.41 m h^{-1}. The initial static water table is unknown, but according to data from post-German water wells, it was found at a level of approximately 6.0 m above sea level. The static water table is presently found at around 2.0 m above sea level (Fig. 2). The Quaternary and Tertiary horizon is supplied by lateral input and infiltration, mainly from the roof layer, but the infrequent increase in salinification may also be indicative of temporary supply from the floor layer. In an environment undisturbed by human activity, water from the Quaternary and Tertiary horizon moved from the upland to the east, in the direction of the Vistula river valley. Since then, the filtration process has been disturbed by well operation.

Analytical methods. Fluoride concentrations in underground water were determined by spectrophotometry with alizarine-zirconium reagent (PN-70/C-04.588).

The impact of environmental factors on fluorine concentrations in the analysed water samples was determined by Principal Component Analysis (PCA) with the use of the CANOCO 4.1 software package. PCA is a highly useful ordination method which supported the multivariate analysis of relations between selected environmental factors and fluoride content in the analysed underground water samples. The method also facilitated the interpretation of complex correlations and a synthetic presentation of the obtained results.

The significance of differences between groups of means was determined by analysis of variance (ANOVA, MANOVA) with the use of Duncan's test as a post-hoc procedure at $P > 0.05$ in the STATISTICAL 7.1 PL software package.

RESULTS AND DISCUSSION

Based on the results of local surveys carried out in 1994-2004 in an area with differently situated water intakes and varied well depth (from <100 m to 150 m), fluoride concentrations were determined within the range of 0.5 $mg \cdot dm^{-3}$ to 2.80 $mg \cdot dm^{-3}$ (Fig. 3 and Fig. 4). The highest fluoride content was found in the Cretaceous horizon (C) – Fig. 1 and Fig. 3, and the lowest concentrations were determined in the shared Quaternary and Tertiary profile (QT) – Fig. 2 and Fig. 4. Fluoride concentrations in water were stable during the investigated period, as indicated by the low coeffi-

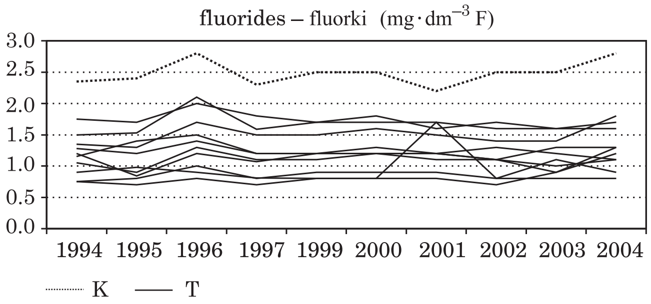

Fig.3. Quality of raw water supplied from the well no 7 from the Cretaceous (K) aquifiers as well as from the wells no 1,2,3,4,5,6,8,9,10,11 from the Tertiary aquifiers in the period of 1994-2004 at the "Motława" intake in Tczew

Rys. 3. Jakość wód surowych pobieranych w latach 1994-2004 ze studni nr 7 z warstw wodonośnych kredy (K) i ze studni nr 1,2,3,4,5,6,8,9,10,11 z warstw trzeciorzędowych (T) z ujęcia "Motława" w Tczewie

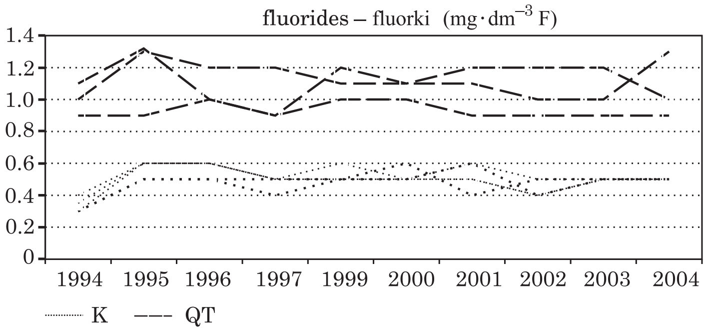

Fig.4. Quality of raw water supplied from the well no K1, K2, K3 from the Cretaceous (K) water horizon as well as from the wells no 1B, 2A, 4, 5, 6 from the common Tertiary and Quarternary aquifiers in the period of 1994–2004 at the "Park" intake in Tczew

Rys. 4. Jakość wód surowych pobieranych w latach 1994–2004 ze studni nr K1, K2, K3 z utworów kredowych (K) oraz ze studni 1B, 2A, 4, 5, 6 ze wspólnej warstwy czwartorzędu i trzeciorzędu (QT) na ujęciu "Park" w Tczewie

cient of variation ranging from 13% for C to 25% for QT, and the absence of statistically significant differences between fluoride concentrations in the successive years of the survey (ANOVA, Duncan's test, $P > 0.05$). The above is indicative of the absence of external sources of pollution and the high isolation of substratum layers, mainly limestone and marl (Fig. 1), where the highest fluoride concentrations were found in the „Motława" intake at a depth of 150 m.

The PCA ordination of factors which determine fluoride concentrations in the analysed underground water samples has revealed that the predominant role is played by the water-bearing horizon and the related depth of the deposit. The axis diagram of factors F1 and F2 (Fig. 5), i.e.

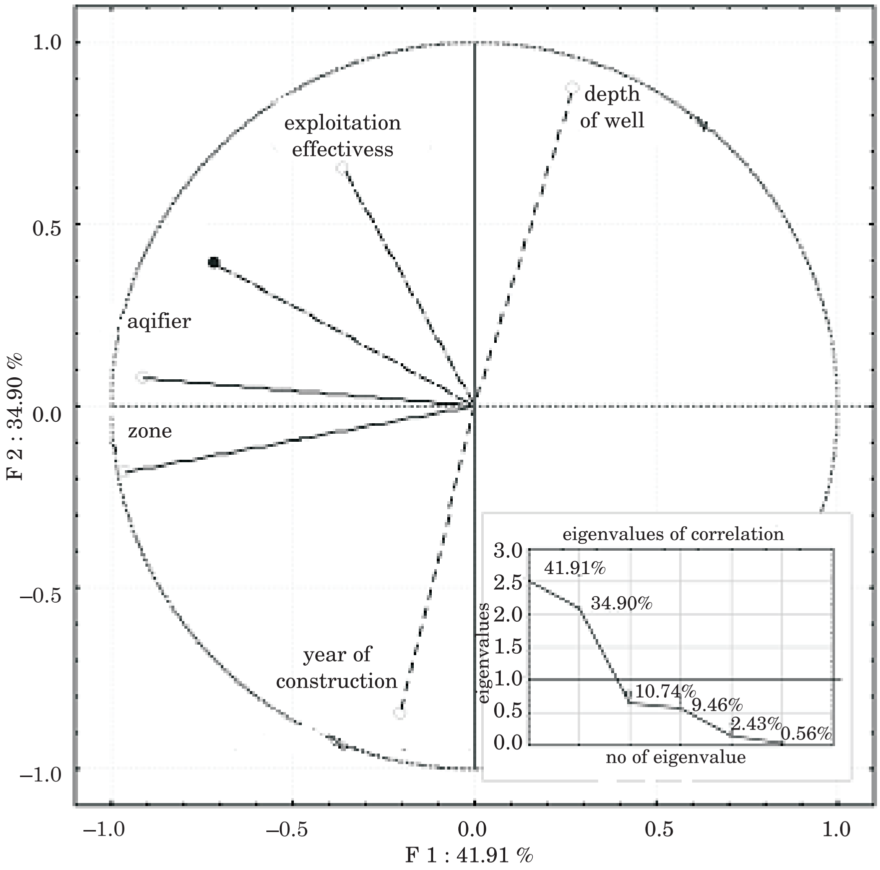

Fig. 5. Principal components analysis (PCA) of the variables influencing fluorides concentrations in undergroundwater in Tczew. Main diagram complemented with the eigenvalues graph

Rys. 5. Analiza komponentów głównych (PCA) w analizie oddziaływania na wielkość stężeń fluorków w wodach podziemnych w Tczewie.
Wykres główny uzupełniono o wykres wartości własnych

the first two proper values, explains 76.81% of total variance (F1 – 41.91%, F2 – 34.90%). Negative values on the F1 axis and positive values on the F2 axis are represented by variables related to the water-bearing horizon and the volume of underground water uptake.

It was found, based on the analysis of fluoride concentrations, that water drawn from different water-bearing horizons form groups of means which are marked by statistically significant differences in Duncan's test (Fig. 6).

Cretaceous horizon water was characterised by median values of 1.1 mg·dm^{-3} within the overall range of 0.8 mg·dm^{-3} to 2.8 mg·dm^{-3}. It should be noted,

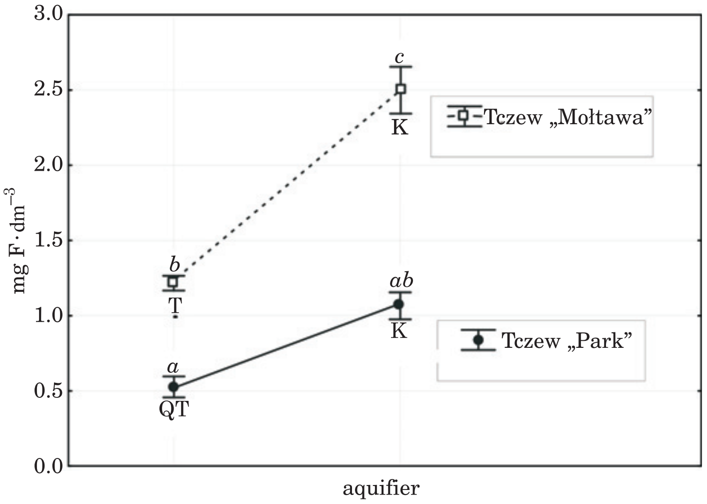

Fig. 6. Average concentation of fluorides in the undergroundwater in relation to water horizon and the depth of uptaken water. Vertical bars denote 95% range of confidence. Different letters denote groups of means that statistically differ in the Duncan test at $P > 0.05$

Rys. 6. Średnia zawartość fluoru w wodach podziemnych w zależności od piętra i głębokości ujmowanej wody. Pionowe zakresy oznaczają 95% przedział ufności. Różne symbole literowe oznaczają grupy średnich różniących się istotnie statystycznie w teście Duncana, gdy $P > 0{,}05$

however, that the thickness of Cretaceous water-bearing horizons (fissured marl deposits) significantly affected the fluoride content of water. Fluoride concentrations increased throughout the entire cross-section of all water-bearing horizons, as indicated by the presented regression equations and statistically significant correlation coefficients: $r = 0.89$ for the „Park” intake and $r = 0.71$ for the „Motława” intake (Fig. 7).

Nevertheless, a reversed system was determined in the same profile, in particular in two layers of the Cretaceous horizon. In the deeper layer reaching 180 m, fluoride concentrations were statistically significantly lower than in water samples drawn from the same horizon at a depth of 100-150 m.

The maximum allowable concentration of fluoride (1.5 mg·dm^{-3}) was exceeded in some of the investigated water samples (38%), mainly from Cretaceous horizons. Water drawn from this profile is not fit for consumption without prior treatment. Fluorine concentrations cannot be lowered to the allowable level with the use of the available technological and economic treatment methods. Due to the simultaneous occurrence of water-bearing horizons with varied fluoride concentrations (Fig. 8), qualitative standards can be met through the mixing of water from various sources.

The results of the study indicate that potable water drawn from the discussed intakes is characterised by satisfactory quality. It follows that

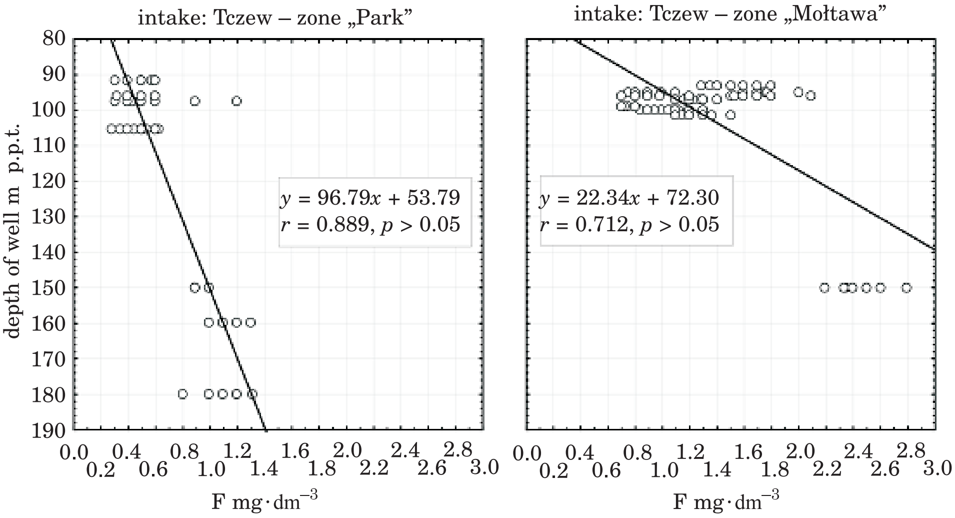

Fig. 7. Changes in fluorides concentrations in the undergroundwater at the intake "Park" and "Motlawa" in Tczew

Rys. 7. Zmiany zawartości fluorków w wodach podziemnych ujęcia Tczew w strefie „Park” i „Motława”

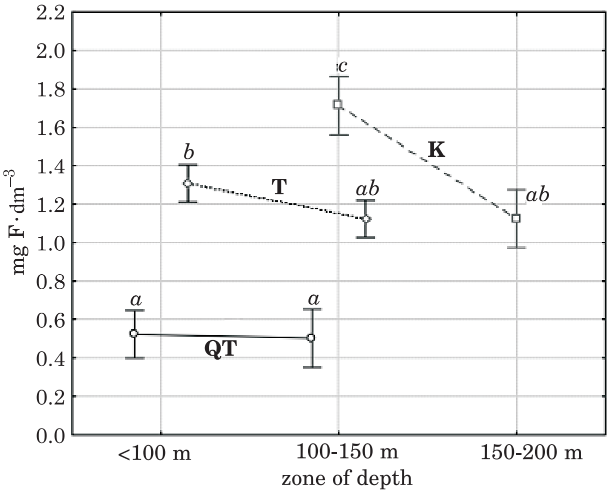

Fig. 8. Differences in fluorides concentrations in relation to water horizon and its depth. Vertical bars denote 95% range of confidence. Different letters denote groups of means that statistically differ in the Duncan test at $P > 0.05$

Rys. 8. Zmiany zawartości fluoru w zależności od warstwy wodonośnej i jej głębokości. Pionowe zakresy oznaczają 95% przedział ufności. Różne symbole literowe oznaczają grupy średnich różniących się istotnie statystycznie w teście Duncana, gdy $P > 0,05$

the Cretaceous horizon in Starogard Lakeland deserves the status of a highly valuable resource which should be preserved through the protection of younger and shallower deposits operated as water intakes. In view of the growing consumption of underground water, rational use of water resources is recommended to guarantee the abundance of water supply for the future generations.

CONCLUSIONS

1. Fluoride concentrations in underground water samples from the Tczew intakes in the Starogard Lakeland varied subject to the investigated water-bearing horizon and the depth of the deposit.

2. Fluoride concentrations ranged from 0.3 to 2.8 mg·dm^{-3}, and the maximum allowable concentration levels (1.5 mg·dm^{-3}) for potable water were exceeded in 38% of the analysed samples.

3. The highest fluoride concentrations were determined in Cretaceous horizons which consisted of fissured marls. Significant differences were observed within the same profile at different water-bearing horizons. Water drawn from bottom layers was characterised by the lowest fluoride concentrations. The highest fluoride concentrations were reported in Cretaceous horizons at a depth of up to 150 m.

4. Mixed potable water drawn from different wells was characterised by the optimum fluoride content and did not require further treatment in this respect.

REFERENCES

Chełmicki W. 2001. *Woda zasoby, degradacja, ochrona.* PWN Warszawa, ss. 42-63.

Indulski J.A. 1989. *Fluor i Fluorki.* PZWL Warszawa: ss. 22-23.

Jackowska I., Bojanowska M. 2007. *Jakość wody z zasobów wód podziemnych Lublina w zależności od miejsca jej poboru.* J. Elementol., 12(1): 39-45.

Kabata-Pendias A., Pendias H. 1999. *Biogeochemia pierwiastków śladowych.* PWN. SA. Warszawa, ss. 397.

Koc J., Krzemieniewski M., Wons M. 2005. *Fluorki w wodach podziemnych z rejonów anomalii geogenicznych*. Inż. Ekol., 13: 207-211.

Koc J., Wons M., Glińska-Lewczuk K., Szymczyk S. 2006. *Content of iron, manganese and flurine in groundwater and after its purification to potable water.* Pol. J. Environ. Stud., 15 (2a): 364-370.

Norma PN-70/C-04588. *Oznaczanie zawartości fluoru*.

Operaty wodnoprawne ujęcia „Motława" i „Park" w Tczewie 2005. Biuro Studiów i Badań Geologicznych. Gdańsk, 3-17.

Paczyński B., Macioszczyk T., Kazimierski B., Mitręga J. 1996. *Ustalenia dyspozycyjnych zasobów wód podziemnych.* MOŚZNiL. Wyd. TRIO Warszawa, 21-45.

PASIUK-BRONIKOWSKA W. 1999. *Chemical transformations in atmospheric waters*. Arch. Ochr. Środ., 1: 9-20.

Rozporządzenie Ministra Zdrowia z 2007 w sprawie jakości wody przeznaczonej do spożycia przez ludzi. Dz. U. Nr 61, poz. 417.

SIKORSKA-JAROSZYŃSKA M., CZELEJ G. 2000. *Fluor w stomatologii i medycynie.* Lublin, 62-65.

Wytyczne WHO dotyczące jakości wody do picia. Tom 1. *Zalecenia*. WHO. 1998. Warszawa, ss. 166-170.

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INFLUENCE OF FILLING IN AN SBR REACTOR ON THE TREATMENT OF LEACHATE FROM MUNICIPAL LANDFILLS*

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Abstract

The aim of the present study was to determine the influence of solid filling on the effectiveness of removal of organic substances (as COD) and ammonium from leachate from municipal landfills in SBR and SBBR reactors. The reactors worked on a laboratory scale reactors working under aerobic conditions at constant hydraulic retention time (HRT) of 3 d.COD values in outflow were similar: on average 635 mg $O_2 \cdot dm^{-3}$ (SBR) and 646 mg $O_2 \cdot dm^{-3}$ (SBBR).

Regardless of the presence or absence of filling, nitrate dominated in the effluent. The average concentration was 693 mg $N_{NO3} \cdot dm^{-3} \cdot h^{-1}$ in SBR and 699 mg $N_{NO3} \cdot dm^{-3}$ in SBBR. The concentrations of ammonium and nitrite were low, less than 2.9 mg $N_{NH4} \cdot dm^{-3}$ and 0.5 mg $N_{NO2} \cdot dm^{-3}$ (SBR), and 3.2 mg $N_{NH4} \cdot dm^{-3}$ and 0.3 mg $N_{NO2} \cdot dm^{-3}$ (SBBR).

The results indicate that the presence of solid filling did not influence the effectiveness of nitrification in activated sludge.

Key words: leachate, SBR, SBBR, activated sludge, ChZT, ammonium.

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WPŁYW OBECNOŚCI WYPEŁNIENIA W REAKTORACH SBR NA EFEKTYWNOŚĆ OCZYSZCZANIA ODCIEKÓW ZE SKŁADOWISK ODPADÓW KOMUNALNYCH

Abstrakt

W pracy badano wpływ obecności wypełnienia stałego w reaktorach SBR i SBBR na skuteczność usuwania substancji organicznych (ChZT) oraz azotu amonowego z odcieków ze składowisk odpadów komunalnych. Reaktory pracowały w skali laboratoryjnej, w warunkach tlenowych. Czas zatrzymania odcieków wynosił 3 d. Wartości ChZT w odpływie z reaktorów kształtowały się na podobnym poziomie, średnio 635 mg $O_2 \cdot dm^{-3}$ (SBR) i 646 mg $O_2 \cdot dm^{-3}$ (SBBR). Niezależnie od obecności wypełnienia, w odciekach oczyszczonych dominował azot azotanowy (V), średnio 693 mg $N_{NO3} \cdot dm^{-3}$ (SBR) oraz 699 mg $N_{NO3} \cdot dm^{-3}$ (SBBR). Stężenia azotu amonowego i azotu azotanowego (III) były niskie i nie przekroczyły: 2,9 mg $N_{NH4} \cdot dm^{-3}$ i 0,5 mg $N_{NO2} \cdot dm^{-3}$ (SBR) oraz 3,2 mg $N_{NH4} \cdot dm^{-3}$ i 0,3 mg $N_{NO2} \cdot dm^{-3}$ (SBBR). W badaniach stwierdzono, że obecność wypełnienia stałego w SBR nie ma wpływu na efektywność oczyszczania odcieków.

Słowa kluczowe: odcieki, SBR, SBBR, osad czynny, ChZT, azot amonowy.

INTRODUCTION

Leachate occurs as a result of rainwater migration through a landfill and the leaching of dissolved organic and inorganic compounds (KEMPA 1983). From the literature data it can be assumed that the dependence between the landfill operation time length and the amount of leachate has not been firmly stated. In contrast, the influence of waste disposal duration on the type, concentration and biodegradability of organic substances and nitrogen in leachate is well-known.

Depending on duration of landfill operation, KURNIAWAN et al. (2006), and earlier KANG et al. (2002) and AMOKRANE et al. (1997) divided landfills into young, in the maturation and stabilization phase (medium) or stabilized (old) ones.

During the first five years of waste disposal, COD in leachate varies within a wide range, from 204 up to 40 000 mg $O_2 \cdot dm^{-3}$, whereas BOD ranges from 18 to 25 000 mg $O_2 \cdot dm^{-3}$ (KANG et al. 2002, EL-FADEL et al. 2002, KURNIAWAN et al. 2006).

Leachate from landfills operating from 5 to 10 years is characterized by the COD value of 1 660–20 000 mg $O_2 \cdot dm^{-3}$, and BOD of 100-4 000 mg $O_2 \cdot dm^{-3}$ (EL-FADEL et al. 2002, KURNIAWAN et al. 2006).

In leachate from landfills operating over 10 years, concentration organic substances is the lowest: from 550 to 8 800 mg $O_2 \cdot dm^{-3}$ (as COD) and from 16.5 to 1 000 mg $O_2 \cdot dm^{-3}$ (as BOD) (EL-FADEL et al. 2002, BILA et al. 2005).

EL-FADEL et al. (2002) concluded from the literature data that the ammonia nitrogen concentration in leachate changes from values close to zero to about 1 250 mg $N_{NH4} \cdot dm^{-3}$, like that of organic nitrogen. In general, concentration of nitrate does not exceed 9.8 mg $N_{NO3}{\cdot}dm^{-3}$ and that of nitrite - 1.5 mg $N_{NO2}{\cdot}dm^{-3}$.

The investigations reported by KACZOREK and LEDAKOWICZ (2002) and SURMACZ-GÓRSKA et al. (2000) suggest that ammonium concentration in leachate from local landfills reaches value of 3 000 mg $N_{NH4}{\cdot}dm^{-3}$. OBRZUT (1997) reports that ammonium in leachate from ten Polish landfills ranged in concentration between 1.7 and 1 520 mg $N_{NH4}{\cdot}dm^{-3}$, with the mean value of 398 mg $N_{NH4}{\cdot}dm^{-3}$.

It is recommended that leachate should be treated by a variety of biological and physicochemical methods, different in the complexity of the process and advancement of technical solutions.

Initially, in the biological leachate treatment, anaerobic or aerated lagoons with long hydraulic retention time were used (SURMACZ-GÓRSKA et al. 1997). The necessity of nitrogen removal from leachate caused higher interest in more effective methods, such as activated sludge (LOUKIDOU, ZOUBOULIS 2001) or combined methods (WELANDER et al. 1997, ROSTRON et al. 2001, KIM et al. 2006).

One of the ways to enhance nitrification efficiency, in comparison with activated sludge alone, are mobile carriers introduced to sludge, which make it possible to lengthen sludge age and affect the increase of biomass concentration in a reactor.

High biomass concentration and long sludge age facilitate more effective removal of organic matter, with participation of slow growing heterotrophic bacteria and maintenance of suitable abundance of nitrifiers. The biomass in a reactor can be retained as a result of immobilization on a carrier, inclusion into a carrier or a combination of both methods. In practice, activated carbon, sand, plastic or sponges are used as carriers (KARAPINAR, KARGI 1996). For synthetic wastewater treatment by activated sludge, ARNZ (2000) used a reactor filled with a porous ceramic carrier (SBBR) and a SBR reactor working only with suspended biomass. The authors obtained higher biomass growth in the SBBR (90%) rather than in the SBR. KARAPINAR and KARGI (1996) applied sponges as a filling in an FBBR reactor. The biomass concentration in the reactor was 55 $g{\cdot}dm^{-3}$, thus being 90% higher in comparison with a reactor without the filling.

Research on enhancement of nitrification has also been conducted using activated sludge with biofilm on filling (mobile or immobile carriers).

The effectiveness of nitrification depends both on the carrier type and the structure of its surface. The investigations by WELANDER et al. (1997) dealt with these problems. The authors examined the influence of the filling type on nitrification in three reactors operated in parallel with different filling types. The leachate came from Hyllstofta, a twenty-year-old municipal and industrial landfill in Sweden, and were pretreated in anaerobic lagoons. The results demonstrated that in reactors with polyethylene pieces and polyethylene pieces with addition of 5% ammonium chloride as the filling, the nitrification rate was nearly identical, and depending on operational conditions changed within the range of about 5.6 to 11 mg $N_{NH4} \cdot dm^{-3} \cdot h^{-1}$. In a reactor with the filling of cellulose, the nitrification rate was evidently higher. Under optimal conditions it reached about 40 mg $N_{NH4} \cdot dm^{-3} \cdot h^{-1}$.

The aim of the present study was to determine the influence of filling in form of sponge of polyvinyl chloride (PVC) on the effectiveness of organics (as COD) and ammonium removal in SBR and SBBR reactors from leachate from municipal landfills.

MATERIAL AND METHODS

In the experiment, leachate collected from a municipal landfill located in Wysieka near Bartoszyce, Warmia and Mazury Province., was used. The landfill has been operated since January 1996. The investigations were conducted in 2004, when the landfill was in the stabilization phase. The characteristics of the landfill leachate are shown in Tables 1. The leachate was characterized by a low BOD_5/COD ratio equal 0.3, with ammonium as a dominating form of nitrogen.

The technological research on the leachate treatment by activated sludge was conducted in SBR reactors (Sequenting Batch Reactor) with volume of 5 dm^3, made of plexiglass and equipped with stirrers of adjustable rotation speed (36 r $min.^{-1}$) and aeration system (2.4 – 4.0 mg $O_2 \cdot dm^{-3}$).

The experiments were carried out in two reactors, at constant hydraulic retention time (HRT) of 3 d. The total operating time of the SBR was 24 h. The reactors worked under aerobic conditions and the operating cycle consisted of filling, aeration, settling and decantation.

Reactor 1 (SBR) worked with activated sludge, whereas reactor 2 (SBBR–Sequenting Batch Biofilm Reactor) contained additional stationary filling in the form of 42 strips of polyvinyl chloride sponge (2×11 cm).

The effectiveness of municipal landfill leachate treatment by activated sludge in SBR and SBBR under aerobic conditions was investigated. The efficiency of leachate treatment was estimated on the basis of organic matter concentration changes, expressed as COD and nitrogen forms (ammonium, nitrite and nitrate) in a reactor's cycle. The analyses were carried out according to HERMANOWICZ et al. (1999).

The differences between the effluent from the two reactors were determined using Statistica 7.1., non-parametric the Kurskal-Wallis test.

Table 1

Physicochemical composition of leachates from the municipal landfill
in Wysieka (Warmia and Mazury Province, Poland)

Parameter	Unit	Value
pH	-	8.2
COD	mg $O_2 \cdot dm^{-3}$	805
BOD_5	mg $O_2 \cdot dm^{-3}$	242
Total N	mg $N \cdot dm^{-3}$	872.2
Organic N	mg $N \cdot dm^{-3}$	170.2
$N\text{-}NH_4$	mg $N_{NH4} \cdot .dm^{-3}$	702
BOD_5/ COD	-	0.3
COD/total N	-	0.92

RESULTS AND DISCUSSION

The values of organic substances (COD) in treated leachate during the experiment are shown in Fig. 1. Initially, concentrations of organic substances fluctuated and then stabilized. This was probably associated with adaptation of activated sludge microorganisms to landfill leachate, which depended on operational conditions. The activated sludge adaptation in the SBR and SBBR was 6 and 11 days, respectively (Fig. 1).

For statistical analysis of the quality of treated leachate, the results obtained after adaptation of activated sludge were used. From the data it was concluded that the COD values were similar: on average 635 mg $O_2 \cdot dm^{-3}$ (SBR) and 646 mg $O_2 \cdot dm^{-3}$ (SBBR).

It can be inferred that the presence of stationary filling in a reactor did not influence the removal of organic matter from leachate.

It was demonstrated, however, that the efficiency of the removal of organic substances (COD) was low, which was caused by the fact that the leachate came from a landfill operated for 8 years, currently in the stabilization phase. The leachate composition from stabilized sites was characterized by relatively low concentration of organic substances (to 5000 mg $O_2 \cdot dm^{-3}$), hardly biodegradable (Amokrane et al. 1997).

Loukidou and Zoudoulis (2001) treated leachate containing organic matter at concentration (COD) of 5000 mg $O_2 \cdot dm^{-3}$, BOD_5/COD ratio equal 0.2 and HRT = 1 d. Using an SBR reactor filled with polyurethane cubes, the authors achieved about 65% reduction of COD and 95% of BOD_5. The low efficiency of organic matter removal (as COD) was caused by partially

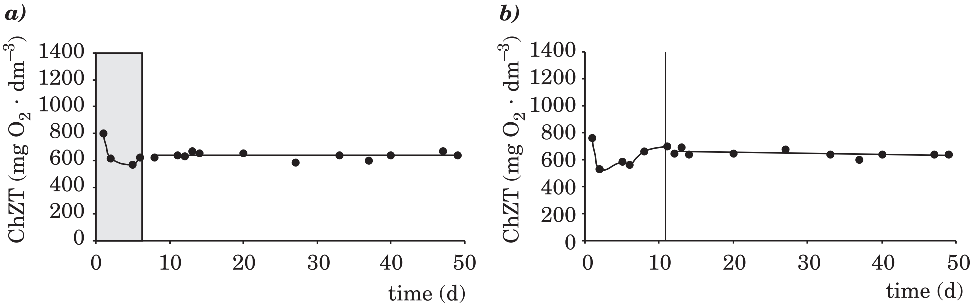

Fig. 1. Concentrations of organic compounds as a COD value in outflow from:
a) SBR; b) SBBR

stabilized leachate from a ten-year-old landfill, containing mainly nonbiodegradable organic compounds.

Rusten and Eliassen (1993) showed that by increasing the aeration phase in the SBR cycle from 61% to 67%, the efficiency of municipal wastewater was raised by about 5% (COD).

In our study, the effectiveness and course of ammonium removal from leachate in SBR and SBBR were also investigated.

Changes in removal of ammonium, nitrite and nitrate followed a similar course, regardless of the presence or absence of the filling in the reactor (Fig. 2). A distinctive feature of ammonium oxidation was that it consisted of two stages of nitrification (in phase II). It was assumed that the ammonium removal rate and increasing nitrate concentration (stage I) were linear in character, according to the zero-order reaction.

When in stage II, the nitrification rate was calculated according to the zero-order equation.

The values of the determined rate of ammonium removal and increasing nitrite and nitrate concentrations in leachate from SBR and SBBR can be found in Table 2. In stage I, the decrease in ammonium concentration was faster (28 mg $N_{NH4} \cdot dm^{-3} \cdot h^{-1}$ – SBR and 28.4 mg $N_{NH4} \cdot dm^{-3} \cdot h^{-1}$ – SBBR) than the increase in nitrite concentration (3.5 mg $N_{NO3} \cdot dm^{-3} \cdot h^{-1}$ for SBR and 1.22 mg $N_{NO3} \cdot dm^{-3} \cdot h^{-1}$ for SBBR). As a result, accumulation of nitrite in sediment water was observed. The maximum concentration of nitrite appeared at 7th h of the cycle. Then the nitrogen concentration was 237 mg $N_{NO2} \cdot dm^{-3}$ in SBR and 158 mg $N_{NO2} \cdot dm^{-3}$ in SBBR. Afterwards, the nitrate concentration began to increase rather notably.

At stage II, the nitrification rate proceeded according to the first-order reaction in comparison with stage I. In SBR, it was 87.6 mg $N_{NO3} \cdot dm^{-3} \cdot h^{-1}$, whereas in SBBR – 80 mg $N_{NO3} \cdot dm^{-3} \cdot h^{-1}$.

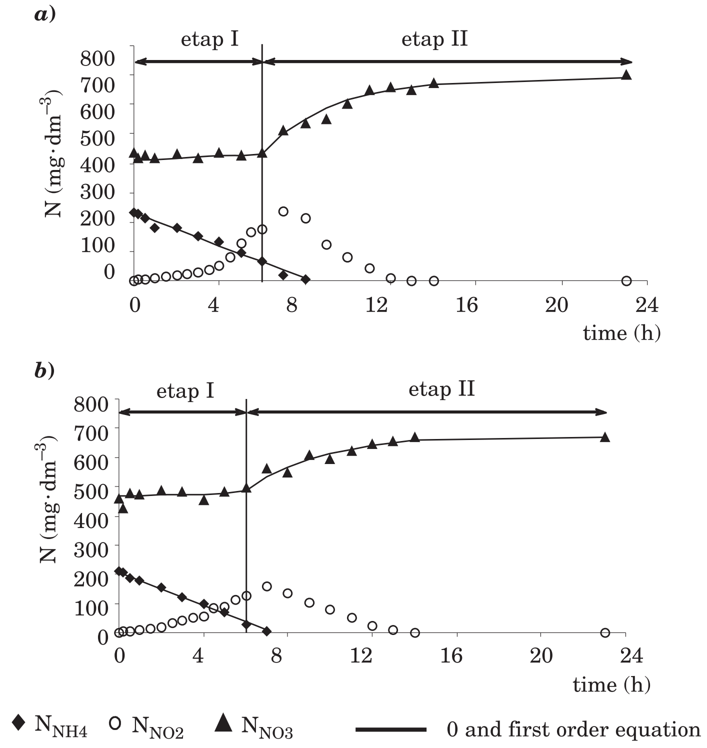

Fig. 2. Changes in concentration of nitrogen forms during an operating cycle of the reactor: a) SBR; b) SBBR

Regardless of the presence or absence of the filling, nitrate dominated in the effluent. Its average concentration was 693 mg $N_{NO3}\cdot dm^{-3}\cdot h^{-1}$ in SBR and 699 mg $N_{NO3}\cdot dm^{-3}$ in SBBR. The ammonium and nitrite concentrations were low, less than 2.9 mg $N_{NH4}\cdot dm^{-3}$ and 0.5 mg $N_{NO2}\cdot dm^{-3}$ (SBR), and 3.2 mg $N_{NH4}\cdot dm^{-3}$ and 0.3 mg $N_{NO2}\cdot dm^{-3}$ (SBBR).

The results suggest that the presence filling did not influence the effectiveness of nitrification in activated sludge.

Yalmaz and Öztürk (2001) claimed that the rate of ammonium loss was kept at a level of 10.5 mg $N_{NH4}\cdot dm^{-3}\cdot h^{-1}$ during the treatment of leachate in SBR reactors.

Welander et al. (1997) demonstrated the influence of the type of filling on the effectiveness of nitrification in leachate. In a reactor filled with cellulose moulders, the nitrification rate was definitely higher (about 40 mg $N_{NH4}\cdot dm^{-3}\cdot h^{-1}$), whereas when filled with polyethylene pieces and polyethylene pieces with an addition of 5% ammonium chloride, it varied from about 5.6 to 11 mg $N_{NH4}\cdot dm^{-3}\cdot h^{-1}$.

Table 2

The constant of ammonium nitrogen removal and nitrate increase rates in SBR and SBBR

Parameter	Unit	Value					
		nitrogen forms					
		ammonium		nitrate			
		SBR	SBBR	etap I		etap II	
				SBR	SBBR	SBR	SBBR
k_1	$mg \cdot dm^{-3} \cdot h^{-1}$	28	28.4	3.5	1.22	-	-
k_2	h-1	-	-	-	-	0.3	0.28
rv	$mg \cdot dm^{-3} \cdot h^{-1}$	28	28.4	3.5	1.22	87.6	80
Correlation coefficient	-	0.99	0.98	0.66	0.71	0.94	0.98
Conformity coefficient	-	0.01	0.02	0.58	0.1	0.11	0.1

Rostron et al. (2001) conducted investigations on synthetic wastewater in CSTR reactors. In a reactor working with suspended biomass, the nitrification rate was 8.64 kg $N \cdot m^{-3} \cdot h^{-1}$. However, when using Linpor moulders, the rate reached 13.68 kg $N \cdot m^{-3} \cdot h^{-1}$, and with Kaldnes moulders, it went up to 12.72 kg $N \cdot m^{-3} \cdot h^{-1}$. The highest nitrification rate (16.8 kg $N \cdot m^{-3} \cdot h^{-1}$) was obtained when biomass immobilized in capsules of polyvinyl chloride (PVC) was applied.

Loukidou and Zoudoulis (2001) achieved 60% reduction of ammonium from leachate. Their experiments were carried out in a reactor filled with polyurethane cubes. The ammonium concentration in leachate was 1 800 mg $N_{NH4} \cdot dm^{-3}$. According to the authors, aeration time of 18 h turned out too short to obtain complete nitrification.

CONCLUSIONS

1. The effectiveness of organic matter removal from leachate was low and at HRT of 3 d, operating time of 24 h and under aerobic conditions, it reached about 20%, with or without filling in a reactor.

2. Ammonium oxidation to nitrate was parallel to the accumulation of nitrite. Nitrification in phase II occurs in two stages. Following ammonium oxidation and maximum nitrite concentration in leachate (stage I), nitrite decreases whereas the nitrate concentration goes up (stage II).

3. Presence of filling in a reactor did not influence the rate of ammonium oxidation in SBR and SBBR reactors.

REFERENCES

Amokrane A., Comel C., Veron J. 1997. *Landfill leachates pretreatment by coagulation - flocculation*. Wat. Res., 31: 2775-2782.

Arnz P., Esterl S., Nerger C., Delgado A., Wilderer P. A. 2000. *Simultaneous loading and draining as a means to enhance efficacy of sequencing biofilm batch reactors*. Wat. Res., 5/34: 1763-1766.

Bila D.M., Montavão A.F., Silva A.C., Dezotti M. 2005. *Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement.* J. Hazard. Mater., B117: 235-242.

El-Fadel M., Bou-Zeid E., Chahine W., Alayli B. 2002. *Temporal variation of leachate quality from pre-sorted and baled municipal solid waste with high organic and moisture content.* Waste Manage., 22: 269-282.

Hermanowicz W., Dożańska W., Dojlido J., Koziorowski B. 1999. *Fizycznochemiczne badanie wody i ścieków*. Arkady, Warszawa.

Kaczorek K., Sójka-Ledakowicz J., Ledakowicz S. 2002. *Porównanie skuteczności metod biologicznych i technik membranowych w oczyszczaniu odcieków z wysypisk*. Inż. Aparat. Chem., 3: 67-68.

Kang K-H., Shin H.S., Park H. 2002. *Characterization of humic substances present in landfill leachates with different landfill ages and its implications.* Wat. Res., 36: 4023-4032.

Karapinar I., Kargi F. 1996. *Effect of particle number density on wastewater treatment performance of a fluidized-bed bioreactor.* Enzyme Microb. Technol., 19: 140-144.

Kim D-J., Lee D-I., Keller J. 2006. *Effect of temperature and free ammonia on nitrification and nitrite accumulation in landfill bacterial community by FISH.* Bio. Technol., 97: 459-468.

Kurniawan T.A., Chan G.Y.S., Lo W-H., Babel S. 2006. *Physico-chemical treatment for removal of recalcitrant contaminants from landfill leachate.* J. Hazard. Mater., B129: 80-100.

Loukidou M. X., Zouboulis A. I. 2001. *Comparison of two biological treatment process using attached-growth biomass for sanitary landfill leachate treatment.* Environ. Pollut., 111: 273-281.

Obrzut L. 1997. *Odcieki z wysypisk komunalnych.* Ekoprofit, 5: 32-36.

Surmacz-Górska J., Miksch K., Kierońska T., Kita M. 1997. *Chemiczne i biologiczne utlenianie zanieczyszczeń występujących w odciekach wysypiskowych.* V Ogóln. Symp. Nauk.-Tech. „Biotechnologia Środowiskowa", ss. 239-247.

Surmacz-Górska J., Miksch K., Kita M. 2000. *Możliwości podczyszczania odcieków z wysypisk metodami biologicznymi.* Arch. Ochr. Środ., 26: 43-54.

Rostron W.M., Stuckey D. C., Young A.A. 2001. *Nitrification of high strength ammonia wastewaters: comparative study of immobilisation media.* Wat. Res., 35: 1169-1178.

Rusten B., Eliassen H. 1993. *Sequencing batch reactors for nutrient removal at small wastewater treatment plants*. Wat. Sci. Technol., 28: 233-242.

Welander U., Henrysson T., Welander T. 1997. *Nitrification of landfill leachate using suspended-carrier biofilm technology.* Wat. Res., 31: 2351-2355.

Yalmaz G., Öztürk I. 2001. *Biological ammonia removal from anaerobically pre-treated landfill leachate in sequencing batch reactors (SBR).* Wat. Sci. Technol., 3/43: 307-314.

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EFFICIENCY OF REMOVAL OF HEAVY METALS FROM MUNICIPAL LANDFILL LEACHATE

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Abstract

The aim of this study was to determine the rate of removal of heavy metals depending on a treatment method applied to leachate from a municipal waste landfill. After the biological treatment, concentrations of Cu, Zn and Ni were observed to have increased. Application of the reagent Fenton caused further growth in Cu, Zn, and also Pb concentrations. The highest concentrations of Cu, Zn and Ni were observed when the Fe^{2+}: H_2O_2 ratio in Fenton was 1:3. The lowest concentrations of these heavy metals were observed at a 1:5 ratio of Fe^{2+}: H_2O_2. The concentration lead, for example, was over 30-fold higher than in raw leachate. There was not correlation between the COD values in raw leachate or in biologically or chemically processed leachate and the concentrations of the analysed metals.

Key words: landfill leachate, activated sludge, Fenton method, heavy metals.

EFEKTYWNOŚĆ USUWANIA METALI CIĘŻKICH Z ODCIEKÓW ZE SKŁADOWISK ODPADÓW KOMUNALNYCH

Abstrakt

W pracy badano wpływ oczyszczania odcieków ze składowisk odpadów komunalnych na stężenie występujących w nich metali ciężkich. Oczyszczanie biologiczne spowodowało wzrost stężenia Cu, Zn i Ni. Po zastosowaniu odczynnika Fentona stwierdzono dalszy wzrost stężenia Cu, Zn, a także Pb. Proporcja Fe^{2+}: H_2O_2 wynosząca 1:3 okazała się niekorzystna w przypadku Cu, Zn i Ni, ponieważ ich stężenie było w tych warunkach najwyższe. W przypadku proporcji Fe^{2+}: H_2O_2 wynoszącej 1:5 zaobserwowano najniższe stężenia Cu, Zn i Ni, podczas gdy stężenie

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Pb było ponad 30-to krotnie wyższe niż w odciekach surowych. Nie stwierdzono korelacji między wartością ChZT w odciekach surowych oraz oczyszczonych biologicznie i chemicznie a stężeniem analizowanych metali ciężkich.

Słowa kluczowe: odcieki, osad czynny, metoda Fentona, metale ciężkie.

INTRODUCTION

Leachate is the term referring to rainwaters migrating through a landfill and leaching dissolved organic and inorganic compounds (SURMACZ-GÓRSKA et al. 1999, NECZAJ et al. 2005).

Leachate occurs when the water content in a landfill exceeds its storage volume, i.e. the maximum water amount which can be retained in the porous material of the landfill (EL-FADEL et al. 2002).

The sources of heavy metals in leachate are industrial waste, e.g. ashes or dyes etc. (ERSES, ONAY 2003), as well municipal waste containing electronic parts, fluorescent lamps, thermometers, batteries, pesticides and others (WARD et al. 2005).

Solubility and mobility of metals are closely connected with transformations in a landfill and depend on its pH, redox, and presence of complexing organic and inorganic substances (BOZKURT et al. 2000).

The highest concentrations of heavy metals occur in leachate from young landfills in the acid fermentation phase and at low pH. At both the maturation and stabilization phases, the pH becomes neutral and solubility of heavy metals decreases (ERSES, ONAY 2003).

With the ageing of a landfill, changes in products of organic matter decomposition occur: from low molecular weight volatile organic acids to humic and fulvic acids. The solubility of high molecular weight organic acids is diverse, but most of them are able to adsorb heavy metals. Therefore, metals adsorbed by humic substances can occur in leachate in the form of colloidal and suspended fractions.

JANSEN and CHRISTETNSEN (1998) investigated heavy metals in leachate from four big municipal landfills in Denmark. The authors showed that colloidal fraction contained 10–60% of total nickel in leachate, 0–95% zinc (therein 80% of 0.001–0.4 µm fraction) and 30-100% of copper. Cadmium occurred in leachate mainly in the dissolved form (26–100%). At the maturation phase of a landfill, metal sulphides can be easily formed. Additionally, metals can be precipitated as carbonates, hydroxides, and even phosphates (ERSES, ONAY 2003).

The concentration ranges of heavy metals in leachate from municipal landfills given by various authors are different, with some being quite high (Table 1).

Table 1

Ranges of concentrations of heavy metals in leachate from municipal landfills ($\mathrm{mg \cdot dm^{-3}}$)

Landfill age (years)	Heavy metals							References
	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
4	<5	18-110	18-71	<1	41-74	2,2-12	21-47	Urase et al. (1997)
5	<60	<13 100	<325	n.b.	<100	<500	<174	Robinson et al. (2005)
5	22-130	50-80	10-90	<17	<70	<1840	220-435	Kulikowska (2002)
8	n.e.	n.e.	n.d.	n.e.	n.d.	<100	0-200	Al.-Yagout, Hamoda (2003)
10	0,2	219	24	n.e.	187	23	74	Szymańska--Pulikowska 2005
>10	<10	200-100	80-100	1200-2000	100-250	<100	250-350	Bila et al. (2005)
Closed	n.e.	n.e.	<200	n.e.	400-600	n.e.	200-4800	Al.-Yagout, Hamoda (2003)
No data	0.13-0.36	6.9-45	n.e.	0.013-0.02	n.e.	2.0-3.5	n.e.	Oygard et al. (2004)

n.e. – not examined
n.d. – not detected

Robinson et al. (2005), who examined leachate from a municipal landfill in Bryn Posteg in England, revealed that the upper chromium concentration was 13.1 $\mathrm{mg \cdot dm^{-3}}$. According to Bila et al. (2005), mercury concentrations in leachate from municipal landfills in Denmark can be as high as 2 $\mathrm{mg \cdot dm^{-3}}$.

It has been demonstrated that leachate treatment methods can be altered as the landfil grows older. Leachate from landfills which have operated for up to ten years are treated mainly by biological methods, whereas that from older landfills is recommended to be treated by multistage systems, combining biological (activated sludge, fluid beds, combined systems) and physicochemical methods (Barbusiński et al. 1997, Surmacz-Górska et al. 1999, Chianese et al. 1999, Rosik-Dulewska 2007, Neczaj et al. 2005, Kim et al. 2006).

Physicochemical methods such reverse osmosis or advanced oxidation are also recommended for treatment of leachate from landfills on which municipal and chemical waste, containing hazardous organic and inorganic substances, are deposited,. Among advantages of these methods is high efficiency of removal of organic substances and heavy metals (above 99%). From Bilstad and Madland (1992) investigations have demonstrated that by using reverse osmosis it is possible to achieve 100% removal efficiency for suspension and chromium as well as nearly 99% removal efficiency for iron, copper and zinc.

The aim of this study has been to determine the extend of the removal of heavy metals from municipal landfill leachate depending on a treatment method.

MATERIAL AND METHODS

In the experiment, leachate collected from a municipal landfill located in Wysieka near Bartoszyce, Province of Warmia and Mazury. The landfill opened in January of 1996.

Leachate samples were collected from a storage reservoir in monthly intervals from May 2004 to April 2006. Overall, 24 samples were collected. The composition of leachate was typical for leachate from landfills in the stabilization phase. Raw leachate contained 875 $mg \cdot dm^{-3}$ of COD.

The filling of the reactor consisted of 42 strips of polyvinyl chloride sponge (2×11 cm). The total operating time of the SBBR was 24 h (filling 23 h, settling and decantation 1h). The experiments were carried out in triplicate.

Next, the leachate samples underwent advanced chemical oxidation by Fenton's method. First, 1 dm^3 of biologically treated leachate was put into the reactor, then $7H_2O$, $FeSO_4$ and H_2O_2 as perhydrol (30% H_2O_2) were added. The pH was adjusted to 3 using 95% H_2SO_4. The experiment lasted for 2 h. The concentration of H_2O_2 was 2 $mg \cdot dm^{-3}$, whereas the Fe^{2+}: H_2O_2 ratios were 1:3, 1:5 and 1:10. All analyses were repeated three times. In total, 9 experiments were carried out.

In the leachate treated biologically and subjected to the advanced oxidation method, the following determinations were performed: level of organic compounds as COD and concentrations of Cd, Cu, Zn, Ni and Pb. COD was analysed by dichromate method according to HERMANOWICZ et al. (1999). Determinations of the heavy metal were carried out using an atomic absorption spectrophotometer AA 280FS (Varian, Australia). Calibration solutions were prepared by dilution of heavy metal standard solutions (obtained from Fluka and acidified with 65% HNO_3) to the concentration of 1 $g \cdot dm^{-3}$.

The relationship between each method of leachate treatment and concentration of heavy metals was tested using Pearson's linear correlation coefficient.

RESULTS AND DISCUSSION

The main processes occuring during removal of heavy metals from leachate are sorption and precipitation. The presence of organic matter and alkaline or neutral environment can be beneficial for the course of these processes (Dewil et al. 2007).

After the biological treatment in the SBBR reactor, concentration of organics as COD decreased by 19% (Table 2). The activated sludge treatment did not affect the concentration of cadmium although it reduced the Pb level by 28% and increased the concentrations of of Cu, Zn and Ni by 91, 234 and 12%, respectively. Similar results were obtained by Urase et al. (1997). Leachate treatment by activated sludge did not change the Cd concentration but decreased the Pb concentration (75%).

Addition of Fenton reagent to leachate caused decrease in COD values from 405 $mg{\cdot}dm^{-3}$ (at 1:3 Fe^{2+}: H_2O_2 ratio) to 460 $mg{\cdot}dm^{-3}$ (at 1:10 Fe^{2+}: : H_2O_2 ratio) – Table 2.

The Fe^{2+}:H_2O_2 ratio of 1:3 turned out unfavourable in the case of Cu, Zn and Ni. For example, it caused the highest, 5-fold, increase in the Cu concentration (Table 2). After adding more H_2O_2 (1:5 Fe^{2+}: H_2O_2 ratio), concentrations of these metals were reduced, reaching the lowest values among all the analysed ratios of both substances. Further increase of H_2O_2 in the mixture (1:10 Fe^{2+}: H_2O_2 ratio) caused increase in the Cu, Zn and Ni concentrations.

At the $Fe^{2+}H_2O_2$ ratio of 1:3, the cadmium concentration was reduced to 3 $\mu g{\cdot}dm^{-3}$, and that of Pb fell below the detection level. Opposite tendency occurred for Cu, Zn and Ni. After increasing the share of H_2O_2 in the mixture (1:5 Fe^{2+}: H_2O_2 ratio), concentrations of these metals were the highest (Table 2).

Table 2

Concentrations of analysed heavy metals in raw leachate and after biological and chemical treatment ($mg \cdot dm^{-3}$)

Heavy metals	Raw leachate (*n*=24)	Leachate after biological treatment (*n*=9)	Leachate after chemical treatment Fe^{2+} :H_2O_2 (*n*=9)		
			1:10	1:5	1:3
Cd	10 (±0.2)	10 (±0.15)	4 (±0.05)	10 (±0.23)	3 (±0.04)
Cu	189 (±9)	362 (±12)	864 (±70)	704 (±55)	1963 (±97)
Zn	181 (±23)	605 (±56)	954 (±68)	787 (±65)	1639 (±109)
Ni	121 (±8)	136 (±15)	96 (±6)	59 (±1)	144 (±5)
Pb	53 (±3)	38 (±6)	n.d.	1730 (±107)	n.d.

n.d. – not detected

The increase of concentrations of heavy metals in the chemically treated leachate could have resulted from decomposition of high molecular weight organic substances to low molecular weight compounds, which occurred under the effect of hydroxyl radicals ($OH^{\bullet}$) generated during Fenton's reaction. In this process, complexes of metals and organic compounds are destroyed, causing release of heavy metals. Acid pH during this process can facilitate solubility of heavy metals in leachate (ERSES, ONAY 2003).

The relevant literature view contains contrary opinions on the results of leachate treatment. ANDREAOTTOLA and CANNAS (1992), URASE et al. (1997) and DEWIL et al. (2007) stated that the treatment method not influence concentration of heavy metals in leachate. However, URASE et al. (1997) reported that the cadmium concentration in leachate remaieds constant, independently of a treatment method. Our results show that the copper concentration decreased by 75% in the biologically treated leachate and by 55% after combining the biological and chemical methods. Also, the Ni concentration declined after using both methods (45% decrease after the biological treatment and 33% - after the combined treatment).

CHIANESE et al. (1999) investigated the influence of organics content (COD) in leachate on the effectiveness of zinc, copper and cadmium removal by advanced oxidation. In their experiment, solution containing metals at a concentration of 20 $mg \cdot dm^{-3}$ and leachate from municipal landfill was supplied to the system. The results revealed that the effectiveness of zinc and copper removal was about 99% and more in the control sample without leachate. After addition of leachate (COD 1 265 $mg \cdot dm^{-3}$) the process efficiency varied from 99.2% to 98.5% (Cu) and from 98.1% to 97.2% (Zn). Removal of cadmium proceeded at constant efficiency (99.5%), independently of organics concentration in leachate.

The statistical analysis of our data, using Pearson's correlation, did not show significant relationship between the COD value and concentrations of the metals in raw and treated leachate. In addition, no correlation between the method of leachate treatment and concentration of the metals was verified. The influence of pH on concentration of heavy metals in leachate was not investigated because the chemical treatment proceeded at constant pH equal 3.

According to ŘYGARD et al. (2004), organics concentration influences content of metals in leachate. At the COD concentration of 3100 $mg \cdot dm^{-3}$ the concentration of cadmium was 200 $mg \cdot dm^{-3}$ whereas that of lead equalled 2700 $mg \cdot dm^{-3}$. For comparison, when the COD concentration was reduced to 310 $mg \cdot dm^{-3}$, the content of the two heavy metals was 360 mg $Cd \cdot dm^{-3}$ and 3500 mg $Pb \cdot dm^{-3}$.

CONCLUSIONS

1. The biological and chemical treatment helped to reduce concentration of organics expressed as COD from 875 mg·dm^{-3} to 713 mg·dm^{-3} (biological process) and to 405 mg·dm^{-3} during chemical oxidation.

2. The COD value did not influence concentration of heavy metals in leachate.

3. The biological methods tested did not cause more efficient removal of heavy metals from leachate. On the contrary, under these conditions Cu, Zn and Ni concentration increased.

4. Using the chemical methods caused 5-fold increase in Cu concentration and 3-fold increase in Zn concentration in leachate.

5. Applying a combination of the biological and chemical methods in leachate treatment did not guarantee efficient removal of heavy metals either. In some cases, it even increased their concentrations.

REFERENCES

AL-YAGOUT A.F., HAMODA M.F. 2003. *Evaluation of landfill leachate in arid climate-a case study.* Environ. Intern., 29: 593-600.

ANDREOTTOLA G., CANNAS P. 1992. *Chemical and biological characteristics of landfill leachate. Landfilling of waste: leachate.* Elsev. Appl. Sc. London and New York, 65-88.

BARBUSIŃSKI K., KOŚCIELNIAK H., MAJER M. 1997. *Oczyszczanie wód podziemnych zalegających pod składowiskiem odpadów przemysłowych.* V Ogólnop. Symp. Nauk.-Tech. „Biotechnologia Środowiskowa”, ss: 219-225.

BILA D.M., MONTAVÃO A.F., SILVA A.C., DEZOTTI M. 2005. *Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement.* J. Hazard. Mater., B 117: 235-242.

BILSTAD T., MADLAND M. V. 1992. *Leachate minimization by reverse osmosis.* Wat. Sci. Technol., 3 (25): 117-120.

BOZKURT S., MORENO L., NERETNIEKS I. 2000. *Long-term processes in waste deposits.* Sci. Total Environ., 250: 101-121.

CHIANESE A., RANAURO R., VERDONE N. 1999. *Treatment of landfill leachate by reverse osmosis.* Wat. Res., 33: 647-652.

DEWIL R., BAEYENS J., APPELS L. 2007. Enhancing the use of waste activated sludge as bio-fuel through selectively reducing its heavy metal content. J. Hazard. Mater., 144: 703-707.

EL-FADEL M., BOU-ZEID E., CHAHINE W., ALAYLI B. 2002. *Temporal variation of leachate quality from pre-sorted and baled municipal solid waste with high organic and moisture content.* Waste Manage., 22: 269-282.

ERSES A.S., ONAY T.T. 2003. *In situ heavy metal attenuation in landfills under methanogenic conditions.* J. Hazard. Mater., B99: 159-175.

HERMANOWICZ W., DOŻAŃSKA W., DOJLIDO J., KOZIOROWSKI B. 1999. *Fizycznochemiczne badanie wody i ścieków.* Arkady, Warszawa.

JENSEN D.L., CHRISTENSEN T.H. 1998. *Colloidal and dissolved metals in leachates from four Danish landfills.* Wat. Res., 33: 2139-2147.

Kim D-J., Lee D-I., Keller J. 2006. *Effect of temperature and free ammonia on nitrification and nitrite accumulation in landfill bacterial community by FISH.* Biores. Technol., 97: 459-468.

Kulikowska D. 2002. *Efektywność oczyszczania odcieków z wysypisk odpadów komunalnych w reaktorach SBR.* Wydz. Inż. Środ., Politechnika Warszawska. (praca doktorska), ss. 35-44;

Neczaj E., Okoniewska E., Kacprzak M. 2005. *Treatment of landfill leachate by sequencing batch reactor.* Desalination, 185: 357-362.

Řygard J. K., Mĺge A., Gjengedal E. 2004. *Estimation of the mass-balance of selected metals in four sanitary landfills in Western Norway, with emphasis on the heavy metal content of the deposited waste and the leachate.* Wat. Res., 38: 2851-2858.

Robinson H.D., Knox K., Bone B. D., Picken A. 2005. *Leachate quality from landfilled MBT waste.* Waste Manage., 25: 383-391.

Rosik-Dulewska Cz. 2007. *Podstawy gospodarki odpadami.* Wyd. Nauk. PWN, Warszawa.

Slack R.J., Gronow J.R., Voulvoulis N. 2005. *Household hazardous waste in municipal landfills: contaminants in leachate.* Sci. Total Environ., 337: 119-137.

Szymańska-Pulikowska A. 2005. *Zanieczyszczenie wód podziemnych w otoczeniu starego składowiska odpadów komunalnych.* Zesz. Probl. Post. Nauk Rol., PAN, Warszawa, 505: 439-444.

Urase T., Salequzzaman M., Kobayashi S., Matsuo T., Yamamoto K., Suzuki N. 1997. *Effect of high concentration of organic and inorganic matters in landfill leachate on the treatment of heavy metals in very low concentration level.* Wat. Sci. Technol., 36: 349-356.

Ward M.L., Bitton G., Townsend T. 2005. *Heavy metal binding capacity (HMBC) of municipal solid waste landfill leachates.* Chemosphere, 60: 206-215.

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CALCIUM IONS IN THE PIG PINEAL GLAND – AN ULTRACYTOCHEMICAL STUDY

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Abstract

The aim of the study was to analyze the distribution of calcium ions in the pig pineal gland at the level of electron microscopy. The investigations were performed on the pineals obtained immediately after slaughter (performed between 11:30 and 12:00 a.m.) from 4- month-old gilts. The fixation procedures were conducted with the use of pyroantimonate, which reacted with calcium ions and formed electron dense precipitates.

The precipitates were found both in the intercellular spaces and in cells - pinealocytes, gial cells, endothelial cells and fibroblasts. The precipitates were much more numerous in the intercellular spaces than in the cells. Amount and distribution of precipitates differed significantly between pinealocytes, therefore two types of cells were distinguished. The first type of pinealocytes included cells containing a small or moderate amount of precipitates. They were usually characterized by light or dark cytoplasm and large variability in number and structure of dense bodies. Pinealocytes classified to the second type possessed large or very large content of precipitates. These cells were characterized by electron dense cytoplasm and showed the presence of numerous dense bodies. In both types of pinealocytes, precipitates were present in the nucleus and in the cytoplasm. In nuclei, precipitates were numerous in nucleoplasma and rather infrequently noted between membranes of the nuclear envelope. In the cytoplasm deposits were found in mitochondria, vesicles and cisterns of smooth endoplasmic reticulum, in the Golgi apparatus and in cytosol. The amount of precipitates in glial cells, endothelial cells and fibrocytes was lower than in pinealocytes.

Key words: pig, pineal gland, calcium ions, ultracytochemical analysis.

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JONY WAPNIOWE W SZYSZYNCE ŚWINI – BADANIA ULTRACYTOCHEMICZNE

Abstrakt

Celem pracy była analiza ultracytochemiczna rozmieszczenia jonów wapniowych w szyszynce świni domowej. Badano szyszynki pobrane bezpośrednio po uboju (wykonanym między godz. 11:30 a 12:00) od loszek w wieku ok. 4 miesięcy. Do utrwalania gruczołów zastosowano pyroantymonian potasu, co umożliwiło związanie jonów wapniowych w postaci elektronowo gęstych precypitatów, których rozmieszczenie określono za pomocą mikroskopu elektronowego.

Precypitaty występowały w przestrzeni międzykomórkowej oraz w komórkach: pinealocytach, komórkach glejowych, komórkach śródbłonka naczyń włosowatych i fibrocytach. Zawartość złogów pyroantymonianu wapnia była znacznie większa w przestrzeni zewnątrzkomórkowej niż wewnątrz komórek. Ze względu na ilość i lokalizację precypitatów możliwe było wyróżnienie dwóch typów pinealocytów. Pierwszy z nich stanowiły komórki zawierające małą lub średnią ilość precypitatów. Komórki te charakteryzowały się elektronowo jasną lub elektronowo gęstą cytoplazmą, a skład ciałek gęstych był zróżnicowany pod względem ilościowym i jakościowym. Drugi typ pinealocytów stanowiły komórki z dużą lub bardzo dużą zawartością precypitatów. Najczęściej charakteryzowały się one elektronowo gęstą cytoplazmą oraz obecnością bardzo licznych ciałek gęstych. W obu typach pinealocytów precypitaty występowały zarówno w jądrze komórkowym, jak i w cytoplazmie. W jądrze stosunkowo liczne precypitaty o zróżnicowanych wymiarach stwierdzono w obrębie chromatyny, natomiast jedynie sporadycznie obserwowano je w przestrzeni między błonami otoczki jądrowej. W cytoplazmie precypitaty występowały w mitochondriach, pęcherzykach i cysternach siateczki śródplazmatycznej gładkiej, strukturach aparatu Golgiego oraz w cytoplazmie podstawowej. Zawartość precypitatów w komórkach glejowych, komórkach środbłonka oraz fibrocytach była znacznie mniejsza niż w pinealocytach.

Słowa kluczowe: świnia, szyszynka, jony wapniowe, analiza ultracytochemiczna.

INTRODUCTION

The mammalian pineal gland is a neurohormonal transducer, which converts neuronal input from the suprachiasmatic nucleus (the main circadian oscillator, which function is controlled by the retina) into the hormonal output – melatonin (REITER 1993). This pineal hormone controls several processes occurring in the diurnal and seasonal rhythm (REITER 1993, ARENDT 1995). Melatonin is also involved in regulation of the immune (AKBULUT et al. 2001), cardiovascular (KRAUSE et al. 2000) and gastro-intestinal systems (BUBENIK, 2002) as well as in modulation of neoplastic processes (BLASK et al. 1989, KARASEK, PAWLIKOWSKI 1999). It is also a very potent scavenger of free radicals and posses a strong cell protective capacity (REITER et al. 2000).

An interest in the study of calcium ions in the pineal gland derives from at least two reasons. The first of them is an important role of calcium in regulation of numerous pineal processes, although many of them are not fully recognized. A special attention is paid to the role of Ca^{2+} in regulation of the melatonin secretion. In the rodent pineal gland, norepinephrine –

the main neurotransmitter controlling the pineal function – increases via activation of α_1-adernoceptors the intracellular free Ca^{2+} concentration in pinealocytes, what potentates the secretory response of these cells to stimulation of β-adrenoceptors (SUGDEN 1993, SUGDEN et al. 1987). The role of calcium in regulation of the pineal activity in non-rodent species has been not investigated. The second aim to study calcium in the pineal gland is the presence of the pineal concretions in several mammals (HUMBERT, PEVET 1991, JAPHA et al. 1976, KRSTIČ 1976, 1986, WELSH 1985). These unique structures consist of organic compounds – mainly proteoglycans and insoluble calcium salts. Other elements: phosphorus, sulfur, magnesium, strontium, zinc, iron, manganese, copper and silicon have been also detected in the pineal concretions (HUMBERT, PEVET 1991, KRSTIČ 1976, KRSTIČ, GOLAZ 1977, WELSH 1985). The biological significance of the pineal concretions is still unknown.

The pig pineal gland shows many species specific features of their morphology and physiology, among them at least three need to be especially emphasized: 1) the presence of numerous electron dense bodies in pinealocytes, 2) the excusive involvement of β-aderenoceptors in stimulation of melatonin secretion by norepinephrine (without α-adrenoceptors participation) and 3) the regulation of melatonin synthesis via changes in serotonin N-acetyltransferase properties (LEWCZUK 2002, WYRZYKOWSKI et al. 1997). The calcified concretions are very rare in the pig pineal and they have been found only in the pineal capsule and connective tissue septa in the glands of three-year-old pigs (LEWCZUK et al. 1994).

The aim of the present work was to analyse the distribution of calcium ions in the pig pineal gland at the level of electron microscopy. In order to localize Ca^{2+} we applied potassium pyroantimonte method, which enables us to visualise calcium in a form of electron dense precipitates.

MATERIAL AND METHODS

The studies were performed on five crossbred female pigs at the age of ca 4 months. The animals were purchased from a commercial farm and kept in the laboratory room, in which natural lighting from windows (sunrise 06:00–06:30, sunset 18:35–19:00) was supplemented during the day with fluorescent illumination providing light intensity of 500 lx at the level of animal heads. Gilts had free access to water and were fed twice daily (9:00, 14:00) with standard food. After 2 weeks the pigs were killed between 11.30 and 12.00 a.m. All procedures on animals were performed in agreement with the Polish law.

The pineal glands were removed no later than 3 minutes after death, divided into small pieces and fixed in a solution containing 2% glutaraldehyde, 2% potassium pyroantimonate and 0.735% potassium acetate for 2 hours at 4°C (pH 7.5). After the first step of fixation, the pieces were rinsed three times (10 min. each) with 0.735% potassium acetate in distilled water, incubated for 2 hours in 1 % aqueous solution of osmium tetroxide containing 2% potassium pyroantimonate and 0.735% potassium acetate. Next, the pieces were washed in potassium acetate solution to remove any unreacted potassium pyroantimonate and to prevent nonspecific precipitation, dehydrated and embedded in Epon 812. Both contrasted with lead citrate and uranyl acetate and uncontrasted ultrathin sections were examined in the transmission electron microscope Tesla BS 500. As control ultrathin sections were decalcified by incubation in 13.5% EDTA at 60°C for 2 hours.

RESULTS AND DISCUSSION

The potassium pyroantimonate method is commonly used for the ultracytochemical localization of calcium ions in many biological samples including the pineal gland (Appleton, Morris 1979, Klein et al. 1972, Krstič 1985, Lewczuk et al 1994, Mentre, Escaig 1988, Pizzaro et al. 1989, Theron et al. 1989, Tutter et al. 1991, Wick, Heple 1982). According to the studies on chemical composition of pyroantimonate deposits, performed using x-ray microanalysis, Ca^{2+} is the predominant (beside small amounts of K, Na, Mg) or the only element associated with antimony, what points to the satisfactory specificity of this method (Suzuki, Sugi 1989, Mentre, Escaig 1988). As concerning sensitivity, the potassium pyroantimonate technique is the only one enabling demonstration of intracellular calcium ions at the level of electron microscopy in the pineal gland (Tutter et al. 1991). The procedures validating the potassium pyroantimonate technique for studies of calcium in the pig pineal gland were performed and discussed in our previous study (Lewczuk et al., 1994). In the present work we treated some ultrathin sections with EDTA to confirm the presence of Ca^{2+} in precipitates. As expected, pyroantimonate deposits were not found after treatment with this chelator.

The reaction product in a form of electron dense precipitates was observed both in intercellular spaces and in cells – pinealocytes, gial cells, endothelial cells and fibroblasts in all studied pineal glands. The intercellular spaces contained extremely numerous, large precipitates, whose presence clearly marked borders between adjacent cells (Fig. 1). The prominent differences in amount of precipitates between extracellular and intercellular compartments reflect the well-known gradient of calcium ions concentration on both sides of plasma membrane and clearly point to the lack of significant ions translocation during fixation.

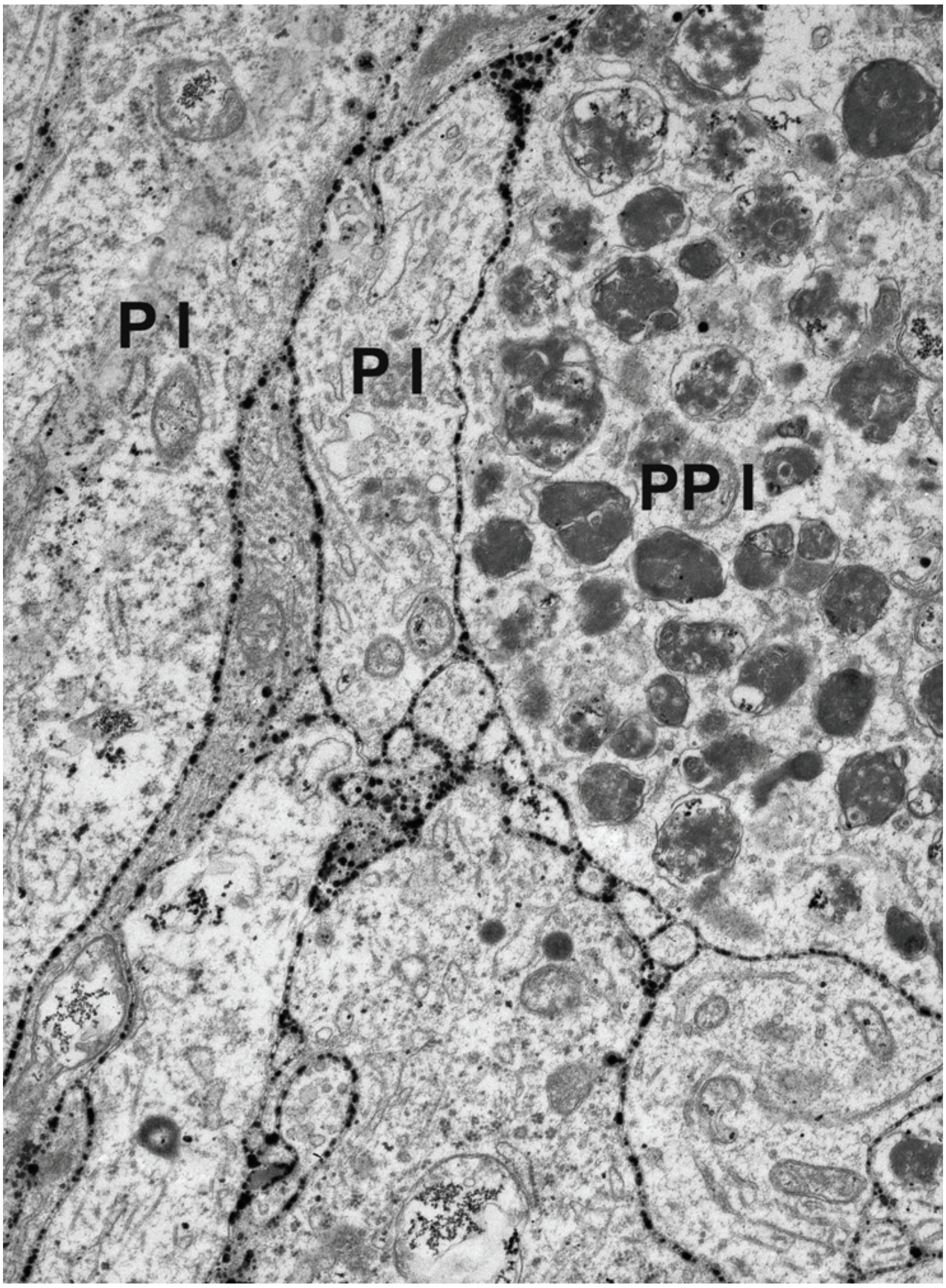

Fig. 1. Numerous precipitates in the intercellular species between neighboring cells and cell processes. Pinealocytes (P I) and the ending of pinealocyte process (PP I) with low amount of precipitates. Mag. 25 000 x

Generally, pyroantimonate deposits were more numerous in pinealocytes than in other cell types. Amount and distribution of precipitates differed significantly between pinealocytes, therefore two types of cells were distinguished (Fig. 1, 2, 3, 4). The first type of pinealocytes included cells containing a small or moderate amount of precipitates (Fig. 1, 2, 4). These cells were usually characterized by low electron density of their cytoplasm, but pinealocytes with the electron dense cytoplasm were also noted among them. Pinealocytes of this type contained various forms of dense bodies, which number varied significantly between cells. In perikarya of these pinealocytes, precipitates were seen both within the nucleus and cytoplasm. In the nucleus relatively numerous precipitates, varying in sizes, were found in the nucleoplasm and sporadically in the space between membranes of the nuclear envelope. In the cytoplasm, small precipitates were observed in mitochondria, vesicles and cisterns of the smooth endoplasmic reticulum and in the Golgi apparatus, whereas single large precipitates were noted in cytosol. In the cell processes and their endings precipitates were noted in mitochondria, vesicles of the smooth endoplasmic reticulum, on the outer surface of dense bodies and in cytosol.

Pinealocytes classified to the second type were characterized by large or very large content of precipitates, both in the cell nucleus and the cytoplasm (Fig. 2, 3, 4). They were usually characterized by electron dense cytoplasm (with a few exceptions) and the presence of numerous dense bodies, which most frequently represent types MBB1C and MBB-2 according the classification proposed by LEWCZUK and PRZYBYLSKA-GORNOWICZ (1994). In perikaryon, mitochondria contained numerous small or few large precipitates, while in the Golgi apparatus and in the smooth endoplasmic reticulum numerous large precipitates were found. Very numerous, large precipitates were observed in cytosol. The endings of cell processes contained numerous precipitates, located mainly in cytosol and sometimes on the surface of dense bodies (Fig. 4).

The obtained results have shown that pig pinealocytes differ significantly each other in the content of calcium ions. It should be stressed that prominent differences in amount of calcium pyroantimonate precipitates have been commonly observed between neighboring pinealocytes. Therefore, we can exclude that the variability in calcium ions content is an artifact of fixation procedures. There is rather loose relationship between the electron density of cytoplasm and Ca^{2+} content. Pinealocytes with low calcium content possessed both light and dark cytoplasm, pinealocytes with high calcium – usually dark. More interesting are differences in amount and structure of dense bodies between pinealocytes with different calcium ions content. Pinealocytes with high level of Ca^{2+} contain numerous dense bodies, among them predominate MBB-2 or MBB-1C. This relationship may be considered as a specific functional state of these cells. The current data largely supplemented our previous observations (LEWCZUK et al. 1994), what

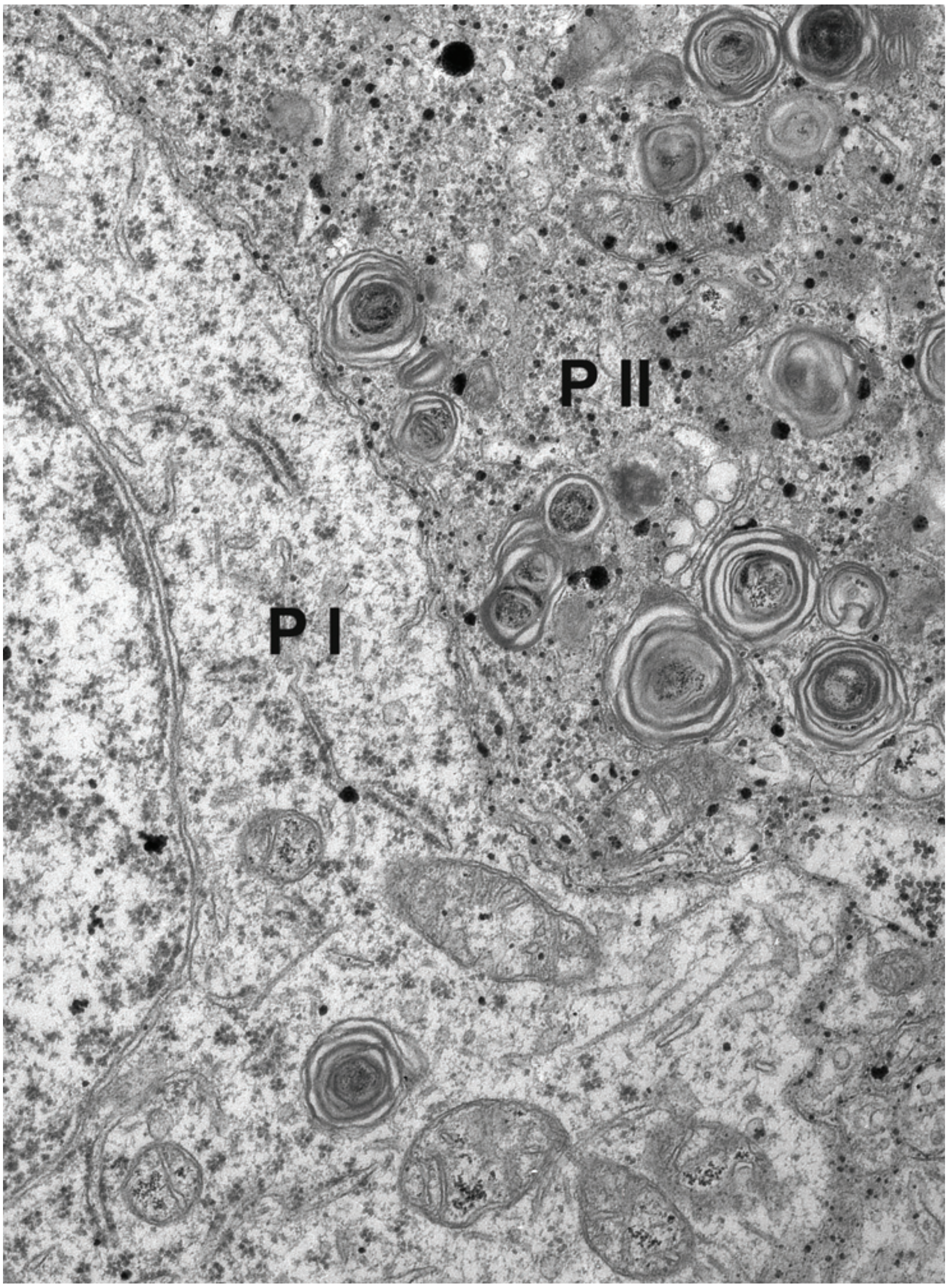

Fig. 2. Variable content of precipitates in two neighboring pinealocytes. Light pinealocyte containing low amount of precipitates (P I) and a dark pinealocyte (P II) with numerous precipitates. Mag. 25 000 x

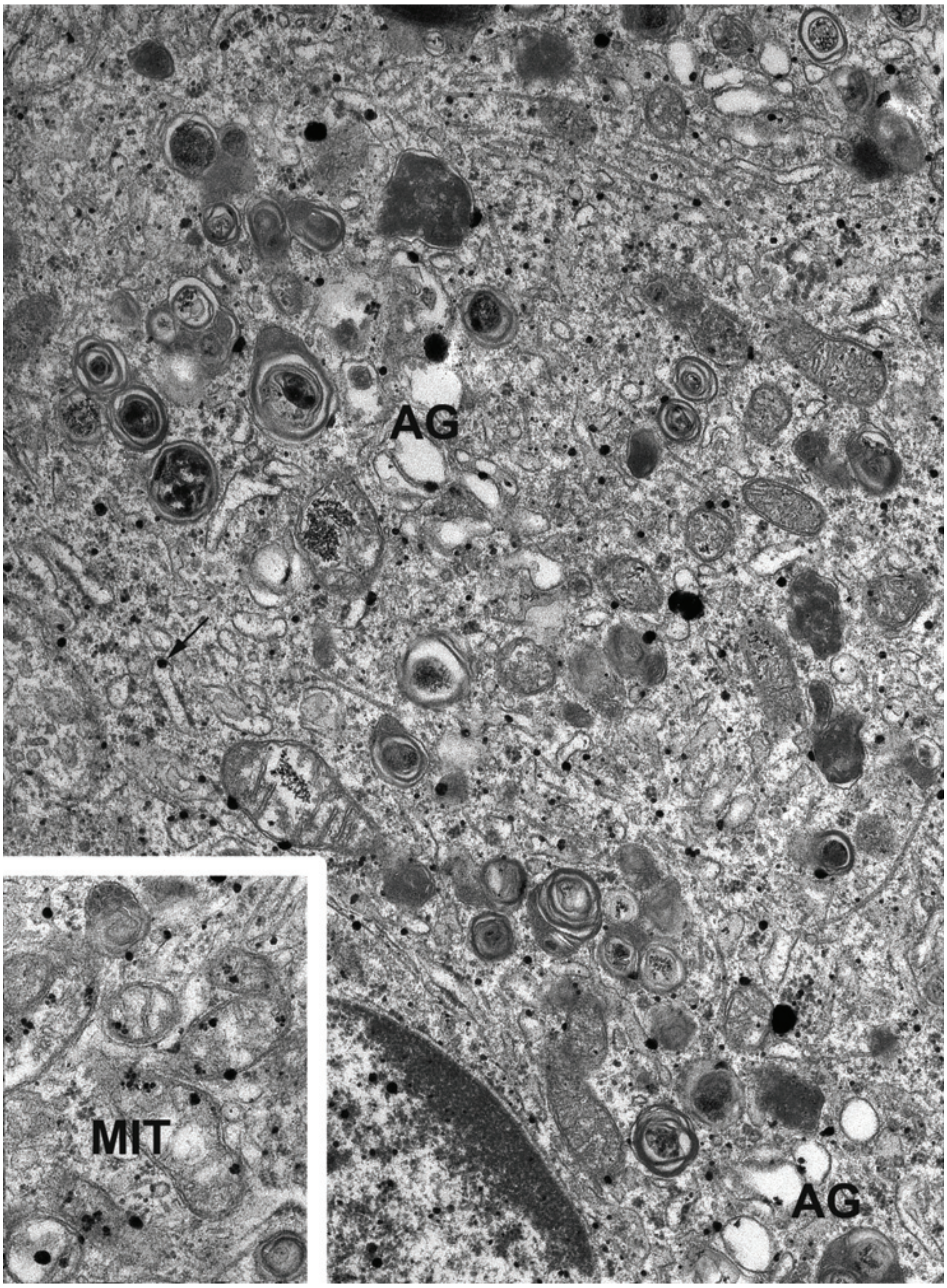

Fig. 3. Dark pinealocyte with numerous precipitates distributed in mitochondria (MIT), the Golgi apparatus (AG), vesicles of endoplasmic reticulum (arrow) and in cytosol. Mag. 25 000 x, insert – 30 000 x

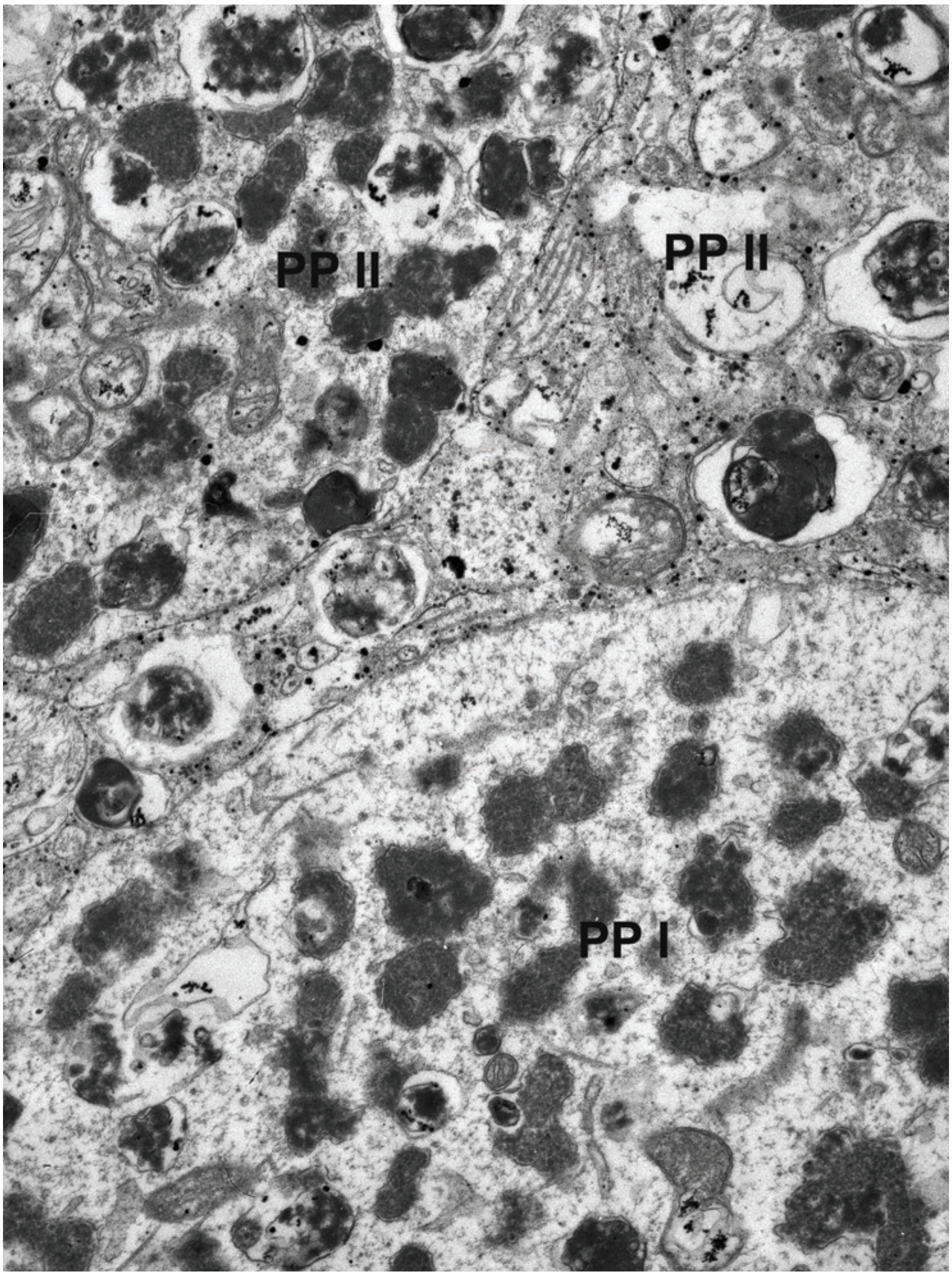

Fig. 4. Endings of light pinealocyte with low content of precipitates (PP I) and dark pinealocytes with numerous precipitates (PP II). Mag. 25 000 x

was possible due to some technical improvements in the fixation procedures and a very-well preservation of cell structure.

The differences in calcium ions content between dark and light pinealocytes were described in the rat pineal gland by PIZZARO et al. (1989). The authors distinguished two kinds of pinealocytes: type I corresponding to the classic light pinealocytes with almost complete absence of calcium pyroantimonate precipitates and type II with dense cytoplasmic matrix and very abundant coarse precipitates inside the cytoplasm and nucleus.

In our study gilts were killed only during the light phase of the diurnal cycle. The investigations performed in the baboon (THERON et al. 1989) and the gerbil (TUTTER at al. 1991) demonstrated some changes in distribution, but not in amount of calcium pyroantimonate deposits between animals killed during the day and the night. A prominent shift from a predominant cytoplasmic localization of Ca^{2+} during the light phase to intravesicular distribution of these ions during the darkness was found in baboon pinealocytes. In contrast, gerbil pinealocytes, when the animals were killed at day time, showed accumulation of precipitates in all compartments of the endoplasmic reticulum including subsurface cisterns, but when the animals were killed at night precipitates were not present anywhere in the endoplasmic reticulum (TUTTER at al. 1991). It should be noted, that in our study subsurface cisterns of pinealocytes did not contain precipitates.

The content of precipitates in glial cells, endothelial cells and fibrocytes was usually low. The deposits were observed in the cell nuclei, mitochondria, the Golgi apparatus, vesicles of endoplasmic reticulum and in cytosol.

CONCLUSIONS

1. The content of calcium ions differ significantly between pinealocytes in the glands taken from immature pigs killed during the daytime.

2. Pinealocytes with high content of calcium ions usually posses numerous dense bodies of type MBB-2 and MBB-1C as well as electron-dense cytoplasm.

3. Pinealocytes with low or moderate calcium content show large variability in the electron density of cytoplasm and in the presence of dense bodies.

REFERENCES

AKBULUT K.G., GÖNÜL B., AKBULUT H. 2001. *The effects of melatonin on humoral immune responses of young and aged rats.* Immunol Invest., 30: 17-20.

APPLETON J., MORRIS D.C. 1979. *The use of the potassium pyroantimonate-osmium method as a means of identifying and localizing calcium at the ultrastructural level in the cells of calcifying systems.* J. Histochem. Cytochem., 27 (2): 676-680.

ARENDT J. 1986. *Role of the pineal gland and melatonin in seasonal reproductive function of mammals.* Oxford. Rev. Reprod. Biol., 8: 266-320.

ARENDT J. 1995. *Melatonin and the mammalian pineal gland.* Chapman & Hall, UK.

BLASK D.E., HILL S.M., PELLETIER D.B., ANDERSON J.M., LEMUS-WILSON A. 1989. *Melatonin: an anticancer hormone of the pineal gland.* In: *Advances in pineal research.* Vol. 3, pp. 259-264.

BUBENIK G.A. 2002. *Gastrointestinal melatonin: localization, function, and clinical relevance.* Dig. Dis. Sci., 47(10): 2336 – 2348.

HUMBERT W., PEVET P. 1991. *Calcium content and concretions of pineal glands of young and old rats. A scanning and x-ray microanalytical study.* Cell Tissue Res., 263: 593-596.

JAPHA J.L., EDER T.J., GOLDSMITH E.D. 1976. *Calcified inclusions in the superficial pineal gland of the mongolian gerbil, Meriones unguiculatus.* Acta Anat. 94: 533-544.

KARASEK M., PAWLIKOWSKI M. 1999. *Pineal gland, melatonin and cancer.* Neuroendocrinol. Lett., 20: 139-144.

KLEIN R.L., YEN S.-S., THURESON-KLEIN A. 1972. *Critique on the K-pyroantimonate method for semiquantitative estimation of cations in conjunction with electron microscopy.* J. Histochem. Cytochem., 20 (1): 65-78.

KRAUSE D.N., GEARY G.G., DOOLEN S., DUCKLES S.P. 2000. *Melatonin and cardiovascular system.* In: *Melatonin after four decades. An assessment of its potential*. Eds. J. OCLESE, Kluwer Acad./Plenum Publ., New York, 299-310.

KRSTIČ R. 1976. *A combined scanning and transmission electron microscopic study and electron probe microanalysis of human pineal acervuli.* Cell Tissue Res., 174: 129-137.

KRSTIČ R. 1985. *Ultracytochemical localization of calcium in the superficial pineal gland of the Mongolian gerbil.* J. Pineal Res., 2 (1): 21-37

KRSTIČ R. 1986. *Pineal calcification, its mechanism and significance.* J. Neural Transm. (Suppl), 21: 415-432.

KRSTIČ R., GOLAZ J. 1977. *Ultrastructural and x-ray microprobe comparison of gerbil and human pineal acervuli*. Experientia, 33: 507-508.

LEWCZUK B. 2002. *Mechanisms of adrenergic regulation of melatonin secretion in the pig pineal gland – in vitro study.* Univ. of Warmia and Mazury, Dissertations and Monographs, 60: 1-160.

LEWCZUK B., PRZYBYLSKA B., WYRZYKOWSKI Z. 1994. *Distribution of calcified concretions and calcium ions in the pig pineal gland.* Fol. Histochem. Cytobiol., 32: 243-249.

LEWCZUK B., PRZYBYLSKA-GORNOWICZ B. 1997. *Effects of sympathicolytic and sympaticomimetic drugs on pineal ultrastructure in the domestic pig.* J Pineal Res., 23: 198-208.

MENTRE P., ESCAIG F. 1988. *Localization of cations by pyroantimonate.* I *Influence of fixation on distribution of calcium and sodium. An approach by analytical ion microscopy.* J. Histochem. Cytochem., 36 (1): 49-54.

PIZZARO M.D.L., PASTOR F.E., GIL A.L., BARRAGAN L.M. 1989. *Ultrastructural study of the distribution of calcium in the pineal gland of the rat subjected to manipulation of the photoperiod*. Histochemistry, 92: 161-169

REITER R.J. 1993. *The melatonin rhythm: both a clock and a calendar.* Experientia, 49: 654-664.

REITER R.J., TAN D.X., OSUNA C., GITTO E. 2000. *Actions of melatonin in the reduction of oxidative stress – a review.* J. Biomed. Sci., 7: 444-458.

Sugden L. A., Sugden D., Klein D. C. 1987. a*1-Adrenoceptor activation elevates cytosolic calcium in rat pinealocytes by increasing net influx.* J. Biol. Chem., 262(2): 741-745.

Sugden D. 1993. *The importance of á1-adrenergic mechanisms in regulating pineal melatonin synthesis.* W: *Melatonin and the pineal gland - from basic science to clinical application.* Eds: Touitou Y, Arendt J, Pevet P, Excerpta Medica, 3-9.

Suzuki S., Sugi H. 1989. *Evaluation of the pyroantimonate method for detecting intracellular calcium localization in smooth muscle fibers by the X-ray microanalysis of cryosections.* Histochemistry, 92: 95-101.

Theron J.J., Biagio R.P., Henning C.N. 1989. *Circadian changes in the ultracytochemical localization of calcium in the pinealocytes of the baboon (Papio ursinus).* Ad.: Adv. Pineal Res., vol 3. R.J. Reiter, S.F. Pang (Eds), John Libbey & Co Ltd, London, pp. 33-38.

Tutter I., Heinzeller T., Seitz-Tutter D. 1991. *Pinealocyte subsurface cisterns* III, *Storage of calcium ions and their probable role in cell stimulation.* J. Pineal Res., 10: 91-99.

Welsh M.G. 1985. *Pineal calcification, structural and functional aspects.* Pineal Res. Rev., 3: 41-68. A.R. Liss (Ed), New York.

Wick S.M., Hepler P.K. 1982. *Selective localization of intracellular* Ca^{2+} *with potassium antimonate*. J. Histochem. Cytochem., 30 (11): 1190-1204.

Wyrzykowski Z., Przybylska-Gornowicz B., Lewczuk B. 1997. *Membrane bounded dense bodies (MBB) of the domestic pig pinealocytes – current state of knowledge.* Ann. Acad. Med. Bial., 42 (Suppl. 2): 185-193.

J. Elementol. 2007, 12(4): 347–360

CAUSES OF LOADING THE WATER OF THE EUTROPHIC LAKE JAGIEŁEK WITH NITROGEN AND PHOSPHORUS COMPOUNDS UNDER THE METEOROLOGICAL CONDITIONS OF OLSZTYN LAKELAND

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Abstract

The causes of the eutrophication of Lake Jagiełek, situated around 6 km south-west of Olsztyn, were investigated in the hydrological years 1998-2004. The catchment area of this water body is situated in the watershed zone of the Łyna and Pasłęka rivers. The lake is subject to advanced eutrophication. As regards precipitation amount, the analysed period consisted of three dry years, two normal years and one wet year. Due to the occurrence of three successive dry years and higher evaporation resulting from increased air temperatures (by 0.5°C on average), the lake shallowed with periodic exposure of bottom sediments in the shoreline zone. The periodic exposure and inundation of sections of the lake bottom has led to intense mineralization of bottom sediments. This process contributes to secondary contamination of surface water with mineral substances, mainly nitrogen and phosphorus compounds. The investigated water body is situated in a watershed zone and is characterised by low and stable electrolytic conductivity (113 $\mu S \cdot cm^{-1}$ on average) and low pH of water (6.72 on average) which periodically reaches 4.70. The concentration levels of biogenic elements (nitrogen and phosphorus compounds) are subject to seasonal fluctuation. Relatively high concentrations of $N\text{-}NO_3$ (1.25 mg dm^{-3} on average) were observed in the winter and spring, while low levels of this compound (0.18 $mg \cdot dm^{-3}$ on average) were reported in the summer and autumn. $P\text{-}PO_4$ concentrations were marked by a growing trend from 0.26 $mg \cdot dm^{-3}$ on average in the spring to 0.70 $mg \cdot dm^{-3}$ on average in the summer. A high water load with biogenic elements, whose concentrations significantly exceeded the allowable and dangerous levels of N and P according to Vollenweider's criteria, speeded up the eutrophication process and stimulated the gradual self-decline of the entire ecosystem. The restoration of ecological balance in the surveyed

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ecosystem should rely on the seasonal nature of climatic and hydrological factors characteristic of the examined area, and should involve the re-introduction of the water body into the horizontal water circulation system.

Key words: lake, eutrophication, precipitation, biogenic elements, nitrogen, phosphorus.

PRZYCZYNY OBCIĄŻENIA WÓD ZEUTROFIZOWANEGO JEZIORA JAGIEŁEK ZWIĄZKAMI AZOTU I FOSFORU NA TLE WARUNKÓW METEOROLOGICZNYCH POJEZIERZA OLSZTYŃSKIEGO

Abstrakt

Przyczyny eutrofizacji jeziora Jagiełek, położonego ok. 6 km na południowy zachód od Olsztyna, badano w latach hydrologicznych 1998–2004. Zlewnia zbiornika jest położona w strefie wododziałowej rzek Łyny i Pasłęki. W zbiorniku stwierdzono zaawansowany stopień eutrofizacji wód. Pod względem ilości opadów, w analizowanym okresie wyróżniono 3 lata suche, 2 normalne i jeden rok wilgotny. Wystąpienie w krótkim okresie kilku lat suchych oraz wzrost parowania w wyniku podwyższenia temperatury powietrza (średnio o 0,5°C) spowodowały wypłycenie jeziora, z okresowym odsłanianiem osadów dennych w jego strefie przybrzeżnej. Skutkiem okresowego odsłaniania i zatapiania części dna zbiornika jest intensywna mineralizacja osadów dennych. Powoduje to wtórne zanieczyszczenie wód powierzchniowych składnikami mineralnymi, głównie związkami azotu i fosforu. W zbiorniku zlokalizowanym w strefie wododziałowej wykazano niskie i stabilne wartości przewodnictwa elektrolitycznego (średnio 113 $\mu S \cdot cm^{-1}$), niski odczyn wody (średnio pH 6,72), osiągający okresowo pH 4,70 oraz sezonową cykliczność stężeń biogenów (związków azotu i fosforu). Stosunkowo wysokie stężenia N-NO_3 (średnio 1,25 mg dm^{-3}) występowały w okresie zimowo-wiosennym, a niskie (średnio 0,18 $mg \cdot dm^{-3}$) w okresie letnio-jesiennym. Stężenia P-PO_4 wykazywały tendencję wzrastającą od średnio 0,26 $mg \cdot dm^{-3}$ wiosną do średnio 0,70 $mg \cdot dm^{-3}$ latem. Duże obciążenie wody substancjami biogennymi, przekraczające wielokrotnie dopuszczalne i niebezpieczne poziomy N i P, przyśpieszyło eutrofizację wody i spowodowało ewoluowanie całego ekosystemu w kierunku stopniowej samolikwidacji zbiornika. Odtworzenie równowagi ekologicznej w badanym ekosystemie, powinno opierać się na sezonowości zjawisk klimatycznych i hydrologicznych występujących w regionie przy ponownym włączeniu zbiornika w poziomy obieg wody.

Słowa kluczowe: jezioro, eutrofizacja, opady, biogeny, azot, fosfor.

INTRODUCTION

Every natural water body and its catchment area form a landscape system where water is the main means of transport and exchange of matter between ecosystems. The physical and geographical characteristics of the catchment area determine both the rate at which matter is transported to the water body as well as the volume of the accumulated substances. Situated at the lowest point in the surrounding area, a water body is the accumulation centre of energy and matter migrating from the catchment (WINTER 2001). Therefore, the catchment area plays a vital role in regulating the process of lake degradation (GLIŃSKA-LEWCZUK 2002, 2005., KOC et al. 1996, KOC, SZYMCZYK 2001).

The morphological parameters of a water body remain in a close relationship with the physical and geographical characteristics of its catchment area (BAJKIEWICZ-GRABOWSKA 1999, GLIŃSKA-LEWCZUK 2005), and they determine the intensity of biogeochemical changes taking place in this body of water (GLIŃSKA-LEWCZUK 2002). Subject to the individual susceptibility of a lake to external influences and to the supply of biogenic elements from the catchment area, clear changes in the physical and chemical properties of water are observed (BAJKIEWICZ-GRABOWSKA 1999, GLIŃSKA-LEWCZUK 2005). The inflow of excessive quantities of nutrients from the catchment into the water body leads to an ecological unbalance. The majority of Polish lakes, in particular water bodies with a small area of several hectares, are characterised by high water fertility which leads to their degradation, overgrowth and disappearance (JĘDRYKA, MACIEJEWSKI 2007). This process is visibly accelerated when the supply of groundwater to the water body is inhibited, a situation which is commonly noted in reclaimed areas. The change in the existing water relations, observed when a part of the catchment is excluded from the process of supplying matter to the water body and when water outflow is blocked, decreases the proportion of allochtonic substances in favour of autochtonic substances in the matter circulation cycle in an aquatic ecosystem.

As regards water bodies situated in a watershed zone, the amount and intensity of precipitation and meltwater input are important factors which determine the physical and chemical properties of water (WEGENER et al. 2007). Although precipitation contributes to surface water pollution (SAPEK 1998), it has a minor effect on water bodies in a watershed zone as regards their pH reaction and electrolytic conductivity which is marked by low ion concentration, in particular ions which are typical of the chemical denudation of the lithosphere, such as carbonates, calcium and others (KOC et al. 2003).

The objective of this study was to identify the factors and causes which have contributed to the strong degradation and the gradual decline of a small lake with the historical name of Jagiełek, situated in the watershed zone of the Łyna and Pasłęka rivers in the Olsztyn area.

MATERIALS AND METHODS

Research site. The topographic catchment of Lake Jagiełek covers an area of 210 hectares. It is situated within the administrative boundaries of the Stawiguda commune, around 6 km south-west of Olsztyn (Fig. 1). The catchment area is located in the watershed zone of the Łyna and Pasłęka

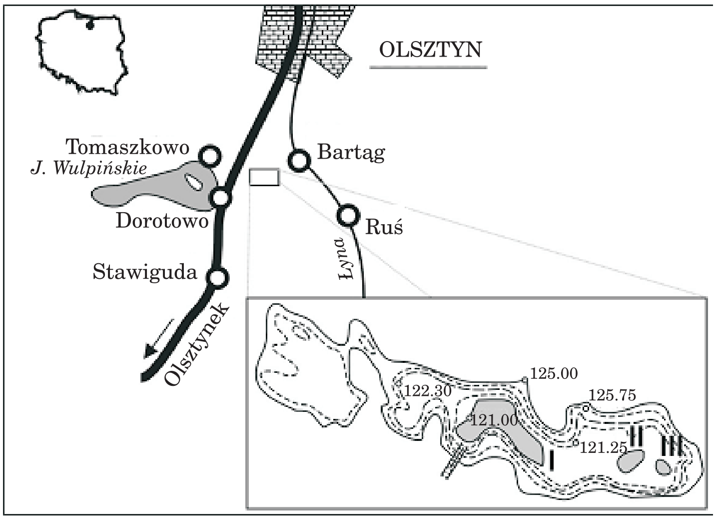

Fig. 1. Location and the contemporary (121,00 m a.s.l.) and former (125,00 m a.s.l.) reach of water table area of Jagiełek Lake

Rys. 1. Lokalizacja i zasięg obszarowy współczesnego (121,00 m n.p.m.) i dawnego jeziora Jagiełek (125,00 m n.p.m.)

rivers. It is an undulating moraine upland area situated at an altitude of 120 to 141 m above sea level. Soil in the catchment area consists of Quaternary deposits in the form of boulder clay with glacial and fluvioglacial sand and gravel interbedding. It comprises impermeable and weakly permeable deposits of boulder clay and slime with silty and loamy sand layers. Sand and gravel layers of glacial origin occur locally on the surface. The catchment comprises mostly soil of quality class V and VI, while class IV soil occupies only a small part of its area. The catchment area features a forest complex comprising mostly uneven-aged pure pine and pine-birch tree stands.

Jagiełek is a remnant of a postglacial lake with features characteristic of a ground moraine body of water. It presently consists of three small but strongly overgrown water bodies – the deepest points of the former postglacial lake (Fig. 2). The largest region occupies an area of 1.27 hectares and it is the only site where the surface water table is maintained throughout the year. The remaining two bodies of water, with an area of 0.24 and 0.09 hectares respectively, are periodically filled with water, mainly in the spring. The present water table level reaches 121 m above sea level on average, with annual amplitude of around 1.70 m. The water table was originally found at 125.00 m above sea level, indicating that the former water body had an area of 25.47 hectares. An analysis of Schroetter's general map of 1803 in the 1: 50 000 scale has shown that those water bodies had been connected in the early 19th century, and that the

Fig. 2. View on three overgrowing reservoirs of the Jagielek lake, aerial photo. September 2004

Rys. 2. Widok na zarastające akweny jeziora Jagiełek, zdjęcie lotnicze – wrzesień 2004

water table of a lake with the Prussian name of *Jagiellen See* was approximately 5.25 m higher than today (Fig. 3). In addition to a decline tendency observed in most natural water bodies, the decrease in the water table area and the lake's capacity has resulted mainly from reclama-

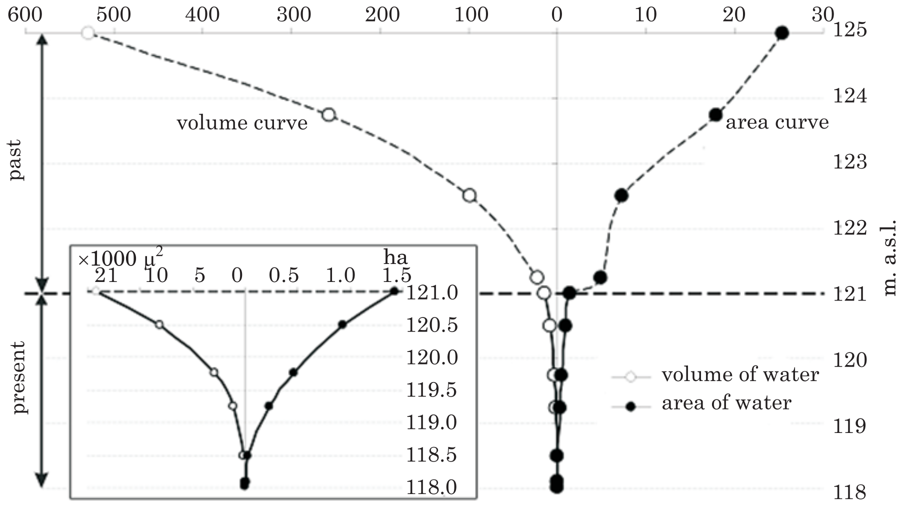

Fig. 3. Volume and area curves of Jagiełek Lake presenting maximal reach (in approximately 1800) and contemporary (2004) water table

Rys. 3. Krzywa powierzchni i pojemności jeziora Jagielek obrazująca maksymalny zasięg zbiornika (ok. 1800 r.) oraz współczesny (2004 r.)

tion works conducted between the two World Wars as well as in the 1960s.

Jagiełek was initially supplied with infiltration and ground water from the catchment with an area of 210 hectares. Water was flowing out of the lake via a canal on the southern side in the direction of Lake Wulpińskie. In the early 1960s, a drainage system was build in the western part of Jagiełek's catchment, but the lake was excluded from the drainage network. As a result, the groundwater level in the lake's vicinity was lowered by around 1 m. The above reduced the area of the groundwater source to 82.16 hectares. Jagiełek developed a quick and short-term response to intense supply of water (mostly meltwater) in the form of high water levels, long-term lowering of the water table which exposed bottom sediments in the summer and autumn low-flow periods. Jagiełek's catchment is a farming area, but the water body is surrounded by a young coniferous forest planted at the turn of the 1960s and 1970s.

Analysis methods. The study to determine the causes of eutrophication of Lake Jagiełek was conducted in Tomaszkowo near Olsztyn in the hydrological years 1998–2004. Water samples were taken once a month only from the largest water body (there is no access to the remaining two water bodies), in accordance with the generally applied methods (HERMANOWICZ et al. 1999). The following determinations were made: ammonium nitrogen ($N\text{-}NH_4$) – by colorimetry with Nassler's reagent, nitrate nitrogen ($N\text{-}NO_3$) – by colorimetry with phenoldisulfonic acid, nitrite nitrogen ($N\text{-}NO_2$) – by colorimetry with phenoldisulfonic acid. Mineral nitrogen was determined as the sum of the above nitrogen forms. Total phosphorus and phosphate concentrations were determined by colorimetry after mineralization with ammonium molybdate and tin chloride as the reducing agent.

Sampling was accompanied by observations of water level in Lake Jagiełek. Meteorological data were provided by from the meteorological station of the University of Warmia and Mazury in Olsztyn, situated at a distance of approximately 300 m from the lake. The mean total annual precipitation in the investigated period for the Olsztyn area was 570.5 mm (Fig. 4). According to KACZOROWSKA'S criterion (1962), the two years (1996 and 1997) preceding the investigated period were classified as normal years as regards precipitation amount, while the analysed period comprised 3 dry years (1999 – 497 mm, 2000 – 474 mm, 2003 – 478 mm), 2 normal years (1998 – 534 and 2001 – 591 mm) and one wet year (2004 – 696 mm). The average air temperature in the surveyed period was 7.8°C, marking an increase of 0.5°C from the long-term average for 1961–2004. Dry and warm years were predominant in the analysed six-year period.

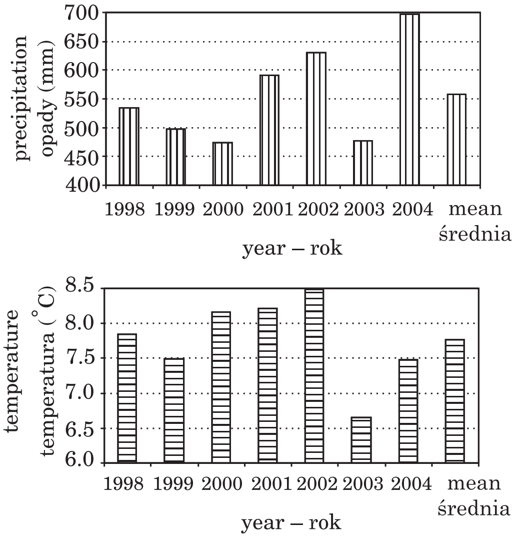

Fig. 4. Variability of precipitation sums in Tomaszkowo in hydrological years 1998–2004

Rys. 4. Zmienność opadów i temperatur w Tomaszkowie
w latach hydrologicznych 1998–2004

RESULTS AND DISCUSSION

The drainage reclamation works conducted in the catchment area of Jagiełek lake minimised the catchment's role as the main supplier of residual substances from farming production. Due to an estimated 40% reduction of the water body's alimentation area and the predominance (60%) of interior areas without an outflow, it should be assumed that the intensity of biogeochemical processes in this ecosystem relies mostly on autochtonic mineral and organic matter (Table 1). The quality of water in Lake Jagiełek is subject to seasonal variation, which is a characteristic feature of strongly eutrophic aquatic environments. The physical and chemical properties of water, presented in Table 1, are indicative of significant changes in the chemical composition of water in the body, mainly mineral forms of nitrogen and phosphorus and, in particular, nitrate nitrogen for which the coefficient of variation reached 245%.

The short-term migration of substances, which is also due to the water body's location in a watershed zone, results in stable and low electrolytic conductivity reaching 113 $\mu S \cdot cm^{-1}$ on average as well as periodically acidic pH of water (6.72 on average) which drops to 4.70.

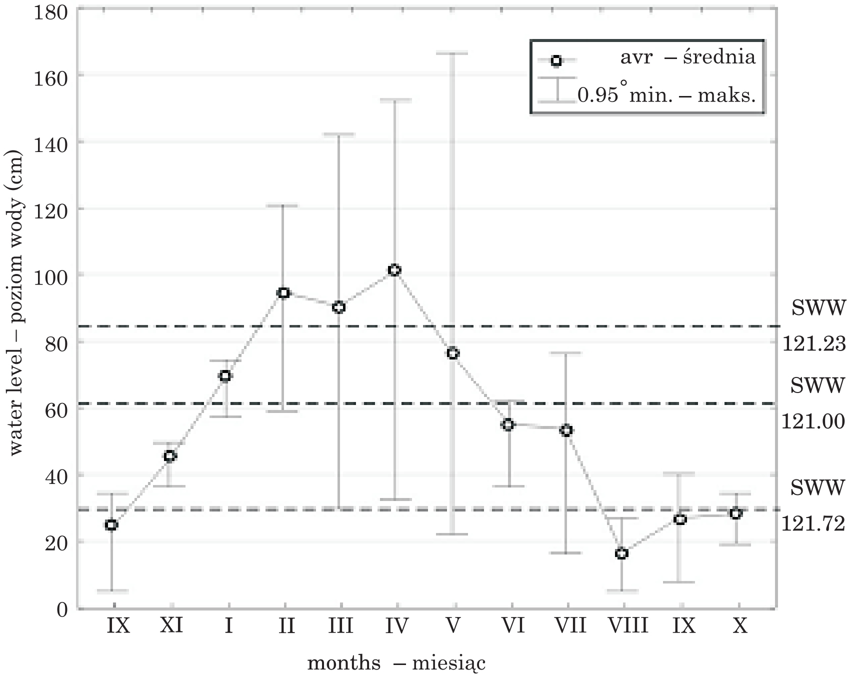

Fig. 5. Changes in water level in Jagiełek lake over the period of one hydrological year. Symbols of SWW, SSW, SNW denote limits of high, medium and low water

Rys. 5. Zmiany położenia lustra wody w jeziorze Jagiełek w ciągu roku hydrologicznego. Symbole SWW, SSW, SNW oznaczają granice stref stanów wody, odpowiednio: średnią wysoką wodę, średnią wodę i średnią niską wodę

Natural processes leading to the overgrowth and silting-up of the water body are caused by the closed cycle of water-contained matter due to the blockage of the surface outflow from the lake. In this environment, meteorological parameters which determine, among others, the circulation rate of water and water-contained matter play a very important role, as demonstrated by the water level amplitude which is 3.5 times higher (170 cm) than in most lakes of the region. The lowest water level was observed in 2003 (amplitude of only 29 cm) which was the driest and the coolest year, while the highest water level (amplitude of 137 cm) were recorded in 1998 which was marked by normal precipitation totals and temperatures approximating the long-term average. The absence of a significant rise in water levels in a wet year, preceded by a dry year, is indicative of a drastic drop in groundwater levels which were supplemented at the expense of lake filling. An analysis of the annual water levels shows two distinctive periods: a period marked by an abundance of water, observed between March and May, due to the melting of the snow and ice cover and soil thawing, and the summer period marked by low water levels (Fig. 5).

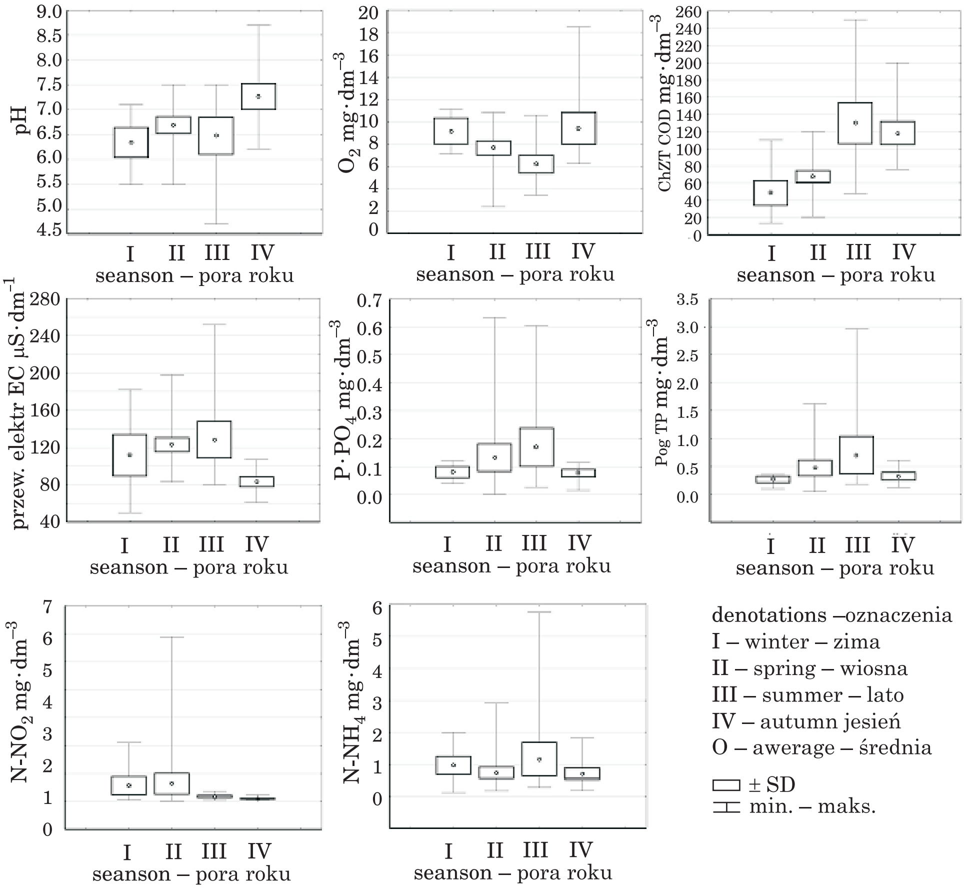

Fig. 6. Seasonal variability of physico-chemical parameters of water in Jagielek lake in the study period of 1998–2004

Rys. 6. Zróżnicowanie sezonowe właściwości fizykochemicznych wody jeziora Jagiełek w wieloleciu 1998–2004

In the spring period of high water, oxygen reserves are supplemented after the oxygen deficit in the winter. Yet both seasons have a significant impact on N-NO_3 concentrations. The highest levels (5.88 mg·dm^{-3}) of nitrate nitrogen are reported in the winter, probably due to a limited rate of phytosorption of nitrogen released in the process of biochemical change (Fig. 6). The lowest concentrations of this nitrate form were observed in the summer and autumn months – 0.18 and 0.10 mg·dm^{-3} respectively, during which substantial quantities of this component were absorbed by plants. Between 1998 and 2004, the N-NO_3 concentrations in the water of the investigated lake were similar to N-NH_4 concentration levels. In the discussed period of study, the concentration of ammonium nitrogen (N-NH_4) in water ranged from 0.11 mg·dm^{-3} in a normal year (2002) to 5.76 mg·dm^{-3} in a wet year (2004). The high N-NH_4 concentration in water in the wet year (autumn) resulted from organic matter mineralization in the summer, and was supported by relatively high temperatures, very low water levels over a period of several preceding years as well as higher precipitation totals which caused ammonium ions from decomposing sediments to be deposited in the water body, thus contributing to secondary contamination (Fig. 7).

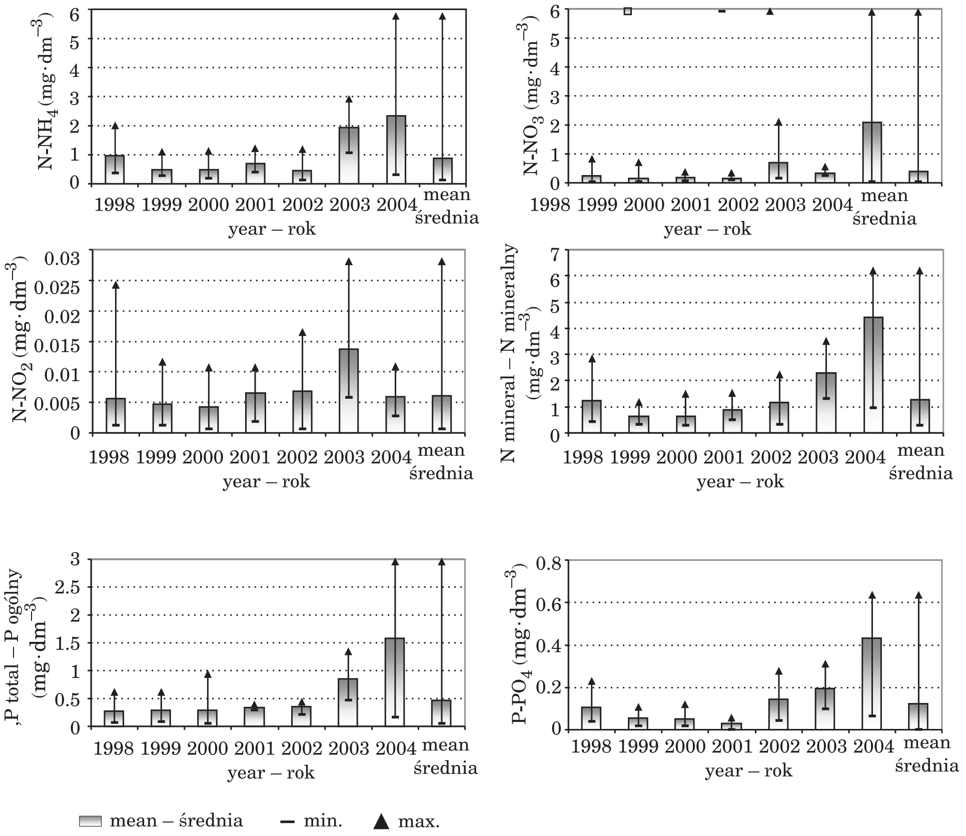

Fig. 7. Changes in mineral forms of nitrogen and phosphorus in Jagiełek Lake water in hydrological years 1998–2004

Rys 7. Zmienność stężenia mineralnych form azotu i fosforu w wodzie jeziora Jagiełek w latach hydrologicznych 1998–2004

From among the discussed nitrogen forms, nitrate nitrogen ($N\text{-}NO_2$) was marked by the smallest fluctuation in concentration levels (from 0.0006 to 0.0028 $mg \cdot dm^{-3}$). Changes in the concentration of nitrate nitrogen in surface layers could be due to the small area of the water body which is characterised by high sedimentation and a high content of anaerobic products of the sediment transformation process (Koc et al. 1996). Higher $N\text{-}NO_2$ concentrations in the lake were observed in the spring which could be due to a lower rate (at lower temperatures) of biochemical change of nitrogen and the extended duration of the first stage of nitrification.

The concentration of mineral nitrogen in Lake Jagiełek clearly indicates that this biogenic element posed the highest load on the investigated water body in the wet year (2004), preceded by drier years (Fig. 7). The above implies that the nitrogen accumulated in bottom sediments was released, leading to secondary contamination of surface waters, which was additionally aided by low water levels.

The high content of phosphorus compounds in shallow water bodies with a limited supply from the catchment is usually ascribed to sediment resuspension. An analysis of seasonal fluctuations in phosphorus concentration in water and hydrometeorological conditions in the investigated period supported this possibility.

The increase in total phosphorus concentrations (0.70 $mg \cdot dm^{-3}$) during low water periods in the summer was statistically significant in comparison with other periods due to the possibility of bottom sediment stim-

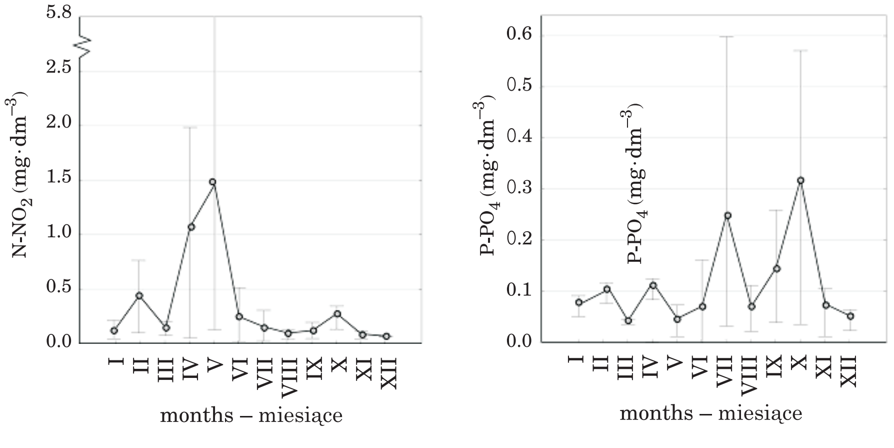

Fig. 8. Monthly changes in the concentrations of $N\text{-}NO_3$ and $P\text{-}PO_4$ in Jagiełek Lake water in a hydrological year from the period of 1998–2004. Vertical bars indicate ranges of minimal and maximal concentrations

Rys. 8 Zmiany stężeń $N\text{-}NO_3$ i $P\text{-}PO_4$ w wodzie jeziora Jagiełek w ciągu roku hydrologicznego na podstawie comiesięcznych wyników badań z okresu 1998–2004. Pionowe słupki oznaczają zakresy minimalnego i maksymalnego stężenia ulation by the wind. In the winter, when the insulating ice cover prevented water movement caused by wind, total phosphorus concentration reached 0.26 $mg \cdot dm^{-3}$. During that period, when the sorption of this element by plants was limited, phosphorus precipitation and its accumulation in bottom sediments increased. Yet in view of the significant rise in water levels in the spring, accompanied by higher phosphorus concentrations in water, it can be assumed that the dilution effect was supported by phosphorus desorption from sediments and the supply of phosphorus in melt and precipitation water. The nature of the annual changes in phosphorus concentration in Lake Jagiełek differed from the changes reported in respect in nitrate levels. While $N\text{-}NO_3$ concentration levels were high in the winter and spring, the concentration of $P\text{-}PO_4$ in Jagiełek was marked by a rising trend in the spring, summer and autumn (Fig. 8).

The dynamics of changes in concentration levels of total phosphorus and its soluble forms ($P\text{-}PO_4$) was influenced by hydrometeorological conditions in particular years of the experimental period. The dominance of dry years in the discussed period has led to a significant drop in groundwater levels which, in turn, intensified the release of nitrogen and phosphorus compounds from bottom sediments into the water. For this reason, the highest concentrations of both total phosphorus (2.96 $mg \cdot dm^{-3}$) and $P\text{-}PO_4$ (0.66 $mg \cdot dm^{-3}$) were noted in the last year (2004) of the investigated period (Fig. 7).

Table 1
Tabela 1

Assessment of the catchment of Jagiełek lake as a source of the matter to the lake
Ocena zlewni jeziora Jagiełek jako dostawcy materii do zbiornika przed melioracją i po melioracji

Property of the catchment Cecha zlewni	Unit Jednostka	Before reclamation Przed melioracjami	After exclusion from the drainage supply Po wyłączeniu z zasilania wodami drenarskimi
Powierzchnia zlewni jeziora	ha	210.00	82.16
Powierzchnia jeziora	ha	25.47	1.60
Ohle's index Wskaźnik Ohlego	%	8.4	51.3
Balance type of a lake Typ bilansowy jeziora	-	flown - through przepływowe	outflowless bezodpływowe
Share of depressions Obszary bezodpływowe	%	45	61
Land use Użytkowanie ziemi	-	arable lands and forest rolniczo-leśna	forest and arable land leśno-rolnicza

Regardless of the season, the water body was characterised by excessive unitary water load with biogenic elements whose concentrations were significantly above the allowable and dangerous levels of N and P according to Vollenweider's criteria (1968), a fact which stimulated the gradual self-decline of the ecosystem (Fig. 2). As shown on the example of the investigated body of water, the proper functioning of an aquatic ecosystem in a strongly drained environment of a watershed zone requires revitalisation despite the limited role played by the catchment as the source of biogenic elements. The restoration of ecological balance in the surveyed ecosystem should rely on the seasonal nature of climatic and hydrological factors characteristic of the examined area, and should involve the re-inclusion of the water body into the horizontal water circulation system. The progressive eutrophication of the lake could be inhibited by increasing landscape diversity and improving the water balance of the catchment.

Table 2
Tabela 2

Physico-chemical properties of water in Jagiełek Lake located near Tomaszkowo in the period of 1998–2004
Właściwości fizykochemiczne wody w jeziorze Jagiełek k. Tomaszkowa w latach 1998–2004

Parameter Wskaźnik	Average Średnia	Median Mediana	Range – Zakres		25% Quartile	75% Quartile	cv (%)
			minimum	maximum			
pH	6.72	6.88	4.70	8.70	6.22	7.30	12
Diss. oxygen O_2 mg·dm^{-3}	7.87	7.65	2.38	18.50	6.32	9.37	38
Temperature °C	13.01	13.90	0.50	29.00	5.50	18.70	65
COD, ChZT mg·dm^{-3}	90.63	80.00	13.50	250.00	53.00	104.00	59
SEC µS·cm^{-1}	112.89	106.00	50.00	252.00	90.00	133.00	35
N-NO_2 mg·dm^{-3}	0.006	0.004	0.001	0.028	0.003	0.007	97
N-NO_3 mg·dm^{-3}	0.39	0.13	0.03	5.88	0.08	0.32	245
N-NH_4 mg·dm^{-3}	0.87	0.51	0.11	5.76	0.35	1.08	112
N_{min} mg·dm^{-3}	1.27	0.92	0.28	6.19	0.49	1.40	105
P-PO_4 mg·dm^{-3}	0.12	0.07	0.00	0.63	0.04	0.12	121
TP Pog mg·dm^{-3}	0.47	0.30	0.05	2.96	0.17	0.45	122

CONCLUSIONS

1. The main cause of intensive geochemical changes leading to eutrophication, hypertrophy and disappearance of water bodies in a watershed zone are the adverse changes in water relations resulting from the lowering of groundwater levels and the exclusion of water bodies from the active system of horizontal water circulation.

2. The example of Lake Jagiełek situated in the Olsztyn Lakeland indicates that the dynamics of biochemical changes in the illustrated ecosystem is determined by meteorological conditions observed in the period of many years as well as in the course of a single year. Drainage reclamation works conducted in the catchment area of Lake Jagiełek inhibited groundwater supply, contributed to the shallowing of the lake and decreased its surface nearly 30-fold, as a result of which the water level became strongly dependent on meteorological conditions.

3. The investigated water body, located in a watershed zone, is marked by stable and low electrolytic conductivity of 113 $\mu S \cdot cm^{-1}$ on average as well as low water pH which periodically reaches 4.70. The above is indicative of short-term migration of precipitation water from the catchment.

4. In an annual cycle, the concentration levels of biogenic elements in Lake Jagiełek were characterised by seasonal fluctuations which differed for every analysed substance. While $N\text{-}NO_3$ concentrations were relatively high (1.25 $mg \cdot dm^{-3}$ on average) in the winter and spring and low in the summer and autumn ((0.18 $mg \cdot dm^{-3}$ on average), $P\text{-}PO_4$ concentrations were marked by a growing trend from 0.26 $mg \cdot dm^{-3}$ on average in the spring to 0.70 $mg \cdot dm^{-3}$ on average in the summer low-flow period.

5. The dynamics of changes in water resources in the investigated lake (amplitude of 170 cm) was due to significant differences in the supply of precipitation water which had a pronounced effect on biogeochemical processes in the ecosystem, mainly sedimentation and resuspension of mineral forms of phosphorus. The precipitation water deficit observed in 1998-2004 significantly lowered the water level in the lake which, consequently, led to organic matter mineralization in bottom sediments and to the release of nutrients into the water. The highest concentrations of mineral forms of nitrogen and phosphorus compounds in the lake were observed in the wet year preceded by two drier years.

6. A high water load with biogenic elements whose concentrations significantly exceeded the allowable and dangerous levels of N and P according to Vollenweider's criteria, speeded up the eutrophication process and stimulated the gradual self-decline of the entire ecosystem.

7. The restoration of ecological balance in the surveyed ecosystem should rely on the seasonal nature of climatic and hydrological factors characteristic of the examined area and should involve the re-introduction of the water body into the horizontal water circulation system.

REFERENCES

Bajkiewicz-Grabowska E. 1999. *Struktura fizyczno-geograficzna układu krajobrazowego zlewnia-jezioro i jej wpływ na tempo naturalnej eutrofizacji jezior.* W: *Funkcjonowanie i ochrona ekosystemów wodnych na obszarach chronionych.* Red. B. Zdanowki, M. Kamiński, A. Martyniak. Wyd. IRŚ, Olsztyn, ss. 99-112.

Glińska-Lewczuk K. 2002. *Wpływ zlewni rolniczej na funkcjonowanie systemu rzeczno-jeziornego na przykładzie zlewni strugi Wólki.* Cz. II. *Nawożenie w kształtowaniu środowiska.* Zesz. Probl. Post. Nauk Rol., 484: 163-174.

Glińska - Lewczuk K. 2005. *Effect of land use and lake presence on chemical diversity of the Łyna River system*. Pol. J.Environ. Stud., 15 (2): 256-269.

Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B., Zerbe J. 1999. *Fizyczno-chemiczne badanie wody i ścieków*. Arkady, Warszawa.

Jedryka E., Maciejewski S. 2007. *Rekultywacja Jeziora Zdworskiego.* Cz. I. *Charakterystyka stanu istniejącego i potrzeby działań renaturyzacyjnych.* Wiad. Mel i Łąk., 1 (412):18-22.

Kaczorowska Z. 1962. *Opady w Polsce w przekroju wieloletnim.* Prz. Geogr. 33, Inst Geograf., PAN.

Koc J., Glińska K., Nowicki Z., Rochwerger A., 1996, *Wpływ sposobu użytkowania terenu na jakość wód powierzchniowych na przykładzie wybranych zlewni Pojezierza Olsztyńskiego.* Inż. Środ. Ekspl. Obiektów Wojsk., WAT: 58-63.

Koc J., Glińska-Lewczuk K., Solarski K. 2003. *Opady atmosferyczne jako medium chemicznej denudacji gleb.* Zesz. Nauk. Post. Nauk Rol., 493: 159-166.

Koc J., Szymczyk S. 2001. *Wpływ użytkowania terenu na eutrofizację wód.* Mat. Konf. nt. *Agrarna oświata i nauka na początku trzeciego tysiąclecia.* T.1. Lwów, ss. 68-77.

Sapek A. 1998. *Udział azotu z opadu atmosferycznego w zanieczyszczeniu zasobów wody.* Zesz. Probl. Post. Rol., 458: 485-495.

Wagener T., Sivapalan M., Troch P., Woods R. 2007. *Catchment classification and hydrologic similarity.* Geography Compass, 1 (4): 901–931

Vollenweider R., 1968. *Scientific fundamentals of the eutrophication of lakes and flowing waters.* OECD, Paris, 139 pp.

Winter T. C. 2001.*The concept of hydrologic landscapes*. J. Am. Wat. Res. Assoc. 37 (2): 335-349.

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CHANGES IN THE CHEMICAL PROPERTIES OF WATER IN A SMALL POND IN VERTICAL PROFILES

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Abstract

The study to determine thermal-oxygen changes and chemical properties of water in a flow-through pond was conducted between April 2004 and March 2005 in three vertical profiles. The study involved the determination of electrolytic conductivity and pH reaction of water as well as the content of nitrate nitrogen and ammonium nitrogen, total phosphorus and sulphates. Thermal stratification was not observed in the investigated pond with the maximum depth of 2.45 m, and oxygen content was represented by a clinograde curve. Biogenic element concentrations in the pond were determined by depth in the vertical profile, and they were subject to seasonal variation. The highest concentrations of mineral substances in water were reported in the bottom layers of the pond. Although the investigated pond is a flow-through water body, it accumulates biogenic elements.

Key words: small pond, thermal profile, water temperature, oxygen profile, biogenic elements.

ZMIANY WŁAŚCIWOŚCI CHEMICZNYCH WODY OCZKA WODNEGO W PROFILACH PIONOWYCH

Abstrakt

Badania nad rozpoznaniem zmian termiczno-tlenowych i właściwościami chemicznymi wody przepływowego oczka wodnego prowadzono od kwietnia 2004 r. do marca 2005 r. w 3 profilach pionowych. Oznaczono przewodność elektrolityczną i odczyn wody oraz zawartość azotu azotanowego i amonowego, fosforu ogólnego i siarczanów. Stwierdzono, że w zbiorniku o głębokości maksymalnej 2,45 m nie przebiega stratyfikacja termiczna, a zawartość tlenu obrazuje krzywa w postaci klinogrady. Stężenia biogenów w wodzie oczka wodnego były uzależnione od głębokości w profilu pionowym i pory roku. Największa zasobność wody zbiornika w substancję mineralną występuje przy dnie. Pomimo przepływowego charakteru zbiornika następuje w nim akumulacja biogenów.

Słowa kluczowe: oczko wodne, profil termiczny, temperatura wody, profil tlenowy, biogeny.

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INTRODUCTION

Due to their small size, ponds generally form a homogeneous environment. Energy and mass circulation in small ponds usually involves the entire water volume which inhibits the development of relatively stable heterogenic systems. The rate and structure of energy and mass exchange between the pond and its surroundings are also determined by factors characteristic of those water bodies. This exchange takes place mostly between water and the atmosphere, while the horizontal exchange with the catchment area is restricted to the inflow of organic matter (DRWAL, LANGE 1985). Ponds are shallow bodies of water which are not marked by significant thermal stratification (BIEDKA, DZIENIS 2001). According to JĘDRCZAK (1992), small ponds are polymictic water bodies which are subject to multiple and full mixing of water in the vertical profile under the influence of wind, also during summer stagnation. In some periods (windless), the mixing process is limited which may lead to a periodical thermal and chemical water stratification.

The development of thermal-oxygen relations and other physical properties of water are investigated mostly in deeper water bodies. The obtained results are used to determine the degree to which lakes are susceptible to degradation. Similar observations carried out in small pond profiles support the investigation of changes in those processes and their causes, not only at various depths, but also in different seasons.

The objective of this study was to investigate thermal and oxygen changes taking place in a small mid-field pond at different times of the year, and to determine changes in the chemical properties of water occurring throughout the year in the vertical profiles of this pond. Since the investigated small pond is a flow-through water body, another aim of this study was to determine the chemical properties of water in the longitudinal profile.

MATERIALS AND METHODS

The study was conducted in a mid-field pond in Wrocikowo near Olsztyn which is supplied mostly by rain, ground and drain water. The investigated pond (covering an area of 0.67 hectares) is a flow-through water body: drain water from the catchment area is supplied to the pond by a drainage ditch (inflow), and water flowing out of the pond is collected also by a drainage ditch (outflow). The pond is characterised by the following morphometric features: maximum length – 127 m, maximum width – 65 m, shoreline length – 327 m, elongation – 1.89, maximum depth – 2.45 m, average depth – 1.11 m, average pond volume (at average water level) – 8701 m^3. For the purpose of determining the thermal-oxygen relations and the chemical properties of water throughout the year, the survey was carried out in April, July, September and November 2004 and in March 2005 (under the ice cover), and the obtained results were interpreted as spring, summer, autumn (September and November) and winter measurements, respectively. Three vertical profiles were identified: on the side of the inflow (L), at the deepest point of the pond (G) and on the side of the outflow (P). Water oxygen content and water temperature were measured with the use of an oxygen probe every 10 cm in every vertical profile of the pond. To determine water reaction and electrolytic conductivity, as well as the content of nitrate nitrogen and ammonium nitrogen, total phosphorus and sulphates in water, samples were taken at four depth levels in L and G profiles, i.e. from the surface (0.1 m), from the central part (0.7 m and 1.5 m) and from the near-bottom layer. In P profile, samples were taken at three depth levels, i.e. from the surface layer (0.1 m), from the central layer (1.0 m) and from the near-bottom layer. Water pH was determined by potentiometry, specific electrolytic conductivity – by conductometry, $N\text{-}NO_3$ – by colorimetry with phenoldisulfonic acid, $N\text{-}NH_4$ – by colorimetry with Nessler's reagent, total phosphorus – by colorimetry with ammonium molybdate and tin chloride, and SO_4^{-2} – by colorimetry with the use of the nephelometric method.

RESULTS

Water temperature in the pond was dependent on air temperature, and was marked by seasonal change (Fig. 1). Over the experimental period, water temperature ranged from +0.1°C in March 2005 to +18.7°C in July 2004. In the spring, the temperature of water in vertical profiles was 8.7°C to 10.6°C. Two layers were distinguished in the analysed vertical profiles: an upper layer (up to 1 m) – marked by a higher temperature and a lower layer - marked by a lower temperature. Similar results were reported by PASCHALSKI (1959) who investigated a three-fold shallower pond in the spring. In the water body analysed in this study, the temperature of the warmer upper layer was nearly uniform (10.6°C – 10.4°C) to a depth of 1 m. The above indicates that this layer is mixed under the influence of wind. The colder lower layer (10.4°C – 8.7°C) was characterized by a significant temperature drop and it was not affected by external factors to the extent reported in the upper layer.

Water temperature measurements pointed to the absence of thermal stratification in the pond during the summer (Fig. 1). The above is due mainly to the relatively low depth of the pond. According to DRWAL and

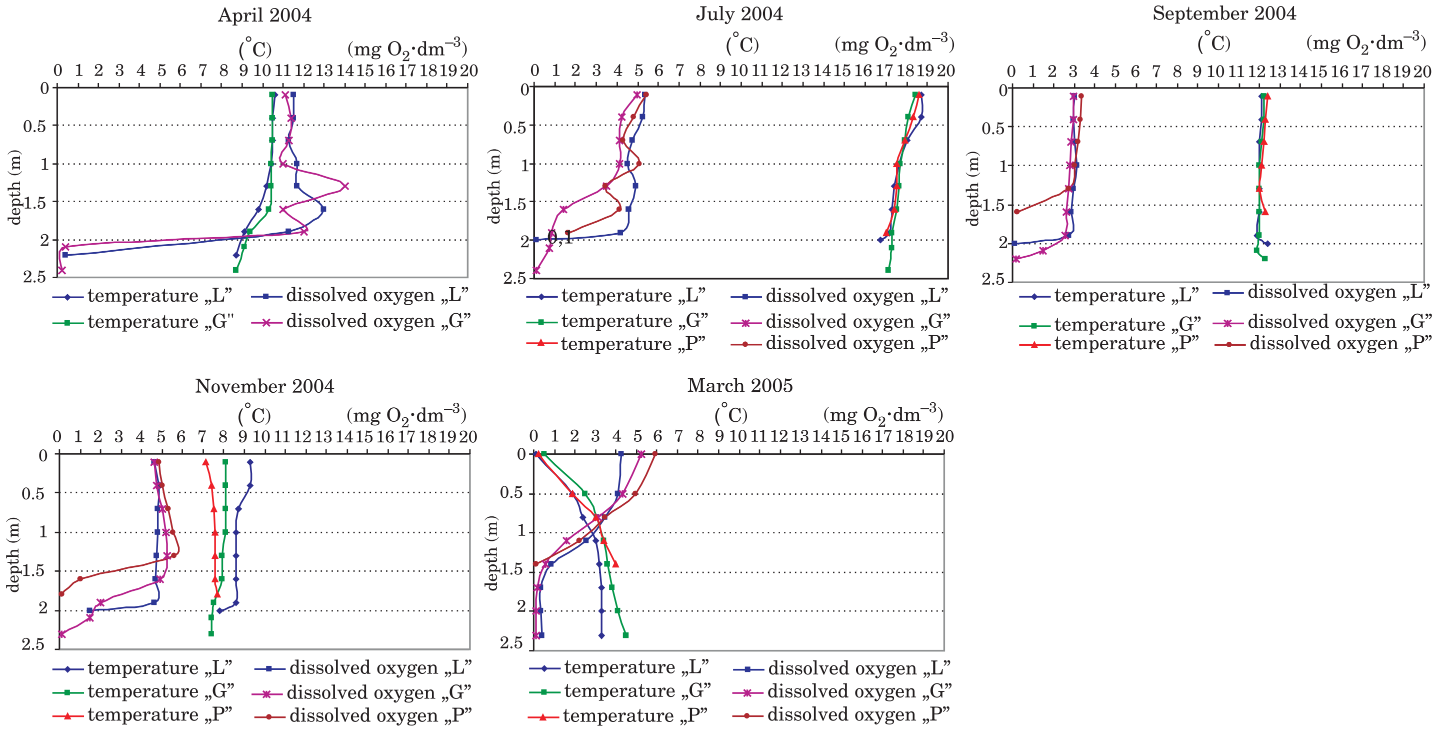

Fig. 1. Seasonal changes of the water temperature and dissolved oxygen in profiles L, G and P of the mid-field pond

LANGE (1985), a clearly pronounced thermal stratification with very high gradients (more than 5°C per meter of depth) may develop in the summer with anticyclonic weather and in the absence of wind. In the investigated pond, the temperature gradient in July reached only 2°C between the surface and the near-bottom layer. In September, water temperature was almost identical (around 2°C) in both the vertical and the horizontal section. The above findings are indicative of autumn circulation in the analysed pond. Dissolved oxygen content in three vertical sections was also most uniform (around 3 mg O_2 dm^{-3}) in the autumn (Fig. 1). In the period when the pond was covered with ice, a reverse thermal stratification was observed in the deepest layers (Fig. 1).

The dissolved oxygen content of water was subject to seasonal modification, reaching from 0.09 mg $O_2 \cdot dm^{-3}$ in July (near the bottom) to 14 mg $O_2 \cdot dm^{-3}$ in April. Positive heterograde oxygen curves were reported in L and G profiles. This could be due to a fast rate of photosynthesis under good trophic conditions and satisfactory light conditions. In July, a clinograde oxygen curve was observed at the deepest point of the pond (G profile) (dissolved oxygen content decreases progressively with depth), where oxygen concentration was lower than in the remaining profiles. In March 2005, when pond water was sampled from under the ice cover, clinograde oxygen curves were reported (Fig. 1). The above testifies to the process of mineralization in the pond, as supported by high values of specific electrolytic conductivity which is characteristic of this season (Fig. 2). This process was also responsible for lowering the pH of water (Fig. 2).

The presented oxygen profiles of the investigated pond (Fig. 1) point to favourable aerobic conditions in the spring, summer and in November. Throughout the entire investigated period (particularly in March 2005 – under the ice cover), an oxygen deficit was observed in near-bottom layers, which is a characteristic feature of stratified lakes.

During the study, the reaction of pond water ranged from pH 5.8 in the bottom layer (July) in L and G profiles to pH 8.05 in April (Fig. 2). Similar results were reported in other ponds (KOC et al. 2002, KOSTURKIEWICZ, FIEDLER 1995, SKWIERAWSKI, SZYPEREK 2002). A slightly acidic reaction was noted in the summer. In the summer, the progressive decrease in pH with depth could result from biological processes occurring in deeper layers of the pond. It should also be noted that the profiles on the side of the inflow (L) and the outflow (P) from the pond, the pH of water was slightly higher than that reported in the profile at the deepest point of the pond (Fig. 2). The higher pH of water and a higher oxygen content in shallower profiles testify to the influence of the littoral zone where photosynthesis takes place (CO_2 consumption leads to a higher pH and a higher oxygen content). Pond water under ice cover had a slightly alkaline reaction.

Throughout the investigated period, the electrolytic conductivity of pond water ranged from 440 $\mu S \cdot cm^{-1}$ (in September 2004, in the surface

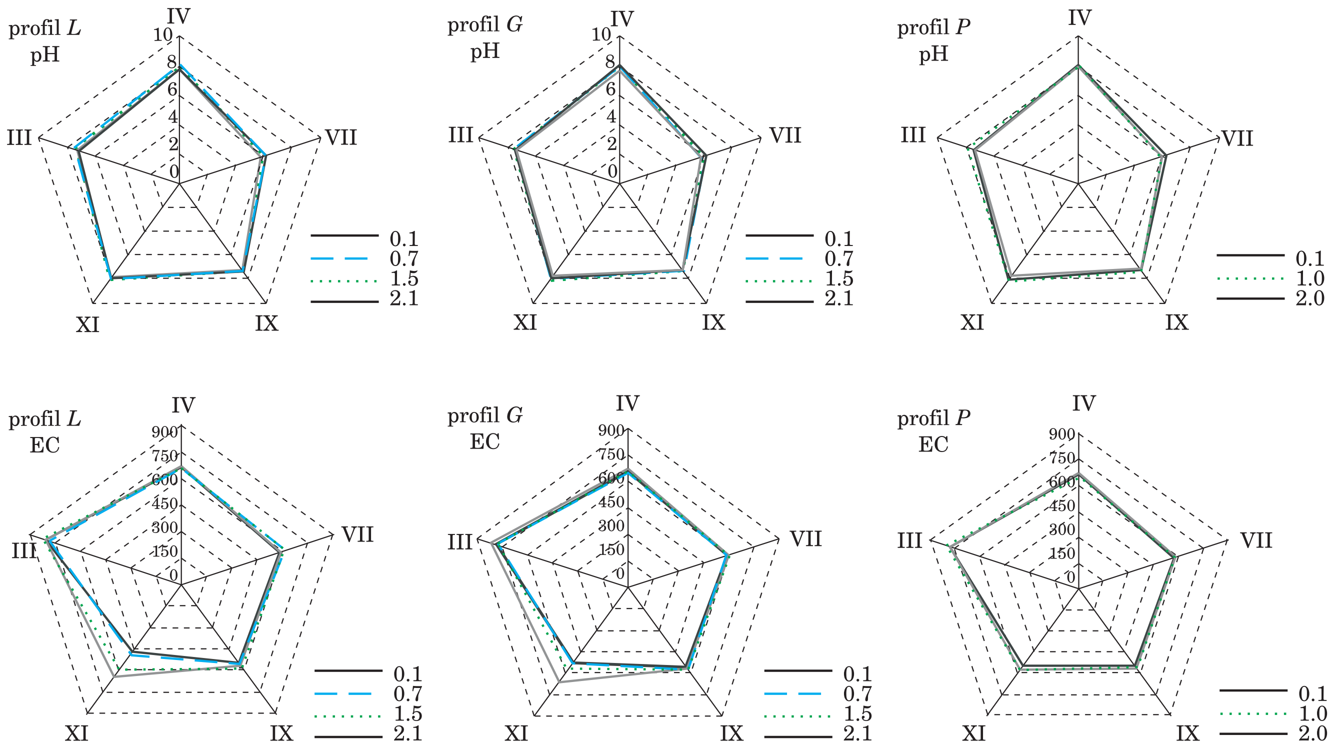

Fig. 2. Seasonal changes of the water reaction and electrolytic conductivity (EC)in profiles L, G and P of the mid-field pond

layer of L profile) to 813 $\mu S \cdot cm^{-1}$ (in March 2005, in G profile) – Fig. 2. The above values are higher than those reported in the lakes of the Masurian Lakeland by ZDANOWSKI and HUTOROWICZ (1994) and in other ponds investigated by KOC et al. (2002). The highest electrolytic conductivity in the examined pond was determined at the bottom (Fig. 2). The above indicates that the bottom layers are marked by higher abundance of mineral substances from the mineralization of organic matter contained in bottom sediments.

The content of nitrate nitrogen in pond water fluctuated throughout the year, reaching from 0.028 $mg \cdot dm^{-3}$ to 2.66 $mg \cdot dm^{-3}$ (Fig. 3). The highest nitrate nitrogen content was observed in April 2004 and March 2005. The increased $N\text{-}NO_3$ concentrations in the spring were most likely caused by significant quantities of nitrogen supplied to the pond with surface runoff from fertilised fields. Significant variations between the investigated profiles were not reported in July, September and November. In March, $N\text{-}NO_3$ concentration levels in pond water dropped significantly in deeper layers (Fig. 3). $N\text{-}NO_3$ concentration in the surface layer was twice that reported in the near-bottom layer, and a similar trend was observed in every profile. The above resulted from clear stratification during that period due to the formation of ice cover which prevented pond water from mixing. An oxygen deficit was also observed in the near-bottom layer (Fig. 1) which reduced nitrate nitrogen to ammonium nitrogen (Fig. 3).

Ammonium nitrogen concentration in the pond ranged from 0.011 $mg \cdot dm^{-3}$ to 1.029 $mg \cdot dm^{-3}$ (Fig. 3) and, similarly to nitrate nitrogen, it was marked by substantial fluctuation throughout the year. Yet the reported values were nearly twice lower than those determined by KOC et al. (2005) in water bodies supplied with drain water in the Sępopol Plain. It could be concluded that the average concentration of ammonium nitrogen in the near-bottom layer of the investigated pond was two-fold higher than in the surface layer (Fig. 3), and this dependency was not observed only in April. The highest variations in ammonium nitrogen concentration levels between the surface and the bottom layers of pond water were found in P profile, smaller differences were reported at the deepest point of the pond (G) and the least significant variations – in L profile.

The highest concentration of total phosphorus was observed at the deepest point of the pond (G) – 0.509 $mg \cdot dm^{-3}$, followed by the profile on the side of the inflow (L) – 0.493 $mg \cdot dm^{-3}$, while the lowest concentration was reported in the profile on the side of the drainage ditch outflow (P) – 0.466 $mg \cdot dm^{-3}$ (Fig. 4). High phosphorus concentrations were determined in July, they were nearly twice lower in November and more than three times lower in March. Similar changes in phosphorus concentration levels throughout the year were observed by KOC et al. (1997) who reported the lowest total P concentrations in the winter. In March, the total phosphorus concentration in the investigated pond was nearly identical in G and P vertical profiles. In general, higher total P concentration levels were found in the bottom layers than the in the surface layers of the pond.

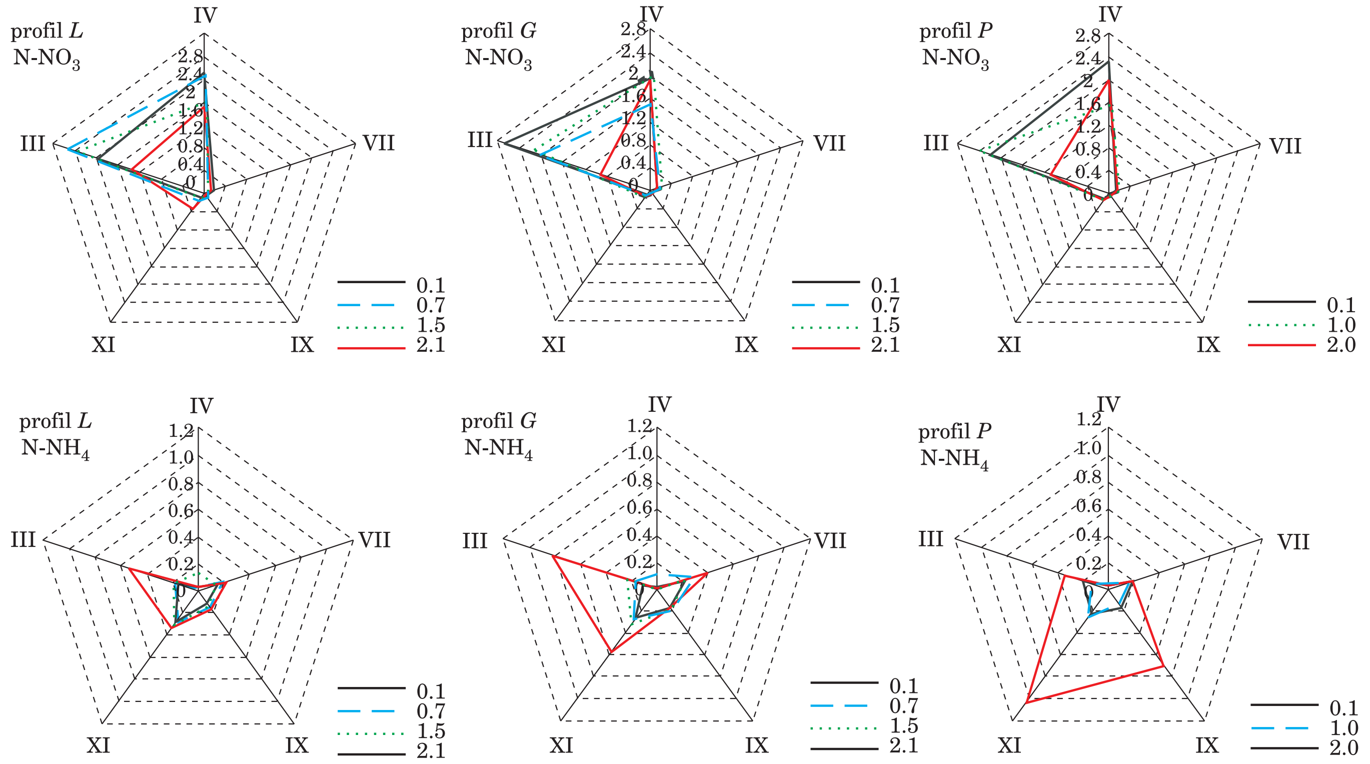

Fig. 3. Seasonal changes of the content of nitrate nitrogen and ammonium nitrogen in the water of mid-field pond in profiles L, G and P

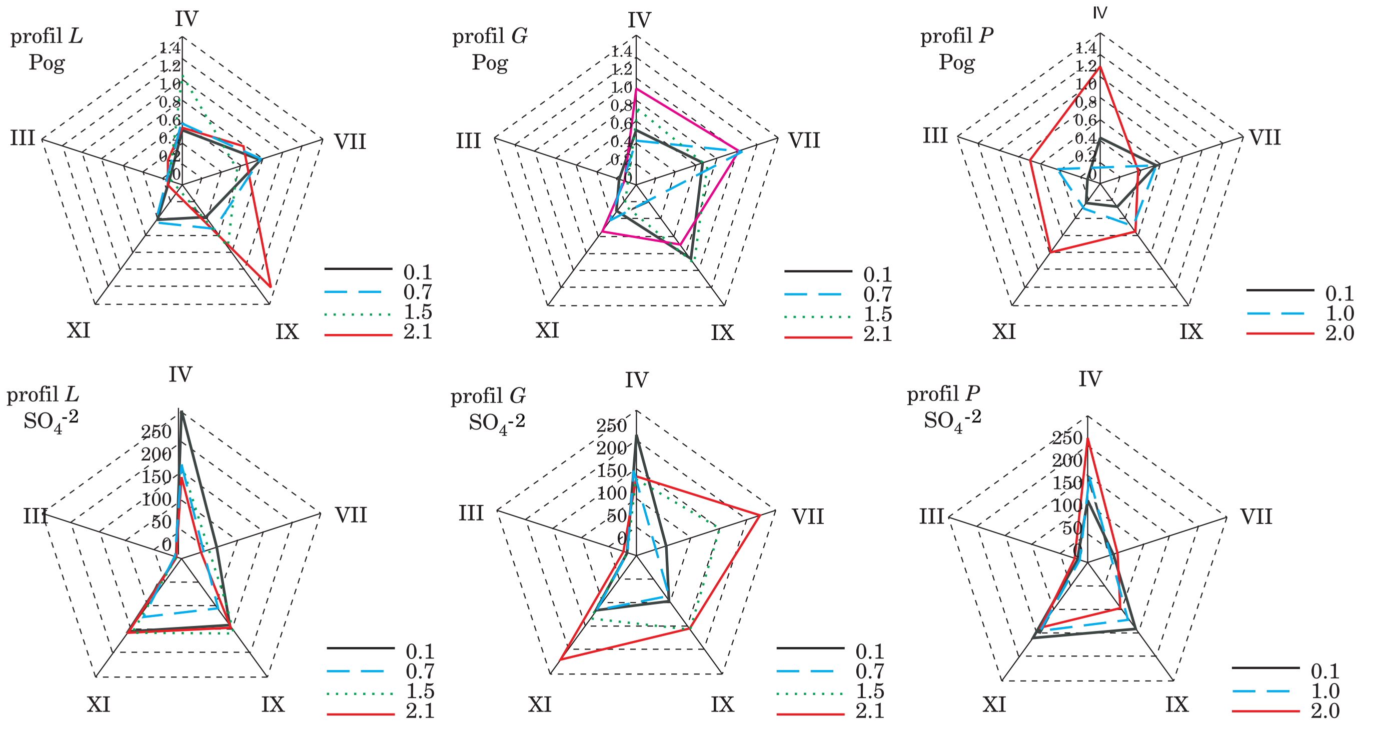

Fig. 4. Seasonal changes of the content of total phosphorus (Pog) and sulphates (SO_4^{-2}) in the water of mid-field pond in profiles L, G and P

Sulphate concentration in pond water ranged from 9.2 mg·dm^{-3} to 250.0 mg·dm^{-3} (Fig. 4). Higher SO_4^{-2} concentrations were reported in the summer, while the lowest – in the winter. The above was due to anaerobic conditions which led to a significant reduction in sulphate concentration levels. In the remaining investigated periods, sulphate concentration in pond water was nearly ten times higher than in March 2005. A significant increase in sulphate concentration levels was observed in the near-bottom layer at the deepest point of the pond in July, September and November (Fig. 4). A similar trend was reported in P profile in April. In the same profile, sulphate concentration dropped progressively at greater depths in September and November.

In view of the above, it can be concluded that the concentration of mineral components in flow-through ponds varies in the longitudinal profile. The content of nitrate nitrogen decreased in the direction from L profile to P profile, while the highest concentrations of total phosphorus and sulphates were observed at the deepest point of the pond (G). Higher nitrate concentrations in L profile than in P profile are most probably due to the supply of significant quantities of nitrate nitrogen via the drainage ditch network. The high content of total phosphorus and sulphates at the deepest point of the pond (G) testifies to the accumulation of those compounds in bottom sediments, followed by their transport to water. Although the investigated pond is a flow-through water body, it accumulates some of the compounds supplied from the catchment area.

CONCLUSIONS

1. The investigated pond is a relatively shallow water body (2.45 m), which explains the absence of thermal stratification with a simultaneous clinograde distribution of dissolved oxygen.

2. Biogenic element concentrations in pond water are determined by depth in the vertical profile. The highest concentrations of mineral substances were observed in the bottom layers, as indicated by the highest electrolytic conductivity values and higher $N\text{-}NH_4$, total phosphorus and sulphate concentrations.

3. Biogenic element concentrations are marked by seasonal fluctuation regardless of the place and depth of water sampling. Nitrate nitrogen concentrations are higher in the spring, higher levels of total phosphorus are observed in the summer, while the autumn is marked by higher ammonium nitrate concentrations.

4. The average concentration of biogenic elements is determined by the place of water sampling in the pond's longitudinal profile. Although the investigated pond is a flow-through water body, it accumulates bio-

genic elements whose concentration in water decreases in the direction from the ditch supplying water to the pond (inflow) to that collecting water from the pond (outflow).

REFERENCES

BIEDKA P., DZIENIS L. 2001. *Zmienność wybranych parametrów fizyczno-chemicznych wód powierzchniowych w profilu pionowym, na przykładzie wybranych jezior Pojezierza Suwalsko-Augustowskiego*. Zesz. Nauk. Politechniki Białostockiej, 142 (15): 57-65.

DRWAL J., LANGE W. 1985. *Niektóre limnologiczne odrębności oczek*. Zesz. Nauk. Wydz. Biol. Geogr. i Oceanogr. UG, 14: 69-82.

JĘDRCZAK A. 1992. *Skład chemiczny wód Pojezierza Antropogenicznego w Łuku Mużakowskim*. Wyd. WSI w Zielonej Górze, 54: 139.

KOC J., CYMES I., SZYPEREK U. 2005. *Możliwości wykorzystania wód w zlewni rolniczej do pojenia bydła.* J. Elementol., 10(2): 341-348.

KOC J., PROCYK Z., SZYMCZYK S. 1997. *Czynniki kształtujące jakość wód powierzchniowych obszarów wiejskich.* W: *Woda jako czynnik warunkujący wielofunkcyjny i zrównoważony rozwój wsi i rolnictwa.* Konf. Nauk.-Tech. PHARE-FAPA-IMUZ AR w Szczecinie, Falenty 1997.

KOC J., SKWIERAWSKI A., CYMES I., SZYPEREK U. 2002. *Znaczenie ochrony małych zbiorników wodnych w krajobrazie przyrodniczym*. Wiad. Mel. Łąk., 45 (2): 64-68.

KOSTURKIEWICZ A., FIEDLER M. 1995. *Oczka wodne w eksploatacji systemów drenarskich na terenach bogato urzeźbionych*. Zesz. Nauk. AR we Wrocławiu, 266, (8): 191-199.

PASCHALSKI J. 1959. *Obserwacje warunków środowiskowych drobnych zbiorników wodnych okolic Warszawy*. Ekol. Pol., ser. A, 7 (1): 1-20.

SKWIERAWSKI A., SZYPEREK U. 2002. *Wpływ rolnictwa na jakość wody w małych zbiornikach wodnych Pojezierza Mazurskiego*. Fragm. Agron. 19 (2): 236-243.

ZDANOWSKI B., HUTOROWICZ A. 1994. *Sainity and trophy of great masurian lakes (Masurian Lakeland, Poland)*. Ekol. Pol., 42 (3-4): 317-331.

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