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This volume contains a part of proceedings from the Second National Conference – *Wetland and Freshwater Ecosystems* held in Augustow, Poland in 18-20 July 2009. Proceedings of the First Conference in Bialowieza, in 2006 were published in special volumes of the Polish Journal of Environmental Studies.

The Conference on wetlands and freshwaters in 2009 with ca 80 participants was organized by the University of Bialystok, Institute of Biology and the Bialystok Technical University, Institute of Environmental Engineering and Protection under the auspices of the Rectors of University of Bialystok and Bialystok Technical University. The Conference took place nearby the border of Biale Lake on the Augustow Canal and very close to Rospuda River Valley, in Poland. The papers were prepared on the basis of oral or poster presentations during conference including results of group and individual discussions.

Much thanks for Prof. dr hab.inż.B.Wiśniowska-Kielian from the Agricultural University in Krakow for Her intensive editor work and Editors of *the Ecological Chemistry and Engineering* for Their help in papers preparation for the print.

Sponsors of conference were: HACH LANGE, MERCK, OLYMPUS, KAWASKA, OMC ENVAG, Kompania Piwowarska and media sponsor LAB.

Conference organizers
Professor Andrzej S. Górniak
Professor Józefa Wiater

Wojciech DĄBROWSKI¹

EFFECTIVENESS OF CONSTRUCTED WETLANDS FOR DAIRY WASTEWATER TREATMENT

EFEKTYWNOŚĆ ZŁÓŻ HYDROFITOWYCH W OCZYSZCZANIU ŚCIEKÓW MLECZARSKICH

Abstract: There are 9 dairy facilities having their own wastewater treatment plants in Podlasie province. In majority, they were built in 70's of the 20th century, when "Promlecz" technology based on high and low-loaded sludge activated chambers dominated. According to data from 2008, the amount of disposed wastewaters is from 470 to 5200 m³ · d⁻¹, at personal equivalent (P.E.) from 7130 to 277 000. Most of wastewater treatment plants requires to be modernized due to their poor technical status along with the increase of production, which is associated with the quantity of generated wastewaters, sludge, and reject water that should be processed. In the case of small treatment plants, the constructed wetland method may be an alternative for advanced and expensive technologies that are usually incorporated during modernization. Vertical and horizontal-flow wetlands can successfully work as a second stage of dairy wastewater purification after their preliminary mechanical and biological treatment. The study was carried out on a base of existing installation designed by the author and working in dairy wastewater treatment plant in Wysokie Mazowieckie. Studies were concentrated upon applying the hybrid system consisting of vertical-flow constructed wetland (VF-CW) and horizontal-flow constructed wetland (HF-CW). Wastewater after de-phosphatation and high-loaded sludge activated chamber were subjected to purification.

Mean pollution concentrations in dairy wastewater taken to the researches were: BOD₅ (234.1 mg O₂ · dm⁻³), COD (332.8 mg O₂ · dm⁻³), Kjeldahl's nitrogen (25.9 mg N_{TKN} · dm⁻³), ammonium nitrogen (13.9 mg N · dm⁻³), total phosphorus (10.9 mg P_T · dm⁻³). BOD₅ removal efficiency was 84.8 %, Kjeldahl's nitrogen 81.0 %, ammonium nitrogen 91.0 %, and total phosphorus 39 %, on average. The study confirmed the usefulness of constructed wetland method applied after mechanical and biological stages at dairy wastewater treatment plants.

Keywords: constructed wetlands, dairy wastewater, nutrients

The agricultural and food industries, namely dairy companies, dominate in north-eastern Poland. There are 9 dairy facilities having their own wastewater treatment plants in Podlasie province. In practice, all the objects have to be modernized due to increasing wastewaters and reject water loads generated during sludge processing. The reject water, that are characterized by considerable quantities of ammonia nitrogen

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content in relation to raw wastewater, make problems with a stable and effective work of the treatment plant. They are usually returned at the beginning of purification process. Among objects listed in Table 1, only two used a technology for efficient removal of carbon, nitrogen, and phosphorus compounds. The remaining ones apply “Promlecz” technology known since the beginning of 70’s of the 20th century. The author proposed to apply constructed wetland systems to purify the dairy wastewater after preliminary mechanical and biological processing. According to up-to-date research and literature references, the hybrid systems (H-CW) appeared to work most efficiently. The hybrid system consists of two beds: vertical-flow and horizontal-flow of wastewaters. In these systems, the horizontal-flow constructed wetland (HF-CW) provides with the effective removal of organic matter, total suspension, and may create a convenient condition for denitrification processes. Vertical-flow constructed wetland (VF-CW) makes possible the easier nitrification processes to occur [1, 2]. Both types are characterized by different working parameters. The VF-CW’s work in cycles, while HF-CW’s continuously. Their application is recognized and described in literature. The constructed wetland systems can be applied for sewage treatment from households, some industries, rain waters, or leachates from waste landfills. They are broadly used at dairy farms, while there is no detailed recommendations referring to applications at dairy wastewater treatment plants.

Here performed study aimed at evaluating the usefulness of constructed wetland technology at dairy wastewater treatment plant. Table 1 presents a general list of parameters at dairy wastewater treatment plants analyzed by the author in a view of the application of constructed wetland system. It also contains principal parameters such as generated wastewater amounts, mean BOD₅, or personal equivalent. Data were collected in 2008.

Table 1

Basic characteristic of dairy wastewater plants in Podlasie province

Plant	Sewage quantity [m ³ · d ⁻¹]	Average BOD ₅ [mg O ₂ · dm ⁻³]	P.E. [-]	Sludge productions [Mg d.m. · yr ⁻¹]
Wysokie Mazowieckie	5 200	3 200	277 000	2 300
Bielsk Podlaski	560	1 050	9 800	95
Grajewo	2 100	1 180	41 300	400
Kolno	1 060	1 800	31 800	224
Zambrow	1 200	850	17 000	108
Sejny	470	910	7 130	36
Monki	600	1 500	15 000	90
Piatnica	1 300	1 620	35 100	250

Taking into account the personal equivalent at particular dairy wastewater purification plants, the constructed wetland systems may be used in the smallest objects, ie in Bielsk Podlaski, Sejny or Monki. In other objects, they can be applied to purify the separated wastewater stream, eg reject water from sewage sludge processing. The main

aim of the researches was to check the possibility of constructed wetlands treating dairy wastewater.

Material and methods

The paper presents results from study upon the installation designed by the author and built at the dairy wastewater treatment plant in Wysokie Mazowieckie. The system consists of the retention reservoir, vertical-flow constructed wetland, intermediate retention reservoir, and horizontal-flow constructed wetland. The vertical wetland was designed according to Brix and Arias [3] and Cooper [4]. It was of 5 m^2 area and 1.0 m of filling depth, while horizontal wetland (5 m^2 area) had 0.65 m deep filling. Both wetlands were grown with specially prepared three-year-old *Phragmites australis* L. seedlings. The dairy wastewaters were preliminarily purified in mechanical system (bars and screen). Then they were supplied to de-phosphatation chamber and low-loaded sludge activated chamber. From there, pumps transport initially purified dairy wastewaters to the retention reservoir of the study installation. Figure 1 presents the scheme of study installation along with the photo taken in spring 2009. Study was carried out in September 2008, and it included 20 series of analyses of wastewaters delivered to vertical and horizontal wetlands, as well as wastewaters flowing out after the purification processes. The vertical-flow constructed wetland worked in cycles with hydraulic load of $0.05 \text{ m} \cdot \text{d}^{-1}$. The horizontal-flow constructed wetland worked

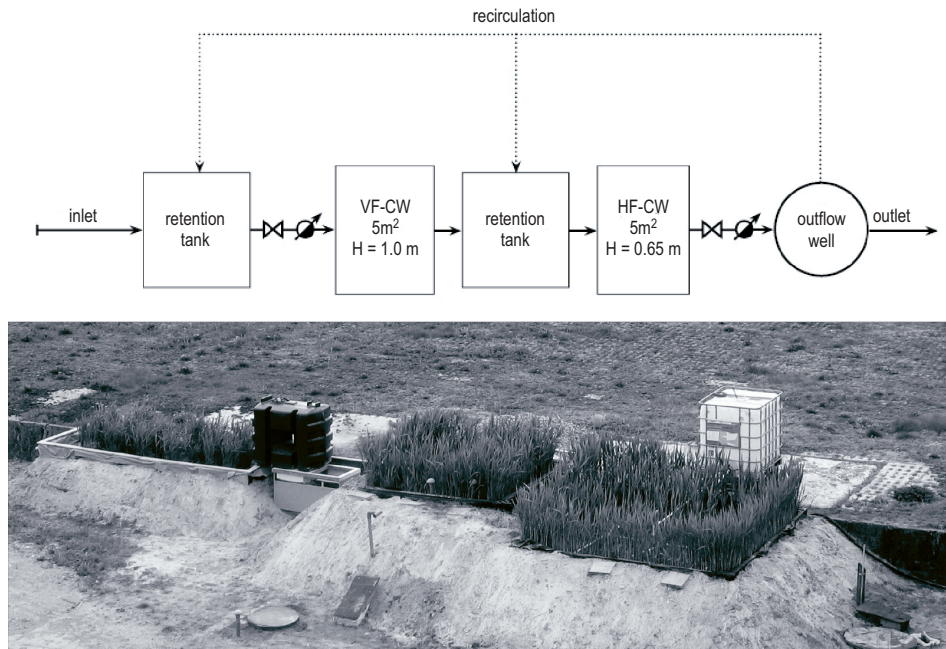


Fig. 1. Flow diagram of the research installation

continuously and was supplied from the intermediate retention reservoir after the vertical-flow part. Analyses included principal indices (BOD₅, COD, TKN-N, NH₄-N, NO₃-N, total P) of contamination set for dairy wastewater treatment plant in Wysokie Mazowieckie. Permissible values for contaminants disposed from the dairy wastewater treatment plant are presented in Table 2 [5, 6].

The analyses were performed in laboratory of Department of Technology in Engineering and Environmental Protection, Technical University in Białystok. All determinations were performed in accordance with Polish Norms.

Results and discussion

Results achieved during the study, after statistical processing, were presented in Table 2.

The BOD₅ value in wastewaters supplied to the vertical-flow constructed wetland was from 228 to 240 mg O₂ · dm⁻³. The average BOD₅ value was at the level of 234.1 mg O₂ · dm⁻³, which at the hydraulic load of 0.05 m · d⁻¹ resulted in load index 23.4 g BOD₅ · m⁻². Mean value of BOD₅ at the outflow from the vertical-flow wetland amounted to 86.1 mg O₂ · dm⁻³, while at the outflow from the hybrid system 35.4 mg O₂ · dm⁻³. The total efficiency of the hybrid system was calculated on a base of mean values at the inflow to the vertical-flow and outflow from the horizontal-flow constructed wetland. In the case of BOD₅, it was 84.8 %, whereas for COD – 85.3 %. The efficiency of Kjeldahl's nitrogen removal was 81 %, while ammonia nitrogen 91 %. High level of Kjeldahl's and ammonium nitrogen removal resulted mainly from the vertical-flow constructed wetland work, because it operates under aerobic conditions and good aeration of a bedding is a result of a cyclic wastewater flow and passive aeration of the bedding by drainage and ventilation systems. Nitrification processes occur in that wetland. Achieved results confirm those from studies upon household and industrial sewage with composition similar to that of dairy wastewaters (eg from dairy farms) conducted in Germany, Ireland and Japan [7–10]. The vertical-flow constructed wetland made possible to perform the denitrification process, which results from different flow characteristics and opportunities to maintain under-oxygenated conditions. It is possible due to the height of the bed filling with wastewater, which is regulated at the outflow of the installation. The nitrate nitrogen content became lower from 8.3 after vertical to 0.8 mg NO₃-N · dm⁻³ after horizontal-flow constructed wetland. The efficiency of the hybrid system for purification of dairy wastewaters was similar to values characteristic for household sewage purified using the same systems [11].

In the case of horizontal-flow constructed wetland, the load of pollution calculated on a base of mean BOD value in wastewater after the vertical-flow part was 8.6 g BOD · m⁻² · d⁻¹. The efficiency of organic substance removal was 14.9 g BOD₅ · m⁻² daily for vertical and 5.1 g BOD₅ · m⁻² daily for horizontal-flow constructed wetland, while about 20 g BOD₅ · m⁻² daily for the whole system. Phosphorus removal efficiency was low amounting to 39 % for the whole system, on average. The phosphorus content at the outflow from the study installation was 6.6 mg P · dm⁻³ at permissible value for dairy wastewater treatment plant in Wysokie Mazowieckie 1.5 mg

Table 2

Effectiveness of Hybrid Constructed Wetland for dairy wastewater treatment

Parameter	BOD ₅	COD	TKN-N	NH ₄ -N	NO ₃ -N	Total P
	[mg O ₂ · dm ⁻³]					
Inlet to VF-CW						
Minimum	228.0	310.0	22.0	9.1	0.10	9.2
Maximum	240.0	380.0	30.0	20.3	0.40	16.3
Mean	234.1	332.8	25.9	13.9	0.24	10.9
Median	233.5	320.0	25.5	13.1	0.20	10.3
Standard deviation	4.6	28.1	2.7	4.1	0.12	2.2
Outlet from VF-CW						
Minimum	79.0	90.0	7.0	5.1	6.30	6.2
Maximum	96.0	112.0	12.8	8.2	11.20	12.3
Mean	86.1	99.7	10.4	6.7	8.30	8.5
Median	85.5	99.5	10.1	6.6	8.20	8.6
Standard deviation	5.9	7.1	2.3	1.2	1.60	1.9
Outlet from Hybrid system VF-HF						
Minimum	28.0	39.0	4.0	0.9	0.2	4.2
Maximum	45.0	56.0	5.9	1.6	1.6	8.4
Mean	35.4	49.0	4.8	1.3	0.8	6.6
Median	34.5	48.6	5.0	1.2	0.7	6.5
Standard deviation	6.8	4.9	0.7	0.3	0.5	1.7
Limits for dairy wastewater after treatment in Mlekovića W.W.T.P.						
Total effectiveness of Hybrid Constructed Wetland [%]	84.8	85.3	81	91	—	39

$\text{P} \cdot \text{dm}^{-3}$. Constructed wetlands are not adapted to intensive removal of phosphorus. In order to improve the efficiency, a special filling in a form of lime gravel or separate filters should be applied [12].

Conclusions

1. The constructed wetlands can be used as the 2nd or 3rd level of dairy wastewater treatment.

2. Vertical-flow constructed wetlands provide with efficient nitrification, while horizontal-flow constructed wetlands make possible to perform the denitrification process.

3. Due to low efficiency of phosphorus removal in hybrid system and quality requirements for purified wastewaters, it is necessary to apply additional elements or special filling helping with phosphorus removal.

Acknowledgments

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References

- [1] Gajewska M., Tuszyńska A. and Obarska-Pempkowiak H.: Polish J. Environ. Stud. 2004, **13**, 149–153.
- [2] Dąbrowski W.: [in:] 7th International Conference Environmental Engineering, May 22–23, 2008, Vilnius, Lithuania 2008, 121–125.
- [3] Brix H. and Arias C.A.: Ecol. Eng. 2005, **25**, 491–500.
- [4] Cooper P.: [in:] International Seminar on the use of Aquatic macrophytes for wastewater treatment in constructed wetlands, May 8–10, 2003, Lisbon, Portugal 2003, 195–217.
- [5] Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006 r. w sprawie warunków jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego. DzU 2006, nr 137, poz. 984.
- [6] Pozwolenie zintegrowane dla Spółdzielni Mleczarskiej Mlekovita w Wysokim Mazowieckiem. Firma EKOM, D. Boruszko, W. Dąbrowski and L. Magrel, Białystok 2005, 107–120.
- [7] Healy M.G., Rodgers M. and Mulqueen J.: Bioresource Technol. 2007, **98**, 2268–2281.
- [8] Kern J.: Seasonal efficiency of a constructed wetland for treating dairy farm wastewater, [in:] Constructed Wetlands for Wastewater Treatment in Cold Climates. U. Mander and P. Jenssen (eds.), WIT Press, Southampton, UK 2003, 197–214.
- [9] Nagasawa T., Inoue T., Kato K., Iiegutsu H., Koba T., Miyaji N., Kitagawa K. and Yangiva S.: [in:] 11th International Conference on Wetland Systems for Water Pollution Control, November 1–7, 2008, Indoore, India 2008, p. 1074.
- [10] Kato K., Inoue T., K., Iiegutsu H., Koba T. and Kitagawa K.: First year performance of real scale hybrid wetland system for the treatment of dairy wastewater in a cold climate in Japan. Wetpol 2007 – 2nd International Symposium on Wetland Pollutant Dynamics and Control, 16–21.09, 2007, University of Tartu, Estonia, Publicationes Instituti Geographici Universitatis Tartuensis 2007, **104**, 150–152.
- [11] Obarska-Pempkowiak H.: Oczyszczalnie hydrofitowe. Wyd. Politechniki Gdańskiej, Gdańsk 2002.
- [12] Arias C.A., Brix H. and Johansen N.H.: [in:] 8th International Conference on Wetland Systems for Water Pollution Control, 16–19 September 2002, University of Dar Es Salaam, Tanzania 2002, 952–960.

EFEKTYWNOŚĆ ZŁÓŻ HYDROFITOWYCH W OCZYSZCZANIU ŚCIEKÓW MLECZARSKICH

Katedra Technologii w Inżynierii i Ochronie Środowiska
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Abstrakt: Na terenie województwa podlaskiego działa 9 zakładów mleczarskich korzystających z własnych oczyszczalni ścieków. W większości są to obiekty z lat 70. ubiegłego wieku, kiedy to w kraju dominowała technologia „Promlecz” oparta na komorach osadu wysoko- i niskoobciążonego. Ilość odprowadzanych ścieków wynosi według danych z roku 2008 od 470 do 5200 m³ · d⁻¹, równoważna liczba mieszkańców (P.E.) waha się od 7130 do 27 7000. Większość oczyszczalni wymaga modernizacji ze względu na ich stan techniczny, jak i wzrost produkcji w zakładach, co przekłada się na ilość generowanych ścieków, osadów i odcieków związanych z ich przeróbką. Metoda hydrofitowa w przypadku małych oczyszczalni mleczarskich może stanowić alternatywę dla zaawansowanych i kosztownych technologii z reguły stosowanych przy ich modernizacji. Złóża o przepływie pionowym i poziomym mogą z powodzeniem pracować jako drugi stopień oczyszczania ścieków mleczarskich po ich wstępnym mechanicznym i biologicznym oczyszczeniu. Wykonane badania przeprowadzono, opierając się na instalacji badawczej zaprojektowanej przez autora i działającej na terenie oczyszczalni ścieków mleczarskich w Wysokiem Mazowieckiem. Badania koncentrowały się na zastosowaniu układu hybrydowego składającego się ze złoża o przepływie pionowym (VF-CW) oraz poziomym (HF-CW). Oczyszczaniu poddano ścieki po komorze defosfatacji i komorze osadu wysokoobciążonego. Średnia wartości wskaźników zanieczyszczeń w ściekach mleczarskich poddanych badaniom wynosiły: BZT₅ (234,1 mg O₂ · d⁻³), ChZT (332,8 mg O₂ · d⁻³), azot Kjeldahla (25,9 mg N_{TKN} · d⁻³), azot amonowy (13,9 mg N-NH₄ · d⁻³), fosfor całkowity (10,9 mg P_T · d⁻³). Efektywność usuwania BZT₅ wynosiła średnio 84,8 %, ChZT 85,3 %, azotu Kjeldahla 81,0 %, azotu amonowego 91,0 % i fosforu ogólnego 39 %. Badania udowodniły przydatność zastosowania metody hydrofitowej po stopniu mechanicznym i biologicznym w oczyszczalniach ścieków mleczarskich.

Słowa kluczowe: złoża hydrofitowe, ścieki mleczarskie, biogeny

Julitta GAJEWSKA¹, Piotr JACAK¹
and Leszek BABIŃSKI²

**INFLUENCE OF ANOXIC CONDITION
ON THE COMPOSITION OF MICROORGANISMS
COLONIZED A CONTEMPORARY WOOD SAMPLES
IN ARCHAEOLOGICAL SITE IN BISKUPIN**

**WPLYW WARUNKÓW BEZTLENOWYCH
NA SKŁAD MIKROORGANIZMÓW
ZASIEDLAJĄCYCH WSPÓŁCZESNE DREWNO
NA STANOWISKU ARCHEOLOGICZNYM W BISKUPINIE**

Abstract: From 2003 year a research project was initiated in Biskupin with monitoring of physical, chemical and microbiological parameters of deposited archaeological wood in wet peat soil on sp1 and sp4 sites. In this paper colonization by microorganisms of a temporary oak wood (*Quercus* sp.) and pine wood (*Pinus sylvestris* L.) deposited during four years in the similar anoxic conditions in flooded sites were observed.

The results of the performed investigations showed on an interesting microbial community as colonizers of wood samples, outside and inside them, including a lignocellulotic bacteria and microscopic fungi, responsible for wood decomposition, and pathogenic, toxinogenic microorganisms, eg: *Pseudomonas aeruginosa*, *Aeromonas hydrophila / caviae*, *Clostridium perfringens* bacteria and *Aspergillus fumigatus*, *Penicillium* spp., and *Candida* spp. fungi.

Keywords: bacteria, microscopic fungi, wood colonization, physical and chemical parameters, Biskupin

Since many years ago on archaeological positions of defensive settlement from VIII century BC of Lusatian culture in Biskupin, physical, chemical and microbiological investigations were provided, on the basis which conservatory works of archaeological wood oak and pine were done. In the aim of recognition the threats, the archeological wood on what be subject in Biskupin, the identification of pine and oak wood

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colonizing bacteria and microscopic fungi in anoxic conditions was conducted [1–4]. This work was widened on oak and pine contemporary wood, kept by 2 years in peat soil on sp1 and sp4 sites, in similar conditions like archaeological wood is still resting [1–3, 5, 6].

The objective of this work was isolation and identification of microorganisms colonized a contemporary oak wood (*Quercus* sp.) and pine wood (*Pinus sylvestris* L.) and estimate the degree of wood colonization, after four year period of deposition in similar conditions to those of the archeological wood: in wet peat soil and in anaerobic condition in sp1 and sp4 measuring stations in Biskupin.

Materials and methods

Investigation was conducted on a contemporary oak and pine wood, which saved in wet peat in anoxic conditions in period 4 years (September 2003–September 2007). The experimental material, cut out from the long of trunks of approximately 240 mm diameter, derived from the outer part of the heartwood zone of oak and sapwood of pine. Dimensions of wood samples were as follow: 100 (L) × 10 (T) × 10 (R) mm. These samples were buried in the archeological site sp1 (No. 72) and sp4 (No. 6) in Biskupin in the layer of peat soil at the depth of 100 cm. At this level archaeological wooden construction from the Lusatian settlement are still deposited. During the experimental period the following physical and chemical measurements were done: level of ground water at sp1 and level of water in the trench at sp4, water reaction (pH) and water conductivity, soil temperature and redox potential, according to the methods described by Babinski et al [7]. After 4 years wooden materials to microbiological examinations were taken, for comparison of microbial colonization on the surface of wood (1–1.5 mm) and internal tissue (3–5.5 mm) and in soil arrounded to wood. For isolation and identification of bacteria, actinomycetes and microscopic fungi, the following media were used: nutrient agar with/without of 10 % mutton blood medium, Bunt and Roviry medium supplemented with 1 % starch and nystatine, King's B medium, Wilson–Blair medium for *Clostridium perfringens* reduced sulphite, Dubos medium with stripes of filter paper as source of carbon, Weimer and Zeikus medium with stripes of filter paper, Copier and Barjac medium for nitrifying bacteria, medium for denitrifying bacteria with nitrate, medium for amonifying bacteria with Winogradski salts and Doebereiner's medium for nitrogen fixing bacteria, and for microscopic fungi Martin's and Sabourad's or Chapek–Dox medium. Cultures were cultivated in 28 °C, and 37 °C for mesophilic strains and 60 °C for thermophilic strains. Anaerobic cultures were placed in an anaerostat (in presence of hydrogen and carbon dioxide, palladium catalyst and methylene blue as indicator of anaerobic condition) or anaerobic station (Juan). For systematic determination of bacteria Api tests bioMerieux with computer analyses programe were used. Microscopic observations and photos documentation by Nikon's E 600 fluorescent microscope with camera and computer were done. Systematic determination of bacteria according to Bergey's Manual of Systematic Bacteriology [8] and to identify fungi – systematics according to Barnett [9] and Fassiatoiva [10] were used.

Results and discussion

The measurements of physical and chemical properties of water and soil were performed on sp1 and sp4 stations, where investigated samples of pine and oak wood were deposited during 4 years. The results of these observations were presented in Table 1.

Table 1

Some selected physical and chemical properties of water and soil from Biskupin

Property	Value	Place of measurement (station)	
		sp1	sp4
Water level		above samples	above samples
Water reaction (pH)	minimum	6.6	6.9
	maximum	7.6	8.8
	mean	7.0	7.8
Water electrical conductivity [$\text{mS} \cdot \text{cm}^{-1}$]	minimum	0.46	0.40
	maximum	2.10	0.96
	mean	1.45	0.59
Soil temperature [$^{\circ}\text{C}$]	minimum	2.1	not measured
	maximum	19.0	
	mean	10.4	
Soil redox potential [mV]	minimum	-410	-240
	maximum	-100	-80
	mean	-240	-180

During resting on archaeological site (August 2003–August 2007), the samples of pine and oak wood always were below of groundwater level (sp1 station) and below a water level in a trench (SP4 station). The average value of water reaction (pH) was neutral, and pH value of trench water was significantly alkalic (even to 8.8). The higher conductivity of groundwater from sp1 station were observed, where average salinity was above twice higher than for a water from trench at sp4 station. The measurements of temperature only in soil of sp1 station were done. The temperature of peat on 100 cm of depth, in the wood samples left in soil, oscillated from 2.1 to 19.0 $^{\circ}\text{C}$. The average value of redox potential was -240 mV on sp1 station and -180 mV in a bed level of a wet trench. Results indicated on the strong reducing conditions present in two wood deposited sites. The changes of water reaction (pH) and conductivity, and soil redox potential followed serial fluctuations according to changes of groundwater level and depending on the change in season of the year. The detailed results of chosen monitoring environmental parameters at wet archaeological sites in Biskupin were described by Babinski et al [7].

The results of microbiological determinations on the settlement of a contemporary oak (*Quercus* sp.) and pine wood (*Pinus sylvestris* L.) showed the high diversity of

physiological groups of soil microorganisms in strictly anaerobic conditions. Results of these investigations were presented in Table 2 (bacteria) and Table 3 (microscopic fungi). One could observe in both samples of wood a temporary and strictly anaerobic bacteria and the microscopic fungi, which could grown in vitro in aero- and anaerobic conditions, when redox potential was very low periodically from -410 mV (minimal value), to -100 mV (maximal value).

Table 2

Colonization of a contemporary oak wood (*Quercus* sp.) and pine wood (*Pinus sylvestris* L.) after 4 years stored in wet peat soil by relative and strictly anaerobic bacteria from soil surrounded wood

Samples	Bacteria
sp1 pine outside	<i>Bacillus polymyxa</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Clostridium perfringens</i> , <i>Clostridium butyricum/bejerinckii</i> , <i>Clostridium thermocellum</i> , <i>Sporocytophaga</i> sp.
sp1 pine inside	<i>Bacillus polymyxa</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Clostridium thermocellum</i> , <i>Sporocytophaga</i> sp., <i>Streptomyces</i> sp.
sp1 oak outside	<i>Bacillus polymyxa</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Clostridium perfringens</i> <i>Micrococcus</i> sp., <i>Clostridium butyricum/bejerinckii</i> , <i>Clostridium thermocellum</i> , <i>Sporocytophaga</i> sp.
sp1 oak inside	<i>Bacillus polymyxa</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Clostridium butyricum/bijerienickii</i> , <i>Clostridium thermocellum</i> , <i>Sporocytophaga</i> sp.
sp4 pine outside	<i>Bacillus polymyxa</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Clostridium perfringens</i> , <i>Clostridium butyricum/bejerinckii</i> , <i>Clostridium thermocellum</i> , <i>Clostridium clostridiiforme</i> , <i>Sporocytophaga</i> sp., <i>Streptomyces</i> sp.
sp4 pine inside	<i>Bacillus polymyxa</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Clostridium perfringens</i> , <i>Clostridium butyricum/bejerinckii</i> , <i>Clostridium thermocellum</i> , <i>Sporocytophaga</i> sp.
sp4 oak outside	<i>Bacillus polymyxa</i> , <i>Pseudomonas fluorescens</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Clostridium perfringens</i> , <i>Micrococcus</i> sp., <i>Clostridium butyricum/bejerinckii</i> , <i>Clostridium thermocellum</i> , <i>Sporocytophaga</i> sp., <i>Streptomyces</i> sp.
sp4 oak inside	<i>Bacillus polymyxa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Clostridium perfringens</i> , <i>Clostridium thermocellum</i> , <i>Sporocytophaga</i> sp., <i>Streptomyces</i> sp.
sp1 soil	<i>Bacillus polymyxa</i> , <i>Bacillus mycoides</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Pantoea</i> spp., <i>Clostridium perfringens</i> , <i>Micrococcus</i> sp., <i>Clostridium butyricum/bejerinckii</i> , <i>Clostridium thermocellum</i> , <i>Clostridium clostridiiforme</i> , <i>Sporocytophaga</i> sp., <i>Streptomyces</i> sp.
sp4 soil	<i>Bacillus polymyxa</i> , <i>Bacillus mycoides</i> , <i>Pseudomonas fluorescens</i> , <i>Pseudomonas aeruginosa</i> , <i>Aeromonas hydrophila/caviae</i> , <i>Enterobacter cloace</i> , <i>Clostridium perfringens</i> , <i>Clostridium butyricum/bejerinckii</i> , <i>Clostridium thermocellum</i> , <i>Clostridium clostridiiforme</i> , <i>Sporocytophaga</i> sp., <i>Streptomyces</i> sp.

In the anaerobic conditions most of isolated and identified microorganisms were able to colonize a surface of oak and pine wood and they could penetrate to inside of wood (on 3–5.5 mm of depth).

Table 3

Colonization of a contemporary oak wood (*Quercus* sp.) and pine wood (*Pinus silvestris* L.) after 4 years stored in wet peat soil by yeasts and hyphal fungi from soil surrounded wood

Samples	Fungi grown in aerobic conditions	Fungi grown in anaerobic conditions
sp1 pine outside	<i>Aspergillus fumigatus</i> , <i>Penicillium</i> spp., <i>Candida</i> spp.	<i>Penicillium</i> spp., <i>Candida</i> spp.
sp1 pine inside	<i>Fusarium oxysporum</i> , <i>Aspergillus fumigatus</i> , <i>Rhizopus oryzae</i> <i>Penicillium</i> spp., <i>Candida</i> spp.	<i>Penicillium roquefortii</i> , <i>Penicillium</i> spp., <i>Candida</i> spp.
sp1 oak outside	<i>Penicillium citrinum</i> , <i>Candida</i> spp.	<i>Mucor piriformis</i> , <i>Penicillium</i> spp., <i>Candida</i> spp.
sp1 oak inside	<i>Mucor piriformis</i> , <i>Aspergillus fumigatus</i> , <i>Penicillium roquefortii</i>	<i>Mucor piriformis</i> , <i>Penicillium roquefortii</i> , <i>Penicillium</i> spp.
sp4 pine outside	<i>Aspergillus fumigatus</i> , <i>Candida</i> spp.	<i>Mucor piriformis</i> , <i>Fusarium oxysporum</i> , <i>Aspergillus fumigatus</i> , <i>Penicillium</i> spp., <i>Candida</i> spp.
sp4 pine outside	<i>Aspergillus fumigatus</i> , <i>Penicillium citrinum</i>	<i>Mucor piriformis</i>
sp4 oak outside	<i>Aspergillus fumigatus</i> , <i>Penicillium roquefortii</i> , <i>Candida</i> spp.	<i>Penicillium terrestre</i> , <i>Candida</i> spp.
sp4 oak inside	<i>Penicillium</i> spp.	<i>Penicillium</i> spp.
sp1 soil	<i>Fusarium oxysporum</i> , <i>Penicillium</i> spp., <i>Candida</i> spp.	<i>Fusarium oxysporum</i> , <i>Penicillium roquefortii</i> <i>Penicillium</i> spp., <i>Candida</i> spp.,
sp4 soil	<i>Phialophora bubaki</i> , <i>Aspergillus fumigatus</i> , <i>Candida</i> spp.	<i>Fusarium oxysporum</i> , <i>Candida</i> spp.

It was observed, that inside oak and pine wood saprophytic producing slime bacteria *Pseudomonas fluorescens* (API 90.7 %), cellulolytic bacteria and producing slime, too, a temperate anaerobic *Bacillus polymyxa*, *Sporocytophaga* sp. as well as strictly anaerobic meso – and thermophilic *Clostridium* spp. strains were present. The pathogenic bacteria were detected also, like *Aeromonas hydrophila/caviae* (Api 87.6 %), *Pantoea agglomerans* (Api 78.8 %), *Pseudomonas aeruginosa* (Api 99.9 %), *Clostridium perfringens* reducing sulphite as well as yeast from *Candida* sp. and *Aspergillus fumigatus*, *Mucor* sp. and *Penicillium* spp. microscopic fungi. *Micrococcus luteus* bacteria in some samples were also detected. In soil samples were present intestinal bacteria from *Enterobacteriaceae* family (eg *Enterobacter cloacae* – Api 94.3 %), which could not penetrate inside wood.

We could isolate pathogenic microscopic fungi colonizing pine and oak wood samples, eg toxinogenic and cancerogenic *Aspergillus fumigatus* strain or yeasts *Candida* sp. dangerous for people, or *Fusarium oxysporium* as plants pathogen; they can grow under an anaerobic condition. These pathogenic bacteria and fungi present in

soil surrounded wooden trenches probably can get throughout from water of Biskupin Lake.

Anoxic conditions are good for growth not only strictly anaerobes, but for a facultative anaerobic bacteria. Due to the deficiency of oxygen in flooded soils, microorganisms inhabiting flooded soils must be able to survive with little to no oxygen. Under anoxic conditions facultative microbes can use alternative (not oxygen) electron acceptors such as nitrate, ferric iron Fe(III), manganese(IV), oxide, sulfate, and carbon dioxide to produce energy and build their biomass. In 2009 Sikora and Blaszczyk [11] showed the important ecological role of Fe(III) reducing bacteria from Bacteria and Archaea domains, their classification and a biotechnological majority. According to Bagramayan et al [12], redox potential is a determinant in the *E. coli* anaerobic fermentative growth and survival. Decrease of redox potential (Eh) down to -550 – -600 mV in the *E. coli* culture was observed during growth in either anaerobic or aerobic conditions.

In present experiments oak and pine wood or soil bacterial isolates classified from different physiological groups with following processes, like: cellulolise, proteolise, amonification, nitrification, denitrification, fermentation of different substrates and their assimilation, possible to recognize on basis their biochemical profiles (Api tests).

Wood colonization processes of living bacterial and fungal microorganisms, with antagonistic and symbiotic or syntrophic relations between them in strictly anoxic conditions can be very interesting studies on wood „microbial community”. Anaerobic microbial processes including denitrification, methanogenesis and methanotrophy are responsible for releasing greenhouse gas (N_2O , CH_4 , CO_2) into atmosphere, and environmental factors, such as redox potential (Ex), pH, acidity, alkalinity, and salinity, are continuously changing [13]. Additionally, in aerobic conditions, gleying process in waterlogged soils occurred, by accumulation of Fe(II) due to reduction of ferric iron into ferrous iron [14]. Fermentative bacteria F(III) – reducing can be mainly isolated from gleyed soils. The black colour of soil is frequently observed in flooded soil. This may result from the formation of iron sulfide (FeS) and pyrite (FeS_2). The potential redox for SO_3^{-2}/S^{-2} is about: -116 mV. Disappearance of sulphate can be under Eh: -150 mV [15]. In authors own experiments, under anoxic conditions, wooden samples saved in wet soil during 4 years and soil samples, surrounded wood, were black. A strictly anaerobic *Clostridium perfringens* bacteria isolated from soil and from wood could reduced sulphite to H_2S , and caused their black colour.

A low redox potential is important for denitrification. In this process, nitrate is reduced to nitric oxide, then nitrous oxide fully reduced to dinitrogen. Microbes responsible include both organotrophs and litotrophs, and this process occurs primarily by facultative anaerobes (eg *Pseudomonas* sp., *E. coli* [2] and strictly anaerobes (eg *Clostridium perfringens* [16]. Many fermentative bacteria can reduce nitrite to ammonium, then pH value of soil can increase rapidly even to pH 10 [2].

Physiological biodiversity of microorganism under anaerobic conditions is connected with decomposition of lignocellulolytic wooden materials (eg *Clostridium* spp., *Sporocytophaga* sp., *Bacillus polymyxa*). Glucose, as end product of cellulose or hemicellulose fermentation, can be very good substrate for next colonizers of pine and oak wood saved in soil [17, 18]. In 2002 Wazny [19] on basis own and numerous

authors papers described decomposition of wood by aerobic and anaerobic bacteria isolated from archaeological wooden samples in contact with water, like *Bacillus* spp., *Cellulomonas* spp., *Cellvibrio* spp., *Corynebacterium* spp., *Ervinia carotovora*, *Clostridium* spp., *Pseudomonas* spp., and *Streptomyces* spp.

In present work, among different wood colonizers, a nitrifying aerobic *Nitrosomonas* sp. bacteria were isolated. According to Strous et al [20], aerobic nitrifying bacteria such *Nitrosomonas* spp. might be involved in Anammox process – as anaerobic ammonium oxidation. This anaerobic ammonium oxidation, recently was described as a new process in which ammonium was converted to dinitrogen gas under anaerobic condition with nitrite as the electron acceptor, described by Vandegraaf et al in 1995 [4].

According to Badura [21] one still can not understand entirely the role of microorganisms in soil mineralization processes; certainly is difficult to recognize a real total number of living cells: fast living as eutrophic cells and slowly growing – as oligotrophic bacteria. A qualitative composition of microorganisms is not completely recognized, because during influence of many parameters, like physical and chemical properties of soil and soil plants on microorganisms growth, which can significantly change kinds of growing microorganisms.

Most of isolated soil and wooden pathogenic or nonpathogenic microbial strains were responsible for the decomposition of a temporary and archaeological wood, deposited in wet soil. Actually we try to find the best method of conservation wooden trenches by using antibacterial and antifungal biocides, in hope, that it will be possible to demonstrate archaeological wood samples after hygienisation in Biskupin Museum, to protection of the archaeological wood monuments for future.

Conclusions

1. The contemporary oak and pine wood, kept by 4 years under anoxic conditions, during very low redox potential parameters, were colonized by different physiological groups of bacteria; oxygenic (Ammonox), a facultative and strictly anaerobic, together with a facultative and strictly anaerobic microscopic fungi.

2. The largest threat for wood can make the cellulolytic or lignocellulytic microorganisms like: *Bacillus polymyxa*, *Sporocytophaga* sp, meso- and thermophilic *Clostridium* spp. bacteria and *Streptomyces* spp. actinomycetes, as well as *Penicillium* sp. and *Aspergillus* sp. microscopic fungi.

3. The present in soil bacteria from family *Enterobacteriaceae* did not colonize samples of the oak and pine wood, kept in anaerobic conditions.

4. It was observed, that *Fusarium* sp. fungi which were present in soil adhered to wood, were absent inside oak and pine wood, probably in consequence of antagonistic activity of the dominant *Pseudomonas fluorescens* strains.

5. We suppose, that maintenance of a contemporary wood and archeological wood, too, for longer time in anoxic conditions (with high concentration of sulfide and very low soil redox potential) in wet archeological site in Biskupin will have positive role in limitation of decomposition saved wood in peat and its biological corrosion in future.

References

- [1] Babiński L., Zborowska M., Gajewska J., Waliszewska B. and Prądyński W.: Folia Forest. Polon., ser. B 2006, **37**, 3–7.
- [2] Cole J.A. and Brown C.M.: FEMS Microbiol. Lett. 1980, **7**, 65–72.
- [3] Gajewska J., Kostecka J. and Babiński L.: Zesz. Probl. Post. Nauk Roln. 2006, **520**, 455–463.
- [4] Gajewska J., Borkowski A. and Babiński L.: Polish J. Environ. Stud. 2006, **15**(5d), 665–669.
- [5] Zborowska M., Babiński L., Gajewska J., Waliszewska B. and Prądyński W.: Folia Forest. Polish, ser. B 2007, **38**, 13–26.
- [6] Vandergraaf A.A., Mulder A., Debruijn P., Jetten M.S.M., Robertson L.A. and Kuenen J.G.: Appl. Environ. Microbiol. 1995, **61**, 1246–1251.
- [7] Babiński L., Fejfer M. and Prądyński W.: J. Wetland Archaeol. 2007, **7**, 51–72.
- [8] Garrity G.M. (ed.): Taxonomic Outline of The Archae and Bacteria. Bergey's Manual of Systematic Bacteriology. Bergey's Manual Trust. Second Edition. XXI, Springer, Verlag, New York 2001, 721 pp.
- [9] Barnett H.L.: Illustrated Genera of Imperfecti Fungi. The Burgess Publishing Company, USA, 1960–1965, 225 pp.
- [10] Fassiátova O.: Plisme a Vleknite Hauby v technice Mikrobiologii (prirucka k. Urcovani). Statni Nakladatelství Technické Literatury, Praha 1979, 255 pp.
- [11] Sikora A. and Błaszczuk M.K.: Adv. Microbiol. 2009, **48**(2), 93–104 (in Polish).
- [12] Bagramayan K., Galstyan A. and Trchounian A.: Bioelectrochemistry 2000, **51**(2), 151–156.
- [13] Schlesinger W.H.: Biogeochemistry: An analysis of global change. Eight printing. Academic Press, San Diego 2005, 558 pp.
- [14] Lovley D.R.: [in:] Origins, Evolution, and Biodiversity of Microbial Life. Seckbach J. (ed.), Kluwer Academic Publishers, Netherlands 2004, 299–313.
- [15] Venk H.R. and Bujakh A.: Minerals. Their constitution and origin. Cambridge University Press, U.S. 2004, 646 p.
- [16] Mitchell R. and Alexander M.: Soil Sci. 1962, **93**, 413–419.
- [17] Gajewska J.: Decomposition of lignocellulosic substrates by thermophilic *Clostridium thermocellum* bacteria. Ed. SGGW, Warsaw 1992, 126 pp. (in Polish).
- [18] Kundzewicz A., Gajewska J., Górska E.B., Jaśkowska H. and Rekosz-Burlaga H.S.: Folia Forest. Polon., ser. B 1993, **24**, 37–45.
- [19] Ważny J.: Wood Industry 2002, **7–8**, 8–13 (in Polish).
- [20] Strous M., Van Gerven E., Ping Z., Kuenen J.G. and Jetten M.S.M.: Appl. Environ. Microbiol. 1997, **63**(6), 2446–2448.
- [21] Badura L.: [in:] Modern methods of investigations soil microorganisms and another environments. Ciesielska A. and Pokojaska-Burdziej A. (eds.), UMCS Toruń, 2007, p. 13 (in Polish).

WPLYW WARUNKÓW BEZTLENOWYCH NA SKŁAD MIKROORGANIZMÓW ZASIEDLAJĄCYCH WSPÓŁCZESNE DREWNO NA STANOWISKU ARCHEOLOGICZNYM W BISKUPINIE

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Abstrakt: Od wielu lat na stanowiskach archeologicznych obronnego osiedla kultury łużyckiej z VIII w. p.n.e. w Biskupinie prowadzone są badania fizykochemiczne, mikrobiologiczne i konserwatorskie zabytkowego drewna archeologicznego. W celu rozpoznania zagrożeń mikrobiologicznych, na jakie wciąż narażone jest to zabytkowe drewno, badania mikrobiologiczne rozszerzono o współczesne drewno dębu (*Quercus* sp.) i sosny (*Pinus sylvestris* L.), przechowywane przez 4 lata w warunkach anoksji w glebie torfowej na stanowiskach sp1 i sp4.

Stwierdzono różnorodność glebowych względnie i bezwzględnie beztlenowych kolonizatorów, np. celulolitycznych bakterii i grzybów mikroskopowych, zdolnych do rozkładu drewna, a także patogenów, np. *Pseudomonas aeruginosa*, *Aeromonas hydrophila/caviae*, *Clostridium perfringens* oraz grzybów *Aspergillus fumigatus*, *Penicillium* spp. i *Candida* spp.

Słowa kluczowe: bakterie, grzyby mikroskopowe, kolonizacja drewna, parametry fizykochemiczne, Biskupin

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GRAVEYARD – POINT SOURCE POLLUTION OF NATURAL WATER BY PESTICIDES

MOGILNIK – PUNKTOWE ŹRÓDŁO ZANIECZYSZCZENIA WÓD NATURALNYCH PESTYCYDAMI

Abstract: The objective of the paper is to evaluate the state of water and soil in the vicinity of the pesticide graveyard in Folwarki Tylwickie and to present a study on the possibility of reducing the migration of pesticides from deposited wastes by using waste sorption agents. Water samples from bored wells, dug wells, piezometers, and soil samples from the vicinity of the graveyard were examined. About 47 biologically active pesticide substances were chosen for monitoring.

In the examined water and soil, among the identified pesticides, dominated the most durable chloroorganic insecticides and their metabolites. Stabilized sewage sludge from a dairy wastewater plant after compost stabilization was used as sorbent. The use of Freundlich's, Langmuir's and BET's isotherms proved that sewage sludge compost has sufficient sorption properties in relation to chloroorganic insecticides. Due to the properties they can be used to construct a sorption shield around the graveyards. In the future, this would allow to apply a sorption screen around the pesticide burial area which reduces pesticide migration into the environment.

Keywords: pesticide graveyard, heavy metals, pesticide, soil, water, sorption isotherm

Pesticides, as toxic compounds, are cancerogenic, teratogenic, embryotoxic and mutagenic. They are detected in all environmental compartments: atmosphere, hydrosphere, geosphere, flora, fauna, and of course, man. Outdated or not used pesticides become very dangerous wastes, that when inappropriately stored, penetrate into the natural environment making a threat for all life forms [1–7]. The past left tens of thousands tons of accumulated pesticide wastes that have been storing continuously since 1950's. Those reserves grew, among others in 1970's when, due to ecological and toxicological reasons, many of these means were withdrawn from the market and agricultural application. Also wrong management, distribution and uncontrolled import of plant protection means have contributed. Part of means was remained at the stores, another part was placed in graveyard buildings which were started in 1970's in a form

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of wells of 3–4 meter deep made of concrete circles of 1–3 meter diameter or built as brick constructions that were buried with 0.5 m thickness soil layer after filling [1, 2].

Previous designing procedures did not take into account the long-term effects of the graveyard exploitation. Neither hydrological conditions, land characteristics, nor environmental conditions were taken into account, and no geological investigations were performed at localizing these objects, which resulted in their building on geological forms with great permeability and sometimes even on water-carrying layers. Supervision made by Sanitary and Epidemiological Stations revealed that 1/3 of graveyards did not meet localization conditions. They were closer than 300 m from water intake points, water reservoirs and agricultural areas. At least 75 graveyards were situated near rivers and lakes, 100 were near drinking water intakes and about 140 of them near residential areas. Among 16 pesticide stores in Podlasie province, 7 of them are localized within Upper Narew river area, and the remaining at the direct neighborhood of other surface flows. Chambers of majority of graveyards are leaky, which is proved by soil and water analyses due to supervisions [1, 6, 7]. There is also possibility to worsen the construction condition along with the occurrence of corroding the concrete bunkers and wells, the outdated pesticides are deposited, and in consequence, a toxic leakage. The leakage can be transported by underground water and then in a form of so-called underground inflow, it is caught by a network of surface waters. Accumulation of outdated pesticides, even after removal, will be a potential source of a threat and natural environment pollution for many years. Accumulation of toxic substances at one place along with confirmed pesticide emission into the underground water make a serious hazard for people. A graveyard contains a variety of substances that reacting to one another can produce often more toxic and mutagenic compounds than the substrates. Although local penetration of poisons into the water or ground may have no direct and significant effects on inhabitants, short filtration way (often through light, permeable and with low sorption capacity soils) makes a great threat for quality of surface water that transports toxins to a considerable distance. Mean flow rate of underground water near the graveyards in Podlasie province is about $80\text{--}100\text{ m} \cdot \text{yr}^{-1}$, which means that in the case of any constructional damage, a constant supply of pollution into the open waters will be happening for many years. Therefore, there is a necessity to search for the solutions to reduce the pesticide migration in an environment as well as to introduce new concepts. Thus, it seems to be purposeful to undertake studies upon application of sorption process using selected natural and waste adsorbents as a screen for pesticides in order to reduce their migration from other graveyards, stores and contaminated soils and concrete [8–13].

The present research was aimed at searching for a possibility to reduce the migration of deposited pesticide wastes by applying natural and waste sorption substances that would make a barrier for plant protection means against penetration to the hydrosphere. It would protect ground and surface waters that are often the source of drinking water for people and animals. In future, it would allow for applying the sorption screen around pesticide burial area, which reduces pesticide migration into the environment, and grown energetic plants – through phytoremediation – would prolong the sorbent vitality and remove pesticides accumulated in aboveground parts by means of combustion.

Material and methods

Experimental area

The size of pesticide migration disposed in graveyard was evaluated on selected objects localized in Podlasie province in Folwarki Tylwickie (53°00' 23°26'). It is an active graveyard consisted of three containers made of ferroconcrete well circles isolated with tar-board and cement (1.26, 1.8 and 1.8 m³ capacities). In total, 5000 kg of expired pesticides and 10 kg of chemicals from Sanitary Station are deposited. The dump was localized on fine and medium sands that have good filtration properties. All dangerous substances leaking from leaky tanks may easily migrate along with rainfalls. Burial ground is set at about 1.6 m depth, whereas underground water is at the level of 2 m. Surface water intake is situated at the distance of about 4.5 km, groundwater about 1 km (bored well 1000 m, dug well 800 m). River Malynka flows nearby (about 1.5 km). Graveyards are localized among brushwood directly in cultivated field, and near protected area and congested housing.

Materials

Determinations of natural water and soil qualities in that area and near the graveyard were carried out. Samples of natural water and soils around the burial ground were collected for analyses. Physicochemical parameters were determined in water samples taken from groundwater near graveyard (piezometers), dug wells (farm wells, bored wells) of surrounding farms, surface water and soil from 1 m depth layer. Analyses of soils, ground and surface waters were carried out in spring, summer and autumn (2006–2008) during rainfalls. Collected water and soil samples were analyzed for remains of pesticides from chloroorganic, phosphoorganic, pyrethroids, nitrophenols, triazines, and phenoxyacids groups being components of the most disposed chemicals. Moreover, heavy metals and other properties influencing on pesticide conversions were determined in water.

Table 1

The characteristic of compost

Sorbent	Properties						
Compost	Manurial [% in d.m.]						
	Ca	Mg	Total N	NH ₄ ⁺ -N	Total P	K	
	5.61	0.46	1.39	0.009	1.47	0.45	
Compost	Metal [mg · kg ⁻¹ d.m.]						
	Pb	Cu	Cd	Cr	Ni	Zn	Hg
	7.0	22.7	0.63	9.9	5.8	210	2.5
Compost	Other [%]						
	pH	Hydration		Dry mass		Organic matter	
	6.7	67.5		34.2		67.5	

On a basis of literature data and own studies, chloroorganic pesticides that most often occurred near the graveyards at the highest concentrations were selected as representative sorbats [1–7]. Individual pure active substances (HCH, DDE, and aldrin) were applied. Sewage sludge compost achieved directly from dairy treatment plant in Sokolka. The characteristic of the compost are given in Table 1.

Sorption procedure

Studies under static conditions were performed in accordance with methodology applied in Belgium, Germany, France, Italy, England, USA, and Poland [8–11, 13, 14]. They were aimed at plotting the adsorption isotherms due to which it is possible to compare the sorption capacities of different adsorbats on different adsorbents. Sorption experiments were carried out by adding a known mass of compost (0.001; 0.002; 0.005; 0.01; 0.025 g per 100 cm³ solution) to glass flasks filled with pesticides aqueous solution. Flasks were shaken in an isothermal water bath shaker at 130 rpm and 20 °C for 24 hours, and were left for 24 hrs in order to reach a sorption equilibrium. Freundlich's and Langmuir's isotherms [8–11, 13–16] were plotted on a base of achieved results applying Statistica software in order to analyze the processes.

Analytical procedure

Pesticide concentrations were determined in collected samples in accordance with an obligatory methodology using gas chromatograph coupled with mass spectrometer (GC/MS/MS 4000) as well as gas chromatograph AGILENT6890 equipped with ECD1 and NPD2 columns. Moreover, after sample digestion according to EPA 3015 procedure using microwave digester Mars 5, also metals concentrations were determined by means of ICP-AES technique, except of mercury determined by means of CV-AAS technique [17, 18].

Results and discussion

In total, 108 of water samples and 54 of soil samples were analyzed. Results are presented in Table 2. The analyses were carried out for 47 biologically active substances from different chemical groups: chloroorganic, phosphoroorganic, pyrethrins, triazines, and others (Table 2).

From the regional point of view, the graveyard is located on a slight morphological slope. Water level corresponds to the area surface. It is a couple of meters deep next to the graveyard. The direction of underground water flow is consistent with the terrain morphology.

Water flows from the graveyard in the direction of Malynka and Suprasl valley. Many toxic substances accumulated in one place and confirmed leaks of pesticides to underground waters pose a serious threat to the environment and local inhabitants. The largest amounts of biologically active substances remains (25.4 %) were found in soil samples. Presence of six of 16 studied chloroorganic compounds was determined. They

were the most stable and the least environmentally degradable agents. Achieved results of soil analyses indicate that large area is polluted with pesticides originating most probably from leaky chambers in the dump. Moreover, phosphoorganic compounds, pyrethrins and herbicides were found. Pesticide levels found are not very high, but their presence indicates the spreading of pollutants within the soil. The highest values were recorded for DDT ($0.927 \text{ mg} \cdot \text{kg}^{-1}$) and atrazine ($0.710 \text{ mg} \cdot \text{kg}^{-1}$) (Table 1). Wolkowicz [7], who studied water and soil near burial grounds achieved similar results in Mlynów, Wagów and Poznań as well as Stobiecki [6] and Morzycka [4] in Wasocz in Podlasie province.

Table 2

List of substances determined by gas chromatography in water and soil samples

Active substance		Method of detection	LD Soil	Conc. Soil	LD Water	Concentration			
						Farm wells	Bored wells	River	Piezometer
						[mg · kg ⁻¹]		[mg · dm ⁻³]	
H	Atrazine	GC-NP	0.01	0.710	0.0001	0.0022	not detected	0.0032	
	Chlorpropham	GC-NP	0.01		0.0006	0.0025		0.0015	
	Dichlorprop	GC-EC	0.08		0.0038				
	Dinoseb	GC-NP	0.03		0.0015	0.0049		0.0040	
	DNOK	GC-NP	0.02		0.0010				
	MCPA	GC-EC	0.10		0.0020	0.0330		0.0025	
	Mecoprop	GC-EC	0.10		0.0033	0.0109		0.0161	
	Simazine	GC-NP	0.02		0.0001				
	2,4-D	GC-EC	0.02		0.0010				
	Trifluraline	GC-NP	0.001	0.016	0.0003				
IC	Carbaryl	GC-NP	0.50		0.0030				
	Carbofuran	GC-NP	0.050		0.0004				
	Pirimicarb	GC-NP	0.008	0.015	0.0001				
	Propoxur	GC-EP	0.050		0.0005	0.0002	0.0001		
OC	Chlorfenson	GC-EC	0.020		0.0002				
	p,p'-DDD	GC-EC	0.004		0.0002	0.0036		0.0020	
	o,p'-DDT	GC-EC	0.001	0.927	0.0002	0.0025	0.0035	0.0030	
	p,p'-DDE	GC-EC	0.0004	0.275	0.0001			0.0005	
	p,p'-DDT	GC-EC	0.005	0.139	0.0002	0.0016	0.0010	0.0020	
	Dieldrine	GC-EC	0.001		0.0010			0.0010	
	DMDT	GC-EC	0.002		0.0010				
	Endrin	GC-EC	0.001	0.012	0.0010			0.0020	
	α-β Endosulfan	GC-EC	0.007		0.0001				
	Endosulfan – sulfate	GC-NC	0.009		0.0001				
	HCB	GC-EC	0.002	0.056	0.0001				
	α-HCH	GC-EC	0.001		0.0001	0.0136		0.0010	
	β-HCH	GC-EC	0.008		0.0002			0.0002	

Table 2 contd.

Active substance	Method of detection	LD Soil	Conc. Soil	LD Water	Concentration			
					Farm wells	Bored wells	River	Piezo-meter
					[mg · dm ⁻³]			
γ-HCH	GC-EC	0.003	0.033	0.0001	0.0016		0.0018	0.0090
δ-HCH	GC-EC	0.004		0.0001	0.0217			0.0004
Methoxychlor	GC-EC	0.003		0.0001			0.0003	0.0002
OP	Bromfenvinfos	GC-EC	0.06		0.0004			
	Chlorfenvinfos	GC-EC	0.02		0.0003			
	Chlorpyrifos	GC-EC	0.05		0.0002			
	Chlorpyrifos – methyl	GC-EC	0.1		0.0002			
	Diazinon	GC-NP	0.08		0.0001			
	Dimethoate	GC-NP	0.01		0.001			
	Fenthion	GC-NP	0.01		0.0002			
	Fenitroton	GC-NP	0.01		0.0002			
	Heptenophos	GC-NP	0.02		0.0004			
	Izofenphos	GC-NP	0.01	0.045	0.0001			
	Methidation	GC-NP	0.01		0.0052			
	Parathion	GC-NP	0.01		0.0001			
	Thiometon	GC-NP	0.02		0.0001			0.0003
	Triazophos	GC-NP	0.01		0.0002			0.0008
P	Cypermethrin	GC-EC	0.05		0.0004			
	Deltamethrin	GC-EC	0.02		0.0005			
	Fenprothrin	GC-EC	0.01		0.0003			

Explanations: H – herbicides, IC – carbamate insecticides, OC – organochlorine insecticides, OP – organophosphorus insecticides, P – pyrethrins, LD – limit of detection, Conc. – concentration.

It was discovered that in the burial grounds there were mixtures of various substances which were products of mutual changes, which gave new molecules of unknown toxic properties. The leak from the burial ground chambers is transported by underground waters and after several tens of meters it is intercepted by a network of surface waters. Average groundwater flow from the burial ground was approx. 80–100 m · yr⁻¹. Water from bored wells localized near burial grounds in land holding, from farm wells in Folwarki Tylwickie and from Malynka river was subjected to analysis for pesticides remains.

In the graveyard in Folwarki Tylwickie most stable chloroorganic insecticides and their metabolites were dominant. Very characteristic was the presence of isomer γ-HCH which is the least degradable of all HCH isomers. These are highly toxic compounds having long periods of half decomposition. Presence of 10.64 % among 47 studied active substances was recorded in water samples. Surface water sample from Malynka river – presence of MCPA (25 μg · dm⁻³), MCPA (23.4 μg · dm⁻³), simazine (161 μg · dm⁻³) and water samples from dug wells were the most polluted. High level of

herbicide in river may be also explained by the surface runoff from fields after autumn agrotechnical operations. Studies of pesticide agents in water samples collected in bored wells did not confirm any of 47 analyzed pesticide. Instead, it confirmed the suggestion that graveyard caused the pollution of the first water bearing layer and surface water. Measurements of physicochemical parameters and heavy metals contents were determined in collected water samples (Table 3). In general, achieved results did not show the presence of elevated values and concentrations of those parameters (pH, conductivity, TOC), nor any heavy metal (in spite of Mn).

Table 3

List of metals determined in water samples

Parameter	Concentration in water		
	Farm wells	Bored wells	River
pH	7.94	7.28	7.88
Conductance [$\mu\text{S} \cdot \text{cm}^{-1}$]	527	477	596
TOC [$\text{mg} \cdot \text{dm}^{-3}$]	23.46	21.10	25.28
Metal [$\text{mg} \cdot \text{dm}^{-3}$]			
Al	0.02585	< 0.01	0.076
Cd	< 0.0005	< 0.0005	< 0.0005
Cr	< 0.002	< 0.002	< 0.002
Cu	< 0.002	< 0.002	< 0.002
Fe	0.2526	0.0381	0.0834
Hg	0.00018	0.00002	0.00025
Mn	0.32813	0.05487	0.0044
Ni	< 0.002	< 0.002	< 0.002
Pb	< 0.00027	< 0.00027	< 0.00027
Zn	0.11858	1.4257	< 0.020

Characteristics of applied sorbents (Table 1) indicate that both meet requirements of compost for natural applications. The adsorption process is described using Freundlich's, Langmuir's or BET's formulae:

$$\begin{array}{ll} \text{Freundlich} & A = kc^{1/n} \\ \text{Langmuir} & A = a_m kc / (1 + kc) \\ \text{BET} & A = ac / (1 + c)(1 + kc) \end{array}$$

Following curves were achieved $A_F = 24378.4 c^{2.16}$ for compost at correlation coefficient of $R = 0.973$, $A_L = 951 c / (1 - 4.4508 c)$ at correlation coefficient of $R = 0.957$, and $A_{BET} = 1005c / (1 + c)(1 - 4.627c)$ at correlation coefficient of $R = 0.956$.

Constants k and $1/n$ were estimated by means of the least squares by Gauss-Newton and Levenberg-Marquardt method applying Statistica software, and then the errors for these constants were evaluated. Figure 1 present adsorption isotherms for studied pesticides on applied compost adsorbents as a function of adsorbate amount adsorbed by adsorbent weight unit (x/m) vs. adsorbate's balance concentration (c_0).

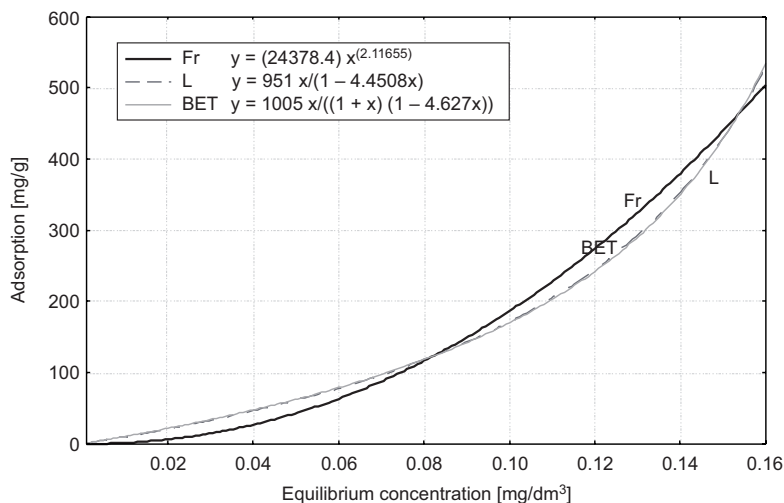


Fig. 1. Sorption isotherms of chloroorganic pesticides on compost

The same group of isotherms according to Giles' classification (S) was achieved for all pesticides [8, 10, 11, 16]. It includes isotherms for systems in which solvent is strongly adsorbed and is competitive for dissolved substance being adsorbed [16]. Isotherm's shape also proves the flat arrangement of adsorbate's molecule at adsorbent's active centers. The isotherms shape testifies also to the fact that the adsorbate particle may be placed vertically or at an angle in the active centre of the adsorbent [9, 16]. Figure 1 apparently shows that, for compost, Freundlich's isotherm does not approach monotonically to limit adsorption within the same balance concentrations range, and it can be predicted as over $500 \text{ mg} \cdot \text{g}^{-1}$.

Knowledge on $1/n$ parameter value in Freundlich's formula allows for assessing the adsorption intensity of a given substance from water phase on adsorbent; value of k constant determines the sorption capacity of an adsorbent at balance concentration in a solution. Higher k value corresponds to higher sorption capacity. In own studies, higher value of k coefficient was achieved for dairy sludge, which proves its usefulness in application as sorption screen around the pesticide graveyard. Constants $1/n$ in Freundlich's formula are directional coefficients of isotherms equal to the tangent of line inclination angle in logarithmic coordinates. Therefore, the higher $1/n$ value, the more intensive adsorption process. Also $1/n$ coefficient for the sludge is two times higher, which proves higher intensity of chloroorganic pesticides retain.

Conclusions

1. It was found pollution of natural water by chloroorganic, carbamate, triazine and phenoxyacetic pesticides and heavy metals.
2. River and dug wells were contaminated with pesticides which was caused by leaking from graveyards.

3. High concentration of herbicide (MCPA, MCPP and simazine) in natural water was caused both by graveyards leaching and surface flow from ploughed fields after agrochemical measures.

4. Sewage sludge compost proved to be the best natural sorbent for the process for migration reduction of chloroorganic pesticides from graveyards.

5. It is indispensable to analyze the Freundlich adsorption isotherm coefficients to get the optimum amount of the sorbent for pesticide detoxication.

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References

- [1] Biziuk M.: *Pestycydy. Występowanie, oznaczanie i unieszkodliwianie*. WNT, Warszawa 2001.
- [2] Foster S.S.D., Chilton P.J. and Stuart M.E.: *J. Inst. Water Environ. Manage.* 1991, **5**(2), 186–193.
- [3] Ignatowicz K.: *Polish J. Environ. Stud.* 2007, **16**(4), 177–181.
- [4] Morzycka B.: Influence of burial grounds on the environment on the basis of examining water samples from water intakes and farm wells from the vicinity of burial grounds in Podlaskie voivodship. Report, Plant Protection Institute 2001, 2002, Instytut Ochrony Roślin, Poznań.
- [5] Siłowicki A.: *Inwentaryzacja odpadów, Środ. Ochr. Rośl. Mater. IOR, Project GEF in Poland 1999, Państwowy Instytut Geologiczny, Warszawa 1999.*
- [6] Stobiecki S.: Report of analysis of waters and soils in the vicinity of Wąsosz. Plants Protection Institute, Poznań 1999.
- [7] Wołkowicz S., Wołkowicz W. and Choromański D.: *Badanie wpływu przeterminowanych środków ochrony roślin (mogilników) na środowisko geologiczne (III etap)*. Państwowy Instytut Geologiczny, Warszawa 2003, 15 p.
- [8] Hameed B.H., Salman J.M. and Ahmad A.L.: *J. Hazard. Mater.* 2009, **163**(1), 121–126.
- [9] Ignatowicz K.: *J. Hazard. Mater.* 2009, **169**(1–3), 953–957.
- [10] Ignatowicz K.: *Przem. Chem.* 2008, **87**(5), 2, 464–467.
- [11] Ochsner T.E., Stephens B.M., Koskinen W.C. and Kookana R.S.: *Soil Sci. Soc. Amer. J.* 2006, **70**, 1991–1997.
- [12] Zbytńiewski R. and Buszewski B.: *Polish J. Environ. Stud.* 2002, **11**(2), 179–184.
- [13] Spadotto C.A. and Hornsby A.G.: *J. Environ. Qual.* 2003, **32**, 949–956.
- [14] Yuh-Shan Ho.: *Polish J. Environ. Stud.* 2006, **15**(1), 81–86.
- [15] Anielak A.M.: *Chemiczne i fizykochemiczne oczyszczanie ścieków*. Wyd. Nauk. PWN, Warszawa, Poland 2000.
- [16] Jankowska M., Świątkowski A., Starostin L. and Ławrinienko-Omiczyńska J.: *Adsorpcja jonów na węglu aktywnym*. Wyd. Nauk. PWN, Warszawa 1991.
- [17] Lambropoulou D.A., Sakkas V.A., Hela D.G. and Albanis T.A.: *J. Chromatogr. A* 2002, **963**, 107–116.
- [18] Woudneh M.B., Sekela M., Tuominen T. and Gledhill M.: *J. Chromatogr. A* 2007, **1139**(1), 121–129.

MOGILNIK – PUNKTOWE ŹRÓDŁO ZANIECZYSZCZENIA WÓD NATURALNYCH PESTYCYDAMI

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Abstrakt: W pracy przedstawiono wyniki badań wody i gleby z okolic mogilnika w Folwarkach Tylwickich oraz możliwość ograniczenia migracji przeterminowanych pestycydów zdeponowanych w mogilnikach

poprzez zastosowanie odpadowych materiałów sorpcyjnych. Próbkę wody ze studni wierconych, kopanych i z piezometrów oraz próbki gleby pobrane w okolicy mogilnika zbadano na obecność 47 biologicznie aktywnych substancji pestycydowych.

W badanych próbkach stwierdzono największe ilości insektycydów chloroorganicznych i ich metabolitów. Do ograniczenia migracji związków chloroorganicznych zastosowano sorbent odpadowy – ustabilizowany osad ściekowy poddany procesowi kompostowania. W celu określenia mechanizmu sorpcji zastosowano równania izotermi Freundlicha, Langmuira i BET. Na podstawie przeprowadzonych badań stwierdzono, że kompost z komunalnego osadu ściekowego może być zastosowany do budowy bariery wokół mogilnika, która ograniczy migrację pestycydów do środowiska.

Słowa kluczowe: mogilnik, metale ciężkie, pestycydy, gleba, woda, izotermie adsorpcji

Elżbieta JEKATIERYNCZUK-RUDCZYK¹

CHANGES OF PHOSPHORUS COMPOUNDS CONCENTRATIONS IN WATERS OF LOWLAND CATCHMENTS WITH VARIOUS ANTHROPOPRESSION LEVELS

ZMIANY STĘŻEŃ ZWIĄZKÓW FOSFORU W WODZIE ZLEWNI NIZINNYCH O RÓŻNYM STOPNIU ANTROPOPRESJI

Abstract: Phosphorus compounds concentrations in surface and interstitial water as well as groundwater within river Krzemianka and river Jaroszwka catchments, that are characterized by various anthropopression levels, were analyzed in the study. These phosphorus compounds concentrations varied along with the increase of anthropopression within the catchment. In waters of river Jaroszwka catchment, only 15 % total phosphorus (TP) was made up by soluble reactive phosphorus (SRP), which indicated the supply of organic contaminants to surface water and groundwater in urban areas. Organic phosphorus form prevailed in all types of waters in studied catchments, and its mean concentrations amounted to: 198 $\mu\text{gP}/\text{dm}^3$ in groundwaters, 208 $\mu\text{gP}/\text{dm}^3$ in interstitial waters, and 139 $\mu\text{gP}/\text{dm}^3$ in surface waters. Higher concentrations of studied phosphorus forms were recorded in interstitial waters, which in the case of intensive river drainage, may contribute to considerable eutrophication of flowing waters.

Keywords: lowland river, interstitial water, SRP (soluble reactive phosphorus), total phosphorus

Phosphorous significantly affects the living organisms, because it is essential in physiological processes. In waters, it can originate from organic plant and animal remains decay, dissolving the minerals, remains of fertilizers, as well as industrial and municipal wastewaters pollution. Increasing phosphorus load in water reservoirs is a main cause of eutrophication process [1, 2].

In river water, bottom sediments and hydraulic connection between surface and groundwaters mainly affect the phosphorus compounds content [3, 4]. In rivers that drains groundwaters, biological processes occurring in sediments may have periodic influences on surface waters by considerable decreasing of their quality [5]. It is associated with intensified supply of interstitial waters to surface ones. That phenomenon is present after heavy rainfalls preceded by a drought. Quality of river waters is

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then significantly worsened, which is expressed as decreased oxygen concentration and elevated concentrations of some chemical parameters, mainly biogens [6].

The study aimed at analyzing the phosphorus compounds concentrations in surface, interstitial, and groundwaters within two lowland catchments with various anthropopression levels.

Material and methods

Determinations of phosphorus compounds were conducted in two catchments of Białystok Height: afforested catchment of river Krzemianka localized within Knyszynska Forest and within urban catchment of river Jaroszwka near the city limits of Białystok [7, 8]. Analysis of phosphorus compounds in surface waters was made in 5 hydrometric profiles of river Krzemianka (7.2 km of water course – Kopisk village, 6.0 km of water course – Białystok–Augustow road, 3.0 km of water course – Rybniki village, 2.0 km of water course – below ponds in Rybniki village, 1 km of water course – afforested area) and in 5 profiles of river Jaroszwka (3.5 km of water course – below Raginis Street, 2.8 km of water course – near Skrzatow Street, 2.2 km of water course, 1.8 km of water course – at Saint Wanda track, final fragment of the river below fish ponds). Phosphorus compounds in shallow groundwaters near riverbeds and interstitial waters collected from 10, 30, 50, and 70 m depths of river bottoms, were analyzed in two hydrometric profiles of river Krzemianka (upper fragment – Białystok–Augustow road and lower section – below ponds in Rybniki village) and single profile of river Jaroszwka (near Skrzatow Street) [6]. Water samples for hydrochemical analyses were collected every two months in 2003–2004. In total, 60 samples of surface water from river Krzemianka, 96 samples of interstitial water, and 24 samples of groundwater from river Krzemianka catchment were collected. Considering the river Jaroszwka, 60 samples of surface, 48 samples of interstitial, and 12 samples of groundwater were collected.

Phosphorus forms were determined by means of spectrophotometry in accordance with ISO norms:

- orthophosphates (SRP) – molybdate method after sample filtration through GF/C filter;
- total phosphorus (TP) – molybdate method after acidification, UV digestion, and pH adjusting against phenolphthalein using diluted NaOH and H₂SO₄ solutions;
- organic phosphorus (OP) was calculated as a difference between TP and SRP.

Statistical processing was made with a help of Statgraphics 5.0 for Windows and Phreeqc Interactive 2.15 software. Statistical difference significance of chemical parameters in various water types was determined applying Duncan's multiple difference test.

Results and discussion

The SRP concentrations in river Krzemianka water amounted from 44 to 110 µgP/dm³. The highest values were recorded in the section closing the catchment, where

arable lands prevailed in adjacent areas [2]. In the forest part of the catchment, average SRP concentrations reached slightly above $70 \mu\text{g}/\text{dm}^3$. Mean TP concentrations in river Krzemianka water also oscillated within wide range from 147 to $717 \mu\text{gP}/\text{dm}^3$ (Fig. 1a).

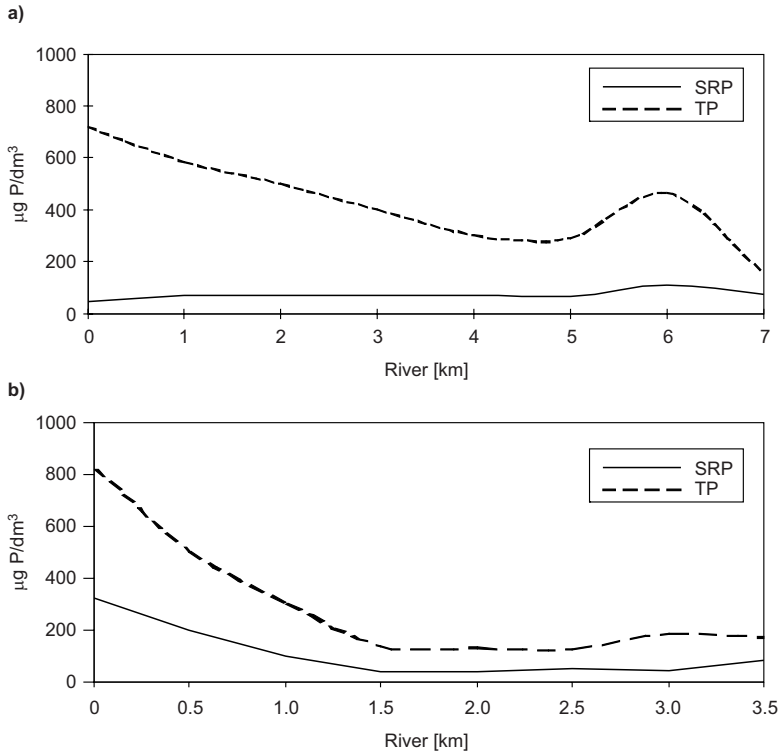


Fig. 1. Changes in concentrations of phosphorus along: a) the Krzemianka river, b) the Jaroszowka river
SRP – soluble reactive phosphorus; TP – total phosphorus

In urban fragment of the river, mean SRP concentrations were much higher than in forest-catchment river ($39\text{--}325 \mu\text{gP}/\text{dm}^3$). Particularly high mineral phosphorus concentrations were recorded in the section that drained the urban area. Average TP concentrations along the river Jaroszowka river changes in similar pattern as SRP: they varied from 125 to $819 \mu\text{gP}/\text{dm}^3$ (Fig. 1b).

Interstitial water from river Krzemianka catchment contained the highest concentrations of SRP, OP, and TP in relation to adjacent aqueous environments (Fig. 2a, b). In afforested part of river Krzemianka catchment, TP and OP concentrations in interstitial water were much higher than in waters adjacent to hyporheic zone. The highest SRP concentration was recorded in catchment of river Jaroszowka, in interstitial water, but differences in particular water types of that phosphorus form were not statistically significant (Fig. 2c). The highest TP and OP concentrations in that section

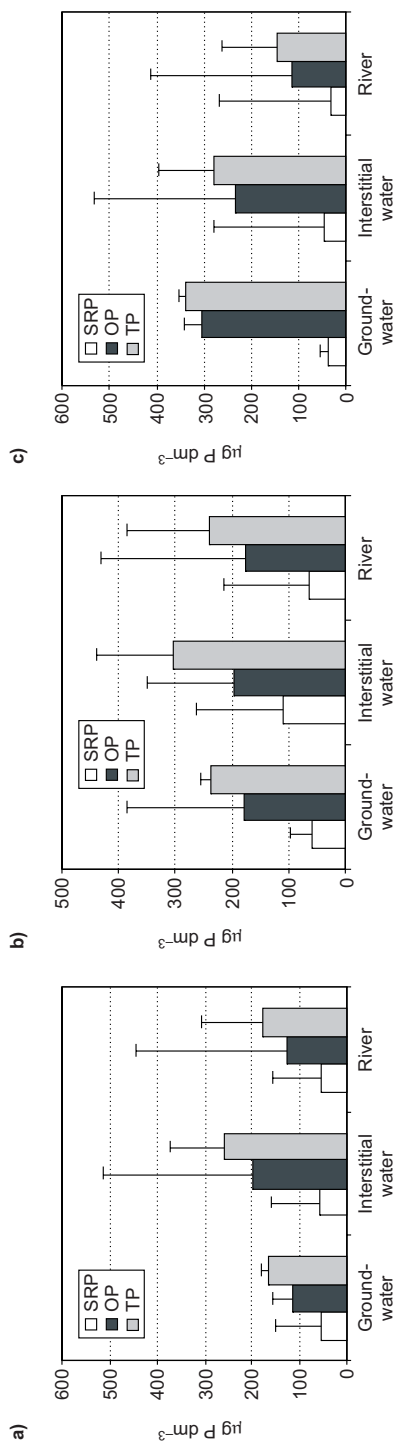


Fig. 2. a) The average (+standard deviation) concentration of phosphorus in groundwaters, interstitial waters and Upper Krzemińska river; b) The average (+standard deviation) concentration of phosphorus in groundwaters, interstitial waters and Lower Krzemińska river; c) The average (+standard deviation) concentration of phosphorus in groundwaters, interstitial waters and Jarosówka river
 SRP – soluble reactive phosphorus; OP – organic phosphorus; TP – total phosphorus

were found in groundwater. High SRP concentrations in river Jaroszowka water originated from leaky cesspits or poorly purified wastewaters. Performed study revealed that interstitial or groundwaters could be a source of phosphorus in small rivers. Vallett et al [9] claimed that phosphorus compounds in interstitial waters enrich surface water. Examinations made by Hendricks and White [10] revealed much higher inorganic phosphorus concentration in groundwaters than surface waters in various hydrological seasons.

Surface, interstitial, and groundwaters of studied catchments contained mineral phosphorus in forms of H_2PO_4^- and HPO_4^{2-} ions, and also CaHPO_4 and MgHPO_4 in lower Krzemianka river catchment. The groundwaters of upper Krzemianka and Jaroszowka rivers were characterized by considerable ability to dissolve the hydroxyapatite (calculated saturation indexes – SI – reached values of -4.13 and -5.57 , respectively), which could increase the amounts of mineral phosphorus dissolved in water of the spring fragments of rivers (Fig. 1a, b). In interstitial and surface waters of those profiles, SI indexes in relation to $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ reached values close to 0. In waters of river Krzemianka catchment, SI values in relation to hydroxyapatite were much lower (from -1.66 in groundwaters to -1.06 in surface waters). SI relating to vivianite – $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ – showed similar tendencies in all profiles: its highest values exceeding -5 were recorded in surface waters.

The SRP to TP ratios in different types of waters in river Krzemianka catchment were similar (Table 1). The SRP made up to about 30 % of TP in both sections of that catchment, which proves the neutrality of the Puszcza Knyszynska aqueous environment [1]. In groundwaters of Jaroszowka, SRP to TP ratio was twice as low as in surface ones. The SRP to OP ratio in river Jaroszowka river was also over twice as high as in groundwaters. Interstitial waters of lower Krzemianka river contained SRP to organic phosphorus ratio even up to 0.55, which was the highest among all recorded ones. It indicates considerable mineral phosphorus load delivered to the waters and originating from the surface areas from cultivated fields.

Table 1

The relationship between forms of phosphorus in waters

Type of water	SRP TP			SRP OP		
	Upper K*	Lower K	J	Upper K	Lower K	J
Groundwaters	0.31	0.25	0.10	0.46	0.32	0.12
Interstitial waters	0.22	0.34	0.16	0.29	0.55	0.19
Rivers	0.30	0.27	0.22	0.42	0.36	0.29

* K – Krzemianka river, J – Jaroszowka river.

Besides the influence of a man's activity, the phosphorus concentration changes may result from phosphate ions adsorbed on silt or organic particles. Such situation could be present in spring fragment of river Jaroszowka, where average SRP concentrations exceeded $300 \mu\text{gP}/\text{dm}^3$. The SRP sorption can occur at high inorganic phosphorus levels, while its low concentrations favor desorption. Under aerobic conditions,

dissolved phosphorus can form complexes with metal oxides and hydroxides giving insoluble sediments. High SI indexes relating to $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and calculated for river water indicate quite great possibility to migrate by mineral phosphorus forms in waters of Białystok Height rivers.

Conclusions

1. Concentrations of phosphorus forms varied along the river course with the change of anthropopression intensity within the catchment.
2. OP prevailed in all water types within studied catchments, and its mean concentrations amounted to $198 \mu\text{gP}/\text{dm}^3$ in groundwaters, $208 \mu\text{gP}/\text{dm}^3$ in interstitial, and $139 \mu\text{gP}/\text{dm}^3$ in surface waters.
3. SRP made up only 15% of TP in river Jaroszwka catchment, which indicates the supply of organic contaminants to surface and groundwaters in urban areas.
4. Higher phosphorus concentrations were recorded in interstitial rather than surface water, which during the intensive river drainage may contribute to significant eutrophication of flowing waters.

References

- [1] Bowes M.J., House W.A. and Hodgkinson R.A.: *Sci. Total Environ.* 2003, **313**, 199–212.
- [2] Withers P.J.A. and Jarvie H.P.: *Sci. Total Environ.* 2008, **400**, 379–395.
- [3] Brunke M. and Gonser T.: *Freshwater Biol.* 1997, **37**, 1–33.
- [4] Sophocleous M.A.: *The state of the science*. Hydrogeol. J. 2002, **10**(1), 52–67.
- [5] Boulton A.J., Findlay S., Marmonier P., Stanley E.H. and Vallett H.M.: *Ann. Rev. Ecol. Syst.* 1998, **29**, 59–81.
- [6] Jekatierynczuk-Rudczyk E.: *Pol. J. Environ. Stud.* 2006, **15**, 453–456.
- [7] Jekatierynczuk-Rudczyk E. and Zieliński P.: [in:] Michalczyk Z. (ed.), *Badania geograficzne w poznaniu środowiska*. Wyd. Uniwersytetu Marii Curie-Skłodowskiej, Lublin, 2004, 301–306.
- [8] Jekatierynczuk-Rudczyk E.: *Ecohydrol. Hydrobiol.* 2008, **8**(1), 77–87.
- [9] Vallet H.M., Fisher S.G. and Stanley E.H.: *J. North Am. Benthological Soc.* 1990, **9**, 201–215.
- [10] Hendricks S.P. and White D.S.: *Arch. Hydrobiol.* 1995, **134**(4), 459–490.

ZMIANY STĘŻEŃ ZWIĄZKÓW FOSFORU W WODZIE ZLEWNI NIZINNYCH O RÓŻNYM STOPNIU ANTROPOPRESJI

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Abstrakt: W pracy przedstawiono zmiany stężeń związków fosforu w rzekach pierwszego rzędu cechujących się różnym nasileniem antropopresji w zlewni (Krzemianka – zlewnia leśna, Jaroszwka – zlewnia w strefie podmiejskiej). Stężenia związków fosforu zmieniały się wzdłuż biegu rzek wraz ze wzrostem antropopresji w zlewni. W wodzie zlewni Jaroszwka zaledwie 15 % TP stanowił SRP, co wskazuje na dopływ zanieczyszczeń organicznych do wód powierzchniowych i podziemnych na terenie miejskim. We wszystkich typach wody w badanych zlewniach przeważał fosfor organiczny, a jego średnie stężenia wynosiły: $198 \mu\text{gP}/\text{dm}^3$ w wodach podziemnych, $208 \mu\text{gP}/\text{dm}^3$ w interstycjalnych i $139 \mu\text{gP}/\text{dm}^3$ w wodach powierzchniowych. W wodzie interstycjalnej stwierdzono większe stężenia badanych form fosforu, co w przypadku intensywnego drenażu rzecznoego może przyczynić do znacznej eutrofizacji wód płynących.

Słowa kluczowe: rzeki nizinne, wody interstycjalne, SRP (rozpuszczalny fosfor reaktywny), fosfor całkowity

Aleksander KIRYLUK¹

**CONCENTRATIONS OF NITRATES(V)
IN WELL WATERS IN THE RURAL AREAS
OF PODLASIE PROVINCE AND THE ASSESSMENT
OF INHABITANTS' HEALTH RISK**

**STĘŻENIA AZOTANÓW(V) W WODACH STUDZIENNYCH
NA OBSZARACH WIEJSKICH WOJEWÓDZTWA PODLASKIEGO
I OCENA RYZYKA ZDROWOTNEGO MIESZKAŃCÓW**

Abstract: The dug wells in some rural areas make up still the source of supply in potable water. In the period of 2008–2009, in the area of the Podlaskie province, the investigations of the nitrates(V) concentrations were conducted in waters of 11 rural wells in the catchments of Słina river. The area of investigations is characterized by quite intensive agricultural utilization (diary cattle farms).

Investigations showed that the concentration of nitrates(V) follows to the level of $26.40 \text{ mg NO}_3 \cdot \text{dm}^{-3}$ in well waters. Investigations showed that inappropriate location of the well in the premises of the farm, the improper technical parameters of the well and the migration of the nitrogen pollution from agricultural areas were the main reasons of the contamination of well waters by nitrates. The margin of health safety of people using the well water was assessed. In 3 among 11 of studied wells, water quality was below the safety health margin. The rest of studied wells contained water about the low safety margin.

Keywords: farmstead, dug wells, well waters, nitrates(V), health risk

According to the data of the end of 2008, in Poland 69.4 % of farmstead on the countryside had the connection to the public water pipe network and used treated water. However, there are essential disproportions between the amount of households located on the countryside and connected to the water pipe network. The most farmstead which use the water pipe network is in following provinces: Łódź (84.3 %), Wielkopolska (81.5 %), Świętokrzyskie (74.3 %) and Opole (72.0 %), but the least in West Pomerania (57.6 %), Warmia and Mazury (58.3 %), Lubuskie (58.8 %) and Małopolska (61.4 %) [1].

Substantial impact on the sanitary state of rural areas has the connection of farmstead to the water-pipe network and sewage treatment plant. In the end of 2008 in Poland

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19.4 % of farmstead used sewerage system. The most of farmsteads, which are seweraged, is in the following provinces: Podkarpackie (35.5 %), Pomerania (29.7 %) and Wielkopolska (24.5 %). The least amount of sewerage farmsteads, is in provinces of: Lublin (9.2 %), Lodz (12.0 %), Lubuskie (13.3 %) and Swietokrzyskie (13.5 %).

In spite of the existing water-pipe networks in the rural areas, it is widely observed that inhabitants of the countryside take water from wells to the direct or farming use but also to water animals and plants. It is caused by economical reasons and in order to cut costs, but it also comes from the conviction that the well water tastes better and is much healthier than piped water, which is not rationally proved. Taking into account chemical and bacteriological properties of dug well water, in many cases it should not be used to direct consumption and to the use in farmsteads.

Rural dug wells are supplied by water coming from first water-bearing layer, below which there are not or are rarely observed waterproof layers, that is why they have the contact with contamination caused by agriculture, mainly by liquid manure or mineral fertilizers. It causes worsening of water quality in the grounds of nitrates and other organic compounds and higher bacteria amount [2, 3]. Usually, this kind of water is not drinkable without previous treatment.

Nitrates(V) and nitrates(III) are ions which can be found in nature and are formed as the result of nitrogen compounds transformation. In natural conditions their concentration in surface water reaches usually some milligrams in 1 dm^3 . It is observed the increase of nitrates(V) content in groundwater, which is caused by agriculture intensification. Their concentration can reach the hundreds of milligrams in 1 dm^3 [4, 5]. The presence of nitrates in water is caused by the use of mineral and natural fertilizers in agriculture and sewage discharge to the surface water and to the ground. The main reasons of well waters contamination in the rural areas are:

- percolation to the ground water of liquid manure and others solutions coming from the wastes of animal production like for example from pile of cow dung or pig and cow house,
- natural processes of washing out of nitrates from plough land, pastures and meadows,
- nitrogen mineralisation in organic soils (mainly boggy soils).

Among the farmstead, the animal production usually occurs there. It results in the forming of animal excrements like cow dung, cow manure and poultry excreta. The activity conducted in the area of farmstead is a source of groundwater contamination by fertilizers ingredients, which means mainly nitrogen and phosphorus compounds [5]. These elements infiltrate into the depth of the soil profile and penetrate not only to the groundwater, but also as a result of ground outflow, to streams located nearby. The speed of their movement and the quantity of elements going into surface and ground waters depends mainly on the soil type.

Rural wells usually are not deep (with the depth of some to dozens meters). Water in these wells is exposed to contaminations from inappropriate stored animal excrements, but also from water flowing from the area of farmstead. Another source of these water contaminations is uncontrolled outflow of domestic sewage flowing from households, which are drained usually to closed wells functioning as cesspools. Contaminations,

which are introduced to ground by infiltration, penetrate into groundwater. In Poland, the main load of nitrogen compounds coming into shallow ground and surface waters has an origin in agriculture [5]. The land use, but also its intensiveness, influences the quantity of nitrogen load introducing into catchment.

In Podlasie province after 1990, there was observed the increase of milk production and nowadays about 25 % of the country production comes from this region of Poland. The largest farms with the dairy cattle breeding of farming character are located in the west part of this province. The clear increase of cattle population and the concentration of this production in this part of the province causes that livestock density is above $3 \text{ DJP} \cdot \text{ha}^{-1}$ (DJP – *large conversion unit*). Such a numerous livestock density and intensive grassland use can cause the excessive concentration of nitrogen compounds and their migration into the environment [6].

The use of well water, especially coming from shallow wells, can be the reason of periodic poisoning and can cause serious human and animal illnesses [7]. Nitrates(V) harmfulness is caused by their reduction into nitrates(III), which can pose direct risk to health causing methemoglobinemia, anemia, but also as the result of exogenic and endogenic processes they can be the source of carcinogenic nitrosamines [8].

The object of the experiment was the assessment of nitrates(V) concentration in well water in the arable areas in Podlasie province and the assessment of inhabitants health risk in these areas, which is caused by the use of water from ground dug well.

Material and methods

The area of the research was the catchment of the Slina river, which is located in the agricultural area, differentiated on the account of use intensiveness. In order to determine nitrates(V) concentrations in well water in the area of this river catchment, there were chosen 11 rural dug wells. The area of the catchment was divided into four parts, which were differentiated by environmental conditions and the way of ground use.

The wells of number 1–4 are situated on the lower course, where in the areas close to the river are mainly grasslands. Meadows, in majority, occur on boggy peat-muck soils. In this part of the valley, there is observed high concentration of dairy cattle breeding (up to do $3 \text{ DJP} \cdot \text{ha}^{-1}$) and intensive meadows and pastures use. The doses of mineral fertilization exceed $250 \text{ kg NPK} \cdot \text{ha}^{-1}$, while fertilization by liquid manure is also used. Cattle grazing in pastures near the stock yard is also done. Within the farmstead, there are located cow dung piles.

The wells of number 5–8 are located in the middle part of the river catchment and the majority of the areas constitute arable lands but also there are little enclaves of grasslands. In this part, the catchment is medium-intensively used, but there is the possibility of biogens flow from the arable lands which are located higher.

The wells of numbers 9–11 occur in the upper part of the river basin. This part of the catchment covers mainly intensively used meadows and pastures. Livestock density amounts $2\text{--}3 \text{ DJP} \cdot \text{ha}^{-1}$ and there is used mineral fertilization and liquid manure in doses similar to lower part of the basin.

The investigations were done in the period of 2008–2009. In the distance of some meters from analyzed wells, there were done soil pits in order to determine taxonomic unit of soil, take soil samples and determine the level of groundwater. Well water samples were taken in 6 periods in 2008 and 6 periods in 2009, so the sampling frequency was done in accordance with Health Minister Order from 2007 [9]. Nitrates(V) in dug well samples were determined by HACH DR-200 spectrophotometer. Statistic analysis of the results was done with the use of Statsoft Statistica 6.0 program. Chemical analysis results were compared with the norms included in the Health Minister Order considering water quality which is destined to consumption by people [9].

To assess the health risk caused by nitrates taken together with water were used suggestions of Alimentary Commission Codex FAO/WHO [10].

The assessment of nitrates risk caused by nitrates taken together with potable water by inhabitants of analyzed rural area was done by calculating of ADI (*Acceptable Daily Intake*), EDI (*Estimated Daily Intake*) and safety margin.

ADI means the quantity of chemical substance which adult can consume during his or her all life, probably without the damage to his or her health in accordance with the knowledge state. The ADI value for nitrates was determined in 1974 by Expert Committee FAO/WHO [11] on the level of $3.65 \text{ mg NO}_3 \cdot \text{kg}^{-1}$ body mass per day. Nitrates in potable water make up about 10 % of total value of ADI taken by nutritious way, so the ADI value taken with water can amount $0.365 \text{ mg NO}_3 \cdot \text{kg}^{-1}$ body mass $\cdot \text{day}^{-1}$ [7]. It was accepted that the average body mass is 70 kg so the ADI value amount $25.55 \text{ mg NO}_3 \cdot \text{day}^{-1}$. The EDI value was calculated on the basis of the formula:

$$\text{EDI} = \text{F} \cdot \text{R}$$

where: F – average daily water consumption [$2 \text{ dm}^3 \cdot \text{person}^{-1} \cdot \text{day}^{-1}$],

R – average level of nitrates(V) content in water.

Safety margin = ADI : EDI; the higher index value, the lower health risk.

On the basis of determined safety margin there were accepted the following ranges:

- < 1 – below the safety margin,
- 1–10 – low safety margin,
- 10–20 – medium safety margin,
- 20–30 – high safety margin,
- > 30 – very high safety margin.

Results and discussion

Impact of wells location and their environmental conditions on nitrates(V) concentration in water

The distance of wells supporting potable water for people and farming needs should amount at least 15 meters from farming buildings, cow dung piles and waste containers [12]. In the analyzed area, 7 wells were located closer than 15 meters from farming buildings. These wells were situated on light permeable soils on sandy deposits. The well of number 4 and 7 were quite shallow and located on light soils (Table 1).

Table 1

Localization and characteristics of farm wells

No. of well	Localization	Type of animal production	Distance of well from inventory buildings	Groundwater level		Soil type near well
				Well depth [m]	Groundwater level	
1	Makowo	Dairy cattle	12	8.5	1.8	Podzolic, loose sand
2	Mazury	Dairy cattle	17	7.0	1.3	Pseudo-podzolic
3	Lopuchowo	Dairy cattle	13	5.0	1.2	Brown developed from loams
4	Hermany	Dairy and fattening cattle	12	8.0	1.7	Podzolic
5	Kobylin Pieniaki	Dairy cattle	30	6.0	2.2	Chernozem
6	Kobylin Kruszewo	Dairy cattle	22	7.0	1.4	Strong loamy sands
7	Zawady	Dairy and fattening cattle	12	3.0	2.2	Podzolic, loose sand
8	Bruszewo	Dairy cattle	23	6.0	1.7	Strong loamy dusty sand
9	Szypulki Szymany	Dairy and fattening cattle	7	7.0	1.9	Light loamy sand
10	Zalesie Labeledzkie	Dairy cattle	12	6.0	1.5	Weakly loamy sand
11	Jablon Zarzeckie	Dairy cattle	10	5.0	2.4	Podzolic, loose sand

Table 2

Nitrites(V) concentrations in well waters within the of catchment area of Slina river in 2008 [$\text{mg NO}_3 \cdot \text{dm}^{-3}$], $n = 66$

No. of well	Determination dates							Mean
	March	May	June	August	September	November		
1	14.4	15.2	8.8	7.6	10.0	14.0	11.7	
2	2.8	6.0	3.2	1.9	3.7	4.1	3.6	
3	17.2	21.6	19.4	20.1	13.2	14.8	17.7	
4	7.4	8.6	4.9	3.3	8.2	2.6	5.8	
5	15.2	22.2	8.0	5.4	6.9	7.6	10.9	
6	15.6	20.6	9.5	5.9	12.4	19.7	13.9	
7	7.2	25.8	18.6	16.8	17.2	16.0	16.9	
8	7.4	3.6	3.1	9.4	5.0	4.2	5.5	
9	14.8	26.4	10.0	15.0	10.8	20.0	16.2	
10	6.2	7.4	6.7	4.6	5.1	4.6	5.8	
11	2.0	13.2	7.6	9.9	9.6	10.0	8.7	
Minimum	2.0	3.6	3.1	1.9	3.7	2.6		
Maximum	17.2	26.4	19.4	20.1	17.2	20.0		
Mean for 2008	10.6							
Median for 2008	9.1							
SD for 2008	6.2							
Minimum for 2008	1.9							
Maximum for 2008	26.4							

SD – Standard deviation.

Table 3

Nitrates(V) concentrations in well waters within the catchment area of Słima river in 2009 [$\text{mg NO}_3 \cdot \text{dm}^{-3}$], n = 66

No. of well	Determination dates						Mean
	March	May	June	August	September	November	
1	5.6	9.8	5.2	4.2	7.2	12.8	7.4
2	3.5	5.3	4.3	4.7	3.9	2.6	4.0
3	9.6	17.7	18.8	4.8	10.1	13.2	12.4
4	3.6	6.8	2.1	1.5	3.2	1.2	3.0
5	10.4	17.5	9.3	15.6	17.2	11.2	13.5
6	7.6	16.7	6.2	3.8	1.9	1.2	6.2
7	11.6	17.6	14.4	12.4	12.8	18.0	14.4
8	18.0	12.4	5.0	5.6	3.7	4.3	8.2
9	17.2	22.0	17.6	11.6	11.2	11.6	15.2
10	5.4	5.8	7.0	4.8	4.8	5.2	5.5
11	10.0	9.6	7.8	9.6	5.4	7.0	8.2
Minimum	3.5	5.3	2.1	1.5	1.9	1.2	
Maximum	18.0	22.0	18.8	15.6	17.2	18.8	
Mean for 2009				8.9			
Median for 2009				5.4			
SD for 2009				5.2			
Minimum for 2009				1.2			
Maximum for 2009				22.0			

SD – Standard deviation.

Higher access to water pipe network of the countryside, gives the possibility of higher water use, however while the lack of sewerage systems in most of the villages, it causes sewerage discharge into water, soil and leaky cesspools. The higher concentration of nitrates(V) was observed in wells of number 2, 7 and 9 (Tables 2 and 3), both in researches of 2008 and 2009. It can be assumed that it was caused mainly by little depth of these wells (3–7 m) but also little distance from inventory buildings.

The concentrations of nitrate nitrogen(V) in analyzed well water were differentiated, both in particular wells but also in particular months. The highest concentrations occurred in May 2008 and 2009.

Nitrates concentration is characterized by seasonal variability. The highest nitrates concentrations occur in early spring, and the least in high vegetation period (Fig. 1).

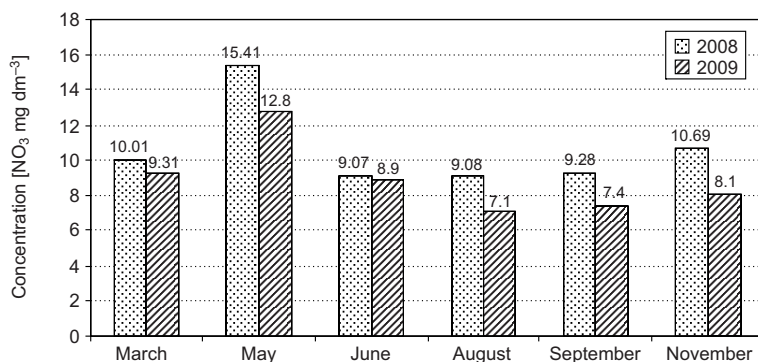


Fig. 1. Seasonal variability of nitrates(V) concentration in well waters in catchment of Slina river

In analyzed well water, there was not found the concentration above the level of $50 \text{ mg NO}_3 \cdot \text{dm}^{-3}$, so there was not exceed permissible standard for potable water [9]. It is assessed that nitrates move into the depth of ground with the speed of 1 m per year. Deeper layers of groundwater can be contaminated after some time and this contamination is stable and can be felt for many years [3, 5].

Nitrates in surface and shallow groundwater come mainly from rural areas. In surface water they fasten their eutrophication. Supply of these ions to the environment in a form of contaminations, to the large extend, is said to be caused by agriculture and human activity. It is estimated that 50–60 % of nitrogen introduced to Baltic Sea, comes from the area sources, which means agricultural lands. It is found that in water from 50 % of dug wells, the level of nitrates exceed permissible standard of $50 \text{ mg NO}_3 \cdot \text{dm}^{-3}$ [13].

Calculated median of nitrates concentrations in analyzed water of wells amounted $9.1 \text{ mg NO}_3 \cdot \text{dm}^{-3}$ in 2008 and $5.4 \text{ mg NO}_3 \cdot \text{dm}^{-3}$ in 2009, and the range of concentrations fluctuated between 1.2 to $26.4 \text{ mg NO}_3 \cdot \text{dm}^{-3}$ (Tables 2 and 3). Higher nitrates concentrations were found in researches in 2008, which can be connected with more intensive migration of nitrates caused by higher atmospheric rainfall in this year. The highest nitrate ions concentration was observed in water samples taken in May 2008 and 2009 from the well of number 7 and 9, which can be caused by technical parameters and the

location of these wells within the farmstead. In analyzed north-eastern region, vegetation starts far later comparing with the region of middle and western Poland, that is why in early spring nitrates were not taken in by plants and migrated together with surface flow. In this period, there is often used liquid manure on grasslands.

Assessment of inhabitants' health risk caused by nitrates(V) contained in water

Calculated values of ADI (*Acceptable Daily Intake*) and safety margin (Table 4) show that in 3 analyzed wells, nitrates concentration was below safety margin ($ADI/EDI < 1$). In the rest of 8 analyzed wells, nitrates concentrations were within the low safety margin ($ADI/EDI < 10$). It can be concluded that water from analyzed wells should not be used as potable water drunk by people.

Table 4

Mean nitrates(V) concentration, value of EDI and safety margin in rural wells waters

No. of well	NO ₃ concentration [mg · dm ⁻³]	EDI value [mg NO ₃ · person ⁻¹ · day ⁻¹]	Mean safety margin ADI/EDI
1	9.56	19.12	1.33
2	3.83	7.66	3.33
3	15.04	30.08	0.84
4	4.45	8.90	2.87
5	12.20	24.40	1.04
6	10.09	20.18	1.26
7	15.70	31.40	0.81
8	6.80	13.60	1.87
9	15.68	31.36	0.80
10	5.63	11.26	2.27
11	8.47	16.94	1.51
Mean	9.78	19.56	1.31

The researches done by Medical University in Bialystok [7], connected with the assessment of health risk and its estimations caused by nitrates presence in potable water consumed by inhabitants of Podlasie province, showed that 1.79 % of urban dwellers and 4.86 % of rural inhabitants took in nitrates(V) with tap water of lowered safety margin.

Water taken from water pipe network (supported by small intakes) can also be of the potential danger for health, because nitrates which are contained in potable water, due to their transformations, can cause various negative effects in human and animal organisms [14].

Conclusions

1. In intensive agricultural used areas of Podlasie province, there is observed water contamination in dug wells in effect of inappropriate location of wells within the

farmstead, improper technical parameters of wells but also nitrogen compounds migration into the environment.

2. Nitrates(V) concentrations ranged between 1.2 to 26.4 mg NO₃ · dm⁻³. These values do not exceed permissible standards for potable water.

3. There was stated clear seasonal variability of nitrates(V) concentrations, and the highest concentration occurred in early spring months.

4. Water in 3 among 11 analyzed wells, showed the relation of ADI/EDI below safety margin, which can caused negative effect on health in case of longer use.

5. There are needed further investigations on the quality of well and tap water in the rural areas, mainly on the grounds of health reasons.

Acknowledgements

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References

- [1] Informacja o stanie infrastruktury technicznej wsi na koniec 2008 roku. Ministerstwo Rolnictwa i Rozwoju Wsi, Departament Gospodarki Ziemią, Wydział Infrastruktury Technicznej i Techniki Rolniczej 2010 [online] <http://bip.minrol.gov.pl>.
- [2] Bombik T., Kolbuszewski T. and Mazurek J.: Zesz. Nauk. WSRP w Siedlcach, Zoot. 1989, **22**, 193–203 [in Polish].
- [3] Durkowski T., Burczyk P., Walczak B. and Wesółowski P.: [in:] Conf. Water as a factor determining the multi-functional development of countryside and agriculture. Proc. of IMUZ 1997, p. 147–152 [in Polish].
- [4] Koc J., Cieciko Cz., Janicka R. and Rochweger A.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 175–183.
- [5] Sapek A. and Sapek B.: Zesz. Eduk. IMUZ 2005, **10**, 27–38.
- [6] Kiryluk A.: Ochr. Środ. Zasob. Natur., IOŚ Warszawa 2008, **35/36**, 88–93.
- [7] Szczerbiński R., Karczewski J. and Filon J.: Roczn. PZH 2006, **1**, 39–48.
- [8] Raczuk J., Biardzka E. and Michalczyk M.: Woda – Środowisko – Obszary Wiejskie 2009, **9**, 1(25), 87–97.
- [9] Rozporządzenie Ministra Zdrowia z dnia 29 marca 2007 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi. DzU 2007, nr 61, poz. 417.
- [10] Alimentary Commission Codex FAO/ WHO: Progress report by WHO on prediction of dietary intake of pesticides. FAO/WHO CXPR 1994, **94/4**.
- [11] Evaluation of certain food additives: Twenty third report of the Joint FAO/WHO Expert Committee on Food Additives. Techn. Rep. Ser. **648**, WHO, Geneva 1980.
- [12] Rozporządzenie Ministra Infrastruktury z dnia 12 kwietnia 2002 r. w sprawie warunków technicznych, jakim powinny odpowiadać budynki i ich usytuowanie. DzU 2002, nr 75, poz. 690.
- [13] Wiśniowska-Kielian B. and Niemiec M.: Ann. UMCS, Sec. E 2006, **61**, 147–156.
- [14] WHO: Guidelines for Drinking-water Quality. Third edition, WHO, Geneva 2004, 417–420.

STĘŻENIA AZOTANÓW(V) W WODACH STUDZIENNYCH NA OBSZARACH WIEJSKICH WOJEWÓDZTWA PODLASKIEGO I OCENA RYZYKA ZDROWOTNEGO MIESZKAŃCÓW

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Abstrakt: Kopane wiejskie studnie przydomowe na niektórych obszarach wiejskich stanowią nadal źródło zaopatrzenia mieszkańców w wodę pitną. W latach 2008–2009 przeprowadzono badania stężeń azotanów(V)

w wodach 11 studni wiejskich na obszarze woj. podlaskiego w zlewni rzeki Ślina. Teren objęty badaniami charakteryzuje się dość intensywnym wykorzystaniem rolniczym (intensywne nawożenie, fermy bydła mlecznego).

Badania wykazały, że w wodach studziennych następuje koncentracja azotanów(V) do poziomu 26,40 mg $\text{NO}_3 \cdot \text{dm}^{-3}$. Głównymi przyczynami zanieczyszczenia wód studziennych azotanami są: niewłaściwe usytuowanie studni w obrębie zagrody, niewłaściwe parametry techniczne studni oraz migracja związków azotu z obszarów rolniczych. Określono margines bezpieczeństwa zdrowotnego mieszkańców korzystających z wód studziennych. Wody z 3 spośród 11 badanych studni wykazują wartość wskaźnika ADI/EDI poniżej marginesu bezpieczeństwa zdrowotnego. Pozostałe badane studnie zawierają wody o małym marginesie bezpieczeństwa.

Słowa kluczowe: zagroda wiejska, studnie kopane, wody studzienne, azotany(V), ryzyko zdrowotne

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SEASONAL CHANGES OF PHOSPHORUS RELEASE FROM THE BOTTOM SEDIMENTS OF RUSALKA LAKE DURING THE RESTORATION PROCESS

SEZONOWE ZMIANY UWALNIANIA FOSFORU Z OSADÓW DENNYCH W JEZIORZE RUSALKA W TRAKCIE ZABIEGÓW REKULTYWACYJNYCH

Abstract: Paper presents a comparative study of phosphorus (P) internal loading from bottom sediments in Rusalka Lake in years 2006 and 2007, when restoration measures were conducted and in 2005, a year before restoration.

Internal loading of P decreased as an effect of applied treatment. The mean loading in 2005 was $9.07 \text{ mg P m}^{-2} \text{ d}^{-1}$, whilst in next two years it was $4.36 \text{ mg P m}^{-2} \text{ d}^{-1}$ and $2.28 \text{ mg P m}^{-2} \text{ d}^{-1}$, respectively. The reduction reached 51 % in 2006 and 75 % in 2007. A domination of P release was noted in 2005 and 2006, amounting in summer to $38.1 \text{ mg P m}^{-2} \text{ d}^{-1}$ in the deepest place of the lake and $15.6 \text{ mg P m}^{-2} \text{ d}^{-1}$ in the littoral zone. A period of accumulation supremacy was observed in spring 2007, reaching $4.9 \text{ mg P m}^{-2} \text{ d}^{-1}$ in the littoral and $2.8 \text{ mg P m}^{-2} \text{ d}^{-1}$ in the profundal.

Keywords: bottom sediments, phosphorus, restoration

Rusalka Lake is a eutrophicated waterbody used for recreational purposes [1]. Deteriorated water quality, especially strong cyanobacterial water bloom, induced to undertake restoration treatment in the form of iron(III) sulphate(VI) (PIX) addition to the water. The addition of iron or alum to increase the sediment's sorption capacity is one of restoration methods aiming at P internal loading reduction [2]. The objectives of iron treatment are: (1) precipitation of P from the water body; (2) increase of the sediment's P-binding capacity; and (3) decontamination or precipitation of hydrogen sulphide [3].

The goal of the studies was to determine seasonal and spatial variability of P release from bottom sediments in Rusalka Lake before and during the restoration process.

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Material and methods

Study area

Rusalka Lake is a man-made reservoir with a surface area of 36.7 ha situated in the north-western part of Poznan City area. Its mean depth is 1.9 m, whilst the maximum depth is 9.0 m. The reservoir was created in 1943 as a result of damming the Bogdanka River valley and clay mining pits existing within the area [4]. As a major part of the bottom stays in contact with epilimnion waters (92 %), this lake should be recognized as a polymictic one. Thermal stratification comprises in summer only the deepest part, covering a small place of the bottom [1]. Due to close distance of the city centre and attractive areas situated around the lake, this waterbody is used for recreational purposes [4, 5]. Phytoplankton blooms caused by Cyanobacteria are observed mainly in summer period [1]. Mean retention time in Rusalka Lake is about 5 months [6]. Restoration measures in Rusalka Lake were conducted in the years 2006–2007 with the application of iron(III) sulphate(VI) (PIX-112). It was entered into the lake with the use of prototyped device by AERATOR company from Poznan. Six treatments were conducted between April and September (930 kg altogether) in 2006, while three in the same time in 2007 (350 kg altogether).

Studies of internal phosphorus loading from the bottom sediments were conducted in years 2005–2007: before (2005) and during the restoration measures (2006–2007). Internal P loading was estimated on the basis of *ex situ* experiments under laboratory conditions. Intact sediment cores were sampled to transparent plastic tubes with the use of a modified Kajak bottom sampler at two research stations every two months. Station 1 was situated in the deepest place of lake (9 m of depth), while station 2 in littoral area (2 m of depth). Each tube contained ca 15 cm of the sediment core together with ca 25 cm of the overlying water. They were kept in laboratory in darkness at the thermal and oxygen conditions similar to natural for about 2 weeks. P content was measured spectrophotometrically after mineralization with ascorbic acid as a reducer [7] every 2–3 days. Obtained data enabled the tracing of P change in water above the sediment and calculation of P release per 1 m² of sediments during 24 h. Internal loading was estimated separately for two zones of bottom sediments: zone I (33.9 ha, depth 0–4 m) and zone II (2.8 ha, depth > 4 m) [8]. The relations between P release indicated in the experiments and water temperature were calculated and used for estimation of the annual internal loading of P from bottom sediments, using temperature data measured in the lake. The total annual loading was a sum of loads calculated for the area of both zones.

Results

Significantly lower values of P release were noted for littoral area of the lake (zone I) than in profundal (zone II). The highest amounts in this zone were obtained in 2005, ranged from 2.3 mg P m⁻² d⁻¹ in January to 15.6 mg P m⁻² d⁻¹ in June. In 2006 noted values were lower – from 0.6 mg P m⁻² d⁻¹ in winter to 5.2 mg P m⁻² d⁻¹ in summer.

P accumulation was observed only in spring 2007 (to $4.9 \text{ mg P m}^{-2} \text{ d}^{-1}$), while in summer P release dominated with maximum in August ($8.6 \text{ mg P m}^{-2} \text{ d}^{-1}$, Fig. 1A). In zone II in 2005 the amounts of released P varied from $8.1 \text{ mg P m}^{-2} \text{ d}^{-1}$ (winter) to $29.8 \text{ mg P m}^{-2} \text{ d}^{-1}$ (autumn), while in 2006 from $14.4 \text{ mg P m}^{-2} \text{ d}^{-1}$ to $35.2 \text{ mg P m}^{-2} \text{ d}^{-1}$. In spring 2007 an accumulation was noted, reaching $2.8 \text{ mg P m}^{-2} \text{ d}^{-1}$, but in summer an intense P loading was found. The value noticed in August 2007 ($48.6 \text{ mg P m}^{-2} \text{ d}^{-1}$) was greatest in entire research period (Fig. 1B).

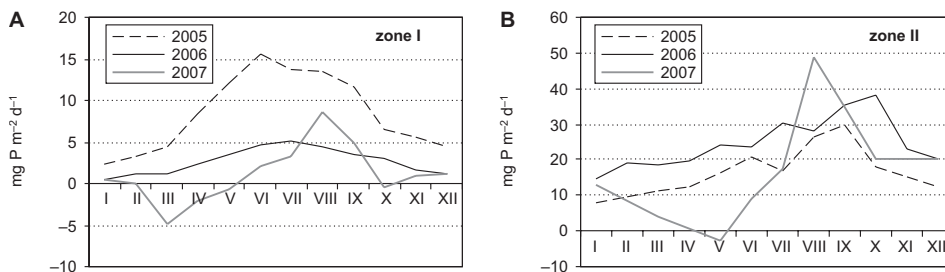


Fig. 1. The domination of P release or accumulation in bottom sediments in zone I (A) and zone II (B)

Total loading from both zones (weighted mean) was higher in 2005 than in years of restoration, reaching $16.0 \text{ mg P m}^{-2} \text{ d}^{-1}$ in June. The lowest values were noted in 2007, except late summer, when P release was greater than in the same time of 2006 (maximum in August 2007 $11.7 \text{ mg P m}^{-2} \text{ d}^{-1}$). An accumulation process was observed from March till May 2007 (Fig. 2).

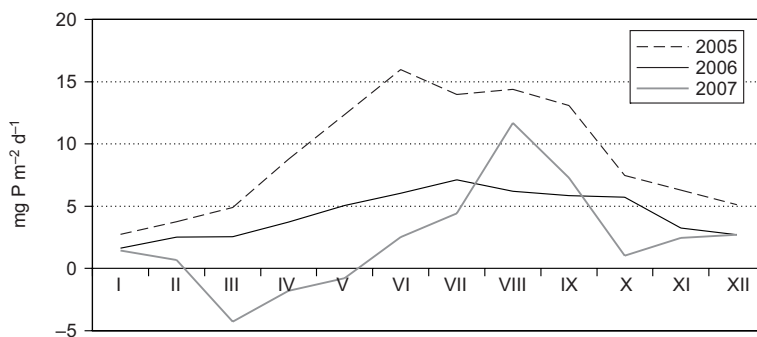


Fig. 2. The domination of P release or accumulation in bottom sediments (weighted mean from both zones)

Seasonal variability of internal loading was noted in both zones. In zone I the lowest values were observed in winter, whilst the greatest in summer. Higher values occurred in 2005 in all seasons with comparison with adequate periods of 2006 and 2007 (Fig. 3A). In zone II the amount of released P increased in summer and autumn. The highest amounts were observed in all seasons in 2006, reaching $32.2 \text{ mg P m}^{-2} \text{ d}^{-1}$, while in 2005 and 2007 did not exceed $27.5 \text{ mg P m}^{-2} \text{ d}^{-1}$ (Fig. 3B).

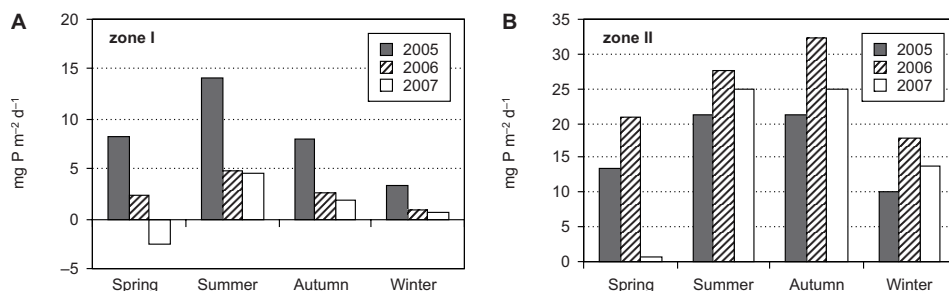


Fig. 3. Seasonal domination of P release or accumulation in bottom sediments of zones I (A) and II (B)

Total P release in both zones was also highest in summer (maximum – 14.8 $\text{mg P m}^{-2} \text{d}^{-1}$ in 2005). P accumulation was observed in spring 2007 (Fig. 4).

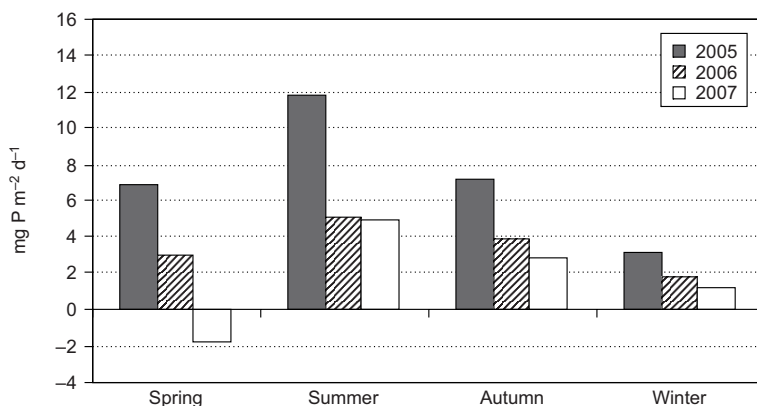


Fig. 4. Seasonal domination of P release or accumulation in bottom sediments (weighted mean from both zones)

The average internal loading in 2005 was $9.07 \text{ mg P m}^{-2} \text{d}^{-1}$ and decreased in 2006 to $4.36 \text{ mg P m}^{-2} \text{d}^{-1}$ in 2006 and to $2.28 \text{ mg P m}^{-2} \text{d}^{-1}$ in 2007. Therefore, the reduction amounted to 51 % in 2006 and 75 % in 2007.

The magnitude of P loads from sediments was higher in zone I as it covers 12 times greater bottom area than zone II. Maximum value was noted in June 2005 (5.28 kg P d^{-1}), while minimum – in February 2007 ($0.003 \text{ kg P d}^{-1}$). P accumulation dominated in spring 2007 (up to 1.68 kg P d^{-1}). In zone II the loads ranged from $0.014 \text{ kg P d}^{-1}$ in April 2007 to 1.36 kg P d^{-1} in August 2007. Marginal accumulation was also noted in that year (0.08 kg P d^{-1}). Total loads from both zones varied from 0.24 kg P d^{-1} to 5.86 kg P d^{-1} . Spring accumulation reached 1.56 kg P d^{-1} . The average load was highest in summer (3.35 kg P d^{-1}) and lowest in spring (0.95 kg P d^{-1}). Total internal P loading to the lake decreased from 1214.5 kg in 2005 to 584.1 kg in 2006 and to 304.7 kg in 2007 (4 times in comparison with the initial year) (Fig. 5).



Fig. 5. The average P loads from bottom sediments in zones I and II in Rusalka Lake in 2005–2007

Discussion

Greater internal P loading from the deeper part of the lake was a result of oxygen deficits occurring in this area [1]. In anaerobic conditions P bound with Fe was released [3, 9]. Hydrogen sulphide presence indicated reducing conditions in the sediments. This compound causes the reduction of Fe(III) and the formation of iron sulphide (FeS). In iron-rich sediments, the colour changes from brown (oxidized status) to black (reduced status) [3]. As zone II covers a marginal area of the bottom in Rusalka Lake, therefore thermal stratification in summer caused that P remained in the deepest place. Due to hot summer and thus rapid stratification formation (early spring) and oxygen depletion in the hypolimnion (data not presented here), high P release was noted in 2006.

In the littoral area good oxygen conditions remained throughout the all research period [1], therefore the amount of released P was lower than in zone II. However, this process was also observed in this zone [9–15]. Similar phenomenon was also noted in restored Uzarzewskie Lake [16]. Under aerobic conditions, P released as a result of microbial mineralization is transferred to the reductant-soluble, labile and pore water pools. In shallow waters pore water P concentrations remain low, probably due to wind-induced sediment resuspension. Large short-term release events result from the onset of anoxia where the reductant-soluble P pool is greatly depleted in mid-summer and winter [17]. As the littoral zone covers the prevalent part of the bottom (92 %), its role in P internal loading is significant.

P loading in littoral zone decreased as a result of applied iron treatment as the sorption complex was enriched with this element. In shallow, aerobic littoral P sorption on Fe was more intense than in profundal. P accumulation was even noted in the lake during spring, reducing the amount of P loads reaching lake ecosystem. It confirms the idea that the duration of internal loading can be reduced significantly by different restoration methods such as dredging to remove accumulated P or addition of iron or alum to elevate the sorption capacity of sediments [18]. Restoration treatment caused significant results rather in littoral area than in the deepest place. Such a great P load reduction was possible as the littoral zone covers over 90 % of bottom sediment. The water quality improvement is expected as the P concentrations in water decreased after restoration.

Acknowledgements

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References

- [1] Gołdyn R., Podsiadłowski S., Kowalczevska-Madura K., Dondajewska R., Szeląg-Wasielewska E., Budzyńska A., Domek P. and Romanowicz W.: *Ocean. Hydrobiol. Stud.* 2010, **XXXIX**(3), 65–80.
- [2] Søndergaard M., Jensen J.P. and Jeppesen E.: *Hydrobiology* 2003, **506–509**, 135–145.
- [3] Søndergaard M., Wolter K.D. and Ripl W.: [in:] Perrow M.R. and Davy A.J. (eds.), *Handbook of Ecological Restoration, Vol. 1, Principles of Restoration.* Cambridge University Press 2002, p. 184–205.
- [4] Gołdyn R., Jankowska B., Kowalczak P., Pułyk M., Tybiszevska I. and Wiśniewski J.: [in:] *The natural environment of the Poznań City.* Poznań City Office, Environment Protection Department, Poznań 1996, p. 45–69 (in Polish).
- [5] Pułyk M. and Tybiszevska E. (eds.): *The report on natural environment status in Wielkopolska province in 1994.* WIOŚ Poznań, The Environment Monitoring Library, Poznań 1995, p. 160 (in Polish).
- [6] Szeląg-Wasielewska E.: *Acta Hydrobiologica* 1992, **34**(4), 341–356.
- [7] Elbanowska H., Zerbe J. and Siepak J.: *Physico-chemical analyses of water.* PWN, Warszawa 1999, 232 p. (in Polish).
- [8] Kowalczevska-Madura K., Gołdyn R. and Dondajewska R.: *Ocean. Hydrobiol. Stud.* 2010, **XXXIX**(4), 135–144.
- [9] Boström B., Andersen J.M., Fleischer S. and Jansson M.: *Hydrobiol.* 1988, **170**, 229–244.
- [10] Kowalczevska-Madura K. and Gołdyn R.: *Polish J. Environ. Stud.* 2009, **18**(4), 635–643.
- [11] Drake J.C. and Heaney S.I.: *Freshwater Biol.* 1987, **17**, 513–523.
- [12] Uchmański J., Szeligiewicz W. and Loga M.: [in:] *Comparative Reservoir Limnology and Water Quality Management,* Straškraba M., Tundisi J.G. and Duncan A. (eds.), Kluwer Academic Publishers, Dordrecht 1993, p. 99–118.
- [13] Kleeberg A. and Dudel G.E.: *Mar. Geol.* 1997, **139**, 61–75.
- [14] Jiang X., Jin X., Yao Y., Li L. and Wu F.: *Environ. Pollut.* 2006, **141**, 482–487.
- [15] Dondajewska R.: *Ocean. Hydrobiol. Stud.* 2008, **37**(2), 89–97.
- [16] Kowalczevska-Madura K., Dondajewska R. and Gołdyn R.: *Limnological Review* 2008, **8**(4), 177–182.
- [17] Spears B.M., Carvalho L., Perkins R., Kirika A. and Paterson D.M.: *Hydrobiology* 2007, **584**, 37–48.
- [18] Søndergaard M., Jensen J.P. and Jeppensen E.: *Sci. World* 2001, **1**, 427–442.

SEZONOWE ZMIANY UWALNIANIA FOSFORU Z OSADÓW DENNYCH W JEZIORZE RUSAŁKA W TRAKCIE ZABIEGÓW REKULTYWACYJNYCH

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Abstrakt: Praca prezentuje zmiany uwalniania fosforu z osadów dennych w jeziorze Rusałka w latach 2006–2007, kiedy prowadzono rekultywację zbiornika z użyciem siarczanu(VI) żelaza(III).

W wyniku przeprowadzonych zabiegów rekultywacyjnych zasilanie wewnętrzne w fosfor z osadów dennych wyraźnie zmniejszyło się. Średnie zasilanie wewnętrzne przed wykonaniem zabiegów rekultywacyjnych wynosiło $9,07 \text{ mg P m}^{-2} \text{ d}^{-1}$, w kolejnym zmniejszyło się do $4,36 \text{ mg P m}^{-2} \text{ d}^{-1}$ (redukcja o 51 %), a w ostatnim roku do $2,28 \text{ mg P m}^{-2} \text{ d}^{-1}$ (redukcja o 75 %). W latach 2005 i 2006 stwierdzano wydzielanie fosforu z osadów dennych, dochodzące w okresie letnim do $38,1 \text{ mg P m}^{-2} \text{ d}^{-1}$ w obrębie głęboczka i do $15,6 \text{ mg P m}^{-2} \text{ d}^{-1}$ w litoralu. W ostatnim roku badań wiosną, nie następowało wydzielanie P z osadów, a kumulacja P osiągnęła $4,9 \text{ mg P m}^{-2} \text{ d}^{-1}$ w litoralu i $2,8 \text{ mg P m}^{-2} \text{ d}^{-1}$ na głęboczku.

Słowa kluczowe: osady dennie, fosfor, rekultywacja

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**SEASONAL CHANGES
IN SELECTED PHYSICOCHEMICAL PARAMETERES
OF SALINE WATER BODIES (CASE STUDY
OF RETENTION-DOSING RESERVOIR “BRZESZCZE”)**

**SEZONOWE ZMIANY
WYBRANYCH PARAMETRÓW FIZYKOCHEMICZNYCH
SŁONYCH ZBIORNIKÓW WODNYCH (NA PRZYKŁADZIE
ZBIORNIKA RETENCYJNO-DOZUJĄCEGO „BRZESZCZE”)**

Abstract: The paper presents results of physicochemical parameters (temperature, pH, conductivity, salinity, oxygenation, oxydation reaction potential, turbidity) in man-made water body.

The conducted studies indicated that anthropogenic saline reservoirs are typified by specific limnic processes. It concern especially myctic processes, which are distinctly different from those known from fresh water lakes. The “Brzeszcze” reservoir is of bradymictic type, characterized by advantage of stagnation over mixing. Differences in conductivity between bottom and surface waters within 3 meters varied from 5.4 mS · cm⁻¹ to 11.8 mS · cm⁻¹. The waters were also characterized by large decrease in oxygenation with depth and between seasons from more than 22 to ca 1 mg O₂/dm³. The hydrological situation in “Brzeszcze” is to the some extent similar an estuary. The movement of waters is determined by the process called “anthropomixing”. Another unusual feature was high short-term changes within 5 minutes in conductivity and turbidity probably associated with waving caused by wind.

Keywords: limnic processes, saline waters, anthropogenic water bodies, halophytes

Coal mine activity causes many negative consequences in natural environment. One of the most serious problems is output of coal mine saline waters. According to hydrological dictionary [1] mining waters are both waters flowing to pits from drained orogen and technological waters introduced with hydraulic stowage. In the area of Upper Silesian Coal Mine Industry majority of mine waters is characterized by high degree of salinity. According to qualitative classification there are four groups of

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mining waters [2]. These are fresh waters (I), industrial waters (II), brackish waters (III) and salt waters. Fresh waters are those in which general content of dissolved substances is estimated at not higher than $1.0 \text{ g} \cdot \text{dm}^{-3}$ and concentration of chloride and sulphate ions ($\text{Cl}^- + \text{SO}_4^{2-}$) lower than $0.6 \text{ g} \cdot \text{dm}^{-3}$. Mineralization of industrial waters ranges from 1.0 to $3.0 \text{ g} \cdot \text{dm}^{-3}$ and concentration of chloride and sulphate ions ($\text{Cl}^- + \text{SO}_4^{2-}$) varies between 0.6 to $1.8 \text{ g} \cdot \text{dm}^{-3}$. Brackish waters are characterized by range of the ion concentration from 3.0 to $7.0 \text{ g} \cdot \text{dm}^{-3}$. Salt waters are waters with mineralization $> 70 \text{ g} \cdot \text{dm}^{-3}$ and concentration ($\text{Cl}^- + \text{SO}_4^{2-}$) $> 42 \text{ g} \cdot \text{dm}^{-3}$.

As it was mentioned before, discharge of salt waters into surface streams caused many negative consequences in fresh water ecosystems. In order to reduce the negative influence of salt waters on environment many technical solutions are applied. One of such solutions is hydrotechnical method. It consists in keeping of salt waters in retention-dosing water bodies and next their controlled discharge into surface streams. Salt water discharge is most frequently performed in the period of high waters state. Then they become strongly diluted, and negative impact on ecosystem is minimalized.

Although, retention-dosing water bodies are objects of anthropogenic origin, however, from time to time they undergo the same processes as natural lakes. It concerns also remaining man-made water reservoirs [3]. High degree of salinity of retentioned waters lead to their distinctiveness of limnic processes in comparison with typical fresh water reservoirs. Therefore, such objects are named as “halinotrophic reservoirs” – the term introduced by Molenda [3]. It concerns only chemical (trophic) traits but it does not take into account genesis of reservoirs. Other halinotrophic reservoirs may be remaining anthropogenic water bodies as subsidence or exploitation hollow reservoirs. The term “halinotrophy” is being more and more popular in hydrological papers eg Jankowski and Rzetala [4].

The main goal of this work is to verify hypothesis that chosen limnic processes (mixing) in anthropogenic salt-water reservoirs are similar to those ones in natural fresh water reservoirs. In particular, it was examined: what seasonal changes in chosen hydro-chemical traits are ie between period of mixing (autumn-spring) and stagnation (winter-summer); whether there is a relationship between degree of oxygenation and content of chlorophyll; and if there is a distinct a relationship between oxygenation and pH in such objects. Finally, it was checked if the vicinity of the studied body halophytes grow.

Material and methods

Localization of the study area

According to physical-geographical division of Poland the investigated reservoir is situated in Oswiecim Valley in Brzeszcze. This water body was opened in 1979. The area of the reservoir is estimated at 27.5 ha and its capacity – $1\,155\,747 \text{ m}^3$. This object is supplied by mining waters from coal mine “Brzeszcze” – $7000 \text{ m}^3 \cdot \text{d}^{-1}$. They are characterized by low degree of salinification and were classified to III group. The reservoir water-storage capacity enables retention of mining waters apart from draining to Wisla River during 4–5 months. Discharge of salt waters to Wisla is performed by

bottom sluices of capacity $80\,000\text{ m}^3 \cdot \text{d}^{-1}$, what facilitates complete emptying of the reservoir within 14 days [5].

Methods

The measurements of selected parameters of water such as: temperature, pH, conductivity, salinity, oxygenation, oxidation reaction potential and turbidity as well as content of chlorophyll *a* were performed directly in the field using 6600 UPG Multi-Parameter Water Quality Monitor with terminal YSI 650 MDS every 0.5 of meter of depth. The measurements were collected every 5 seconds within 10 minutes. The point of profile studies were located in the deepest site in the water body close to flood-gate. Also these parameters were collected in other parts of the reservoir. Within a 5 m distance from the bank of the reservoir floristic inventory of vascular plants were done. Nomenclature of plant names follows Mirek et al [6]. The relationship between oxygenation and pH as well as oxygenation and content of chlorophyll for whole data set was examined by Spearman rank correlation using free R software (<http://www.r-project.org>).

Results

The conducted studies indicated that in the water body “Brzeszcze” there are high vertical gradients of selected traits of water environment. Even in autumn and spring differences in conductivity are to be found (Fig. 1).

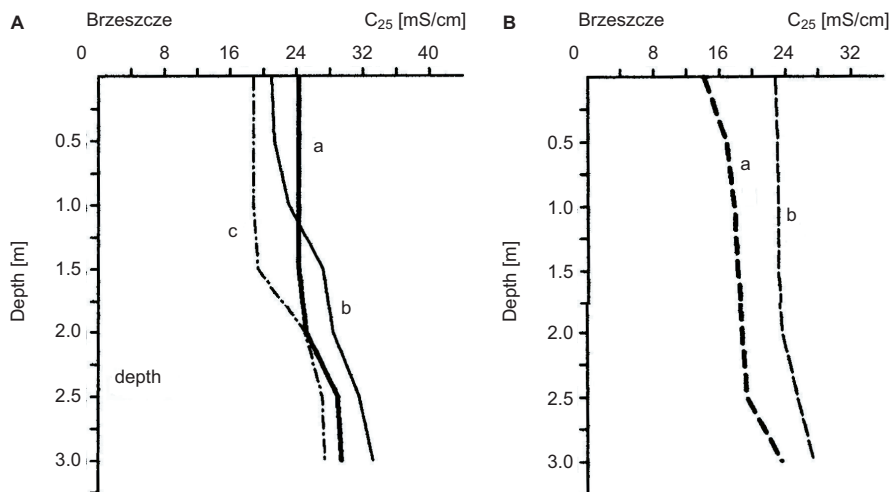


Fig. 1. Changes in conductivity of waters in vertical profile; A – autumn-spring (mixing): a – autumn 2008, b – spring 2008, c – spring 2006; B – winter-summer (stagnation): a – winter 2006, b – summer 2008

Despite that, maximal depth of reservoir during the studies amounted to 3 m (it can change due to level of accumulation) difference in conductivity of surface and bottom waters amounted to $5.4\text{ mS} \cdot \text{cm}^{-1}$. Higher differences were noted in spring – 11.8

$\text{mS} \cdot \text{cm}^{-1}$. Also in summer differences in conductivity between surface and bottom layer were apparent – $5.3 \text{ mS} \cdot \text{cm}^{-1}$.

Also “Brzeszcze” reservoir is typified by high vertical gradients of an oxygenation from the highest ca $22 \text{ mg O}_2/\text{dm}^3$ to the ca $1 \text{ mg O}_2/\text{dm}^3$. Both in spring, summer and in autumn in surface layer high oxygenation of water is being observed (Fig. 2).

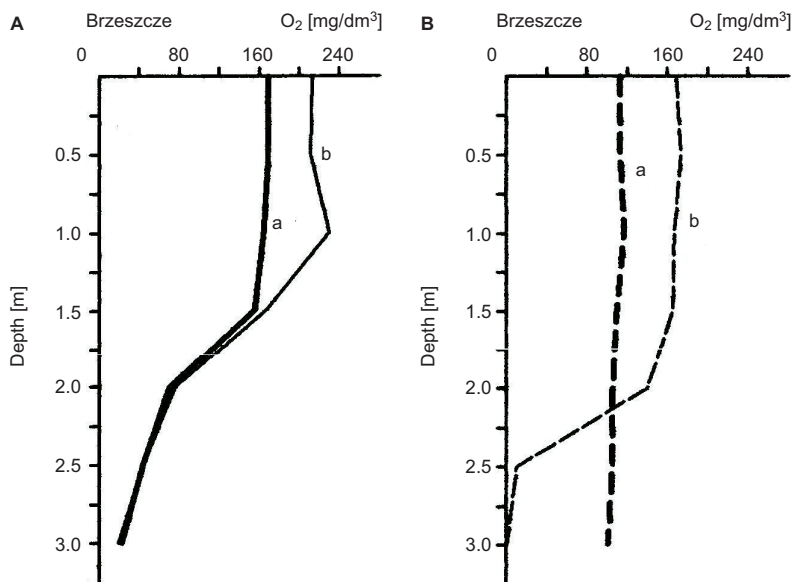


Fig. 2. Changes in oxygenation [$\text{mg O}_2/\text{dm}^3$] in vertical profile; A – autumn-spring: (mixing) a – autumn 2008, b – spring 2008; B – winter-summer (stagnation): a – winter 2006, b – summer 2008

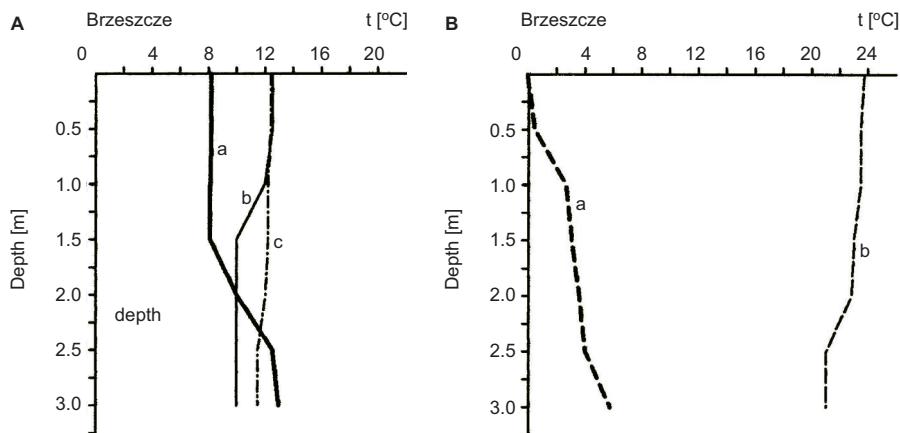


Fig. 3. Changes in temperature [$^{\circ}\text{C}$] of waters in vertical profile; A – autumn-spring (mixing): a – autumn 2008, b – spring 2008, c – spring 2006; B – winter-summer (stagnation): a – winter 2006, b – summer 2008

Analysis of temperature of water during spring shows that it is lower and not too much differentiated and amounts to ca 12 °C in whole vertical profile (Fig. 3).

Also in remaining periods gradients of temperature are low and do not exceed 4 °C. Despite this considerable gradients in conductivity are observed.

The aforementioned oxygenation of water is also manifested by a high value of correlation coefficient between value of oxygenation [%] and pH (Fig. 4).

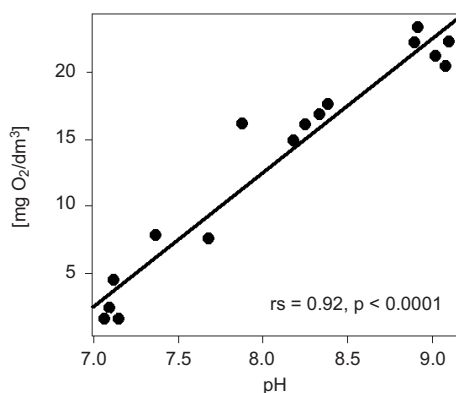


Fig. 4. Relationship between oxygenation [O_2/dm^3] and pH; data from three profile points

It is also confirmed by relationship between content of chlorophyll and value of oxygenation [%] (Fig. 5).

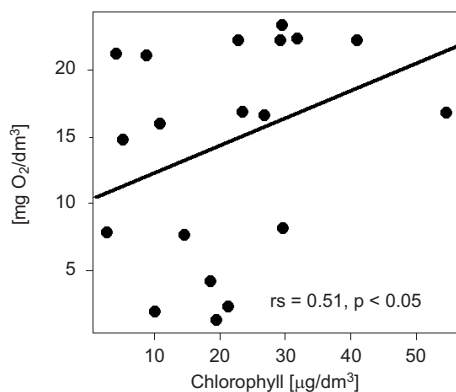


Fig. 5. Relationship between oxygenation [O_2/dm^3] and content of chlorophyll; data from three profile points

Since in surface layer saturation of oxygen in water is observed thus with increasing depth its successive decrease occurs. In bottom zone even in spring and autumn very low oxygenation of water below 2 mg O₂/dm³ was recorded. However, in summer there are anaerobic conditions.

Apart from gradients in vertical profile in water body dynamic changes in physical parameters of surface waters were noted. When waving was moderate (height of wave 0.25 m) conductivity within 10 min varied in the range from 20.023 to 21.609 $\text{mS} \cdot \text{cm}^{-1}$ (Fig. 6).

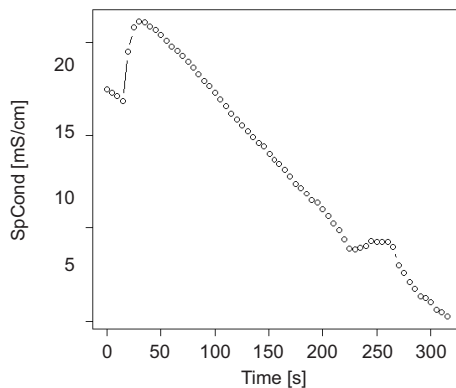


Fig. 6. Changes in conductivity of waters of Brzeszcze reservoir (online measurements every 5 seconds)

Thereby amplitude amounted to 1.585 $\text{mS} \cdot \text{cm}^{-1}$. Such high dynamics was noted at the case of turbidity which varied from 26 to 87 NTU (Fig. 7).

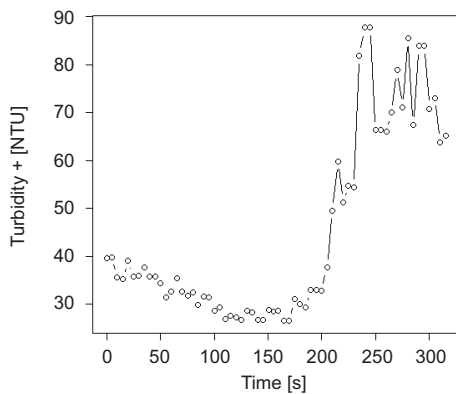


Fig. 7. Changes in turbidity of waters of Brzeszcze reservoir (online measurements every 5 seconds)

Dynamic changes of this parameter were the aftermath of resuspension of bottom sediments in littoral zone.

Discussion

Based on the studies it can be inferred that water body “Brzeszcze” is of bradymictic type, characterized by advantage of stagnation over mixing. Hampered mixing is an

aftermath of high differences in water density. Despite of this process, in this reservoir there is water circulation at the horizontal level in relation to inflow – outflow. Saline waters with higher density dropped to the bottom, whereas those ones with lower density remained in surface layer. Observed very high gradients in water mineralization are not frequently to be found in shallow reservoirs. Such reservoirs belong to group of polymictic water bodies characterized by many cycles of mixing within a year. Especially surprising are very high differences in mineralization of waters in spring and autumn. It is a period where temperature of water is constant, in which even in deep reservoirs thermal and density gradients decreased [7].

Additionally salt waters from surface layer are diluted by groundwaters and rainfall. The hydrological situation in “Brzeszcze” is to the some extent similar to an estuary. There are conditions for forming of salt-water wedge on which river fresh water are moved [8]. This reservoir is characterized by specific processes of water movement which can be determined as “anthropomixing”. The examples anthropomictic water bodies are also tanks responsible for water circulation in power plants [9].

When oxygenation of waters is concerned it should be concluded that such considerable oxygenation of water is a consequence of photosynthesis. Such relationship which is the effect of photosynthesis was revealed in numerous experimental studies [10, 11].

Taking into account seasonal changes and high vertical gradients in oxygenation similar results were obtained by Lange and Maslanka [12] in shallow lake Wierzcholek in Pomerania region. However, their observations concerned only summer. In spring and autumn there completed mixing took place and bottom waters releasing methane and sulphur hydrogen simultaneously becoming oxygenated. Also Molenda [13] reported similar oxygen conditions in shallow subsidence reservoir “Maroko” localized in Katowice. Deoxidation of bottom waters and high oxygenation of surface waters is a result of eutrophization of waters of reservoir [14]. Together with increasing depth value of redox potential changes. In surface layer always processes of oxidation take place but in bottom reduction processed were present.

Another very interesting feature of studied anthropogenic saline reservoir is very high dynamic short-term changes of physical parameters. The periodical changes within a day (in one hour intervals) in case of conductivity are known from literature [15] and can be high. In the cited study short-term changes were due to strong impact by the sea. Such changes could be result of hydrometeorological conditions (state of Baltic sea, speed and direction of wind, value of runoff from the catchment). In this study changes both in conductivity and turbidity probably are associated only with wind even if its wind speed was not very high but caused waving what influenced changes in physicochemical parameters of waters.

As it was aforementioned the water body “Brzeszcze” is a salt-water reservoir. Waters of the water body affect vegetation in littoral zone. It is reflected by the occurrence of halophyte species as *Puccinellia distans* – indicator of salt waters, obligatory halophyte [16], as well as abundant in this are facultative halophytes [17] *Chenopodium glaucum*, *Daucus carota*, *Agrostis capillaris*, *Trifolium repens*, *Calamagrostis epigeios* and *Centaurea jacea*. There were other present species assigned the

latter group eg *Equisetum arvense*, *Potentilla anserina*, *P. reptans*, *Plantago lanceolata*, *P. major*, *Achillea millefolium* and *Taraxacum officinale*.

Conclusions

1. The conducted studies indicated that halinotrophic reservoirs are typified by specific limnic processes. It concern especially myctic processes, which are distinctly different from those known from fresh water lakes. The hydrological situation in such objects can be similar to estuaries.

2. Conductivity and turbidity seem to be very unstable parameters probably due waving caused by wind, therefore they should be analyzed with a special caution.

References

- [1] Magnuszewski A. and Soczyńska U. (eds.): Międzynarodowy słownik hydrologiczny. Wyd. Nauk. PWN, Warszawa 2001.
- [2] Rogoż M.: Poradnik hydrogeologa w kopalni węgla kamiennego. Wyd. Śląsk, Katowice 1987.
- [3] Molenda T.: [in:] Jeziora i sztuczne zbiorniki wodne procesy przyrodnicze oraz znaczenie społeczno-gospodarcze. Uniwersytet Śląski, Sosnowiec 2005, p. 161–168.
- [4] Jankowski A.T. and Rzętała M.: [in:] Natural and human environment of Poland. A geographical overview, M. Degórski (ed.), PAN, Warszawa 2006, p. 86–92.
- [5] Wilk Z. (ed.): Hydrogeologia polskich złóż kopalin i problemy wodne górnictwa, t. 1. Uczelniane Wydawnictwa Naukowo-Dydaktyczne AGH, Kraków 2003, 610 p.
- [6] Mirek Z., Piękoś-Mirkowa H., Zając A. and Zając M.: Flowering plants and pteridophytes of Poland a checklist. PAN, W. Szafer Institute of Botany, Kraków 2002.
- [7] Choiński A.: Limnologia fizyczna Polski, Wyd. Nauk. UAM, Poznań 2008.
- [8] Allen P.A.: Procesy kształtujące powierzchnię Ziemi. Wyd. Nauk. PWN, Warszawa 2000.
- [9] Rzętała M.: Funkcjonowanie zbiorników wodnych oraz przebieg procesów limnicznych w warunkach zróżnicowanej antropopresji na przykładzie regionu górnos Śląskiego. Wyd. Uniwersytetu Śląskiego, Katowice 2008.
- [10] Neverova-Dziopak E.: Ekologiczne aspekty ochrony wód powierzchniowych. Ofic. Wyd. Politechniki Rzeszowskiej, Rzeszów 2007.
- [11] Tsvetkova L.L., Neverova-Dziopak E. and Usanov B.P.: [in:] Mat. 2 Międzunarodnaja jewroazjatska konf. "Putireszenija ekologiczeskich problem transportnych korridorow", St. Pieterburg, Russia 2000, p. 213–224.
- [12] Lange W. and Maślanka W.: Struktura tlenowa wybranych jezior Pojezierza Pomorskiego, Rocznik Fizycznogeograficzny, T. 1, Uniwersytet Gdańsk 1996.
- [13] Molenda T.: Rewitalizacja ekosystemów wodnych w warunkach zróżnicowanej antropopresji (na przykładzie Ekologicznego Systemu Obszarów Chronionych Katowic). Praca doktorska (maszynopis), Katowice 2002.
- [14] Lampert W. and Sommer U.: Ekologia wód śródlądowych. Wyd. Nauk. PWN, Warszawa 1996.
- [15] Cieśliński R.: [in:] Anthropogenic and Natural Transformations of Lakes. Polskie Towarzystwo Limnologiczne, vol. 3, pp. 53–58, Toruń 2009
- [16] Mirek Z. and Trzcńska-Tacik H.: Ecol. Pol. 1981, **29**(3), 343–352.
- [17] Wróbel M., Tomaszewicz T. and Chudecka J.: Polish J. Ecol. 2006, **54**(2), 303–309.

**SEZONOWE ZMIANY WYBRANYCH PARAMETRÓW FIZYKOCHEMICZNYCH
SŁONYCH ZBIORNIKÓW WODNYCH
(NA PRZYKŁADZIE ZBIORNIKA RETENCYJNO-DOZUJĄCEGO „BRZESZCZE”)**

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Abstrakt: Praca przedstawia wyniki badań parametrów fizykochemicznych wód (temperatura, pH, przewodność (przewodność), zasolenie, natlenienie, zawartość chlorofilu *a*, mętność) w zbiorniku pochodzenia antropogenicznego.

Przeprowadzone badania wykazały, że antropogenne słone zbiorniki wodne charakteryzują się specyficznymi procesami limnicznymi. Dotyczy to w szczególności procesów miksji, które są zupełnie inne niż w naturalnych akwenach wodnych. Zbiornik retencyjno-dozujący „Brzeszcze” należy zaliczyć do typu bradymiktycznego o przewadze stagnowania nad mieszaniem. Różnice w przewodności pomiędzy przydennymi a przypowierzchniowymi wodami w obrębie 3 metrów głębokości wahają się od $5,4 \text{ mS} \cdot \text{cm}^{-1}$ do $11,8 \text{ mS} \cdot \text{cm}^{-1}$. Wody charakteryzowały się również silnym spadkiem natlenienia wraz z głębokością i między porami roku z ponad $22 \text{ mg O}_2/\text{dm}^3$ do około $1 \text{ mg O}_2/\text{dm}^3$. Sytuację hydrologiczną w zbiorniku „Brzeszcze” można w pewnym sensie porównać do tych, jakie panują u ujścia rzek do mórz. W zbiorniku tym występują specyficzne procesy ruchu wód, które można by określić jako antropomiksja. Inną niezwykłą cechą są krótkookresowe, zachodzące w ciągu 5 min, duże zmiany przewodności i mętności, związane prawdopodobnie z falowaniem wywołanym przez wiatr.

Słowa kluczowe: procesy limniczne, wody słone, zbiorniki antropogenne, halofity

Marcin NIEMIEC¹ and Barbara WIŚNIEWSKA-KIELIAN¹

ASSESSMENT OF HEAVY METAL POLLUTION OF RAINWATERS FLOWING DOWN THE ROAD No. 4 TAKEN FROM RETENTION RESERVOIRS

OCENA ZANIECZYSZCZENIA METALAMI CIĘŻKIMI WÓD OPADOWYCH SPŁYWAJĄCYCH Z DROGI Nr 4 POBRANYCH ZE ZBIORNIKÓW RETENCYJNYCH

Abstract: Storm sewage flowing down the roads are collected in roadside retention, infiltration and evaporating reservoirs. Those reservoirs are the elements of rainy sewage system and the pre-cleaning process of runoff from surface of road carrying the considerable load of pollutants takes place in them. The aim of the study was to estimate the quality of rainwaters taken from retention reservoirs situated along the main-road No. 4 from Krakow to Bochnia section. Water samples were taken from the both sides of the road and Zn, Cu, Ni and Pb contents were determined.

Heavy metal concentrations in rainwaters collected from retention reservoirs are not high and in no cases exceed the standards admissible for surface waters. Considerable differences in the contents of analyzed metals were assessed between individual reservoirs. Higher concentrations were determined in water from tanks situated on the southern side of the route than on the northern one. Low concentrations of heavy metals in waters in the retention reservoirs may be a result of considerable amounts of organic and mineral suspension absorbing these pollutants in the bottom sediments.

Keywords: rainwaters, runoff, retention reservoirs, heavy metals, self-purification, water quality

Fast spreading urbanized areas and growing number of roads and highways lead to considerable quantities of rainwaters flowing off heavily anthropologically transformed terrains forming storm sewage [1]. They may contain great amounts of pollutants posing a hazard for the natural ecosystems [2]. The most serious agents polluting the runoffs include organic matter, heavy metals, oil derivatives or compounds extracted with petroleum ether [3]. Polish legislation [4] regards rainwaters as sewage which cannot be discharged into the receiver of water without pre-purification. The law on environmental protection describes rainwaters and snow-melt waters from polluted areas, cities,

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industrial areas, car-parks and roads, supplied to the ground or waters, by means of sewer systems. Introducing these waters to reservoirs or to the ground requires a special water supply and sewage effluent disposal consent. According to Decree of the Minister of Environment it is necessity of purification of rainwaters flowing down the roads to the level of total suspension at the outflow not more than $100 \text{ mg} \cdot \text{dm}^{-3}$ and $15 \text{ mg} \cdot \text{dm}^{-3}$ of oil derivative substances [4]. Retention, infiltration and evaporating tanks are constructed in order to collect, clean and evaporate rainwater from road drainage. They are situated, especially evaporating tanks, in the areas with high groundwater levels, where water discharge directly into the receiving water is difficult. Storing water originating from drainage of main road and highway with great throughput allows also to block these pollutants and to protect the neighbouring water ecosystems and groundwaters against pollution. Organic matter is capable of binding pollutants, particularly oil derivatives and some heavy metals, which together with the suspension become element of bottom sediments. Processes of water self-purification occurring in the reservoirs diminish the risk of pollutant penetration into the adjacent ecosystems with floodwater runoff or water overflow in the tanks.

The paper aimed at an assessment of quality of storm sewage collected in retention reservoirs situated along the national road No. 4 from section between Krakow and Bochnia.

Material and methods

Water samples were collected in May 2007 from 22 tanks. The national road No. 4 runs in the east-west direction. The water samples were taken from 11 basins on the southern side of the road and from 11 basins on its northern side. Water was filtrated and acidified with nitric acid and total concentrations of zinc, copper, lead and nickel were assessed after 10 times condensation using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) in JY 238 Ultrace Jobin Yvon Emission apparatus.

Results and discussion

Lead content in rainwaters from all analyzed retention tanks ranged widely, from 0.0023 to $0.021 \text{ mg} \cdot \text{dm}^{-3}$, and one may see considerable differences of this element concentrations registered in individual basins (Fig. 1).

Relative standard deviation for all basins was 69 %. Lead quantities found in road drainage waters were not high and only in 4 cases limit values for the highest quality class waters were exceeded, while only one sample was classified to the third quality class [6]. Wiśniowska-Kielian and Niemiec [7] found on average three times smaller contents of this element in waters of the Dunajec River and its tributaries. Lead content in storm sewage runoff from heavily anthropogenically transformed areas is generally very high. Gobel et al [8] registered mean contents of $0.225 \text{ mg Pb} \cdot \text{dm}^{-3}$ in drainage waters from German expressways, whereas this element concentrations in runoffs from German car-parks were on the level of $0.170 \text{ mg} \cdot \text{dm}^{-3}$. On the other hand Gnecco et al [9] registered lead contents of 0.006 – $0.025 \text{ mg Pb} \cdot \text{dm}^{-3}$ in the runoffs from urban

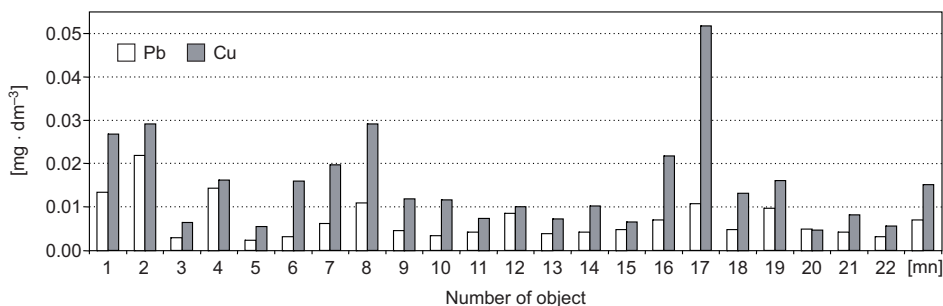


Fig. 1. Lead and copper concentration [$\text{mg} \cdot \text{dm}^{-3}$] in rainwater taken from retention tanks; mn – the arithmetical mean of all measurements

roads in Italy, which approximates the values obtained in the presented research. Barret et al [10] report lead concentrations in surface runoffs from housing estates in Austin, Texas, on the level of $0.016 \text{ mg} \cdot \text{dm}^{-3}$, whereas $0.041 \text{ mg} \cdot \text{dm}^{-3}$ was detected in runoffs from the city roads in the same place. Nordeidet et al [11] found lead content in runoffs from highways in the vicinity of Oslo on the level of even $0.7 \text{ mg} \cdot \text{dm}^{-3}$. Ball et al [12] stated that vehicle traffic intensity affects lead concentrations in the surface runoffs the most, despite withdrawal of lead as the fuel supplement.

Copper concentrations in the analyzed waters ranged from 0.0046 to $0.0517 \text{ mg} \cdot \text{dm}^{-3}$ (Fig. 1) with mean for all objects $0.0152 \text{ mg} \cdot \text{dm}^{-3}$. The average value of this element found in the Thames River water was $0.004 \text{ mg} \cdot \text{dm}^{-3}$ [13], whereas Wisniowska-Kielian and Niemiec [7] registered this element value in the Dunajec waters ranging from 0.0001 to $0.032 \text{ mg} \cdot \text{dm}^{-3}$. Like in case of lead, considerable differences in copper concentrations were assessed between individual objects; relative standard deviation was 74 %. A similar as for lead concentrations trend for this metal level between the investigated reservoirs was observed. Concentrations of this metal were not high and only five samples were classified to the 2nd water quality class, while water from only one tank was assigned to 3rd quality class [6]. Kayhanian et al [14] found mean contents of copper in the runoffs from California roads of $0.035 \text{ mg} \cdot \text{dm}^{-3}$, however the same authors point to great, sometimes several hundred-fold differences in this element levels between individual samples. Nordeidet et al [11] stated copper concentrations in the runoffs from expressways near Oslo of $0.1 \text{ mg} \cdot \text{dm}^{-3}$, while its contents noted in urban areas distanced from the highways were between 0.035 and $0.05 \text{ mg} \cdot \text{dm}^{-3}$.

Nickel concentrations in rainwaters collected from retention tanks were not high and fluctuated from 0.85 to $8.75 \mu\text{g} \cdot \text{dm}^{-3}$ (Fig. 2).

Critical value for 1st class of waters quality is $10 \mu\text{g} \cdot \text{dm}^{-3}$ therefore, with respect to their nickel concentrations, all analyzed samples were classified to waters of the best quality class [6]. Higher content of this element was found in the Thames water [13] and in dam reservoirs and rivers in the Upper Silesia Region [15]. Gobel et al [8] stated $24 \mu\text{g Ni} \cdot \text{dm}^{-3}$ in runoffs from German highways. The same author reports Ni concentrations of $10 \mu\text{g} \cdot \text{dm}^{-3}$ in runoffs from roads other than highways. Kayhanian et

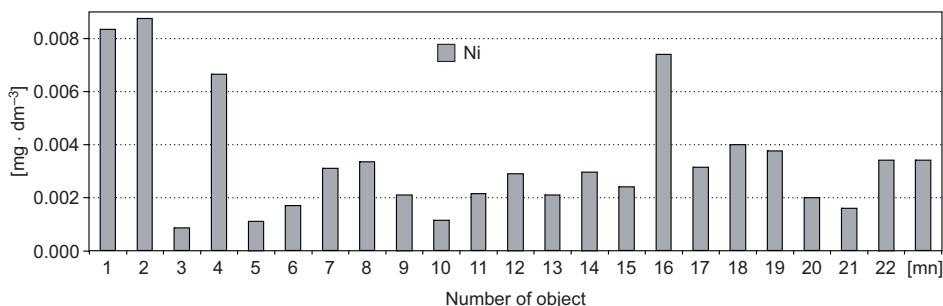


Fig. 2. Nickel concentration [$\text{mg} \cdot \text{dm}^{-3}$] in water of retention tanks; mn – the arithmetical mean of all measurements

al [14] in their research noted similar mean values in runoffs from California highways to obtained in the present investigations.

The quantities of zinc in the analyzed waters ranged from 0.26 to 0.492 $\text{mg} \cdot \text{dm}^{-3}$ (Fig. 3), whereas relative standard deviation for all basins was 82 %. Only two samples had greater amounts of this metal than the contents admissible for the 1st class quality of waters [6]. Kayhanian et al [14] report 0.241 $\text{mg} \text{Zn} \cdot \text{dm}^{-3}$ in runoffs from California highways and only 0.075 $\text{mg} \cdot \text{dm}^{-3}$ in runoffs from uninhabited areas. The highest concentrations of zinc are found in the runoffs from roofs covered with zinc coated sheets. Gromaire-Mertz et al [16] found over 30 $\text{mg} \text{Zn} \cdot \text{dm}^{-3}$ in runoffs from the roofs of houses in Paris, whereas zinc concentrations assessed by Gnecco et al [9] in the runoffs from Italian roads were reaching 0.081 $\text{mg} \cdot \text{dm}^{-3}$ and runoffs from roofs revealed about five times greater Zn amounts. Wisniowska-Kielian and Niemiec [7] report on average about four times lower zinc content in water of the Dunajec River and its tributaries than found in the analyzed waters.

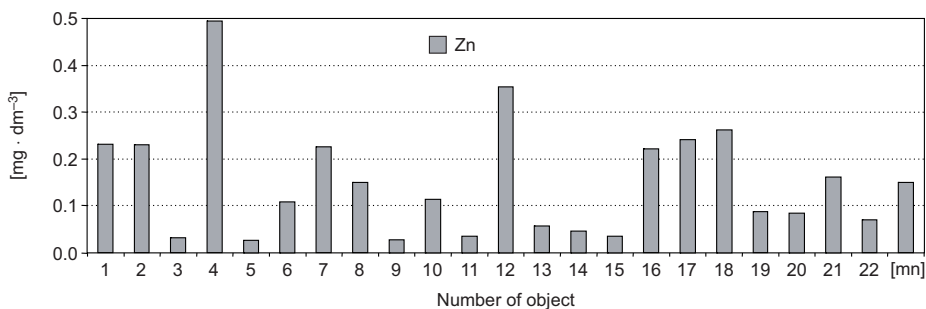


Fig. 3. Zinc content [$\text{mg} \cdot \text{dm}^{-3}$] in water of retention tanks; mn – the arithmetical mean of all measurements

The studied waters collected from retention reservoirs did not reveal high heavy metal concentrations and according to legal regulations could be discharged into wastewater receivers [4]. Much higher concentrations are registered in rivers and reservoirs situated in industrialized areas. Kostecki [15] states almost five times higher

concentrations of copper and zinc and over ten times greater contents of lead in the Klodnica River water flowing through the Upper Silesia Region.

Higher concentrations of all elements were registered in the reservoirs situated on the southern side of the road than in these on the northern side. This might have been caused by faster water evaporation in these tanks, which increased metal concentrations. Substantial differences in the contents of examined elements were found between the individual reservoirs. Wu et al [17] point to considerable differences in pollutant concentrations in runoffs from roads. Great differences of heavy metal contents in runoffs from antropogenically transformed areas are determined by precipitations, their frequency and intensity. The character of catchments is also very important, therefore element concentrations in runoffs may be vastly different between similar catchments [18]. Most elements originate from dry deposition and during rainfall are washed off the hardened surfaces [19]. The amount of metals in runoffs from roads depends on the contents of solid dust particles suspended in water, which greatly depends on traffic density [20]. Kazemi [21] found the strongest affinity of dust particles below 20 μg to heavy metals, ie the one whose largest numbers originate from vehicle traffic. Kayhanian et al [14] also point to relationships between dissolved and suspended metals. The values of suspended metals may be even several thousand times higher than the amounts dissolved in water [15, 22].

Metals, which are mostly present in a dissolved form are more mobile and bioavailable for living organisms. Lead poses the greatest hazard, while copper and nickel the smallest because these elements occur mainly in the unavailable forms. From among the investigated metals copper, zinc and lead are counted among pollutants strongly associated with intensity of motorization. Nickel assessed in runoffs from roads and highways originates mainly from other sources [12].

Conclusions

1. Heavy metal concentrations in waters collected from retention reservoirs situated along the national road No. 4 are not high and in no cases exceed the standards admissible for surface waters.

2. Considerable differences in the contents of analyzed metals were assessed between individual reservoirs.

3. Higher concentrations were determined in water from tanks situated on the southern side of the route than on the northern one.

4. Low concentrations of heavy metals in waters in the retention reservoirs may be a result of considerable amounts of organic and mineral suspension absorbing these pollutants in the bottom sediments.

References

- [1] Pratt G., Mantle J.D. and Schofield P.A.: *Water Sci. Technol.* 1989, **21**(8–9), 769–778.
- [2] Vaze J. and Chiew F.H.S.: *J. Environ. Eng.* 2004, **130**(4), 391–396.
- [3] Khan S., Lau S.L., Kayhanian M. and Stenstrom M.K.: *J. Environ. Eng.* 2006, **132**(3), 415–422.

- [4] Rozporządzenie Ministra Środowiska z dnia 29 listopada 2002 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego. DzU 2002, nr 212, poz. 1799.
- [5] Eriksson E., Baun A., Scholes L., Ledin A., Ahlman S., Revitt M., Noutsopoulos C. and Mikkelsen P.S.: *Sci. Total Environ.* 2007, **383**(1–3), 41–51.
- [6] Rozporządzenie Ministra Środowiska z dnia 11 lutego 2004 r. w sprawie klasyfikacji dla prezentowania stanu wód powierzchniowych i podziemnych, sposobu prowadzenia monitoringu oraz sposobu interpretacji wyników i prezentacji stanu tych wód. DzU 2004, nr 32, poz. 284.
- [7] Wiśniowska-Kielian B. and Niemiec M.: *Ecol. Chem. Eng.* 2004, **11**(8), 823–831.
- [8] Göbel P., Dierkes C. and Coldewey W.G.: *J. Contamin. Hydrology* 2007, **91**(1–2), 26–42.
- [9] Gnecco I., Berretta C., Lanza L.G. and La Barbera P.: *Atmos.c Res.* 2005, **77**(1–4), 60–73.
- [10] Barrett M.E., Zuber R.D., Collins E.R., Malina J.F., Jr., Charbeneau R.J. and Ward G.H.: A review and evaluation of literature pertaining to the quantity and control of pollution from highway runoff and construction (2nd edition). CRWR, University of Texas 1995, Rep. 239.
- [11] Nordeidet B., Nordeide T., Åstebøl S.O. and Hvitved-Jacobsen T.: *Sci. Total Environ.* 2004, **334–335**, 231–238.
- [12] Ball J.E., Wojcik A. and Tilley J.: Stormwater Quality from Road Surfaces – Monitoring of the Hume Highway at South Strathfield. University of New South Wales 2000, 204 p.
- [13] Neal C., Neal M., Hill L., and Wickham H.: *Sci. Total Environ.* 2005, **360**(1–3), 254–271.
- [14] Kayhanian M., Suverkropp C., Ruby A. and Tsay K.: *J. Environ. Manage.* 2007, **82**(2), 279–295.
- [15] Kostecki M.: *Arch. Ochr. Środow.* 2000, **26**(4), 75–94.
- [16] Gromaire-Mertz M.C., Garnaud S., Gonzalez A. and Chebbo G.: *Water Sci. Technol.* 1999, **39**(2), 1–8.
- [17] Wu J.S., Allan C.J., Saunders W.L. and Evett J.B.: *J. Environ. Eng.* 1998, **124**(7), 584–592.
- [18] Förster J. and Herrmann R.: Eintrag und Transport von organischen Umweltchemikalien über verschiedene Dächer in das Kanalsystem, Hydrologie bebauter Gebiete, Stoffaustausch aus der Kanalisation. Weinheim (VCH Verlagsgesellschaft) 1996.
- [19] Irish L.B., Barrett M.E., Malina J.F. and Charbeneau R.J.: *J. Environ. Eng.* 1998, **124**(10), 987–993.
- [20] Herrmann R., Daub J., Striebel T. and Robien A.: [in:] Schlussbericht des BMBF_Verbundprojektes Niederschlag, FKZ: 02WA93214, Band 1, München (Oldenbourg-Verlag) 1998, pp. 73–97.
- [21] Kazemi A.: *Schwermetallbelastung von Straßenkehrriecht auf Straßen mit unterschiedlicher. Kfz-Frequenz*, Forum Städte-Hygiene, Hannover 1989, **40**(2), 153–156.
- [22] Graham A. and Parker R.L.: *Geolog. Soc. Amer.* 2003, **35**(6), 144.

OCENA ZANIECZYSZCZENIA METALAMI CIĘŻKIMI WÓD OPADOWYCH SPŁYWAJĄCYCH Z DROGI Nr 4 POBRANYCH ZE ZBIORNIKÓW RETENCYJNYCH

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Abstrakt: Ścieki opadowe spływające z dróg są zbierane w przydrożnych zbiornikach retencyjnych, infiltracyjnych i odparowujących. Te zbiorniki są elementami systemu kanalizacji i zachodzi w nich proces podczyszczania spływów z dróg niosących znaczny ładunek zanieczyszczeń. Celem badań była ocena jakości wód opadowych pobranych ze zbiorników retencyjnych usytuowanych wzdłuż drogi krajowej nr 4 na trasie Kraków – Bochnia. Próbkę pobierano z obydwu stron drogi i oznaczono w nich zawartość Zn, Cu, Ni i Pb.

Stężenie metali ciężkich w wodach opadowych pobranych ze zbiorników retencyjnych nie było duże i w żadnym przypadku nie przekroczyło wartości dopuszczalnych dla wód powierzchniowych. Stwierdzono wyraźne różnice zawartości analizowanych metali w próbkach z poszczególnych zbiorników. Wyższe zawartości metali oznaczono w wodach opadowych ze zbiorników usytuowanych po południowej stronie drogi niż po północnej stronie. Małe stężenie metali ciężkich w wodach opadowych ze zbiorników retencyjnych może być wynikiem dużej zawartości zawiesin organicznych i mineralnych absorbujących te zanieczyszczenia w osadach dennych.

Słowa kluczowe: wody opadowe, zbiorniki retencyjne, metale ciężkie, samooczyszczanie, jakość wody

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PHYTOSOCIOLOGICAL AND ECOLOGICAL ANALYSIS OF LOWER SECTION OF THE KWACZA RIVER BEFORE RESTORATION (SLUPIA RIVER BASIN)

ANALIZA FITOSOCJOLOGICZNO-EKOLOGICZNA DOLNEGO ODCINKA RZEKI KWACZY PRZED RENATURYZACJĄ (DORZECZE SŁUPI)

Abstract: The 2.5 km long section of the Kwacza River (tributary of the Slupia River) was investigated in 2007 in terms of hydrochemistry and phytosociology. The aim was to assess the quality of river waters as well as to identify vegetation composition before the planned restoration of the river. Hydrochemical research was conducted four-times (spring, summer, autumn and winter) at the beginning and at the end of the studied river section. Additionally, hydrochemical measurements were performed in the Slupia River above the outlet of Kwacza in order to compare the results. Vegetation was studied according to the Braun-Banquet method and the results were presented in the form of phytosociological table.

The performed chemical analyses indicated that the river along its whole length had unclassified waters and the parameter which caused that situation was phosphorus content. Mineral forms of nitrogen over the vegetation period accumulated considerably due to biosorption in plants. The analysis of 174 phytosociological records revealed the presence of 15 phytocoenoses of *Potametea* and *Phragmitetea* classes, including seldom observed in Pomerania plant communities of *Ranunculion fluitantis* (*Callitricho-Batrachion*) alliance. The dominant position in the riverbed of *Sagittario-Sparganietum emersi* plant society as well as the dynamic development of *Elodeetum canadensis* were the result of water contamination which could further lead to elimination of valuable *Callitricho-Batrachion* plant communities of *Ranunculion fluitantis* alliance. The planned renaturation works should be conducted carefully due to the presence of legally protected plant species and natural habitats. First the water and sewage management should be regulated in the whole Kwacza drainage area.

Keywords: vegetation, river macrophytes, water hydrochemistry, renaturation, Kwacza River, tributary of Slupia River

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A river valley is a specific type of complex ecosystem with spatial continuity but also variability in transverse and longitudinal sections. Its structure is very rich, with considerable biological diversity [1, 2].

Phytosociological and ecological research of small Pomeranian rivers has been fragmentary so far, therefore their results can not be the basis of ecological state assessment according to the Water Framework Directive 2000/60/EC [3]. The investigations were focused on selected plant species, for example *Callitriche* sp. [4] or species of alliance *Ranunculion fluitantis* (= *Callitriche-Batrachion*) [5]. There is a lack of complex research on the ecology of river phytocoenoses in terms of their species composition, structure, distribution and dynamics.

The Slupia River with its tributaries is one of the main Pomeranian rivers, valuable from the natural point of view due to the presence of salmonid fish spawning grounds [6]. Therefore, the discussed area has been included in the European ecological network called Nature 2000 [7]. However, at the same time, it is a highly anthropogenically transformed river, particularly in its middle watercourse, which destabilizes the functioning of riparian ecosystems [8]. The Kwacza River, one of the largest tributaries of Slupia, was highly transformed at the beginning of the XX century. The applied regulation works mostly consisted in riverbed straightening and the application of weirs [8]. The water and sewage management in the discussed river basin has not been regulated so far. Transformations the riverbed as well as water contamination have caused changes in habitat conditions of river hydrobionts.

Therefore, the restoration works have been carried out since 2007 in the lower Kwacza River section. They constitute the part of research project "Protection of Atlantic salmon and migratory trout spawning grounds in the Slupia river basin", managed by the Slupia River Basin Landscape Park and financed by EkoFundusz. Restoration of the river consisted in the application of various deregulation solutions, which effects has been monitored. The biomonitoring includes various, interdisciplinary environmental analyses [9].

The aim of this study was to reveal macrophyte structure and its dependence on hydrochemical conditions in the outlet section of the Kwacza River, before restoration.

Material and methods

Study area

The Kwacza River is a left-sided tributary of the middle Slupia River and drains the area of 85 km². Its length is equal to 21 km. According to the physico-geographical division of Poland [10] Kwacza is located in the mesoregion Rownina Slupska (313.43) being a part of macroregion Pobrzeze Koszalinские (313.4).

The hydrological regime of Kwacza is characterized by ground, rain and snow supply. Mean water flow is 0.97 m³ · s⁻¹. Unitary outflows from the drainage area are rather high compared with other rivers of the region and amount to 13 dm³ · s⁻¹ · km⁻². Water supply of the Kwacza River measured as annual outflow is equal to 34.89 mln m³ with more than half (54 %) occurring in winter [11].

The Kwacza hydrographic network consists in small watercourses, often highly transformed by hydrotechnical works, particularly in the outlet section. Almost the whole river basin is meliorated. Riparian areas has been considerably drained and now are used as grassland [12]. The present structure of use of the river basin is predominated by arable areas, particularly in the upper and middle parts of the discussed basin [8].

The research included vegetation and hydrochemical analyses of Kwacza waters. 10 sampling profiles K1–K10 (Fig. 1) were located at the 2.5 km long outlet section of the Kwacza River, at sites the restoration works were planned [9]. In this study was used the results of hydrological research conducted within the framework of Kwacza restoration project [11]. Hydrochemical carting was performed 4 times (spring, summer, autumn and winter) in 2007 at 10 profiles located along the water course (Fig. 1). At each profile samples were taken from 3 sampling sites – by both river banks and in the middle of riverbed. In this study we only compared site K1 (beginning of the studied section) with K10 (end of the studied section). Additionally, hydrochemical analyses of Slupia waters above the outlet of Kwacza were performed (Table 1). The following physicochemical parameters were measured every three months using multi-parameter water quality sonde YSI 6600: water temperature, electrolytic conductivity (SEC), reaction (pH), redox potential (Eh), dissolved oxygen concentration, oxygen saturation, turbidity, chlorophyll content, dry residue, salinity as well as $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Cl concentrations. At the same time water samples were taken for the purpose of laboratory analyses, in which PO_4 , total phosphorus, Ca, Na, K and Mg contents were determined using the appropriate methodology [13]. Water quality classification into 5 grades was performed according to the Decree of the Minister of Environment from the

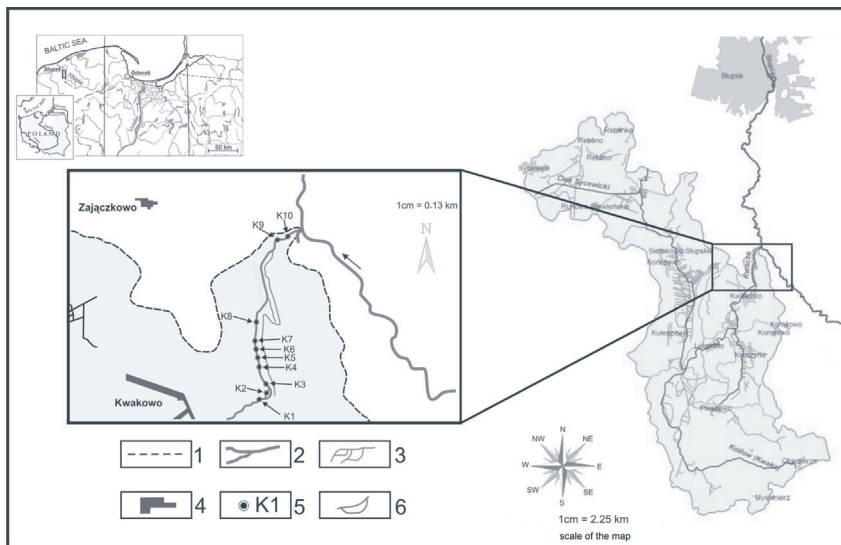


Fig. 1. The Kwacza River Basin and location of the research object: 1 – range of the river basin, 2 – rivers, 3 – melioration ditches, 4 – town/village, 5 – research sites – profiles, 6 – new riverbed sections

Table 1
 Physico-chemical parameters of the Kwacza waters (sampling site K1 and K10) against the background of physicochemical characteristics of the Słupia River; \pm SD – standard deviation; CV – coefficient of variability; II, III, IV, V denoted in superscript – classes of waters quality according to the Decree of the Minister of Environment [11, 14]

Parameter	Kwacza K 1					Kwacza K 10					Słupia (142 km)				
	Average	Max	Min.	\pm SD	CV	Average	Max	Min.	\pm SD	CV	Average	Max	Min.	\pm SD	CV
Water temperature [°C]	10.06	16.26	3.27	4.78	47	10.04	16.43	3.15	4.82	48	9.36	17.02	2.76	5.67	61
Electrolytic conductivity [$\text{mS} \cdot \text{cm}^{-1}$]	0.37	0.39	0.35	0.01	3	0.37	0.39	0.36	0.01	3	0.35	0.37	0.34	0.01	3
Reaction [pH]	7.72	8.03	7.45	0.21	3	7.73	8.29	7.34	0.28	4	7.72	8.08	7.05	0.35	5
Eh [mV]	153	210	66	46	30	154	198	125	31	20	157	212	82	53	34
Turbidity [NTU]	6.20	20.96	1.63	6.77	109	5.64	17.42	1.78	5.50	98	4.34	10.80	1.78	3.35	77
Chlorophyll [$\mu\text{g} \cdot \text{dm}^{-3}$]	8.34	13.47	3.85	2.98	36	7.88	13.95	4.01	3.16	40	7.73	19.89	3.51	6.19	80
Dissolved oxygen [$\text{mg} \cdot \text{dm}^{-3}$]	8.25	12.15	3.29	3.22	39	8.91	13.84	3.13	3.95	44	7.98	13.16	2.04	4.13	52
Oxygen saturation [%]	74.0	113.6	28.4	30.3	40.9	80.5	133.2	27.0	38.1	47.3	70.2	101.6	17.3	36.1	51.3
COD_5 [$\text{mg} \cdot \text{dm}^{-3}$]	23.04 ^{III}	43.60	12.80	10.10	44	23.74 ^{III}	44.40	13.60	10.61	45	14.42 ^{II}	17.20	12.00	2.23	15
Dry residue [$\text{mg} \cdot \text{dm}^{-3}$]	0.24	0.25	0.23	0.01	3	0.24	0.25	0.24	0.01	3	0.23	0.24	0.22	0.01	3
Ash content [$\text{mg} \cdot \text{dm}^{-3}$]	0.18	0.19	0.17	0.01	4	0.18	0.19	0.17	0.01	4	0.17	0.18	0.16	0.01	4
Ca [$\text{mg} \cdot \text{dm}^{-3}$]	53.74	59.00	47.50	3.85	7	56.49	60.40	53.00	3.63	6	50.00	55.20	45.70	3.96	8
Na [$\text{mg} \cdot \text{dm}^{-3}$]	8.56	10.00	4.80	1.71	20	9.11	9.60	8.30	0.52	6	8.38	10.00	3.20	2.60	31
K [$\text{mg} \cdot \text{dm}^{-3}$]	2.49	2.80	2.00	0.33	13	2.56	3.00	2.10	0.29	11	2.33	2.70	2.00	0.33	14
Mg [$\text{mg} \cdot \text{dm}^{-3}$]	6.76	9.70	5.30	1.48	22	6.54	8.40	5.30	1.12	17	6.93	10.60	5.10	1.94	28
Cl [$\text{mg} \cdot \text{dm}^{-3}$]	24.99	44.37	11.47	12.73	51	25.40	35.23	15.38	8.55	34	19.03	29.80	9.00	8.60	45
HCO_3 [$\text{mg} \cdot \text{dm}^{-3}$]	119	128	114	5	5	119	128	114	5	5	137	185	114	30	22
$\text{NO}_2\text{-N}$ [$\text{mg} \cdot \text{dm}^{-3}$]	0.030	0.069	0.007	0.024	80	0.037	0.086	0.012	0.028	77	0.022	0.058	0.004	0.023	103
$\text{NO}_3\text{-N}$ [$\text{mg} \cdot \text{dm}^{-3}$]	0.70	0.99	0.20	0.25	35	0.70	1.15	0.26	0.27	38	0.38	0.79	0.13	0.21	57
$\text{NH}_4\text{-N}$ [$\text{mg} \cdot \text{dm}^{-3}$]	0.15	0.67	0.01	0.22	151	0.13	0.66	0.01	0.22	169	0.15	0.58	0.01	0.20	137
N_{min} [$\text{mg} \cdot \text{dm}^{-3}$]	0.88	1.10	0.71	0.13	15	0.87	1.18	0.68	0.18	21	0.55	1.01	0.18	0.34	61
$\text{PO}_4\text{-P}$ [$\text{mg} \cdot \text{dm}^{-3}$]	0.28 ^{II}	0.37	0.21	0.07	25	0.28 ^{II}	0.43	0.20	0.09	33	0.15	0.21	0.11	0.04	30
P_{total} [$\text{mg} \cdot \text{dm}^{-3}$]	1.18 ^V	1.78	0.76	0.37	32	1.04 ^V	1.56	0.64	0.35	34	0.83 ^{IV}	1.51	0.25	0.49	60

11th of February 2004 on the classification used in surface and ground water quality assessment, guidelines for monitoring and the interpretation of results [14].

Vegetation research was performed in July 2007 along the 2.5 km long outlet section of the Kwacza River. For the purpose of biomonitoring, the detailed floristic lists were made at 10 sampling profiles located along the water course, at which restoration works were supposed to be performed [9]. At each profile there were 3 lists prepared, separately for 3 sampling sites. Apart from the selected profiles also all the distinct vegetation lobes were analysed. Altogether 174 phytosociological records were taken which later were presented in the form of synthetic table (Table 2). It included the number of phytosociological records, number of species, cover of herb layer and the area of vegetation lobes. The constancy degree and cover coefficient for a given plant species were calculated from at least 5 phytosociological records. Additionally the frequency of occurrence and cover coefficients for the consecutive species were given in the Table 2. The nomenclature was used according to Mirek [15]. The share of rare and endangered species was determined on the basis of the following studies by Zukowski and Jackowiak [16] and Jasnowska and Jasnowski [17]. The syntaxonomy of plant communities used was according to Matuszkiewicz [18] as well as Brzeg and Wojterska [19].

Results and discussion

Hydrochemical parameters and water quality

The Kwacza River is considerably influenced by anthropopression in terms of physico-chemical parameters, even more than the Slupia River. That results in higher concentrations of most of the factors connected with anthropogenic source of supply comparing to Slupia [11].

The analysis of concentrations of nitrogen mineral forms in the Kwacza River revealed that they accumulated by biosorption mainly in the river valley (buffering zone). The contents of $\text{NO}_3\text{-N}$ at sites K1 and K10 were significantly lower than the average for the whole study period (ie $0.7 \text{ mg} \cdot \text{dm}^{-3}$) and reached the level of $0.57 \text{ mg} \cdot \text{dm}^{-3}$. The low content of nitrates is typical for eutrophic waters, when in summer nitrates are removed mainly by aquatic vegetation. Conducted study indicated the increase in nitrate concentration over winter both in Kwacza and Slupia Rivers and then the content of $\text{NO}_3\text{-N}$ was higher at site K10 than at K1.

The concentration of $\text{NH}_4\text{-N}$ over the study period varied considerably and showed the downward trend along the watercourse. The coefficient of variability (CV) for ammonium nitrogen at site K1 was high and equal to 151 % while at site K10 it reached 169 %. $\text{NH}_4\text{-N}$ content was by around 12 % lower at K10 than at K1.

Among the other parameters analysed the attention should be paid to COD-Cr as an indicator of rate of biogeochemical processes. The level of COD at sites K1 and K10 reached on average $23 \text{ mg} \cdot \text{dm}^{-3}$ and varied between 12.80 and $44.40 \text{ mg} \cdot \text{dm}^{-3}$. The section of the Kwacza River to be restored underwent higher fluctuations in COD (CV = 44–45 %) comparing with the Slupia waters (CV = 15 %).

The quality of Kwacza waters as regards most of the studied physicochemical parameters was rather good as the average values were slightly lower than thresholds for I class waters of very good quality. However, according to the Decree of the Minister of Environment [14] which introduced the five-grade scale, the quality of Kwacza waters was bad due to the concentration of total phosphorus which exceeded the threshold level for V class waters of bad quality. According to that decree, bad quality waters:

a) do not meet the requirements for surface waters used as the source of drinking water,

b) biological characteristics of such waters reveals changes consisting in the disappearance of considerable part of populations due to anthropopression.

As for the rest of the parameters, COD values decreased the Kwacza water quality down to III class waters of satisfactory quality while phosphates(V) to II class waters of good quality.

Vegetation

At the lower section of the Kwacza River were found 40 hydrophyte species which represented 21 families. Those families had various share of the consecutive species. The most abundant group were the families with singular species: *Alismataceae*, *Iridaceae*, *Potamogetonaceae*, *Typhaceae* and *Lemnaceae*. The remaining families were represented by 2–5 taxa. Vegetation in the Kwacza River was predominated by *Sparganium emersum*, *Callitriche cophocarpa*, *Berula erecta*, *Elodea canadensis* and *Batrachium aquatile*. Those species occurred most frequently and reached the highest cover coefficient values (Table 2). Rather small areas in the riverbed were covered by *Scirpus sylvaticus*, *Glyceria maxima*, *Iris pseudacorus*, *Sparganium erectum*, *Phragmites australis* and *Mentha aquatica*. One of the species – *Ribes nigrum* – was legally protected. As for rare and endangered species we observed *Butomus umbellatus* (peat land flora) and *Rumex aquaticus*, endangered in the area of West Pomerania and Greater Poland. The species typical of *Calitricho-Batrachion* rivers also occurred in Kwacza and those were: *Batrachium fluitans*, *Batrachium aquatile*, *Callitriche cophocarpa*, *Berula erecta*, *Veronica beccabunga*, *Veronica anagalis-aquatica* and *Butomus umbellatus* [18].

The Kwacza riverbed was inhabited by 15 phytocoenoses (plant societies and communities) belonging to 2 vegetation classes. Five of them were freshwater macrophyte communities of *Potametea* class while 10 belonged to rush communities with aquatic plants of *Phragmitetea* class (Table 2).

Phytosociological and ecological characteristics of selected plant communities

The *Sagittario-Sparganietum emersi* society was as key community in the studied river section. It formed low rushes on the riverbed at the depth not exceeding 1 m. Only one species (*Sparganium emersum*) typical of the society was always present. The

average frequency of occurrence reached *Callitriche cophocarpa* while rather rarely appeared *Elodea canadensis*. The remaining species occurred seldom and among them the highest cover coefficient reached *Mentha aquatica*. The number of species in the studied lobes varied between 1 and 10 (3 on average) while their cover ranged from 4 to 100 % of the studied area (40 % on average) (Table 2).

The *Elodeetum canadensis* society formed submerged waterweed thicket, often 2–4 species aggregations at the river bottom, predominated by *Elodea canadensis*. *Sparganium emersum* and *Callitriche cophocarpa* reached the average frequency of occurrence. The rest of the species – *Glyceria maxima*, *Carex riparia* and *Phalaris arundinacea* – appeared rarely. The area of the studied lobes amounted to 2–25 m² while their coverage ranged between 50 and 100 % (74 % on average).

Considerable share of *Sagittario-Sparganietum emersi* phytocoenoses (93 lobes with the area of 5–80 m²) as well as the presence of *Elodeetum canadensis* can be explained by point source inflow of nutrients, mainly nitrogen and phosphorus compounds. *Sparganium emersum* represents communities rather insensitive to contamination [18, 20, 21]. The presence of communities with the predominant role of *Elodea Canadensis* is typical for contaminated, eutrophic waters [18, 22, 23].

Phytocoenoses predominated by *Callitriche cophocarp* also covered considerable riverbed area. Smaller lobes (1–4 m²) with *Callitriche cophocarpa* were oval or lenticular. *Sparganium emersum* was common as well, while the remaining species appeared rarely. Altogether we found 15 species in the studied lobes and their number varied between 1 and 13 (3 on average).

The *Beruletum submersae* society occurred in the coastal zone as well as in the deeper zones (submerged form *Berula erecta* fo. *submersa*). The studied lobes contained 13 species (3 on average) and rare species prevailed. As regards cover coefficient, some lobes were predominated by *Mentha aquatica*.

The *Callitricho-Batrachion* communities were represented by two plant societies – *Ranunculetum aquatilis* and *Ranunculo-Sietum erecto-submersi*. The *Ranunculetum aquatilis* society contained not large number of species, between 1 and 7 (3 on average), but *Batrachium aquatile* was present permanently. *Callitriche cophocarpa* and *Sparganium emersum* also occurred frequently. Average occurrence but high cover coefficient reached *Elodea canadensis*. In turn, the *Ranunculo-Sietum erecto-submersi* society consisted of larger number of species, between 3 and 12 (7 on average). *Batrachium aquatile* and *Berula erecta* were present permanently, opposite to *Callitriche cophocarpa*. As for the accompanying species, high coverage reached *Sparganium emersum* and *Mentha aquatica*.

Communities predominated by *Callitriche cophocarpa* and *Berula erecta* were probably the impoverished forms of *Callitricho-Batrachion* phytocoenoses from alliance *Ranunculion fluitantis* (= *Callitricho-Batrachion*), which occur in cool, clean and well oxygenated waters [18]. Regulation works in the past as well as the constant inflow of biogenes probably caused changes in the structure and distribution of the studied phytocoenoses. The presence of *Ranunculion fluitantis* communities depends on many factors [24]. According to Puchalski [5], the ecological factors that influence the structure and distribution of those communities are: mid climate conditions, hydro-

logical stability of rivers, groundwater supply, light conditions, water transparency and the availability of biogenes (mainly nitrogen and phosphorus). One can conclude that the possible unavailability of biogenes for plants in the Kwacza River was compensated by the inflow from anthropogenic sources. The performed hydrochemical analyses revealed, that nitrogen compounds underwent biosorption by plants over the vegetation period.

Conclusions

1. The results of hydrochemical and phytosociological analyses are the basis of further ecological study after the planned restoration of the 2.5 km long section of the Kwacza River.

2. Synthetic analysis of vegetation indicated the presence of 15 syntaxa, both societies and communities. Among them there were *Callitricho-Batrachion* communities of *Ranunculion fluitantis* (*Callitricho-Batrachion*) alliance, rare in the Pomerania. They included the *Ranunculetum aquatilis* and *Ranunculo-Sietum erecto-submersi* societies.

3. The studied flora contained 40 vascular plant species. The rare and legally protected species were also present. Particular attention should be paid to the species typical of *Callitricho-Batrachion* rivers: *Batrachium aquatile*, *B. fluitans*, *Callitriche cophocarpa*, *Berula erecta*, *Veronica beccabunga*, *Veronica anagalis-aquatica*, *Butomus umbellatus*.

4. Chemical analyses of the Kwacza River indicated low water quality and the parameter which contributed to that situation the most was content of total phosphorus of anthropogenic origin. Mineral nitrogen forms over the vegetation period accumulated in macrophytes by biosorption. Further inflow of biogenes (mainly nitrogen and phosphorus) may cause the development of *Sparganium emersum* and *Elodea canadensis* phytocoenoses. They reveal high biomass production and considerable expansibility which can lead to the disappearance of valuable *Callitricho-Batrachion* communities of *Ranunculion fluitantis* alliance.

5. Restoration of the Kwacza River should be planned carefully due to the presence of legally protected plant species and natural habitats according to the Appendix I of the Habitat Directive. First the attention should be paid to the water and sewage management in the whole Kwacza river basin.

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References

- [1] Gacka-Grzeškiewicz E.: [in:] Nature friendly management of river basins. W. Puchalski and K.J. Pawelczuk (eds.), Politechnika Koszalińska, Koszalin 2002, pp. 22–24 (in Polish).
- [2] Pawlacyk P.: *Przegl. Przyrod.* 1995, 6(3–4), 235–255 (in Polish).

- [3] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal of the European Communities L 327, 22.12.2000.
- [4] Bączkiewicz A., Szoszkiewicz A., Cichocka J., Celiński K., Drapikowska M. and Buczkowska K.: *Biolog. Lett.* 2007, **44**(2), 103–114.
- [5] Puchalski W.: *Lowland and piedmont rivers with Callitriche-Batrachion (code 3260)*. Handbook of natural habitat protection Nature 2000. Ministerstwo Środowiska, Warszawa 2008, p. 1–81 (in Polish).
- [6] Dębowski P., Grochowski A., Miller M. and Radtke G.: *Roczn. Nauk. PZW* 2000, **13**, 109–136 (in Polish).
- [7] Osadowski Z.: [in:] *Ecological and landscape studies in sustainable development*. M. Kistowski (ed.), Gdańsk 2004, p. 177–183 (in Polish).
- [8] Osadowski Z. and Flis A.: [in:] *Short-term effects of ecological restoration of small river basins in the example of the Kwacza River*. K. Obolewski (ed.), Park Krajobrazowy “Dolina Stupi” i Akademia Pomorska, Słupsk 2009, p. 33–48 (in Polish).
- [9] Obolewski K., Osadowski Z. and Miller M.: *Nauka, Przyroda, Technologia* 2009, **3**(3), #95 [online] http://www.npt.up-poznan.net/pub/art_3_95.pdf (in Polish).
- [10] Kondracki J.: *Regional geography of Poland*. PWN, Warszawa 1998 (in Polish).
- [11] Obolewski K., Glińska-Lewczuk K., Osadowski Z. and Kobus S.: *Polish J. Environ. Stud.* 2008, **17**(2c), 39–46.
- [12] Osadowski Z.: [in:] *Mechanisms of anthropogenic changes of the plant cover*. B Jackowiak and W. Żukowski (Eds), Publications of the Department of Plant Taxonomy of the Adam Mickiewicz University in Poznań, 2000, p. 235–247.
- [13] Hermanowicz W., Dojlido J., Zerbe J., Dożańska W. and Kosiorowski B.: *Physico-chemical analyses of water and sewage*. Wyd. Arkady 1999, p. 1–35 (in Polish).
- [14] Decree of the Minister of Environment from February 11th 2004 on the classification used in surface and ground water quality assessment, guidelines for monitoring and the interpretation of results. DzU 2004, nr 32, poz. 284 (in Polish).
- [15] Mirek Z., Piękoś-Mirkowa H., Zając A. and Zając M.: *Flowering plants and pteridophytes of Poland a checklist*. Polish Academy of Sciences, W. Szafer Institute of Botany, Kraków 2002, p. 1–235.
- [16] Żukowski W. and Jackowiak B.: *Vascular plant species endangered with extinction in the West Pomerania and Greater Poland regions*. Prace Zakładu Taksonomii Roślin UAM, Poznań 1995, **3**, 27–69 (in Polish).
- [17] Jasnowska J. and Jasnowski M.: *Chrońmy Przyr. Ojczystą* 1977, **33**(4), 5–14 (in Polish).
- [18] Matuszkiewicz W.: *Guide for identification of plant communities in Poland*. Wyd. Nauk. PWN, Warszawa 2005 (in Polish).
- [19] Brzeg A. and Wojterska M.: [in:] *Vegetation of the Greater Poland and south-pomeranian lake district*. M. Wojterska (Ed.), Przewodnik sesji terenowych 52 Zjazdu PTB, Poznań 2001, p. 34–110 (in Polish).
- [20] Marketa Sagova-Mareckova M. and Kvet J.: *Hydrobiol.* 2002, **479**, 131–141.
- [21] Marketa Sagova-Mareckova M., Petrussek A. and Kvet J.: *Aquatic Ecology* 2009, **43**, 903–913.
- [22] Ozimek T., Donk E. and Gulati R.: *Hydrobiology* 1993, **251**, 13–18.
- [23] Samecka-Cymerman A. and Kempers A.J.: *Water, Air, Soil Pollut.* 2003, **145**, 139–153.
- [24] Mony C., Mony J.F., Thiebaut G. and Muller S.: *Biodivers. Conserv.* 2006, **15**, 3383–3400.

ANALIZA FITOSOCJOLOGICZNO-EKOLOGICZNA DOLNEGO ODCINKA RZEKI KWACZY PRZED RENATURYZACJĄ (DORZECZE SŁUPI)

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Abstrakt: Na 2,5-kilometrowym odcinku rzeki Kwaczy (dopływ Słupi) przeprowadzono w 2007 roku badania hydrochemiczne i fitosocjologiczne. Celem badań było określenie jakości wód w rzece oraz rozpoznanie flory i roślinności makrofitów przed planowaną renaturyzacją rzeki. Badania hydrochemiczne

przeprowadzono czterokrotnie (wiosna, lato, jesień i zima) na początku (K1) i na końcu badanego odcinka rzeki (K10). Dodatkowo, w celach porównawczych, wykonywano pomiary hydrochemiczne wód Słupi powyżej ujścia rzeki Kwaczy. Na całym odcinku rzeki badano roślinność metodą Braun-Blanquet, a wyniki zestawiono w formie syntetycznej tabeli fitosocjologicznej. Analizy chemiczne wykazały, że rzeka na całej długości prowadzi wody pozaklasowe, a parametrem obniżającym klasę jakości była zawartość fosforu. W okresie wegetacji mineralne formy azotu ulegały znacznej akumulacji w wyniku biosorpcji przez rośliny. Na podstawie analizy 174 zdjęć fitosocjologicznych stwierdzono w korycie rzeki 15 fitocenoz z klasy *Potametea* i *Phragmitetea*, w tym rzadko opisywane na Pomorzu zbiorowiska ze związku *Ranunculion fluitantis* (*Callitricho-Batrachion*): *Ranunculetum aquatilis*, *Ranunculo-Sietum erecto-submersi* i *Beruletum submersae*. Dominujący udział w korycie rzeki zespołu *Sagittario-Sparganietum emersi* oraz dynamiczny rozwój płatów *Elodeetum canadensis* jest efektem zanieczyszczenia wód, co z czasem może doprowadzić do całkowitego wyparcia cennych zbiorowisk rzek włosienicznikowych ze związku *Ranunculion fluitantis*. Planowane prace renaturyzacyjne należy przeprowadzać z dużą ostrożnością ze względu na obecność prawnie chronionych gatunków roślin i siedlisk przyrodniczych. W pierwszej kolejności należy uporządkować gospodarkę wodno-ściekową w obrębie całej zlewni rzeki Kwaczy.

Słowa kluczowe: roślinność, makrofity rzeczne, hydrochemia wód, renaturyzacja, rzeka Kwacza, dorzecze Słupi

Jan PAWLUCZUK¹

DYNAMICS OF MINERAL NITROGEN FORMS CONTENT IN OMBROPHILOUS ORGANIC SOIL AND IN UNDERGROUND WATER

DYNAMIKA ZAWARTOŚCI MINERALNYCH FORM AZOTU W OMBROFILNYCH GLEBACH ORGANICZNYCH I W WODACH GRUNTOWYCH

Abstract: The determination of dynamics mineralisation of organic nitrogen compounds in ombrophilous organic soil and in underground water at Zielony Mechacz and Budwity objects was the aim of these researches.

Habitat conditions, and especially aqueous properties of the raised bog significantly influenced on mineralisation dynamics of organic nitrogen compounds and on the quantity of accumulated $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in soil and in underground water. In ombrophilous organic soil in the reserve, where natural habitat conditions are kept as well as in peat soil located in peat mine; the mineralisation of the organic compounds in studied seasons was small. In the case of raised bog, very small quantities of nitrates have been found. Only in the case of bog's forest peat which was located on the boundary between the reserve and the peat mine the content of that form of nitrogen was average and large. It means about stopping the nitrification process and the degradation of peat soil. The concentration of the mineral nitrogen compounds in underground water land ombrophilous peat bog was differentiated and depended on the dynamics of organic matter mineralisation carrying out in ombrophilous organic soil.

Keywords: mineralization, raised bog, groundwater, habitat conditions

In the areas where the exploitation of peat deposits is carried out the level of underground water is artificially reduced. The deep dehydration of deposits earmarked for mining also causes the lowering of water in area neighbouring with the mine. The enlarged quantity of air in the soil initiates many physical and chemical processes which lead to organic compounds decomposition which releases considerable quantities of biogenic components [1]. In the mineralisation process of organic nitrogen is released mineral nitrogen ($\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$), which is assimilated through plants. In organic soil deeply drained comes to the intensive freeing of mineral nitrogen

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which quantity often exceeds alimentary needs of plants. The unused nitrogen can diffuse to underground water and causes its eutrophication [2, 3]. In the aspect of environment protection, the dehydration of peat bog and connected with that process and an organic nitrogen compounds mineralisation poses a threat to the existence of these habitats. That is why one should control processes causing the changes of peat soils as a result of their dehydration [4]. So far the researches on the mineralisation of organic nitrogen compounds were carried out mainly in peat soils of reophilic peat bog [5, 6].

The mineralisation course of organic nitrogen compounds in the peat soil of ombrophilous peat bog in different seasons of a year, and the researches on nitrate and ammonium content in underground water of that soil have not been carried out yet, that is why such researches were undertaken. The determination of mineralisation dynamics of organic nitrogen compounds in the peat soil of raised bog in the various seasons of a year considering existing habitat conditions was the aim of these researches. The seasonal changes of nitrate and ammonium content have been also shown in underground water of these soils.

Materials and methods

Dynamics of mineral nitrogen compounds content in ombrophilous peat soil and underground water at Zielony Mechacz and Budwity objects were studied. The raised bog of the area 366 hectares is located in Maldyty community in Warmia and Mazury province, in the eastern part of Iława Lake district [7]. The stratigraphic researches of layers have confirmed that raised bog of the continental type was formed in the continental glacier process of a shallow moraine lake, created after the retreat of the Scandinavian continental glacier in the Holocene period [8]. Under eutrophical conditions the lake covering followed by detritus gyttia deposition which depth fluctuates from 0.5 m to 3.5 m. After filling a lake with sediment deposits started to appear the vegetation of reophilic peat bog vegetation, creating layers of sedge and sedge-alder swamp forest peat, covering on the gyttia. Overgrowing the aqueous reservoir was carried out from banks to the centre of a lake. The development of bog boric habitats took place in further structural constituent [9–11]. No larger aqueous watercourse does not get into the lake basin what created favourable conditions for oligotrophication of the habitat. Poor and acid rains were the main source supplying water into the habitat, therefore ombrogenic type of hydrological supplying was dominating – THZ [12]. The depth of the formed high bog at Zielony Mechacz and Budwit was about 4.5 metres. It is characterized by a faint degree of decomposition (R1) and does not show larger morphological differentiation. The Hypnum-moss peat provided litter raised bog is a sedge low moor peat. These researches have confirmed that at Zielony Mechacz and Budwit is a boggy peat soil, ombrophilic in the accumulation phase, formed from a weak decomposed peat PtIIIaa. On account of profitable aqueous properties and a weak decomposition degree, that soil should rate to the Prognostic Humidity Complex of Soils – wet A and to Potential Hydrological Humidity Habitat – ombrogenic wet. The high peat bog is characterized by diverse

aqueous conditions. There are undisturbed aqueous conditions in its south part where, the boggy process takes place. The reserve "Zielony Mechacz" has been formed in that area of 94.3 hectares in order to "preserve and protect sites of glacial relict such as the "moroszka" raspberry (*Rubus chamaemorus*) and a "raised bog" [13]. The northern part of peat bog possesses disturbed aqueous relations because of the desiccation of this terrain in order to exploitation of the peat. At present where the mining of peat was finished, the reclamation process of the soil is carried out.

The mineralisation rate of organic nitrogen compounds in peat soil and the content of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in underground waters of the soils were studied in the vegetation season and in winter in the period 1999–2001 as well as in 2008. The presented results of the mineral nitrogen release course were the continuation of broadened researches about mineralisation intensity of organic nitrogen compounds in peat soils in four seasons on the background of diverse habitat conditions of young glacial areas [6]. The researches have been carried out in four soil open pits on a raised bog, strongly boggy formed from the peat weakly decomposed (PtIIIaa). Three soil open pits were situated in the south part of a raised bog, provided with a reserve protection. The mineralisation rate of organic nitrogen compounds in the reserve soils was studied in periodically dried ombrophilic peat soils located at the border of the reserve and the mine (open pit I) and in peat soils with undisturbed aqueous conditions (open pit II, open pit III).

The fourth soil open pit was located in the northern part of peat bog on terrains after the former mine of the peat, where the renaturation process is carried out. The GPS satellite navigation system permitted to co-ordinate geographical positions of soil open pits. From layers: 5–10, 25–30, 35–40 and 50–60 cm, the soil samples with small cylinders of the capacity about 100 cm^3 , were taken with preserving structure, where: the ash (by combustion of soil samples at $550 \text{ }^\circ\text{C}$), volumetric mass density after desiccation of samples at $105 \text{ }^\circ\text{C}$, general porosity (calculated on the basis of mass volumetric density and the ash content), the moisture of soils (determined with the drier method), reaction of soils (pH measured with a potentiometric method in H_2O and in $1 \text{ mol} \cdot \text{dm}^{-3}$ KCl solutions), total nitrogen content with Kjeldahl method [14] have been determined. The content of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the soil was studied in the extract of 1 % K_2SO_4 after 14-day incubation at $28 \text{ }^\circ\text{C}$ [15]. The evaluation of $\text{NO}_3\text{-N}$ was carried out, based on border numbers according to Gotkiewicz [16]. In piezometers installed next to soil open pits, levels of underground water have been measured and the water was taken to chemical analyses. Nitrate nitrogen in underground waters was determined by colorimetric method with disulfonic acid while ammonium nitrogen with Nessler's solution [17].

Results and discussion

Physical and chemical proprieties of soils at Zielony Mechacz and Budwit objects are typical for the oligotrophic raised bog with a low (R1) decomposition degree (Table 1).

The ash content of peat was very low especially in layers below 75 cm (2.0 to 1.5 % of dry residue). The volumetric mass density of peat bog was also very low and did not

Table 1
Physical and chemical properties of ombrophilous organic soil bog at Zielony Mechacz
and Budwity objects

Layer [cm]	Level	Ash content [% d.m.]	Volume density [g · cm ⁻³]	Specific density	Total porosity [%]	pH in 1 M KCl	pH in H ₂ O	Profile I	Profile II	Profile III	Profile IV
								total N [%]			
5–10	Otwy*	4.2	0.081	1.508	94.8	2.8	3.6	1.03	1.07	0.88	0.96
15–20	Otwy	5.7	0.080	1.527	95.0	2.7	3.6	—	—	—	—
25–30	Otwy	6.7	0.105	1.538	93.1	2.9	3.8	1.00	0.99	0.85	0.93
35–40	Otwy	3.3	0.079	1.498	95.0	2.9	4.0	0.91	0.77	0.75	0.82
55–60	Otwy	3.2	0.079	1.497	94.8	2.9	3.8	0.81	0.41	0.49	0.79
75–80	Otwy	2.0	0.081	1.482	94.5	2.9	3.7	—	—	—	—
95–100	Otwy	1.5	0.079	1.478	94.6	2.7	4.2	—	—	—	—

* Otwy – raised bog peat.

exceed $0.1 \text{ g} \cdot \text{dm}^{-3}$. Specific mass density in studied layers of peat bog on average was $1.5 \text{ g} \cdot \text{dm}^{-3}$ and it was insignificantly lowering in deeper layers. The raised bog – Zielony Mechacz and Budwity was characterized by a high general porosity, (93–95 % vol.). So high porosity is connected with a low degree of peat decomposition and testifies about exceptionally small refinement of the soil and huge possibilities of water accumulation. The reaction of the peat was qualified as the strong acidic [18].

The content of total nitrogen in studied raised peat was insignificantly diversified and in the comparison with eutrophical peat was low. In the soil open pit I it fluctuated from 1.03 to 0.81 %, in the open pit II from 1.07 to 0.41 %, it was the lowest in the open pit III – from 0.88 % to 0.49 %. However, it fluctuated from 0.96 to 0.79 % in the open pit IV, on the terrain of the former mine.

The studied soils of a raised bog differed in levels of underground water and moisture (Table 2).

Table 2

Average moisture [%] and underground water levels [cm] of Zielony Mechacz and Budwity raised bog

Profile GPS coordinates	Layer [cm]	Seasons of the year			
		Spring	Summer	Autumn	Winter
		Moisture of soil [%]			
Profile I GPS: N 53°54' 669"; E 19°41' 836"	5–10	68.29	61.98	73.60	71.30
	25–30	69.98	63.65	64.00	69.90
	35–40	75.57	78.65	61.80	76.35
	50–60	79.78	82.32	71.30	75.80
Profile II GPS: N 53°54' 645"; E 19°41' 873"	5–10	75.89	79.87	82.19	80.50
	25–30	79.98	77.45	84.34	85.55
	35–40	84.57	83.98	80.38	83.95
	50–60	89.58	89.53	89.76	95.60
Profile III GPS: N 53°54' 427"; E 19°41' 677"	5–10	95.51	94.90	94.10	97.55
	25–30	96.00	95.40	96.60	96.45
	35–40	97.82	96.50	96.30	96.90
	50–60	97.86	94.50	95.50	97.80
Profile IV GPS: N 53°54' 615"; E 19°41' 546"	5–10	91.80	89.80	87.20	88.00
	25–30	91.93	84.80	85.70	87.60
	35–40	94.53	90.25	96.50	97.25
	50–60	97.87	95.35	91.80	97.30
Underground water level [cm]					
Piezometer I		67	115	78	68
Piezometer II		30	35	25	15
Piezometer III		*	3	*	*
Piezometer IV		*	5	2	5

* Water on the surface of soil.

The mine bordering on the reserve caused that the lowest level of underground water was kept in the piezometers I. The underground water was on the depth from 67 cm to

115 cm there. The higher level of underground water and its insignificant variations during the year occurred in the piezometer II. The level of underground waters was kept on the depth from 15 to 35 cm in studied seasons of the year. In piezometers III and IV the underground water was the most often kept on the surface of the soil or from 2 to 5 cm below its surface. The studied peat soils differed in its moisture. The high moisture of peat bog in all seasons of the year kept in open pits III and IV (from 84.8 to 97.8 % vol.). The lowest moisture was characterized the top layers of soils of a raised bog situated near the mine. In the open pit I moisture in the layer 5–10 cm was kept in the range 61.9 to 73.6 % vol. and in the open pit II from 75.9 to 82.2 % vol., respectively.

During the year larger differences in moisture occurred only in layers 5–30 cm, in the open pit I and II of peat bog. In the deeper layers of these open pits similarly as in remaining studied ones was high moisture. Prevailing aqueous conditions at Zielony Mechacz and Budwity high bog are profitable from the soil protection point of view, because they limit changes proceeding in organic soils. The aqueous proprieties of a raised bog and kept their naturalness degree, had a significant effect on the mineralisation dynamics of organic nitrogen compounds, and on the quantity of accumulated $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the soil and in underground water. In ombrophilous organic soil in the reserve where natural habitat conditions are kept as well as in peat soils located on terrains after the former peat mine the mineralisation of organic matter where the renaturation process happens was also small (Table 3). The biggest amount of mineral nitrogen was released in peat soils of boggy forest located on the boundary of the reserve near the former pit mine (an open pit I). The large release of mineral nitrogen in that soil especially happened in the summer periods in surface layers. The predominated form in the mineralisation process of organic nitrogen compounds was $\text{NO}_3\text{-N}$, which content in the soil was high and average, however the affluence of these soil layers in $\text{NH}_4\text{-N}$ was smaller and ranged 7.3–8.3 $\text{mg} \cdot \text{dm}^{-3}$. In the remaining seasons the mineralisation rate in the soil of an open pit I was smaller. The content of $\text{NO}_3\text{-N}$ in spring was low whereas in autumn was low and average. In the peat soil located near the former mine the ratio of $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ in the vegetation season was above the unity, what testifies about convenient conditions to the course of the nitrification process. The inhibition of organic nitrogen compounds mineralisation in winter was stated. The content of N-NO_3 was very low whereas $\text{NH}_4\text{-N}$ content did not exceed 3.9 $\text{mg} \cdot \text{dm}^{-3}$.

In peat soil on the terrain of the former mine, low contents of mineral nitrogen have been found. The $\text{NH}_4\text{-N}$ form was predominated, which content did not exceed 5.7 $\text{mg} \cdot \text{dm}^{-3}$, and the affluence of the peat in $\text{NO}_3\text{-N}$ was very low. In II and III open pits in all studied layers of soil profile were very small quantities of $\text{NO}_3\text{-N}$. The larger seasonal fluctuations of nitrates were not also found as it took place in the case of a reophilic peat bog mineralisation process. The largest concentrations of mineral nitrogen appeared in underground water in a piezometer I, installed on the boundary between the reserve and the mine, and in the piezometer IV in the terrain of the former mine (Table 4).

Table 4

Average nitrogen content of underground water at Zielony Mechacz and Budwity objects

Season	GPS coordinates: N 53°54' 669"; E 19°41' 836"			GPS coordinates: N 53°54' 645"; E 19°41' 873"			GPS coordinates: N 53°54' 427"; E 19°41' 677"			GPS coordinates: N 53°54' 615"; E 19°41' 546"		
	NO ₃ -N	NH ₄ -N	N-min	NO ₃ -N	NH ₄ -N	N-min	NO ₃ -N	NH ₄ -N	N-min	NO ₃ -N	NH ₄ -N	N-min
[mg · dm ⁻³]												
Spring	0.463	0.967	1.430	0.259	0.328	0.587	0.238	0.318	0.556	0.441	0.787	1.228
Summer	0.890	0.568	1.458	0.300	0.431	0.731	0.241	0.314	0.555	0.483	0.897	1.380
Autumn	0.569	0.867	1.436	0.234	0.622	0.856	0.231	0.312	0.543	0.426	0.825	1.251
Winter	0.576	0.797	1.373	0.201	0.342	0.543	0.221	0.310	0.531	0.451	0.796	1.247
Average	0.624	0.800	1.424	0.248	0.431	0.679	0.233	0.313	0.546	0.450	0.826	1.276

The high concentrations of mineral nitrogen in water of the piezometer I were connected with the large dynamics mineralisation of organic matter and its acid reaction which favoured washout of mineral nitrogen compounds to underground water. Whereas the high concentrations of mineral nitrogen in the water after the mine exploitation are connected with washout of these compounds to deeper layers in the period, when these soils were dried and the peat was exploited and the organic matter mineralisation took place there. The $\text{NH}_4\text{-N}$ form was predominated in all water sections, and the largest its concentration appeared mostly in autumn.

Conclusions

1. The dynamics of organic nitrogen compounds mineralisation in ombrophilous peat soils in Zielony Mechacz and Budwit objects is distinctly limited through prevailing habitat conditions. The raise of underground water level in terrains after exploitation of peat, favours the renaturation process and significantly limits the discharge rate of mineral nitrogen forms both in peat in the terrain of the former mine, and in peat in the terrains of the neighbouring reserve.

2. In raised bog of Zielony Mechacz and Budwity objects very small quantities of nitrates have been stated and only in boggy forest peat appeared the influence of the mine on raising that mineral nitrogen content form to average and high quantities. At present the low rate of the nitrification process does not pose any threat to ombrophilous peat soils; however the renaturation process of these soils should be continued.

3. The concentration of mineral nitrogen compounds in underground water of the ombrophilous boggy forest peat was differentiated and depended on mineralisation dynamics of organic matter in soils. The highest concentrations of mineral nitrogen have been found in underground water of boggy forest peat located on the boundary between the peat mine and the terrain after exploitation. It is the intensification effect of the nitrification process and washout of these compounds.

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References

- [1] Gotkiewicz J. and Gotkiewicz M.: [in:] *Gospodarowanie na glebach torfowych w świetle 40-letniej działalności Zakładu Doświadczalnego Biebrza*. Bibl. Wiad. IMUZ 1991, **77**, 59–77.
- [2] Kiryluk A. and Wiater J.: *Roczn. AR Poznań*, 342, Melior. Inż. Środow. 2002, **23**, 193–199.
- [3] Sapek B.: *Zesz. Probl. Post. Nauk Roln.* 1996, **440**, 331–341.
- [4] Gotkiewicz J.: [in:] *Torfowiska i mokradła*. Monografia. SGGW, Warszawa 2007, pp. 63–74.
- [5] Pawluczuk J. and Gotkiewicz J.: *Acta Agrophys.* 2003, **1(4)**, 721–728.
- [6] Pawluczuk J.: *Zesz. Probl. Post. Nauk Roln.* 2001, **476**, 243–250.
- [7] Kondracki J.: *Geografia regionalna Polski*. Wyd. Nauk. PWN, Warszawa 2001.
- [8] Pawluczuk J. and Gotkiewicz J.: *Biul. Nauk. Uniw. Warm.-Mazur. w Olsztynie* 2000, **9**, 121–133.
- [9] Abromeit J.: *Flora von Ost- und Westpreußen*. I. 1. Hälfte (IX), Berlin 1898, pp. 1–400.
- [10] Polakowski B.: *Chrońmy Przyr. Ojcz.* 1960, **6**, 38–39.

- [11] Steffen H.: Pflanzensozioologie. Bd 1. Vegetationskunde von Ostpreussen. Verlag von Gustav Fisher, Jena 1931, pp. 406.
- [12] Okruszko H.: Roczn. Glebozn. 1988, **29**(1), 127–152.
- [13] Zarządzenie Ministra Leśnictwa i Przemysłu Drzewnego z dnia 15 maja 1962 r. w sprawie uznania za rezerwat przyrody. Monitor Polski 1962, nr 51, poz. 252.
- [14] Sapek A. and Sapek B.: Metody analizy chemicznej gleb organicznych. Wyd. IMUZ 1997, **115**, pp. 150.
- [15] Gotkiewicz J.: Roczn. Nauk Roln. 1974, F–**78**(4), 8–34.
- [16] Gotkiewicz J.: Zróżnicowanie intensywności mineralizacji azotu w glebach organogenicznych związane odrębnością warunków siedliskowych. IMUZ, Falenty 1973, Rozpr. hab. **11**, pp. 111.
- [17] Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B. and Zerbe J.: Fizyczno-chemiczne badanie wody i ścieków. Wyd. Arkady, Warszawa 1999, pp. 556.
- [18] Okruszko H.: [in:] Gospodarowanie na glebach torfowych w świetle 40 letniej działalności Zakładu Doświadczalnego Biebrza, Bibl. Wiad. IMUZ 1991, **77**, 87–103.

DYNAMIKA ZAWARTOŚCI MINERALNYCH FORM AZOTU W OMBROFILNYCH GLEBACH ORGANICZNYCH I W WODACH GRUNTOWYCH

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Abstrakt: Celem badań było określenie dynamiki mineralizacji organicznych związków azotu w ombrofilnych glebach organicznych i w wodach gruntowych na obiektach: Zielony Mechacz i Budwity.

Warunki siedliskowe, a zwłaszcza właściwości wodne torfowiska wysokiego, istotnie wpływały na dynamikę mineralizacji organicznych związków azotu oraz na ilość gromadzonego N-NO₃ i N-NH₄ w glebie i w wodach gruntowych. W ombrofilnych glebach organicznych w rezerwacie, w którym zachowane są naturalne warunki siedliskowe, jak również w glebach torfowych położonych na terenach po byłej kopalni torfu, mineralizacja materii organicznej w badanych sezonach była niewielka. W torfach wysokich stwierdzono bardzo małe ilości azotanów, a jedynie w torfach boru bagiennego położonego na granicy między rezerwatem i kopalnią zawartość tej formy azotu była średnia i duża. Świadczy to o zahamowaniu procesu nitryfikacji i degradacji gleb torfowych. Stężenie mineralnych związków azotu w wodach gruntowych ombrofilnych torfowisk było zróżnicowane i zależało od zachodzącej w ombrofilnych glebach organicznych dynamiki mineralizacji materii organicznej.

Słowa kluczowe: mineralizacja, torfowisko wysokie, woda gruntowa, warunki siedliskowe

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EFFECT OF SEWAGE SLUDGE IN SOIL ON Cd, Pb AND Zn ACCUMULATION IN THE *Linum usitatissimum* L.

WPLYW OSADÓW ŚCIEKOWYCH W GLEBIE NA AKUMULACJĘ Cd, Pb ORAZ Zn W *Linum usitatissimum* L.

Abstract: Sewage sludge is the product of the process of wastewater treatment. Sludge may be considered hazardous waste requiring costly disposal procedures, or may be perceived as a source of nutrients for use on agricultural land. Experiments were carried out in simulated natural conditions in pots set in the land to a depth of 50 cm with variations of graded mixture of natural sediments and soils. Sewage sludge sedimentation was added into the weighed quantity of soil in the proportions: sludge – soil = 1:2 (var. K1), 1:3 (var. K2), 1:4 (var. K3), 1:5 (var. K4), 1:6 (var. K5). Control variant (K0) without the presence of sewage sludge has also been sown with all varieties. Studied crop were the varieties of flax and linseed. Flax and linseed varieties variously accumulated particular metallic elements, the highest concentrations were recorded for Zn, followed by the Pb and Cd. The lowest concentrations of Cd and Pb were analyzed in the seed ($0.121 \text{ mg} \cdot \text{kg}^{-1}$) and the highest concentrations of Cd and Pb were detected in the stem ($\text{Cd} = 0.396 \text{ mg} \cdot \text{kg}^{-1}$) and capsules ($\text{Pb} = 1.881 \text{ mg} \cdot \text{kg}^{-1}$). The highest concentration of Zn was found in the capsule ($115.015 \text{ mg} \cdot \text{kg}^{-1}$) and lowest in the root ($33.782 \text{ mg} \cdot \text{kg}^{-1}$). Trend of accumulation of Cd was: stem > capsule > root > seed, Pb: capsule > stem > root > seed, Zn: capsule > seed > root > stem. The results of studied experiments show that the particular varieties of fiber and linseed have different variability in the ability to draw heavy metals from the soil and consequently different phytoremediation potential.

Keywords: *Linum usitatissimum* L., flax, linseed, cadmium, lead, zinc

Sewage sludge is the product of the process of wastewater treatment. Sludge may be considered hazardous waste requiring costly disposal procedures, or may be perceived as a source of nutrients for use on agricultural land. For application of sewage sludge on agricultural land at the Czech Republic the concentration limits of chosen risk elements

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have to be respected and the only these sewage sludges which are in the agreement with the respective regulation are allowed to be used. Limit (maximum) concentrations in sludge are for Cd $5 \text{ mg} \cdot \text{kg}^{-1}$, Cu $500 \text{ mg} \cdot \text{kg}^{-1}$, Pb $200 \text{ mg} \cdot \text{kg}^{-1}$, Zn $2500 \text{ mg} \cdot \text{kg}^{-1}$, As $30 \text{ mg} \cdot \text{kg}^{-1}$, Cr $200 \text{ mg} \cdot \text{kg}^{-1}$ and Ni $100 \text{ mg} \cdot \text{kg}^{-1}$ d.m. Bioavailability of heavy metals is not directly correlated with their total concentrations in soil or sludge. Availability of heavy metals from sewage sludge to the plants is mainly determined by soil properties. Mobility of metals in the soil after application of sewage sludge depends mainly on chemical and physical properties of sludge – soil. Metals originated from sewage sludge are mainly accumulated in the surface layers of soil and Zn is the most accessible for the organisms. Sewage sludges contains high levels of organic and inorganic nutrients, but the availability of toxic metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in cultivated crops [1, 2] is considered to be the main problem. Knowledge of the crops characteristics on contaminated sites and their potential ability to transfer metal contaminants in the harvested plant parts can be a very important finding for future phytoremediation applications. Studies in the plants [3] for the ability to accumulate Cd, Pb and Zn in soil enriched sewage sludge showed differences between crops and their varieties.

Materials and methods

The experiment was conducted at the agricultural research institute Agritec, Ltd. of Sumperk, located in the middle Europe in the North Moravia part of the Czech Republic at $49^{\circ}58'21.213''\text{N}$ latitude, $16^{\circ}58'0.341''\text{E}$, longitude and 329 m above the sea level. The experiment was conducted during the growing season April–August 2005, 2006 and 2007. This growing periods of the years were characterized by average monthly temperatures between $8.3 \text{ }^{\circ}\text{C}$ and $20.5 \text{ }^{\circ}\text{C}$. Average monthly maximal temperatures fluctuated between 20.4 and 35.2 and the average monthly minimal temperatures between $-6.0 \text{ }^{\circ}\text{C}$ and $8.0 \text{ }^{\circ}\text{C}$. The total rainfall was 297.5 mm in 2005, 365.7 mm in 2006 and 247.5 mm in 2007, respectively compared with long-term average rainfall 339.5 mm in the monitored growing periods. Experiments were carried out in simulated natural conditions in pots set in the land to a depth of 50 cm with variations of graded mixture of natural sediments and soils. Sewage sludge sedimentation was added into the weighted quantity of soil in the proportions: sludge – soil = 1:2 (var. K1), 1:3 (var. K2), 1:4 (var. K3), 1:5 (var. K4), 1:6 (var. K5). Control variant (K0) without the presence of sewage sludge has also been sown with all varieties. Jitka, Laura, Viola, Mercury, Venica, Hermes, Jordan, Escalina, Viking, Tabor, Bonet, Agatha, Super, Marilyn, Ilona, Elektra, Atalante, Flanders, Lola and Biltstar were the studied flax and linseed varieties. Harvested plants were dried, separated into the stem, capsules, root and seed and analyzed.

Table 1

Chemical characterization of natural soil used in the experiments

	pH/CaCl ₂	K	P	Mg	Ca	N-NH ₄	N-NO ₃	Cd	Pb	Zn
mg · kg ⁻¹ d.m.	6.75	171	73	201	2047	3.89	6.5	0.25	32.8	56.4

Table 2

Chemical characterization of used sewage sludge

pH	mg · kg ⁻¹ d.m.								%	mg · kg ⁻¹ d.m.		g · kg ⁻¹ d.m.			
	Pb	Cd	Cu	Zn	Cr	Ni	As	Hg	N total	N-NH ₄	N-NO ₃	P total	Ca	Mg	K
8.05	57.6	1.7	198	1250	155	28.1	4.3	1.9	4.8	9410	49.9	28	33.3	6.27	5.05

The digestion of plant materials was performed in a microwave oven operating system (Milestone, ETHOS D) with an energy output 0–400 W (0–100 % potency, respectively). Approximately 0.5 g of dry plant materials were placed into the teflon microwave digestion vessels, then 5 cm³ of 65 % HNO₃ and 1 cm³ of 30 % H₂O₂ were added to each sample. Plant samples were digested using the optimized microwave programs. After cooling to room temperature the digested samples were diluted to a final volume of 25 cm³ with deionized water. Blank samples were prepared simultaneously. These solutions were stored in a refrigerator at 4 °C until the analysis was carried out. The total contents of elements (Cd and Pb) in the digests were determined by graphite furnace atomic absorption spectroscopy (SOLLAR M, Unicam Ltd., Cambridge, U.K.) equipped with Zeeman and deuterium background correctors, a graphite furnace GF95 and an auto-sampler. For the determination of Zn there was used flame atomic absorption spectroscopy. For this work, the deuterium lamp was used as background corrector for determination of Zn and Cd, the Zeeman corrector was employed for determination of Pb. The wavelengths used for quantification were: λ = Cd 228.8 nm; Pb 217.0 nm and Zn 213.9 nm. Certified reference materials IRM 9035 kohlrabi-haulm ÚKZÚZ Brno were applied for quality assurance of analytical data. The results data were statistically analyzed by using the statistical package program Statistica, using analysis of variance and multiple comparisons and correlation.

Results and conclusions

The highest concentration was found in zinc (15.51–375.2 mg · kg⁻¹ d.m.), followed by lead (Pb) with (0.01–5.85 mg · kg⁻¹ d.m.) and the lowest concentration was detected in cadmium (0.007–5.22 mg · kg⁻¹ d.m.). Individual studied metals were variously accumulated into organs of flax and linseed. The application of sewage sludge influenced the level of Cd content in all flax organs. Lead and zinc content in flax and linseed plants fluctuated in the respective variants and did not show significant increasing tendency in all organs by the increasing content of sewage sludge into the soil similarly as Balik et al [4] investigated by Zn accumulation in oat. By mutual evaluation of concentration of heavy metals in different organs the highest accumulation of cadmium was found in stem, lead (Pb) and zinc in capsules. On the contrary, the lowest concentration of cadmium and lead (Pb) was detected in seed and the lowest concentration of zinc was found in root. Cadmium was more accumulated by linseed varieties, whereas lead (Pb) and zinc were more accumulated by flax varieties. Variant with the highest sewage sludge content 1K significantly ($p \geq 0.05$) concentrated

Table 3

Heavy metal (Cd, Pb and Zn) uptake/accumulation ($\text{mg Cd, Pb, Zn} \cdot \text{kg}^{-1}$ d.m.; $\text{g Cd, Pb, Zn} \cdot \text{ha}^{-1}$) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested cultivars (data for 20 flax and linseed cvs.). Analysis of variance; mature plants; field-simulated experiment 2005–2007

	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
	$\text{mg Cd} \cdot \text{kg}^{-1}$				$\text{g Cd} \cdot \text{ha}^{-1}$			
1K = 1:2	0.376 ^b	0.566 ^c	0.535 ^c	0.164 ^c	0.420 ^b	3.972 ^b	0.428 ^c	0.147 ^c
2K = 1:3	0.323 ^a	0.444 ^{bc}	0.514 ^{bc}	0.154 ^{dc}	0.312 ^a	2.489 ^a	0.414 ^c	0.166 ^c
3K = 1:4	0.313 ^a	0.375 ^{ab}	0.409 ^b	0.128 ^{cd}	0.297 ^a	1.960 ^a	0.321 ^b	0.130 ^{bc}
4K = 1:5	0.309 ^a	0.335 ^{ab}	0.285 ^a	0.111 ^{bc}	0.288 ^a	1.560 ^a	0.216 ^a	0.123 ^{bc}
5K = 1:6	0.302 ^a	0.296 ^a	0.265 ^a	0.092 ^{ab}	0.312 ^a	1.447 ^a	0.220 ^a	0.088 ^{ab}
Control	0.298 ^a	0.362 ^{ab}	0.263 ^a	0.074 ^a	0.279 ^a	1.627 ^a	0.224 ^a	0.056 ^a
	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
	$\text{mg Pb} \cdot \text{kg}^{-1}$				$\text{g Pb} \cdot \text{ha}^{-1}$			
1K = 1:2	1.135 ^a	0.929 ^{ab}	1.699 ^a	0.573 ^b	1.247 ^{bc}	6.065 ^b	1.469 ^a	0.606 ^b
2K = 1:3	1.045 ^a	0.886 ^{ab}	1.716 ^{ab}	0.657 ^b	0.984 ^{ab}	4.082 ^a	1.345 ^a	0.785 ^b
3K = 1:4	1.037 ^a	0.887 ^{ab}	1.713 ^{ab}	0.612 ^b	0.911 ^a	3.864 ^a	1.399 ^a	0.685 ^b
4K = 1:5	1.067 ^a	0.832 ^{ab}	1.982 ^b	0.593 ^b	0.954 ^{ab}	3.312 ^a	1.526 ^a	0.695 ^b
5K = 1:6	1.103 ^a	0.748 ^a	2.271 ^c	0.547 ^b	1.009 ^{ab}	3.408 ^a	1.860 ^b	0.655 ^b
Control	1.574 ^b	0.901 ^b	1.907 ^{ab}	0.328 ^a	1.480 ^c	3.587 ^a	1.645 ^{ab}	0.237 ^a
	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
	$\text{mg Zn} \cdot \text{kg}^{-1}$				$\text{g Zn} \cdot \text{ha}^{-1}$			
1K = 1:2	37.893 ^b	39.085 ^c	117.638 ^a	74.811 ^b	37.753 ^b	201.409 ^b	95.831 ^a	70.388 ^b
2K = 1:3	36.266 ^b	35.804 ^{ab}	112.596 ^a	74.131 ^b	31.369 ^a	169.973 ^{ab}	91.689 ^a	69.161 ^b
3K = 1:4	36.321 ^b	36.389 ^{bc}	109.012 ^a	74.229 ^b	30.925 ^a	159.728 ^a	87.910 ^a	67.894 ^b
4K = 1:5	32.193 ^a	34.010 ^{ab}	116.041 ^a	70.867 ^b	28.795 ^a	139.656 ^a	91.797 ^a	65.107 ^b
5K = 1:6	30.925 ^a	32.759 ^a	116.468 ^a	71.595 ^b	29.846 ^a	151.355 ^a	101.151 ^a	68.433 ^b
Control	29.092 ^a	46.713 ^d	118.333 ^a	61.426 ^a	27.559 ^a	200.091 ^b	99.684 ^a	42.769 ^a

Table 4

Correlation HMs between individual plant organs

	Cd				Pb				Zn			
	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
Root		0.41	-0.01	0.13		-0.07	0.06	-0.46		0.32	0.41	-0.04
Stem	0.41		0.15	0.12	-0.07		0.27	0.09	0.32		0.40	-0.26
Capsule	-0.01	0.15		0.23	0.06	0.27		-0.18	0.41	0.40		-0.23
Seed	0.13	0.12	0.23		-0.46	0.09	-0.18		-0.04	-0.26	-0.23	

cadmium into all organs in contrary to control variant of Table 8. The found Cd concentration indicates trend of accumulation in the direction of stem > capsule > root > seed, similarly to work Jiao et al [5], who found decreasing direction of accumulation at harvest time: stem>seed. The trend of lead (Pb) transport was following: capsules > stem > root > seed. The concentration of lead (Pb) in root was equal in all variants enriched by sludge. However, it was significantly ($p \geq 0.05$) lower in comparison with the control. On the other hand, the concentration of lead (Pb) in a seed had completely opposite tendency and varied in stem and capsules. The trend of zinc concentration was: capsule > seed > root > stem and the highest was in the capsule, but between the individual variant was balanced and insignificantly higher in the control variant. The zinc content in a stem was different in individual variants with significantly highest content of the control. Zinc accumulated in root shows significant ($p \geq 0.05$) influence on variants with higher content of sludge (Table 3). While studying concentration of zinc in a seed there was found significantly ($p \geq 0.05$) increasing content of element with increasing amount of sludge in soil. Table 3 represents total accumulation of heavy metals, so-called absorption factor, that is absorption of risk element by crop per area unit ($\text{g} \cdot \text{ha}^{-1}$). By biomass of above-ground mass, on contrary of total crop mass, was absorbed off 89 % Cd, 85 % Pb and 91 % Zn. Stem had the highest absorption factor of all three elements (mean $2.176 \text{ g Cd} \cdot \text{ha}^{-1}$, $4.053 \text{ g Pb} \cdot \text{ha}^{-1}$ a $170.369 \text{ g Zn} \cdot \text{ha}^{-1}$). Cd absorption was higher in linseed varieties (except of root), in contrary to Pb and Zn absorption was higher from flax (except of capsules and seeds). These trends of absorption by individual organs of flax and linseed plants were found out from resultant analyses of gained data: Cd = stem > root > capsule > seed, Pb = stem > capsule > root > seed, Zn = stem > capsule > seed > root. Absorption of Cd by all parts of plant was significant ($p \geq 0.05$) for variants with higher content of sludge in soil. Absorption of Pb was above all significant ($p \geq 0.05$) for variant 1 K and absorption of Zn was after application of sewage sludge significant only for root, stem and seed also in variant 1K. When studying extract of cadmium from soil substrate and sewage sludge Piotrowska and Cyplik et al [5] came to similar conclusions. They learned increased content of Cd in root. By mutual evaluation of accumulation of monitored heavy metals there was found correlative dependence of Cd accumulation into stem and root ($r = 0.414$) and correlation in accumulation Pb between roots and stem ($r = -0.456$) and stem and capsules ($r = 0.411$), see Table 4. The results show, that individual varieties of flax and linseed have different variability in ability to accumulate heavy metals from soil. Variety of linseed Flanders showed the highest concentration of Cd in root, capsules and seed (Table 5). This variety had significantly ($p \geq 0.05$) higher concentration Pb in seed. In variety of flax Jitka was found the highest concentration of Pb in stem and capsules (Table 6). An interesting fact was, that the highest concentrations of Zn were always found in flax varieties (root – Viola, stem – Marylin, capsule – Hermes, seed – Jordán) (Table 7), but by mathematics analyses of calculation of absorption factor, the highest found absorption in root and stem was by variety of flax Jordan (root: $40.191 \text{ g} \cdot \text{ha}^{-1}$, stem: $238.298 \text{ g} \cdot \text{ha}^{-1}$), but linseed Biltstar ($145.187 \text{ g} \cdot \text{ha}^{-1}$) drew off more into capsules and variety linseed Atalante ($105.443 \text{ g} \cdot \text{ha}^{-1}$) – seed. The variety of flax Jordan presents the highest accumulative potential of Pb in stem ($5.812 \text{ g} \cdot \text{ha}^{-1}$), variety

Table 5
Cadmium uptake/accumulation ($\text{mg Cd} \cdot \text{kg}^{-1} \text{ d.m.}$; $\text{g Cd} \cdot \text{ha}^{-1}$) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested variant. Mean; mature plants; field-simulated experiment 2005–2007

Variety	$\text{mg Cd} \cdot \text{kg}^{-1}$				$\text{g Cd} \cdot \text{ha}^{-1}$			
	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
Hermes	0.338	0.320	0.446	0.103	0.396	1.828	0.271	0.089
Jitka	0.308	0.445	0.414	0.159	0.238	2.719	0.338	0.118
Venica	0.319	0.316	0.221	0.100	0.364	1.917	0.177	0.122
Merkur	0.303	0.340	0.376	0.100	0.272	1.589	0.259	0.078
Bonet	0.293	0.408	0.390	0.103	0.236	2.127	0.218	0.086
Tábor	0.347	0.449	0.394	0.111	0.314	2.629	0.295	0.110
Viola	0.369	0.368	0.276	0.096	0.310	2.218	0.198	0.075
Viking	0.359	0.352	0.417	0.095	0.378	1.888	0.366	0.082
Agatha	0.346	0.477	0.423	0.143	0.409	3.518	0.308	0.130
Escalina	0.277	0.317	0.386	0.100	0.276	1.747	0.295	0.104
Ilona	0.312	0.377	0.366	0.108	0.323	2.004	0.214	0.092
Super	0.286	0.356	0.348	0.128	0.256	1.506	0.244	0.097
Elektra	0.320	0.326	0.307	0.087	0.380	2.166	0.181	0.056
Marylin	0.366	0.417	0.434	0.121	0.425	2.257	0.368	0.115
Jordán	0.277	0.384	0.359	0.132	0.328	2.697	0.292	0.096
Laura	0.315	0.383	0.334	0.118	0.337	1.885	0.262	0.119
Atalante	0.305	0.433	0.412	0.142	0.304	2.418	0.432	0.227
Flanders	0.253	0.351	0.465	0.181	0.232	1.176	0.433	0.234
Lola	0.349	0.430	0.450	0.119	0.230	1.301	0.351	0.188
Biftstar	0.363	0.681	0.353	0.168	0.353	3.986	0.573	0.149

Table 6

Lead uptake/accumulation ($\text{mg Pb} \cdot \text{kg}^{-1} \text{ d.m.}$; $\text{g Pb} \cdot \text{ha}^{-1}$) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested variant. Mean; mature plants; field-simulated experiment 2005–2007

Variety	$\text{mg Pb} \cdot \text{kg}^{-1}$				$\text{g Pb} \cdot \text{ha}^{-1}$			
	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
Hermes	1.183	0.808	2.117	0.557	1.256	3.949	1.430	0.558
Jitka	1.073	1.087	2.343	0.600	0.892	5.679	2.029	0.491
Venica	1.184	0.855	1.609	0.556	1.239	4.725	1.336	0.791
Merkur	1.305	0.927	1.754	0.526	1.076	4.203	1.283	0.489
Bonet	0.983	0.792	1.927	0.488	0.769	3.410	1.312	0.503
Tábor	1.081	0.781	1.773	0.489	0.922	3.930	1.378	0.550
Viola	1.241	0.895	2.018	0.441	1.063	5.191	1.451	0.420
Viking	1.192	0.835	1.683	0.494	1.289	4.431	1.688	0.554
Agatha	1.075	0.889	1.595	0.551	1.265	4.997	1.260	0.577
Escalina	1.231	0.905	2.145	0.584	1.183	4.573	1.681	0.680
Ilona	1.137	0.868	2.252	0.552	0.971	4.053	1.425	0.537
Super	1.260	0.816	1.942	0.569	1.034	3.132	1.489	0.480
Elektra	1.135	0.717	1.804	0.610	1.209	3.949	1.120	0.444
Marylin	0.988	0.779	1.961	0.561	1.029	4.124	1.585	0.542
Jordán	1.172	0.961	1.989	0.551	1.341	5.812	1.508	0.399
Laura	1.022	0.958	1.782	0.546	1.046	4.329	1.496	0.663
Atalante	1.399	0.778	1.555	0.557	1.435	2.945	1.647	0.993
Flanders	1.171	0.873	1.802	0.706	1.042	2.330	1.798	1.028
Lola	1.279	0.865	1.882	0.540	0.875	2.263	1.485	0.852
Biftstar	1.089	0.888	1.690	0.558	1.015	3.038	2.414	0.662

Table 7
Zinc uptake/accumulation ($\text{mg Zn} \cdot \text{kg}^{-1}$ d.m.; $\text{g Zn} \cdot \text{ha}^{-1}$) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested variant. Mean; mature plants; field-simulated experiment 2005–2007

Variety	$\text{mg Zn} \cdot \text{kg}^{-1}$				$\text{g Zn} \cdot \text{ha}^{-1}$			
	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
Hermes	34.294	36.921	135.152	71.530	36.526	192.214	98.000	55.428
Jitka	33.999	40.694	129.667	74.767	26.131	186.563	102.144	57.474
Venica	32.650	36.408	99.740	69.987	34.164	201.528	85.222	79.613
Merkur	35.134	37.249	106.248	67.710	27.776	139.086	79.856	50.648
Bonet	30.806	36.673	106.958	71.125	23.425	159.847	75.637	59.507
Tábor	31.629	37.803	118.981	73.572	27.314	194.948	96.153	69.966
Viola	39.568	37.117	113.759	70.604	33.161	191.841	86.379	54.142
Viking	33.834	35.481	104.983	71.288	32.062	172.937	110.961	58.642
Agatha	27.904	35.919	95.629	68.144	29.928	196.964	73.999	60.813
Escalina	38.104	37.651	115.926	66.891	34.197	171.101	87.882	66.153
Ilona	33.716	37.754	117.925	75.498	30.299	180.807	83.819	54.311
Super	33.841	33.071	113.186	72.918	27.123	127.095	86.779	50.431
Elektra	33.253	35.448	102.679	68.958	36.946	198.972	64.145	43.104
Marylin	33.567	41.392	128.114	76.284	36.403	217.994	108.826	66.334
Jordán	33.267	38.469	118.469	77.860	40.191	238.298	95.295	54.282
Laura	38.074	39.442	118.162	75.613	37.109	164.529	98.155	72.798
Atlante	31.946	34.034	102.243	70.049	29.886	130.248	100.939	105.443
Flanders	29.330	39.133	132.313	62.120	24.190	103.126	121.591	71.819
Lola	32.471	38.986	123.902	64.099	21.179	95.162	92.572	79.537
Biftstar	38.241	39.559	116.255	74.512	32.816	144.111	145.187	68.726

Table 8

Heavy metal (Cd, Pb and Zn) uptake/accumulation ($\text{mg Cd, Pb, Zn} \cdot \text{kg}^{-1} \text{ d.m.}$; $\text{g Cd, Pb, Zn} \cdot \text{ha}^{-1}$) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested cultivars and variant (data for 20 flax and linseed cvs. and 5 variant mixture sludge and soil). Analysis of variance; mature plants; field-simulated experiment 2005–2007

	$\text{mg} \cdot \text{kg}^{-1}$					$\text{g} \cdot \text{ha}^{-1}$				
	Root	Stem	Capsule	Seed		Root	Stem	Capsule	Seed	
Flax	0.321 ^a	0.377 ^a	0.368 ^a	0.113 ^a		0.328 ^a	2.168 ^a	0.268 ^a	0.098 ^a	
	0.318 ^a	0.474 ^a	0.420 ^a	0.153 ^b		0.280 ^a	2.220 ^a	0.447 ^b	0.199 ^b	
Linseed	1.141 ^a	0.867 ^a	1.918 ^a	0.542 ^a		1.099 ^a	4.405 ^b	1.467 ^a	0.542 ^a	
	1.235 ^a	0.851 ^a	1.732 ^a	0.590 ^a		1.092 ^a	2.644 ^a	1.836 ^b	0.884 ^b	
Flax	33.978 ^a	37.343 ^a	114.099 ^a	72.047 ^b		32.047 ^b	183.420 ^b	89.578 ^a	59.603 ^a	
	32.997 ^a	37.928 ^a	118.679 ^a	67.695 ^a		27.018 ^a	118.162 ^a	115.072 ^b	81.381 ^b	

of linseed Atalante in root ($1.435 \text{ g Pb} \cdot \text{ha}^{-1}$), variety of linseed Biltstar in capsules ($2.414 \text{ g Pb} \cdot \text{ha}^{-1}$) and variety of linseed Flanders in seed ($1.028 \text{ g Pb} \cdot \text{ha}^{-1}$) (Table 6). Linseed Flanders had higher accumulative potential Cd in seed ($0.234 \text{ g} \cdot \text{ha}^{-1}$). Stem and capsules absorbed more Cd by linseed Biltstar ($3.986 \text{ g} \cdot \text{ha}^{-1}$, $0.573 \text{ g} \cdot \text{ha}^{-1}$) (Table 5). By monitoring of studied heavy metals during years there was found out various significant ($p \geq 0.05$) influence on their concentration an accumulation into parts of flax.

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References

- [1] Maxted A.P., Black C.R., West H.M., Crout N.M.J., McGrath S.P. and Young S.D.: *Phytoextraction of cadmium and zinc from arable soils amended with sewage sludge using *Thlaspi caerulescens*: development of a predictive model*. Environ. Pollut. 2007, **150**, 363–372.
- [2] McGrath S.P., Zhao F.J. and Chaudri A.M.: *Bioavailability of heavy metals from sewage sludge and some long-term effects on soil microbes in agricultural ecosystems*, [in:] Irradiated sewage sludge for application to cropland. IAEA, Vienna 2002, pp.199–216.
- [3] Bjelkova M., Vetrovcova M. and Griga M.: *The effect of sewage sludge-amended soil on Cd, Pb and Zn accumulation by hemp (*Cannabis sativa* L.) plants*, [in:] 4th Eur. Bioremed. Conf., Chania, Crete, Greece, 2008 p. 273.
- [4] Balik J., Tlustos P., Szakova J., Pavlikova D. and Cerny J.: *The accumulation of zinc in oat grown in soils treated by incubated sewage sludge with peat and straw*. Rostlinná výroba 2002, **48**(12), 548–555.
- [5] Jiao Y., Grant C.A., Bailey L.D.: *Effects of phosphorus and zinc fertilizer on cadmium uptake and distribution in flax and durum wheat*. J. Sci. Food Agricult. 2004, **84**(8), 777–785.
- [6] Piotrowska-Cyplik A. and Czarnecki Z.: *Phytoextraction of Pb, Cr and Cd by hemp during sugar industry anaerobic sewage sludge treatment*. EJPAU 2005, **8**(1), #3.

WPLYW OSADÓW ŚCIEKOWYCH W GLEBIE NA AKUMULACJĘ Cd, Pb ORAZ Zn W *Linum usitatissimum* L.

Abstrakt: Osad ściekowy jest produktem procesu oczyszczania ścieków. Osady ściekowe mogą być uznane za odpady niebezpieczne, wymagające kosztownych procedur usuwania, lub mogą być postrzegane jako źródło składników odżywczych do stosowania na gruntach rolnych. Badania przeprowadzono w symulowanych warunkach naturalnych – w doniczkach umieszczonych w ziemi na głębokości 50 cm, zawierających mieszaninę naturalnych osadów i gleb. Osady ściekowe dodano do odważonej ilości gleby w proporcjach: osady – gleba = 1:2 (var. K1), 1:3 (var. K2), 1:4 (var. K3), 1:5 (var. K4), 1:6 (var. K5). Wariant kontrolny (K0) bez obecności osadów ściekowych również obsiano wszystkimi odmianami. Badano odmiany lnu włóknistego i lnu oleistego. Odmiany lnu włóknistego i oleistego różnie kumulowały zwłaszcza metale; najwyższe stężenia zanotowano dla Zn, a następnie Pb i Cd. Najniższe stężenia Cd i Pb były analizowane w materiale siewnym ($0,121 \text{ mg} \cdot \text{kg}^{-1}$), a najwyższe stężenia Cd i Pb stwierdzono w łodydze (Cd = $0,396 \text{ mg} \cdot \text{kg}^{-1}$) i kapsułkach nasiennych (Pb = $1,881 \text{ mg} \cdot \text{kg}^{-1}$). Najwyższe stężenie Zn stwierdzono w kapsułkach nasiennych ($115,015 \text{ mg} \cdot \text{kg}^{-1}$), a najniższe w korzeniach ($33,782 \text{ mg} \cdot \text{kg}^{-1}$). Trend akumulacji Cd: łodyga > kapsułka nasienne > korzeń > nasiona, Pb: kapsułka nasienne > łodyga > korzeń > nasiona, Zn: kapsułka nasienne > nasiona > korzeń > łodyga. Wyniki badań i eksperymentów pokazują, że poszczególne odmiany lnu włóknistego i lnu oleistego wykazują zmienność umiejętności akumulacji metali ciężkich z gleby, a tym samym różne potencjały fitoremediacji.

Słowa kluczowe: *Linum usitatissimum* L., len włóknisty, len oleisty, kadm, ołów, cynk

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CLASSIFICATION OF DIFFERENT-SIZED AEROSOL MONITORING DATA

KLASYFIKACJA DANYCH MONITORINGOWYCH FRAKCJI AEROZOLU O RÓŻNYCH ROZMIARACH CZĄSTEK

Abstract: The present study deals with the application of self-organizing maps (SOM) of Kohonen for the classification of aerosol monitoring data sets from two sampling points (Arnoldstein and Unterloibach) located close to the border between Austria and Slovenia. The goal of the chemometric data treatment was to find some specific patterns in the classification maps for five different aerosol fractions collected in four different seasons of the year. The results obtained indicated a distinct separation of the ultrafine particles (PM 0.01–PM 0.4) from the other fractions which underlines their specific effect on human health. Seasonal separation but only between summer and winter sampling is also observed.

Keywords: chemometrics, classification, self-organizing maps, aerosol fraction, seasonal sampling

Assessment of the air pollution at sites of interest requires consequent and constant monitoring of carefully selected parameters. This usually results in a dataset with complex and multiway structure. For instance, consider a data set obtained as a result of monitoring air pollution described by several parameters measured at different sampling sites over 10 years. Possible multivariate statistical approaches to interpret and model such a data set are PARAFAC [1, 2], PARAFAC2 [3, 4] and Tucker3 [5, 6]. Such data can be seen as 3-way data array arranged as *sampling site* × *parameters* × *time* and thus explored with approaches dealing with 3-way data structure. Another opportunity for interpretation and classification of such type of data seems to be the application of self-organizing maps (SOM) of Kohonen which offer significant advantages in treating multidimensional data sets [7–12].

In the present study a more complex dataset is analyzed. It has been of a great interest [13] to monitor the concentration of different chemical components in the

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aerosol samples collected at two sampling sites scattered in the region of the Austrian province Carynthia close to the Slovenian border during spring, summer, autumn and winter. Additionally, the samples were classified in five particle size fractions in order to reveal differences, if they exist, in behavior of fine and coarse particles with respect to the concentrations of chemical components measured in the samples over the four seasons of the monitored year. It is substantial to note that industrial activity could be found on the Slovenian territory since on the Austrian side no industry is available.

The aim of the present study is to classify the monitoring data set from industrial region of Austria by the use of self-organizing maps of Kohonen in order to reveal the relationship between particle size and seasonality with respect to the air quality of the region in consideration. It is our conviction that this study will bring the better understanding of the complex processes that take place in the local area of interest. Besides, the increasing intensity of production of nanomaterials put on the agenda of the society the problem of possible hazards due to the emission of ultrafine particles in the atmosphere. Therefore, the main tasks of this model study are to find out if the different aerosol fractions and their seasonal distribution form different patterns in the classification schemes. No similar study has been ever performed up to our knowledge.

Experimental

The data set contains concentrations of 16 chemical components (Na, NH_4^+ , K, Ca, Mg, Cl^- , NO_3^- , SO_4^{2-} , C, Cd, Cu, Fe, Mn, Pb, V and Zn) and the amount of dust [$\mu\text{g}/\text{Nm}^3$], measured in triplicate in spring, summer, autumn and winter, in five different particle size fractions (PM0.04-PM0.1, PM0.1-PM0.4, PM0.4-PM1.6, PM1.6-PM6.4, PM6.4-PM25) at the two sampling sites Unterloibach and Arnoldstein, Carynthia, Austria.

Sampling sites

Two sampling sites are considered both located in the Austrian province Carynthia near to the Austrian-Slovenian border.

The sampling site Unterloibach is located in the Austrian province Carynthia at height 629 m a.s.l. (latitude $46^\circ 32'18''$ and longitude $14^\circ 48'52''$). The site is a typical rural one and is located near to the border with Slovenia. At a distance (northeast direction) of nearly 15 km a lead smelter is still active (on Slovenian territory) and in the eastern direction, again in Slovenia, a steel work is producing special quality steels. In southern direction one could detect the biggest Slovenian coal power station, which delivers over 75 % of the electricity for the country.

The sampling site Arnoldstein is also located in the Austrian province Carynthia at height 564 m a.s.l. (latitude $46^\circ 33'31''$ and longitude $13^\circ 42'12''$). The site is close to a small settlement with 700–800 m distance from an industrial region. At present three

different industrial enterprises – for waste recycling, for polymer production, and for steel finishing are active.

Sampling procedure

The aerosol data collection was gathered in the period between March 1999 and February 2000. The sampling was performed by the use of a high – volume sampler (Digital DHA-80), which is a completely automated device. The aerosol particles of the class PM₁₀ are collected on a daily basis on quartz fiber filters (QAT-UP, Pallflex, USA) allowing in this way determination of the carbon content. Additionally to the sampling by high-volume sampler four seasonal sampling campaigns by low-pressure impactor (LPI 75/0.04 according to Berner) were carried out.

Analytical procedure

The determination of the water-soluble ions (cations: sodium, ammonium, potassium, magnesium and calcium; anions: chloride, nitrate, sulfate) was performed by the use of two ion-chromatographic systems after extraction of the filters by deionised water in ultrasonic bath for 20 min.

The concentration of the heavy metals was determined by the use of atomic absorption spectrometry. One quarter of the filter was cut by a ceramic scissor and the sample was weighted and extracted with 10 cm³ 10 % HNO₃.

The analytical procedure for determination of carbon (total carbon, TC, black carbon, BC and organic carbon, OC) used the developments of the well-established approaches of [14] for sample burning in oxygen atmosphere (TC), optical determination (BC) and the difference between TC and BC for OC determination.

The complete description of the sampling devices, the pre-sampling preparation of the filters and the chemical analysis procedure could be found in [13].

Statistical data analysis

The SOM is an algorithm used to visualize and interpret large high-dimensional data sets [15]; it is an unsupervised pattern cognition method similar to cluster analysis. The main advantage of SOM is the simultaneous classification of variables and objects (sampling locations). Typical applications are visualizations of process states or financial results by representing the central dependencies within the data on the map. The map consists of a regular grid of processing units called neurons.

A model of some multidimensional observations, possibly a vector consisting of features (variables), is associated with each unit. The map attempts to represent all available observations with optimal accuracy using a restricted set of models. At the same time the models become ordered on the grid so that similar models are close to each other and dissimilar models far from each other. Fitting of the model vectors is usually carried out by a sequential regression process, where $t = 1, 2, \dots$ is the step

index. For each sample $x(t)$, the winner index c (best matching unit – BMU) is first identified by the condition:

$$\forall i, \|x(t) - m_c(t)\| \leq \|x(t) - m_i(t)\|$$

When the BMU has been found, the weight vectors of the SOM are updated so that the BMU is moved closer to the input vector in the input space.

Then, all the model vectors or a subset of them belonging to the nodes centered around node $c = c(\mathbf{x})$ are updated as:

$$m_i(t+1) = m_i(t) + h_{c(x),i}(x(t) - m_i(t))$$

Here, $h_{c(x),i}$ is the “neighborhood function”, a decreasing function of the distance between the i -th and c -th nodes on the map grid. This regression is usually reiterated over the available objects.

The trained map can be graphically presented by 2D planes for each variable, with the variable distribution values being indicated by different colors on the different regions of the map. Additionally, the node “coordinates” (vectors) can be clustered by the non-hierarchical K-means classification algorithm.

All calculations concerning SOM classification were performed by a free Teuvo Kohonen toolbox (SOM Toolbox 2.0), which can be downloaded together with documentation from <http://www.cis.hut.fi/projects/somtoolbox/>. Matlab 6.5 software as an environment was used. The statistical tests were performed by the use of software package STATISTICA 6.0.

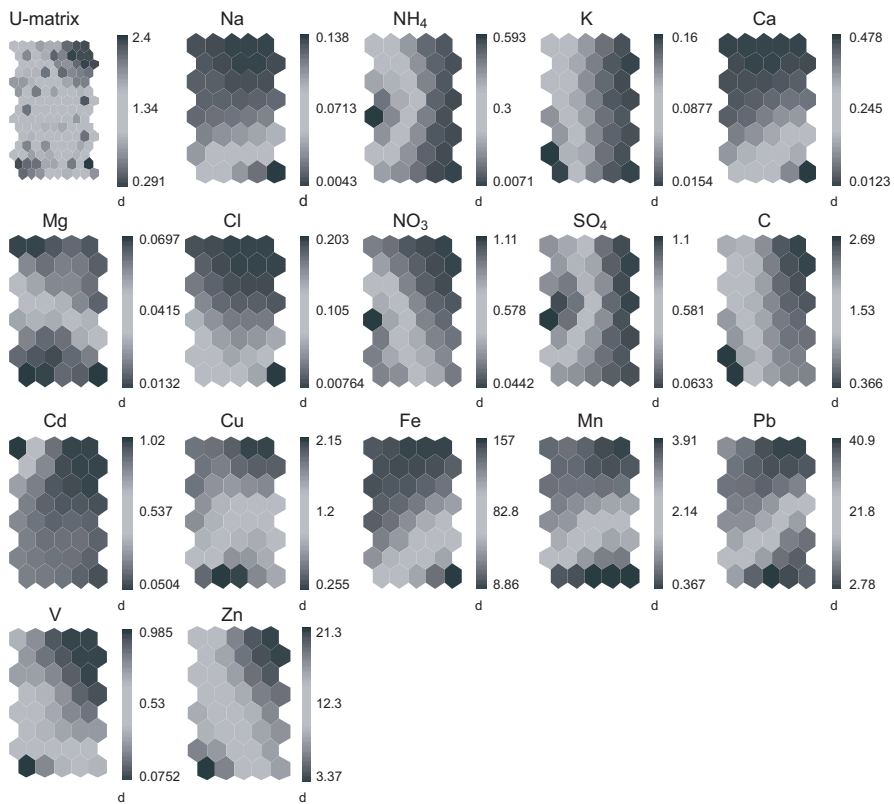
Results and discussion

Since the main target of the study was to find specific relationships between the season of sampling and the aerosol fraction, the data set was divided into two major parts: Arnoldstein monitoring results and Unterloibach monitoring results.

Site Arnoldstein

In Fig. 1 the self-organizing maps for all aerosol fractions and all sampling seasons are shown.

Several typical patterns could be detected from the classification maps. There is a group of classification objects (seasons, fractions) which are characterized by highest concentrations of calcium, sodium, iron, manganese, lead, copper and to some extent chloride (these objects are located at the right down corner of the SOMs). It might be assumed that this pattern reflects the effects of industrial impact around the sampling site. Another pattern is formed by the maps similarity of vanadium, zinc, carbon and to some extent potassium (highest concentrations of the analytes on the left down corner of the SOMs). This pattern is probably a reflection of the impact of combustion processes (oil, gasoline, coal, wood burning) in the neighborhood. The role of the atmospheric



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Fig. 1. Self-organizing maps for site Arnoldstein (all fractions, all seasons)

transfer of secondary aerosol is indicated by the formation of the third pattern where a resemblance is found in the maps of nitrate, sulfate, and ammonium (the highest concentrations of these major components of the aerosol are found on the middle of the left side of the SOMs). Magnesium and cadmium indicate a different distribution and do not resemble any of the patterns already defined. It may be assumed that magnesium shows this specificity due to the crustal impact of the Alpine region and cadmium – due to the ore content for the lead smelter production.

In Fig. 2 the grouping of the variables is indicated.

The variables classification panes show a slightly different grouping as compared by the empirical comparison of patterns of similarity between the general SOMs. Calcium, iron and sodium form the group probably related to the metallurgical impact of the Slovenian neighborhood. This group is very close to the one to which anthropogenic origin could be attributed – lead, manganese, copper. The effect of the secondary aerosol transport is indicated by the link between sulfate and ammonium and the burning sources are presented by the formation of group

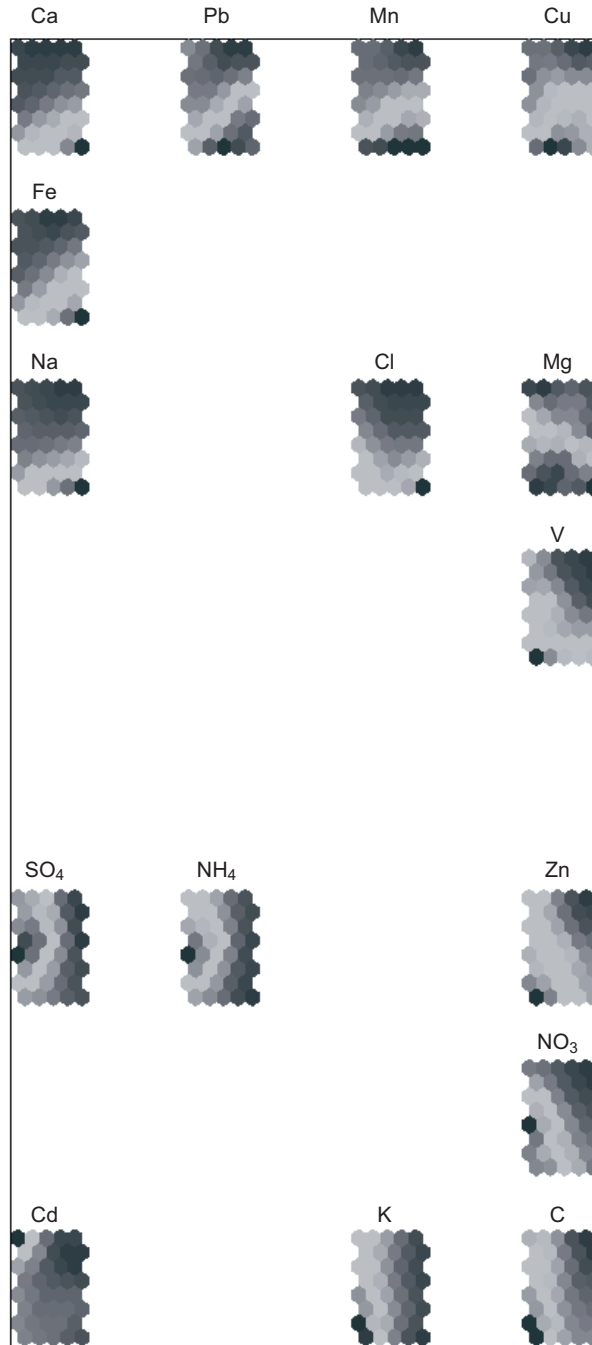


Fig. 2. The classification planes of the variables (Arnoldstein site)

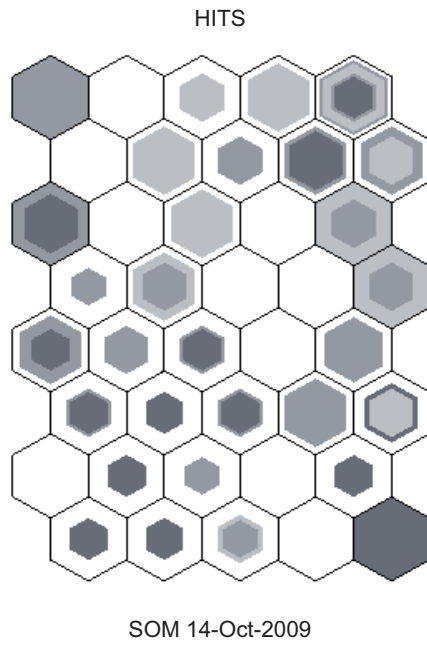


Fig. 3. Formation of seasonal clusters (Arnoldstein site)

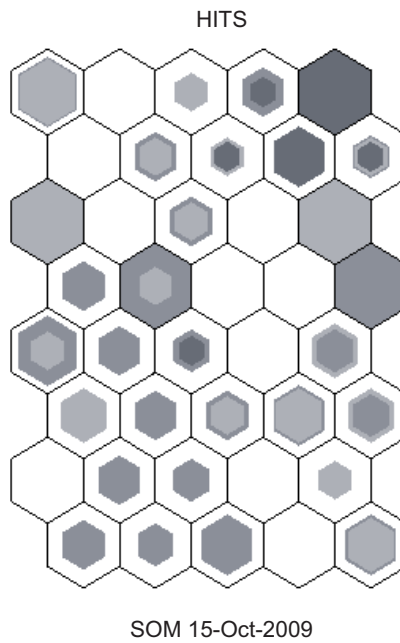


Fig. 4. Classification of the aerosol fractions (Arnoldstein site)

of similarity between potassium and carbon. Again, cadmium is located apart from the other chemical parameters reflecting the strong and specific impact of the lead smelter.

One important goal of the study was to try to find seasonal effects from the monitoring data collected in all seasons of the year. In Fig. 3 the classification of all aerosol fractions with respect to the seasonal distribution of the dust is shown.

It is obvious that the separation between summer and winter samples at Arnoldstein site is well expressed. The typical summer samples are dominantly located in the bottom part of the hit diagram since the winter samples are concentrated in the upper part. The other two seasons (spring and autumn) are not so distinctly separated from the rest of the samples. Therefore, one could introduce individual summer and winter pattern of the samples since the third one (for the spring and the autumn) is of non-specific character.

It is important to note that in the winter period the total amount of particulate matter, of the pollutant concentrations (arsenic, cadmium, chromium, copper, iron, manganese, nickel, lead, vanadium, zinc), and the carbon content all of them marking the anthropogenic impact have their highest concentrations. During the summer period these concentrations are lowest. Higher winter concentrations show also sodium, potassium, calcium and magnesium being related to the crustal impact to the total amount of the aerosol. The spring-autumn pattern is characterized by highest levels of the ions related to the secondary aerosol transfer – nitrate, sulfate and ammonium.

Since a more or less specific classification was found for the seasonal factor, it was interesting to check if such specificity could be found for the separate aerosol fractions. The results could be use when assessing the effects of different-sized aerosol particles on human welfare and health. This problem is quite interesting with respect to the increasing role of the nano-sized technologies.

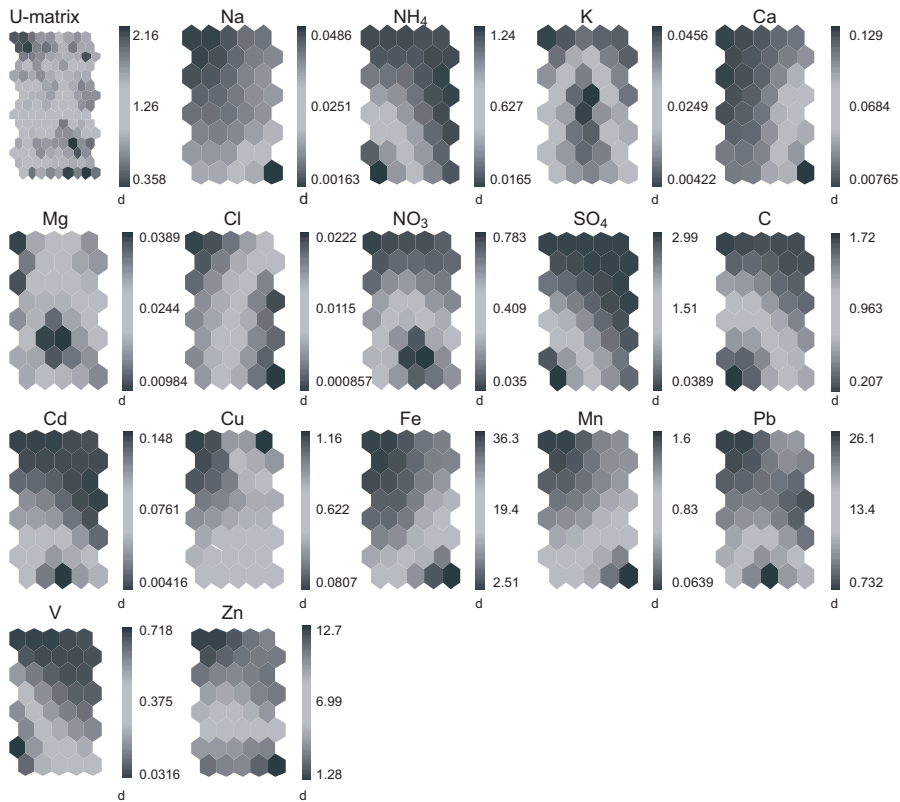
In Fig. 4 the hit diagram with classification results for all five fractions for all seasons (Arnoldstein site) is presented.

The finest aerosol fraction (PM_{0.04}-PM_{0.1}) is clearly separated from the other four and forms a well-defined cluster (upper right corner of the diagram). The “ultrafine” pattern is discriminated from the others by the lowest concentrations of chemical species in this particular fraction.

The next two fractions (PM_{0.1}-PM_{0.4} and PM_{0.4}-PM_{1.6}) form a “fine mixed” pattern characterized by increasing level of concentrations reaching its maximum in fraction (PM_{0.4}-PM_{1.6}). A similar mixing (“coarse mixture”) is observed for the coarse fractions (PM_{1.6}-PM_{6.4} and PM_{6.4}-PM₂₅). In the latter case the concentration of the chemical components starts decreasing after reaching the maximum of the “fine mixed” pattern.

Site Unterloibach

Next four figures (Figs. 5–8) illustrate the classification results for the different seasons and fractions of the aerosol samples collected at the Unterloibach site.



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Fig. 5. Self-organizing maps for site Unterloibach (all fractions, all seasons)

From the general maps (Fig. 5) the patterns formed are including the pattern of the industrial impact (sodium, calcium, chloride, manganese, iron, zinc), the second mixed pattern of combustion processes and secondary emissions (ammonium, carbon, sulfate and vanadium) and the third combined pattern reflecting anthropogenic and crustal influences (nitrate, lead, cadmium, potassium and magnesium). The specific position of copper on the general maps location reflects site specificity related to copper ore treatment.

Almost the same configuration could be derived from the classification planes of the variables (Fig. 6).

It is interesting to note that for this particular site the seasonal classification differs substantially from that of Arnoldstein site (Fig. 7). No distinct division between seasons is found and it proves the significant difference of the air quality and its seasonal parameters at the two sites.

However, the classification of the aerosol fractions resembles almost completely the separation at site Arnoldstein (Fig. 8). A very clear separation of the “ultrafine” fraction

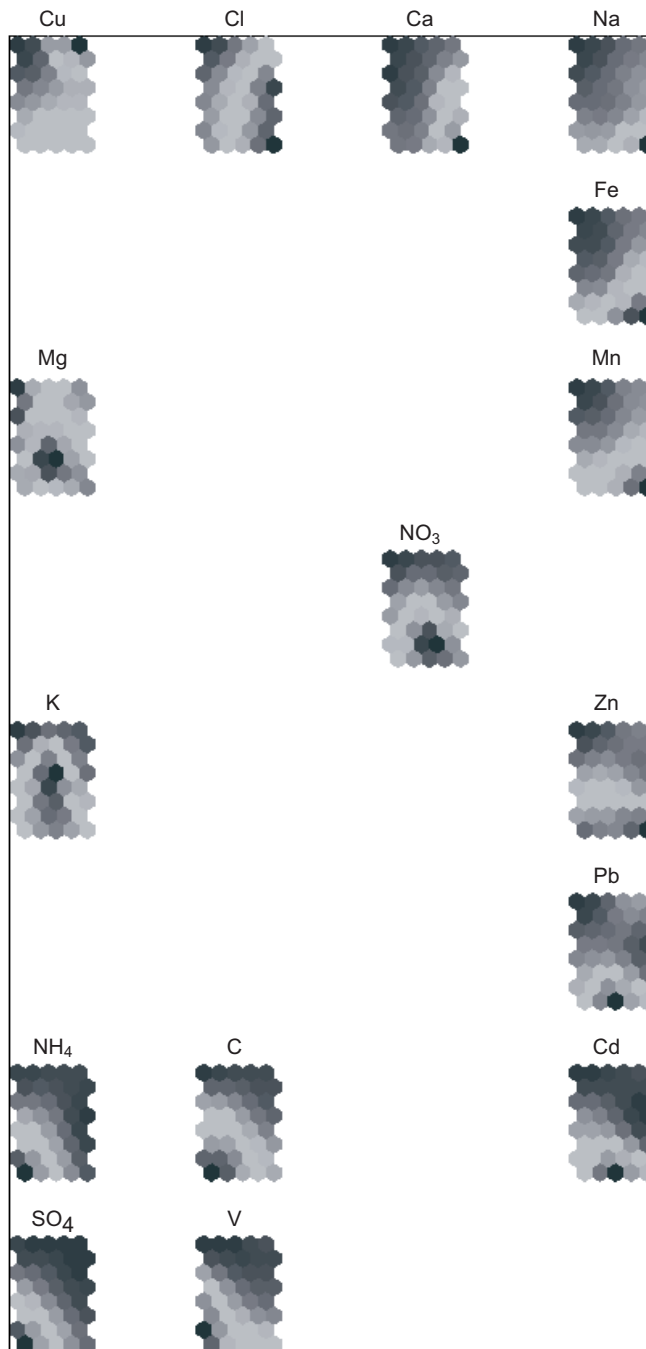


Fig. 6. The classification planes of the variables (Unterloibach site)

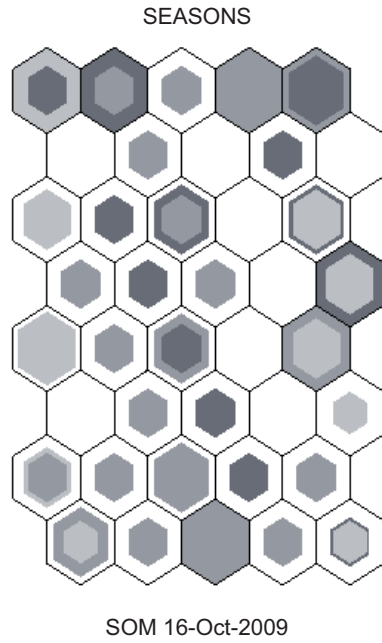


Fig. 7. Formation of seasonal clusters (Unterloibach site)

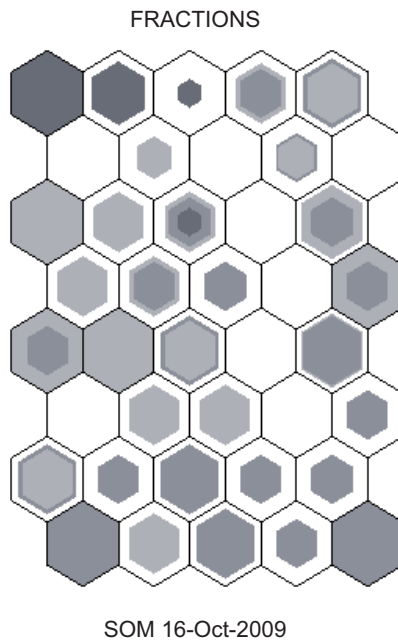


Fig. 8. Classification of the aerosol fractions (Unterloibach site)

from the rest of the fractions is observed since the other four fractions are of mixed character.

Conclusions

The most significant results from the study carried out was the classification of the aerosol fractions and separating a “ultrafine” fraction pattern characterized by lowest concentrations of the chemical parameters but a very stable and not mixable with the other fraction patterns system. This is an indirect proof of the special physicochemical and probably health-affecting role of the fine aerosol fractions in the ambient atmosphere. Besides, there is a clear separation of the aerosol effects between winter and summer seasons which indicates that the health hazards could be different in different seasons. Finally, the site location is also an separate factor which should be interpreted in all possible air quality assessments.

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References

- [1] Bro R.: Chemomet. Intell. Lab. Syst. 1997, **38**, 149–171.
- [2] Faber N., Bro R. and Hopke P.: Chemomet. Intell. Lab.Syst. 2003, **65**, 119–137.
- [3] Kiers H., Ten Berge J. and Bro R.: J. Chemomet. 1999, **13**, 275–294.
- [4] Bro R., Anderson C.A. and Kiers H.A.L.: J. Chemomet. 1999, **13**, 295–309.
- [5] Henrion R.: Chemomet. Intell. Lab. Syst. 1994, **25**, 1–23.
- [6] Geladi P.: Chemomet. Intell. Lab. Syst. 1989, **7**, 11–30.
- [7] Tsakovski S., Simeonova P., Simeonov V., Freitas M.C., Dionosio I. and Pacheko A.M.G.: J. Radioanal. Nucl. Chem. 2009, **281**, 17–22.
- [8] Wen G., Guo X., Huang D. and Liu K.: IEEE Int. Conf. on Neural Networks – Conf. Proc. Art. 4371093, 2007, 991–996.
- [9] Stanimirova I. and Simeonov V.: Chemomet. Intell. Lab. Syst. 2005, **77**, 115–121.
- [10] Astel A., Tsakovski S., Barbieri P. and Simeonov V.: Water Res. 2007, **41**, 4566–4578.
- [11] Tsakovski S., Kudlak B., Simeonov V., Wolska L. and Namiesnik J.: Anal. Chim. Acta 2009, **631**, 142–152.
- [12] Kolehmainen M., Martikainen H., Hiltunen T. and Ruuskanen J.: Environ. Monit. Assess. 2000, **65**, 277–286.
- [13] Lavric T.: Composition and Sources of Aerosols (PM10) in the border Region Carynthia – Slovenia – Italy. Ph.D. Thesis, Technical University of Vienna, Vienna 2002.
- [14] Puxbaum H. and Rendl J.: Microchim. Acta 1983, 263–272.
- [15] Kohonen T.: Self-Organizing Maps. Springer, New York 2001.

KLASYFIKACJA DANYCH MONITORINGOWYCH FRAKCJI AEROZOLU O RÓŻNYCH ROZMIARACH CZĄSTEK

Abstrakt: Przedstawiono wyniki badań monitoringowych próbek aerozolu atmosferycznego pobranych z dwóch punktów pomiarowych (Arnoldstein i Unterloibach) z pobliza granicy między Austrią i Słowenią.

Dane zinterpretowano z wykorzystaniem samoorganizujących się map (SOM) Kohonena. Celem chemometrycznej interpretacji danych było znalezienie charakterystycznych struktur na mapach klasyfikacji dla pięciu różnych frakcji aerozoli, zebranych w czterech różnych porach roku. Uzyskane wyniki wskazują na wyraźne oddzielenie najdrobniejszych cząstek (PM 0,01 – PM 0,4) od innych frakcji, co wskazuje na ich specyficzne działanie na zdrowie człowieka. Obserwuje się również zmiany sezonowe, ale tylko między próbkami pobranymi latem i zimą.

Słowa kluczowe: chemometria, klasyfikacja, mapy samoorganizujące się, frakcja aerozolowa, próbkowanie sezonowe

Mirosław WIATKOWSKI¹

INFLUENCE OF MSCIWOJOW PRE-DAM RESERVOIR ON WATER QUALITY IN THE WATER RESERVOIR DAM AND BELOW THE RESERVOIR

WPLYW ZBIORNIKA WSTĘPNEGO MŚCIWOJÓW NA JAKOŚĆ WODY W ZBIORNIKU ZAPOROWYM I PONIŻEJ ZBIORNIKA

Abstract: The paper presents results of research carried out in the period of November 2006 – October 2008 and focused on the influence of the Msciwojow pre-dam reservoir on the quality of water in the main reservoir and below. The following water quality indicators were determined: NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , water temperature, pH, electrolytic conductivity, dissolved oxygen and chlorophyll *a*. The measurements were carried out for the Msciwojow reservoir, located on the Wierzbiak river in Lower Silesia province (south-western part of Poland).

Contribution of the pre-dam reservoir to the reduction of pollutants in water of the Wierzbiak and Zimnik rivers flowing into the main reservoir was analyzed. During the performed analyzes the following reductions of the main physico-chemical indicators in the pre-dam reservoir were observed, ie nitrates(V) by 69.9 %, phosphates by 32.9 %, nitrates(III) by 63.2 % and ammonia by 62.9 %. The increase of water temperature, pH and dissolved oxygen was also recorded. In the study the quality of water flowing into the Msciwojow reservoir, outflowing water and water stored in the pre-dam and in the main reservoir was assessed. The obtained results showed that the pre-dam reservoir contributed to the improvement of the quality of water flowing into the main reservoir. Proposals for defining dimensions of pre-dam reservoirs and designing principles were presented.

Keywords: pre-dam, water reservoir, pre-dam reservoir efficiency, water quality, water protection

Small water reservoirs, due to their location in the lowest part of the catchment, collect pollutants from the entire catchment area, which testifies to their high sensitivity to processes occurring in the catchment. Apart from their main functions (flood control, agricultural irrigation, fish-farming, water power generation and recreation) they also play an important role in the development of water resources and natural amenities, constituting a key element in water quality protection [1–5]. Small water reservoirs are usually located in agricultural catchments and they form ecosystems accumulating biogenic substances, such as nitrogen and phosphorus compounds as well as various

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pollutants. These processes may result in deterioration of water in reservoirs, their eutrophication and alluviation. Phosphorus and nitrogen compounds transported by rivers generally come from point and area sources [6–8]. For many years attempts have been made to stop biogenic substances at the reservoir inlets. The reduction of their inflow, particularly phosphorus and nitrogen, as well as prevention from alluviation can be achieved in many ways and with different effects. One of these methods is construction of a pre-dam reservoir [9].

Examples of using pre-dam reservoirs to reduce the inflow of nutrients to the main reservoir and the effectiveness of such actions can be found in literature [6, 10–14]. The main functions of pre-dam reservoirs are: stopping the bed load, suspended sediments and fertilizing substances; visual improvement of the landscape at the end of backwater; preventing from uncovering in backwater areas at the main reservoir drawdowns; protecting from eutrophication and landscape deformation; providing additional storage of water in the pre-dam reservoir; storing up water for emergency situations; and recreation purposes (water sports) [14].

Pre-dam reservoirs are constructed directly in front of the main reservoir, usually at its backwater part or aside [15–16].

The aim of this study was to assess the influence of the pre-dam reservoir on the reduction of pollutants in water supplying the main reservoir and below it. Based on the Msciwojow pre-dam reservoir some guidelines for setting up dimensions of such reservoirs were presented.

Study area and methodology

The Msciwojow reservoir was constructed by dividing the Wierzbiak river with an earth dam at 35 + 375 km of its course. A watercourse called Zimnik also flows into the river (Fig. 1). Before the construction of the reservoir Wierzbiak and Zimnik valleys converged at the place of the present bowl. The Msciwojow reservoir is situated in the municipality of Msciwojow, county of Jawor, Lower Silesia province. The Wierzbiak catchment at the reservoir dam's profile covers the area of 47.0 km², including the partial surface area of Zimnik, ie 14.3 km². The main functions of the reservoir are: flood control, providing water for irrigation of agricultural areas, recreation and fishing. The reservoir has been operating since 1999. Its bowl was divided into the main reservoir and a pre-dam with a sedimentation tank and biological barriers (the main reservoir is separated from the pre-dam by a biological barrier III) (Fig. 1). Such a solution resulted from the necessity of partial removal of biogenic substances and suspended solids from the inflowing water in the pre-dam reservoir. Biological barriers are in the form of levees. Their role is to direct the flow to extend the retention time in the pre-dam reservoir. This prolongs the contact of water with water plants and microorganisms, which by absorbing the biogenic substances improve its quality.

The total capacity of the Msciwojow reservoir at a normal operational fill level (NPP) is 735000 m³ and the filling area – 34.59 ha. The average depth of the reservoir is 2.0 m. As far as the pre-dam reservoir is concerned, its total capacity at the normal operational fill level amounts to 175000 m³, whereas the filling area is 14 ha. The

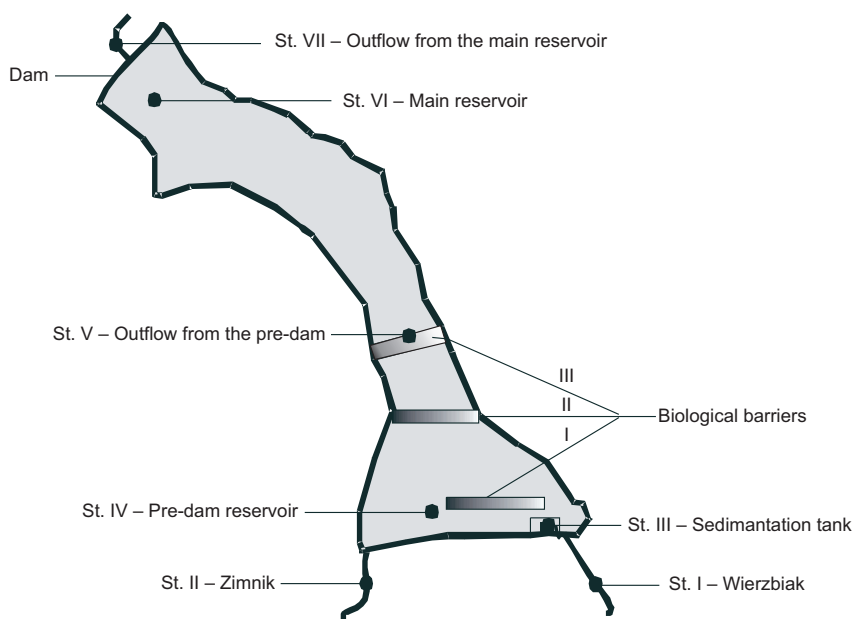


Fig. 1. Location of the Msciojow reservoir on Wierzbiak and Zimnik rivers. Sampling points: St. I – Wierzbiak (reservoir inlet); St. II – Zimnik (reservoir inlet); St. III – sedimentation tank; St. IV – bowl of the pre-dam reservoir; St. V – outflow from the pre-dam; St. VI – main reservoir; St. VII – outflow from the main reservoir

average depth of the pre-dam reservoir is 1.3 m. The average flow in the reservoir profile amounts to $0.171 \text{ m}^3 \cdot \text{s}^{-1}$, ie $0.122 \text{ m}^3 \cdot \text{s}^{-1}$ (the Wierzbiak river) and $0.049 \text{ m}^3 \cdot \text{s}^{-1}$ (the Zimnik river) [6]. The average retention time in the main reservoir is about 38 days and in the pre-dam – about 12 days.

The reservoir catchment is used for agricultural purposes. There is no sewerage system in the catchment. Wastewater from the Msciojow reservoir, mainly municipal and domestic effluents, are discharged directly to the Wierzbiak and Zimnik rivers, above the reservoir.

The quality of water in the reservoir area was measured once a month at 7 sampling points: above the Msciojow reservoir, on the Wierzbiak river, at 37 + 540 km of its course (St. I); on the Zimnik river, at 0 + 800 km (St. II); in the sedimentation tank (St. III); in the pre-dam reservoir (St. IV); at the outflow from the pre-dam reservoir (St. V); in the main reservoir (St. VI) and at the outflow from the main reservoir (St. VII) – Fig. 1.

At the reservoir inlet and outlet water samples were collected from the subsurface layer in the stream. In the reservoir water was sampled at the depth of about 50 cm below the water-table. The following parameters were determined: NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , water temperature, pH, electrolytic conductivity, dissolved oxygen and chlorophyll *a*. The latter one was determined by the Province Inspectorate of Environmental Protection in Opole according to PN-86/C-05560/02 standard. Water pH, electrolytic

conductivity and water temperature were measured *in situ*. Determination of water quality chemical indicators was performed in the laboratory of the Department of Land Protection University of Opole. Additional analyses of water quality were carried out in the laboratory of the Department of Construction and Infrastructure at Wrocław University of Environmental and Life Sciences.

Based on the average values of the selected water quality indicators for the Wierzbiak (St. I) and Zimnik rivers (St. II) flowing into and out of the Mściwojow reservoir, obtained during a 2 years' measurement period and hydrometric measurements – loads [kg] of inflowing and outflowing pollutants were calculated.

In order to assess the impact of the pre-dam reservoir on the quality of water in the main reservoir and below, the average values of particular physico-chemical indicators of the Wierzbiak (St. I) and Zimnik rivers (St. II) were determined according to the following equations:

$$\bar{W}_{iD} = \frac{C_{Xi} W \cdot QW + C_{Xi} Z \cdot QZ}{QW + QZ} \quad (1)$$

where: \bar{W}_{iD} – average concentration of i physico-chemical indicator in water flowing into the reservoir bowl [mg/dm³];

$C_{Xi}W$, $C_{Xi}Z$ – average concentration of i physico-chemical indicator in Wierzbiak and Zimnik rivers [mg/dm³];

QW , QZ – water volume of Wierzbiak and Zimnik in Δt [m³].

Changes [%] of nitrate(V), nitrate(III) and ammonia loads in the pre-dam and the main reservoir were calculated based on the difference between their average values in the inflowing water (St. I and St. II), water flowing out of the pre-dam reservoir (St. V) and water flowing out of the main reservoir (St. VII).

The quality of the Wierzbiak and Zimnik water flowing into the reservoir, water at the reservoir outlet as well as water stored in the reservoir was assessed according to the Regulation on the ways of classifying the uniform parts of surface water bodies [17]. Assessment of the eutrophication process was presented and the sensitivity of the analyzed water to nitrogen compounds coming from agricultural sources was determined in the context of the above-mentioned Regulation [18].

Results and discussion

Characteristics of water flowing into the Mściwojow reservoir, water stored in the sedimentation tank, pre-dam reservoir and the main reservoir, as well as water flowing out of the pre-dam and the main reservoir in the period of 2006–2008 is presented in Table 1.

It can be noticed that the highest averaged values in water flowing into the reservoir (St. I and St. II) were recorded for nitrates(V), nitrates(III), phosphates and electrolytic conductivity. In the sedimentation tank (St. III) the highest values were found for water temperature and dissolved oxygen, whereas in the pre-dam reservoir (St. IV) – for water pH.

Table 1

Characteristics of water flowing into the Msciwojow reservoir (St. I, St. II), water in the sedimentation tank (St. III) and pre-dam reservoir (St. IV), water flowing out of the pre-dam reservoir (St. IV), water in the main reservoir (St. V) and water flowing out of the main reservoir in November 2006 – October 2008

Water quality indicator	Inflow to the pre-dam reservoir (Wierzbiak) St. I	Inflow to the pre-dam reservoir (Zimmik) St. II	Sedimentation tank St. III	Pre-dam reservoir St. IV	Outflow from the pre-dam reservoir St. V	Main reservoir St. VI	Outflow from the main reservoir St. VII
Nitrates(V) [mg NO ₃ ⁻ /dm ³]	<u>10.6–61.0</u> 31.39	<u>12.1–44.0</u> 32.83	<u>2.2–35.00</u> 22.61	<u>0.8–35.0</u> 12.18	<u>0.80–31.0</u> 9.58	<u>0.80–25.0</u> 5.63	<u>0.8–26.0</u> 8.80
Nitrites(III) [mg NO ₂ ⁻ /dm ³]	<u>0.03–0.66</u> 0.22	<u>0.02–0.5</u> 0.22	<u>0.07–0.59</u> 0.21	<u>0.003–0.3</u> 0.1	<u>0.003–0.23</u> 0.081	<u>0.003–0.15</u> 0.054	<u>0.003–0.20</u> 0.071
Ammonia [mg NH ₄ ⁺ /dm ³]	<u>0.03–0.82</u> 0.26	<u>0.05–2.60</u> 0.67	<u>0.05–0.50</u> 0.16	<u>0.05–0.26</u> 0.13	<u>0.03–0.33</u> 0.14	<u>0.05–0.64</u> 0.19	<u>0.05–2.56</u> 0.34
Phosphates [mg PO ₄ ³⁻ /dm ³]	<u>0.2–1.6</u> 0.61	<u>0.28–2.00</u> 0.77	<u>0.13–1.34</u> 0.57	<u>0.17–1.46</u> 0.56	<u>0.05–1.26</u> 0.44	<u>0.06–1.2</u> 0.45	<u>0.10–1.97</u> 0.61
Water temperature [°C]	<u>2.0–23.4</u> 10.41	<u>2.1–23.2</u> 10.25	<u>2.0–25.9</u> 11.86	<u>2.1–27.2</u> 11.34	<u>2.0–27.5</u> 11.60	<u>2.0–27.6</u> 11.13	<u>2.5–26.1</u> 10.51
Reaction (pH) [-]	<u>7.2–8.6</u> 7.83	<u>7.0–8.3</u> 7.64	<u>7.1–9.8</u> 8.41	<u>7.1–9.4</u> 8.46	<u>6.90–9.50</u> 8.42	<u>7.2–9.10</u> 8.36	<u>7.4–9.1</u> 8.1
Electrolytic conductivity [µS/cm]	<u>662–783</u> 715.41	<u>437–901</u> 706.45	<u>578–743</u> 668.82	<u>556–708</u> 641.38	<u>545–676</u> 618.86	<u>532–887</u> 624.30	<u>532–887</u> 617.81
Dissolved Oxygen [mg O ₂ /dm ³]	<u>8.02–13.86</u> 10.60	<u>7.03–11.73</u> 8.63	<u>8.69–17.5</u> 13.3	<u>8.57–13.87</u> 11.68	<u>8.43–13.66</u> 10.84	<u>8.76–13.48</u> 10.96	<u>4.23–13.0</u> 8.0

The analyzed data also show that at St. V sampling point (outflow from the pre-dam) higher values of water temperature, water pH and dissolved oxygen were observed in comparison with St. I and St. II (inflow to the reservoir). At St. VII (outflow from the main reservoir) the values of ammonia and phosphates were higher than at St. V.

In the summer season water blooms were observed in the Msciwójow reservoir (St. IV and St. VI). In 2008 the content of chlorophyll *a* in the reservoir varied from $56.4 \mu\text{g}/\text{dm}^3$ (01.07.2008) to $107.6 \mu\text{g}/\text{dm}^3$ (26.08.2008). The values of chlorophyll *a* exceeded the limit values for water quality indicators defined for uniform parts of surface water bodies, such as lakes and other natural water reservoirs from class V [17].

Wierzbiak and Zimnik water (St. I and St. II) flowing to the Msciwójow reservoir as well as water from the sedimentation tank (St. III) and the pre-dam reservoir (St. IV) were classified as eutrophic. At the above-mentioned sampling points the annual average concentration of nitrates exceeded the limit value ($10 \text{ mg NO}_3 \cdot \text{dm}^{-3}$) and the concentration of chlorophyll *a* exceeded the limit value ($25 \mu\text{g}/\text{dm}^3$) defined in the Regulation of the Minister of the Environment from 2008 [17]. Moreover, it was found out that Wierzbiak water was sensitive to nitrogen compounds coming from agricultural sources as the concentrations of nitrates were higher than the values ($50 \text{ mg NO}_3 \cdot \text{dm}^{-3}$) defined in the Regulation [18].

From nine water quality indicators analyzed in the Msciwójow reservoir seven (except for phosphates and nitrates(III)) are taken into consideration in the water quality classification [17].

The analysis of Wierzbiak and Zimnik water quality (St. I and St. II) showed that the values of N-NH_4^+ , water pH, electrolytic conductivity and dissolved oxygen did not exceed the limit values of water quality indicators for uniform parts of surface water bodies in natural watercourses, such as rivers of class I. However, concentrations of N-NO_3^- and water temperature were higher than the limit values defined for class II [17].

The analysis of Wierzbiak water below the reservoir (St. VII) showed that values of N-NO_3^- , N-NH_4^+ , electrolytic conductivity and dissolved oxygen did not exceed the limit values of water quality indicators for uniform parts of surface water bodies in natural watercourses, such as rivers of class I. However, water temperature and pH were higher than the limit values defined for class II [17].

In order to assess the impact of the Msciwójow pre-dam reservoir on the quality of water stored in the main reservoir and below it, downstream the Wierzbiak river, physico-chemical indicators describing the quality of water in front of the reservoir (St. I and St. II), at the outlet from the pre-dam reservoir (St. V) and below the reservoir (St. VII) were analyzed. The following four indicators were selected: nitrates(V), nitrates(III), ammonia and phosphates. Changes in the loads of the above-mentioned chemical compounds are presented in Table 2.

Table 2 shows that in the investigated period the load of nitrates(V) decreased by 69.9 % (St. V) while flowing through the pre-dam reservoir, and after passing through the main reservoir (St. VII) further reduction was observed (by 8.1 % in comparison with sampling point St. V).

Table 2

Changes in loads of nitrates(V), nitrates(III), ammonia, phosphates, and total suspended solids [$\text{kg} \cdot \text{d}^{-1}$] at sampling points St. I, St. II, St. V and St. VII in the period of November 2006 – October 2008

Water quality indicator	Average value in water [$\text{kg} \cdot \text{d}^{-1}$]			% Changes in the pre-dam reservoir (among St. I, St. II and St. V)	% Changes in the main reservoir (between St. V and St. VII)
	Inflow to the reservoir (St. I and St. II)	Outflow from the pre-dam reservoir (St. V)	Outflow from the main reservoir (St. VII)		
Nitrates(V) [kg N-NO_3^-]	106.098	31.950	29.358	69.9	8.1
Nitrates(III) [kg N-NO_2^-]	0.989	0.364	0.319	63.2	12.4
Ammonia [kg N-NH_4^+]	4.334	1.609	3.907	62.9	142.8 (increase)
Phosphates [kg P-PO_4^{3-}]	3.092	2.075	2.876	32.9	38.6 (increase)

The load of nitrates(III) in the pre-dam reservoir was reduced by 63.2 % and after passing through the main reservoir it was still reduced by 12.4 % in comparison with St. V sampling point.

As far as ammonia is concerned, the reduction of its load in the pre-dam reservoir (St. V) in comparison with waters flowing into the reservoir (St. I and St. II) was 62.9 %. The same parameter for water flowing through the main reservoir (St. VII) went up by 142.8 % in comparison to St. V (Table 2).

Concentration of phosphates in water flowing to the Msciwojow reservoir decreased after passing through the pre-dam reservoir. The average load of phosphates in water flowing through the pre-dam reservoir went down by 32.9 % in comparison with St. I and St. II sampling points. After further flow of water through the main reservoir the value for phosphates increased by 38.6 % (Table 2).

According to literature pre-dam reservoirs can improve the quality of water in the main reservoirs. The analysis of the Msciwojow pre-dam reservoir, carried out in the period of 2000–2002 [6], shows that its efficiency was: 66.5 % for nitrates(V), 50 % for nitrates(III), 34.3 % for ammonia and 52.8 % for phosphates. According to Benndorf et al [10–11] the phosphate reduction efficiency calculated on the basis of measurements carried out in 13 pre-dam reservoirs in Germany varied from 14 % at an average retention time of 12 hours in Forchheim pre-dam reservoir to 66.5 % at the retention time of 12 days in Hassel pre-dam reservoir. Information on the elimination of phosphates can also be found in [12]. The authors of this study report on high efficiency of pre-dam reservoirs ranging from 52 % to 74 %.

Effectiveness of the pre-dam reservoir Brzozki on the Pratwa river (Opole province) as described by [19] is 36.5 % for nitrates(V), 28.6 % for nitrates(III), 51.6 % for phosphates and 57.1 % for total phosphates.

Research studies carried by Skonieczek and Szymczyk [20], Skonieczek and Koc [21] showed that a small water reservoir (pond) significantly contributed to the reduction of concentrations and loads of phosphorus and nitrogen compounds in the

water of Szabruk watercourse (near Olsztyn) flowing through the reservoir. The average annual reduction of the total phosphorus was 58 % and phosphates P-PO_4^{3-} – 60 %.

Proposals for defining dimensions of pre-dam reservoirs and designing principles

In order to investigate to what an extent a water reservoir is liable to eutrophication and whether it is necessary to build a pre-dam reservoir in backwater some calculations must be made. Below calculations made for the Msciwojow reservoir in the period of 2006–2008 are presented. Based on Vollenweider's criterion [22], in Benndorf's modification [23], and at the assumption that the concentration of phosphates in the potential reservoir (St. I and St. II) is $0.66 \text{ mg PO}_4^{3-} \cdot \text{dm}^{-3}$ (according to equation 1), it was found out that the amount of phosphates per 1 m^2 of the reservoir was $3.28 \text{ g P-PO}_4 \cdot \text{m}^{-2} \cdot \text{a}^{-1}$ at the ratio of the average reservoir depth of 2,0 m to the retention time. The load of inorganic nitrogen flowing into the reservoir was $305.3 \text{ Mg N} \cdot \text{a}^{-1}$. According to Kajak [15] the real loads are usually much higher than the dangerous loads. The annual loads vary from a dozen or so to even more grams of phosphorus and almost 200 g of nitrogen per 1 m^2 of the reservoir surface area. Therefore, the Msciwojow reservoir must be classified as a polytrophic lake. It must be noted here, that calculations were made only for phosphorus and nitrogen coming from inflows and a direct catchment or internal load from sediments were not taken into consideration. Therefore, in order to protect the Msciwojow reservoir against pollutants flowing from the catchment the construction of the pre-dam reservoir in backwater was proposed as early as at the designing stage [24].

To achieve proper operation of the pre-dam reservoir its dimensions should be defined in such a way so that they would guarantee proper operation of the reservoir throughout the entire operating period. Pre-dam dimensioning procedure, based on the Msciwojow reservoir and research studies [10, 25, 26], is presented below. Calculations were made for the assumed retention time in the pre-dam reservoir of 5–15 days [6, 10–12, 25]:

a) For Wierzbiak and Zimnik rivers feeding the Msciwojow reservoir the average flow $\text{SQ} = 0.171 \text{ m}^3 \cdot \text{s}^{-1}$, and taking into consideration the retention time $\Delta t = 5$ days the required capacity of the pre-dam reservoir $V_{\text{zb_wst}}$ should be:

$$V_{\text{pre-dam}_5} = 86400 \cdot \Delta t \cdot \text{SQ} = 0.0738 \cdot 10^6 \text{ m}^3 \quad (2)$$

b) At the assumed retention time in the pre-dam reservoir $\Delta t = 12$ days (according to Benndorf [10] it is the optimum retention time):

$$V_{\text{pre-dam}_{12}} = 86400 \cdot \Delta t \cdot \text{SQ} = 0.1773 \cdot 10^6 \text{ m}^3 \quad (3)$$

c) Assuming the retention time in the pre-dam reservoir $\Delta t = 15$ days:

$$V_{\text{pre-dam}_{15}} = 86400 \cdot \Delta t \cdot \text{SQ} = 0.2216 \cdot 10^6 \text{ m}^3 \quad (4)$$

d) The second criterion determining the operational capacity of the pre-dam reservoir refers to rising flows (flood discharge). Two years' high flow $Q_{50\%}$ (without the volume of the assumed bed load) should be retained in the reservoir for 12 hours. Assuming that:

- capacity of the main reservoir $V_{\text{main_res}} = 0.735 \cdot 10^6 \text{ m}^3$,
 - rising flow (flood discharge) $Q_{50\%} = 5.5 \text{ m}^3 \cdot \text{s}^{-1}$,
 - volume of the sediments $V_o = 0.01 \cdot V_{\text{main_res}} = 0.0735 \cdot 10^6 \text{ m}^3$
- the capacity of the pre-dam reservoir should be:

$$V_{\text{pre_dam}} = Q_{50\%} \cdot 0.5 \cdot 86400 + V_o = 0.2376 \cdot 10^6 \text{ m}^3 \quad (5)$$

e) The current capacity of the Msciwojow pre-dam reservoir is $V = 0.175 \cdot 10^6 \text{ m}^3$. However, according to equations 2–5 the reservoir capacity should be 0.0738–0.2376 10^6 m^3 . It must be pointed out here, however, that too high capacity of the pre-dam reservoir is not recommended if wastewater management in the reservoir catchment is changed.

For the assumed parameters of the pre-dam reservoir a potential average annual reduction of phosphorus can be estimated, based on relationships presented in [27]. The average annual water flow Q [m^3/d] in the watercourse feeding the pre-dam reservoir and the average annual retention time at Msciwojow pre-dam $t = V/Q$ [days] should be assumed (where V – capacity of the existing or planned pre-dam reservoir; Q – average annual flow). Then the average annual phosphorus reduction for the previously defined parameters of the pre-dam reservoir should be about 60 %. It should be stressed here, that this is the best method for pre-dam reservoirs provided that the phosphorus load is not too big. Otherwise, it must be assumed that the reduction will be lower [27]. Such a situation was in the case of the Msciwojow reservoir in 2006–2008.

Based on the gained experience as well as literature data some recommendations for the optimum operation of pre-dam reservoirs can be given. Firstly, they should be located at the river inflow to the reservoir bowl. Their average depth should not exceed 3 m, which enables optimum use of light in the process of primary production of phytoplankton. The flow rate should guarantee longer contact of water with vegetation in the pre-dam reservoir and with microorganisms, which absorb biogenic substances contributing to the improvement of water quality. Moreover, the pre-dam reservoir should be equipped with an upper spillway to enable the release of surface water with the lowest phosphorus concentrations. It is also recommended that the pre-dam reservoir should be cleaned on a regular and stage-by-stage basis.

Conclusions

Based on the research carried out in the Msciwojow reservoir in the period of 2006–2008 the following conclusions can be drawn:

1. Wierzbiak and Zimnik water (St. I and St. II) flowing to the Msciwojow reservoir was classified as eutrophic due to the concentration of phosphorus, nitrogen and chlorophyll a . It was also found out that the Wierzbiak water was sensitive to nitrogen

pollutants coming from agricultural sources. This justified the construction of the pre-dam reservoir in backwater of the Mściwojow reservoir.

2. The pre-dam reservoir contributes to the changes of water quality in the Wierzbiak and Zimnik rivers. Changes of selected water quality indicators observed at the inflow to the Mściwojow pre-dam reservoir and at its outflow confirm its significant role in the retention of the analyzed indicators. Water retention in the pre-dam reservoir resulted in the reduction of pollutant loads: nitrates(V) by 69.9 %, nitrates(III) by 63.2 %, ammonia by 62.9 % and phosphates by 32.9 % (Table 1 and Table 2)

3. Water flowing out of the main reservoir (St. VII) shows lower values of the analyzed biogenic substances than water flowing into the reservoir (St. I and St. II) – (Table 2).

4. In order to avoid water eutrophication it is necessary to reduce the concentrations of biogens in water flowing to the reservoir. One of the solutions is the construction of the pre-dam reservoir, which will contribute to the improvement of water quality in the main reservoir and extend its operating time. This should be taken into consideration not only in designing new reservoirs but also in the case of the existing ones (provided that location conditions are favorable).

5. The proposed methodology for the preliminary assessment of the pre-dam efficiency in the reduction of phosphorus can be applied to Polish reservoirs and it should be verified on a larger number of facilities. The presented guidelines concerning the designing process should be taken into account at the construction of reservoirs.

6. It is recommended that the research initiated in the Mściwojow reservoir should be continued. This would contribute to the development of more comprehensive methodology for reduction of pollutants in pre-dam reservoirs as well as to a more detailed analysis of the processes taking place in the reservoirs.

References

- [1] Nyc K. and Pokładek R.: *Rola małej retencji w kształtowaniu ilości i jakości wód*. Zesz. Nauk. AR we Wrocławiu, Inż. Środow., 2004, **XIII**(502), 343–352.
- [2] Mioduszewski W.: *Rola małej retencji w kształtowaniu i ochronie zasobów wodnych*. Zesz. Nauk. AR we Wrocławiu, Inż. Środow. 2004, **XIII**(502), 293–305.
- [3] Pływaczyk L.: *Mala retencja wodna i jej uwarunkowania techniczne*, [in:] *Ekologiczne aspekty melioracji wodnych*, Tomiałojć L. (ed.), Wyd. Inst. Ochrony Przyrody PAN, Kraków 1995, 141–148.
- [4] Miler A. T.: *Stan obecny małej retencji wodnej oraz perspektywy jej rozbudowy na przykładowych terenach leśnych w Wielkopolsce*. Infrastruktura i Ekologia Terenów Wiejskich/Infrastruct. Ecol. Rural Areas, PAN, 2009, **4**, 231–237.
- [5] Tucholski S., Duda M. and Skonieczek P.: *Self-Purification of waters polluted with sewages in the retention reservoir*. Ecol. Chem. Eng. 2007, **14**(S2), 253–262.
- [6] Wiatkowski M., Czamara W. and Kuczewski K.: *Wpływ zbiorników wstępnych na zmiany jakości wód retencjonowanych w zbiornikach głównych*. Monografia nr 67. Wyd. Inst. Podstaw Inżynierii Środowiska PAN, Zabrze, 2006, 121 pp.
- [7] Hejduk L. and Banasik K.: *Zmienność stężenia fosforu w górnej części zlewni rzeki Zagożdżonki*. Przegl. Nauk. Inż. Kształt. Środow. 2008, **4**(42), 57–64.
- [8] Koc J., Cymes I., Skwierawski I. and Szperek U.: *Znaczenie ochrony małych zbiorników wodnych w krajobrazie rolniczym*. Zesz. Probl. Post. Nauk Rol. 2001, (476), 397–407.
- [9] Wiatkowski M. and Czerniawska-Kusza I.: *Use of Jedlice preliminary reservoir for water protection of Turawa dam reservoir*. Oceanolog. Hydrobiol. Stud. 2009, **XXXVIII**(1), 83–91.

- [10] Benndorf, J., Pütz K., Krinitz H. and Henke W.: *Die Funktion der Vorsperren zum Schutz der Talsperren vor Eutrophierung*. Wasserwirtschaft Wassertechnik 1975, **25**(1), 19–25.
- [11] Benndorf J., Pütz K. and Kraatz W.: *Zur Funktion der Vorsperren*, Int. Symp. EUTROSYM '76, Karl-Marx-Stadt, DDR, 1976, 25–41.
- [12] Benndorf, J., Hallebach R. and Pütz K.: *Die Leistung von Vorsperren bei der Rückhaltung der Pflanzennährstoffe aus Abwässern und landwirtschaftlich genutzten Flächen*. Limnologica (Berlin) 1976, **10**(2), 617–622.
- [13] Pütz K. and Benndorf J.: *The importance of pre-reservoirs for the control of eutrophication of reservoirs*. Water Sci. Technol. 1998, **37**(2), 317–324.
- [14] Czamara W., Czamara A. and Wiatkowski M.: *The use of pre-dams with plant filters to improve water quality in storage reservoirs*. Arch. Environ. Protect. 2008, **34**, 79–89.
- [15] Kajak Z.: *Hydrobiologia-Limnologia, Ekosystemy wód śródlądowych*. Wyd. Nauk. PWN, Warszawa 2001, 360 pp.
- [16] Żbikowski A. and Żelazo J.: *Ochrona środowiska w budownictwie wodnym*. Mat. inf., Ministerstwo Ochrony Środowiska Zasobów Naturalnych i Leśnictwa, Warszawa 1993.
- [17] Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008 roku w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych. DzU 2008, nr 162, poz. 1008.
- [18] Rozporządzenie Ministra Środowiska z dnia 23 grudnia 2002 roku w sprawie kryteriów wyznaczania wód wrażliwych na zanieczyszczenie związkami azotu ze źródeł rolniczych, DzU 2002, nr 241, poz. 2093.
- [19] Wiatkowski M.: *Poprawa jakości wód w zbiornikach malej retencji za pomocą osadników wstępnych*, [in:] Zapobieganie zanieczyszczeniu, przekształcaniu i degradacji środowiska, Kasza H. (ed.), Zesz. Nauk. ATH w Bielsku-Białej, Inż. Włók. i Ochr. Środow. 2006, **24**(7), 326–335.
- [20] Skonieczek P. and Szymczyk S.: *Redukcja zanieczyszczenia wód azotem w stawie zasilanym odpływami z oczyszczalni ścieków*, Chem. Inż. Ekol. 2005, **12**(3), 407–414.
- [21] Skonieczek P. and Koc J.: *Role of preliminary reservoirs in reducing phosphorus inflow from agricultural and afforested catchment areas to the lake*. Ecol. Chem. Eng. A 2008, **15**(12), 1347–1357.
- [22] Vollenweider R. A.: *Advances in defining critical loading levels for phosphorus in lake eutrophication*. Mem. Ist. ital. Idrobiol. 1976, **33**, 53–83.
- [23] Benndorf J.: *A contribution to the phosphorus loading concept*. Int. Revue ges. Hydrobiol. 1979, **64**, 177–188.
- [24] Projekt zbiornika wodnego Mściwojów na rzece Wierzbiak, Instytut Inżynierii Środowiska, Akademia Rolnicza we Wrocławiu, Wrocław 1995.
- [25] Ciepielowski A., Garbulewsky K., Król P., Kubrak E. and Żbikowski A.: *Small retention reservoirs*. [In:] Podstawy Melioracji Rolnych, vol. 2., Prochal P. (ed.), Państwowe Wydawnictwo Rolnicze i Leśne, Warszawa 1987, 420 pp.
- [26] Wiatkowski M.: *Hydrochemical conditions for localization of small water reservoirs on the example of Kluczbork reservoir*. Arch. Environ. Protect. 2009, **35**(4), 129–144.
- [27] DWA Regelwerk. Merkblatt DWA, Wirkung, Bemessung und Betrieb von Vorsperren zur Verminderung von Stoffeintragen in Talsperren, Hennef 2005, 32 pp.

WPLYW ZBIORNIKA WSTĘPNEGO MŚCIWOJÓW NA JAKOŚĆ WODY W ZBIORNIKU ZAPOROWYM I PONIŻEJ ZBIORNIKA

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Abstrakt: W pracy przedstawiono wyniki badań, przeprowadzonych w okresie od listopada 2006 do października 2008 r., dotyczące wpływu zbiornika wstępnego na jakość wody w zbiorniku głównym Mściwojów i poniżej zbiornika. Pomiarami objęto następujące wskaźniki jakości wody: NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , temperaturę wody, pH, przewodność elektrolityczną (konduktywność), tlen rozpuszczony i chlorofil *a*. Badania przeprowadzono na zbiorniku Mściwojów zlokalizowanym na rzece Wierzbiak, w woj. dolnośląskim (Polska południowo-zachodnia).

Analizowano wpływ zbiornika wstępnego na zmniejszenie się zanieczyszczeń w wodach rzek zasilających zbiornik główny (Wierzbak i Zimnik). Badania wykazały, że w zbiorniku wstępnym ma miejsce obniżanie się podstawowych wskaźników fizyczno-chemicznych wody: azotanów(V) o 69,9 %, fosforanów o 32,9 %, azotanów(III) o 63,2 % i amoniaku o 62,9 %. Znotowano wzrost temperatury wody, odczynu i tlenu rozpuszczonego. W pracy przedstawiono ocenę jakości wód dopływających do zbiornika Mściwojów i z niego odpływających, wód retencjonowanych w zbiorniku wstępnym i głównym. Na podstawie otrzymanych wyników badań stwierdzono, że zbiornik wstępny przyczynia się do poprawy jakości wody dopływającej do zbiornika głównego. Podano propozycje zasad wymiarowania zbiorników wstępnych i zalecenia do ich projektowania.

Słowa kluczowe: zbiornik wstępny, zbiornik wodny, skuteczność zbiornika wstępnego, jakość wody, ochrona wód

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EVALUATION OF EFFICIENCY SELECTED SECONDARY SAMPLING METHODS IN SOIL STUDIES

OCENA SKUTECZNOŚCI WYBRANYCH METOD OPRÓBKOWANIA WTÓRNEGO W BADANIACH GLEB

Abstract: The purpose of the work was to compare effectiveness of common secondary sampling methods for assessing the distribution of soil pollution. The study case is based on an example of assessing the spatial distribution of soil contamination with lead in Slawkow area (Upper Silesian Industrial Region). This comparison was made in regard to both precision of the spatial estimation and minimization the cost of measuring campaign. The special attention was given to the often applied secondary sampling designs such as threshold radial (also known as adaptive cluster sampling) and adaptive fill sampling. These two methods were tested in typical municipal and suburban environment in Slawkow area. The work contains also detailed statistical and geostatistical analysis of above-mentioned contamination, and elaboration of series of its spatial distributions using numerous alternative sampling designs. The determined sampling plans make it possible to find compromise between ecological and financial aspects. A combination of the obtained results with the legal regulations in force concerning concentrations of heavy metals in soils are the basis for reliably estimation the ecological hazard arising from the soil contamination with lead in the Slawkow area.

The results of performed analyses show that better efficiency in terms of cost and precision of measuring campaign gives rather coarser preliminary sampling design followed by appropriate secondary sampling then use the one-stage very dense measuring grid. However, the effectiveness of both threshold radial and adaptive fill secondary sampling designs is much worse than secondary sampling designs based on geostatistical methods using eg minimization of maximum or mean kriging variance criterion.

However, it was also found that the effectiveness of both threshold radial and adaptive fill secondary sampling designs is significantly worse than secondary sampling designs based on geostatistical methods. Therefore, when a larger environmental research is envisaged the collaboration with experienced geostatisticians is always the right choice.

Keywords: secondary sampling designs, heavy metals, soils, ecological risk, geostatistics

The choice of appropriate sampling design is essential in different soil related surveys. This arises from the fact, that our knowledge on soil in their natural state is never fully known and collecting samples as well as laboratory analysis is expensive and time consuming, especially when investigations are performed on large areas. Secondary sampling is very important stage of many environmental studies, which can

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significantly improve the analysis by relatively low cost. Secondary sampling design can refine a model, get a deeper insight into studied phenomenon, clarify situation and thus make right decision.

The goal of the work was a case-study based evaluation of effectiveness of commonly used secondary spatial sampling designs such as threshold radial design (also known as adaptive cluster sampling) and adaptive fill design for delineation of the extent of the area polluted with heavy metals.

Site description and data collection

Study area was located in Slawkow city and its vicinity (Upper Silesian Industrial Region). The studies were performed using soil samples from the archives of the Polish Geological Institute [1, 2]). The whole measuring campaign led to the collection of 2672 soil samples and 330 samples of water sediments. All samples were collected on the basis of a very dense grid pattern. The sampling points were placed in an regular way and the average distance between the neighbouring points was almost constant reaching about 250 [m]. The aim of the analysis was to determine the concentrations of Ag, Al, As, Ba, C_{org}, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, S, Sr, Ti, V and Zn, as well as pH. (For our analysis only 1393 Pb samples were used.) These measurements resulted in the preparation of “Detailed Geochemical Map of Upper Silesia in the scale 1:25 000, a promotional sheet Slawkow”. Soil samples weighing about 0.5 kg were collected with a penetrometer of 8 cm in diameter, at a depth of 0.0 to 0.2 cm. The samples were dried at room temperature and then sieved through a 1 [mm] sieve. Finally, analytical samples weighing (100 g) were obtained by quartering, and then concentrations were determined analytically. Lead concentrations in samples collected from the Slawkow area were determined by the ICP-AES method, using a Philips 8060 emission spectrometer with plasma excitation. The details of measurements campaign as well as of analytical methods are given in [1, 2].

All values of lead concentrations in soils were expressed in [mg/kg]. A detailed map of sample point locations was shown in Fig. 1.

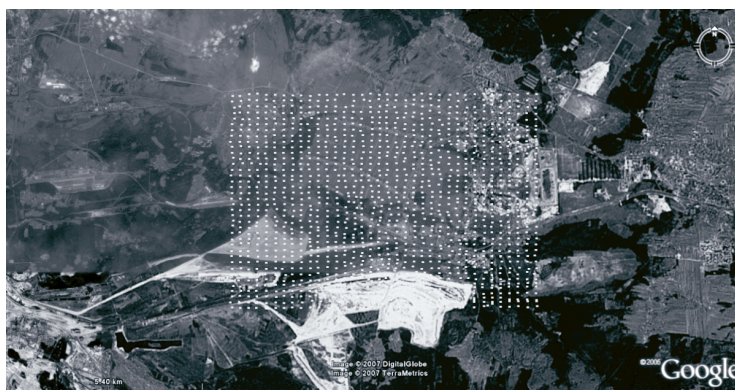


Fig. 1. Satellite view of Slawkow with sample point locations (exhaustive data set)

A satellite view of study area with sample point locations (exhaustive data set) were shown in Fig. 1, and the map of this area is given in Fig. 2.

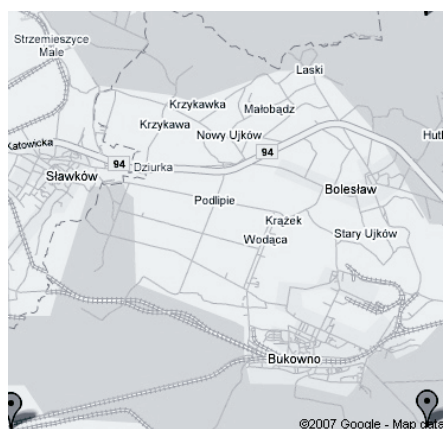


Fig. 2. Detailed map of study area

Secondary sampling strategies and geostatistical methods

In order to limit the time consuming analyses we focused in our work on two commonly used secondary sample designs [3, 4]:

1) Threshold Radial (TR) Secondary Sample Designs (also known as Adaptive Cluster Sampling) which is a straightforward secondary sample design that places samples in a radial pattern around existing data points that exceed a decision threshold. Threshold radial can be useful in situations where one have a lot of very low or undetected samples and one or two very high measurements.

2) Adaptive Fill (AF) Secondary Sample Designs. In this case, samples are placed in the largest spatial gaps among data points. Unlike Threshold Radial, this design gives no regard to the measured values, only their relative positions.

A set of new sample candidates is defined by a grid (much like a spatial model) that overlays the data points and acknowledges site boundaries, polygons, and whether layers are active or not. From this set of N candidates the first winning location is simply that value which has the maximum distance to its closest neighbor. The design searches for the second location among the remaining candidates by comparing with the $N + 1$ locations. If there are ties among the two locations, then the tie breaker method is used. The process repeats until one of the following becomes true:

- the total number of samples has been located,
- there are no remaining candidates,
- no remaining candidate satisfies the minimum distance constraint.

To study soil contamination with lead, it was necessary to obtain the spatial distribution of lead concentrations in soils, as well as the spatial distribution of estimation errors. This was done using geostatistical methods. The ordinary kriging was selected as the most appropriate technique for our analysis. Ordinary kriging is the most

effective linear estimator as it assumes that the average value of the estimation error equals zero, and thus minimises the variance of the estimation error [5–11].

The series of spatial distribution of lead concentrations in soils were produced. In the first step preliminary coarse sampling designs (systematic or random) were chosen from the very dense exhaustive data set shown in the Fig. 1. These designs were treated as pre-information for subsequent sampling. Then above-described spatial distributions were created by careful variogram modeling and kriging technique. At this stage all modeled spatial distributions of lead concentrations in soils were validated using cross-validation methods [12]. Each of the data points was individually removed from the data set, and after that, its value was modeled and subsequently compared with the measured one. Next, the scatter plots of estimated values versus the measured ones were calculated. Using these scatter plots several estimation errors were carefully calculated. Furthermore, modeled spatial distributions were validated using true values taken from exhaustive data set.

Another important feature of sampling design is always the total cost of measuring campaign calculated on the basis of the cost of single measurement. By comparing the quality of the spatial distribution with the total cost of measurements it was possible to evaluate the efficiency of the sampling grid under investigation. Then, it was decided what type of secondary sample design should be applied, and how many additional measurements should be used. This allowed for significant reduction of uncertainty by relatively low cost. Then all above-described analyses were repeated once or twice. For clarity multistage sampling process was abbreviated. For instance, the abbreviation “200 (S) + 200 (TR)” means, that preliminary sample of 200 nodes grid was systematic (S), and furthermore 200 additional points were added using threshold radial sampling (TR) technique. Analogously, the abbreviation “100 (R) + 100 (AF)” means, that preliminary sample of 100 nodes grid was simple random (R), and furthermore 100 additional points were added using adaptive fill sampling (AF) technique.

Analyses were performed using Arc Gis software (namely, FIELDSD, Geostatistical Analyst and Spatial Analyst components) [13].

Results and discussion

Below, in Figs. 4–7 exemplary sampling designs are presented (eg systematic and random preliminary sampling design followed by threshold radial and adaptive fill secondary samplings) with the appropriate spatial distributions of lead contamination. The scale used in all figures is given in Fig. 3.

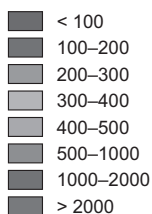


Fig. 3. The scale used in Fig. 4–7 to describe spatial distribution of lead contamination. The lead concentrations are expressed [mg/kg]

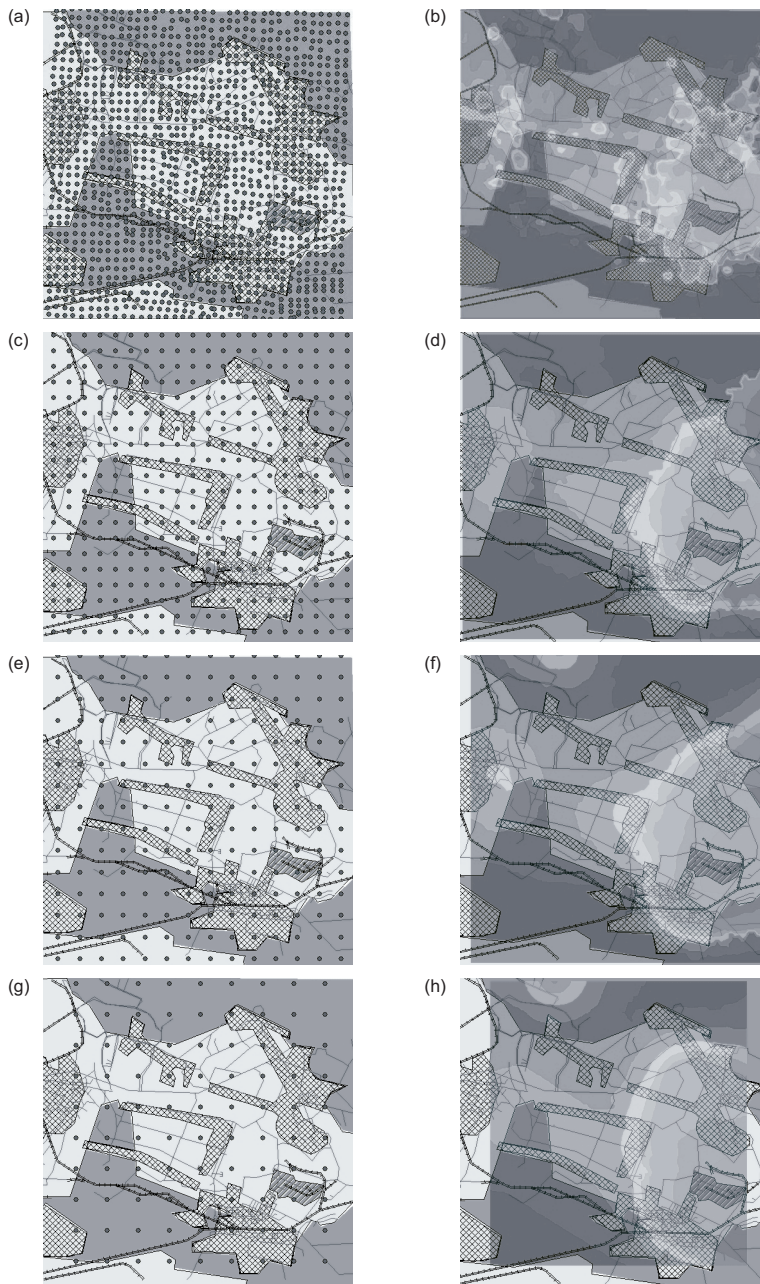


Fig. 4. Systematic sampling designs with decreasing number of observations (left) and appropriate spatial distribution of lead contamination (right): (a), (b) – 1393 measurement points (excessive dataset); (c), (d) – 400 (S) measurement points; (e), (f) – 200 (S) measurement points; (g), (h) – 100 (S) measurement points; (a) show excessive dataset; (c), (d), (e), (f), (g) and (h) shows preliminary sampling designs

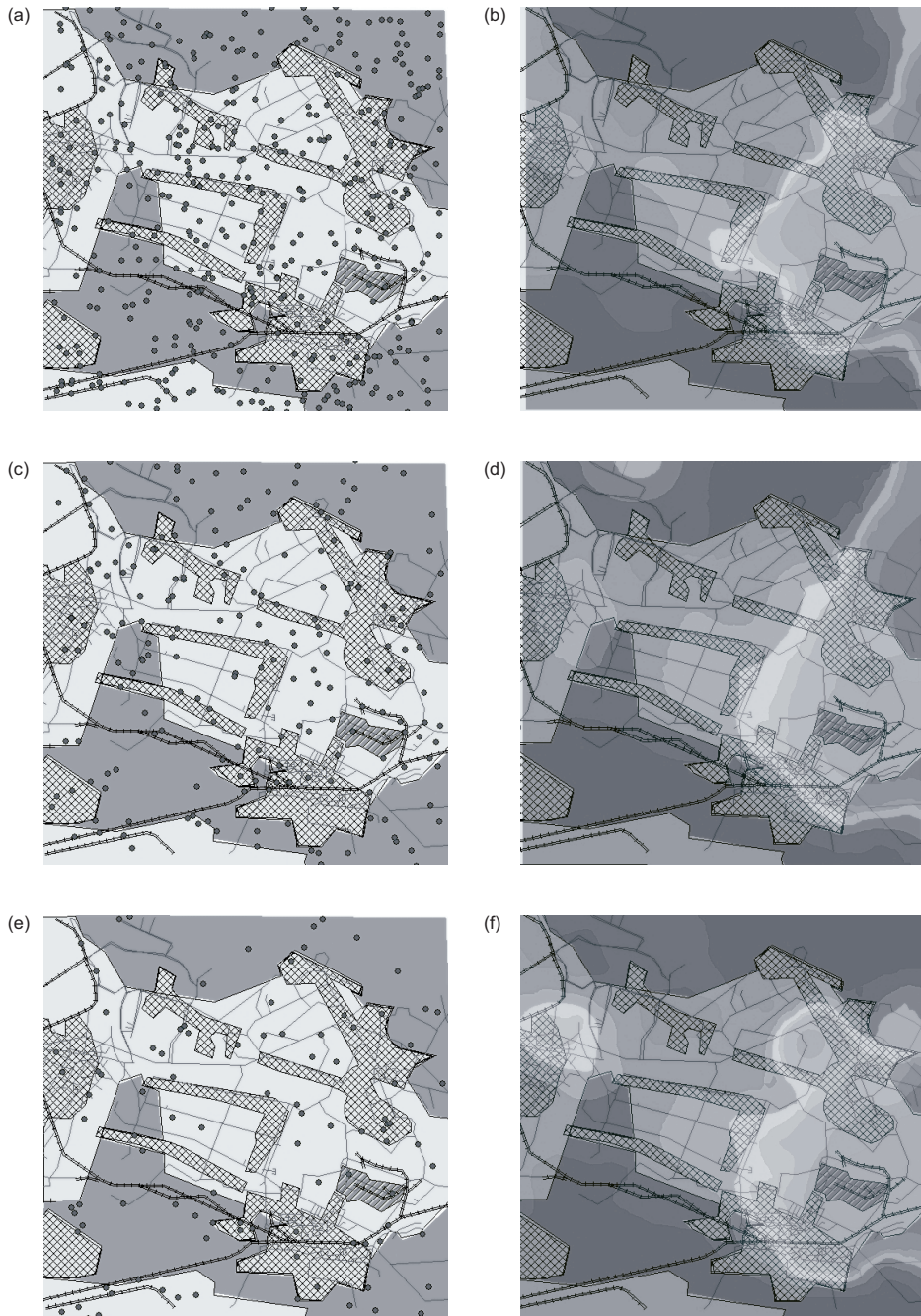


Fig. 5. Preliminary, simple random sampling designs with decreasing number of observations (left) and appropriate spatial distribution of lead contamination (right): (a), (b) – 400 (R) measurement points; (c), (d) – 200 (R) measurement points; (e), (f) – 100 (R) measurement points

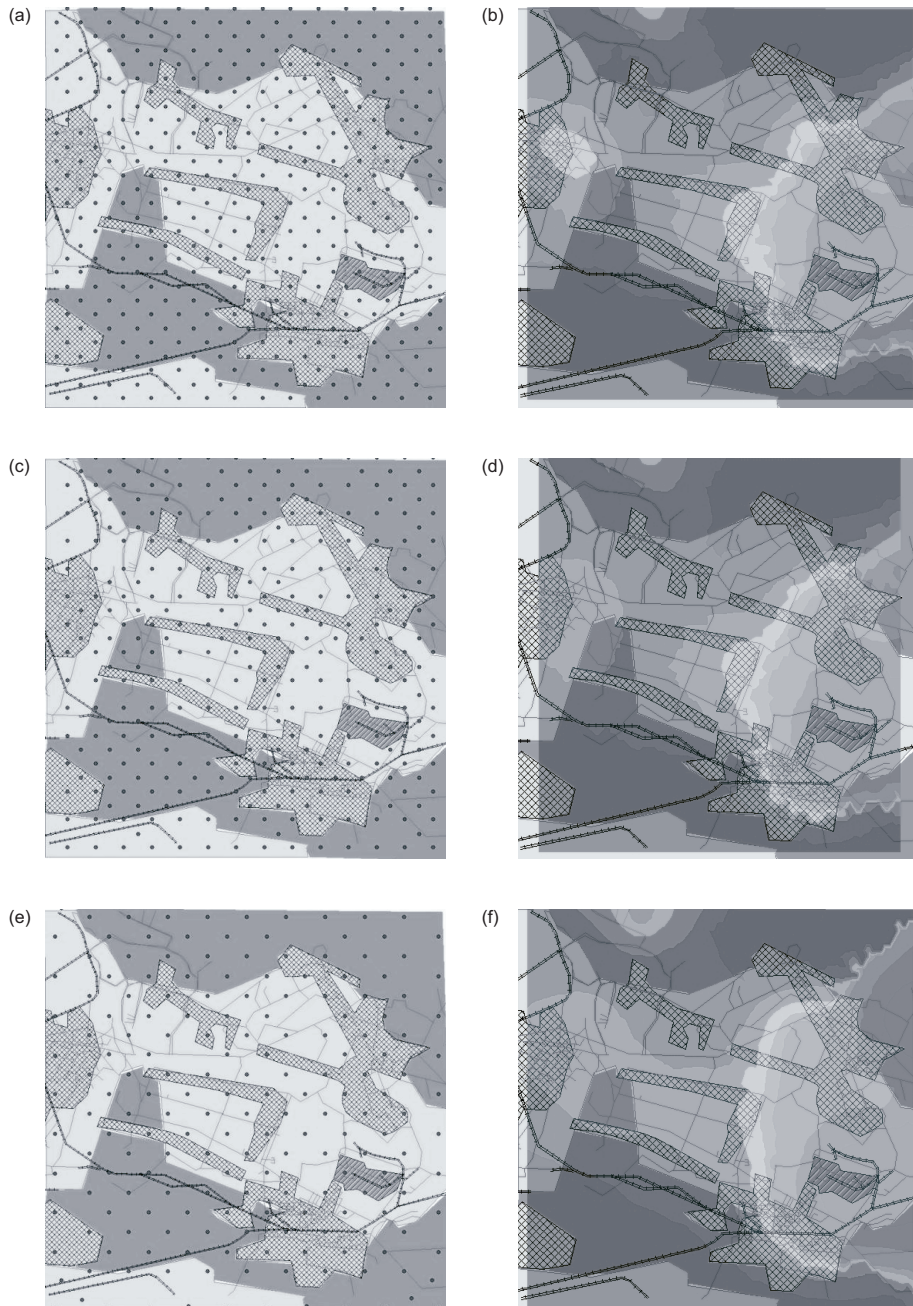


Fig. 6. Improvement of preliminary, systematic sample designs using threshold radial secondary sampling (left) and appropriate spatial distribution of lead contamination (right): (a), (b) – 200 (S)+200 (TR) measurement points; (c), (d) – 200(S)+100 (TR) measurement points; (e), (f) – 100(S)+100 (TR) measurement points

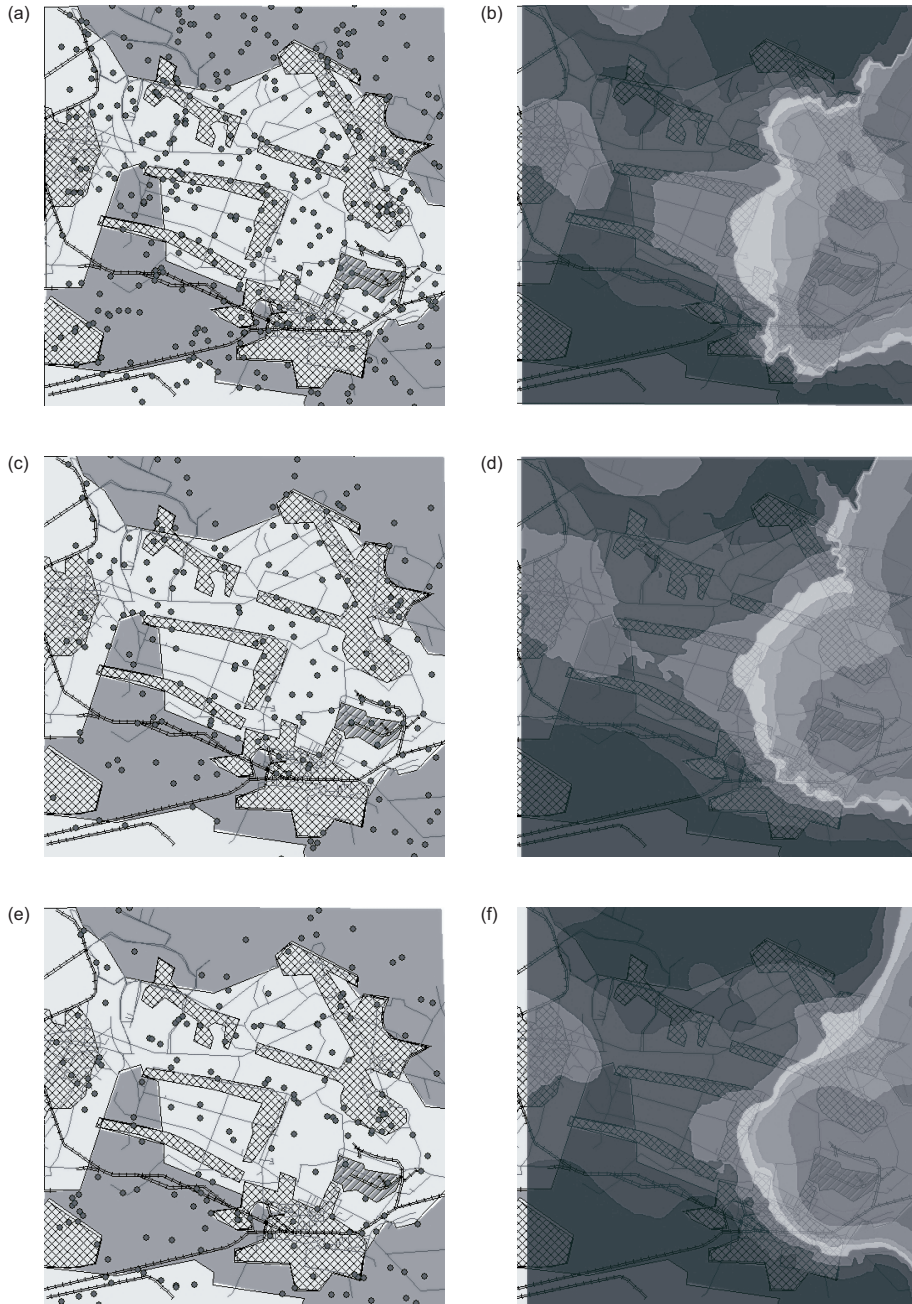


Fig. 7. Improvement of preliminary, systematic sample designs using adaptive fill secondary sampling (left) and appropriate spatial distribution of lead contamination (right): (a), (b) – 200 (R)+200 (AF) measurement points; (c), (d) – 200 (R)+100 (AF) measurement points; (e), (f) – 100 (R)+100 (AF) measurement points

Table 2

The exemplary cross-validation summaries for sampling designs obtained using threshold radial method

		Stage I – Preliminary sampling: Systematic (S) or Simple Random (R)					
Sampling design		100 (S)	200 (S)	400 (S)	100 (R)	200 (R)	400 (R)
Error							
Mean prediction error		0.841	1.570	1.657	-6.760	-5.101	1.013
Root-mean square prediction error		470	756	1477	553	784	648
Average kriging prediction error		449	796	1420	524	659	678
Mean standardized prediction error		0.00172	0.00156	0.00116	-0.00728	-0.00756	0.00139
Root mean square standardized prediction error		1.033	0.953	1.041	0.972	1.150	0.934
Stage II – Threshold Radial							
Sampling design		100 (S) + 100	200 (S) + 100	200 (S) + 200	100 (R) + 100	200 (R) + 100	200 (R) + 200
Error							
Mean prediction error		3.505	16.45	-4.728	2.65	-8.074	-2.469
Average kriging prediction error		1388	2765	815.8	465	927	832.4
Average kriging prediction error		1355	2671	798.4	501	930	744.9
Mean standardized prediction error		0.00192	0.00738	-0.00504	0.00113	-0.00821	-0.0040
Root mean square standardized prediction error		1.026	1.254	1.013	0.893	0.988	1.11
Stage III – Threshold Radial							
Sampling design		100 (S) + 100 + 100	200 (S) + 100 + 100		100 (R) + 100 + 100	200 (R) + 100 + 100	
Error							
Mean prediction error		0.241	17.42		-0.118	-10.44	
Root-mean square prediction error		410	2931		456.2	1461	
Average kriging prediction error		413	2572		470.1	1716	
Mean standardized prediction error		0.00078	0.00522		0.00010	-0.00646	

Tables 1 and 2 show the cross-validation errors for exemplary sampling designs obtained using adaptive fill method and using threshold radial method, respectively. At first glance, the above-shown results seem to be rather ambiguous. However, detailed analysis of estimation errors for numerous multistages sampling designs proved that better results in terms of cost and precision give very often coarser preliminary sampling designs followed by appropriate chosen secondary sampling than use of the onestage very dense measuring grid. This result arises from the fact that although mostly used dense regular sampling grids, are relatively precise, but in the same time they are very costly. (Preliminary random sampling designs give unbiased results, but in general, are less precise than systematic sampling designs.) Multistage sampling allows for treating the intermediate results as the preinformation for subsequent sampling. This make it possible to better control and tune the whole sampling process according to circumstances occurring during sampling campaign.

However, we also observed that the effectiveness of both threshold radial and adaptive fill secondary sampling designs is much worse than secondary sampling designs based on geostatistical methods. These advanced methods are very flexible and use many different criteria eg minimization of maximum, or mean kriging variance [14]. The geostatistical methods take precisely into account spatial correlations that are present in spatial distributions under study. The threshold radial and adaptive fill secondary sampling designs are still derived from classical sampling theory and do not use effectively whole information present in data sets.

But these sampling designs are much simpler, and therefore easier to use. The choice of multistage sampling strategy depends on the qualifications and the experience of surveyors. Nevertheless, according to our many-years experience, we would strongly recommend use of geostatistical multistage procedures than improved sampling procedures derived from classical sampling theory. When a larger environmental research is envisaged the collaboration with experienced geostatisticians is always the right decision.

Conclusions

The choice of proper sampling design is crucial in different soil studies and in many cases even more important than high accuracy of laboratory chemical analyses. Secondary sampling is significant stage of many environmental studies, which can significantly improve the analysis by relatively low cost. This is especially important in complicated urban and suburban environment.

In this work the focus was given on secondary sampling designs such as threshold radial and adaptive fill sampling. The results of systematic analyses show that better efficiency in terms of cost and precision of measuring campaign gives coarser preliminary sampling design followed by appropriate secondary sampling then use the one-stage dense measuring grid.

The effectiveness of both threshold radial and adaptive fill secondary sampling designs can be worse than sophisticated secondary sampling designs based on geostatistical methods that make effective use of spatial correlations among measure-

ment points. On the other hand, the secondary sampling methods considered here are often much simpler to perform and always easier to use for analyzes than geostatistical methods and therefore they are reasonable alternative for them.

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References

- [1] Lis J. and Pasieczna A.: Szczegółowa Mapa Geochemiczna Górnego Śląska, Państwowy Instytut Geologiczny, Warszawa 1999.
- [2] Lis J. and Pasieczna A.: *Szczegółowe kartowanie geochemiczne na Górnym Śląsku*. Zesz. Nauk. Politech. Śląskiej, Górnictwo 2005, **267**, 173–182.
- [3] Stewart R. and Purucker T.: SADA Technical Support: Using Secondary Sampling Strategies, University of Tennessee, Knoxville 2000.
- [4] Guidance on choosing a sampling design for environmental data collection, United States Environmental Protection Agency, Office of Environmental Information, Washington DC 2002.
- [5] Journel A.G. and Huibregts C.J.: Mining Geostatistics, Academic Press, London 1978.
- [6] David M.: Handbook of Applied Advanced Geostatistical Ore Reserve Estimation, Elsevier Scientific Publishing, Amsterdam 1988.
- [7] Isaaks E.H. and Srivastava R.M.: An introduction to applied geostatistics, Oxford University Press, New York 1989.
- [8] Goovaerts P.: Geostatistics for natural resources evaluation, Oxford University Press, New York 1997.
- [9] Demougeot-Renard H., Foquet C. and Renard P.: *Forecasting the number of soil samples required to reduce remediation cost uncertainty*. J. Environ. Qual. 2004, **33**, 1694–1702.
- [10] Zawadzki J.: *Geostatistical methods for continuity correlation evaluation: Studies of Fe, Pb and Zn concentrations in soil*. Inżynieria Ochr. Środ. 2002, (3–4), 369–391.
- [11] Carlen C., Critto A., Nathanail P. and Marcomini A.: *Risk based characterisation of a contaminated industrial site using multivariate and geostatistical tools*. Environ. Pollut. 2000, **111**(3), 417–427.
- [12] Kohavi R.: *A study of cross-validation and bootstrap for accuracy estimation and model selection*. Proc. 14th Internat. joint Conf. Artificial Intelligence, San Francisco, USA 1995, **2**, 1137–1145.
- [13] ArcGIS 9; What is ArcGIS 9.1, ESRI 2005.
- [14] Groeningen van J.W.: *Constrained optimisation of spatial sampling – a geostatistical approach*. PhD Thesis, Wageningen Agricultural University and ITC, Wageningen, Netherlands 1999.

OCENA SKUTECZNOŚCI WYBRANYCH METOD OPRÓBKOWANIA WTÓRNEGO W BADANIACH GLEB

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Abstrakt: Celem pracy było porównanie efektywności wybranych metod opróbkowania dodatkowego, wykonywanego w celu wyznaczenia rozkładu zanieczyszczenia gleby. Studium przypadku zostało oparte na przykładzie wyznaczania rozkładu przestrzennego zanieczyszczenia gleby ołowiem w okolicach Sławkowa (Górnośląski Okręg Przemysłowy). Głównymi kryteriami efektywności metod opróbkowania dodatkowego były oceny dokładności rozkładu przestrzennego oraz koszty kampanii pomiarowej. Szczególną uwagę zwrócono na często stosowane opróbkowanie dodatkowe metodami uzupełniania promieniowego (zwanego również adaptacyjnym opróbkowaniem klastrowym) oraz wypełniania adaptacyjnego. Te dwie metody były przetestowane w typowym miejskim i podmiejskim środowisku, na terenie i w okolicach Sławkowa. Praca zawiera również statystyczną i geostatystyczną analizę omawianego zanieczyszczenia gleby, określenie jego

ciągłości przestrzennej, jak również wyznaczenie serii rozkładów przestrzennych zanieczyszczenia gleby ołowiem przy wykorzystaniu wyżej wymienionych metod opróbkowania dodatkowego.

Wyznaczone sieci pomiarowe pozwoliły na znalezienie kompromisu pomiędzy aspektem ekologicznym i finansowym. Rezultaty analizy statystycznej i geostatystycznej wraz z obowiązującymi uregulowaniami prawnymi dotyczącymi zawartości metali ciężkich w glebie są podstawą do rzetelnego określenia potencjalnego ryzyka ekologicznego wynikającego z zanieczyszczenia gleb ołowiem w okolicach Sławkowa.

Rezultaty wykonanych analiz pokazują, że lepszą skuteczność określaną kosztem i precyzją kampanii pomiarowej daje najczęściej rzadsze opróbkowanie wstępne uzupełnione odpowiednim opróbkowaniem dodatkowym, niż jednoetapowa kampania pomiarowa z gęstą siecią pomiarową.

Jednakże zarówno metoda uzupełniania promieniowego oraz wypełniania adaptacyjnego są mniej precyzyjne niż wieloetapowe procedury opróbkowania wykorzystujące zaawansowane metody geostatystyczne. Metody te znacznie lepiej wykorzystują informację o korelacjach przestrzennych zawartą w zbiorach danych. Pomimo większej złożoności tych metod autorzy zalecają ich stosowanie lub współpracę ze specjalistami z zakresu statystyki i geostatystyki środowiska w sytuacjach, gdy planowane są znaczące badania środowiska naturalnego.

Słowa kluczowe: opróbkowanie dodatkowe, metale ciężkie, ryzyko ekologiczne, geostatystyka

Varia

Invitation for ECOpole '11 Conference

CHEMICAL SUBSTANCES IN ENVIRONMENT



We have the honour to invite you to take part in the 20th annual Central European Conference ECOpole '11, which will be held in **12–15 X 2011** (Thursday–Saturday) at the Conference Center “Rzemieślnik” in Zakopane, PL.

The Conference Programme includes oral presentations and posters and will be divided into five sections:

- SI Chemical Pollution of Natural Environment and Its Monitoring
- SII Environment Friendly Production and Use of Energy
- SIII Risk, Crisis and Security Management
- SIV Forum of Young Scientists and Environmental Education in Chemistry
- SV Impact of Environment Pollution on Food and Human Health

The Conference language is English.

The Conference Opening Lecture will be delivered by the **Nobel Prize Winner Professor Dr. Paul Jozef CRUTZEN**.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
- extended Abstracts (4–6 pages) in the semi-annual journal *Proceedings of ECOpole*
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15.07.2011** and for the Extended Abstracts: **1.10.2011**. The actualised list (and the Abstracts) of the Conference contributions

accepted for presentation by the Scientific Board, one can find (starting from 15.07.2011) on the Conference website.

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

At the Reception Desk each participant will obtain a CD-ROM with abstracts of the Conference contributions as well as Conference Programme (the Programme will be also published on this site).

Further information is available from:

Prof. dr hab. Maria Waclawek

Chairperson of the Organising Committee
of ECOpole '11 Conference

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**Zapraszamy
do udziału w Środkowoeuropejskiej Konferencji
ECOpole '11
w dniach 12–15 X 2011**

**SUBSTANCJE CHEMICZNE
W ŚRODOWISKU PRZYRODNICZYM**



Będzie to dziewiętnasta z rzędu konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w Ośrodku Konferencyjno-Wypoczynkowym „Rzemieślnik” w Zakopanem.

Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego.

Obrady konferencji ECOpole '11 będą zgrupowane w pięciu sekcjach:

- SI Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring
- SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie
- SIII Zarządzanie środowiskiem w warunkach kryzysowych
- SIV Forum Młodych (FM) i Edukacja prośrodowiskowa
- SV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi.

Pan Profesor Dr Paul Jozef CRUTZEN – Laureat Nagrody Nobla
wygłosi referat inauguracyjny.

Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie;
- rozszerzonych streszczeń o objętości 4-6 stron w półroczniku *Proceedings of ECOpole*;
- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna (Ecol. Chem. Eng.)* ser. A i S oraz niektórych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*.

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 15 lipca 2011 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2011 r. na stronie internetowej

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Prof. dr hab. Maria Waclawek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole '11

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