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Wojciech BARAN[1*], Ewa ADAMEK[1],
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ASSESSMENT OF SULFONAMIDES OCCURRENCE IN THE BIOSPHERE

OCENA WYSTĘPOWANIA LEKÓW SULFONAMIDOWYCH W BIOSFERZE

Abstract: Sulfonamides, derivatives of *p*-aminobenzenesulfonic acid, have been used in the treatment of patients with bacterial diseases since 1940s. According to the Anatomical Therapeutic Chemical Classification (ATC) they are included in a group of antibacterial agents, intended mainly for internal use, commonly known as antibiotics. Sulfonamides are also used as herbicides and feed additives in agriculture. It is estimated that their annual world consumption in veterinary medicine only can be up to 15 thousand Mg (tons).

At present, sulfonamides are detected in almost 100 % of environmental samples which are checked from the point of view of antibiotics contents. Typically, the determined concentrations of sulfonamides are lower than $\mu g \cdot dm^{-3}$ but in liquid manure they were even detected at the 100 $mg \cdot kg^{-1}$ level. An environmental risk caused by sulfonamides, estimated based on their ecotoxicity, is not great. However, there are evidences that they take part in generating drug resistance of microorganisms. Newly arisen drugresistance genes can be transferred between different strains of bacteria, *eg* by conjugation. As a result, these genes may occur in pathogenic bacteria present in the ecosystems that have not previously been exposed to antibiotics.

The aim of this paper was to present the problems connected with the occurrence of sulfonamides in different ecosystems. Based on the available literature from 2004 to 2010 the characterization of the potential resistance of sulfonamides in the environment and their ecotoxicity was carried out. Moreover, the problems of drugresistance to sulfonamides and the risk assessment with allowing their antimicrobial activity were presented.

Keywords: sulfonamides, ecotoxicity, drugresistance

Introduction

The global increase in human prosperity and a general fear of a pandemic have caused that the world consumption of drugs has increased systematically. Unfortunately,

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Poland is one of the leaders in this field. After use, large amounts of drugs are discharged into the environment with human and animal excretions as well as unused waste [1]. A persistence of pharmaceuticals in the environment, the rate of their spreading and their ability to accumulate in the biosphere are different. However, their high biological activity indicates that drugs, even in trace amounts, can cause significant changes in the biosphere. An example of such changes can be widely described in the last decade of the 20th century the phenomenon of feminization of fish caused by anthropogenic pollution of European rivers by sex hormones or increasing frequency of zoonotic infection (*ie* human diseases acquired from vertebrate animals) [2]. For these reasons, pharmaceuticals are currently classified as particularly dangerous pollutants for the environment. In result, researches and multinational projects (*eg* REMPHARMAWATER, Poseidon, Knapp, ERAPHARM) are carried out to find answer to the following questions:

– Which pharmaceuticals have the greatest environmental risk?
– How can effectively control the amounts and effect of drugs on the environment?
– How can successfully reduce their release into the environment?

Antivirotics (antibiotics) are a group of pharmaceuticals, whose effect on the environment can be particularly harmful from human health viewpoint. In almost 100 % of environmental samples tested for the content of antibiotics traces of tetracyclines and sulfonamides were detectable [1–16]. The aim of the present study was to discuss problems and issues related to the occurrence of sulfonamides in the environment. The potential risk assessment on the environment and effect of sulfonamides on human health were considered as particularly important. It was used also the data of the ecotoxicity of sulfonamides and information relating to drug resistance.

Structure and physicochemical properties of sulfonamides

Since the early 1940s, over 150 substances, sulfanilamide derivatives have applied in human and veterinary medicine (Fig. 1). They have a free amino group (-N^4H_2) at one end and a substituted, amide nitrogen atom (N^1) at second end.

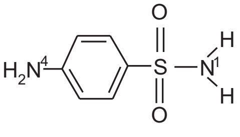


Fig. 1. Sulfanilamide

Common names of selected sulfonamides, sulfanilamide derivatives and their chemical structure are presented in Table 1.

Sulfonamides are amphoteric and polar molecules (Fig. 2). Their amino nitrogen (N^4) is protonated at pH 2–3 while the amide nitrogen (N^1) is deprotonated at pH 4.5–11 [7, 17].

Sulfonamides presented in text (except sulfaguanidine and sulfasalazine) are small molecules (molar mass 177–300 g · mol^{-1}), soluble in water (7.5–1500 mg · dm^{-3}), and

Table 1

Common (non-systematic) names and structure of selected sulfonamides

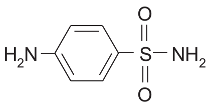
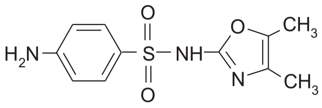
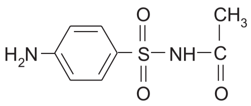
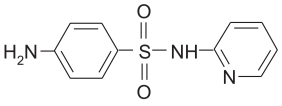
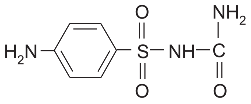
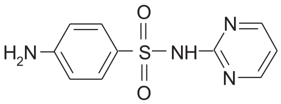
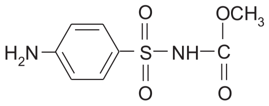
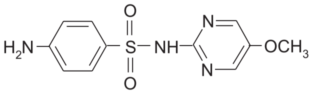
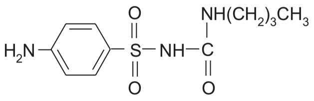
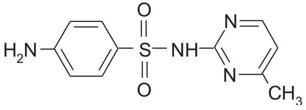
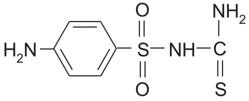
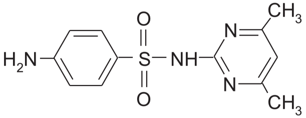
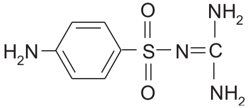
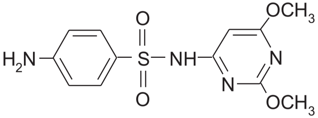
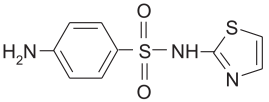
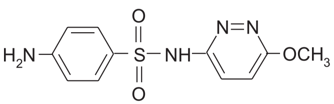
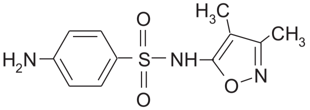
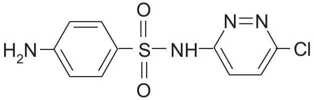
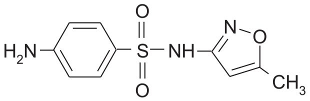
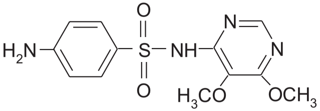
Name of sulfonamide/ CAS number	Abbreviation	Chemical structure	Name of sulfonamide/ CAS number	Abbreviation	Chemical structure
Sulfanilamide 63-74-1	SAD		Sulfamoxole 729-99-7	SMM	
Sulfacetamide 144-80-9	SCT		Sulfapyridine 144-83-2	SPY	
Sulfacarbamide 547-44-4	SC		Sulfadiazine 68-35-9	SDZ	
Asulam 3337-71-1			Sulfamethoxine 651-06-9	SMO	
Carbutamide 339-43-5			Sulfamerazine 127-79-7	SMR	

Table 1 contd.

Name of sulfonamide/ CAS number	Abbreviation	Chemical structure	Name of sulfonamide/ CAS number	Abbreviation	Chemical structure
Sulfathiourea 515-49-1	STU		Sulfadimidine/ Sulfamethazine 57-68-1	SDM	
Sulfaguanidine 57-67-0	SGM		Sulfadimethoxine 122-11-2	SDT	
Sulfatiazole 72-14-0	STZ		Sulfamethoxy-pyridazine 80-35-3	SMP	
Sulfafurazole 127-69-5			Sulfachloro-pyridazine 80-32-0	SCP	
Sulfamethoxazole 723-46-6	SMX		Sulfadoxine 2447-57-6	SDX	

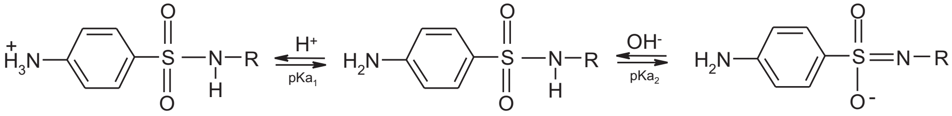


Fig. 2. Acid-base dissociation constants of sulfonamide

with low value of Henry's constant ($1.3 \cdot 10^{-12}$–$1.8 \cdot 10^{-8}$) [6, 7, 18]. They are only slightly sorbed by soil (soil partition coefficient values are 0.6–7.4 $dm^3 \cdot kg^{-1}$ [6]). This is the reason that sulfonamides are easily and quickly spread in the environment but it should limit their accumulation in defined biotopes. Sulfonamides practically do not adsorb onto activated carbon [1, 3]. They are classified as photo- and thermally stable substance (DT_{50} > 1 year) [18]. They can undergo alkaline hydrolysis, coupling reaction with phenols and amines and can react easily with the hydroxyl radicals $HO^{\bullet}$ ($k = 5.8–7.1 \cdot 10^9\ mol^{-1} \cdot s^{-1}$) [7, 8, 19, 20]. Possible ways of decomposition of sulfonamides were described in detail by Garcia-Galan et al [8].

Antibacterial activity of sulfonamides

The discussed sulfonamides are a group of synthetic bacteriostatic drugs classified by the WHO to the group of antibacterial drugs for systemic use (the subgroup J01E) [21]. They cause inhibition of proliferation of microorganisms (bacteria) that produce folic acid. The mechanism of this process is based on competitive antagonism of sulfonamide with *p-aminobenzoic acid* (PABA). During the biosynthesis of folic acid, PABA bonds with dihydropteridine, and then with glutamic acid. Sulfonamides, due to their similarity in structure, can replace PABA and to block the biosynthesis of PABA and folic acid in bacterial cells. In result, it is possible the inhibition of nucleic acids synthesis and, in consequence, proteins [16, 22]. Sulfonamides inhibit also the permeability of bacterial cell wall for glutamic acid which is also essential component in the folic acid synthesis. However, they do not inhibit the growth of microorganisms that:

- need the presence of folic acid in the environment,
- possess a high concentration of PABA or
- have modified metabolic pathways (drug resistant).

Biotransformation of sulfonamides is mainly based on their acetylation or glucuronidation [7, 8]. The metabolites of sulfonamides do not possess their biological activity. However, it can be easily restored *in vitro* conditions [23].

Biodegradability of sulfonamides

The opinions of researchers on the biodegradability of sulfonamides are divided [1, 3, 7, 15, 18]. The cause of this may be, for example, differences in microbial activity of matrix, stability of various sulfonamides, inoculum used, and applied methods to assess their degradation [1].

The results of standardized tests such as the ISO 11734:1995 and OECD 301D and the assessment of soil microbial activity suggests that most of the sulfonamides do not undergo natural biodegradation [18, 24, 25]. Probably the best described sulfonamide in the literature namely sulfamethoxazole was practically regarded as a non-biodegradable compound in the eight of the twenty three articles describing its resistance to biodegradation: 3 in pure water, 1 in seawater, 2 in natural water and 3 in wastewater or active sludge). According to Weifen et al, in the presence of shrimp (*Penaeus chinensis*) the DT_{50} value for sulfametoxazole was 5.68 h [26] and Ingerslev and Halling-Sorensen have determined that the presence of microorganisms in activated sludge the DT_{50} for sulfonamides can be only 0.3 day [27]. It is not excluded that in these cases most of the sulfonamides may be incorporated in microorganisms and /or undergo only slight reversible transformations such as acetylation [8, 23]. It was also describes the rapid disappearance of sulfonamides in soil and manure however, it may be an effect of binding between sulfonamides and organic or mineral particles [23, 28, 29] or be caused by photochemical processes [30, 31].

Reassuming, most researchers recognize sulfonamides as poorly or non-biodegradable compounds values in the range from a few to tens of days) [32]. Sulfamethoxazole, sulfadiazine and sulfachloropyridazine are considered as more resistant to biodegradation while sulfathiazole or sulfamethazine are less resistant. Moreover, sulfonamides may also bioaccumulation [1, 6].

Ecotoxicity of sulfonamides

Toxicity of sulfonamides to higher organisms is not high. According to the EU directive 93/67/EEC sulfonamides under investigation can be classified as non-toxic or harmful [33]. However, according to “Environmentally Classified Pharmaceuticals 2009” they are highly toxic drugs [32].

Sulfonamides are practically non-toxic to most microorganisms tested [3, 16, 34], including selected strains of bacteria such as *Vibrio fischeri*, *Enterococcus feacalis*, *Escherichia coli*, *Pseudomonas aeruginosa*, or *Staphylococcus aureus*. For example, the $L(E)C_{50}$ values determined using the Microtox ® test (*Vibrio fischeri*) ranged from 16.9–78.1 $mg \cdot dm^{-3}$ (for sulfamethoxazole) to > 1000 $mg \cdot dm^{-3}$ (for sulfathiazole) [34, 35]. A highly toxic effect of sulfomethoxazole on *Vibrio fischeri* (EC_{50} = 0.083 $mg \cdot dm^{-3}$) has been described by Ferrari et al [36].

Strong bacteriostatic properties cause that sulfonamides can significantly change the functioning of non-selected organisms living in the environment [36]. Thiele-Bruhn and Beck have showed that the pouring out of urine, containing even a very low concentration of sulfapirydine (0.0071–0.056 $mg \cdot kg^{-1}$), into the soil results in a significant reduction in microbial activity [37]. It was found that in the case of sulfapirydine the EC10 values for soil organisms ranged from 0.00014 to 0.16 $mg \cdot kg^{-1}$ (the microbial Fe(III) reduction test) and from 0.0071 to 0.056 $mg \cdot kg^{-1}$ (the substrate-induced respiration test) [38].

However, the most sensitive to the presence of sulfonamides were bioindicators containing chlorophyll [6, 16, 34]. In the case of sulfamethoxazole, the NOEC values for algae (*Pseudokirchneriella subcapitata* and *Synechococcus leopolensis*) and gibbous duckweed (*Lemna gibba*) were 0.09 [36, 39], < 0.0005–0.103 [36, 40] and 0.01

mg · dm^{-3} [3], respectively. It means that even very low concentrations of sulfonamides may significantly affect the growth and development of plants. Results described in the literature indicate that sulfonamides do not exhibit mutagenic or carcinogenic (teratogenic) activity [34].

It is not excluded that sulfonamides may accumulate in the various organisms in the food chain, and then it may lead to a local increase in toxic effects induced by these drugs [6, 7]. In addition, toxic effects of sulfonamides and other drugs can exhibit a synergism [39, 40]. Particularly large data on the sulfonamides ecotoxicity are summarized in articles by Garcia-Galan et al [16] and Isidori et al [34].

Estimated usage of sulfonamides

The accurately assessment of the global consumption of all drugs is difficult or even impossible. The authors of the Knappe project (*Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters*) estimate that global consumption of pharmaceuticals used in human and veterinary medicine rises and reaches 100,000 Mg (tons) per year. In turn, based on the Union of Concerned Scientists information, Sarmach et al have indicated that at the beginning of the 21st century Americans consumed 16000 Mg of antibiotics per year. Sulfonamides used in veterinary medicine accounted for approximately 2.3 % of the total amount of antibiotics. In European countries, this value ranged from 11 to 23 % [6]. According to other authors, the all world consumption of antibiotics belonging to group J01 alone (antibacterial for systemic use) was ranged from 100000 to 200000 Mg per year, including from 50 to 75 % were used in veterinary medicine and animal husbandry [1, 18]. Reassuming, it is possible that each year even more than 20000 Mg of sulfonamides having bacteriostatic properties is introduced into the biosphere (without drugs introduced as herbicides).

Since the end of 20th century, Scandinavia and other countries in Europe and North America have imposed restrictions on the use of antibiotics (including sulfonamides) in animal husbandry. Among other, the use of antibiotics as growth promoters in animal husbandry in the European Union [41] has banned since January 1, 2006. However, reports on the consumption of pharmaceuticals in different countries do not showed the reduction in their use. For example, in Denmark in the years from 1990 to 2004, the consumption of antibiotics in veterinary medicine has increased from 53.4 to 112.5 Mg [42].

Removal of sulfonamides from wastewater

A part of sulfonamides used in veterinary medicine reaches (in manure) directly into the soil. However, the great majority of these compounds enter wastewater. Opinions on the effectiveness of sulfonamide removal in conventional biological-mechanical treatment plants are divergent. Similar differences occur during the assessment biodegradability of drugs [1, 3, 14, 15, 18, 23, 27, 30, 43]. Based on the analysis of recent publications on this subject it shows that most of the sewage treatment plants using activated sludge remove 25 to 90 % of sulfonamides from wastewater. For example, according to the data published in the 2010, sulfamethoxazole was removed from the selected *sewage* *treatment plants* (STPs) in Spain in the range 30–92 % [43]. However, there were also described cases in which the concentration of sulfonamides in effluent was higher than in influent [3, 44, 45]. For example, in a pilot STP in Austria the efficiency of removal of sulfamethoxazole ranged from – 280 to 61 % [44].

It is also important that a large part of sulfonamides may be adsorbed in STPs by the biomass [46]. Obviously, the high degradation efficiency of sulfonamides in wastewater was obtained using the various *advanced oxidation processes* (AOP) [1, 3, 47–51] such as the use of O_3, Cl_2, ClO_2 [1, 47–49, 52], Fenton reaction [47, 50] or photocatalytic processes [23, 47, 49, 50]. Unfortunately, the application of these methods is costly and can also be harmful to the environment due to the formation of highly toxic intermediates [52]. Sulfonamides can be removed from wastewater by nanofiltration and reverse osmosis with nearly 100 % efficiency but in these cases then there may be a problem with wastewater containing concentrated solutions of toxins (including sulfonamides) [1, 3, 18, 53, 54].

A conclusion of this problem may be the data from the article by Turkdogan and Yetilmezsoy [53]. The authors have estimated that 80 % of used antibiotics enter the environment despite the use of various processes in STPs (based on the data from Turkey, without regard to sulfonamides).

Occurrence of sulfonamides in the environment

The first information containing quantitative data about the presence of sulfonamides in river water was published in 1982 [6]. However, systematic studies on the quantitative determinations of sulfonamides in environmental matrices became possible after the development of the highly sensitive analytical methods. According to *American Environmental Protection Agency* (EPA) data, the limit of detection during the routine analytical procedures using SPE/HPLC-MS/MS technique for the selected sulfonamides is below the 10^{-9} g · dm^{-3} (*eg* for sulfadimethoxine, the limit of detection is $1 \cdot 10^{-10}$ g · dm^{-3}). A detailed statement of analytical techniques and limits of detection of drugs (including sulfonamides) in environmental samples has been discussed by Garcia-Galan et al [16] and Seifrtova et al [55]. At such a level of detection, sulfonamides are detected practically in all of the surface water [56, 57] and wastewater samples [10, 43, 58]. Sulfonamides concentrations in the environment undergo significant fluctuations which are mainly dependent on the type of matrix and the type of sulfonamide. Sulfamethoxazole is a sulfonamide mostly detected in the environment (40–50 % of described results). Garcia-Galan et al [58] have described, in detail, the frequency of occurrence of 19 selected sulfonamides in wastewater. According to Bialk-Bielinska et al [59], the literature data concerning the determination of sulfonamides in environmental samples may contain significant errors. For example, the recovery of sulfonamides from soil samples may be in the range from about 5 to nearly 294 %. Additionally, the results obtained may depend on the sampling site, day of the week [60] and even on the time of day [61]. A summary of the occurrence of sulfonamides depending on the matrix is given in Table 2. The presented data are based on some the selected review articles [1, 12, 15] and values described in the literature.

Table 2

Some data on the occurrence of sulfonamides in the environment

Matrix	Mean[1]/ the most of ten described sulfonamides	n^2	Mean[1]	n^2	Mean	n^2	Mean	n^2	Maximal values	References
	Based on our literature studied		[1]		[12]		[15]			
Drinking waters	2.1 (0–8.5) μg · dm^{-3} (Sulfamethoxazole)	4	—		0.4 ng · dm^{-3}	5	—		8.5 μg · dm^{-3} (PEC for Sulfamethoxazole)	[5]
Bottled mineral water	0.164 ng · dm^{-3} (Sulfadimethoxine)	1	—				—		1.1 ng · dm^{-3} (N_4-acetylsulfamethazine)	[62]
Ground water	0.80 (0.0099–1.11) μg · dm^{-3} (Sulfamethoxazole)	11	0.167 (0.017–0.47) μg · dm^{-3}	12	66.53[3] (max 1600) μg · dm^{-3}	60	0.183 μg · dm^{-3}	6	3.461 μg · dm^{-3} (Sulfacetamide)	[63]
	0.053 (0.0002–0.09148) μg · dm^{-3} (Sulfadimethoxine)	3							< 1.11 μg · dm^{-3} (Sulfamethoxazole)	[11]
Surface water	0.87 (0.015–18) μg · dm^{-3} (Sulfamethoxazole)	38	0.156 (0.004–1) μg · dm^{-3}	51			0.339 μg · dm^{-3}	9	19.2 μg · dm^{-3} (Sulfamethazine)	[64]
	2.26 (0.0108–19.2) μg · dm^{-3} (Sulfamethazine)	12							> 25 μg · dm^{-3} (all sulfonamide)	[62]
Sea water	0.0475 μg · dm^{-3} (Sulfamethoxazole)	1	—	—			—	—	0.0475 μg · dm^{-3} (Sulfamethoxazole)	[65]
Drainflow/ leachte	379.78 (0.66–703.2) μg · dm^{-3} (Sulfachloropyridazine)	2	—	—	—	—	—	—	703.2 μg · dm^{-3} (Sulfachloropyridazine)	[66]
Influent/ wastewater	46.58 (0.05–1340) μg · dm^{-3} (Sulfamethoxazole)	31	1.485 (0.02–9) μg · dm^{-3}	15	11.972 (max 1158.68) μg · dm^{-3}	57	—	—	1340 μg · dm^{-3} (Sulfamethoxazole; from pharmaceutical production)	[56]
	61.11 (0.0269–500) μg · dm^{-3} (Sulfamethazine)	17							1158.68 μg · dm^{-3} (Sulfathiazole; agricultural wastewater)	[67]

Table 2 contd.

Matrix	Mean[1]/ the most of ten described sulfonamides	n[2]	Mean[1]	n[2]	Mean	n[2]	Mean	n[2]	Maximal values	References
	Based on our literature studied		[1]		[12]		[15]			
Hospitals wastewater	17.78 (0.3–79.9) μg · dm^{-3} (Sulfamethoxazole)	6					—	—	12.8 μg · dm^{-3} (Sulfamethoxazole)	[68]
	1.28 (0.353–2.2) μg · dm^{-3} (Sulfadiazine)	2							PEC 92.8 μg · dm^{-3} (all sulfonamides)	[69]
Effluent	0.517 (0.00366–6) μg · dm^{-3} (Sulfamethoxazole)	30	1.189 (0.0632–4.7) μg · dm^{-3}	21			1.123 μg · dm^{-3}	3	6.0 μg · dm^{-3} (Sulfamethoxazole)	[70]
	1.26 (0.005–4.27) μg · dm^{-3} (Sulfathiazole)	4							4.27 μg · dm^{-3} (Sulfathiazole; effluent of agricultural STP)	[67]
Sludge (after WWTP)	22.56 (0.01–113) μg · kg^{-1} (Sulfamethoxazole)	6	68 20 μg · kg^{-1}	1	—	—	—	—	197 μg · kg^{-1} (Sulfapyridine)	[71]
	99.1 (1.2–197) μg · kg^{-1} (Sulfapyridine)	2							31 μg · kg^{-1} (Sulfamethazine)	[72]
Soil	211.6 (0.16–860) μg · kg^{-1} (Sulfonamides)	10	837.74 (1–9520) μg · kg^{-1}	12	—	—	—	—	400 μg · kg^{-1} (Sulfathiazole; agricultural soil)	[73]
			48.45[4] (1–304) μg · kg^{-1}	11					PEC 860 μg · kg^{-1} (Sulfachloropyridazine; soil pore water estimation)	[74]
Manure	27.30 (0.23–167) mg · kg^{-1} (Sulfamethazine)	7	32.803 (0.020–167) mg · kg^{-1}	13	—	—	—	—	395.730 mg · kg^{-1} (Sulfadimethoxine; in bedding-day 0)	[75]
	59.07 (35.2–91) mg · kg^{-1} (Sulfadiazine)	3							167 mg · kg^{-1} (Sulfamethazine)	[76]
Waste landfill			—	—	—	—	—	—	1600 μg · dm^{-1} (all sulfonamides)	[77]

[1] Calculated based on maximum values given in tables; [2] n-number of papers; [3] natural waters; [4] without a soil sample containing 9520 μg · kg^{-1} sulfadiazine (immediately after application).

Sulfonamide concentrations in samples increase as follows: seawater < ground water < surface water < raw municipal sewage < treated sewage < hospital sewage < activated sludge < soil < runoff from farmland < leachates from landfill < manure. In our opinion, due to the very low concentrations of sulfonamides and small number of positive tests, the presence of trace amounts of these drugs in drinking water is not a significant problem. Their maximum concentrations were found in fresh removed bedding [75] and manure from pigs fed diets with the addition of sulfonamides, mainly sulfamethazine [76]. However, as we consider the more worrying is the fact that this sulfonamide occurred in almost 50 % of samples (the average concentration of drug was 7 mg · kg^{-1}). Additionally, sulfadiazine was also determined in tested samples (max 35.2 mg · kg^{-1}). It is important, that even short-term storage of manure can result in a significant reduction in concentrations of sulfonamides [75].

Generation of drug resistance

In populations of bacteria that are sensitive to specific antibiotics can also intrinsically occur strains resistant to at least one drug. In consequence, these resistant bacteria can survive, multiply and be spread to others in the family. A potentially possible correlation between the presence of anti-infectives in the environment and drug resistance was observed in the 20th century [6, 78]. For example, the ECO-SENS project has collected and analyzed the drugs resistance data in 17 European and American countries, since 1960. In Nicole Kemper's article on the influence of veterinary antibiotics on the environment the author has formulated the following thesis: "Resistance is provoked by repeated exposition of bacteria to sub-lethal dosages of antibiotics, as realized by continuing manuring with contaminated faeces on land used agriculturally" [9]. Moreover, the generation of drug resistance as a result of the transfer of "resistance" genes (horizontal gene transfer) in the environment has also significance [79–81]. In this case, resistant strains may occur in ecosystems theoretically not exposed to chemotherapeutics. For example, Pallecchi et al have described the occurrence of drug resistance in 67 % of members of the Guarani Indian community of Alto Los Athletic (Bolivia) [80]. There is also the possibility that drug resistance against one group of drugs may favour the generation of drug resistance to other drugs or disinfectants [82]. Due to the high importance of pathogens' resistance to human health, a program of monitoring for microorganisms resistance in Europe and the Americas was implemented [79, 83].

A significantly increased resistance against sulfonamides was observed in these bacteria strains that have in cells:

- overproduction of glutamic acid, or (PABA),
- overproduction of *dihydropteroate synthase* (DHPS) coded by plasmid DNA,
- increased activity of *dihydrofolate reductase* (DHFR),
- a reduction in the permeability of bacterial cell wall,
- there is no synthesis of folic acid (it is taken with food),
- a synthesis of the modified DHPS enzyme having no affinity for sulfonamide.

In environmental matrices the presence of organisms resistant to sulfonamides can be determined by detection of specific resistance-genes sul1, sul2, and sul3 or plasmids R388, RSF1010, pUVP4401 [84–86]. The most often, the mechanism of bacterial resistance to sulfonamides has been described in isolates of *Escherichia coli*, *Salmonella enterica*, *Shigella* spp from manure of farm animals, from meat and meat products, from healthy humans and urinary infections, and wastewater. The available data on the bacterial resistance to sulfonamides are presented in Table 3.

Table 3

Dissemination of sulfonamide resistance genes (sul1, sul2 and sul3) in the environment

Matrix	Total of sulfonamide-resistant isolates positive for sul1-3 genes [%]	Total of sulfonamide--resistant isolates [%]	References
Pigs	11–84 (sul1), 19–54 (sul2), 3–46 (sul3)	50–97	[84]
Swine		81	[87]
Cattle		22	
Dogs and cats		20	
Laying hens		26	
Pigs	18 (sul1), 20 (sul2), 18 (sul3)	50	[88]
Wild small mammals	5 (sul1), 1 (sul2)	6	
Danish broiler faeces, and meat	11 (sul1), 82–100 (sul2)	15–18	[89]
Broiler meat	26 (sul1), 61 (sul2), 8 (sul3)	45	
Foodstuffs	69.8 (sul1), 36.9 (sul2), 1.4 (sul3)	92.5	[86]
Wastewater directly from swine farms	92 (Σ sul1, sul2, sul3)		[90]
Shrimp ponds	43 (Σ sul1, sul2, sul3)		
City canal/fish ponds	72 (Σ sul1, sul2, sul3)		
Water-sediment and Manure	14 (sul1), 96 (sul2)		[91]
Faecal samples	100 (Σ sul1, sul2, sul3))		[92]
Urina UK 1991	43 (Σ sul1, sul2, sul3)	39.7	[85]
UK 1999	53.9 (Σ sul1, sul2, sul3)	46	
UK 2004	57.5 (Σ sul1, sul2, sul3)	45.5	
Healthy humans	33 (sul1), 91 (sul2), 5 (sul3)		[89]
Human	16 (sul1), 97.5 (sul2)	74	[80]
Animal, food and human		100	[42]

Some most important facts related to drug-resistance:

– the use of antibiotics in veterinary medicine increases the drug-resistance of microorganisms including also cross-resistance [6, 94],

– the presence of sulfonamides in the environment increases the antimicrobial resistance of microorganisms [6, 9],

– number of bacterial strains resistant to sulfonamides increases systematically in recent years [78, 85],

– sulfonamides have shown the highest drug resistance, almost twice higher than tetracyclines and many times higher than other antibiotics [87].

The environmental risk assessment

The majority of researchers have used the method recommended by the *European Medicines Evaluation Agency* (EMEA) for the environmental risk assessment. This method uses the results of toxicological studies and is based on the calculation the *Hazard Quotient* (HQ) as the ratio of *predicted exposure concentration* (PEC) to the *predicted no-effect concentration* (PNEC) [1, 3, 10, 15, 16, 32, 34, 54, 95]. The way of determination of these values described in detail by Koschorreck et al, Kim et al and Lopes de Souza et al [18, 35, 95]. A similar method base on calculation of the MEC/PNEC ratio where MEC is the measured environmental concentration [1, 5, 34, 43, 96]. Typically, value of the HQ < 1 indicate that substance analyzed can be considered as environmentally safe. According to Environmentally Classified Pharmaceuticals (2009) the risk is specified as:

– insignificant if PEC/PNEC < 0.1,

– low if PEC/PNEC ratio 0.1–1,

– moderate if PEC PNEC 1–10,

– high if PEC/PNEC > 10 [32].

A comprehensive review of the data on HQ values for 5 selected sulfonamides are shown in the article by Garcia-Galan et al [16]. Although the presented HQ values are mainly obtained for sulfamethoxazole however they significantly differ among themselves. The selected data on the HQ value made based on the available literature and the above-cited article [16] are shown in Table 4.

Theoretically, for the sulfadimethoxine; in bedding-day 0 and Lemna gibba ($MEC_{max} = 395.73\ mg \cdot kg^{-1}$ [75], EC_{50} $0.248\ mg \cdot dm^{-3}$ [16]), $HQ_{max} = 1.6 \cdot 10^6$ where $HQ_{max} = MEC_{max}/PNEC$ and $PNEC = EC_{50}/1000$.

However, the discussed-above maximum HQ values have probably negligible importance. According to Schwab et al [5] the present concentrations of sulfonamides do not pose a risk to human health. Moreover, according to Environmentally Classified Pharmaceuticals (2009) environmental risk of sulfonamides is specified as insignificant [32]. On the other hand, data on the quantity of these drugs in matrices such as manure, wastewater from agricultural fields and pharmaceutical industry indicate that in these cases sulfonamides can cause serious problems for the environment. Moreover, often it does not take into account changes in the genotype of microorganisms. In contrast to the toxic effect, these changes can easily be easily transferred, even to species in other biocenosis.

Table 4

Ecotoxicological data on the HQ value (based on the available literature)

Matrix	Mean for all sulfonamides	n[1]	Mean for all sulfonamides [16]	n[1]	Maximum values calculated based on data from Table 2 $HQ_{max} = MEC_{max}/PNEC$	Maximum values presented in the literature		
						Values	Comments	References
Drinking water	0.0097	1	—	—	$8.5^2/0.05^3 = 170$ (sulfamethoxazole)	0.0097 (sulfamethoxazole)	HQ = PEC/PNEC for children, for combined drinking water/wsh consumption	[5]
Surface water	6.256 (0.002–59.3)	15	11.116 (0.002–59.3)	8	$18/0.05^3 = 360$ (sulfamethoxazole) $19.2/201 = 0.9552$ (for sulfamethazine and *Daphnia magna*)	59.30 (sulfamethoxazole)	HQ = PEC/PNEC Acute toxicity test on surface waters in Germany	[36]
Wastewater	2.916 (0.001–22.96)	9	—	—	$1340/0.05^3 = 26800$ (sulfamethoxazole)	22.96 (sulfamethoxazole)	HQ = MEC/PNEC algae	[43]
Aquatic environment	2.114 (0.00089–6.3)	3	1.464 (0.03–6.3)	7	—	6.3 (sulfamethoxazole)	HQ = PEC/PNEC The PEC of test pharmaceuticals was estimated based on several conservative assumptions in Korea	[35]
Hospital sludge	3.278 (0.03–15.1)	7	—	—	$12.8/0.05^3 = 256$ (sulfamethoxazole)	15.1 (sulfamethoxazole)	HQ = PEC/PNEC for hospital effluent in Germany	[69]

[1] n-number of data; [2] PEC; [3] PNEC = NOEC/10 for *Synechococcus leopolensis*.

Conclusion

Antibacterial sulfonamides are a group of drugs still commonly used in human and veterinary medicine.

1. The used sulfonamides can be spread almost entirely into the environment in biologically active form or can recover the activity.
2. Probably sulfonamides introduced into the environment remain there for a long time and can spread easily in it and infiltrate even the groundwater.
3. Attendance of sulfonamides in tested environmental samples is very high.
4. The highest concentrations of sulfonamides are found in manure from livestock.
5. Opinions on the possibility of sulfonamides removing in conventional sewage treatment plants (STPs) are divergent.
6. Effective methods for the elimination of sulfonamides can be: nanofiltration, reverse osmosis and AOP.
7. Sulfonamides have very low toxicity to higher organisms, and from this point of view they are not a really threat to people's health.
8. Sulfonamides are highly toxic for microorganisms, algae and certain plants.
9. Sulfonamides occurring in the environment favour the generation of drug resistance.
10. Sulfonamide resistance genes may be transferred in the environment.

According to the authors of the National Programme for Protection of Antibiotics [41], microorganisms with relatively low pathogenic risk due to acquired resistance mechanisms may be the major factors threatening the health and human life. In result, it can lead to the spreading of diseases which are commonly considered to be "overcome." These facts indicate that the presented problem has a serious global importance in ecology and the limitations of antibiotic consumption in individual countries do not solve it.

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OCENA WYSTĘPOWANIA LEKÓW SULFONAMIDOWYCH W BIOSFERZE

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Abstrakt: Sulfonamidy, pochodne kwasu *p*-aminobenzenosulfonowego są znanymi od lat 30. XX w. lekami przeciwbakteryjnymi. Według klasyfikacji anatomiczno-terapeutyczno-chemicznej (ATC) zaliczane są do grupy leków przeciwbakteryjnych do stosowania wewnętrznego powszechnie nazywanych antybiotykami.

Mają one również właściwości roślinobójcze oraz są wykorzystywane jako dodatki do pasz w rolnictwie. Szacuje się, że jedynie w weterynarii ich roczne światowe zużycie może wynosić nawet 15 tys. Mg (ton).

Obecnie w niemal 100 % próbek środowiskowych badanych pod kontem zawartości antybiotyków wykrywane są sulfonamidy. Zazwyczaj ich oznaczane stężenia są niższe niż 1 μg · dm^{-3}, niemniej w gnojowicy wykrywano sulfonamidy w ilościach przekraczających nawet 100 mg · kg^{-1}. Ryzyko środowiskowe powodowane przez sulfonamidy oceniane na podstawie ich ekotoksyczności nie jest wielkie. Jednak istnieją dowody na to, że biorą one udział w generowaniu lekooporności mikroorganizmów. Takie geny lekooporności mogą być przenoszone pomiędzy różnymi szczepami bakterii, np. na drodze koniugacji. W rezultacie geny te mogą się pojawić u bakterii chorobotwórczych obecnych w ekosystemach uprzednio nie narażonych na kontakt z antybiotykami.

Celem pracy jest omówienie problematyki występowania sulfonamidów w poszczególnych ekosystemach. Na podstawie dostępnej literatury obejmującej ostatnią dekadę dokonano charakterystyki potencjalnej trwałości w środowisku i ekotoksyczności sulfonamidów. Omówiono również problematykę lekooporności na sulfonamidy i dokonano oceny ryzyka z uwzględnieniem ich działania przeciwbakteryjnego.

Słowa kluczowe: sulfonamidy, ekotoksyczność, lekooporność

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PARTICULATE MATTER AND ELEMENTS – A CASE STUDY OF LAND-USE CHANGE “BEFORE-AFTER” ON THE EXAMPLE OF A NEW ROAD WITH MEDIUM TRAFFIC

PYŁ ZAWIESZONY I PIERWIASTKI – STUDIUM PRZYPADKU ZMIANY SPOSOBU UŻYTKOWANIA TERENU NA PRZYKŁADZIE NOWEJ DROGI O ŚREDNIM NATĘŻENIU RUCHU

Abstract: Emissions from road traffic play a key role for the impact on entering several types of pollutants into the air, causing that the troposphere (not only in the vicinity of roads) depends on the intensity and type of the transport. Due to exploitation of vehicles and road surfaces, gaseous pollutants and particulates are released into the atmosphere. The paper presents results of research studies on the concentration of PM_{10} dust, and the concentration of heavy metals (Al, Cd, Cu, Cr, Ni, Pb and Zn), which it contains. The PM_{10} concentration measurements were performed using MicroPNS HVS16 sets of dust collectors with control modules. Qualitative and quantitative indications of heavy metals were performed using AAS. The presented approach differs from the previous ones with the method of obtaining results for the reference state, which previously were set out in the same sites, in which later were investigated the effect of motor traffic on the qualities of the air. Samples of the airborne particulate matter and surface dust were collected twice in the same area for a period of 28 days in April 2004 (an area without human intervention) and 2012 (an area of operation). The study was conducted on the area of the current section of the northern ring road of Opole (PL). It was shown that the land-use change, which is the exploitation of new road, causes PM_{10} concentration increase and raise of the designated heavy metals in the air. Based on the estimated EF and Wilcoxon test it was stated that transport significantly affects the level of Pb, Cd, Zn and Cu. It was indicated that the speed of vehicles is one of the key factors influencing the degree of air degradation. It was also concluded that the former approach applied in the assessment of the air quality being based on the comparison of its quality at source and the quality in areas away from human activity, is justified.

Keywords: road traffic, PM_{10}, heavy metals, AAS

Introduction

Road transport interferes in the environment, affecting all of its components: the atmosphere, soil, water, surface soil, geological structure, vegetation and animal world.

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Air pollution, in terms of environmental protection, is considered as one of the most important problems related to transport activities since road traffic emission is a major source that releases several types of toxic substances into the atmosphere [1].

Besides the gaseous pollutants, carriers of toxic compounds in the form of particulate matter are also released into the atmosphere, as a result of vehicles and road surfaces exploitation. The dust pollution emissions generated during use of any form of transport are divided into two categories [2]: direct (exploitation of vehicles and roads, and ground resuspension); indirect (caused by chemical reactions with the primary air pollutants). Airborne particulate matter generated by transport is characterised by a wide diversity in size and chemical composition. Equivalent diameters of particles range from several nanometers to 100 micrometers [3]. From the perspective of human health protection, fractions smaller than 10 mm defined as PM_{10}, that cause significant respiratory, circulatory and nervous systems problems, are considered the most dangerous [4, 5]. For this reason, in many countries, including all EU countries, permissible limits of ambient air concentrations of PM_{10} and heavy metals, which they contain, were introduced [6, 7].

The main sources of particulate matter and contained therein inorganic compounds being released by road transport, except the exhaust gases [8, 9], are: wear of abrasive parts of vehicles (tires, brake linings), substrate resuspension, abrasion of road surface (asphalt) and – in the countries with moderate climate – chemical agents used for road maintenance [2, 10–14]. Road transport, both in the developed and developing countries, is the main source of solid particle emission [15]. As it was indicated in [16], the estimated percentage of road traffic in total PM_{10} emission from anthropogenic sources, amounts to approximately 56 %. However, in Europe the percentage is estimated at the level of 50 % [17].

Particulate pollutants coming from land transport pose a significant threat because they contain toxic inorganic compounds. The primary compounds enriching atmospheric aerosol are, primarily: Ba, Cd, Cr, Cu, Fe, Ni, Pb and Zn [14]. The composition of exhaust emissions from vehicles depends on several factors, primarily on the type of fuel used (most of the solid particles is generated during combustion of diesel fuel) [18], engine type and age, configuration of the exhaust system and air protection equipment [19]. The main source of Ba, Cu, Fe and Zn is the wear of brake linings and discs [20]. Mechanical abrasion of tires causes mainly the release of Zn [2] and additionally triggers the release of Cd, Cu, Cr, Ni and Pb [21]. Mechanical abrasion of road surface causes the emission of Cr, Ni, Pb and [22]. Final important source that releases the solid particles into the air is the road surface resuspension, which causes the level increases of Cd, Cl, Cu, Pb and Zn in the air [23].

Analysing the available literature data, it can be said that:

– road traffic generates significant amount of pollutants and is the main source of anthropogenic airborne particulate matter,

– the highest concentrations of pollutants occurs within 10–50 m from the road and decreases with distance,

– the traffic intensity, the age of vehicles and the quota of the various types have considerable impact on the amount of the pollutants emitted,

– previous research studies on determining the impact of road traffic on the air quality were carried out by comparing the obtained results to the quality results for areas that were not directly affected by transportation and located in other areas.

So far, no comparative studies for the area were conducted, in which selected qualitative and quantitative parameters of the air – before and during the exploitation of the carriageway will be specified. The article is a case study of land-use change "BEFORE--AFTER" on the example of a new medium traffic road. The main objective of this study was to analyse and evaluate the changes in the volume of atmospheric immission that are typical particulates generated by road traffic. The scope of the investigation consisted of carrying out two medium-term measurement campaigns in the same area, *ie* in its original state (before the road was constructed) and during the phase of its constant exploitation. The research hypothesis assumed that the change in the land use does not contribute to an increase in the degree of the ambient air pollution.

Materials and methods

Measurement site and monitoring period, weather conditions

Research studies on the real impact of transport route on the air quality were conducted on the northern section of the Opole ring road (50°38′32″ N, 18°00′36″ E, Silesian Lowland, Poland, Central Europe). The examined, newly built section of the National Road E94 is an extension of the existing ring road, and its length is 3.5 km. The road was built as an answer to the need to transfer the transit out of the centre of the city of Opole and was commissioned in 2007. Before October 2004 (start of construction work), the area was a barren land (75 %) and forestry (25 %). The average daily traffic intensity is approximately 11500 vehicles. The generic structure of motor vehicles is as follows (2010): motorcycles 0.004 %; passenger cars 65.26 %; *light-duty vehicles* (LDV) 9.93 %; *heavy-duty vehicles* (HDV) 24.126 %; coaches 0.53 %; farm tractors 0.15 %.

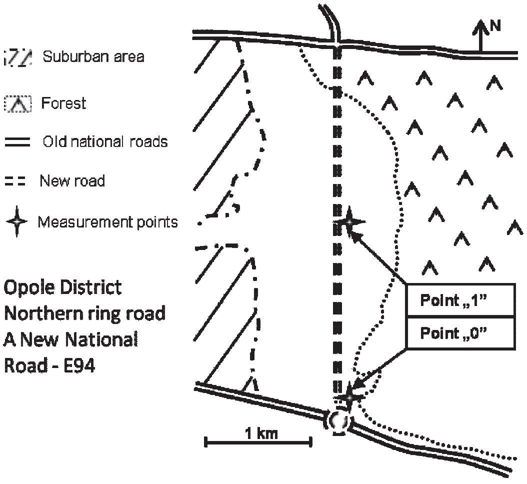

Fig. 1. The map of the area and location of the measurement points

The map of the area and location of the measurement points are shown in Fig. 1.

The measurement campaigns were carried out twice in April 2004 and 2012. In both measurement periods, the measuring media were located in two points: Point ‘0’ (p0) in braking/acceleration zone and Point ‘1’ (p1) in the vehicle zone of steady-movement. Measuring media were situated at distance of 1700 m from each other. The samplers’ location points were 10 m from the western end of the planned/and the existing road. The airborne particulate matter measurements were carried out continuously for 28 days.

The methodology of sampling and analysis

The procedure for estimating the PM_{10} concentration volume was conducted in accordance with guidelines of the European Standard [24]. Daily measurements of the PM_{10} airborne particulate matter, at both sampling points (p0 and p1) were carried out in the same periods using Micro PNS HVS16 sets of dust collectors with control modules. The indicated flow rate was 68 m^3/h. Whatman glass microfiber filters, grade GF/A with a diameter of 150 mm were used as separators for particulate matter. Filters were seasoned for 24 h in constant temperature and humidity conditions, before they were used, and then weighed on a differential dosing scales (repeatability coefficient 2 μg). PM_{10} fraction was collected on a filter during automatic, periodical (24 h) change of filters from tray. The filters were seasoned and weighed again after aspiration. The content of PM_{10} [$\mu g/m^3$] fraction was measured on the basis of the following formula (1).

$$C = (m_1 - m_0)/V \tag{1}$$

where: C – PM_{10} [$\mu g/m^3$] concentration,
m_1 – mass of the filter sputtered with dust [g],
m_0 – the mass of the clean filter [g],
V – volume of the air which has flow through the filter [m^3].

The expanded concentration measurement uncertainty (U) did not exceed 3.1 %.

Determination of heavy metals (Al, Cd, Cr, Cu, Ni, Pb and Zn) was conducted using the air-acetylene flame AAS method (*atomic absorption spectrometry* – SOLAAR M6 spectrometer – for Cr acetylene – N_2O flame).

In the case of PM_{10}, using glass disk, circles with a diameter of 36 mm were cut out from sputtered glass microfiber filters. The samples were taken up based on the US EPA 3052 method. Each PM_{10} sample (on glass microfiber filter – 36 mm) was placed in a Teflon lab dish filled with a mixture of nitric(V) acid (9 cm^3) and hydrofluoric acid (3 cm^3). The samples were mineralised in a microwave mineralizer MILESTONE, Standard D. The product, a subject to mineralisation, was put into measuring beaker (25 cm^3) and then it was refilled with deionized water. Microwave digestion time was 15 minutes (in this 5 minutes for raising the temperature to 180 °C in and 10 minutes for keeping the temperature at 180 °C).

The AAS quality control was performed by carrying out the concurrent analyses of reference material; SRM 1648a (particulate matter). Table 1 shows the concentrations of metal elements in the reference materials and the accuracy obtained using AAS method.

Table 1

AAS data for reference materials

Element	AAS		SRM 1648a – particulate matter		D* [%]
	Mean	SD	Certyfied value	Uncertainty	
	[mg/kg]				
Pb	0.598	0.03	0.655	0.033	–9.5
Ni	74.6	1.2	81.1	6.8	–8.7
Cu	572	14.5	610	70	–6.6
Cr	374	9.9	402	13	–7.5
Zn	4591	162	4800	270	–4.6
Cd	69.4	0.9	73.7	2.3	–6.2
Al	3.26	0.5	3.43	0.13	–5.2

* Deviation: the difference between the AAS and the certified values, divided by the certified value, and expressed in [%].

Expanded uncertainties for the determination of heavy metals are: 11 % for Cd, 10 % for Cr, 21 % for Cu and Zn, 20 % for Al and Ni, 13 % for Pb (PM_{10}), 14 % for Cd, 12 % for Cr, 23 % for Cu and Zn, 19 % for Ni, 16 % for Pb (dust surface). The quantititation limits are: [$\mu g/m^3$] 0.001 (Cr, Cu, Ni, Pb), 0.01 (Al, Zn), 0.0005 (Cd), [mg/kg] 0.02 (Cd, Cu), 0.03 (Zn), 0.06 (Cr, Ni, Pb).

Results and discussion

The PM_{10} concentration values obtained in both periods of the research studies are shown in Fig. 2. The results of the measured average PM_{10} concentration values for the considered measuring points indicate that the exploitation of transportation routes affects the airborne particulate matter emission. The average concentration value from both points amounted to 32.21 $\mu g/m^3$ in the base year, and to 39.44 $\mu g/m^3$ in 2012. The permissible values related to the calendar year (40 $\mu g/m^3$) were not exceeded. A relative rise in ‘after-before’ concentration amounted to the level of 22.5 %. Higher values of PM_{10} concentration were observed at the p0. The area representing the acceleration and braking of vehicles zone was characterised by a relative increase of 29.6 % (only 14.7 % was obtained at p1). This result confirms that the vehicle speed affects the amount of the emitted pollutants. On the other hand, the results at the p0 are also influenced by the proximity of the old and exploited (also in 2004) road. Wilcoxon signed-rank test was used for comparison of concentrations measured at both

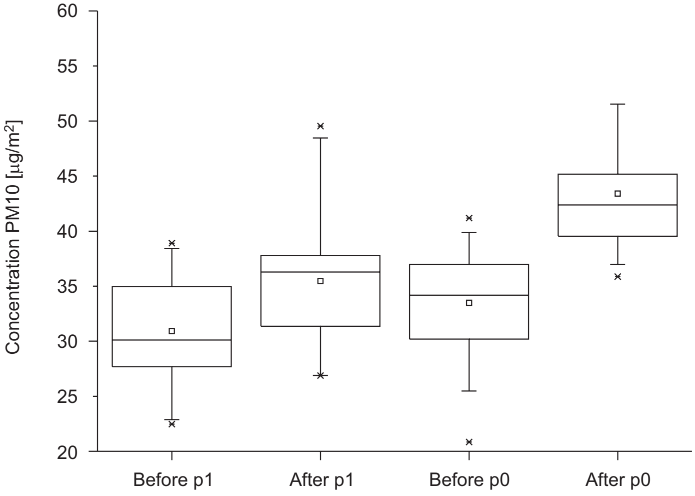

Fig. 2. PM10 concentration in 2004 and 2012. Boxes show the range between the 25th and 75th percentiles. The whiskers extend from the edge of the box to the 5th and 95th percentile of the data. The horizontal line inside indicates the median value

points during both periods. The two-tailed critical value that corresponds to the level of confidence was considered in the research studies, and the critical p-value was 0.05. The statistical analysis showed that the land use change leads to an increased burdens related to the environment.

The relationship of the measured concentrations of PM_{10} in the areas of linear sources and in the areas of reference (M/B) is presented in Table 2. The results indicate that the commonly accepted approach to relate the results of research on the impact of road traffic with the results obtained in distant areas is justified. High values of the M/B coefficient, obtained in Galicia and Euskadi may contradict to this conclusion. However, one should bear in mind that PM_{10} measurements for the main area were conducted in an area with heavy road traffic.

Table 2

PM_{10} relations: road traffic – background

References	Main area (M)	Background (B)	M/B
[25]	Zabrze (road)	Zabrze (city)	1.18
[26]	Guangzhou (city-road)	semi rural area	1.10
[27]	Hualien (road)	Henghuen (national park)	1.63
[28]	Ag.Sofia (city-traffic)	Panorama (suburban)	1.94
[29]	Euskadi (road)	Euskadi (rural)	2.43
[29]	Canary Is. (road)	Canary Is. (rural)	1.97
[29]	Galicia (high traffic)	Galicia (rural)	2.89
This study	with road	without road	1.22

It is worth mentioning that the obtained average value of PM_{10} concentration was at the similar level that was measured by other authors on the roads with similar traffic. Querol et al [29] obtained the PM_{10} concentrations at the range of 33–54 $\mu g/m^3$, Yang [27] at 39.4 $\mu g/m^3$. Higher M/B values, which they have measured, indicate lower concentration value obtained in the areas of reference. On the other hand, it may indicate that the area analysed in the study in 2004 was enriched with dust from natural sources and the nearby town.

Table 3 presents average concentrations of the determined heavy metals in PM_{10} [$\mu g/m^3$]. The results supported by statistical analysis (the Wilcoxon test) show that the exploitation of the carriageway greatly impacts the enhanced immission level of the analysed heavy metals. Except for Al, a remarkable increase in concentrations of metals in the air is observed in 2012 to 2004. The mean results from the two measurement points indicate that the largest increase is related with Cu (3.35), Zn (3.13) and Pb (3.05). Concentrations of Cd and Cr have increased more than twice, and Ni concentration increased by 30 %. Cd, Cr, Ni and Pb concentrations during the stable exploitation of the road, are at the same values as can be measured on the road with similar traffic intensity [13, 30, 31].

Table 3

Average concentration of heavy metals In PM_{10}

[$\mu g/m^3$]	Pb	Ni	Cd	Cu	Cr	Zn	Al
avg before p0	0.0096	0.0047	0.00092	0.0095	0.0018	0.0308	0.0621
avg after p0	0.0293	0.0064	0.00258	0.0320	0.0053	0.0885	0.0655
avg before p1	0.0086	0.0043	0.00088	0.0087	0.0017	0.0242	0.0642
avg after p1	0.0259	0.0054	0.00204	0.0288	0.0049	0.0839	0.0625
avg before	0.0091	0.0045	0.00090	0.0091	0.0018	0.0275	0.0632
avg after	0.0276	0.0059	0.0023	0.0304	0.0051	0.0862	0.0640

The exception is concentration of Zn, which on the examined area was significantly higher. This compound primarily arises from tire wear and mechanical abrasion of road surface, and taking into consideration the quality of road surfaces in Poland (which are the worst one in the whole EU and perhaps even in Europe) than such result does not surprise. Higher concentrations of Cu were also noticed, which may confirm the above statement. A minor increase in the concentration of Al (1.3 %) suggests that for this compound exists different source of origin than transport (confirmed by the Wilcoxon test). A number of quantitative occurrences of particular metals in the air (Zn > Cu > Pb > Ni > Cr > Cd) is almost identical as in studies of other cited authors (Zn > Cu > Pb > Ni > Cd > Cr).

Next to the values of PM_{10} concentration, speed and technical aspects of driving vehicles (braking/accelerating) have also evident impact on emission levels of solid particulates. Significantly higher concentration values of compounds are observed in the slow movement zone (p0). Wherein, the result is undoubtedly affected by the proximity of the adjacent and exploited road, what took place also in 2004.

The relative difference in concentrations of heavy metals in PM_{10} between acceleration/braking and stabilized movement zones in 2012 amounted to: 26.5 % for Cd, 19.2 % for Ni, 12.9 % for Pb, 11.3 % for Cu, 7.3 % for Cr and about 5 % for Zn and Al. It means that travelling at quasi-uniform speed (often > 100 km/h) is more ‘green’ than dynamic changes of speed, and it also supports the opinion of [32].

High values of *relative increase rates* (RIR) seem to confirm the previously given information about the impact of transport as the main source of emission of heavy metals being examined. The RIR fraction was calculated on the basis of the following formula (2).

$$RIR = [(A - B) / B] \cdot 100 \% \qquad (2)$$

where: A – data with road (2012),
B – data without road (2004).

RIR for Cu, Zn, Pb, Cr and Cd assumed the values; 234.6, 213.3, 204.9, 186.2, 156.8, respectively. Slight increase of Ni (30.2) and Al (1.3) resulting mainly from the abrasion processes of tyres and road surface can indicate that this are not the dominant compound emitted by transport means [3].

Figure 3 presents a scatter plot which depicts the relation between the average concentrations of heavy metals directly marked in the suspended particulate matter before and after the change in land use. Significant quantitative changes were observed. Compared with 2004, in 2012 the concentration of Cu, Zn, Pb, Cr and Cd in PM_{10} increased by 2.7, 2.6, 2.5, 2.4, 2.1 times, respectively. Only in the case of Ni the observed increase was slight.

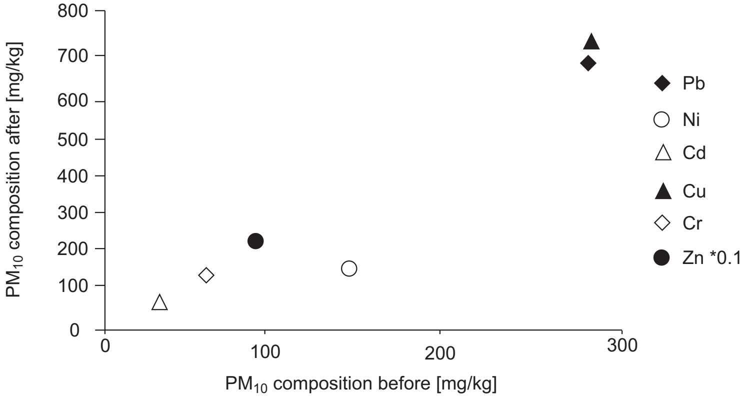

Fig. 3. Before – After scatter plot of heavy metals determined in particulate matter

The research results are often interpreted with the *Enrichment Factor* (EF) by which they are usually compared with concentrations of aluminium, scandium or silicon in relation to the concentration of accumulated in airborne particulate matter [31]. Scandium, silicon and aluminium rarely enrich the atmospheric aerosol from anthropogenic sources. Proportional amount of the examined compound in relation to the reference element in soil and in PM_{10} may indicate the source of origin. It is assumed that EF > 10 indicates that the pollution is of anthropogenic origin, whereas the EF of < 7 indicates geological origin [33]. The Enrichment Factor, calculated with the formula (3), was used to complete the measurement data analysis. Aluminium was used as the background element in this study paper because its soil concentration was stable and ambient concentration was little impacted with human activity. In calculations, data about the values of the concentrations of elements included in the soil of the Opole Region, was obtained from [33, 34].

$$EF_i = (C_i/C_{\mathrm{Al}})_{\mathrm{air}}/(C_i/C_{\mathrm{Al}})_{\mathrm{soil}} \tag{3}$$

where: C_i – is the concentration of element in the environmental sample,
C_{Al} – concentration in the reference material (aluminium) in the air and soil.

Figure 4 shows the EF values for the elements identified in the PM_{10} in 2004 and in 2012.

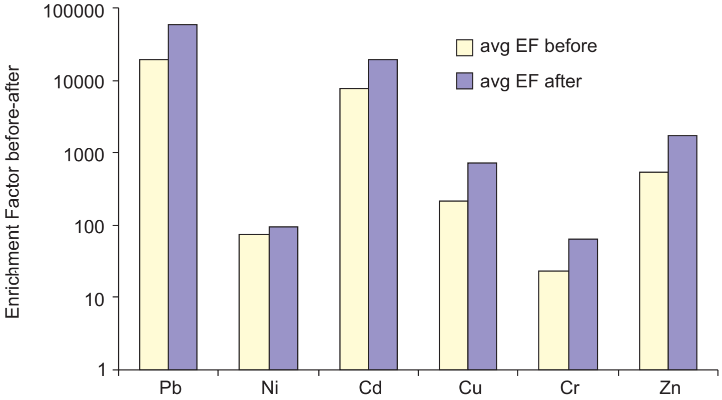

Fig. 4. Enrichment Factor for elements in 2004 (before) and 2012 (after)

According to the applied classification, all the elements identified in the PM_{10} originate from anthropogenic sources (EF > 10). It is undoubtedly influenced by the proximity of the surface emitter, which is the city of Opole. However, the change in land use, where the research is conducted, contributes to the enrichment factor increase. This applies to all elements, although in the case of Ni this increase is not significant. A high value obtained in the case of Pb ($EF \approx 6 \cdot 10^4$) and Zn ($\approx 2 \cdot 10^3$) is also interesting. It is probably connected with local conditions, as other authors who examined the influence of road transport, obtained different EF values: $\approx 3 \cdot 10^5$ for Pb and $\approx 2 \cdot 10^2$ for Zn [31], $\approx 5 \cdot 10^2$ for Pb and $\approx 6 \cdot 10^2$ for Zn [30]. The situation is similar in the case of EF for Cd ($\approx 2 \cdot 10^4$), which was estimated by Gaudry and others to be one order of magnitude lower. A similar value was obtained at the motorway in

France in the case of Ni and Cr (≈ 9 · 10 and ≈ 7 · 10), respectively [31]. EF value for Cu (≈ 7 · 10^2) is identical as observed by other cited authors. In accordance to the research objective, the relation between the EF identified in 2012 and the one marked in 2004 is important. The obtained values of: 2.5 (Cd), 2.8 (Cr), 3.3 (Cu), 1.3 (Ni), 3.0 (Pb) and 3.1 (Zn) finally confirm the thesis according to which the road transport significantly influences the air quality.

Conclusions

The research paper aimed at demonstrating the scale of the impact of transportation route on the air quality. The results obtained directly, in the 'before – after' relation, confirm observations of other authors and indicate that the exploitation of roads and motor vehicles causes high emission of gaseous and dust pollutants into the environment. Therefore, the adopted research hypothesis should be rejected. It is obvious that in the period prior to the change of use, the land was also enriched by anthropogenic pollution. However, 'adding' another source, a source directly affecting the environment, visible led to negative change in the air (and surface) quality. A significant influence of the speed of vehicles as a factor affecting the scale of polluting the air with toxicants, becomes visible. Hence, it is recommended that the amount of zones causing the 'slow-down' of road traffic in the newly-designed and modernised junctions should be limited. The values of measured PM_{10} concentrations and heavy metals in the air are lower than those obtained on motorways and roads with heavy traffic. However, the characteristic relations between the analysed pollutants, identified using indicators, can be considered as retained. The above stated thesis does absolutely not incapacitate the method of conducting the research at source and the comparitions of results with the data from distant areas. Such method is reasonable and recommended. It seems that the obtained results can help to deepen the knowledge about environmental conditions of exploitation of communication routes, although they are limited to traffic with medium intensity.

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PYŁ ZAWIESZONY I PIERWIASTKI – STUDIUM PRZYPADKU ZMIANY SPOSOBU UŻYTKOWANIA TERENU NA PRZYKŁADZIE NOWEJ DROGI O ŚREDNIM NATĘŻENIU RUCHU

Katedra Techniki Cieplnej i Aparatury Przemysłowej
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Abstrakt: Emisja z ruchu drogowego jest istotnym źródłem wprowadzania szeregu rodzajów zanieczyszczeń do powietrza, co powoduje, że jakość troposfery (nie tylko w sąsiedztwie dróg) uwarunkowana jest intensywnością i rodzajem transportu. W wyniku eksploatacji pojazdów i nawierzchni jezdnych do atmosfery uwalniane są zanieczyszczenia gazowe oraz pyłowe. Praca przedstawia wyniki badań dotyczących koncentracji pyłu PM_{10} i zawartych w nim metali ciężkich (Al, Cd, Cu, Cr, Ni, Pb i Zn). Pomiary stężenia PM_{10} wykonano przy użyciu zautomatyzowanych zestawów pobierania pyłów MicroPNS HVS16. Oznaczenia jakościowe i ilościowe metali ciężkich wykonano przy użyciu spektrometrii AAS. Zaprezentowane podejście różni się od dotychczasowych sposobem uzyskania wyników dla stanu odniesienia. Koncentracje analizowanych związków określono w tych samych miejscach, w których później badano wpływ ruchu pojazdów silnikowych na jakość powietrza. Próbki pyłu zawieszonego pobierano dwukrotnie na tym samym terenie przez okres 28 dni w miesiącu kwietniu, w 2004 (teren pozbawiony ingerencji ludzkiej) i 2012 r. (teren eksploatowany). Badania prowadzono na obszarze obecnego odcinka północnej obwodnicy Opola (PL). Wykazano, że zmiana sposobu użytkowania terenu, jakim jest eksploatacja nowej drogi, powoduje wzrost stężeń PM_{10} i oznaczanych metali ciężkich w powietrzu. Na podstawie wyznaczonej wartości współczynnika wzbogacania (EF) i analizy testem Wilcoxona stwierdzono, że transport wydatnie wpływa na poziom Pb, Cd, Zn i Cu. Wykazano, że prędkość pojazdów jest jednym z kluczowych czynników wpływających na stopień degradacji powietrza. Ponadto stwierdzono, że dotychczasowa metoda wykorzystywana przy ocenie jakości powietrza polegająca na porównaniu jego jakości u źródła z jego jakością na terenach oddalonych od działalności człowieka jest uzasadniona.

Słowa kluczowe: ruch drogowy, PM_{10}, metale ciężkie, ASA

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DYNAMICS OF AIR POLLUTION EMISSION FROM NITROGEN PLANTS "PULAWY" AS THE RESULT OF ENVIRONMENTALLY FRIENDLY ACTIONS

DYNAMIKA EMISJI ZANIECZYSZCZEŃ POWIETRZA Z ZAKŁADÓW AZOTOWYCH „PUŁAWY" JAKO WYNIK DZIAŁAŃ PROEKOLOGICZNYCH

Abstract: The paper concerns the dynamics of pollutants emission from Nitrogen Plants in Pulawy and its concentration in the ambient air (immission) in 25 years – since the beginning of the implementation of programs to protect the environment for present with particular reference years 2007–2009, which the research project on the biogeochemistry of nitrogen in ecosystems of the region influenced by Nitrogen Plant "Pulawy" in Pulawy was carried out. Environmentally friendly actions initiated in 1985 resulted in a significant reduction quantity of pollutants emitted by Nitrogen Plants "Pulawy", average about 65 %, while increasing the output by about 50 %. The greatest reduction was achieved in the case of: ammonia emission by 88 %, fertilizer dust by 85 %, ash particulates by 80 %, nitrogen oxides by 62 %, and sulfur dioxide by 27 %.

Keywords: nitrogen plants, air pollutants, emission, immission

Nitrogen Plants "Pulawy" since its inception (1966) have produced nitrogen fertilizers (ammonium nitrate and urea), and since the seventies, the caprolactam and melamine. The products are fabricated on the base of semi-finished products generated in the Works (ammonia, nitric acid, urea and carbon dioxide) and raw materials supplied from the outside (natural gas, benzene and sulfur). The rapid development of the company resulted in the construction successive investments expanding previously offered assortment of chemical products. Sale of chemicals is now 40 % of the total production and gradually increases. Now its production for the year is [1] as follows: total ammonium nitrate (nitrate solution) 1 103 850 Mg, granulated ammonium nitrate 919 875 Mg *urea ammonium nitrate solution* (UAN) 1 000 000 Mg, urea (total) 924 000 Mg, granulated Urea 600 000 Mg, melamine 92 000 Mg, carpolactam 65 000

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Mg, ammonium sulfate 156 000 Mg, hydrogen peroxide 10 000 Mg, liquefied carbon dioxide, 74 250 Mg (AdBlue 100 000 Mg)

Individual production units of Plants produce and emit specific pollutants:

– dusts of ammonium nitrate, urea, melamine and ash;

– gaseous pollutants – SO_2, CO_2, NO_x, CO, NH_3 organic vapors (toluene, benzene, cyclohexane, hydrogen cyanide).

In addition, the emission components are subject to adsorption processes in the atmosphere, condensation, coagulation, also taking part in photochemical or ion reactions, a result of which may be formed products with properties different to the original issue [2]

In the first period of the action of Nitrogen Plants "Pulawy" in the years 1969–1985 experienced an intense degradation of the surrounding environment [3–9] and in 1990 Plants, were on the Polish "List 80" the biggest polluters of the environment [10], among others due to: excessive emissions of nitrogen oxides, excessive emissions of ammonia, under use of cooling water, excessive emissions of hydrocarbons, especially cyclohexane, groundwater abstraction for production purposes, excessive emission of dust and gas from the power station, excessive load of pollutants discharged to surface waters.

Only since 1985, this situation has changed, when a company involved in the implementation of programs for environmental protection. As a result there has been a significant reduction in emissions and the negative impact of factories on the environment.

The aim of this study was to analyze the dynamics of emission by Nitrogen Plants in Pulawy and immission of pollutants in the ambient air in 25 years – since the beginning of the implementation of programs to protect the environment for present with particular reference years 2007–2009, which the research project on the biogeochemistry of nitrogen in ecosystems of the region influenced by Nitrogen Plant "Pulawy" in Pulawy was carried out.

Methods

Emission data were determined from the continuous measurements made in the Nitrogen Plant "Pulawy" in Pulawy, in factory power plant and installation of nitric acid, periodic measurements of the main sources of pollutants from technological processes and balances made on the basis of technological indicators for other sources of emissions.

In emission measurements, the following devices were utilized:

– GASMET DX-4000 (measure of gases emissions);

– EMIOTEST-2594 (measure of dust emissions);

– MGA MRU-5 (the measurement of greenhouse gases).

This work has been mainly used for measurements of nitrogen emissions, namely: ammonia, nitrogen oxides, sulfur dioxide, fertilizer particulates (dust: ammonium nitrate, urea, ammonium sulfate). In order to determine the size of distributed pollutants in ambient air at designated points were made 60-minute measurements of immission.

Air samples were collected with devices SAG 12V COM connected to a scrubber containing a solution absorbing identified contaminants. Then the samples were determined: NH_3 spectrophotometric indophenol method according to PN-Z-040009-2; NO_2 spectrophotometric method with reagent Saltzmana according to PN-Z-04009-9.

Results and discussion

Table 1 shows the relative growth of emissions of key gaseous pollutants and particulate pollutants emitted into the atmosphere by Nitrogen Plants "Pulawy", adopting emissions for 100 when conducting environmental actions in 1985. The greatest reduction was achieved in the case of ammonia emissions by as much as 88 %, nitrogen oxides by 62 %, ash particulates by 80 %, fertilizer particulate by 85 % and sulfur dioxide by 27 %. Generally, the amount of emitted pollutants decreased by about 65 %, while global production increased by 50 %, compared with 1985.

Table 1

The relative changes in emissions from Nitrogen Plants "Pulawy"

Type of emission	1985	1990	1995	2000	2005	2010
Ammonia (NH_3)	100	152	125	16	11	12
Nitrogen oxides (NO_x)	100	136	84	52	31	38
Ash dusts	100	73	31	32	34	20
Fertilizer dust	100	54	32	21	14	15
Sulphur dioxide (SO_2)	100	163	142	94	78	73

Individual production units of Nitrogen Plants "Pulawy" produce and emit specific pollutants:

– Power Plant: ash dust, gaseous pollutants – SO_2, CO_2, NO_x, CO;
– Urea manufacture: gas ammonia, urea dust;
– Ammonium nitrate manufacture: ammonium nitrate dust;
– Manufacture of nitric acid: nitric oxides;
– Manufacture of caprolactam: SO_2, sulfuric acid mist, carbon monoxide, organic vapors (toluene, benzene, cyclohexane, hydrogen cyanide);
– Manufacture of melamine: ammonia, melamine dust.

Percentage of major pollutants in the total emission from Nitrogen Plant of "Pulawy" to the atmosphere shown on the chart (Fig. 1) indicates the dominant role of sulfur dioxide (SO_2) – 56 % and nitric oxide NO – 27 %. These pollutants are a total of over 83 % of emitted gases and dust into the atmosphere. It should be emphasized that these compounds in addition to the environmental impact significantly increase the proton charge and lead to acidification [11–14]. One mole of the SO_2 creates the appearance of 2 moles of protons, while the nitric oxide is the source of one mole of H^+. Acidifying effect, directly or indirectly as a result of physiological, biochemical and chemical processes in soil also indicate: of gaseous pollutants – ammonia (NH_3) and nitric oxide (I), N_2O and fertilizer dust – ammonium nitrate (NH_4NO_3), urea ($CO(NH_2)_2$) and ammonium sulfate $(NH_4)_2SO_4$. This may lead to increased chemical degradation of the environment and biological homeostasis disorders [15].

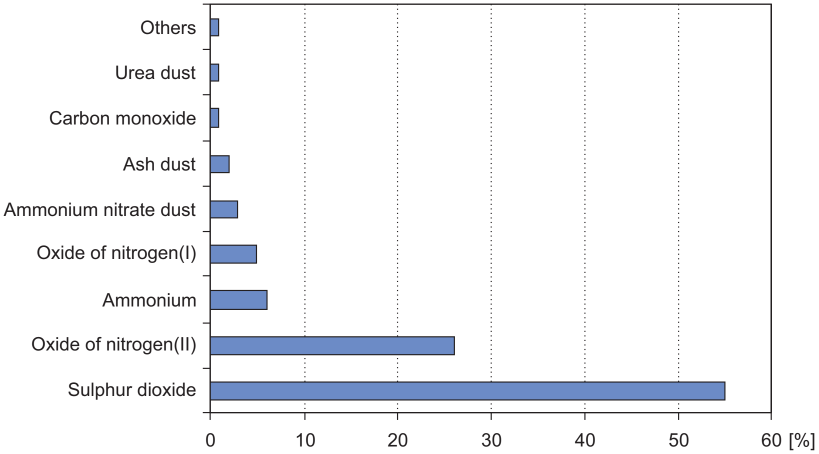

Fig. 1. Share of main pollutants emitted to the atmosphere of Nitrogen Plants “Pulawy” in 2009 [%] (Nitrogen Plant 2010)

Differentiation of air emissions in the years 2007–2009 from Nitrogen Plant “Pulawy” shown in Fig. 2 confirms the downward trend, particularly in relation to sulfur dioxide SO_2 and NO_x. There was lower variation and an increasing trend in the case of fertilizer dusts (Fig. 3) and ammonia NH_3 emissions into the atmosphere in the last three years.

In addition to gaseous pollutants as nitrogen oxides and ammonia significant role in the eutrophication and disruption of ecosystems around the Nitrogen Plant “Pulawy”

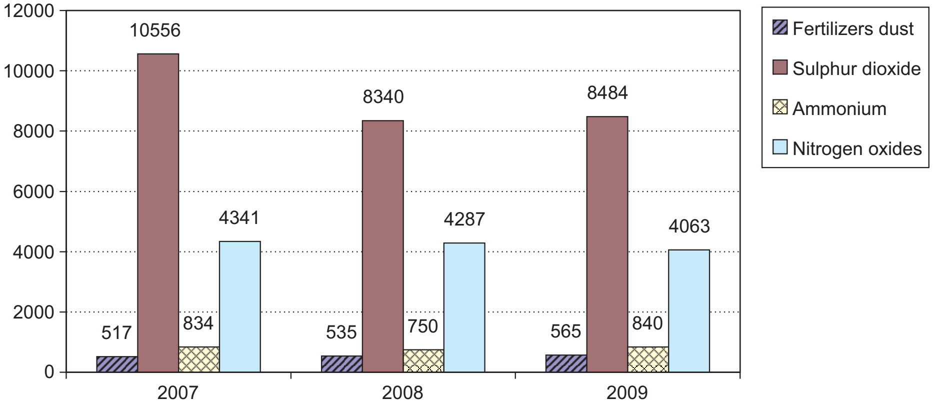

Fig. 2. Emissions of selected contaminants from Nitrogen Plants “Pulawy” in the years 2007–2009 [Mg]

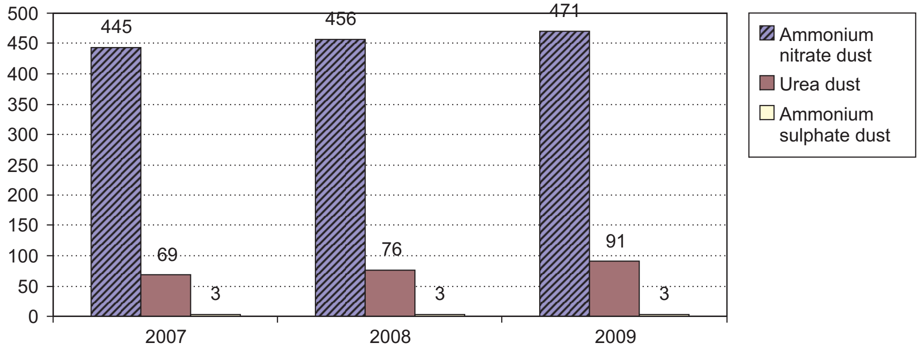

Fig. 3. Fertilizer dust emission by Nitrogen Plants "Pulawy" in 2007–2009 [Mg]

play fertilizer dusts of ammonium nitrate NH_4NO_3, urea $(CO(NH_2)_2)$ and ammonium sulfate $(NH_4)_2SO_4$. Particulate pollution is usually deposited in a much smaller distances from the emitter than gas.

Immission (Table 2) as the amount of particulate matter or gas in a unit volume of air (the concentration of pollutants or level of substances in the air) [16] in the study area has a significant impact on chemical and biological properties of soils, as well as on health, growth and assimilation organs of experimental plants. Differentiation of the major gaseous pollutant immission emitted into the atmosphere by Nitrogen Plants "Pulawy" is given for example, at several points from the year 2008.

Table 2

Some results of immission measurements made by Nitrogen Plants "Pulawy" in 2008

Months	Point – I			Point – II			Point – VIII		
	NH_3	NO_2	SO_2	NH_3	NO_2	SO_2	NH_3	NO_x	SO_2
	$[mg \cdot m^{-3}]$								
January	**0.703**	0.037	0.008	0.038	0.041	0.005	0.127	0.033	0.002
February	0.279	0.103	0.010	0.040	0.049	0.006	0.108	0.087	0.008
March	0.217	0.031	0.000	0.201	0.065	0.002	0.050	0.040	0.000
April	0.036	0.075	0.008	0.048	0.055	0.010	0.050	0.080	0.020
May	0.024	0.021	0.006	0.040	0.031	0.005	—	—	—
June	0.076	0.040	0.004	**0.533**	0.038	0.005	0.001	0.043	0.005
July	0.015	0.036	0.000	0.064	0.039	0.001	0.000	0.047	0.000
August	0.620	0.049	0.002	0.397	0.041	0.000	0.083	0.072	0.008
September	0.305	0.028	0.000	0.064	0.030	0.004	0.033	0.047	0.005
October	**0.426**	0.060	0.012	0.053	0.045	0.010	0.054	0.102	0.000
November	0.062	0.042	0.007	0.181	0.072	0.004	0.010	0.019	0.000
December	0.000	0.026	0.009	0.037	0.025	0.010	0.022	0.028	0.009
Average	0.195	0.046	0.006	0.141	0.044	0.005	0.049	0.054	0.005

The average concentration of pollutants in the individual study points were characterized by great diversity in the year, largely because they are dependent on not only the emission of pollutants but also the direction and strength of winds and weather conditions at the time of the measurement. Exceeding of the allowable concentration have been found only in the case of ammonia at the points nearest emitters.

Conclusions

Environmentally friendly actions initiated in 1985 resulted in a significant reduction of quantity of pollutants emitted by Nitrogen Plants "Pulawy", average about 65 %, while increasing the output by about 50 %.

The greatest reduction was achieved in the case of: ammonia emissions by 88 %, fertilizer dust by 85 %, ash particulates by 80 %, nitrogen oxides by 62 %, and sulfur dioxide by 27 %.

The permissible average concentrations of pollutants in the air were exceeded in some months only in the case of NH_3 at the points closest to the issue, on the direction of prevailing winds in that area. Despite a marked reduction of emissions from Nitrogen Plants "Pulawy", substances accumulated in the environment are still pose a potential threat to the still unstable ecosystems.

A detailed analysis of pollutants emissions from Nitrogen Plants "Pulawy" significantly reduced during the last 25 years demonstrated in the years 2007–2009 variation, which locally may have still an adverse impact on the functioning of ecosystems.

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DYNAMIKA EMISJI ZANIECZYSZCZEŃ POWIETRZA Z ZAKŁADÓW AZOTOWYCH „PUŁAWY” JAKO WYNIK DZIAŁAŃ PROEKOLOGICZNYCH

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Abstrakt: Praca dotyczy dynamiki emisji zanieczyszczeń powietrza z Zakładów Azotowych „Puławy” i stężenia zanieczyszczeń w otaczającej atmosferze w 25 latach – od początku realizacji programu proekologicznego do teraźniejszości, ze szczególnym uwzględnieniem lat 2007–2009, w których prowadzono projekt badawczy dotyczący biogeochemii azotu w ekosystemach rejonu oddziaływania Zakładów Azotowych “Puławy”. Działania proekologiczne zainicjowane w roku 1985 spowodowały znaczącą redukcję zanieczyszczeń emitowanych przez Zakłady Azotowe „Puławy”, średnio około 65 %, przy jednoczesnym zwiększeniu produkcji o około 50 %. Największą redukcję osiągnięto w przypadku: amoniaku o 88 %, pyłu nawozowego 85 %, cząstek popielnych 80 %, tlenków azotu 62 % i ditlenku siarki 27 %.

Słowa kluczowe: zakłady azotowe, zanieczyszczenia powietrza, emisja, imisja

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CHEMICAL SUBSTANCES IN NATURAL ENVIRONMENT OF ORGANIC FARMS

CHEMICZNE SUBSTANCJE W ŚRODOWISKU PRZYRODNICZYM EKOLOGICZNYCH GOSPODARSTW ROLNYCH

Abstract: The study contains data of 4 966 organic farms positively controlled by Certification Body Ekogwarancja PTRE, which constituted 28.4 % of all farms controlled in 2009. There were used 19 biological plant protection products in analyzed farms in 2008.

Among used plant protection products 15 of them were registered in Poland and published on Institute of Plant Protection List and 4 of them were registered in European Union but banned in Poland.

Under monitoring there were collected 74 samples of plant material, 54 samples of fruits and vegetables and 2 samples of soil in order to check out chemical pesticide residues not allowed in organic farming. Totally there were collected samples from 130 farms, which constituted 2.62 % of all controlled farms not allowed substances were revealed in 20 samples, which constituted 15.38 % of all collected samples.

Keywords: organic farming, farm, plant protection, pesticides

The organic farming is a system of agricultural production based on an use of natural processes within given farm. According to this, organic fertilizers generated in a farm are used for plant growing and exclusively own fodders are applied in animal breeding.

The high-quality food, that must not be produced using substances harmful – even in theory – for human’s health, is the most important goal. It is the system that excludes synthetic agents as artificial fertilizers, chemical pesticides, growth regulators, etc. However, no permission for synthetic substances is not sufficiently equivalent condition to organic farming. If the environment contamination is high, even the most “organic” farm is not able to produce the high-quality food, because high levels of harmful substances contained can be expected. Therefore, organic farms should be localized only in pure area. Current EU regulations on organic farming set the details for organic production, processing, controlling, marking, and importing methods, while no qualitative parameters for organic food products, nor the status of agricultural environment where

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they have been produced, are not included [1]. However, commonly used means of conventional farming penetrate out of their application sites, thus their remains can be found in many ecosystems, even where they had never been applied. In consequence, those substances are identified in organic food as well [2]. It accounts for the fact that organic food is not free from remains of illegal agents. Many literature references define organic food as a food produced with no synthetic means use, but it is not defined as completely free from synthetic agents [3].

Despite of the fact that EU Council Regulation (EC) No. 834/2007 does not obligate to analytical determination of a final product quality, while only forces to comply with organic production technology, analyses of organic food for chemical pesticides remains or heavy metals contents, are more commonly performed. Institutional producers' norms setting the limits of prohibited synthetic means in organic food, become binding.

A great variety of chemicals and elements harmful for human, animal, and plant's health exists in a natural environment. Cadmium, lead, nickel, copper, and zinc are considered as items indicating the soil environment contamination level. Sulfur is also included, because it has an exclusively strong impact on Polish soils acidity. At plants – besides the same elements (except from sulfur) – nitrates are additional harmful substances monitored [4].

The pesticide remains in a soil are sometimes a subject to very complex transformations resulting in more toxic substances formation than the initial ones. Some of them are very durable in soils and contaminate the environment to significant degree. Inorganic pesticides and chlorine carbohydrates withdrew from a production are in this group.

Material and methods

The research consists of data collected from 4 966 organic farms that were inspected by certifying body *Ekogwarancja PTRE,* which constituted 28.4 % of all farms controlled in 2009 [5]. The survey on the type and quantity of permissible plant protection means applied in organic farms was conducted in 2008. Number of 130 farms was selected, then plant and soil samples were collected to test for chemical pesticide remains illegal in organic farming, in 2009 and the first half of 2010. Achieved results are presented in a form of detected means types, number of samples with illegal substances identified, as well as type of plant material the prohibited agents were found: crops, vegetables, fruit trees, and berries.

Results and discussion

The certifying body *Ekogwarancja PTRE* inspected 4 908 organic farms, including 4 813 that were positively judged in 2008 [6]. That group comprised of 3 207 organic farms. The remaining experienced the first or the second year of conversion. Biological plant protection means were used in 585 farms, which made up 12.2 % of all controlled farms. Total number of 4966 farms were inspected in 2009. Within the frames of monitoring, 74 plant material, 54 fruits and vegetables, and 2 soil samples were collected to test for pesticide remains, which are prohibited in organic farming. In total, samples from 130 farms were collected, *ie* 2.6 % of all inspected farms. The pesticide remains were identified in 20 samples, which made up 15,4 % of all samples tested.

The organic farming is the only system of agricultural production that is regulated in details by legal acts [7]. The EU Council Regulation (EC) No. 834/2007 is a principle set of regulations concerning the organic farming [2]. In Art. 12 pt. 1, let. g, it is said that *"the prevention of damage caused by pests, diseases and weeds shall rely primarily on the protection by natural enemies, the choice of species and varieties, crop rotation, cultivation techniques and thermal processes"*. The statement informs that prophylaxis leading to create such an ecosystem within a farm that would be harmful for agrophages, is an obligation. This task is not easy, and even impossible to some hazardous organisms. When the prophylaxis does not bring expected effects, letter h of the same Article can be quoted: *"in the case of an established threat to a crop, plant protection products may only be used if they have been authorized for use in organic production under Article 16"*. This act describes only the exceptional situations when biological pesticide can be applied, and furthermore, it can be used only for confirmed threat to a crop, which excludes the prevention activities [8].

Therefore, the use of biological pesticides is not common among organic farmers. The certifying body *Ekogwarancja PTRE* positively inspected 4 813 farms in 2008 and only 585 of them applied biological plant protection products, which made up 12.2 % of all positively inspected farms. Nevertheless, these numbers do not suggest that remaining almost 90 % of controlled farms had not encountered the plant protection problems. Unfortunately, most of farmers who make a decision to perform an organic farm, count on subsidies for that purpose. Such farms are typically extensive.

In small farms, the agricultural goods are utilized for their owner's and families' needs. Cereals are grown in such farms. Sometimes they own small areas of potatoes with continuous problem of beetle that is manually removed. The organic farms group is also composed of such, the owners of which live in distant cities. The area of these farms is most frequently covered by permanent meadows cut not more than once a year. No fertilizers nor plant protection means are applied in these large – often several hundred hectares – farms.

Surveyed farms used 19 biological plant protection products in 2008, including 14 registered in a current IOR Poznan list. Miedzian was the most readily applied substance by 252 farms, then Bioczos – in 136 farms, Siarkol – in 35 farms, as well as Grevit and Novodor – in 30 farms. Among plant protection products used, there were also such, the active substance of which are listed in EU Council Regulation, but are not registered in Poland yet. In this case, applying such agents is not conflicting with EU law; however, it is not allowed in a view of Polish act on plant protection [9].

Another issue is associated with use of means for plants, for which a given product was not registered. It probably results from quite short list of permissible chemicals as well as the thrift of owners who register the agents only for the most common – *ie* most profitable – plant species.

Among preparations applied in farms certified by *Ekogwarancja PTRE*, there is lime sulfur that is forbidden in Poland not only in organic farming. However, Annex II, Table 6 of EU Council Regulation (EC) No. 889/2008 [10] mentions that agent as allowed in organic farming. The problem of using the lime sulfur is discussed from time to time in Polish horticultural journals. *Ekogwarancja PTRE* has been allowed [11] by Ministry of Agriculture and Rural Development to test the lime sulfur under organic farming conditions, hence the agent appears in the list of permissible means applied in farms certified by that body.

In 2009 and the first half of 2010, the certifying body *Ekogwarancja PTRE* made additional inspection in 130 farms by means of collecting the plant and soil material samples. The choice of particular farms resulted from the suspicion of controllers made during the earliest obligatory control on the use of illegal products and laboratory determinations of purchase centers that perform analyses of organic products supplied.

Table 1

Plant protection means used in organic farming

	Number of farms where the mean was used	Name of plant protection mean	Amount of the mean used [kg]
1	252	Miedzian	3276.2
2	136	Bioczos	1904.0
3	35	Siarkol	714.0
4	30	Grevit	75.8
5	30	Nowodor	77.0
6	8	Biosept	5.6
7	30	Biochikol	111.8
8	7	Cuproflow	83.0
9	5	Bovecol	655.0
10	14	Tiotar	378.0
11	6	Antifung	215.0
12	9	Madex	19.2
13	4	Treol	62.0
14	1	Spruzit	1.0
15	4	Promanal	34.0
16	4	Ciecz kalifornijska (*Lime sulfur*)	2130.0
17	2	Beauveria basiana	120.0
18	5	Spintor	3.7
19	3	Paroil	77.0

Total number of 130 samples were subject to analyses, including 110, at which no illegal means residues were detected, unlike 20 remaining ones, where remains of synthetic pesticides were found. Unfortunately, as comparing with previous year controls, that number increased [5]. Following plant materials composed the 110 pure samples subject to determinations (in brackets – number of particular samples):

– horticultural and berry plants: apple (10), strawberry fruit (18), raspberry leaf (16), black currant leaf (15), strawberry leaf (25), red currant fruit (1);

– ground vegetables: cucumber leaf (6), onion and chives (4), pumpkin (2), carrot leaves and root (2), parsley leaves and root (2), lettuce leaf (1), tomato leaf (1), pepper leaf (1), cabbage leaf (1), zucchini (1), dill (1), broccoli (1);

– herbs: valerian leaf (1), chamomile inflorescence (1).

Twenty samples contained residues of synthetic pesticides not allowed in organic farming (Table 2): most in ground vegetables – 12 samples, including parsley leaves – 5 samples, cucumber (leaf and fruit) – 4 samples, and carrot and dill – 1 sample each. Of berry group, raspberry (leaves) – 2 samples, strawberry (leaves) – 3 sample, and black berry (fruits) – 1 sample, were the most contaminated.

Table 2

Illegal means used in organic farming

Cultivation group	Analyzed material	Number of samples	Active substance	Type of the mean
Horticultural and berry plants:	Raspberry leaf	2	Chloropiryfos Fenheksamid Heksytiazoks Pirymetanil	Fungicide Fungicide Acaricide Fungicide
	Strawberry leaf	3	Chloropiryfos Tetrakonazol	Fungicide Fungicide
	Black currant fruit	1	Fluvalinat Karbendazym	Insecticide Fungicide
Ground vegetables:	Parsley leaf	5	Chloropiryfos Azoksystrobina	Fungicide Fungicide
	Cucumber leaf	3	Chloropiryfos Dimetoat Alfa-cypermetryna Bifentryna Ditiokarbaminiany Chlorotalonil	Fungicide Insecticide Fungicide Insecticide Fungicide Fungicide
	Parsley root	1	Azoksystrobina	Fungicide
	Cucumber fruit	1	Chloropiryfos	Fungicide
	Carrot root	1	Azoksystrobina	Fungicide
	Dill herb	1	Chloropiryfos	Fungicide
	Soil	2	DDT, DDE	Insecticide

Residues of DDT – withdrawn in Poland at least 50 years ago! – were detected in the soil. Apparently, it is still problematic for Polish agriculture. Surprisingly, majority of not allowed but used means were fungicides, the number of which is the largest on IOR Poznan list of products permissible in organic farming [12]. Therefore, farmers have a wide choice, but maybe they consider chemical means more efficient or do not know a spectrum of allowed fungicides. Only a single product appeared on a list of permissible insecticides – Spintor. This dramatic situation causes that facing the impossibility of pest control, farmers unfortunately reach for illegal products.

Conclusions

1. Achieved results indicate the need to continue and widen the scope of the control on residues of plant protection means in samples collected from agricultural goods produced by organic means.

2. Results also indicate that plant protection in organic farming system is not satisfactory and the number of farms applying plant protection means is insignificant.

3. Residues of illegal pesticides found in plant material may result not only from their use, but also contamination from adjacent conventional cultivations.

4. Considerable interests of farmers in organic system of a farm management forces the science and administration a task to work out a new and more efficient techniques of plant protection.

5. The increase of organic production faces the barrier of efficient protection of plants sensitive to agrophages.

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CHEMICZNE SUBSTANCJE W ŚRODOWISKU PRZYRODNICZYM EKOLOGICZNYCH GOSPODARSTW ROLNYCH

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Abstrakt: Praca zawiera dane z 4 966 gospodarstw rolnych, pozytywnie skontrolowanych przez jednostkę certyfikującą Ekogwarancja PTRE, co stanowi 28,4 % wszystkich polskich gospodarstw objętych kontrolą w 2009 r. [1]. W badanych gospodarstwach używano w 2008 r. 19 biologicznych środków ochrony roślin.

W ramach monitoringu pobrano w 2009 r. i pierwszej połowie 2010 r. 74 próbki materiału roślinnego, 54 próbki owoców i warzyw, 2 próbki gleby w celu zbadania pozostałości chemicznych pestycydów, niedozwolonych w rolnictwie ekologicznym. Razem pobrano próbki z 130 gospodarstw, stanowiących 2,62 % wszystkich kontrolowanych gospodarstw. Wykryto pozostałości w 20 próbkach, co stanowi 15,38 % wszystkich badanych próbek.

Słowa kluczowe: rolnictwo ekologiczne, gospodarstwa rolne, ochrona roślin, pestycydy

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EFFECTS OF SEWAGE SLUDGE ON THE ACCUMULATION OF HEAVY METALS IN URBAN SOILS

WPŁYW STOSOWANIA OSADÓW NA GROMADZENIE SIĘ METALI CIĘŻKICH W MIEJSKICH GLEBACH

Abstract: The aim of this study was to evaluate the accumulation of heavy metals in soil fertilized with municipal sewage sludge from the Municipal Wastewater Treatment Plant in Sokolka. The study was conducted on four specially prepared test areas along main streets of Bialystok. The experimental plots were sown with two lawn grass mixtures: Eko and Roadside, and three doses of sewage sludge 0.0 (control), 7.5 kg/m^2 and 15.0 kg/m^2 were used. The study included the determination of dry matter and content of Pb, Cu, Zn, Ni and Cd in soil. The heavy metal content in soil was in the acceptable level for soils of urban areas defined in the regulation of the Ministry of the Environment on the standards of the quality of soil. The general content of Zn in soil was significantly correlated with the concentrations of Pb ($r = 0.4$), Cu ($r = 0.9$) Mn ($r = 0.5$) and Ni ($r = 0.4$), while the concentrations of Ni with the level of Cd and Cu (respectively, $r = 0.4$ and 0.5). There was also a correlation between the content of Cd and Ni indeed ($r = 0.4$), Cu and Pb ($r = 0.6$) and Cu and Mn ($r = 0.7$) at $\alpha = 0.05$. The biomass of grass mixtures obtained depended on the applied sludge dose and the location. Moreover, biomass was correlated with the content and composition of soil organic carbon and granulometric composition, respectively ($r = 0.6$, and $r = 0.5$). Soil properties, arising from its particle size, were indeed correlated with the content of metals in the soil. The content of sand was negatively correlated with the concentrations of Zn ($r = -0.8$), Pb ($r = -0.5$), Cu ($r = -0.9$), Mn ($r = -0.5$) and Ni ($r = -0.6$), and the concentrations of silt and clay were positively correlated with the level of Zn, respectively, ($r = 0.8$ and $r = 0.6$), Cu ($r = 0.9$ and $r = 0.7$) and Ni ($r = 0.6$ and $r = 0.7$) at $\alpha = 0.05$. The pH values measured in water and 1 M KCl for all soil samples ranged from 6.94 to 8.02, which means that in every measure point studied heavy metals concentrations in the soil are not a threat to the environment.

Keywords: heavy metals, soil, sewage sludge

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Introduction

Green areas, including lawns, meet a number of key ecological functions, protective and aesthetic necessary to man [1]. Still evolving communication industry and transport are dangers which cause that urban soil require remediation treatment because of their progressive chemical degradation that leads to a sustainable and progressive deterioration of their properties [2]. According to Grejnert [3], urban soil is usually formed from municipal construction landfill, which means that the structure is more dense, has lower content of humus, lower water content and water permeability, and weaker biological activity.

Sludges can be the source of the organic substance used for agricultural purposes and in the remediation of soils [4]. It is estimated that 35–40 % of municipal waste is organic fraction. Organic matter and nutrients contained in the waste are potential which should return to the natural cycle and should be used by plants [5, 6]. According to Szwedziak [7], sludges introduced into the upper layers of the soil are the source of many nutrients to plants, affect soil-forming processes and contribute to increased soil biological activity.

Sludges for reclamation should be stable and conform to the standards regarding heavy metal content and hygienic sanitary conditions [8], converted to the consistency of a solid, which makes it satisfy the requirements of agro fertilizer [9]. The use of sludge in remediation has a double benefit; on the one hand, sewage sludge are treated, on the other hand, one returns to use land transformed by human activity or not used [10]. But in addition to the use of sludge there are also pros and cons. However, as noted Kalembasa and Malinowska [11], such organic substance is introduced into the contaminated soil may increase the mobility of heavy metals as a result of complexation of the low molecular weight organic compounds. As a result, it may lead to the situation that we will not be able to determine the actual risk they pose to the environment, or their availability to living organisms, the risk to human health, to water movement and uptake by plants [12].

The aim of this study was to evaluate the accumulation of heavy metals (Cd, Cu, Ni, Pb and Zn) in soil fertilized with municipal sewage sludge from the Municipal Wastewater Treatment Plant in Sokolka.

Materials and methods

The study was conducted in four specially prepared test areas (90 m^2 each) along main streets of Bialystok (Hetmanska Str., Piastowska Str., Popieluszki Str. and Raginisa Str.). Each test area was divided into 3 blocks (30 m^2 each) and each of them was divided into 6 plots in 5 m^2 area. In fall of 2010 test areas were fertilized with stabilized municipal sewage sludge from the Municipal Wastewater Treatment Plant in Sokolka and three doses of sewage sludge 0.0 (control), 7.5 kg/m^2 and 15.0 kg/m^2 were used. Doses of sewage sludge were established according to Kiryluk [13] who found in several years' study that the most effective doses for turfing of municipal waste disposal areas were those above 40 Mg(t)/ha.

Before the establishment of the experiment both sewage sludge and soil from each combination were analyzed according to the Directive of Evironmental Minister from July 13th, 2010 concerning municipal sewage sludges [14]. The analyses were done by the Regional Chemical and Agricultural Station in Bialystok (Tables 1 and 2). Additionally, soil pH in water and in 1 M KCl were determined.

Table 1

Selected physical and chemical properties of soils at four studied locations

Properties	Hetmanska Str.	Piastowska Str.	Popieluszki Str.	Raginisa Str.
pH	7.9	7.7	7.6	7.4
Sand [%]	75.9	71.9	75.7	84.4
Silt [%]	22.0	25.4	22.3	14.7
Clay [%]	2.1	2.7	2.0	1.0
Textural class	loamy sand	sandy loam	loamy sand	sand
P_2O_5 [mg · 100 g^{-1}]	7.3	18.4	22.0	10.0

In the experiment two grass mixtures were used: Eko from Nieznanice Plant Breeding Station which included 30 % of *Lolium perenne* cv. Niga, 15.0 % of *Poa pratensis* cv. Amason, 22.6 % of *Festuca rubra* cv. Adio and 32.4 % of *Festuca rubra* cv. Nimba and Roadside from Barenbrug which included 32.0 % of *Lolium perenne* cv. Barmedia, 5 % of *Poa pratensis* cv. Baron, 52.0 % of *Festuca rubra rubra* cv. Barustic, 5.0 % of *Festuca rubra commutata* cv. Bardiva (BE) and 6.0 % of *Festuca rubra commutata* cv. Bardiva (NL).

Table 2

Selected properties of municipal sewage sludge

Properties	
pH	6.7
Dry weight [%]	19.3
Organic matter [% d.m.]	58.4
Total P [% d.m.]	2.7
Total N [% d.m.]	4.0
Ammonium N [% d.m.]	0.1
Ca [% d.m.]	5.5
Mg [% d.m.]	0.7
Pb [mg · kg d.m.$^{-1}$]	23.5
Cd [mg · kg d.m.$^{-1}$]	< 0.5
Cr [mg · kg d.m.$^{-1}$]	58.0
Cu [mg · kg d.m.$^{-1}$]	194.0
Ni [mg · kg d.m.$^{-1}$]	22.0
Zn [mg · kg d.m.$^{-1}$]	1459.0
Hg [mg · kg d.m.$^{-1}$]	1.0

Plants for the dry matter determination were taken every 3–4 weeks throughout the growing season, then they were dried in an oven at 105 ^{o}C for 24 h, then at 75 ^{o}C until complete evaporation of water.

The determination of particle size was done by the Casagrande areometric method modified by Proszynski, which consists in measuring the density of soil suspension during progressive sedimentation of soil particles at a constant temperature. Density measurements were made with the Proszynski hydrometer, and the density of the soil suspension were read in the periods indicated in the tables developed by Proszynski [15].

In October 2011 the samples of soil (0–20 cm) were collected. Heavy metals concentrations in studied soils were determined using *Atomic Absorption Spectrometry* AAS. The samples were mineralized in temperature about 450 ^{o}C and remains were dissolved in 3 mol/dm^3 HCl and extracted in *aqua regia* (3 : 1 mixture HCl and HNO_3) in 80 ^{o}C (PN-ISO 11047:2001) [16].

The obtained results were analyzed with ANOVA and coefficients of variation, means and standard deviations were calculated. Correlation between heavy metals concentration in above ground of plants and in soil fertilized with different doses of sewage sludge was calculated using Pearson's correlation factor r for $p \le 0.05$. The results of obtained dry matter were analyzed using multivariate analysis of variance at a significance level $\alpha = 0.05$, in Tukey's test.

Results and discussion

In view of the growing deficit of organic matter in the soil of our country and insufficient production of manure it is necessary to look for other sources of organic matter and nutrient [17]. According to Kalembasa and Malinowska [11], it seems to be interesting to analyze the aspect of the use of sludge in perennial crops, which gradually releases the nutrients for plant growth at a satisfactory level. Sludge may be a good base of nutrients to grow grass in particular on urban soils. The addition of sewage sludge of Municipal Sewage Treatment Plant in Sokolka into the soil has a positive impact on the development of the mixtures of grasses Roadside and Eko (Fig. 1). However, a psychological barrier associated with the source, the specific structure of the post-fermentation sludge, especially high content of some heavy metals mean that it is hard to find buyers who could reasonably use it [18].

The permanent increase of municipal sewage sludge and the prohibition of storage options after 1st January 2013, as well as trends towards reducing the use for agricultural purposes, make very important and still relevant problem of disposal of municipal sewage sludge [19]. As noted by Merrington and Smernik [20], one of the serious risks of application of sewage sludge may be transfer of heavy metals from sludge into soil. According to Singh and Agrawal [21], the concentration of heavy metals in sludge depends on such factors as: the origin of sediment, wastewater treatment process and the process of treatment of sewage sludge; in turn, the bioavailability of metals brought to precipitate into the soil is determined by the properties of soil, such as pH, organic matter content, redox potential, as well as the size of the applied dose of sludge. Some metals due to the different nature of the physical/chemical properties may show affinity to the other components of sewage sludge and soil to which they are added [22].

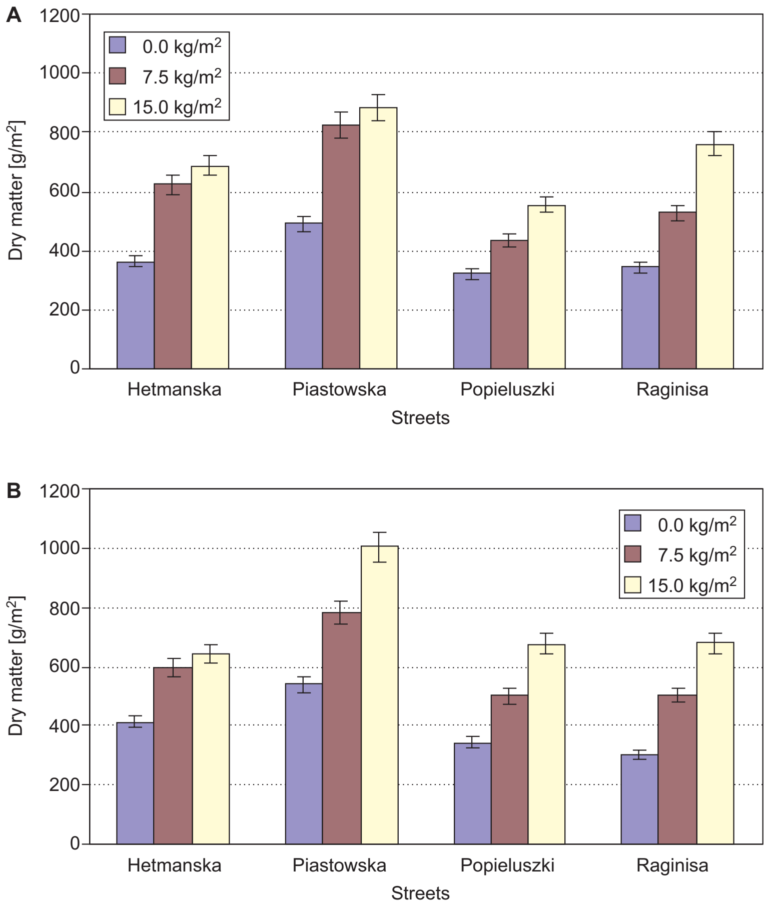

Fig. 1. The effect of sewage sludge dose on produced dry matter of aboveground parts of grass mixtures (A – Eko, B – Roadside) grown in close proximity of main streets of Bialystok (Hetmanska Str., Piastowska Str., Popieluszki Str. and Raginisa Str.)

The dynamics of changes in forms of metals is the most intense in the top layer of the soil and depends on diverse populations of microorganisms, organic matter, *cation exchangeable capacity* (CEC) and the biological interaction associated with microorganisms activity rhizosphere and also on the plant itself [23]. The greatest variability of heavy metals in soils showed zinc (68.1 %), whose content in soils ranged from 24.0 to 246.0 mg/kg d.m., the smallest factor of variability, in turn, in soil had nickel (5.6 %) whose concentrations in soil was from 39.9 to 48.8 mg/kg d.m. (Table 3).

According to Gambus and Grabowski [24], content and distribution of heavy metals in soil profiles are determined by the amount of organic matter, soil physicochemical properties and conduct soil-forming processes. Wilk and Gworek [22] point out that the mixing of sludge with the soil heavy metals forms undergo transformation that alters their bioavailability due to changes in their equilibrium and kinetic reactions in the soil.

Table 3

Concentrations of heavy metals in soil fertilized with different doses of sludge

Street	Grass mixtures	Dose of sewage sludge [kg/m^2]	Cd	Cu	Mn	Ni	Pb	Zn	pH		Sand [%]	Silt [%]	Clay [%]	C_{org} [%]	C : N
			[mg/kg d.m.]						KCl	H_2O					
Hetmanska	Eko	0	1.3	13.0	261.5	44.3	30.0	61.0	7.3	7.7	64	25	11	1.5	4.9
		7.5	0.7	13.3	223.9	44.4	24.0	51.0	7.4	7.8	68	23	9	1.6	4.8
		15.0	1.1	13.1	239.3	46.3	27.5	52.5	7.2	7.6	65	26	9	1.7	6.0
	Roadside	0	0.9	13.2	260.8	47.3	27.5	58.5	7.2	7.7	67	22	11	1.3	6.3
		7.5	0.9	15.3	247.5	46.9	29.0	57.0	7.3	7.7	63	26	11	1.8	4.7
		15.0	0.8	13.7	269.3	48.8	26.5	50.5	7.4	7.6	56	30	14	2.0	6.1
Piastowska	Eko	0	1.1	17.7	300.6	44.9	39.0	92.0	7.3	7.5	57	30	13	1.9	3.9
		7.5	0.8	26.8	321.9	47.4	45.5	246.0	7.1	7.4	44	39	17	1.9	5.5
		15.0	1.2	24.8	341.5	46.2	51.5	243.0	6.9	7.3	55	34	11	2.3	6.0
	Roadside	0	0.5	19.7	309.1	45.6	58.0	155.5	7.3	7.6	46	39	15	2.1	4.9
		7.5	0.7	19.8	324.7	43.9	39.5	130.0	7.3	7.4	49	38	13	2.1	5.2
		15.0	0.5	22.1	365.3	47.8	45.5	171.5	7.1	7.4	52	36	12	2.1	5.0
Popiełuszki	Eko	0	0.4	19.0	415.6	44.2	35.5	90.5	7.5	7.6	59	28	13	1.2	3.9
		7.5	0.9	18.4	403.4	44.1	38.5	84.0	7.3	7.5	57	32	11	2.4	6.3
		15.0	0.5	19.1	376.8	43.8	120.0	85.5	7.3	7.4	58	31	11	1.4	4.3
	Roadside	0	0.3	18.4	384.4	44.2	42.0	85.0	7.4	7.6	53	35	12	1.2	3.5
		7.5	0.3	17.9	387.7	42.5	38.5	77.5	7.2	7.4	59	30	11	1.6	5.5
		15.0	0.6	19.0	383.1	45.9	40.0	93.5	7.0	7.3	63	26	11	1.6	3.9

Table 1 contd.

Street	Grass mixtures	Dose of sewage sludge [kg/m^2]	Cd	Cu	Mn	Ni	Pb	Zn	pH		Sand [%]	Silt [%]	Clay [%]	C_{org} [%]	C : N
			[mg/kg d.m.]						KCl	H_2O					
Raginisa	Eko	0	0.5	10.1	242.5	39.9	21.5	31.0	7.8	8.0	75	18	7	0.6	1.8
		7.5	0.2	9.5	227.6	40.9	21.0	31.5	7.6	7.7	73	18	9	1.1	5.0
		15.0	0.5	11.1	245.3	41.3	19.5	37.5	7.4	7.3	73	22	5	3.3	6.5
	Roadside	0	0.8	8.5	223.0	39.9	20.0	24.0	7.4	7.6	77	17	6	0.5	1.6
		7.5	1.2	13.8	173.1	47.1	24.50	58.0	7.3	7.5	60	30	10	2.1	6.5
		15.0	0.7	13.0	160.7	47.3	25.5	60.0	7.1	7.2	57	31	12	2.48	8.4
Coefficients of variation [%]			43.1	29.1	25.2	5.6	55.4	68.1	2.5	2.5	14.56	22.74	24.4	35.7	29.6
Standard deviation			0.3	4.7	74.4	2.5	20.5	60.4	0.2	0.2	8.80	6.50	2.68	0.62	1.5
Mean			0.7	16.2	295.4	44.8	37.1	88.6	7.3	7.5	60.42	28.58	11.0	1.73	5.0

Some metals are absorbed by organic matter, clay minerals, oxidized forms of iron, manganese and calcium carbonates contained in the soil. The result is a reduction in the concentration of metals in dissolved form. Such soluble trace elements such as copper, a part of zinc, cadmium and nickel are part of a complex with organic substances such as fulvic acid.

The differentiation of the geochemical background in Poland is mainly related to the variable chemical composition of the rocks from which they arise. Against this background a number of regional and local anomalies can be distinguished of geological and anthropogenic origin [25]. The content of cadmium in soils ranged from 0.4 to 1.3 mg/kg d.m., when the natural values were < 0.5 ppm [25]. Thus, it was slightly higher than the geochemical background, but also much smaller than the permissible content, as defined in the Regulation of the Ministry of the Environment [26]. The copper content in the soils was not very diverse – it ranged from 8.5 to 26.8 mg/kg d.m. The average copper content is therefore the natural values of this element in Polish soils (20–40 ppm) [25]. The nickel content in soils oscillated between 39.9–48.8 mg/kg d.m., so it is obvious that it was higher than the geochemical background set for Ni (< 5 ppm) given by Lis and Pasieczna [25] and, as in the case of cadmium, nickel content was within the limit values for concentrations of urban soils as defined in the Regulation of the Ministry of the Environment [26].

The statistical analysis revealed significant correlations between the different metals in the studied soils. The total content of Zn in the soil was significantly correlated with the content of Pb ($r = 0.4$), Cu ($r = 0.9$) Mn ($r = 0.5$), and Ni ($r = 0.4$), and the Ni content to the level of Cd and Cu (respectively, $r = 0.4$ and $r = 0.5$) at $p \leq 0.05$. There was also a significant correlation between the content of Cd and Ni ($r = 0.4$), Cu and Pb ($r = 0.6$), and Cu and Mn ($r = 0.7$) with $\alpha = 0.05$.

According to Rosada [27], pH of the soil was an important determining factor of solubility of heavy metals and equilibrium of adsorption and desorption processes of hydrogen and metals cations. Acidity reception soils ranged from 7.2 to pH 8.0, and the acidity of the replacement of pH 6.9 to 7.8 (Table 3), which means that at any point, the soil was alkaline, and test soil contained therein, and heavy metals present little risk to the environment. There was a significant negative correlation between soil pH and the content of metals in soils. The pH, measured in 1 M KCl was significantly correlated with the content of Zn ($r = -0.6$), Cu ($r = -0.7$), Ni ($r = -0.6$), while the pH measured in water with Zn ($r = -0.5$) and Cu ($r = -0.5$) at $\alpha = 0.05$. The coefficient of variation of the measured pH in water and 1 M KCl showed the same level (about 2.5 %).

The soil particle size is an essential factor determining value of soil. Knowledge of soil particle size allows analyzing their genesis and prediction other properties such as susceptibility to erosion and the response to the pollution [28]. Properties of the soil, arising from its particle size examined for individual streets and grass mixtures, were indeed correlated with the metal concentrations in the soil. Sand content was substantially correlated with the concentrations of Zn ($r = -0.8$), Pb ($r = -0.5$), Cu ($r = -0.9$) Mn ($r = -0.5$) and Ni ($r = -0.6$), and content of silt and clay was positively correlated respectively, with the level of Zn ($r = 0.8$ and $r = 0.6$), Cu ($r = 0.9$ and $r = 0.7$) and Ni ($r = 0.6$ and $r = 0.7$) in the $\alpha = 0.05$.

According to Paluszek [29], properties of soils, icluding soil granulometric composition, affect the soil fertility and growth of plant biomass. There was an important correlation between biomass and soil granulometric composition. The silt content was positively correlated with dry matter ($r = 0.5$), while sand content negatively ($r = –0.4$). The biggest variability showed clay content (24.4 %), its content in the soil ranged from 5.0 to 17.0 %, while the smallest coefficient of variation was noted for sand (14.6 %).

Organic matter in soil is the main element, which shall decide on its quality, and in consequence, for the creation and sustainability aggregates of soil. Additionally, among other things soil water retention, soil biodiversity and the density depend on content of organic matter [30]. The studies carried out show that soil in urban areas is characterized by a very low content of C_{org}. Even sludge doses used in our experiment did not cause any significant increase in carbon content. The highest value of organic C (3.3 %) was observed at the highest fertilization with sewage sludge applied (15.0 kg/m^2), while the lowest at 0.0 kg/m^2 approximately 0.5 % of the plots in Raginisa Street. The analysis of the correlation between the content of the biomass and the amount of C_{org} soil showed a significant correlation ($r = 0.6$).

Soils fertilized with sewage sludge and without sludge fertilization were characterized by a narrow ratio of C : N. Under the conditions of application of used sewage sludge doses (7.5 and 15.0 kg/m^2), the C : N was higher (ranged from 4.7 to 6.3 with 7.5 kg/m^2, and from 3.9 to 8.4 when 15.0 kg/m^2) in the soil than in the plots in which no sludge was used (Table 3). According to Starck [31], products produced in the metabolism of C and N are not only trophic substances, but also compounds which give information on the current status of supply of cells in the carbon and nitrogen, and the ratios of carbon and nitrogen compounds.

For effective treatment of the soil, plants should be characterized by high resistance to harsh environmental conditions and have the ability to accumulate xenobiotics from the soil, as well as rapid growth and high biomass production [32]. The grass in urban areas can meet the above requirements, it should be provided with the conditions for rapid growth and high biomass production. The soil must therefore be characterized by high fertility and abundance to allow for rapid growth [33]. According to Siuta [34], reclamation of sewage sludge doses are 100–150 Mg/ha depending on the status of volunteer plants.

The highest dry matter was observed in the plots located in Piastowska Street. With the increase of the dose of sludge dry weight increased for both analyzed grass mixtures (Eko and Roadside), respectively at a dose of sludge fertilization of 0.0 kg/m^2 – 490 and 540 g/m^2, at 7.5 kg/m^2 – 824 and 782 g/m^2, and at 15.0 kg/m^2 – 883 and 1003 g/m^2 (Fig. 1). The lowest dry matter of mixture Eko was observed on plots located in Popieluszki Street for all used doses of sludge: at 0.0 kg/m^2 – 320 g/m^2, at 7.5 kg/m^2 – 436 g/m^2 and at 15.0 kg/m^2 – 554 g/m^2, and dry matter of the grass mixture was similar to those and Popieluszki and Raginisa Streets: the lowest without sludge fertilization – about 325 g/m^2, at 7.5 kg/m^2 – 500 g/m^2 and at 15.0 kg/m^2 – 675 g/m^2. The statistical analysis (Table 4) showed a significant effect of fertilization with sewage sludge used, date and location of sampling plots the growth and development of grasses tested.

Table 4

Analysis of variance for dry matter production

Factors of analysis	$LSD_{0.05}$
	Dry matter
A (mixtures of grass)	ns*
B (dose of sewage sludge)	14.19
C (sampling time)	14.19
D (localization)	18.25
A × B	ns
A × C	ns
A × D	ns
B × C	34.35
B × D	42.23
C × D	42.23
A × B × C	ns
A × B × D	ns
A × C × D	ns
B × C × D	ns

* ns – non-significant difference.

Conclusions

1. The concentrations of heavy metals in soils along main streets of Bialystok is characterized by considerable local variation.

2. The application of sewage sludge (7.5 and 15.0 kg/m^2) from the Urban Waste Water Treatment Plant in Sokolka into urban soils improves properties of the these soils and had a positive effect on growth and development of analyzed lawn grass mixtures and their remediation capacity.

3. In the soil humus levels an increase in content of Cd and Ni in comparison with their content in the bedrock was observed, but did not exceed allowable content for urban soils as referred to in the regulation of the Ministry of the Environment (2002).

4. Physical and chemical properties of the soils (C_{org} content, grain size, relatively high pH) after the addition of sewage sludge create possibilities for immobilization of heavy metals by incorporating them into organic complexes.

5. Based on the results of our work we recommend the use sewage sludge as fertilizer in particular urban soils that require remediation treatments due to the fast-advancing degree of degradation.

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WPŁYW STOSOWANIA OSADÓW NA GROMADZENIE SIĘ METALI CIĘŻKICH W MIEJSKICH GLEBACH

Wydział Budownictwa i Inżynierii Środowiska
Politechnika Białostocka

Abstrakt: Celem badań była ocena gromadzenia się metali ciężkich w glebach nawożonych komunalnymi osadami ściekowymi z Miejskiej Oczyszczalni Ścieków w Sokółce. Badania przeprowadzono w Białymstoku na czterech specjalnie przygotowanych powierzchniach badawczych wzdłuż głównych ciągów komunikacyjnych. Na poletkach wysiano dwie mieszanki traw gazonowych: Eko i Roadside oraz zastosowano trzy dawki osadu ściekowego: 0 (kontrola), 7,5 kg/m^2 i 15 kg/m^2. Przeprowadzone badania obejmowały oznaczenia suchej masy oraz zawartości następujących metali ciężkich: Cd, Cu, Mn, Ni, Pb oraz Zn w glebie. Analiza stężenia metali ciężkich w badanych glebach wykazała, że zawartość Cd, Cu, Mn, Ni, Pb i Zn mieści się w wartościach stężeń dopuszczalnych dla gleb terenów miejskich określonych w rozporządzeniu Ministerstwa Środowiska w sprawie standardów jakości gleby oraz standardów jakości ziemi. Zawartość ogólna Zn w gruntach była istotnie skorelowana z zawartością Pb (r = 0.42), Cu (r = 0.92) Mn (r = 0.47) oraz Ni (r = 0.42), natomiast zawartość Ni z poziomem Cd i Cu (odpowiednio, r = 43 i r = 46). Stwierdzono również istotnie korelację między zawartością Cd i Ni (r = 0.43), Cu i Pb (r = 0.56) oraz Cu i Mn (r = 0.70) przy $\alpha = 0.05$. Uzyskana biomasa mieszanek traw zależała od zastosowanej dawki osadu ściekowego oraz lokalizacji. Ponadto była ona skorelowana z zawartością węgla organicznego i składem granulometrycznym gleby, odpowiednio (r = 0.60 i r = 0,47). Właściwości gleby, wynikające z jej uziarnienia, były istotnie skorelowane z zawartością metali w glebie. Zawartość piasku była ujemnie skorelowana z zawartością Zn (r = –0.76), Pb (r = –0.47), Cu (r = –0.85) Mn (r = –0.48) oraz Ni (r = –0.61), a zawartość pyłu oraz iłu była dodatnio skorelowana odpowiednio, z poziomem Zn (r = 0.77 i r = 0.64), Cu (r = 85 i r = 73) oraz Ni (r = 56 i r = 66) przy $\alpha = 0.05$. Wartości pH zmierzone w wodzie i w 1 M KCl dla wszystkich badanych próbek gleby mieściły się w granicach od pH 6.94 do pH 8.02, co oznacza, że w każdym z punktów pomiarowych odczyn gleby był obojętny, a badana gleba i zawarte w niej metale ciężkie nie stanowią większego zagrożenie dla środowiska.

Słowa kluczowe: metale ciężkie, biomasa, osady ściekowe

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EFFECT OF LIMING AND SEWAGE SLUDGE ADDITION ON THE DISTRIBUTION OF THE FRACTION OF HEAVY METALS IN SOIL CONTAMINATED WITH NICKEL

WPŁYW WAPNOWANIA I DODATKU OSADU ŚCIEKOWEGO NA ROZMIESZCZENIE FRAKCJI WYBRANYCH METALI CIĘŻKICH W GLEBIE ZANIECZYSZCZONEJ NIKLEM

Abstract: The total content of Zn and Cr and its distribution in fractions separated according to the BCR procedure was determined in soil taken after a three-year pot experiment. The following factors were taken into account in the experiment: I – liming (0 Ca and Ca according to 1 Hh of soil as $CaCO_3$); II – addition of sludge (without addition of sludge and addition of sludge from the wastewater treatment in Siedlce, applied at 2 gC $\cdot$ kg^{-1} of soil); III – varied level of contamination with nickel (0, 50 and 100 mgNi $\cdot$ kg^{-1} of soil as aqueous solution of $NiCl_2 \cdot 6\ H_2O$). Orchard grass (*Dactylis Glomerata* L.) was used as the test plant. The total content of Zn and Cr in soil was determined by ICP-AES, and the fractions of those metals by the 3-step BCR procedure. The total content of the metals in the analysed soil did not exceed the highest acceptable standards. Liming reduced the metal content in the exchangeable, reducible and organic matter-related fraction and increased their content in the residual fraction.

Addition of sludge reduced the Zn and Cr content in the reducible and residual fraction and increased their total content and share in the organic matter- and sulphides-related fraction. No effect of the varied Ni amount on the total content of Zn and Cr or their distribution in the fractions has been found.

Keywords: soil, nickel, liming, sewage sludge, sequential extraction procedure, zinc, chromium

Heavy metals play an important role in contamination and degradation of the natural environment, including the soil. Their characteristic features include accumulation in the environment, especially in live organisms, which increases the intensity of their interactions [1].

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The behaviour of heavy metals in soils (solubility, mobility, availability) is affected mainly by: soil pH, red-ox potential and presence of mineral (iron and manganese compounds, silty minerals) and organic (soil humus) colloids [2–4].

The total content of heavy metals in the soil cannot be regarded as an indicator of their bioavailability [5]. Organic matter present in soil as humic substances as well as that introduced to the soil (substrate) with natural, organic, organic and mineral fertilisers, restricts the amount of heavy metals available to plants [6, 7].

Among soil's ecotoxicologic features, the speciation of heavy metals is of special importance as it can be related to their bioavailability. Commonly applied methods of sequential extraction enable identification of the chemical fraction of heavy metals in the soil environment as well as evaluation of their availability and potential toxicity to the biotic elements of the trophic chain [8–10].

Identification of element species combined with modern statistical methods allow a range of factors to be determined, such as bioavailability, accumulation, migration, toxicity, solubility and sorption [11].

The aim of this study was to determine the effect of liming and the application of sludge on the content of zinc and chromium in different fractions separated in accordance with the BCR procedure in soil contaminated with nickel.

Materials and methods

Soil after a three-year pot experiment, conducted in a random arrangement in triplicate, was used in the study. The experiment was conducted in the years 2006–2008 at the experimental facility of the Siedlce University of Natural Sciences and Humanities. The following factors were considered: I – liming (no liming and liming according to 1 Hh of soil as $CaCO_3$); II – addition of sludge (control and addition of sludge from a wastewater treatment plant in Siedlce, used in amounts corresponding to 2 gC $\cdot$ kg^{-1} of soil); III – varied contamination of soil with nickel (0, 50 and 100 mgNi $\cdot$ kg^{-1} of soil as aqueous solution of $NiCl_2 \cdot 6H_2O$). Liming, sludge and nickel were applied in April–May 2006. Orchard grass (*Dactylis glomerata* L.) whose 4 cuts were harvested each season, was used as the test plant. The soil material used in the experiment was taken from the layer of 0–20 cm of grey-brown podsolic soil with the granulometric composition of loamy sand [12]. The main properties of the soil before the experiment are shown in Table 1.

Table 1

Some properties of soil used in the pot experiment

pH 1 M KCl	C_{org}	N_{tot}	Available		Total		
			P	K	Ni	Cr	Zn
	[g $\cdot$ kg^{-1} of soil]		[mg $\cdot$ kg^{-1} of soil]		[mg $\cdot$ kg^{-1} of soil]		
5.6	7.9	0.98	69	75	5.67	2.46	7.93

The chemical composition of the sludge used in the experiment is shown in Table 2 [9].

Table 2

Chemical composition of sewage sludge from Siedlce

Component	[g · kg^{-1} d.m.]	Component	[mg · kg^{-1} d.m.]
N	60.5	Cd	1.99
P	31.2	Pb	50.5
K	4.28	Ni	20.6
Ca	39.6	Fe	10850
Mg	8.42	Cu	137.7
C_{org}	371	Zn	1276.8
MO	640	Cr	30.14
Dry matter [g · kg^{-1}]		180	

To make the experiment results more accurate, 15 dm^3 pots, each containing 10 kg of soil, were put into additional containers to prevent the solution from leaking out of the pots. The pots were placed in the open and moisture of 60 % of field water capacity was maintained in them. The soil was analysed after the last cut of the test plant, in the third year of the experiment. The soil pH was determined in 1 mol/dm^3 KCl by the potentiometric method. The total zinc and chromium content in soil was determined by the ICP-AES method following the sample mineralisation in a muffle furnace at a temperature of 450 °C and dissolving the ash in a 10 % solution of HCl. The metal fractions were determined by the three-step method of sequential fractionation, proposed by *Community Bureau of Reference* (BCR) [13]. The method diagram is provided in Table 3.

Table 3

A diagram of the BCR metal sequential extraction method [10]

Fraction	Name fractions	Extraction reagents	pH
F_1	Exchangeable and acid soluble	0.1 M CH_3COOH	3.0
F_2	Reducible	0.5 M $NH_2OH \cdot HCl$	1.5
F_3	Oxidisable	8.8 M H_2O_2 + 1 M CH_3COONH_4	2.0
F_4	Residual	Calculated as difference between total content and sum three previously separated fractions	—

The results were worked out statistically by analysis of variance with the Fisher--Snedecor distribution, according to the F.R. Anal. Var 4.1 program and the value of $LSD_{0.05}$ was calculated by Tukey's test. Moreover, a linear correlation analysis was also performed to determine the relationship between the features under study.

Results and discussion

This study has shown clearly that the total content of the metals – zinc and chromium – in the analysed soil, taken after completion of a three-year pot experiment, did not exceed the value of the geochemical background and lay within the range of natural values [2, 14]. Similar values of chromium content in podsolic soils have been found by Kalembasa and Pakula [3] and Pakuła and Kalembasa [15].

The total zinc content in the soil under study (Table 4) ranged from 7.90 to 14.20 mg · kg^{-1} of soil and it significantly depended on liming and the addition of sludge. Liming resulted in a slight, yet statistically proven, increase in the content of the metal in the soil under study, which can be attributed to the fact that the calcium fertiliser introduced to the soil was probably contaminated with zinc compounds.

Table 4

The content [mg · kg^{-1} of soil] of zinc in fractions determined by the BCR method in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1	0.66	0.68	0.70	0.39	0.37	0.37
	F_2	20.2	2.06	2.05	2.47	2.35	2.41
	F_3	1.52	1.63	1.60	1.26	1.30	1.30
	F_4	3.70	3.53	3.55	3.88	4.00	3.98
Sum of fractions	Σ	7.90	7.90	7.90	8.00	8.02	8.06
Sludge from Siedlce	F_1	0.47	0.45	0.47	0.37	0.39	0.38
	F_2	4.78	4.81	4.74	4.19	4.27	4.22
	F_3	4.04	4.06	4.05	3.50	3.51	3.55
	F_4	4.61	4.48	4.64	6.14	6.03	5.95
Sum of fractions	Σ	13.9	13.8	13.9	14.2	14.2	14.1
			F_1	F_2	F_3	F_4	Σ
$LSD_{(0.05)}$ for:							
liming			0.013	0.047	0.053	0.196	0.157
sludge from Siedlce			0.013	0.047	0.053	0.196	0.157
doses of nickel			n.s.	n.s.	n.s.	n.s.	n.s.

n.s. – not significant.

Sludge from the wastewater plant in Siedlce significantly increased the total zinc content in soil (the amount of zinc introduced to soil with the waste material is equal to 6.88 mg · kg^{-1}).

The content of the metal in the sequentially isolated fractions in soil (Table 4 and 5) varied significantly, with the variance being caused both by liming and by the addition of sludge. Liming significantly reduced the amount of zinc in the exchangeable fraction (F_1) and in that related to organic matter (F_3) and increased its amount in the residual fraction (F_4). The effect of the factor analysed here on the content of zinc in the fraction associated with iron and manganese oxides (F_2) was unclear. Liming in control pots significantly increased the content of the zinc fraction, whereas the opposite effect was observed in soils to which sludge was added, which can be attributed to the interaction of both the factors analysed in the experiment.

Table 5

The percentage share of the zinc fraction in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1 F_2 F_3 F_4	8.61 25.60 19.24 46.55	8.61 26.08 20.63 44.68	8.86 25.95 20.25 44.94	4.88 30.87 15.75 48.50	4.61 29.30 16.21 49.88	4.59 29.90 16.13 49.38
Sum of fractions	Σ	100	100	100	100	100	100
Sludge from Siedlce	F_1 F_2 F_3 F_4	3.38 34.39 29.06 33.17	3.26 34.86 29.42 32.47	3.38 34.10 29.14 33.38	2.61 29.51 24.65 43.23	2.75 30.07 24.72 42.46	2.70 29.93 25.18 42.19
Sum of fractions	Σ	100	100	100	100	100	100

Organic matter introduced into soil as sludge reduced the content of the analysed metal in the exchangeable fraction (F_1) and in the residual one (F_4), increased its content in the fraction associated with organic matter and with sulphides (F_3), without clearly differentiating its content in the reducible fraction (F_2).

Earlier studies [16] have provided similar findings concerning organic waste material.

This study did not find a significant effect of a varying content of nickel in soil on the total content of zinc or its distribution in different fractions. The average percentage of the metal under study in the isolated fractions can be shown in the following sequence of decreasing values: $F_4 > F_2 > F_3 > F_1$.

The total content of chromium in the analysed soil ranged from 2.40 to 2.61 mg · kg^{-1} of soil. Both the total content and its content in each fraction depended significantly on liming and the addition of sludge (Table 6 and 7). No effect of the factors under analysis were observed on the content of chromium in the residual fraction (F_4).

Introducing calcium carbonate to the soil resulted in a slight increase in the total chromium content, which – as with zinc (that has been discussed above) – can be attributed to contamination of the calcium fertilisers.

Since chromium in the amount of 0.16 mg · kg^{-1} of soil was introduced with sludge, this factor significantly differentiated the metal content.

A chemical analysis showed a varied content of chromium in the sequentially isolated fractions (Table 6 and 7). The smallest portion of the analysed metal was isolated in the exchangeable fraction (F_1): 2.28–4.28 % of its total content, and the largest was in the residual fraction (F_4): 24.72–58.81 % of the total content.

Table 6

The content [mg · kg^{-1} of soil] of chromium in fractions determined by the BCR method in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1	0.099	0.102	0.100	0.085	0.087	0.084
	F_2	0.289	0.286	0.290	0.358	0.350	0.357
	F_3	0.660	0.680	0.690	0.580	0.570	0.570
	F_4	1.352	1.342	1.350	1.417	1.438	1.429
Sum of fractions	Σ	2.40	2.41	2.43	2.44	2.44	2.44
Sludge from Siedlce	F_1	0.073	0.070	0.075	0.059	0.062	0.064
	F_2	0.376	0.362	0.360	0.305	0.273	0.294
	F_3	0.861	0.873	0.878	0.730	0.740	0.780
	F_4	1.220	1.255	1.247	1.496	1.565	1.462
Sum of fractions	Σ	2.53	2.56	2.56	2.59	2.61	2.60
			F_1	F_2	F_3	F_4	Σ
LSD$_{(0,05)}$ for:							
liming			0.003	n.s.	0.017	n.s.	0.015
sludge from Siedlce			0.003	0.006	0.017	n.s.	0.015
doses of nickel			n.s.	0.008	n.s.	n.s.	n.s.

n.s. – not significant.

Table 7

The percentage share of the chromium fraction in the analysed soil

Fertilisation	Fractions	Liming					
		0 Ca			Ca to 1 Hh		
		Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
		0	50	100	0	50	100
Without organic fertilisation	F_1	4.13	4.23	4.12	3.48	3.57	3.44
	F_2	12.04	11.87	11.93	14.67	14.34	14.63
	F_3	27.50	28.22	28.40	23.77	23.36	23.36
	F_4	56.33	55.68	55.55	58.08	58.73	58.57
Sum of fractions	Σ	100	100	100	100	100	100
Sludge from Siedlce	F_1	2.89	2.73	2.93	2.28	2.38	2.46
	F_2	14.86	14.14	14.06	11.78	10.46	11.31
	F_3	34.03	34.10	34.29	28.19	28.35	30.00
	F_4	51.11	49.03	48.72	57.75	58.81	56.23
Sum of fractions	Σ	100	100	100	100	100	100

The average percentage of the chromium fractions can be shown in the following sequence of decreasing values: $F_4 > F_2 > F_3 > F_1$. A similar sequence has been presented in studies by Bacon et al [17], Kalembasa and Pakula [3] and Pakula and Kalembasa [16].

Wherever liming was applied, it reduced the portion of the metal in the exchangeable fraction (F_1), which leads one to the conclusion that it is a good method to immobilise chromium, and to reduce its toxicity as a result. This factor also reduced the portion of the metal in the fraction bound with organic matter and sulphides (F_3).

Sludge introduced into soil reduced the portion of chromium in the exchangeable fraction (F_1) and in the reducible fraction (F_2) and increased its content in the fraction bound with organic matter and with sulphides (F_3). No effect of the factor under analysis was observed on the content of chromium in the residual fraction (F_4).

The statistical analysis did not confirm any significant effect of increasing the content of nickel in soil on the total content of chromium and its portion in the fractions determined according to the BCR procedure, except for the fractions associated with iron and manganese oxides (F_2), but the effect was not clearly defined.

Table 8 shows the values of pH of the soil, determined in 1M KCl solution, ranging from 5.80 to 6.80.

Table 8

pH of soil in 1 M KCl

Fertilisation	Liming					
	0 Ca			Ca to 1 Hh		
	Dose of nickel [mg · kg^{-1} of soil]			Dose of nickel [mg · kg^{-1} of soil]		
	0	50	100	0	50	100
Without organic fertilisation	5.97	5.84	5.80	6.64	6.59	6.80
Sludge from Siedlce	5.99	5.80	5.80	6.60	6.71	6.72
LSD$_{(0,05)}$ for:						
liming	0.165					
sludge from Siedlce	n.s.					
doses of nickel	n.s.					

n.s. – not significant.

The pH value of limed soil was significantly higher than that of unlimed soil. No effect of the other two factors on the feature was observed.

Significant relationships were observed in the analysed soil between the parameters under examination, which were confirmed by the analysis of correlation.

The values of the correlation coefficient are given in Tables 9 and 10.

Particularly noteworthy is a highly significant negative correlation coefficient between the pH of soil and the portion of zinc in the exchangeable fraction (F_1).

Table 9

Simple correlation coefficients between fractions of zinc and selected properties of soil

Parameter	Fractions			
	F_1	F_2	F_3	F_4
Zn_{tot}	n.s.	0.974**	0.976**	0.840**
pH	–0.766**	n.s.	n.s.	n.s.

n.s. – not significant; ** α = 0.01.

Table 10

Simple correlation coefficients between fractions of chromium and selected properties of soil

Parameter	Fractions			
	F_1	F_2	F_3	F_4
Pb_{tot}	–0.943**	n.s.	0.691*	n.s.
pH	n.s.	n.s.	n.s.	n.s.

n.s. – not significant; * α = 0.05; ** α = 0.01.

It can be concluded that both of the factors examined in the experiment (liming and applying sludge) modified the total content of zinc and chromium in soil and their portion in fractions isolated according to the BCR procedure. Both lime and sludge increased the total amount of both the metals under study in the soil. Liming significantly reduced the amount of both metals in the exchangeable fraction (F_1) and in that bound to organic matter and sulphides (F_3); it also reduced the portion of zinc in the fraction associated with iron and manganese oxides (F_2).

Sludge reduced the portion of both metals in the exchangeable fraction (F_1) and increased its content in the fraction bound to organic matter and sulphides (F_3).

Both calcium carbonate and sludge reduced the mobility of the heavy metals under study in soil, which is in line with the findings of a study conducted by Karczewska et al [18].

This study has not shown a significant effect of an increasing content of nickel in soil on the total content of zinc and chromium in the soil and their portion in fractions isolated according to the BCR procedure.

Conclusions

1. The total content of zinc and chromium did not exceed the value of the geochemical background.

2. The smallest amount of zinc and chromium in the analysed soil was found in the exchangeable fraction (F_1), and the largest amount was in the residual fraction (F_4).

3. Liming reduced the portion of both metals in the exchangeable fraction (F_1) and in the fraction associated with organic matter and with sulphides (F_3); it also increased their total content.

4. Sludge reduced the portion of zinc and chromium in the exchangeable fraction (F_1) and increased its content in the fraction bound to organic matter and with sulphides (F_3).

5. This study did not find a significant effect of a varying content of nickel in soil on the total content of zinc and chromium in soil and its distribution in different fractions.

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WPŁYW WAPNOWANIA I DODATKU OSADU ŚCIEKOWEGO NA ROZMIESZCZENIE FRAKCJI WYBRANYCH METALI CIĘŻKICH W GLEBIE ZANIECZYSZCZONEJ NIKLEM

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Abstrakt: W glebie branej po trzyletnim doświadczeniu wazonowym badano ogólną zawartość Zn i Cr oraz ich rozmieszczenie we frakcjach wydzielonych według procedury BCR. W doświadczeniu uwzględniono następujące czynniki: I – wapnowanie (0 Ca i Ca wg 1 Hh gleby w formie $CaCO_3$); II – dodatek osadu ściekowego (bez dodatku osadu ściekowego i dodatek osadu ściekowego pochodzącego z oczyszczalni ścieków w Siedlcach, stosowanego w dawce odpowiadającej ilości 2 gC · kg^{-1} gleby); III – zróżnicowane zanieczyszczenie gleby niklem (0, 50 i 100 mgNi · kg^{-1} gleby w formie roztworu wodnego $NiCl_2 \cdot 6H_2O$). Rośliną testową była trawa – kupkówka pospolita (*Dactylis glomerata* L.). Ogólną zawartość Zn i Cr w glebie oznaczono metodą ICP-AES, a frakcje tych metali 3-stopniową metodą BCR. Ogólna zawartość badanych metali w analizowanej glebie nie przekraczała dopuszczalnych norm. Wapnowanie spowodowało zmniejszenie udziału obu metali we frakcji wymiennej, redukowalnej i związanej z substancją organiczną oraz zwiększenie ich ogólnej zawartości i udziału we frakcji rezydualnej.

Dodatek osadu ściekowego wpłynął na zmniejszenie ilości Zn i Cr we frakcji redukowalnej i rezydualnej oraz zwiększenie ich ogólnej zawartości i udziału we frakcji związanej z materią organiczną i siarczkami. Nie wykazano wpływu zróżnicowanej ilości Ni w glebie na ogólną zawartość Zn i Cr oraz ich rozmieszczenia w wydzielonych frakcjach.

Słowa kluczowe: gleba, nikiel, wapnowanie, osad ściekowy, analiza sekwencyjna, cynk, chrom

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CONTENTS OF IRON, MANGANESE AND ZINC IN THE SEDIMENTS OF RAINWATER RESERVOIRS SITUATED ALONG THE NATIONAL ROAD No. 4

ZAWARTOŚĆ ŻELAZA, MANGANU I CYNKU W OSADACH ZE ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

Abstract: The research aimed at identification and assessment of iron, manganese and zinc contents in bottom sediments of retention reservoirs – the receivers of rainwater runoff from the national road No. 4. The samples were collected in 2007 and 2008 from the top layer 0–10 cm of the sediments accumulated on the bottom of the reservoirs situated on both sides of the road along the section of about 10 km between the Sulkow and Suchoraba villages. Heavy metal concentrations were determined with ICP-AES method in solutions after the previous mineralization of the sediments in a muffle furnace and in a mixture of concentrated $HClO_4$ and HNO_3 acids (2:3, v/v).

The contents of individual metals in the analyzed sediments ranged from 7.25 to 18.11 gFe $\cdot$ kg^{-1} d.m., from 283 to 3225 mgMn $\cdot$ kg^{-1} d.m. and from 60.06 to 507.5 mgZn $\cdot$ kg^{-1} d.m. Average contents of Fe, Mn and Zn were: 11.84 g, 761 mg and 187 mg $\cdot$ kg^{-1} d.m., respectively. Iron content in the analyzed sediments depended on the sampling date, but no effect of the reservoirs localization on this metal content in the sediments was registered. Neither unambiguous influence of sampling date nor the reservoir distance from Krakow on manganese content in the analyzed sediments was noted. On the other hand, considerable differences in zinc content in the sediment taken from the individual reservoirs and dependant on sampling date were observed. Successive diminishing of zinc amount in the sediments was noted with increasing distance from Krakow.

Keywords: rainwater reservoirs, sediments, metals content, Fe, Mn, Zn

Vehicle transport is one of major sources of environmental pollution. Diesel engines emit considerable amounts of primary pollutants, such as: nitrogen oxides, sulphur dioxide and dusts, they also cause a formation of a secondary pollution, *eg* ozone. A vast number of pollutants enter the environment also in result of car brakes and both tyres and road surface abrasion. Dusts are carriers of many dangerous pollutants, such

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PAHs or heavy metals. These components emitted to the atmosphere find their way to the ground with precipitations and become a component of rainwater, particularly in sealed areas. Intensive development of vehicle transport which happened in the second half of the 20th century generated a new dispersed source of pollution. Construction of heavily loaded communication routes in the developed countries posed a danger of introducing excessive amounts of pollutants to the ecosystems situated in close vicinity to the roads. Storing of water originating from thoroughfare drainage and high throughput highways allows retain these pollutants, protecting the neighbouring water ecosystems and ground waters against enrichment in toxic substances. *Environmental Protection Agency* (EPA) attaches great importance to this type of pollution, which locally may lead to environment degradation. Pollution linear distribution and dispersion on the terrain make protection of the environment additionally difficult. Many researchers of the problem are convinced that in highly urbanized areas coefficient rainwater pose now the greatest hazard for surface and underground water quality [1–3], therefore the facilities for temporary rainwater retaining and pretreatment must become an inevitable element of high throughput highways in order to efficiently protect the environment. The method of rainfall waste water cleaning, yielding the best results, is the use of retention reservoirs. Creating conditions for suspension sedimentation in them favour immobilization of heavy metals and organic impurities. Rainwater may be also cleaned of heavy metals by means of their infiltration through organic sorbents. Organic matter contained in the sorbents causes heavy metal binding [4]. Exploitation of such retention reservoirs leads to formation of a considerable amount of sediments whose utilization may pose a problem due to excessive quantities of pollutants. Considerable quantities of iron and zinc occur in runoffs from roads because of their common use in vehicle transport. These elements enter the runoffs from car bodies and undercarriage elements corrosion, but are also emitted during fuel burning. Because of that iron and zinc content in the sediments from rainwater reservoirs may be considerable and pose a hazard to the environment.

Presented research aimed at determining iron, manganese and zinc contents in the sediments from reservoirs of rainwater running of the surface of national road No. 4.

Material and methods

Sediments from retention reservoirs which are the receivers of rainwater runoffs from the national road No. 4 were sampled along the *ca* 10 km section, between the Sulkow and Suchoraba villages. Parameters of the reservoirs and the catchment were given in Table 1.

The samples were collected in May 2007 and in April and June 2008. Analyzed were sediments from a total of 11 reservoirs: 3 in Sulkow, 1 in Biskupice, 1 in Przebieczany, 2 in Bodzanow and 4 in Suchoraba. The mean sample was formed from initial samples collected from the whole area of the reservoirs. A laboratory sample was representative for the whole reservoir. The sediments were collected from the surface layer to the depth of 10 cm. Collected sediments were dried in the open air, dry mineralized in a muffle furnace at 450 ^{o}C and digested in a mixture of $HClO_4$ and HNO_3 acids (2 : 3, v/v).

Table 1

Characteristic of researched stormwater ponds

No.	No. of object	Localization	Capacity of reservoir (V)	Retention time of water in pond (t)	Total catchment area sealed (F_1)	Total catchment area green areas (F_2)	Flow (Q)
			[m^3]	[min]	[ha]	[ha]	[$dm^3 \cdot s^{-1}$]
1	20	Sulkow	118.4	31.1	0.29	1.85	71
2	21	Sulkow	176.9	29.4	0.29	5.97	119
3	22	Sulkow	86.2	29.7	0.18	2.67	58
4	33	Biskupice	93.0	24.2	0.39	2.58	77
5	32	Przebieczany	81.5	37.8	0.17	1.29	45
6	36	Bodzanow	98.0	25.8	0.62	0.69	87
7	37	Bodzanow	127.0	30.4	0.39	4.08	127
8	41	Suchoraba	101.6	27.2	0.36	2.64	95
9	43	Suchoraba	—	—	0.37	3.88	94
10	45	Suchoraba	194.8	32	0.36	5.17	119
11	55	Suchoraba	218.0	27.7	0.53	9.91	156

The material prepared in this way was dissolved in HCl acid and the concentration of iron, manganese and zinc was assessed using ICP-AES method in JY 238 ULTRACE apparatus (Jobin Yvon Emission). Organic matter content was determined on the basis of weight loss during calcination at 550 °C. The methods were validated on the basis of internal reference materials.

Results and discussion

Iron contents in the analyzed sediments from rainwater reservoirs ranged from 7.25 $g \cdot kg^{-1}$ to 18.11 $g \cdot kg^{-1}$ with an average of 11.84 $g\ Fe \cdot kg^{-1}$ (Table 2).

Table 2

Parameters of heavy metals quantity in sediments from stormwater ponds

Element	Following sampling	Minimum	Maximum	Mean	Median	RSD* [%]
		[$mg \cdot kg^{-1}$ d.m.]				
Fe	I	7249	12168	9427	9115	14.63
	II	9206	16000	11945	11687	17.36
	III	9744	18106	14140	12525	21.35
Mn	I	283	701	480	449	26.93
	II	321	1925	725	517	65.78
	III	287	3225	1079	617	88.82
Zn	I	60.1	339	148	117	55.92
	II	82.3	326	193	183	46.12
	III	62.4	507	221	210	58.94

* RSD – *Relative standard deviation.*

The greatest amounts were assessed in the sediments taken at the third sampling time. There was a half more than the quantities found in the sediments from the first sampling date and by about 30 % more than in the sediments taken on the second one. No effect of the reservoirs localization on this metal content in the sediments was registered.

Iron contents determined in the sediment of individual reservoirs differed slightly (Fig. 1).

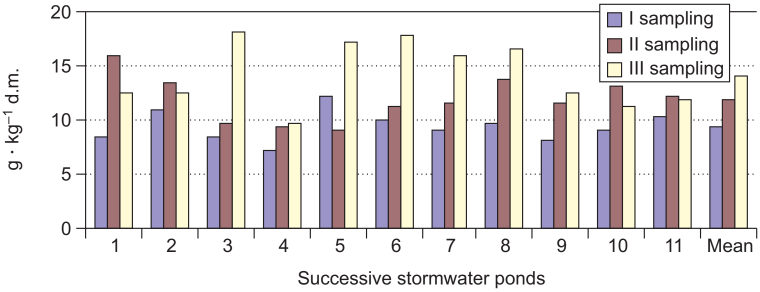

Fig. 1. Iron content in sediment from successive stormwater ponds

Relative standard deviation (RSD) for the sediments from all reservoirs was about 20 %. The amounts of iron in the studied sediments indicate its anthropogenic enrichment. Wisniowska-Kielian and Niemiec [5] assessed iron content between 7 and 25 $g \cdot kg^{-1}$ in bottom sediments of the Dunajec River. These are values comparable with registered in the presented investigations. Mayer et al [6] report iron contents in the sediment of the reservoir receiving stormwaters in Toronto ranging from 23 $g \cdot kg^{-1}$ to 27 $g \cdot kg^{-1}$. Huert-Diaz et al [7] determined this metal content in the sediments of two ports in Baja, Mexico (Ensenada and Suazal) within narrower range from 54.6 to 89.0 $g \cdot kg^{-1}$. The studied areas are threatened with strong anthropopressure both from the ships and rainfall runoffs from the port area. The sediments from the Ensenada port contained much greater amounts of iron than those from Suazal port. Suazal port is 26 years older and 10 times bigger. The source of iron from the vehicle movement is in the first place wearing out of engines and vehicle parts. The common use of this metal for car construction suggests that much bigger quantities should be found in this type of sediments than in the sediments from reservoirs under lesser anthropopressure. The data obtained in the presented investigations and the literature data indicate that the amounts of iron in the sediments from urbanized areas are not higher than observed in the natural reservoirs. Iron contents in river and lake sediments of Poland are comparable, even bigger than obtained in the presented research and reported by other authors [8, 9]. The cause may be poor iron binding with sediments and this element removal to the environment with excessive waters from the reservoirs. The literature data point to a slight diversification of iron amounts in runoffs from urbanized areas, from roads and highways.

Manganese content in the investigated sediments ranged widely from 283 $mg \cdot kg^{-1}$ to 3225 $mg \cdot kg^{-1}$. Average content of this element in the analyzed sediments amounted 761 $mg \cdot kg^{-1}$ (Fig. 2).

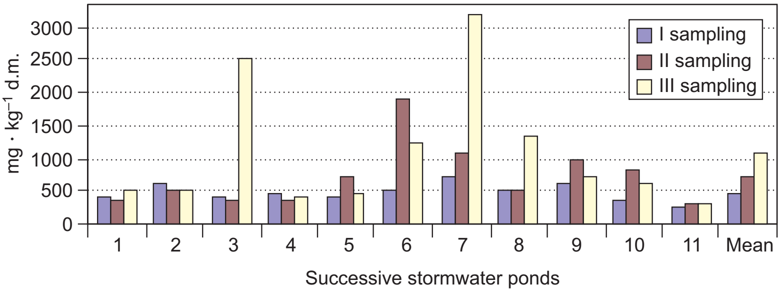

Fig. 2. Manganese content in sediment from successive stormwater ponds

No unequivocal effect of either the sampling date or the reservoir distance from Krakow on manganese content in the sediments was observed. Sediments collected in June 2008 from the reservoirs No. 22 and 36 and the sediments taken in April 2008 from the reservoir No. 36 contained very big quantities of manganese (over 1900 mg Mn · kg^{-1}). The other sediments revealed an approximate content. Manganese is emitted to the environment from communication sources, mainly from wearing of engines [6]. It may occur in considerable amounts in sediments from antropogenically transformed areas, therefore monitoring of this element contents in materials of this type is conducted. Huert-Diaz et al [7] studied the sediments from two ports in Baja, Mexico, stated manganese quantities ranging from 337 mgMn · kg^{-1} to 1090 mgMn · kg^{-1}. However, these authors point to a higher content of this element in Ensenada port than in Suazal port. Rosenkrantz et al [10] reported very low average amounts of this element, fluctuating from 31 mgMn · kg^{-1} to 131 mgMn · kg^{-1}, in the sediments from rainwater reservoirs in Melbourne, Australia. Datry et al [11] in the studies of sediments from infiltration pools of rainfall runoffs in the vicinity of Lyon noted manganese content on reached 429 mg · kg^{-1}.

Sediments from the studied reservoirs revealed a big content of zinc, in the range from 60.1 mg · kg^{-1} d.m. to 507.5 mg · kg^{-1} d.m. and assumed the average value of 187.5 mg · kg^{-1} (Fig. 3). The highest contents of this element were determined in the sediments collected in June 2008 (3rd sampling time), whereas the lowest in the sediments collected in April 2008 (2nd sampling). Considerable differences were

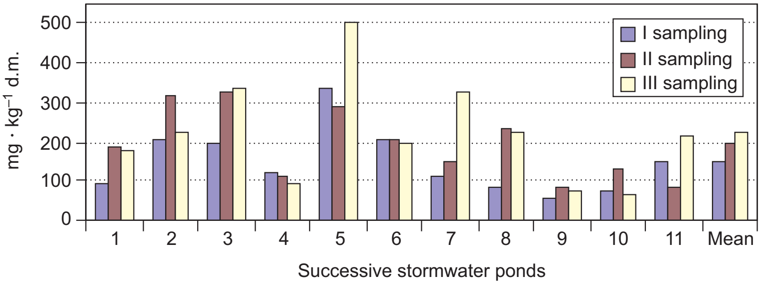

Fig. 3. Zinc content in sediment from successive stormwater ponds

assessed in this metal content in the sediments from individual reservoirs. Relative variability of zinc contents in the sediments from the reservoirs was from 45 to 59 % and was the highest for the third sampling. Successive diminishing of zinc content in the sediments was observed with increase of distance from Krakow. Average content of this metal in sediments from 6 reservoirs situated closest to Krakow was 288.6 mg, whereas in the other reservoirs reached 227.8 mgZn · kg^{-1}.

Zinc is one of major pollutants in runoffs from anthropogenically transformed areas. The main source of zinc from vehicle transport is abrasion of tyres and this element leaching from galvanized steel surfaces [6]. Therefore considerable quantities are found both in the runoffs from highways and from built-up areas. Rosenkrantz et al [10] reported that quantities of this element in the sediments from rainwater reservoirs in Melbourne, Australia, ranged from 508 mgZn · kg^{-1} to 2230 mgZn · kg^{-1}. Duong and Lee [12] stated average content of this element in the sediments from runoffs from the cities in South Korea of between 120 mgZn · kg^{-1} and 160 mgZn · kg^{-1}. Mayer et al [6] investigated the effect of anthropogenic reservoirs collecting rainwater on amphibiotic organisms settling these reservoirs. Even at this element value reaching 80 mg · kg^{-1} the authors reported unfavourable influence on amphibiotic organisms inhabiting these reservoirs. Camponelli et al [13] reported that zinc leached from aged tire debris is bioavailable to developing wood frog (*Rana sylvatica*) and accumulated in sediments may influence its population dynamics. On the other hand Datry et al [11] reported this element quantities in the sediments from infiltration pools of rainwater runoff in the vicinity of Lyon ranging from 329 mg · kg^{-1} to 1542 mg · kg^{-1}. Mayer et al [6] stated that the sediments from the reservoir receiving stormwater in Toronto contain between 262 mgZn · kg^{-1} and 519 mgZn · kg^{-1}. Jartun et al [14] report average zinc contents in the sediments of runoffs in Bergen, Norway, reaching 403 mgZn · kg^{-1}. Birch and McCready [16] tested zinc content in street dust and in sediments originating from reservoirs gathering rainwater in Sydney. Average zinc content in street dust amounted 502 mg · kg^{-1}, whereas in the sediments over 1700 mgZn · kg^{-1}, with maximum amounting 11300 mg · kg^{-1} [16]. Therefore, zinc concentrations in sediments of the analyzed reservoirs were not high and generally lower than reported by other authors. Basing on the data of Lis and Pasieczna [17], zinc contents below 100 mgZn · kg^{-1} may be consider as natural. Assuming these criteria 21 % of samples revealed a natural content of this element whereas 80 % points to anthropogenic enrichment.

Metals contained in runoffs from roads and other sealed areas become a hazard to surface and underground waters. The literature data for similar materials in the world indicate a considerable variability of pollutant concentrations, which is conditioned by many factors, such as: total pollutant quantity emitted per area unit, the weather conditions and kind of surface. Collecting and pretreatment of rainfall waters running off roads in specially adjusted facilities allows to improve their quality through sedimentation of pollutants together with the suspension to the sediments. The analyzed reservoirs collect water from the road of a daily throughput of 34000 cars. Moreover, the catchments of these reservoirs are characterized by a small share of hard surfaced areas in total catchment area. At systems collecting water from catchments with higher proportion of hard surfaced areas one should expect higher contents of the examined metals in sediments. Pretreated water generally meets the standards of sewage disposal to water or to the ground [18]. However, there is a possibility of excessive pollutant concentration in forming sediments. Harmful substances bound in sediments may under some conditions become mobile and carried by rainfall water and may flow into surface hydroecosystems and underground waters. Proper exploitation of rainwater reservoirs requires a periodic removal of sediments. The problem of disposal of sediments formed as a result of purification of road runoffs will aggravate with increasingly larger number of constructed facilities for runoff water pretreatment. As has been mentioned earlier, metal contents in sediments increase during their exploitation, therefore their harmful effect may increase in result of mobilization of metals contained in the sediments. In the studies conducted by Clement et al [19] majority of sediments formed in urban retention ponds as a result of sedimentation of pollutants contained in runoffs from high traffic roads located in various parts of France, had no acute or chronic ecotoxicological effect for aquatic surface ecosystems after 21 days of exposure. On the other hand Camponelli et al [13] found that zinc contained in sediments can result in measurable physiologic outcomes (greater time to metamorphosis and smaller mass) in population dynamics of wood frogs (*Rana sylvatica*).

Conclusions

1. Sediments from the investigated rainwater reservoirs revealed much smaller iron content than analogous sediments collected from reservoirs in various cities of the world.
2. Content of iron was increased in the analyzed sediments taken from most reservoirs in successive sampling date, but in case of manganese and zinc there was no evident dependence with the date of sampling.
3. Zinc content in sediments of the studied reservoirs was diminishing regularly with increasing distance from Krakow agglomeration. Content of iron and manganese did not depend on the reservoir localization.
4. Considering iron, manganese and zinc contents, the analyzed sediments do not pose a hazard to the environment.

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ZAWARTOŚĆ ŻELAZA, MANGANU I CYNKU W OSADACH ZE ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

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Abstrakt: Celem badań było oznaczenie i ocena zawartości żelaza, manganu i cynku w osadach dennych zbiorników wód deszczowych usytuowanych wzdłuż drogi krajowej nr 4. W 2007 i 2008 r. pobrano próbki osadów ze zbiorników będących odbiornikami spływów deszczowych z jezdni i drogi krajowej nr 4 na odcinku 10 km, pomiędzy Sułkowem i Suchorabą. Osady pobrano z ich wierzchniej warstwy (0–10 cm) z każdego zbiornika. Zawartość metali ciężkich w osadach oznaczono po uprzedniej mineralizacji materiału w piecu muflowym oraz w mieszaninie kwasów $HClO_4$ i HNO_3 (2:3, v/v), metodą ICP-AES.

Zawartości poszczególnych metali w analizowanych osadach wahały się od 7,25 do 18,11 gFe $\cdot$ kg^{-1} s.m., od 60,05 do 507,5 mgZn $\cdot$ kg^{-1} s.m. oraz od 283 do 3225 mgMn $\cdot$ kg^{-1} s.m. Średnie zawartości Fe, Zn, Mn wynosiły odpowiednio: 11,84 g, 187,5 mg oraz 761 mg $\cdot$ kg^{-1} s.m. Zawartość żelaza w analizowanych osadach była zależna od terminu pobrania próbek, nie stwierdzono natomiast wpływu usytuowania zbiorników na zawartość tego metalu w osadach. Nie stwierdzono jednoznacznego wpływu terminu pobrania ani oddalenia zbiornika od Krakowa na zawartość manganu w osadach. Stwierdzono znaczne różnice zawartości cynku w osadach z poszczególnych zbiorników oraz w zależności od terminu pobrania próbek. Zaobserwowano sukcesywne zmniejszanie się ilości cynku w osadach w miarę oddalania się od Krakowa.

Słowa kluczowe: zbiorniki wód deszczowych, osady, zawartość metali, Fe, Mn, Zn

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and Barbara WIŚNIOWSKA-KIELIAN[1]

POST-EFFECT OF INCREASING BOTTOM SEDIMENT ADDITIVES TO THE SUBSTRATUM ON NICKEL UPTAKE BY PLANTS

NASTĘPCZY WPŁYW WZRASTAJĄCYCH DODATKÓW OSADU DENNEGO DO PODŁOŻA NA POBRANIE NIKLU PRZEZ ROŚLINY

Abstract: The aim of the studies was an estimate of post-effect of bottom sediment additives to the substratum on nickel uptake by plants, under conditions of pot experiment. Components of substratum were very acid soil and bottom sediment dredged from Roznow Reservoir. Bottom sediment share ranged from 0 to 16 % of total substratum mass. Test plants were grown in orders: maize (*Zea mays* L.) and faba bean (*Vicia faba* L. var. *minor*), as well as oat (*Avena sativa* L.) and narrowleaf lupine (*Lupinus angustifolius* L.). After vegetation period plants were harvested on green mass. Content of Ni in mineralizats obtained from plant material was determined using ICP-AES method. The total quantity of Ni removed with yield of plants depending on species and part of plant was compared and changes affected by bottom sediment share in substratum as well as previous plant cultivation were estimated.

Under conditions of increased sediment share in substratum significantly higher amounts of nickel were accumulated in roots than in shoots of the plants. On average the highest Ni contents were determined in roots and shoots of faba bean, while the lowest ones in maize roots and shoots. Bottom sediment additions in an amount exceeding 4 % of the substrate mass caused a decrease of Ni content in the aboveground parts of all test plants and sediment additions greater than 10 % reduced these metal content in roots of faba bean and lupine, in comparison with plants from control objects. In case of maize and oat all doses of sediment caused an increase of Ni content in roots. In spite of additional Ni load with applied bottom sediment its increased content in plant tissue of aboveground parts of most test plant was not stated. One may explain this dependence by decreased Ni availability to plants as a result of sediment ability to substratum deacidification.

Considering total Ni uptake the highest its amounts were removed with yield of maize, and the lowest with yield of oat. Significantly higher amount of nickel was taken from the soil in case of maize and faba bean cultivation than in case of variant with oat and lupine. This was due to significantly higher maize biomass yield in comparison with other test plants. The Ni translocation coefficients (TC) (content in shoots *versus* content in roots) as well as bioaccumulation coefficients (BC) (content in shoots *versus* content in soil) for individual plants were calculated. The highest average value of TC was affirmed for faba bean (0.5), lower

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ones for oat (0.29) and lupine (0.21), and the lowest one for maize (0.15). The average values of BC for individual plants decreased as follow: 0.74 – faba bean, 0.37 – oat, 0.31 – lupine, 0.16 – maize.

Keywords: bottom sediment, nickel, plants, uptake, translocation and bioaccumulation coefficient

The formation of sediments in reservoirs over time leads to their silting. There are many ways of their recultivation, however, each of which is associated with the problem of management of dredged sediments from the bottom of the reservoir [1]. Agricultural use of waste materials such as sludge or sediments is the most desirable method of their utilization [2]. Nowadays there are many attempts of agricultural use of materials like bottom sediments, sewage sludge or incineration ashes. These materials are used as so-called indirect fertilizers and may be consider as a source of organic matter and mineral compounds of calcium, phosphorus and nitrogen or materials containing significant amounts of silt and clay fractions [3, 4].

Bottom sediments are rich in mineral elements necessary for proper growth and development of plants. They also have the capacity to soil neutralization, which favors the processes of immobilization of pollutants contained therein. They also show high sorption capacity because of considerable silt and clay content and as a rule large content of organic matter [5]. In case of agricultural use of bottom sediments it is necessary to pay attention at the content of heavy metals in material introduced to the soil, due to the possibility of their entering the human food chain. McBride [6] states that attention should be paid in the absence of basic knowledge about the processes which heavy metals are subject, in each concrete situation of use of waste material for soil amendment. Heavy metals in the environment are not biodegradable, but subjected to processes of biotransformation only [7].

Due to the location of water reservoirs in lower points of the basin, they are becoming receivers of pollutants from upper parts of the catchment area. The chemical composition of sediments of individual reservoirs depends on the type and land use of catchments, as well as on the topography of the terrain [5] According to Polish legislation the bottom sediments from superficial standing or flowing water reservoirs used in earth works are not counted among waste but they should suit standards of soil and earth quality and should fulfill the criteria of admissible values of toxic substances contents, indicated in the enclosure of Minister of Environment regulation [8], for soils occurred in purposed place. Bottom sediment the most often contained elevated amount of trace metals like: zinc, copper, nickel, cadmium, chromium, lead and mercury. Trace elements introduced to the soils may cause an increase of their content in cultivated plants and next enter to human food chain [9]. Many fertilizers used in conventional agriculture contain undesirable substances such as heavy metals, which does not exclude their agricultural use. Bottom sediments dredged from reservoirs contain high amount of calcium carbonate and as a rule magnesium carbonate which may cause the soil neutralization. Deacidification of the substrate during growth of the plants leads to constraint the amount of mobile forms of heavy metals and their availability to plants.

The aim of the study was to estimate the impact of bottom sediment additives to the substratum on nickel uptake by plants and to assess the suitability of this sediment used to soil amendment as material for fertilization and deacidification.

Material and methods

A pot experiment was carried out in 2005 in vegetation hall of University of Agriculture in Krakow. The very acid soil and bottom sediment dredged from Roznow Reservoir were used as components of the substratum (Table 1).

Table 1

The basic properties of components of the substrate

Component	pH		Hh	C_{org}	N_{tot}	P_2O_5	K_2O
	KCl	H_2O				acc. to Egner-Riehm	
			[mmol(+) · kg^{-1}]	[g · kg^{-1}]		[mg · kg^{-1}]	
Sediment	7.20	8.31	—	3.65	1.19	41.3	116
Soil	4.40	5.86	12.2	4.73	0.524	94.3	246

The sediment share in substratum increased as follows: 0, 1, 2, 4, 6, 8, 10, 12, 14 and 16 % of total mass amounting 4 kg d.m. per pot (Table 2).

Table 2

Share of the substratum components and total Ni content in individual experimental objects

Component	Share of substratum component [%]									
Soil	100	99	98	96	94	92	90	88	86	84
Sediment	0	1	2	4	6	8	10	12	14	16
Total Ni content [mg · kg^{-1} d.m.]										
Substratum	5.85	6.25	6.64	7.43	8.22	9.01	9.80	10.59	11.38	12.17

The samples (both roots and shoots) of plants grown at those mixtures were studied material. Test plants were grown in two sequences: maize (*Zea mays* L., 'Prosna F_1' Cv.) and faba bean (*Vicia faba* L., var. *minor*, 'Nadwislanski' cv.) as well as oat (*Avena sativa* L., 'Chwat' cv.) and narrowleaf lupine (*Lupinus angustifolius* L., 'Sonet' cv.). After the vegetation period plants were harvested on green mass, dried and the quantity of shoots and roots biomass was measured. Total content of heavy metals in plant material were determined after dry mineralization and dissolving in hot nitric acid, while in samples of substratum after dry mineralization of organic matter and digestion in a hot mixture of concentrated acids: HNO_3 and $HClO_4$ (3:2; v/v). Heavy metals concentrations in obtained solutions were assayed by ICP-AES method.

Results and discussion

Soil and bottom sediment used in experiment contained relativity high amount of Ni: 5.85 mg · kg^{-1} and 45.33 mg · kg^{-1} of d.m., respectively [10].

With increasing share of bottom sediment in substratum total nickel content increased as well (Table 2). In spite of additional Ni load, with applied small additions of bottom sediment (1–4 %), nickel content in all of the test plants shoots as well as faba bean and lupine roots stayed at higher but similar level in comparison with plants of control objects. A decrease of Ni content in mentioned parts of test plants was found when share of sediment in substratum raised to 10 %. Different response was observed in case of oat and maize roots which accumulated enhanced quantities of Ni almost parallel to its increasing up content in substratum. The higher than 10 % additions of bottom sediment to the substratum caused decrease of Ni content in shoots and roots of all test plants (Fig. 1). On average the highest amount of Ni was found in shoots and roots of faba bean and the lowest ones in both these parts of maize.

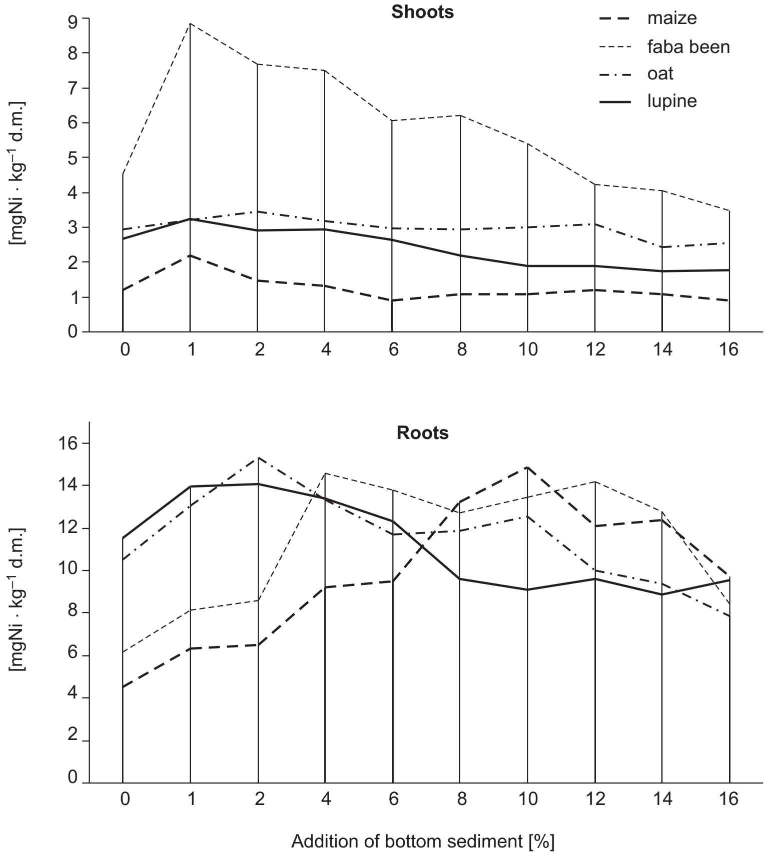

Fig. 1. Ni contents in shoots and roots of test plats depend on share of the bottom sediment in substratum

Heavy metals absorption by plants from substratum depends on many factors [11]. In general, under conditions of soils contaminated with trace elements, it is substantial to reduce their availability to plant, using different methods. Limitation of heavy metals availability, absorption and their entering human food chain should be an effect of these efforts. Ni quantities removed with yield of test plant roots were significantly higher than of aboveground biomass (Fig. 2).

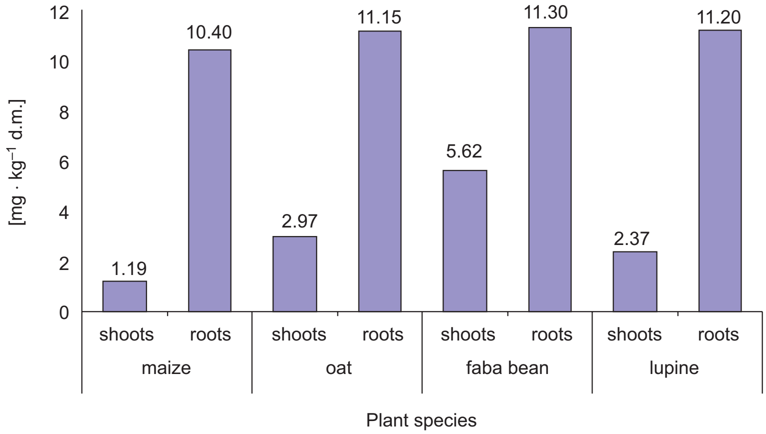

Fig. 2. The average Ni contents in plant tissues of individual species

Considerably great quantities of Ni were accumulated in roots, because nickel absorption by these parts of plant is mainly a passive process and almost proportional to amount of its soluble forms occurring in substratum [9]. The amount of nickel removed by maize increased with successive additions of bottom sediment, and the highest uptake for this plant was stated at a 10 % share of bottom sediment in the substrate. In case of other test plants increasing share of bottom sediment did not affected significant changes of nickel uptake from the substrate (Fig. 3).

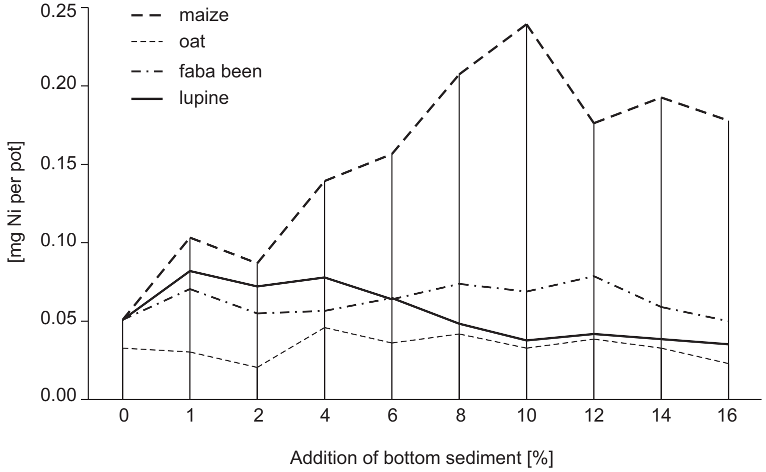

Fig. 3. Amount of Ni removed with yield of test plants depend on sediment addition to the substratum

On average, the most quantities of Ni were removed with yield of maize, what was associated with significantly higher biomass production by this plant, in comparison with the other tests plants, cultivated in presented experiment (Fig. 4). On average, significantly higher amounts of nickel was uptake in plant succession: maize and faba bean (0.221 mg per pot) than with yield of second one – oat and lupine (0.083 mg per pot). This was due to significantly higher amount of total biomass yield of maize and faba bean in this pot experiment.

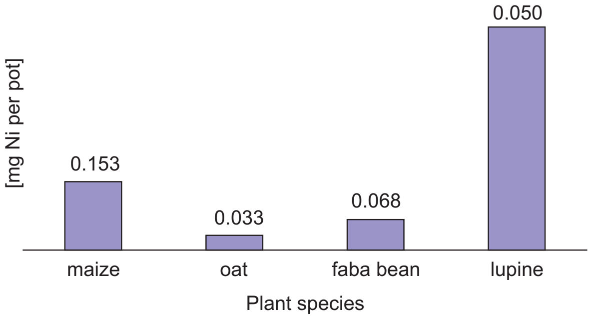

Fig. 4. The average total amount of Ni removed with yield of test plants

Bioaccumulation coefficient (BC) expresses relation between element content in plant and its content in soil. In general, with increasing share of bottom sediment in the substratum the values of Ni bioaccumulation coefficient calculated for individual test plants decreased (Fig. 5).

Analysis of calculated values of Ni BC showed that on average the highest amounts of this metal was accumulated in aboveground parts of faba bean, while the lowest ones

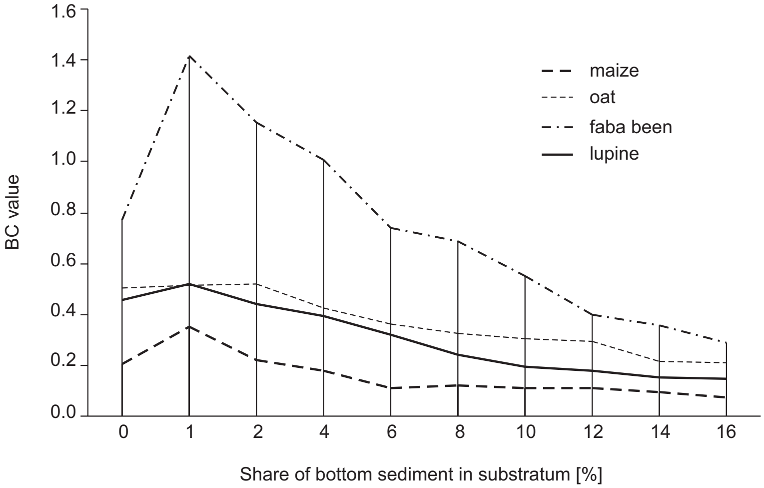

Fig. 5. The value of BC of Ni for shoots of test plants depending on bottom sediment share in substratum

in shoots of maize. Significantly higher values of BC were noted in case of faba bean comparison with the other plants (Fig. 5). In accordance with the data of other authors [12] dicotyledonous plants accumulated more Ni than monocotyledonous ones, independently on contamination level of substratum.

On average, the lowest values of BC were stated in case of plants, which accumulated the smallest amounts of Ni in their aboveground parts (Fig. 6). The lowest average content of this element were affirmed for shoots and roots of maize. The highest average content of Ni was found in aboveground parts of lupine and in roots of faba bean.

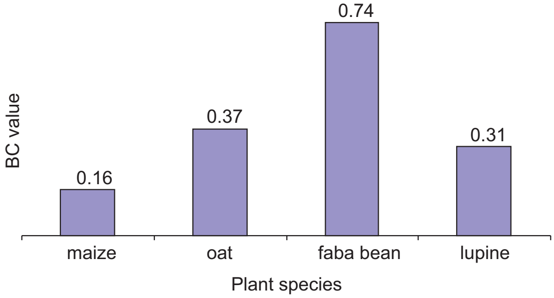

Fig. 6. The average *bioaccumulation coefficient* values (BC) for Ni in plants shoots

The translocation coefficient (TC) is a ratio of trace element content in shoots *versus* its content in roots. It informs about scale of substances movement from roots to above-grounds parts of plant. There are many plants defense mechanisms, generated by plants cultivated under conditions of contaminated substratum. One of them is reduction or prevention of toxic substances transport to vegetative and generative parts [13]. This relationship is confirmed by the low values of Ni translocation coefficient calculated for tests plants (Fig. 7).

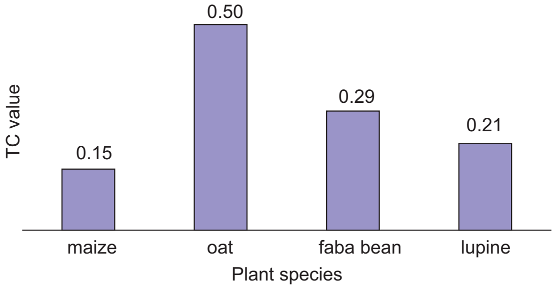

Fig. 7. The average *translocations coefficient* (TC) values calculated for individual plant

The values of translocation coefficients for all test plants did not exceed 0.7 and were considerable lower than observed in case of wild plants species belonging to different biological families which ranged from 1 to 4.4 [14]. The highest average translocation coefficient value was stated in case of faba bean (0.5), lower one for oat (0.29) and lupine (0.21) while the lowest value of TC was noted for maize (0.15).

With increasing share of bottom sediment in substratum decreased the values of translocation coefficient (Fig. 8). One may explain this dependence by decreasing Ni solubility after application of sediment, because of its ability to substratum neutralization. Increase of substratum pH value during plants growth period caused decrease of nickel availability to plants and in consequence decrease Ni content in roots, what resulted in relative increase of translocation coefficient value [15]. Bottom sediment dredged from Roznow Reservoir affected the properties of substratum similarly like liming and caused an increase of pH value up to neutral one. According to Sapek [16] liming is one of the paramount factors which reduce heavy metals mobility, therein Ni, in soil – plant system.

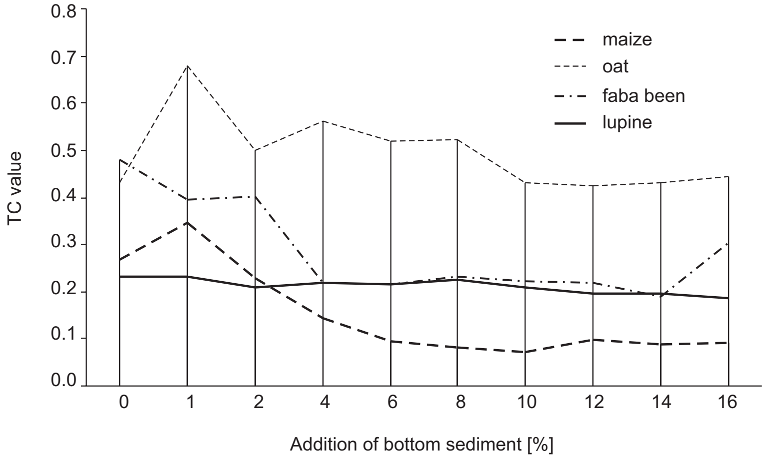

Fig. 8. The value of Ni translocation coefficient (TC) in tested plants dependent on share of bottom sediment in substratum

Conclusions

1. Under conditions of increased share of sediment in substratum significantly higher amounts of Ni were accumulated in roots than in shoots of the plants.

2. Bottom sediment additions in an amount exceeding 4 % of the substratum mass caused a decrease of Ni content in aboveground parts of all test plants and roots of faba bean and lupine. Sediment additions greater than 10 % reduced nickel content in all these parts of test plant below its level in plants of control objects.

3. All sediment additions cause an increase of Ni content in roots of maize and oat, and its share in substratum higher than 10 % decrease nickel content in roots of these plants but Ni level was still higher than in plants of control objects.

4. On average, the highest Ni contents were determined in lupine roots and faba bean shoots, while the lowest ones in maize roots and shoots.

5. The highest total quantities of Ni were removed with yield of maize, and the lowest one with yield of oat.

6. In a spite of additional nickel load with bottom sediment applied in experiment an increase of Ni accumulation in plants was not observed because of sediment ability to substratum neutralization and increase of sorption capacity.

7. With increasing share of bottom sediments in substrate decrease of value of BC in case of all tests plants was noted.

8. Rise of bottom sediment share in substrate caused a decrease of TC in case of all plants in comparison with control objects as a result of limitation of Ni content in roots.

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NASTĘPCZY WPŁYW WZRASTAJĄCYCH DODATKÓW OSADU DENNEGO DO PODŁOŻA NA POBRANIE NIKLU PRZEZ ROŚLINY

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Abstrakt: Celem badań była ocena następczego wpływu dodatku osadu dennego do podłoża na pobranie niklu przez rośliny w warunkach doświadczenia wazonowego. Jako komponenty podłoża użyto glebę lekką, bardzo kwaśną oraz osad denny bagrowany ze Zbiornika Rożnowskiego. Udział osadu dennego wynosił od 0 do 16 % całkowitej masy podłoża. Rośliny uprawiano w kolejności: kukurydza (*Zea mays* L.) i bobik (*Vicia* *faba* L. var. *minor*) oraz owies (*Avena sativa* L.) i łubinu (*Lupinus angustifolius* L.). Po okresie wegetacji rośliny zebrano na zieloną masę. Zawartość Ni w mineralizatach uzyskanych z materiału roślinnego oznaczono metodą ICP-AES. W pracy porównano całkowitą ilości Ni odprowadzoną z plonem roślin testowych w zależności od gatunku i części rośliny oraz oszacowano zmiany powodowane dodatkiem osadu dennego do podłoża, a także następstwem roślin po sobie.

W warunkach zwiększającego się udziału osadu w podłożu znacznie większe ilości niklu zostały zgromadzone w korzeniach niż w łodygach roślin. Średnio najwięcej Ni zawierały korzenie łubinu i bobiku, a najmniej korzenie i łodygi kukurydzy. Dodatki osadu dennego w ilości przekraczającej 4 % masy podłoża powodowały zmniejszenie zawartości Ni w częściach nadziemnych wszystkich roślin testowych, a dodatki osadu większe niż 10 % zmniejszyły zawartość tego metalu w korzeniach łubinu i bobiku, w porównaniu z obiektami kontrolnymi. W przypadku kukurydzy i owsa wszystkie dawki osadu powodowały wzrost zawartości Ni w korzeniach. Pomimo zwiększonego ładunku Ni w podłożu wprowadzonego z zastosowanym osadem dennym nie następował wzrost zawartości tego metalu w częściach nadziemnych większości roślin testowych. Taką zależność można tłumaczyć ograniczeniem dostępności Ni dla roślin na skutek odkwaszającego działania osadu dennego do podłoża.

Biorąc pod uwagę całkowite pobranie Ni, najwięcej tego metalu zostały odprowadzone z plonem kukurydzy, a najmniejsze z plonem owsa. Znacznie więcej niklu pobrały z gleby rośliny uprawiane w następstwie kukurydza–bobik niż w następstwie owies–łubin. Było to spowodowane znacznie większym plonem biomasy kukurydzy w porównaniu z pozostałymi roślinami testowymi, co przełożyło się na znacznie większe pobranie niklu z podłoża. Obliczono *współczynniki translokacji* Ni (WT) (zawartość w częściach nadziemnych *versus* zawartość w korzeniach) oraz *współczynnik bioakumulacji* (WB) (zawartość w częściach nadziemnych *versus* zawartość w glebie) dla poszczególnych roślin. Najwyższą średnią wartość WT stwierdzono dla bobiku (0,5), niższą dla owsa (0,29) i łubinu (0,21), a najniższą dla kukurydzy (0,15). Średnie wartości WB dla poszczególnych roślin malały następująco: 0,74 – bobik, 0,37 – owies, 0,31 – łubin, 0,16 – kukurydza.

Słowa kluczowe: osad denny, nikiel, rośliny, pobranie, współczynnik translokacji, współczynnik bioakumulacji

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SPATIAL DISTRIBUTION OF VARIOUS FORMS OF IRON IN HEAVY METAL POLLUTED SOILS

ROZKŁAD PRZESTRZENNY RÓŻNYCH FORM ŻELAZA W GLEBACH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

Abstract: The paper aimed to determine the content of total and soluble iron forms in the top soil horizon (0–10 cm) and present their spatial diversification in the area of zinc and lead ores presence in the vicinity of ZGH "Boleslaw" Mining and Metallurgical Plant in Bukowno near Olkusz.

In 139 soil samples total iron content was determined after sample digesting in concentrated mineral acids (HNO_3 + $HClO_4$) and soluble forms were extracted with 1 mol · dm^{-3} HCl and with 1 mol · dm^{-3} NH_4NO_3 solutions. Fe content in the obtained extracts was assessed by means of atomic absorption spectrometer with flame atomizer.

A considerable accumulation of iron, seriously exceeding the amounts most frequently noted in the soils of Poland was determined in the analyzed samples. Extractant solutions used for iron dissolving in the investigated soils were characterized by different abilities to release this element. Diluted hydrochloric acid dissolved on average 21.5 % and ammonium nitrate solution on average only below 0.1 % iron in soil. The highest contents of iron soluble in diluted hydrochloric acid were assessed in the areas with the highest total content of this metal to the north and north-west of ZGH "Boleslaw" and in the vicinity of post-flotation wastes settlement tanks. On the other hand, the greatest quantities of iron released with ammonium nitrate solution were found in the vicinity of Pomorzany Mine and on the most acidified soils of the analyzed area.

Keywords: iron, solubility, heavy metals, bioavailable forms

Iron chemistry in soils depends on many factors. It is most dependent on a number of soil physical and chemical properties which cause a reduction or increase in its solubility and bioavailability [1–3].

Amounts of this element contained in soil solution are usually very small and the bigger the lower the value of soil pH. Plants absorb iron as Fe^{2+} ions or in a chelate form. Their content in soil is the smallest at pH 6.5–8.0 [1, 4].

Two opposite phenomena: sorption and desorption [5, 6] affect iron solubility and bioavailability. Sorption occurs according to three basic processes:

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– arresting ions by mineral and organic elements of sorption complex,
– biological accumulation,
– precipitation of insoluble compounds.

These processes lead to limiting iron mobility and solubility. The opposite process – desorption increases this element bioavailability and mobility, among others by dissolving and mineralization of organic compounds. Intensity of these phenomena is conditioned by many physical and chemical properties of (not only soil) environment [4].

Limiting iron bioavailability to plants in result of its adsorption by mineral and organic soil colloids is a positive phenomenon. The result of this process is protection of subsequent links of food chain against the negative effect of excessive amounts of this element on plant healthiness [7].

The paper aimed to determine the total content of iron and its soluble forms in the top soil horizon (0–10 cm) and present their spatial diversification in the area of zinc and lead ores presence in the vicinity of ZGH “Boleslaw” Mining and Metallurgical Plant in Bukowno near Olkusz.

Material and methods

Analysis of iron mobility was conducted in soil samples collected in the Malopolska province near the town of Olkusz in the communes of Boleslaw and Bukowno, situated between two city agglomerations: Krakow and Silesia. Development of mining and zinc-lead ore processing in the region of Olkusz is connected with shallow deposits of metalliferous dolomites in this area in which beside zinc and lead also accompanying elements, such as Fe, Ag, Cd, Tl and As are present [8–11].

Iron is one of the elements accompanying ores extracted in the Olkusz vicinity. It belongs to the most mobile elements in soil, occurs in different forms, among others as concretion and hydroxides and colloidal forms which have a serious influence on soil forming processes but also on trace elements sorption and their solubility and bioavailability to plants [1].

Iron occurs in the soils of the investigated area in the amounts from 41 to 8.2 g $\cdot$ kg^{-1} [12], at an average content of this metal in the soils of Poland *ca* 20 g $\cdot$ kg^{-1} [13]. Therefore it may be expected that this element would enter the food chain with greater intensity.

The researched area covered 100 km^2 in the vicinity of ZGH “Boleslaw” Mining and Metallurgical Plant in Bukowno. Soil samples were collected from June to August 2008 from the top soil horizon (0–10 cm) in 139 points marked on the map (Fig. 1). Sampling places were determined according to previously assumed experimental design. One sample was collected from the area of 1 km^2, whereas in the areas situated in the immediate vicinity of ZGH “Boleslaw” Plant, density of sampling increased to 2 samples per 1 km^2.

Collected soil material was dried in the air and sifted through a plastic sieve with 2 mm mesh. Potentially bioavailable iron compounds were extracted from the collected soil samples by Rinkis method [14] using 1 mol $\cdot$ dm^{-3} HCl solution. Fe quantity actually bioavailable to plants was assessed by the method using 1 mol $\cdot$ dm^{-3} NH_4NO_3

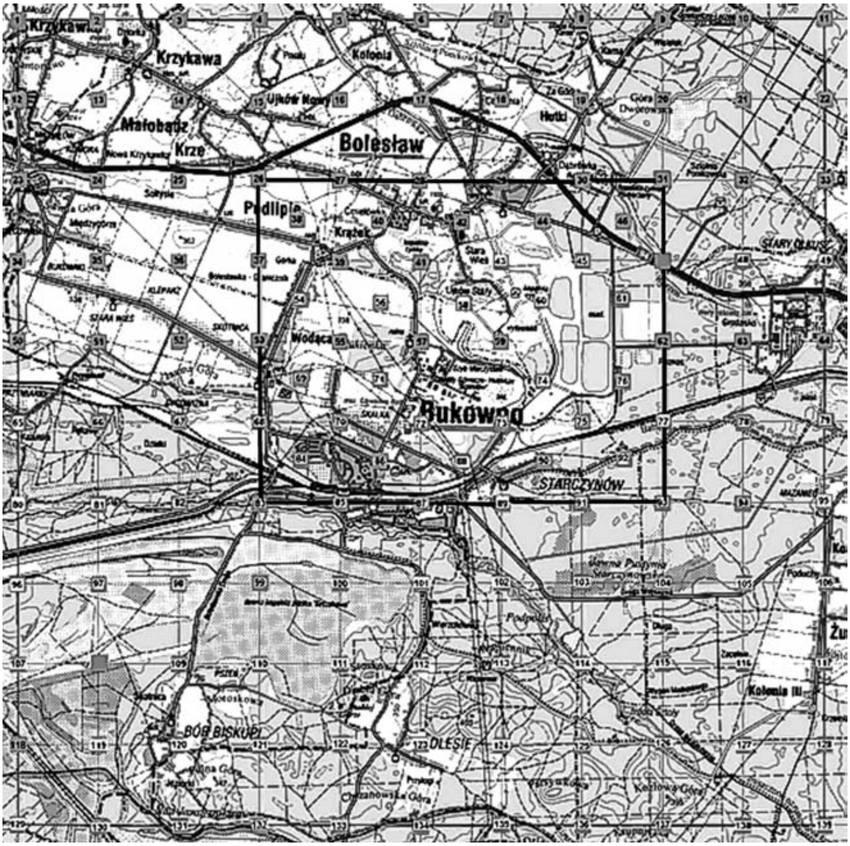

Fig. 1. Places of soil sampling (based on [15])

solution as an extractant [14]. Total Fe content in soil was determined after its dissolving in a mixture of nitric(V) and perchloric(VII) acids (2:1. v/v) following previous mineralization of organic matter in a muffle furnace at 450 ^{o}C [16]. In the solutions prepared in this way iron content was assessed on *Solaar M6 atomic absorption spectrometer* with *flame atomizer*.

The soil basic physicochemical properties were also determined using methods generally applied in agro-chemical laboratories [16]:

– granulometric composition by aerometric Bouyoucose-Casagrande method in Proszynski's modification,

– soil reaction (pH) in 1 mol · dm^{-3} KCl suspension by potentiometric method,

– organic carbon content using Tiurin method.

The obtained results were analyzed by means of Microsoft Excel 2003 calculation sheet. The maps of spatial distribution of bioavailable iron contents in soil, extracted by 1 mol · dm^{-3} HCl and NH_4NO_3 were created using Surfer 8.0 packet. The maps prepared in this way were applied on the maps of the investigated area.

Results and discussion

While analyzing the data presented in Table 1 one may notice not only a considerable diversification of each analyzed forms of iron in the studied soils but also considerable differences between computed values of arithmetic mean, geometric mean and median which describe the assessed amounts of this element.

Table 1

Statistical characteristics of Fe content in the analysed soil samples

Parameter	Fe content [mg · kg^{-1} d.m.]		
	Total	Soluble	
		in HCl solution	in NH_4NO_3 solution
Minimum value	676.2	54.2	0.50
Maximum value	60282.8	6612.9	61.8
Arithmetic mean	6795.5	1392.6	7.2
Geometric mean	4485.0	996.5	3.9
Median	3908.7	1141.2	3.3
Relative standard deviation [%]	128.6	83.6	139.9

This evidences a considerable deviation of these values from normal distribution, caused by a natural and anthropogenic "enrichment" of the environment in the investigated area concerning iron content. At normal distribution of element contents the above-mentioned statistical features would be equal. On the other hand, at a considerable deviation of the normal distribution of data set, geometric mean is more approximate to the middle value of the set (median) than arithmetic mean, therefore in such cases, geometric mean better characterizes the analyzed data pool and is often used to describe the polluted environment [17].

Extractant solutions used for iron extraction from the soils collected around the ZGH "Boleslaw" Mining and Metallurgical Plant near Olkusz were characterized by different potential of this element desorption. Diluted hydrochloric acid dissolved on average 21.5 % of the iron amount assessed using concentrated mineral acids, whereas ammonium nitrate solution extracted on average only less than 0.1 % of this amount of iron. The content of potentially bioavailable iron in the analyzed samples assessed after extraction with 1 mol · dm^{-3} HCl solution ranged widely from 54.2 to 6612.9 mgFe · kg^{-1} d.m. On the other hand, amounts of iron directly available to plants, extracted with 1 mol · dm^{-3} NH_4NO_3 solution ranged from 0.5 to 61.8 mgFe · kg^{-1} d.m. (Table 1, Fig. 2). Relative standard deviation computed for this feature points to the greatest variability of the iron forms contents released by ammonium nitrate solution (Table 1). Relative standard deviation of iron extracted from the analyzed soils with diluted hydrochloric acid was visibly lower (83.6 %), despite the fact that the range of diversification of its contents released by both extractants was almost identical. Minimal iron content determined using HCl solution made up 0.82 % and when NH_4NO_3

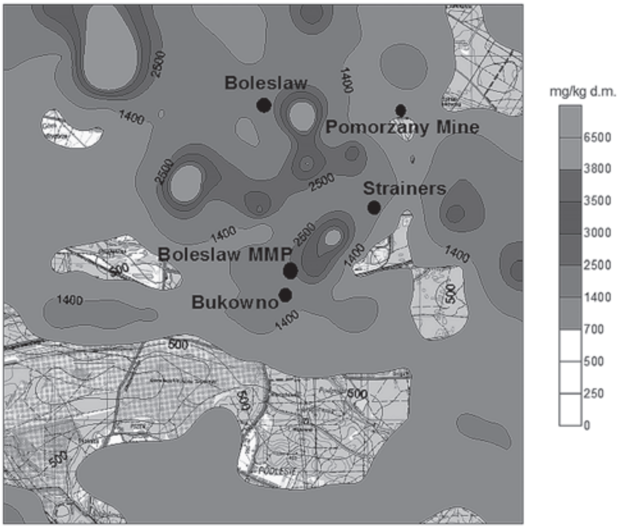

Fig. 2. Spatial distribution of iron content extracted with 1 mol · dm^{-3} HCl in soils around ZGH "Boleslaw" (based on [15])

solution was applied – 0.81 % of the maximum quantity of this element dissolved by both mentioned above extractants.

1 mol · dm^{-3} hydrochloric acid solution was identified in 1986 in Poland as a group extractant for an assessment of microelement contents, including iron, in mineral soils. Limit numbers for this method were published in "Fertilizer recommendations" issued by the Institute of Soil Science and Plant Cultivation [18].Three soil classes were indentified characterized by low, medium and high content of this element.

The investigated region reveals evidently elevated total iron content in soil resulting from both high natural content of this element in the parent rock and anthropogenic activity in this region. However, the assessment of determined contents of iron soluble in diluted hydrochloric acid reveals that only 5 % of samples were characterized by a high content of this metal, whereas as many as 63 % of samples were classified to soils with medium iron content (Table 2). Almost one third of samples contained small amounts of iron.

Table 2

Assessment of iron soluble by 1 mol · dm^{-3} HCl
(on the basis of Fertilizer recommendations [18])

Class of iron content	Estimation of content	Fe content [mg · kg^{-1} of soil]	Share of soils
III	Low	< 700	32
II	Medium	700–3800	63
I	High	> 3800	5

Spatial diversification of the amounts of iron extracted from the soils in ZGH "Boleslaw" Plant neighbourhood using both compared methods points to a dissimilarity and specific activity of applied extractant solutions (Fig. 2 and 3).

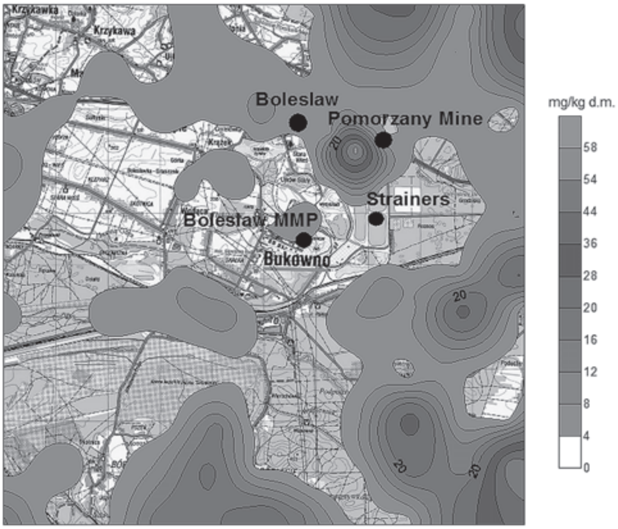

Fig. 3. Spatial distribution of iron content extracted with 1 mol · dm^{-3} NH_4NO_3 in soils around ZGH "Boleslaw" (based on [15])

The highest contents of iron soluble in diluted hydrochloric acid, exceeding 3800 mg · kg^{-1} of soil were assessed to the north and north-west of ZGH "Boleslaw" Plant but also in the vicinity of post-flotation wastes settlement tanks and in the vicinity of Boleslaw town. These regions usually overlie with the areas of the highest total content of this metal in the analyzed soils. Correlation coefficient describing the relationship between these forms of iron in the investigated soils is 0.64 and is significant at the significance level $\alpha \le 0.001$ (Table 3). Quantities of iron extracted from the researched soils using 1 mol · dm^{-3} HCl were also strictly, positively correlated with their contents of floatable particles and organic substance.

Table 3

Effect of selected soil properties on solubility of iron – linear correlation coefficients

Content of Fe soluble in	pH	Content			
		Fe_{tot}	Clay fractions	Colloidal clay	Organic carbon
1 mol · dm^{-3} HCl	0.33*	0.64*	0.54*	0.34*	0.54*
1 mol · dm^{-3} NH_4NO_3	–0.43*	0.00	0.01	–0.08	0.36*

* Significant at $\alpha \le 0.001$.

As has been mentioned earlier, ammonium nitrate solution extracted on average only *ca* 0.1 % of the total iron content in the studied soils. The greatest quantities of this form of iron were assessed in the most polluted area: north of ZGH "Boleslaw" close to Pomorzany Mine and in the north-eastern and south-eastern part of the area under investigations (Fig. 3), where most acidified soils occur [19]. In the other areas covered by the investigations, mainly light soils prevail with considerable proportion of various metals carbonates [8, 9], which suggests poor solubility and bioavailability of iron in the soil substratum. These findings confirm the opinions that this method is used to assess the amounts of elements approximate to assimilated by plants [20]. This conclusion is further corroborated by the values of correlation coefficients compiled in Table 3. Amounts of iron extracted by ammonium nitrate positively depended on the content of soil humus but negatively on changes of the analyzed soils pH.

These observations are best verified by the analysis of iron contents in plants in the area under investigations.

Conclusions

1. Statistical analysis of results of iron contents in soils around ZGH "Boleslaw" Plant in Bukowno points to a big accumulation of this element, considerably exceeding amount most frequently registered in the soils of Poland.
2. Solutions used for iron extraction in the analyzed soils were characterized by different abilities to release this element. Diluted hydrochloric acid extracted on average 21.5 % whereas ammonium nitrate solution on average less than 0.1 % of iron contained in soil.
3. Limit numbers suggested for the assessment of the amount of iron dissolved in 1 mol $\cdot$ dm^{-3} HCl reveal that 32 % of the analyzed soils had low and only 5 % high contents of this element.
4. The highest iron contents extracted by diluted hydrochloric acid were determined in the areas with the highest total content of this metal located to the north and north-west of ZGH "Boleslaw" and in the vicinity of post-flotation waste settlement tanks. On the other hand the greatest amounts of iron released by ammonium nitrate were registered in the neighbourhood of Pomorzany Mine and in the most acidified soils in this area.

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ROZKŁAD PRZESTRZENNY RÓŻNYCH FORM ŻELAZA W GLEBACH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

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Abstrakt: Celem pracy było określenie całkowitej zawartości i rozpuszczalnych form żelaza w wierzchniej warstwie gleby (0–10 cm) oraz przedstawienie ich przestrzennego zróżnicowania, na obszarze występowania rud cynku i ołowiu, w sąsiedztwie Zakładów Górniczo-Hutniczych „Bolesław" w Bukownie koło Olkusza.

W 139 próbkach gleby określono całkowitą zawartość żelaza po trawieniu próbki w stężonych kwasach mineralnych (HNO_3 + $HClO_4$), a rozpuszczalne formy ekstrahowano roztworem 1 mol · dm^{-3} HCl oraz roztworem 1 mol · dm^{-3} NH_4NO_3. Zawartość Fe w uzyskanych ekstraktach oznaczono spektrometrem absorpcji atomowej z atomizerem płomieniowym.

W przebadanych próbkach gleby stwierdzono duże naturalne i antropogenne nagromadzenie żelaza, znacznie przekraczające ilości najczęściej spotykane w glebach Polski. Roztwory ekstrakcyjne użyte do rozpuszczania żelaza w badanych glebach, charakteryzowały się odmiennymi możliwościami uwalniania tego pierwiastka. Rozcieńczony kwas solny rozpuszczał średnio 21,5%, a roztwór azotanu amonu przeciętnie tylko mniej niż 0,1% całkowitej ilości żelaza zawartego w glebie. Największe zawartości żelaza rozpuszczalnego rozcieńczonym kwasem solnym oznaczono w terenach z największą całkowitą zawartością tego metalu na północ i północny zachód od ZGH „Bolesław" oraz w pobliżu osadników odpadów poflotacyjnych. Natomiast największe ilości żelaza ekstrahowanego roztworem azotanu amonu stwierdzono w sąsiedztwie Kopalni Pomorzany i na najbardziej zakwaszonych glebach badanego obszaru.

Słowa kluczowe: żelazo, rozpuszczalność, metale ciężkie, formy przyswajalne

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CHANGES OF HEAVY METAL CONTENTS IN SLUDGE FROM SELECTED TREATMENT PLANTS IN THE WESTERN MALOPOLSKA REGION IN 1995–2009

ZMIANY ZAWARTOŚCI METALI CIĘŻKICH W OSADACH Z WYBRANYCH OCZYSZCZALNI ŚCIEKÓW ZACHODNIEJ MAŁOPOLSKI W LATACH 1995–2009

Abstract: In presented research were analyzed changes in the contents of cadmium, chromium and lead for the period 15 subsequent years (1995–2009) in sludge originating from 9 major treatment plants in western Malopolska Region, where usually municipal sewage is being treated. The analyses were conducted using methods which are recommended as referential in Poland.

Chromium accumulation in the analyzed sewage sludge was most diversified (14–6000 mg · kg^{-1} d.m.), its content in many samples from Myslenice, Krakow-Plaszow, Proszowice, Slomniki and Dobczyce exceeded the level of 5000 mg · kg^{-1} d.m., which conditions the agricultural use of these materials. The highest chromium concentration – 6000 mg · kg^{-1} d.m. was assessed in the sludge from Myslenice in 1997. In 2009 this content was even 150-fold lower. A 11-fold decrease in the average chromium accumulation in sludge samples from all analyzed treatment plants was noted during the investigated period. Diversification of lead and cadmium contents in the studied sewage sludge was much lower than chromium. The greatest amounts of these metals were usually assessed in the sludge from Krzeszowice (on average 126.5 mgPb and 3.79 mgCd · kg^{-1} d.m.), whereas the lowest contents of cadmium were noted in Proszowice and lead in Dobczyce. The average lead content in sludge from all studied treatment plants diminished 3.5-fold and cadmium amount by 2.4-fold over the 15-year period of investigations.

Keywords: cadmium, chromium, lead, sewage sludge, pollution reducing

The amount of sewage sludge produced in treatment plants has been growing proportionately to the amount of annually treated sewage. 567.3 thousand Mg (tons) of sludge were produced in Poland in 2008, of which 44.9 thousand d.m. in the area of the Malopolska province [1]. As a rule it contains considerable amounts of nitrogen, phosphorus and organic substance, which suggests its environmental or agricultural application (as fertilizer). It is also the most economical way of sludge management [2].

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In the initial period of the presented investigations, about 50 % of sewage sludge was used in agriculture and for reclamation [3], whereas currently the amount decreased to 38 % [1]. In practice this application is often impossible due to an excessive accumulation of heavy metals in the sludge and its sanitary pollution with eggs of digestive tract parasites (*Ascaris* sp., *Trichuris* sp., *Toxocara* sp.) and pathogenic bacteria, particularly *Samonella* sp. [4]. Even if the sanitary condition may be improved by composting or intensive liming, yet reduction of heavy metal concentrations on a major scale is practically impossible [5–7]. For this reason a considerable part of produced sludge is stored at treatment plants. By the end of 2008 as much as 599 thousand Mg (tons) d.m. of sludge was deposited in the areas of sewage treatment plants in Poland [1]. Sludge analyses conducted for many years in Poland and worldwide [3, 8, 9] indicate a downward trend for heavy metal content in sludge from municipal sewage, however simultaneously there are cases when these metals permissible contents in sludge are exceeded.

According to the Decree of the Minister of the Environment on municipal sewage sludge [4], analyses of the sludge are conducted in treatment plants depending on the number of inhabitants they serve: up to 10 thousand of inhabitants – once in 6 months, 10–100 thousand once in 4 months and over 100 thousand – once in two months. It results from a considerable diversification of the chemical composition of the sludge produced in various treatment plants and changes of the composition over time.

Research was undertaken to analyze the changes of heavy metal contents in sludge originating from 9 major treatment plants in western Malopolska region, *ie* from Dobczyce, Krakow-Plaszow, Krzeszowice, Myslenice, Niepolomice, Proszowice, Skala, Skawina and Slomniki during successive 15 years of investigations (1995–2009). These treatment plants usually treat municipal sewage, whereas municipal-industrial sewage flows only into Krakow-Plaszow treatment plant.

Materials and methods

Between 2 and 8 representative sludge samples, with some exceptions, were collected in the investigated treatment plants each year in May and November, since 1995. Because of extension and modernization of the treatment plant in Proszowice, sludge sampling in this treatment plant started in May 1996. Analyzed treatment plants are situated at the distance no longer than 35 km from Krakow and daily each treats mechanically and biologically between 800 and 5000 m^3 of municipal sewage which flows in by urban drainage or is supplied by septic tankers. Standing out among the analyzed treatment plants is the plant in Krakow-Plaszow, where usually over 100 000 m^3 of municipal sewage polluted with industrial pollutants flows in daily. Mostly it is only mechanically treated before reaching the sewerage system.

After stabilized and dehydrated sewage samples were supplied to the laboratory, they were homogenized and then stored fresh until analysis in closed glass vessels, at the temperature of 2–5 ^{o}C. The analyses were conducted using the methods which in Poland have been accepted as referential methods of research on sewage sludge [4]. After drying at 105 ^{o}C and determining dry mass content, the samples were digested in a mixture of concentrated nitric(V) and perchloric(VII) acids (3 : 2, v/v) and heavy metal concentrations in the obtained mineralizates were assessed by means of *atomic absorption spectrophotometer* (AAS) or by *emission absorption spectrometer with inductively coupled plasma* (ICP-AES). The analysis were conducted in 2 replications and they were repeated if the relative error was higher than 5 %.

Results

The paper presents only changes in accumulation of cadmium, chromium and lead in the analyzed sewage sludge. These are metals, whose presence in sewage from the researched treatment plants and changes during the time of the investigations were most strongly diversified. Presented results are mean values for the individual years of the investigations and were converted into the metal content in the sludge dry mass.

The highest diversification of heavy metal content in the analyzed sewage sludge was noted for chromium, whose contents in the samples from Proszowice, Slomniki, Dobczyce and Myslenice were described by the relative standard deviation approximate to 100 % (Table 1). The highest chromium concentration (on average 6000 mg $\cdot$ kg^{-1} d.m.) was assessed in 1997 in the sludge from Myslenice. However, this content was reduced 150-fold (Fig. 1) in 2009. The unnatural origin of chromium in the analyzed sludge from some treatment plants has been indicated by the values of geometric mean content of this metal in the studied sludge, much closer to median than arithmetic means. Exceedance the level of 500 mg $\cdot$ kg^{-1} d.m. which conditions agricultural utilization of the sludge was registered in the samples collected in the above-mentioned treatment plants and in the plant in Plaszow, where municipal-industrial sewage is being treated (Fig. 1).

The exceedance was noted only during one year of the investigations in Dobczyce, for 2 years in Slomniki, for 3 years in Proszowice, for 6 years in Plaszow and for 10 years (until 2004) in Myslenice. If we assume geometric mean, which better than arithmetic mean describes chromium content in all analyzed sludge samples, from Myslenice as 100, then its content in the analogous sludge from Krakow-Plaszow will be 58, from Slomniki 16, from Proszowice 11, whereas in the sludge from Skawina only 5.8, from Krzeszowice 3.6 and from Skala 3.4. All analyzed sludge samples from Skala and Krzeszowice and most samples from Skawina contained less than 100 mgCr $\cdot$ kg^{-1} d.m. In 1997 a considerable increase was noted in chromium assessed in sewage sludge from three treatment plants in: Krakow-Plaszow, Proszowice and particularly from Myslenice to which sewage from the local tannery was inflowing. Over the whole 15-year period of the investigations chromium content in the sewage from treatment plants receiving sewage polluted with this metal (Myslenice, Slomniki, Proszowice and Plaszow) diminished several dozen times (in Myslenice even 15-fold) and several fold in the other treatment plants.

Diversification of lead and cadmium contents in the analyzed sewage sludge was considerably smaller than chromium (Table 1, Fig. 1).The greatest amounts of lead occurred usually in the sludge from Krzeszowice (on average 126.5 mg), whereas elevated quantities of cadmium, respectively: 3.79 and 3.65 were noted in Krzeszowice

Table 1

Heavy metals contents in sewage sludge from 9 selected sewage treatment plants in western Malopolska Region [mg · kg^{-1}] in 1995–2009

Value	Niepolomice	Dobczyce	Plaszow	Krzeszowice	Myslenice	Skala	Skawina	Slomniki	Proszowice
Cadmium									
Minimum	1.48	1.37	1.79	2.21	1.12	2.33	1.32	1.03	1.32
Maximum	4.11	4.04	5.44	5.59	4.05	8.07	4.12	4.64	3.14
Average	2.71	2.39	3.95	3.63	2.40	4.17	2.48	2.33	1.90
Median	2.50	1.96	4.15	4.00	2.24	3.50	2.10	2.10	1.75
RSD* [%]	28.0	35.3	30.7	30.3	33.7	38.5	36.0	40.2	26.5
Chromium									
Minimum	22.1	50.4	171.1	15.9	258.9	20.0	14.2	57.5	27.2
Maximum	400.3	750.4	1750.0	49.8	6000.0	90.2	99.7	1280.0	1180.0
Average	143.4	155.3	702.0	35.2	1953.6	37.8	63.0	275.8	312.8
Median	66.9	80.0	490.0	33.7	1245.0	26.0	60.0	100.0	94.0
RSD [%]	82.0	131.8	61.2	26.6	81.3	65.7	42.1	129.2	126.8
Lead									
Minimum	29.1	28.4	43.4	54.0	47.6	40.6	11.1	14.1	25.5
Maximum	90.2	90.4	230.2	220.3	180.2	170.2	136.4	185.2	112.2
Average	59.7	56.7	122.3	141.5	97.2	99.2	82.9	78.2	63.7
Median	54.0	45,.0	96.5	125.0	73.8	67.5	70.0	55.0	52.0
RSD [%]	27.3	35.0	47.2	38.4	43.9	42.4	42.1	62.6	41.6

* Relative standard deviation.

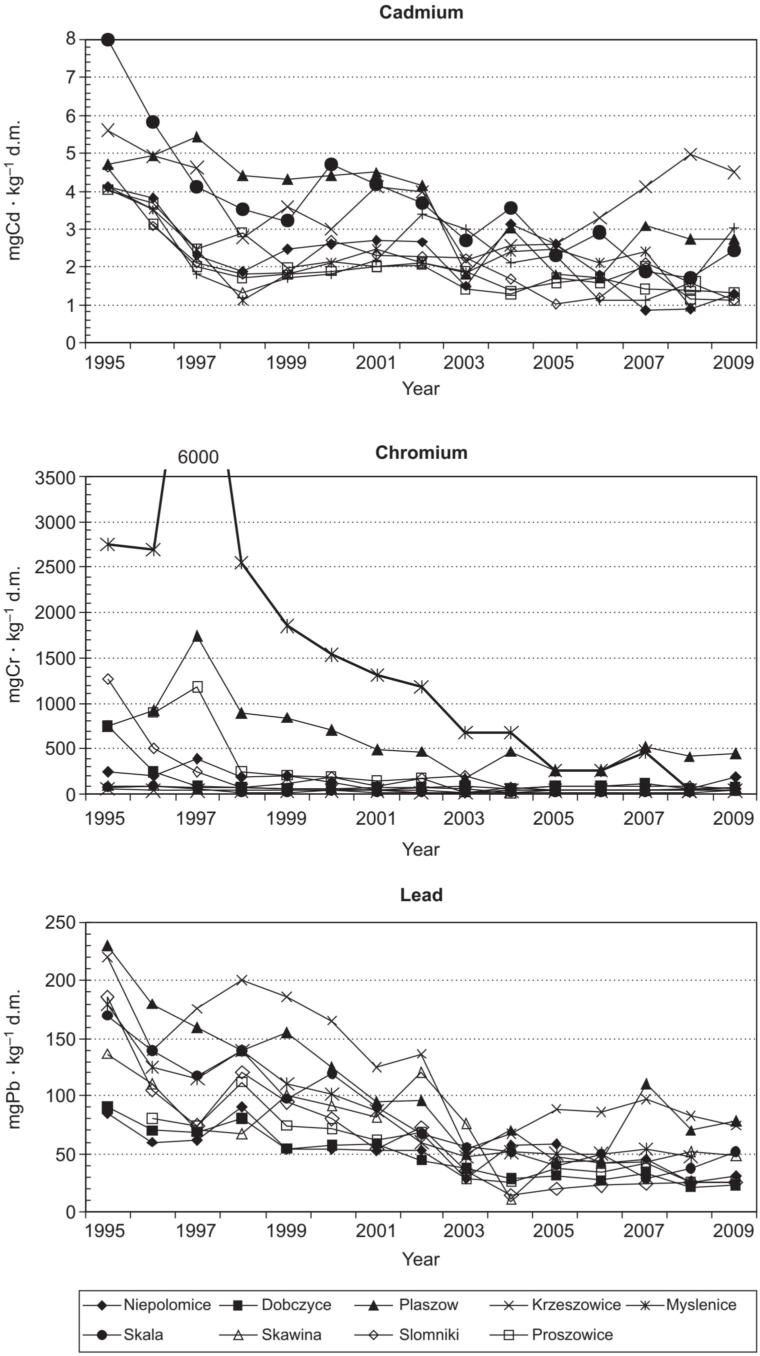

Fig. 1. Contents of heavy metals in sewage sludge from treatment plants of western Malopolska Region in 1995–2009

and Skala. These cities are situated in the area under the influence of the Olkusz region of lead and zinc ores extraction and within the range of pollution emitted by the Upper Silesia Region. Relatively big quantities of lead and cadmium were found also in the sludge from Krakow-Plaszow polluted with the industrial sewage and dust washed off the Krakow agglomeration streets. The lowest contents of lead were assessed in the sludge from Dobczyce and cadmium from Proszowice; these were respectively 2.6 and 2.1 times lower than the highest contents. Mean lead content in sludge from all investigated treatment plants diminished 3.5-fold and cadmium content 2.4-fold over the 15-year period of the investigations. It should be also emphasized that in the three first years of the research a markedly higher content of cadmium and lead was assessed in the sludge from a majority of the investigated treatment plants. In the subsequent years these metals content in sewage sludge was decreasing much more slowly, or as in the case of cadmium, remained on a similar level.

Discussion

Sludge forming at municipal sewage treatment as a rule is abundant in biogenic substances, mainly nitrogen and phosphorus. It is also a good source of organic substance, which when applied to the soil may improve soil humus balance, at the same time improving the soil physical properties and its sorption capacities [10–12]. However, at these beneficial properties the sludge may be also a source of sanitary contamination, contamination with organic toxins, *eg polycyclic aromatic hydrocarbons* (PAHs) which move easily in the soil profile [13], or with heavy metals strongly bound in the top soil layer [2, 14].

The main source of heavy metals contained in municipal sewage sludge is their occurrence in various household waste materials discharged into the sewer system and the roadway runoff from vehicles and emitted by industries [8, 15]. Because of considerable biological harmfulness of these elements, metal contents must be checked both in the sludge and in the soil at each of its agricultural or environmental application. Limit contents of metals conditioning agricultural or reclamation use of municipal sewage sludge in Poland are as follows: 10 mg of cadmium and 500 mg of chromium and lead per 1 kg d.m. of sludge [4]. Sludge polluted with industrial sewage from Krakow-Plaszow cannot be used for the purposes mentioned above.

Among municipal sewage sludge monitored in the presented investigations, all analyzed samples contained smaller quantities of cadmium and lead than limit values stated for these metals. Only chromium content in the sludge from Dobczyce, Slomniki and Proszowice was higher, whereas in the case of sludge from Myslenice it was many times higher than assumed threshold value. Such high accumulation of chromium in sewage sludge from these treatment plants in previous years was mainly caused by the sludge contamination with technological solutions from the process of chromium hide tanning (in Myslenice, Proszowice and Dobczyce) or with galvanizing solutions (Krakow-Plaszow and Slomniki). Once the sources of chromium in the sludge were identified, its excessive content was reduced in the sludge from Dobczyce, Proszowice and Slomniki already after 2–3 years of the investigations. On the other hand considering the treatment plant in Myslenice, only in the samples collected there in 2005 less than 500 mgCr was assessed whereas some samples from 1997 contained even 8000 mgCr · kg^{-1} of sludge d.m.

Changes in cadmium and lead concentrations in the sludge from monitored treatment plants were progressing more slowly than in case of chromium, but in all treatment plants a notable reduction in these metals contents was observed over the 15-year period of research. Relative standard deviations describing the diversification in these metals contents in sludge from individual treatment plants range from 26.5 % (Cd content in sludge from Proszowice) to 62.6 % (Pb in Slomniki). A decrease in the cadmium and lead contents in the sludge during the investigated period most probably is the result of limiting metal bearing dust emission into the atmosphere and general improvement of the environment quality in the Malopolska Region. Many sources of emission and points of heavy metal pollution, mainly with cadmium, lead and zinc were once documented in this region; these processes were especially intensified in the seventies and eighties of the previous century [15, 16].

Similar trends were observed in the countries of Western Europe. For example, average cadmium content in sewage sludge in Switzerland in 1975–1999 declined from 25.2 to 1.7 mg, in Germany in 1982–2000 it decreased from 4.0 to 1.3 mg, whereas in the same years (1982–2000) lead content diminished from 190 to 60 mg · kg^{-1} d.m. [8].

Despite the fact that reduction of cadmium content in the studied sewage sludge was the lowest among all analyzed metals (on average 2.4-fold in all treatment plants) it should be assessed as most beneficent from the perspective of diminishing the risk of the environment pollution with this metal. This metal has very strong toxic effect on living organisms (particularly people and animals) but at the same time labile, forming relatively readily soluble bonds, easily entering the food chain [2–7].

Conclusions

1. The contents of cadmium and lead assessed in 1995–2009 in all sludge samples originating from municipal sewage treatment in the treatment plants of the western Malopolska Region do not limit their agricultural or reclamation application. The condition was not fulfilled for chromium content in many sludge samples originating from municipal sewage with tannery (Myslenice, Proszowice and Dobczyce) or galvanizing sewage (Slomniki) supplement.
2. During the 15-year period of the investigations mean cadmium content in the sludge from all 9 monitored sewage treatment plant diminished on average 2.1-times, lead concentrations 3.5-times and chromium even 11-times.
3. Diminished accumulation of heavy metals in sewage sludge should increase the potential of fertilizer applications of these materials abundant in biogenic components and organic substance.

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ZMIANY ZAWARTOŚCI METALI CIĘŻKICH W OSADACH Z WYBRANYCH OCZYSZCZALNI ŚCIEKÓW ZACHODNIEJ MAŁOPOLSKI W LATACH 1995–2009

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Abstrakt: W prezentowanych badaniach analizowano zmiany zawartości kadmu, chromu i ołowiu w okresie 15 kolejnych lat (1995–2009) w osadach pochodzących z 9 większych oczyszczalni ścieków zachodniej Małopolski, w których na ogół oczyszczane są ścieki komunalne. Analizy przeprowadzono metodami zalecanymi w Polsce jako metody referencyjne.

Nagromadzenie chromu w badanych osadach ściekowych było najbardziej zróżnicowane (14–6000 mg · kg^{-1} s.m.), a jego zawartość w wielu próbkach, pochodzących z Myślenic, Krakowa-Płaszowa, Proszowic, Słomnik i Dobczyc, przekraczała poziom 500 mg · kg^{-1} s.m., warunkujący rolnicze wykorzystanie tych materiałów. Największą zawartość chromu – 6000 mg · kg^{-1} s.m., oznaczono w osadzie z Myślenic w 1997 r. W 2009 r. zawartość ta była aż 150-krotnie mniejsza. Zmniejszenie średniego nagromadzenia chromu w próbkach osadów z wszystkich badanych oczyszczalni w badanym okresie było 11-krotne. Zróżnicowanie zawartości ołowiu i kadmu w badanych osadach ściekowych było znacznie mniejsze niż chromu. Największe ilości tych metali notowano zwykle w osadach z Krzeszowic (średnio 126,5 mg Pb i 3,79 mg Cd · kg^{-1} s.m.), a najmniejsze kadmu w Proszowicach i ołowiu w Dobczycach. Średnia zawartość ołowiu w osadach z wszystkich badanych oczyszczalni zmniejszyła się w 15-letnim okresie prowadzenia badań 3,5-krotnie, a kadmu 2,4-krotnie.

Słowa kluczowe: kadm, chrom, ołów, osady ściekowe, zmniejszenie zanieczyszczenia

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CONTENT OF HEAVY METALS IN SOIL AND IN PINE BARK IN SKALKI TWARDOWSKIEGO LANDSCAPE PARK IN KRAKOW

ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE I KORZE SOSNY W PARKU KRAJOBRAZOWYM SKAŁKI TWARDOWSKIEGO W KRAKOWIE

Abstract: Among the components of natural environment, the soil is the main center of accumulation of many chemical substances, among others pollutions such as heavy metals. In order to evaluate pollution of the environment the soil samples were taken with the use Morris square frame 25 cm by 25 cm in around 40-year old pine grove as well as in the meadow situated nearby, in Skalki Twardowskiego Landscape Park, that is a part of Bielansko Tyniecki Landscape Park. In the grove, necrotic bark of the common pine (*Pinus sylvestris* L.) was taken as well. The environmental condition was analyzed owing to the detection of reaction of the soil, its humidity, content of heavy metals, pH and content of the metals in the pine bark obtained near the area where the soil samples were taken. It was detected that the soils of the researched areas had slightly alkaline reaction, whereas humidity was slightly higher in the meadow. What is more, the analysis of the results concerning the pine barks from the grove indicates considerable acidity (pH 3.33–3.97). The concentration of the metals such as Pb, Zn and Cd was higher in the soil of pine grove, while Cu slightly higher in the meadow. In meadow and grove soil content of the Cd was almost two times above the norm, whereas content of the other metals complied with norms. The content of Cu in bark pine was similar to content of Cu in soil, while content of Pb, Cd and Zn in bark was lower than it was in the soil.

Keywords: heavy metals, necrotic bark of pine, pH soil, pH bark pine

The ever-increasing soil pollution resulting from environmental emission of various pollutants produces substantial adverse changes in the soil that manifest, among others, as its acidification or alkalisation, saltiness, ionic equilibrium disturbance and an increase in its heavy metals content. Among components of natural environment, the

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soil is the principal centre of accumulation of chemical substances, including pollutants. Like in the case of acidification processes, the degree of heavy metal soil pollution depends on its resistance resulting from its sorption capacity. Due to the sorption complex and intense exchange of matter and energy with other environmental components, the soil is able to retain chemical substances migrating through water and the air [1]. In this way, in the process of pollutant circulation, the soil plays the role of a protective filter against compounds that enter waters and, at the same time, becomes increasingly polluted. Soil also belongs among the components of the natural environment more sensitive to the effects of pollution, including pH changes caused by human activity. For this reason, many habitat experts define it as a "mirror" of the environment [2].

Physicochemical properties of the soil affect the plant uptake of various elements and their incorporation into food chain. A pH value greater than 6.5 definitely decreases the amount of soluble forms of metals in the soil and limits their uptake and accumulation by plants [3]. Acidity is one of the key factors determining the course of many soil processes, affecting the functioning and efficiency of entire geoecosystems. Basically, it affects the living conditions of soil organisms, the availability of macro- and micronutrients necessary for plant growth, and the processes of nitrification and the presence of toxic heavy metals, especially aluminium.

In an acidic environment, plants may take up large amounts of these elements (particularly cadmium, zinc, nickel) even from not very polluted soils [4, 5]. Trace elements systematically brought into the soil accumulate in its top layer, because they are bonded by the soil sorption complex and only very slowly move into the depths of the soil profile.

Because of its sensitivity and constant presence in the test site, exposed to the impact of the changing environment, tree bark is a good bioindicator [6]. The bark of deciduous trees is inherently less acidic than the bark of coniferous trees [7]. Clear changes occur in its physical and chemical properties due to air pollution [8]. The method based on the use of aqueous extracts of the tree bark is simple, cheap and appropriate in the assessment of air pollution. It has been used by many researchers [7, 9]. Using it may determine the pH, which decreases under the influence of sulphur dioxide and nitrogen oxides in the air, as well as the electrolytic conductivity, the concentration of sulphates in the bark extract, and the absorption capacity of certain chemical elements. The pH also depends on the species, age and the health of the trees, and on the soil they grow on, the storage tests, techniques, harvest time and the degree of porosity of the cortex [9–11]. Last time the bark is also used to asses the poluttion of organic and inorganic compounds, such as polycyclic aromatic hydrocarbons (PAHs), organochlorine compounds, ammonium nitrate [12].

An exceptionally sensitive biomarker of environmental pollution is the outer bark of common pine (*Pinus sylvestris* L.) – the most widespread tree species in Poland, from which it is easy to collect its outer layer [10]. To evaluate the pollution level are applied, among others, such physicochemical properties of the bark as the pH of water extracts and the capability to absorb some chemical elements.

The aim of the studies was to determine the acidification degree and Pb, Cd, Cu and Zn accumulation in the soil and the outer bark of the pine on sites located in a protected area in the Park Skalki Twardowskiego belonging to the Bielansko-Tyniecki Landscape Park in Krakow.

Material and methods

In order to evaluate pollution of the environment the soil samples were taken with the use of Morris square frame 25 cm by 25 cm in around 40-year old pine grove as well as in the meadow situated nearby, in Skalki Twardowskiego Landscape Park in Krakow. The frame was thrust into the soil on the depth of 10 cm. In each particular site a series consisted of 16 tests on the surface of 1 m^2. Series of samples was taken on the selected sites during autumn 2008. In the grove, necrotic bark of the common pine (*Pinus sylvestris* L.) was taken as well. The environmental condition was analyzed owing to the detection of reaction of the soil, its humidity, content of heavy metals, pH and content of the metals in the pine bark obtained near the area where the soil samples were taken.

In a pine grove, from which soil was sampled, outer bark samples were taken from four *ca* forty year old trees, having similar size of 40 to 50 cm breast height diameter, *ca* 2 to 4 m away from each other. The bark, four samples from each tree, was taken from the trunk at the height of 1.5 m above the ground. The determination of the bark toxicity level was carried out by evaluating its pH value and, next, lead, cadmium, copper and zinc contents were determined.

In order to determine the pH value, the bark samples were dried at 65 ^{o}C for 3 hours, and next they were ground in mortar and pulverised using impact mill. From each sample, 2 g each of bark powder was weighed and 8 cm^3 distilled water added. After 48 hours, pH was measured using a WTW 330 pH-meter.

Chemical analyses of heavy metals were performed by determining the contents of general forms of lead, cadmium, copper and zinc using the AAS method. Dried samples of bark and soil (2.5 g) were subjected to mineralisation process. For this purpose dry water was poured over 3 cm^3 of 65 % HNO_3 and heated for about 4 hours. The filtered liquid was poured into measure flasks and filled with distilled water to volume of 25 cm^3. In solutions of the soil prepared in that manner the content of heavy metals on the spectrometer of atomic absorption was determined (Cole-Parmer, BUCK 200A).

Results and discussion

The soil from the studied sites in the Landscape Park Skalki Twardowskiego showed slightly alkaline pH, from 7.36 to 7.78 (Table 1). The moisture content of the soil from the meadow was 28.6 % and was by several per cent higher than in the soil from the grove (Table 1).

Table 1

Soil moisture and pH in the soil and in the pine bark

Selected parameters	Soil in the grove	Soil in the meadow	The pine bark
Dampness of soil [%]	20.95 (20.2–21.7)	28.55 (25.2–31.9)	—
pH value	7.65 (7.56–7.74)	7.57 (7.36–7.78)	3.71 (3.31–3.97)

However, the results concerning the bark from *ca* 40-year old pine trees from the grove point to its significant acidity. The pH of the analysed pine bark from the studied grove ranged from pH 3.33 to pH 3.97, despite the fact that the soil from this site was slightly alkaline, which resulted from its location on calcareous ground (Table 1). Similar pH values of the pine bark obtained in their study Samecka-Cymerman et al [7] and Harju et al [8].

Average concentrations of heavy metals studied in a pine grove soil were as follows: Pb 59 mg $\cdot$ kg^{-1} d.m., Zn 72 mg, Cu 11 mg and Cd 2 mg $\cdot$ kg^{-1} d.m. However, in the meadow soil demonstrated more than 51 mg of Pb, 65 mg Zn, 13 mg Cu and Cd about 2 mg $\cdot$ kg^{-1} d.m. The concentration of metals such as Pb, Zn and Cd was higher in the pine grove soil, whereas Cu slightly higher in the meadow in the landscape park (Fig. 1). The critical concentrations of the metals in the soils containing the anthropogenic contaminations, according to Kabata-Pendias et al are: 70 mg Pb, 150 mg Zn and 1 mg Cd/kg [13, 14]. The obtained results concerning cadmium are characterised by exceeding the levels indicated by Kabata-Pendias [13]. In the grove soil and in the meadow, the limit value was exceeded more than twice, and in the meadow, almost twice (Table 2).

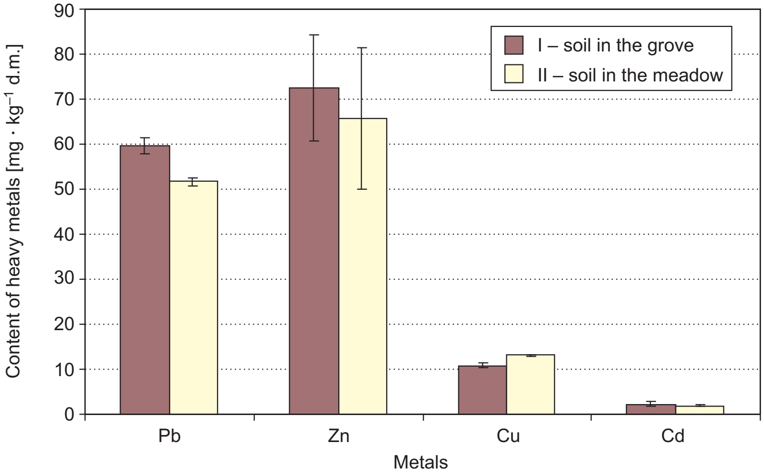

Fig. 1. Content of heavy metals in soil

Table 2

Content of Pb, Zn, Cu, Cd in soil and in pine bark [$mg \cdot kg^{-1}$]

Heavy metals	Soil in the grove	Soil in the meadow	The pine bark	The critical concentrations	
				Kabata-Pendias*	Minister of Environment Regulation**
Pb	59.63 (58.29–60.96)	51.70 (51.08–52.33)	41.86 (24.16–59.55)	70	100
Zn	72.47 (64.07–80.87)	65.72 (54.54–76.91)	32.37 (30.75–33.99)	150	300
Cu	10.85 (10.43–11.26)	13.05 (12.91–13.2)	10.23 (5.07–15.39)	—	150
Cd	2.32 (2.03–2.6)	1.90 (1.82–1.98)	1.56 (1.49–1.62)	1	4

* The critical concentrations according to Kabata-Pendias [13]; ** limit values for the heavy metal content set out in the Minister of Environment Regulation on the soil quality and farmland quality standards (Polish Journal of Laws DzU 2002, No. 165, item 1359 of 4 October 2002 [15].

However, concentrations of heavy metals found do not exceed the limits stipulated in the Minister of Environment Regulation on the soil quality and farmland quality standards (Polish Journal of Laws DzU 2002 No. 165, item 1359 of 4 October 2002) (Table 2).

No cases of exceeding the limit values for metals were found for Group B soils (a group covering the land rated as farmland excluding the land under ponds and the land under ditches, the woodland and tree- and bush-covered land, wasteland, as well as built-up and urban areas, excluding industrial areas, mine lands and transport areas) [15].

In the soil environment, heavy metals demonstrate diverse mobility. Lead is strongly bonded by organic matter of soil top layer and only slightly migrates into the depth of the profile, copper is a little more mobile, and zinc relatively easily moves into the depths of the soil. The total metal content of forest litter is determined, beside the deposition rate, also by the humification conditions of the vegetable material and the balance of metal accumulation and leaching processes. Heavy metal toxicity depends on the roles they play in the metabolic processes of the organisms and their susceptibility to bioaccumulation. Metal toxicity is not only the result of its content in the environment, but primarily its biochemical role in metabolic processes and mechanisms of absorption, accumulation and excretion by living organisms. The capability of heavy metals to penetrate to higher plants depends on the soil properties and the conditions prevailing in the environment, as well as the physical and chemical form in which the element occurs.

The lead and zinc contents in the pine bark were significantly lower than in the soil, in which the studied trees grow. Zinc is an essential element in the process of regulating the metabolism of living organisms. In comparison with other trace elements, zinc is much less toxic to animals and humans. Zinc is a common element in the tissues of plants and animals. Just as in plants, in animals zinc interacts with a variety of physiological processes and with various elements, primarily cadmium and copper.

Soils are the place where most of the lead of anthropogenic origin, such as from vehicle exhausts, waste incineration, lead smelting, and use of paint, accumulates. This element is strongly bound in soils and accumulates in the humus layer. Although it is barely mobile, in acidic and sandy conditions can easily be absorbed by plants, which poses an immediate threat to living organisms participating in the food chain. In the soils studied, lead concentration was 51.7–59.6 ppm d.m. and in the pine bark 41.8 ppm. In the studies, the Pb content did not exceed the limit value [13, 15].

In the pine bark, 10.23 mg/kg copper was found and this value was comparable with that analysed in the grove soil (Table 2, Fig. 2).

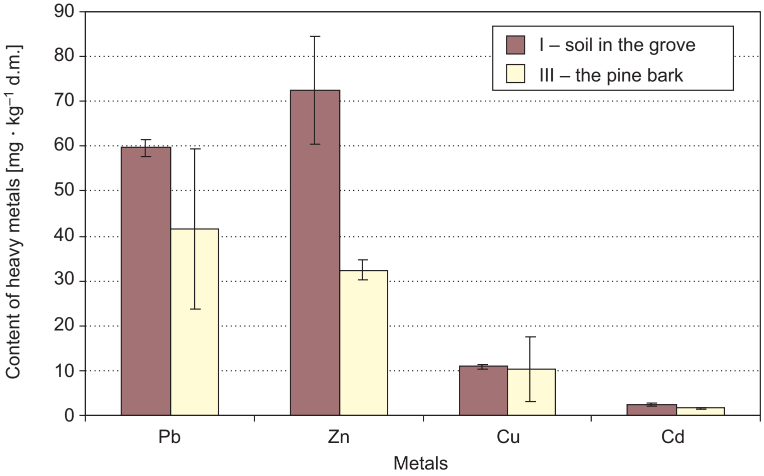

Fig. 2. Content of heavy metals in soil and in pine bark

Copper is a metal present in the soil in the form of very mobile bonding. Its content is closely related to the particle size composition and the pH of the soil; lowering the pH will increase the occurrence of copper. The natural copper content in soils not contaminated ranges from 10 mg/kg for light soils to 25 mg/kg for heavy soils [13]. The copper content in the analyzed soils does not exceed the acceptable limit given by the Regulation of the Minister of the Environment on soil and land quality standards [15].

The lowest cadmium content was found in the pine bark. It was *ca* 1.56 mg per kg, but according to Kabata-Pendias, it was also a value slightly in excess of the limit [13]. Cadmium content in the pine bark from the grove was slightly lower than in the grove soil and meadow in the Landscape Park Skalki Twardowskiego (Table 2, Fig. 1, 2).

Cadmium is relatively easily and intensively taken up by plants, in general proportionally to its concentration in the environment [14] Cadmium introduced into the soil is readily soluble in an acidic medium, and its mobility increases in light soils. It then becomes readily taken up by plants and incorporated into the food chain. It is considered dangerous to humans and animals as it is easily absorbed and long remains in the body. Plants accumulate cadmium in the roots, and its toxic effects may interfere with the processes of photosynthesis.

The cadmium concentration in the bark of necrotic pine correlated with its concentration in the soil. Slosarz [16] obtained a higher Cd content in the bark of pine trees in the Niepolomicka primeval forest (2 ppm) than in the soil (0.88 ppm d.m.) in which the trees grew [16].

Slosarz's results of the research carried out in the Niepolomicka primeval forest in fresh mixed forest indicate that the soil accumulated larger quantities of copper, zinc and lead, while the bark accumulated larger amounts of cadmium [16].

The results indicate that both the pine bark and the soil contaminants are good indicators of acidifying compounds and investigated metals. Confirm the results of Marko-Worlowska and Slosarz [16, 17].

Conclusions

1. The results indicate that the concentrations of heavy metals do not exceed the standards set out in the Regulation of the Minister of the Environment on soil quality standards and earth quality standards for group B – a group covering the land rated as farmland excluding the land under ponds and the land under ditches, the woodland and tree- and bush-covered land, wasteland, as well as built-up and urban areas, excluding industrial areas, mine lands and transport areas (Polish Journal of Laws DzU 2002, No. 165, item 1359 of 4 October 2002).
2. The results of the analysis of the tree bark collected from model trees with surfaces at varying distances from the source of emissions may be used to illustrate the dispersion range of the pollution.
3. The pH of pine bark indicated its much higher acidity than that of the soil in which these pine trees grew.
4. The soil had higher accumulation of lead, cadmium and zinc occurs in the soil than in the pine outer bark.

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ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE I KORZE SOSNY W PARKU KRAJOBRAZOWYM SKAŁKI TWARDOWSKIEGO W KRAKOWIE

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Abstrakt: Spośród komponentów środowiska przyrodniczego gleba jest głównym ośrodkiem akumulacji wielu substancji chemicznych, w tym również zanieczyszczeń, takich jak metale ciężkie. Dla oceny zanieczyszczenia środowiska pobierano próbki glebowe przy użyciu ramy Morrisa o wymiarach 25 × 25 cm w ok. 40-letnim zagajniku sosnowym oraz na pobliskiej łące w Parku Skałki Twardowskiego w Krakowie należącym do Bielańsko-Tynieckiego Parku Krajobrazowego. W zagajniku pobierano również korę martwicową sosny zwyczajnej (*Pinus sylvestris* L.). Badano stan środowiska, określając odczyn gleby, jej wilgotność, zawartość metali ciężkich oraz pH i zawartość metali w korze sosny pozyskanej w pobliżu miejsca pobierania gleby. Stwierdzono, iż gleby badanych stanowisk wykazywały odczyn słabo zasadowy, zaś wilgotność była nieznacznie większa na łące. Natomiast wyniki dotyczące kory sosen z zagajnika wskazują na jej znaczne zakwaszenie (pH 3.33–3.97). Koncentracja metali, takich jak Pb, Zn i Cd była wyższa w glebie zagajnika sosnowego, natomiast Cu nieznacznie wyższa na łące. W glebie łąki, jak i w glebie zagajnika ilość kadmu przekraczała prawie dwukrotnie normę, a pozostałych metali mieściła się w normie. Zawartość miedzi w korze sosny była porównywalna do zawartości w glebie, podczas gdy ilość Pb, Cd i Zn w korze była mniejsza niż w glebie.

Słowa kluczowe: metale ciężkie, kora sosny, pH gleby, pH kory sosny

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Barbara GRAJPEL and Justyna OLSZEWSKA

HOW CAPSAICIN CHANGES THE TOXICITY OF PYRETHROIDS IN AMERICAN COCKROACH (*Periplaneta americana*)

W JAKI SPOSÓB KAPSAICYNA ZMIENIA TOKSYCZNOŚĆ PYRETROIDÓW W STOSUNKU DO KARACZANA AMERYKAŃSKIEGO (*Periplaneta americana*)

Abstract: Intensive use of insecticides has led not only to enhanced environment pollution, but most of all, to an increase in insects' resistance to the chemicals in use. That is why presently the scientists focus on searching for new, alternative means to aid crop protection. One of the ways to achieve it is finding a compound which, when added to an insecticide, magnifies significantly its toxicity against the pests and in the same time it is safe for people. In the presented study we have attempted to analyse whether the active compound of pepper, capsaicin, increases toxicity of a pyrethroid (Bulldock 025 EC) against American cockroach, a main insect factor causing allergies and asthma in people. The effect of the tested substances was measured by means of changes observed in hemolymph pH and acute toxicity test, performed in various ambient temperatures (15 °C, 25 °C and 35 °C). The results of the experiments suggest that the tested substances affect significantly acid-base homeostasis. Moreover, it was demonstrated that different concentrations of capsaicin have different influence on insecticidal properties of the tested pesticide in higher ambient temperatures. It was established that simultaneous application of capsaicin (in 10^{-8} M concentration) and pyrethroid (LD_{50}) causes an increase in death rate among the intoxicated insects. These results give hopes as for applicability of capsaicin as a synergist of pyrethroid insecticides against *Periplaneta americana*, especially in conditions in which the toxicity of the pesticide itself is lower (ie in higher ambient temperatures).

Keywords: capsaicin, pyrethroids, cockroach, death rate, changes in pH

There are many organisms, both vertebrates and invertebrates, associated with human environment. Among them, the cockroaches found their niche in blocks of flats, warehouses, public toilets, hot spots and so on. One of the most popular synanthropic cockroach species is American cockroach (*Periplaneta americana*). It is widely

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recognisable as a pantry pest, but the same cannot be said about its role as an allergic factor. So far the following cockroach allergens have been isolated: Bla g2 (inactive aspartic proteinase), Bla g4 (calycin), Bla g5 (glutatione S-transferase), Bla g6 (troponin) and group I of cross allergens including Bla g1 and Per a (arylophorin), as well as Per a 7 (tropomyosin) [1].

The research conducted on children in poor city districts in the United States showed that the exposition to cockroach-derived allergens plays a significant role in asthma pathogenesis. The most common allergens in children's bedrooms were Bla g1 and Bla g2 [2, 3]. Among the methods of preventing asthma the most important is to clear the place of cockroaches using non-toxic traps and safe insecticides.

In our study we have been trying to pick up a substance which is safe for mammals, but when added to an insecticide, it raises its activity. We have decided to use a neurotoxin – capsaicin. It is an organic compound of amide structure responsible for spicy taste of red pepper. Capsaicin activates TRPV1 receptor, which is localised on endings of Aδ and C nerve fibres. Activation of this receptor results in burning sensation and affects mammalian and insect thermoregulation [4–6]. Long history of this spice use proves that it is safe for human, so it meets the pivotal condition laid down for synergists of insecticides. The aim of the study was to investigate whether capsaicin meets the second key provision – raising the insecticide's toxicity. Since the tested pyrethroid shows a negative temperature coefficient [7], the most important was to determine how capsaicin affects the pyrethroid's toxicity in high ambient temperatures.

Thus, the objective of the presented research was to test whether capsaicin may cause an increase in toxicity of pyrethroid insecticides in different ambient temperatures and whether capsaicin can be used as a synergist of these insecticides in wide spectra of temperature.

Materials and methods

In the experiments adult *Periplaneta americana* of both sexes were used. The animals were bred in insectariums of Department of Animal Toxicology and Department of Biophysics at the Nicolaus Copernicus University in Torun, at constant temperature of 22–25 ^{o}C and under a natural photoperiod. During the whole time of stay in the breeding premises the insects had unlimited access to water and food.

The substances in use

In the research a natural neurotoxin, capsaicin (product of Sigma) was used. In regards to its poor solubility in water, two kinds of solvents were used: alcohol (product of POCH – Polish Chemical Reagents) and a mixture of alcohol and Tween 80 (product of Sigma). In order to obtain proper solutions, a 1 M solution of capsaicin in alcohol 96 % or in a mixture of alcohol 96 % and Tween 80 in 1:1 relation was prepared. This initial solution was subsequently used for preparing a 10^{-8} M solution of capsaicin (the alcohol and Tween concentration was 0.1 %).

In the experiments a pyrethroid insecticide, Bulldock 025EC in LD_{50} dose was used. Its active compound is beta-cyfluthrin.

Method of application

The substances were administered in volume of 10 mm^3 (μl) on the insects' dorsum, under the wings, near the thoracic ganglia.

Abbreviations used in the paper

C – the insects administered saline; A – alcohol 0.1 %; AT – a mixture of alcohol and Tween; k8 – capsaicin solved in alcohol in 10^{-8} M concentration; P – pyrethroid.

Temperature-dependant survival rate

The intoxicated animals (n = 20) were placed for three days in glass cubical chambers (13 × 13 × 13 cm). A shelter and isolation for the insects was made of cardboard containers. The glass cubes were placed in rooms of defined temperatures: 15 ^{o}C, 25 ^{o}C or 35 ^{o}C. During the experiments water and food for the animals were provided. In 12-hour intervals the survival rate was noted, dead individuals removed and water and food changed.

Determining of the insects' hemolymph pH

The hemolymph pH assessment was performed after three days since application. In order to measure the hemolymph pH, the insects' body fluids were collected using thin capillary tubes, which were placed between the body segments right under the second pair of legs. The hemolymph was placed in ependorph tubes thermostated in temperatures equal to the ones in the experiments (15 ^{o}C, 25 ^{o}C or 35 ^{o}C). The pH value was measured using Lazar Research Laboratories PHR (146 Micro Combination pH electrode) and Hanna Instrument microprocessor pH meter. Calibration was performed on standard pH buffers (4.01 and 7.01). The measurements were taken at the temperatures relevant to the experimental ones, after 10 s since putting the electrodes in. After each measurement pH value was checked in the buffers.

Results and discussion

An influence of joint and separate application of pyrethroid and capsaicin in three different ambient temperatures (15 ^{o}C, 25 ^{o}C or 35 ^{o}C) on the insects' death rate was studied. Since it is known that every change in the organism's homeostasis may lead to disturbances in its functioning, a decision to investigate whether the xenobiotics administration affects acid-base homeostasis and whether the changes are correlated with the toxicity of the substances in use was made. As applying both the solvents themselves and capsaicin in various configurations may cause changes in insects' body fluids pH as well as in their death rate, the results are presented as differences observed in relation to the control group (the insects administered only saline) (Fig. 1).

The insects' death rate assessment

The assessment of the capsaicin effect on insecticidal activity of the pyrethroid was conducted after 72 hours since the intoxication on the basis of acute toxicity test.

Table 1

Changes in insects' death rate after co-application of pyrethroid (P) with substances: alcohol 0.1 % (A), a mixture of alcohol and Tween 80 (AT), capsaicin in 10^{-8} M concentration, dissolved in alcohol 0.1 % (k8) and solved in a mixture of alcohol and Tween 80 (kT80) at temperatures of 15 °C, 25 °C and 35 °C.

The substance tested	Changes in the insects' death rate [%]		
	15 °C	25 °C	35 °C
P	95	35	5
PA	75	0	25
PAT	80	80	85
Pk8	75	70	50
PkT8	60	40	75

Application of pyrethroid caused the highest death rate at temperature of 15 °C – 95 %, while at 25 °C – 35 % and at 35 °C – only 5 % (Table 1). It was established that co-application of A and pyrethroid at temperatures of 15 °C and 25 °C caused a decrease in the insecticide's activity (death rate fell by 20 % and 35 %, respectively). At temperature of 35 °C their co-operation led to an increase in the death rate by 20 %. However, unexpectedly, adding AT to pyrethroid only gave the highest results in the toxicity test. The intoxicated insects' death rate was almost equal at various temperatures (15 °C – 80 %, 25 °C – 80 % and 35 °C – 85 %), thus while in colder environment the toxicity fell by 15 %, at higher temperatures it rose by 35 % and 45 %, respectively.

The results of the performed experiments suggest that the tested concentration of capsaicin affects insecticidal activity of the pyrethroid in various ways. While analysing co-operation of capsaicin with the insecticide it was noted that co-application of the pesticide and k8 caused an increase in the insects' death rate by 35 % and 45 % at 25 °C and 35 °C, respectively, however, application of kT8 raised the toxicity by as much as 70 %, but only at the temperature of 35 °C. At temperature of 15 °C every combination of capsaicin and pyrethroid caused lowering of the death rate by 20 % in the case of Pk8 and 35 % in the case of PkT8 in comparison with the toxicity of the pyrethroid itself.

Analysing the insects' hemolymph pH

On the basis of bibliographical data [8] and unpublished own studies it was concluded that in control insects pH value slightly lowers along with the rise in temperature. Application of the pyrethroid reversed this relation: the lowest pH was noted at the temperature of 15 °C – 6.70 ± 0.18 and the highest at 35 °C – 7.31 ± 0.02. At 25 °C it was 7.27 ± 0.02 and was higher than in the insects administered saline (C) by 0.31 ± 0.01 ($p < 0.001$). After co-application of alcohol 0.1 % and insecticide at 15 °C a shift by 0.20 ± 0.01 ($p < 0.001$) towards more acid values of the insects' hemolymph pH was noted. At 25 °C a slight increase in the pH value – by 0.08 ± 0.01 ($p < 0.05$) was observed (Fig. 1). PAT administration caused a decrease in pH value by 0.58 ± 0.01 ($p < 0.001$) at 15 °C. At 25 °C and 35 °C a minor increase in hemolymph pH was statistically insignificant. While analysing the effects of combinations of pyrethroid and capsaicin it can be noted that in both cases only changes at 15 °C were statistically significant (a decrease by 0.11 ± 0.01, $p < 0.05$ and by 0.19 ± 0.01, $p < 0.001$ for Pk8 and PkT8, respectively). In every case at 25 °C and 35 °C the insects' hemolymph pH was similar to this noted in a control group and it was 6.96 ± 0.01 and 6.97 ± 0.01 for Pk8, respectively and 6.94 ± 0.04 and 7.00 ± 0.01 for PkT8, respectively.

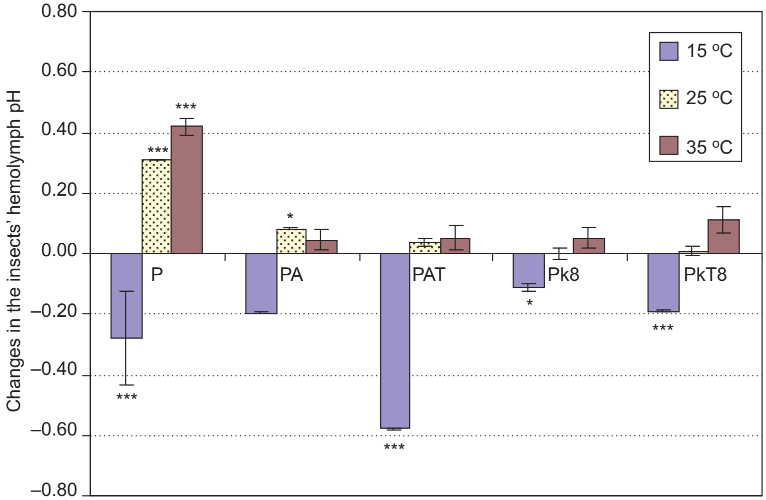

Fig. 1. Changes in the insects' hemolymph pH triggered by co-application of pyrethroid (P) with substances: alcohol 0.1 % (A), a mixture of alcohol and Tween 80 (AT), capsaicin in 10^{-8} M concentration, solved in alcohol 0.1 % (k8) and a mixture of alcohol and Tween 80 (kT8) at temperatures of 15 °C, 25 °C and 35 °C (* – $p < 0.05$, ** – $p < 0.01$, *** – $p < 0.001$)

When comparing the toxicity of the insecticide itself at the three experimental ambient temperatures it can be noted that it is 19-fold lower at 35 °C than at 15 °C, which is consistent with the fact that the tested insecticide is characterised by a negative temperature coefficient [7]. Our earlier studies showed that capsaicin cannot be used separately against cockroaches [9]. However, in the presented study we have demonstrated that when added to a pyrethroid pesticide, it affects markedly its toxicity. Average death rate at all ambient temperatures was 45 %; after co-application of pyrethroid and alcohol – 33 %; after co-application of pyrethroid with a mixture of Alcohol and Tween – 81 %; after co-application of pyrethroid and capsaicin – 65 % and after co-application of pyrethroid and capsaicin dissolved in a mixture of alcohol and Tween – 58 %. Although a synergistic effect of capsaicin is poor, reaching only 20 %, an addition of kT8 to pyrethroid renders its toxic properties less susceptible to ambient temperatures (at 35 ^{o}C the toxicity of PkT8 was higher than of the pyretroid itself by as much as 70 %). Thus, a potential separate and joint use of the substances, depending on the season or ambient temperature (eg in hot spots) should be considered. However, a more attention should be paid to the results of acute toxicity test in the case of joint insecticide and a mixture of alcohol and Tween 80 application, where at every tested temperature the cockroaches' death rate was almost the same, ~80 %. Tween 80 (polyoxyethylenesorbitan monooleate) is a nonionic surfactant used as a food ingredient (E433), applied along with substances limiting absorption of cholesterol [10] and also as a vector for antineoplastic drugs [11]. Thus, Tween 80 as a synergist might be considered as safe and the results obtained as highly advantageous. Nevertheless, it must be taken into account that studies on microorganisms proved that it changes markedly membrane fluidity and it affects many enzymes' synthesis [12], so as far as pyrethroid and a mixture of alcohol and Tween 80 may be used at homes, the case is not that simple for crops, since its potential effect on soil microorganisms should be considered.

Every tested combination of the insecticide and capsaicin caused also temperature--dependent changes in the hemolymph pH. Noteworthy is the fact that in the case of application of the pyrethroid itself a certain dependency between ambient temperature, hemolymph pH and death rate was observed: an increase in ambient temperature was accompanied by a decrease in death rate and a rise in pH values. However, addition of any of the tested substances triggered such various changes that all attempts to find a uniform pattern for them failed. For instance, although joint application of pyrethroid with capsaicin and pyrethroid with capsaicin dissolved in a mixture of alcohol and Tween 80 reduced the effect of pyrethroid itself on acid-base homeostasis (total difference in pH is 0.52 and 0.40, respectively), this change was not accompanied by a change in these substances' toxicity. However, the fact that the measurements were conducted 72 hours after intoxication and that the results obtained come from the individuals which survived the experiment should be taken into account. Thus, in order to investigate more thoroughly the relation between death rate and changes in hemolymph pH, it is necessary to measure time-dependent changes in pH in relation to progressing paralysis caused by the applied substances. Nevertheless, the tolerance of cockroaches to changes in their hemolymph pH (the range of changes covered one whole pH unit, from 6.4 to 7.4) is noteworthy.

The results obtained allow to assume that capsaicin may be used as a toxicity magnifier for pyrethroid insecticides against *Periplaneta americana*, although only in specific environmental conditions (ie high ambient temperature). The death rate observed in the experiments was independent of the changes in pH caused by application of the xenobiotics, as joint intoxication with pyrethroid and a mixture of alcohol and Tween 80 resulted in 80 % death rate and in the same time – lowering the value of pH by 0,57 at 15 ^{o}C, while in higher temperatures death rate remained the same

(80 %), but the changes in pH were significantly lower, reaching only 0.04 and 0.05 in 25 °C and 35 °C, respectively.

Acknowledgements

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W JAKI SPOSÓB KAPSAICYNA ZMIENIA TOKSYCZNOŚĆ PYRETROIDÓW W STOSUNKU DO KARACZANA AMERYKAŃSKIEGO (*Periplaneta americana*)

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Abstrakt: Intensywne stosowanie insektycydów doprowadziło nie tylko do wzrostu zanieczyszczenia środowiska, ale przede wszystkim do wzrostu oporności owadów na stosowane środki. Dlatego też uwaga badaczy koncentruje się obecnie na poszukiwaniu alternatywnych metod walki ze szkodnikami. Jedną z nich może być znalezienie substancji, która dodana do insektycydu, w sposób znaczący podniesie jego toksyczność dla owadów i zarazem będzie bezpieczna dla ludzi. W prezentowanej pracy podjęto próbę oceny czy aktywny składnik papryki – kapsaicyna, zwiększy toksyczność pyretroidu (Bulldock 025EC) w stosunku do karaczana amerykańskiego, będącego głównym czynnikiem wywołującym alergie i astmę u ludzi. Toksyczność badanych substancji określano na podstawie zmian odczynu hemolimfy oraz testów toksyczności ostrej, wykonanych w trzech różnych temperaturach otoczenia (15 °C, 25 °C i 35 °C). Z przeprowadzonych doświadczeń wynika, że badane substancje w sposób znaczny zmieniają równowagę kwasowo-zasadową.

Wykazano także, że testowane stężenia kapsaicyny w różny sposób wpływają na aktywność owadobójczą zastosowanego insektycydu w wyższych temperaturach otoczenia. Stwierdzono, że jednoczesna aplikacja kapsaicyny (w stężeniu 10^{-8} M) i pyretroidu (LD_{50}) powoduje wzrost śmiertelności intoksykowanych owadów. Na podstawie otrzymanych wyników można przypuszczać, że kapsaicynę będzie można stosować jako synergetyk dla insektycydów z grupy pyretroidów w stosunku do *Periplaneta americana*, zwłaszcza w tych warunkach środowiska, w których toksyczność pyretroidu jest mniejsza (duże temperatury otoczenia).

Słowa kluczowe: kapsaicyna, pyretroidy, karaczan, śmiertelność, zmiany pH

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METHODS OF CONTROL OF SYNANTHROPIC GERMAN COCKROACH (*Blattella germanica* L.) IN VARIOUS URBAN ECOSYSTEMS

METODY KONTROLI I ZWALCZANIA SYNANTROPIJNYCH KARACZANÓW (*Blattella germanica* L.) W RÓŻNYCH EKOSYSTEMACH MIEJSKICH

Abstract: The German cockroach (*Blattella germanica* L.) is an omnivorous species. It feeds on leftovers, animal food and also on book hardcover. The presence of cockroaches around municipal structures allows these pest for reproducing and increasing the population numbers in various synanthropic ecosystems. Intensive development of cockroach populations is one of the main reasons of allergies, bronchial asthma and other human diseases. Moreover, cockroaches may transport bacteria and disease vectors on their body and in faeces. For these reasons the control of cockroach invasion is not only an aesthetic problem but also an important issue of health care.

In this paper an attempt was made to estimate the composition and numbers of insects living in various synanthropic ecosystems with the use of pheromone traps. Than appropriate insecticides were applied to control the pest.

Changes in the species structure of cockroaches were traced using pheromone based glue traps placed in selected sites like Warsaw hospital, private apartment, shop and bakery. Larvae and males prevailed on traps; females were caught in lower numbers. Females had cocoons which affected the number of caught larvae. Besides, other animals were caught in the glue trap such as the Oriental cockroach, flies, ants and house mice attracted by an easy access to food.

Keywords: synanthropic organisms, the Oriental cockroach (*Blatta orientalis*), the German cockroach (*Blatella germanica*), control methods

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The occurrence of synathropic insects is largely affected by city infrastructure. In cities we observe clusters of residential houses accompanied by public buildings like hospitals, crëches, schools, shops and supermarkets. Waste bins are often situated nearby. Depending on location, they are emptied daily or once a week. This makes favourable conditions for invasion and spreading of cockroaches but also of rodents, birds and mammals looking for an easy access to food in the city agglomeration.

Isolation from other buildings is an important factor for public buildings which often form separate complexes. Hospitals or large shops (supermarkets) in Warsaw are routinely surveyed for the presence of synanthropic insects and rodents attracted by easily accessible food. This may decrease the population growth of synanthropic insects and their further invasion to apartments.

Residential blocks, where one staircase contains from 5 to 100 flats depending on the construction period, present a bigger problem. An excellent location for the population of the German cockroach, other insects and synanthropic rodents is residential blocks built up in the 1960s and 1970s in the centre of Warsaw. Studies were performed in a flat there. An occupant complained about the invasion of cockroaches. In the centre of Warsaw flats are often rented by students and foreigners working in fast food bars situated in Warsaw and neighbouring communes. Therefore, in such flats, half-finished food products are often prepared and stored. This offers an excellent base for the development of synanthropic insect populations. Another threat is posed by open rubbish chutes on each floor with remaining food leftovers. One may often find there large junk which does not fit into dustbins. This makes a good base for the German cockroaches to occupy and stay outside their feeding period. Cockroaches were seen walking late evening in the corridor near the flat where pheromone traps had been laid. In large communities of people like those living in residential blocks, repairs in flats or in common grounds may leave numerous cracks which facilitate movement of insects and even of rodents.

The next problem is with the costs of disinfection of large residential objects. Many residents do not attempt to control pests thus facilitating their development. This is a result of ignorance about the harmfulness of synanthropic animals on one hand and of the aspiration to live "ecological" life on the other. Means used in the insect and rodent extermination are often toxic or cause an allergic reaction in residents. The problem is also with their improper application. A frequent error made by disinfection firms is an excessive dilution of insecticides, not obeying the methods of their application and a lack of preliminary analyses as to what pest they are dealing with in a given area.

The German cockroach (*Blattella germanica* L.) is a synanthropic species whose life cycle is bound with humans, especially with their building infrastructure. It occurs worldwide, its presence is limited only by temperature [1–3]. The presence of cockroaches around municipal structures allows them to reproduce and increase the number of their populations in various synanthropic ecosystems. They easily migrate through electric and hydraulic connections, dry hydraulic siphons, through cracks in the wall and draughty window frames. They may also get to houses with purchased food, in books, shoe bags etc. Cockroaches search for food more with olfactory than with visual receptors [1, 4]. Rivault [5] found that single cockroaches are able to migrate at a distance of 3 to 85 m a day. This affects colonization of new spaces by these insects where they actively search for food. Jeanson et al [6] found under laboratory conditions that cockroaches, unlike other animals, are not territorial. They only attempt to keep 3–12 mm distance from each other. Therefore, their population may rapidly develop and exist in a given area.

Omnivory enables their survival under variable local conditions [7, 9]. The whole life cycle of the German cockroach lasts 100 days. It is assumed that the active population of cockroaches is composed of 80 % nymphs and 20 % of adults [1, 9, 10]. Intensive development of cockroach population is one of the reasons of allergy, bronchial asthma and other human diseases. Moreover, cockroaches may transmit bacteria and diseases on their bodies and in faeces [11, 12]. In hospitals cockroaches may transmit pathogens responsible for infections [7, 13, 14]. For these reasons the control of cockroach invasion is not only an aesthetic problem but also an important issue of health care. The German cockroach is a subject of studies carried out by many scientists worldwide who search for new chemical and other control methods [15–17].

Material and methods

Pheromone-glue traps were the study material. These traps do not contain any chemical means; therefore they may be safely used in any space. Attracting substance is contained in the tablet made of a herbal mixture of patented composition which gives an effect of natural insect pheromone.

The studies were carried out in selected Warsaw hospitals, private apartments and bakeries. Insect detectors were placed in various rooms (bathrooms, kitchens, stores, water distributors). Traps were displaced in places with potentially available water or moisture (such places are preferred and searched for by cockroaches) and in places where food may possibly be found. Such places included hosepipes delivering water, the rears of refrigerators near water condensers, surroundings of bathtubs, shower bases, microwave cookers, places of food distribution, dish washers and the rears of bookshelves and cupboards used to keep food in original wrapping.

Insect detectors were exposed in particular rooms for one month with the description on each trap of the date and place of exposition. At the same time a protocol was prepared with detailed description of places of trap exposition. Persons who could have a contact with traps were informed on the necessity of leaving them in place. After the study period all traps were collected in a bag with the description of the object of origin.

The numbers and species of attracted insects were analysed in the Chair of Biology of Animal Environment of Warsaw University of Life Sciences SGGW (WULS-SGGW).

Based on the numbers and types of growth forms of insects one may select appropriate control means and apply proper concentrations of chemicals to achieve efficient and safe insect elimination whether by spraying with low or high pressure facilities or by using insecticide paste (in places where aerosols could not be used).

Results and discussion

Pheromone-glue trap is used to estimate insect intestation in a given area. Nymphs of cockroaches were most frequently caught in glue traps (Fig. 1). Many larvae hatched from cocoons carried by females were also found there. Most such newly hatched larvae were found in the apartment and the least – in bakery. This resulted from the fact that the young hatched from the cocoon carried by female even after its death. The young are a potential source of reconstruction and development of the German cockroach population in a given area.

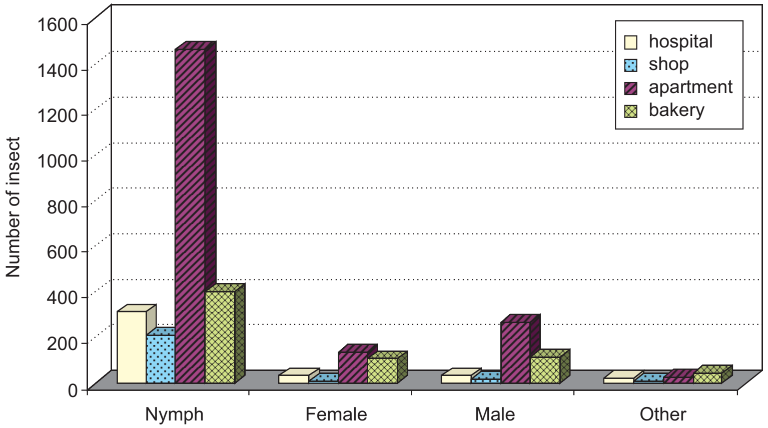

Fig. 1. Mean number of German cockroaches (*Blattella germanica*) caught in pheromone-glue traps

In this experiment only the population of cockroach from bakery was less active. Most active cockroaches were found in the apartment (1899 individuals including 1469 nymphs) compared with the bakery, where only 408 nymphs were noted. The least nymphs (214) were recorded in the shop (Fig. 1).

The catching in a given trap depended also on the place of its exposition (Photo 1). The greatest number of cockroaches in various growth stages was noted in traps placed near refrigerators, food stores, taps and microwave cookers.

This was a results of their physiology and tendency to hide from people's sight. Apart from the German cockroach the traps caught also other synanthropic insects like the oriental cockroach, silverfish, moths or house mice (Photo 2). The latter are attracted to such trap by easy access to highly protein food such as immobilised insects.

Performed experiments showed that glue traps attracted more males than females (Fig. 1) which was especially visible when the insects had been starved before [18, 19]. It is important due to a high reproducibility of cockroaches (Fig. 1). Up to 40 young may hatch from one cocoon.

A big problem presented by cockroaches is their ability to colonise new areas and a lack of territoriality [20]. *B. germanica* unlike other invertebrates and vertebrates is not a territorial animal and most often occupies places with easy access to food and water.

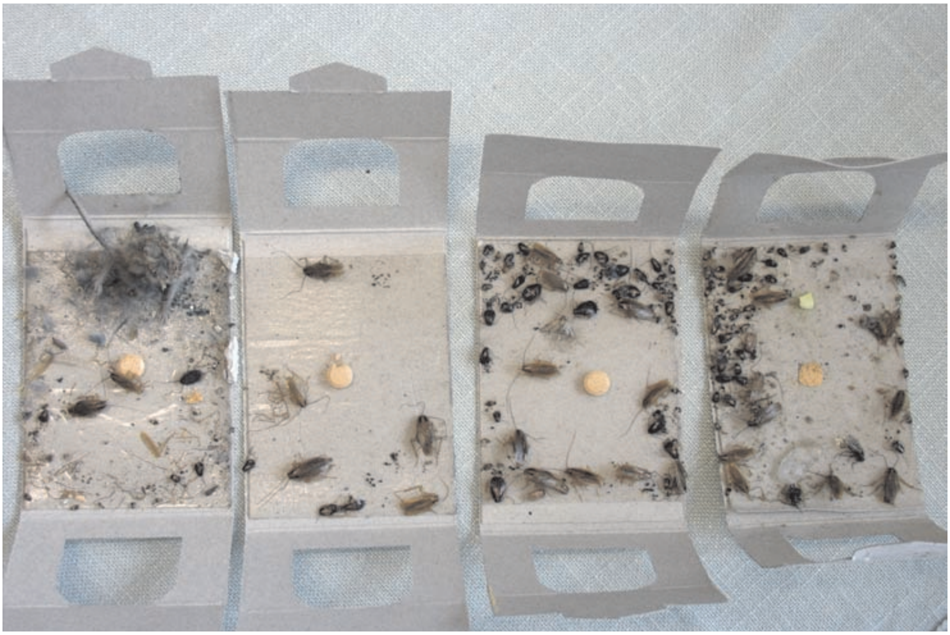

Photo 1. The German cockroach (*Blattella germanica*) in pheromone-glue traps from an apartment

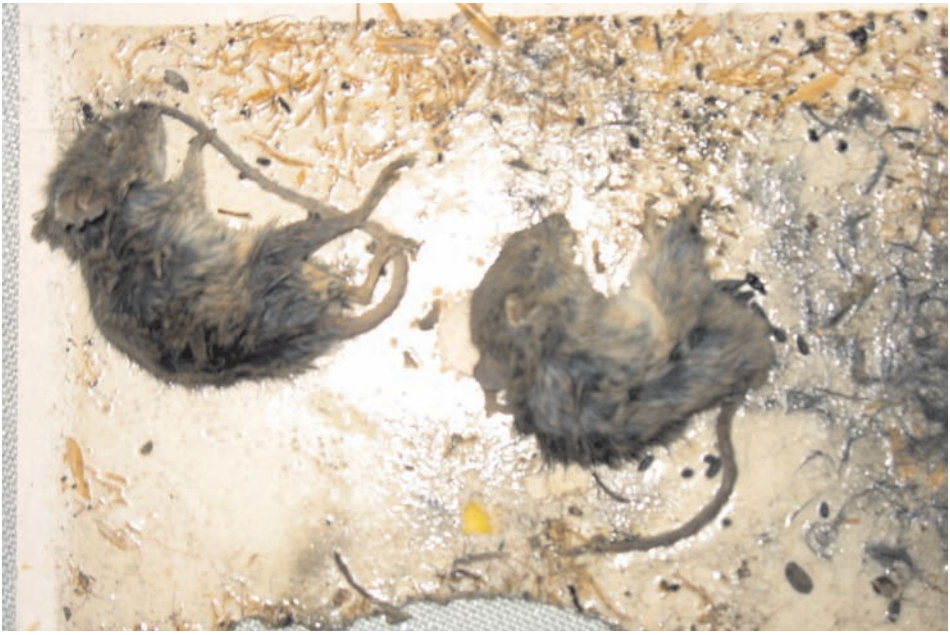

Photo 2. Glue trap from a shop with caught house mice (visible traces of feeding by other individuals can be seen at the bottom)

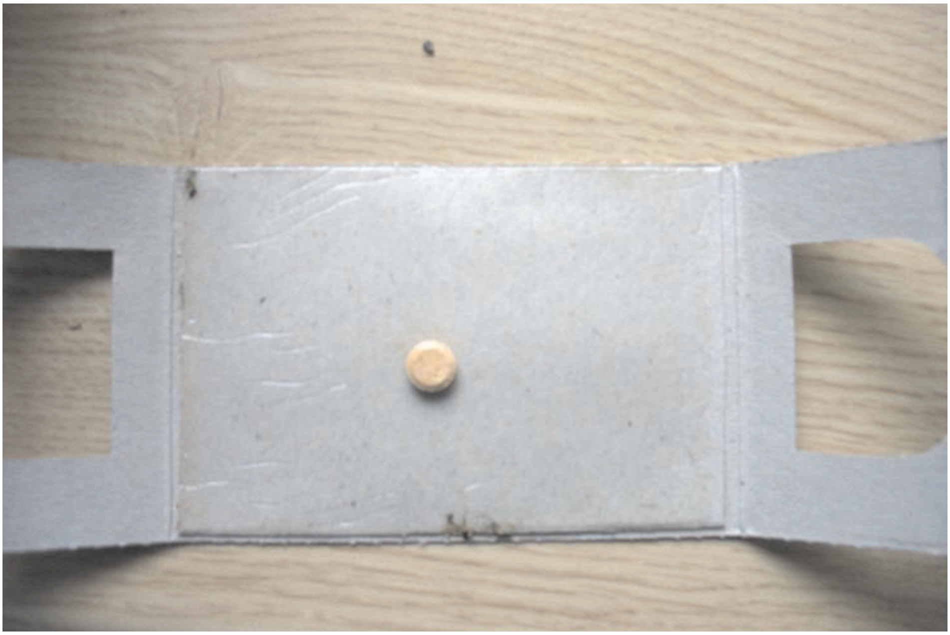

Photo 3. Pheromone-glue traps from hospital kitchen after application insecticides

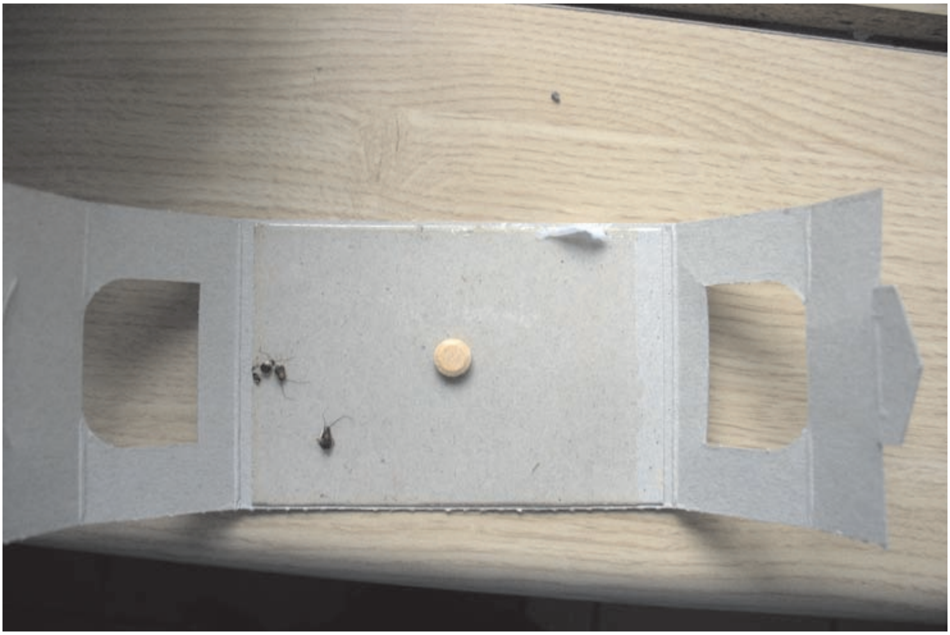

Photo 4. Pheromone-glue traps from an apartment after application insecticides

The factor that determines its occurrence is also a possibility of finding a hiding place to wait for the end of human activity. Cockroaches often hide near generators, in thick curtains and in the casing of household goods.

In contrast with laboratory studies, more larvae and nymphs were found in samples obtained in the field (Fig. 1). This finding confirmed the observations made by Stejskal et al [21] who used artificial barriers on the way to traps. Studies carried out in Warsaw hospitals showed also a higher efficiency of pheromone-glue traps in catching cockroaches as compared with chemical means containing permetrin, deltametrin or other active substances [7, 13, 14, 24]. Pheromone-glue traps showed primarily where to expose chemical means. On analysed grounds pest extermination was done after sampling due to finding many cockroaches and rodents (Fig. 1). After chemical treatment glue traps were exposed again. The traps caught no or a few insects, mainly nymphs (Photos 3 and 4).

Application of insecticides against cockroaches results in health effects in the users of rooms where chemical control means are used [9, 25]. In such case food stored or prepared in a given place becomes also contaminated [15, 16, 26]. Moreover, the insects are good food for rodents (Photo 2) which apart from insects are a serious problem for the service and food processing industries [26].

Summary

Performed studies showed that using pheromone-glue traps allowed for estimating the structure of caught insects. The nymphs of the German cockroach and larvae newly hatched from cocoons dominated there. The density of insects in a trap enabled application of appropriate killing agents in a given area. Consequently, this decreases the contamination of a given area by insecticides and decreases a chance of appearance of other synanthropic organisms.

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METODY KONTROLI I ZWALCZANIA SYNANTROPIJNYCH KARACZANÓW (*Blattella germanica* L.) W RÓŻNYCH EKOSYSTEMACH MIEJSKICH

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Abstrakt: Karaczan niemiecki (*Blattella germanica* L.) jest gatunkiem wszystkożernym, żywi się resztkami ze stołu, karmą dla zwierząt, nie gardzi także oprawami książek. Obecność populacji prusaków wokół struktur miejskich pozwala tym szkodnikom rozmnażać się i doprowadzać do wzrostu ich populacji w różnych ekosystemach synantropijnych.

Intensywny rozwój populacji prusaków jest jedną z głównych przyczyn alergii, astmy oskrzelowej i innych chorób u ludzi. Dodatkowo prusaki należą do organizmów przenoszących choroby i bakterie na swoim ciele oraz w swoich odchodach. Z tego względu kontrola inwazji karaczanów nie jest tylko kwestią estetyki, ale także ochroną zdrowia.

W niniejszej pracy podjęto się oszacować skład i liczebność owadów występujących w różnych ekosystemach synantropijnych. W tym celu wykorzystano pułapki feromonowo-klejowe. Następnie na ich podstawie zastosowano środki owadobójcze zwalczające je. Wykorzystując pułapki lepowe na bazie feromonów rozłożonych w wybranych punktach, takich jak szpital warszawski, prywatne mieszkanie oraz piekarnia, spróbowano prześledzić zmianę strukturową karaczanów. Na łapanych pułapkach przeważały larwy, następnie samce, w mniejszym stopniu łapały się samice. U samic stwierdzano wystąpienie kokonu, dlatego miało to wpływ na liczbę larw. Oprócz tego na pułapkę lepową łapały się inne zwierzęta, takie jak: karaczan wschodni, muchy, mrówki oraz myszy domowe zwabione łatwym dostępem do pokarmu.

Słowa kluczowe: synantropy, karaczan wschodni (*Blatta orientalis*) i karaczan niemiecki (*Blattella germanica*), metody zwalczania

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CHARACTERISTICS OF INDICATORY ALGAE AGAINST THE BACKGROUND OF PHYSICAL-CHEMICAL CONDITIONS IN SMALL WATER BODIES ON THE EXAMPLE OF AN EXCAVATION IN BIESTRZYNNIK

CHARAKTERYSTYKA GLONÓW WSKAŹNIKOWYCH NA TLE WARUNKÓW FIZYCZNO-CHEMICZNYCH W MAŁYCH ZBIORNIKACH WODNYCH NA PRZYKŁADZIE WYROBISKA W BIESTRZYNNIKU

Abstract: The paper presents the results of the researching of microflora (phytobenthos and plankton) and physical-chemical indicators in the water region created after extraction of sand in the locality of Biestrzynnik. The excavation is not a place for rest and recreation. It used to be available for anglers only for a period of several years. The water region has a well developed littoral zone and numerous species of fish attractive for anglers are found in its waters. Samples for microscopic examination and physical-chemical examinations of water were collected. The participation of indicatory species was 50 %. They belonged to *Bacillariophyceae*, *Chlorophyta*, *Cyanophyceae* and *Chrysophyceae.* Among them, species from the ecological group of saproxenes were dominant. With regard to adopted 5-degree scale, *Cymbella ventricosa*, *Nitzschia hungarica*, *Navicula radiosa*, *Cocconeis placentula*, *Nitzschia acicularis*, *Nitzschia hungarica*, *Cosmarium botrytis* had very large population. The results of physical-chemical analyses indicated low polluted water. Selected taxa of indicatory algae with large populations were linked with the values of water pollution indicators. The algae mainly belonged to the group of saproxenes and singly to saprophiles. The examined water body has natural, aesthetic and recreational values.

Keywords: phytomicrobenthos, diatoms, index organisms, water quality, physical and chemical indexes

The examined excavation in Biestrzynnik (a village in Opole province, municipality of Ozimek) is located about 10 kilometres north-east of the locality of Turawa near a storage reservoir (impoondment lake). The reservoir, together with surrounding forests, is a part of Protected Landscape Area. In this area numerous species of wild animals are found, *ia* roe-deer, beaver, wild boar and heron. The area where the village of Biestrzynnik is located is a part of Stobrawsko-Turawskie Forests complex.

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The aim of the conducted research was to determine whether and to what extent the values of physical-chemical indicators and the composition of plant organisms in benthos and plankton change. The paper presents the characteristics of indicatory taxa of numerous populations in relation to the values of water pollution indicators.

Description of the research area

Even in the 1980s in the XX century a sand mine operated in Biestrzynnik. The material was obtained with the use of open-cast method. Some small water bodies were created in former sand excavations, including several fishponds. The water regions are situated below underground water level, whose table is at the depth of 1.3–2.5 metres [1]. The examined excavation is filled mainly with ground water and rainwaters. It is a 2-hectare water body without flow. The average depth is 2 metres, and the maximum is 4 metres. The water body is surrounded by a mixed forest with prevailing pine (Fig. 1 and 2).

The excavation is not open for general recreational use. In the years 1995–2005 the water body was only available for anglers, whose admission and fishing were under control. The lure of fish was allowed. The times of fishing were a period of an intense development of watermilfoil (*Myriophyllum* sp.) which occupied a lot of places, creating underwater meadows.

From the beginning of the 1990s a rational stocking of fishponds was implemented, which resulted in the presence of numerous fish species attractive for anglers: rudd (*Scardinius erythrophthalmus*), roach (*Rutilus rutilus*), carp (*Ciprinus carpio*), bream

Fig. 1. Research area in Biestrzynnik – water body (photo by M. Ostrowska)

Fig. 2. A part of a developed excavation in Biestrzynnik (photo by M. Ostrowska)

(*Abramis brama*), perch (*Perca fluviatilis*), pike-pearch (*Sander lucioperca*), pike (*Esox lucius*), eel (*Anguilla anguilla*), ide (*Leuciscus idus*), crucian (*Carassius carassius*), white amur (*Ctenopharyngodon idella*).

The water body has a well-developed littoral zone broadleaf cattail (*Typha latifollia*) and narrowleaf cattail (*Typha angustifolia*), common reed (*Phragmites communis*), manna grass (*Glyceria aquatica*), sweet flag (*Acorus calamus*), sedges (*Carex* sp.), spike rush (*Heleocharis palustris*), common rush (*Juncus conglomeratus*), soft rush (*Juncus effusus*) and meadow rush (*Juncus inflexus*). In water, watermilfoil (*Myriophyllum* sp.) is dominant, and shining pondweed (*Potamogeton luceus*) and various-leaved pondweed (*Potamogeton gramineus*) are also found.

Nearby the water body, kingfishers (*Alcedo atthis*) reside, mallards (*Anas platyrhynchos*) stop during flights, as well as black-headed gulls (*Larus ridibundus*). There are a lot of edible frogs (*Rana esculenta*), and grass snakes (*Natrix natrix*) are found in water. Insolated edges of the excavation are the residence of sand lizards (*Lacerta agilis*), and on the forest margin blindworm (*Anguis fragilis*) resides.

Material and methods

Samples for microscopic and physical-chemical examinations of water were collected from 1997 to 2006. The researching did not spread over the whole vegatation- and non-vegetation seasons.

Microbenthos was collected in the same place regardless of water level from the bottom of the reservoir covering the area of about 10 cm^2. Plankton was sampled with a plankton net made of miller's gauze number 25 by pouring 50 litres of water through it. In a laboratory, three liquid microscopic preparations were made from each sample. 2–3 drops of sludge or sample water with plankton were placed on a slide and the solution was covered with 24 × 24 mm cover glass. The species were identified, individual specimen were counted in each preparation with the magnification of 200 and 400 x. Dry preparations were also made for precise marking of diatoms [2–4]. The algae were tested with the qualitative-quantitative method in a 5-degree scale, examining the whole glass with the magnification of 200 x, and species were marked on the basis of the keys of several authors: [2, 5–9]. Basic groups and species of benthic and planktonic algae were listed and compared.

Samples of water for analyses were collected 4 metres away from the shore at the depth of about 50 cm with Ruttner water sampler. The range of the analysis of physical--chemical indicators of water included: the temperature of water, reaction, dissolved oxygen, biochemical oxygen demand (BOD_5), forms of nitrogen and phosphorus, calcium, iron [10]. Marking was done with a MERCK laboratory set for water examination and a photometer.

The results and discussion

In the water body in Biestrzynnik, 126 species of algae were identified in phytobenthos and plankton altogether (Fig. 3). 63 indicators of water quality were found. Saproxenes were dominant – 50 species, which accounts for 79 % of all indicators (Fig. 4), (Table 1).

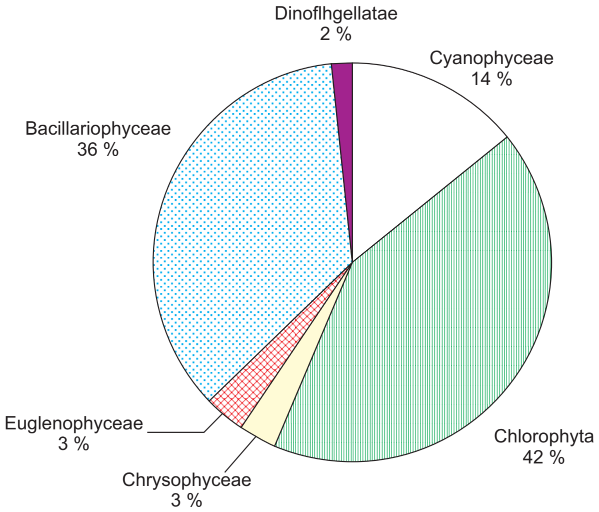

Fig. 3. Higher systematic units at algae in the excavation in Biestrzynnik

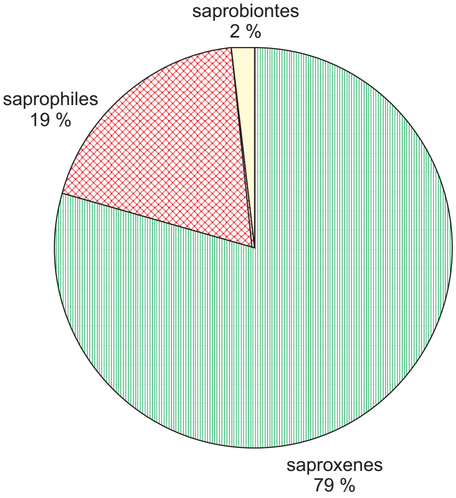

Fig. 4. Indicatory algae in the excavation in Biestrzynnik

Table 1

The list of benthic and planktonic indicatory algae in the excavation

Systematic unit	Ecological unit	Benthos	Plankton
CYANOPHYCEAE			
Anabaena spiroides Klebahn	sn	+	
Aphanizomenon flos-aquae (L.) Ralfs	sn	+	+
Microcystis aeruginosa flos-aquae Kützing	sn	+	+
Nostoc linkia (Roth) Born. et Flah.	sn	+	
Oscillatoria chalybea (Mertens) Gomont.	sl	+	+
Oscillatoria princeps Vaucher	sl	+	
Oscillatoria splendida Greville	sl	+	
Oscillatoria tenuis Agardh.	sl	+	
Pseudanabaena constricta (Szafer) Lauterborn syn.	st	+	
CHLOROPHYTA			
Chlorococcales			
Ankistrodesmus falcatus (Corda) Ralfs.	sn	+	
Crucigenia tetrapedia (Kirchn.) W. et G.S. West	sn	+	
Pediastrum boryanum Menegh.	sn	+	
Pediastrum duplex Meyen.	sl	+	
Scenedesmus acuminatus (Laherh.) Chodat.	sn	+	
Scenedesmus quadricauda (Turp) Breb.	sn	+	
Chaetophorales			
Stigeoclonium tenue (Ag.) Kütz.	sl	+	

Table 1 contd.

Systematic unit	Ecological unit	Benthos	Plankton
Ulothrichales			
Ulotrix zonata Kütz.	sn	+	
*Cladophora glomerat*a (L.) Kütz.	sn	+	+
Conjugatophyceae			
Closterium acerosum (Schrank) Ehrenb.	sl	+	+
Closterium ehrenbergii Menegh.	sn	+	
Cosmarium botrytis Menegh.	sn	+	+
Spirogyra crassa (Kützing) Czurda	sn	+	
CHRYSOPHYCEAE			
Dinobryon divergens Imhoff	sn	+	+
Synura uvella Ehrenberg	sn	+	
Uroglena volvox Ehrenberg	sn	+	+
EUGLENOPHYCEAE			
Euglena acus Ehr.	sn	+	
Euglena viridis Ehr.	sl	+	
BACILLARIOPHYCEAE			
Centrophycideae			
Melosira granulata (Ehr.) Ralfs.	sn	+	
Pennatophycideae			
*Amphora ovali*s Kütz.	sn	+	
Asterionella formosa Hass.	sn	+	
Caloneis amphisbaena (Bory) Cl.	sn	+	
Cocconeis placentula Ehr.	sn	+	+
Cymatopleura elliptica (Breb.) W. Sm.	sn	+	
Cymbella cistula (Hemp.) Grun.	sn	+	
Cymbella ventricosa Kütz.	sn	+	
Diatoma elongatum (Lyngb.) Ag.	sn	+	+
Diatoma vulgare Bory	sn	+	
Epithemia turgida (Ehr.) Kütz.	sn	+	
Epithemia sorex Kütz.	sn	+	
Fragilaria capucina Desm.	sn	+	
Fragilaria construens (Ehr.) Grun.	sn	+	
Fragilaria crotonensis Kitt.	sn	+	
Gomphonema constrictum Ehr.	sn	+	
Gomphonema parvulum (Kütz) Grun.	sn	+	
Meridion circulare Ag	sn	+	
Navicula cryptocephala Kütz.	sl	+	
Navicula exiqua (Greg.) O. Mull	sn	+	
Navicula gracilis Ehr.	sn	+	

Table 1 contd.

Systematic unit	Ecological unit	Benthos	Plankton
Navicula radiosa Kütz.	sn	+	
Navicula viridula Kütz.	sl	+	
Nitzschia acicularis W. Sm.	sl	+	
Nitzschia hungarica Grun.	sn	+	
Nitzschia sigmoidea (Ehr.) W. Sm.	sn	+	
Nitzschia vermicularis (Kütz.) Grun.	sn	+	
Nitzschia palea (Kütz.) W. Sm.	sl	+	
Pinnularia maior (Kütz.) Cl.	sn	+	+
Stauroneis phoenicentron Ehr.	sn	+	
Suriella ovata Kütz.	sn	+	
Synedra acus Kütz.	sn	+	
Synedra ulna (Nitzsch.) Ehr.	sn	+	+
Tabellaria fenestrata (Lyngb.) Kütz.	sn	+	
Tabellaria flocculosa (Roth.) Kütz.	sn	+	+
DINOFLHGELLATAE (PYRROPHYTA)			
Ceratium hirundinella (O.F.M.) Bergh.	sn	+	+

sn – saproxene, sl – saprophile, st – saprobiont.

They belonged to *Bacillariophyceae*, *Chlorophyta*, *Cyanophyceae* and *Chrysophyceae*. *Cymbella ventricosa*, *Navicula radiosa*, *Cocconeis placentula*, *Nitzschia acicularis*, *Nitzschia hungarica*, *Cosmarium botrytis* were numerously represented in the samples with regard to adopted 5-degree scale [2, 9].

The values of selected physical-chemical indicators in the water of the region were as follows:

- pH: 6.8–8.2.
- Dissolved oxygen content: 8.0–13.0 $mgO_2 \cdot dm^{-3}$.
- Water temperature: 6.5–24 °C.
- Biochemical oxygen demand in waters of the river: 0.3–3.8 $mgO_2 \cdot dm^{-3}$.
- Ammonium nitrogen: 0.039–0.16 $N\text{-}NH_4\,mg \cdot dm^{-3}$, ammonia: 0.05 $mgNH_4 \cdot dm^{-3}$.
- Nitrate(III) nitrogen value: 0.003–0.0076 $mgN\text{-}NO_2 \cdot dm^{-3}$, nitrates(III) in concentration 0.01–0.025 $mgNO_2 \cdot dm^{-3}$.
- Nitrate nitrogen: 0.45–1.81 $mgN\text{-}NO_3 \cdot dm^{-3}$. Nitrates(V): 18–23 $mgNO_3 \cdot dm^{-3}$.
- Phosphates content: 0.032–0.1 $mgPO_4 \cdot dm^{-3}$.
- Total iron: in concentration 0.01–0.23 $mgFe \cdot dm^{-3}$.
- Calcium concentration ranged: 12–28 $mgCa \cdot dm^{-3}$.

Subject to analysis were selected species of indicatory algae [2, 9, 11] represented by large populations in relation to values of water pollution indicators. The algae mainly belonged to the group of saproxenes and singly to saprophiles and were represented by *Chlorophyta*, *Bacillariophyceae*, *Cyanophyceae* i *Chrysophyceae*:

Cosmarium botrytis is a widely spread species resistant to organic pollution [9]. It was present in large numbers in the reservoir when the values of physical-chemical indicators equalled: pH 7.8–8.2, dissolved oxygen content 8.0–8.5 $mgO_2 \cdot dm^{-3}$, BOD_5 within the limits 1.0–1.2 $mgO_2 \cdot dm^{-3}$ and the content of nitrates(V) 18 $mgNO_3 \cdot dm^{-3}$, phosphates 0.032 $mgPO_4 \cdot dm^{-3}$, and iron 0.01 $mgFe \cdot dm^{-3}$.

Nitzschia acicularis were identified in a very large number only with the following values of selected physical-chemical indicators: pH 6.8–7.2, dissolved oxygen content $mgO_2 \cdot dm^{-3}$, BOD_5 0.2–3.8 $mgO_2 \cdot dm^{-3}$, nitrates(III) concentration 0.025 $mgNO_2 \cdot dm^{-3}$, nitrates(V) concentration 23 $mgNO_3 \cdot dm^{-3}$, iron 0.0l $mgFe \cdot dm^{-3}$ and the lack of phosphates.

Cymbella ventricosa was numerously represented on the research stand with the pH slightly above 8, oxygen content 8.5 $mgO_2 \cdot dm^{-3}$, BOD_5 1.0 $mgO_2 \cdot dm^{-3}$ the lack of ammomum nitrogen, nitrate(V) nitrogen content 1.81 $mgN\text{-}NO_3 \cdot dm^{-3}$, phosphates 0.032 $mgPO_4 \cdot dm^{-3}$.

Navicula radiosa is a common benthic species, mainly of the litoral zone of stagnant and flowing waters [9]. It developed most intensely by the pH 8.2, dissolved oxygen content 8.5 $mgO_2 \cdot dm^{-3}$, BOD_5 1.0 $mgO_2 \cdot dm^{-3}$, nitrates(III) 0.003 $mgN\text{-}NO_2 \cdot dm^{-3}$, nitrate(V) nitrogen 1.81 $mgNO_3 \cdot dm^{-3}$ and phosphates 0.032 $mgPO_4 \cdot dm^{-3}$.

Nitzschia hungarica developed very intensely and intensely only by the following values of physical-chemical indicators: pH 7.2–8.2, dissolved oxygen content 8.2–8.5 $mgO_2 \cdot dm^{-3}$, BOD_5 0.3–1.0 $mgO_2 \cdot dm^{-3}$, nitrate nitrogen 0.003 $mgN\text{-}NO_3 \cdot dm^{-3}$, nitrate nitrogen 1.13–1.81 $mgN\text{-}NO_3 \cdot dm^{-3}$and phosphates 0.032 $mgPO_4 \cdot dm^{-3}$.

Cocconeis placentula and *Navicula cryptocephala* were numerously represented only when the physical-chemical indicators in water achieved the following values: pH 7.8, dissolved oxygen – 8.0 $mgO_2 \cdot dm^{-3}$, BOD_5 – 1.2 $mgO_2 \cdot dm^{-3}$, ammonia – 0.05 mg $NH_4 \cdot dm^{-3}$, nitrates(III) – 0.025 $mgNO_2 \cdot dm^{-3}$, nitrates(V) – 18 $mgNO_3 \cdot dm^{-3}$ and iron – 0.01 $mgFe \cdot dm^{-3}$.

Tabellaria flocculosa i *Dinobryon divergens* were numerously represented when the water pH was 6.8, dissolved oxygen content was 13 $mgO_2 \cdot dm^{-3}$, BOD_5 3.8 $mgO_2 \cdot dm^{-3}$, concentration of ammonium nitrogen 0.078 $mgN\text{-}NH_4 \cdot dm^{-3}$ and nitrate(V) nitrogen 0.45 $mgN\text{-}NO_3 \cdot dm^{-3}$.

Oscillatoria splendida and *Oscillatoria tenuis* are species found throughout the year in benthos and plankton of stagnant and flowing waters [9]. They developed intensely in the reservoir when the water pH was 7.2, dissolved oxygen content 10.5 $mgO_2 \cdot dm^{-3}$, BOD_5 1.5 $mgO_2 \cdot dm^{-3}$, ammonium nitrogen concentration 1.5 $mgN\text{-}NH_4 \cdot dm^{-3}$, nitrate(III) nitrogen 0.008 $mgN\text{-}NO_2 \cdot dm^{-3}$, nitrate(V) nitrogen 1.81 $mgN\text{-}NO_3 \cdot dm^{-3}$, phosphates 0.1 $mgPO_4 \cdot dm^{-3}$and iron – 0.23 $mgFe \cdot dm^{-3}$.

Aphanizomenon flos-aquae is a common alga that forms blooms in water bodies in summer [9]. An intense development of this blue-green alga in the excavation took place in June 1997, when water pH was 6.8, dissolved oxygen content 8.2 $mgO_2 \cdot dm^{-3}$, BOD_5 1.8 $mgO_2 \cdot dm^{-3}$, ammonium nitrogen concentration 0.039 $mgN\text{-}NH_4 \cdot dm^{-3}$.

In the researched reservoir, out of 53 taxa of green algae there were 23 species of *Chlorococcales*, which accounted for 43 % of the total number of this class of algae. The presence of species from the order of *Chlorococcales* may be connected with a greater concentration of nitrogen compounds in water [12]. Blue-green algae, on the other hand, need a considerable concentration of phosphorus to develop. The low ratio

N : P is favourable for them [13]. A smaller number of *Cyanophyceae* species in relation to *Chlorococcales* species (23) observed in tests suggests a lower content of phosphorus compounds in comparison with nitrogen compounds.

Some species of diatoms indicate a good oxygenation of water, especialIy *Cymbella* and *Fragilaria* are considered to be indicators of a large oxygen content [2, 5, 7, 14]. Species indicating good oxygenation of water in a water region: *Meridion circulare*, *Cymbella cistula*, *Fragilaria construens*, *Cymbella ventricosa*, *Diatoma vulgare*, *Diatoma elongatum*, *Navicula radiosa*, *Fragilaria capucina* were found in the samples.

Among species of algae occurring mainly in polluted waters, representatives of *Euglena,* blue-green algae of *Oscillatoria* type and species of diatoms *Nitzschia acicularis*, *Nitzschia palea* were identified. The populations of these species were not significant.

Conclusions

Chlorophyta and *Bacillariophyceae* were the basic groups of alga during the examinations of the water of the reservoir, with the largest number of types and species and the most frequent occurance of their populations in large numbers.

The participation of indicatory species was 50%. Among them, species from the ecological group of saproxenes were dominant. The remaining indicatory species belonging to other ecological groups occurred sporadically and in small populations. On the basis of species composition of algae and their indicatory value, the waters of the examined reservoir can be regarded as low polluted. Indicatory algae significantly represented in the reservoir are: *Cosmarium botrytis*, *Nitzschia acicularis*, *Cymbella ventricosa*, *Navicula radiosa*, *Nitzschia hungarica*, *Cocconeis placentula*, *Navicula cryptocephala*, *Tabellaria flocculosa*, *Dinobryon divergens*, *Aphanizomenon flos-aquae*, *Oscillatoria splendida* and *Oscillatoria* tenuis. They belonged mainly to saproxenes.

Ranges of values of physical-chemical indicators in the years of the research conducting were at a low level. The results of physical-chemical analysis indicated insignificant variability of water quality. The water reaction did not favour the development of acidophilic species of algae. Environmental conditions (water poor in nutrients) did not favour the development of numerous species of algae.

The reservoir has natural, aesthetic and recreational value. It seems proper to take these types of water ecosystems into consideration in hydrobiological research.

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CHARAKTERYSTYKA GLONÓW WSKAŹNIKOWYCH NA TLE WARUNKÓW FIZYCZNO-CHEMICZNYCH W MAŁYCH ZBIORNIKACH WODNYCH NA PRZYKŁADZIE WYROBISKA W BIESTRZYNNIKU

Zakład Kształtowania Środowiska
Uniwersytet Opolski

Abstrakt: Praca prezentuje badania mikroflory (fitobentosu i planktonu) oraz wskaźników fizyczno-chemicznych wody akwenu powstałego po wydobyciu piasku w miejscowości Biestrzynnik. Wyrobisko nie jest miejscem wypoczynku i rekreacji. Było jedynie przez kilka lat udostępnione dla wędkarzy. Akwen ma silnie rozwiniętą strefę brzegową, a w wodzie jest wiele atrakcyjnych dla wędkarzy gatunków ryb. Pobierano próbki do badań mikroskopowych i fizykochemicznych wody. Udział gatunków wskaźnikowych wynosił 50%. Należały do *Bacillariophyceae, Chlorophyta, Cyanophyceae i Chrysophyceae*. Wśród nich przeważały gatunki z grupy ekologicznej saproksenów. Bardzo liczne populacje w próbkach pięciostopniowej skali miały: *Cymbella ventricosa*, *Nitzschia hungarica*, *Navicula radiosa*, *Cocconeis placentula*, *Nitzschia acicularis*, *Cosmarium botrytis*. Wyniki analizy fizyczno-chemicznej wskazywały na mało zanieczyszczoną wodę. Powiązano z wartościami wskaźników zanieczyszczenia wody wybrane gatunki glonów wskaźnikowych o dużych populacjach. Glony należały głównie do grupy saproksenów i pojedynczo do saprofili. Badany akwen ma walory przyrodnicze, estetyczne oraz rekreacyjne.

Słowa kluczowe: fitomikrobentos, okrzemki, organizmy wskaźnikowe, jakość wody, wskaźniki fizyczno-chemiczne

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Wiesław KOŹLAK[1]

EVALUATION OF POSSIBILITY TO USE SODIUM WATER GLASSES PRODUCED IN POLAND TO REMOVE Ag^+ IONS FROM AQUEOUS MEDIA[*]

OCENA MOŻLIWOŚCI WYKORZYSTANIA KRAJOWYCH SZKIEŁ WODNYCH SODOWYCH DO USUWANIA JONÓW Ag^+ Z MEDIÓW WODNYCH

Abstract: Systems containing sodium water glass produced at Zakłady Chemiczne in Rudniki and silver nitrate were examined by turbimetric method based on obtaining dissolved silver silicate. From turbidimetry waveform we obtained results indicating that silver silicate is formed immediately in initial phase of measuerment and has no further increase of turbidity in time. The values of turbidity and surface tension of studied system depend on the value of Mk. Low-module silicates can be treated as more useful in removing Ag^+ ions from water media.

Keywords: sodium water glasses, silver nitrate, toxicity, turbidimetry, tensiometry, colloidal silver silicates

In the Institute of Chemistry, Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology, the Plock Branch the systematic studies on the properties and structure of aqueous solutions of sodium silicate have been carried out for many years [1, 2].

Sodium water glasses possess innumerable application advantages [3, 4]. It was demonstrated that they can be used for the removal of toxic metals from the environment components, such as surface waters and soils. Because of their abundance and wide uses, the metals are grave pollutants of the ecosystems [5–9]. The harmfulness of metals is based on their ability to accumulate in living organisms and their chronic

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toxicity. The health effects of regular intake of even trace amounts of heavy metals can manifest themselves after several months or even years. Children and ailing people are particularly susceptible to the toxic action of heavy metals [10].

In the Institute of Chemistry, studies were recently undertaken to evaluate the possibility to use sodium water glasses to remove toxic metals from, *ia*, aqueous media.

The aim of this study, being the continuation of widely scoped investigations, is the analysis of the possibility of reaction between different-moduli sodium silicates and Ag^+ ions.

Properties, toxicity and forms of silver ions occurring in waters

The Ag symbol is derived from the Latin name of silver, argentum. Silver (Ag) is a noble metal, rather neutral for living organisms. However, the excess of Ag damages cell membranes and causes the necrosis of liver tissues (similar to the effect caused by the lack of selenium (Se) and vitamin E), influences the concentration of Cu in kidneys and liver when the Wilson illness is ascertained (liver-lenticular degeneracy) and protects RNA from the excess of zinc (Zn). Moreover, the increase of silver amount in food causes the chromatosis of skin and mucous membranes (blue-greyish spots) called “agryria” and not harmful [11, 12].

Ag accumulates in coals (0.1–20 ppm), petroleum, zooplankton (10–20 ppm) and root tissues of some plants (up to 50 ppm). Cow milk contains typically 0.05 ppm of silver which can act as a bactericidal agent. Ag in the concentration of 25 mg/m^3 is toxic for microorganisms.

Silver is a rather rare element, occurring mainly as native silver, argentite (Ag_2S) and cerargyrite (AgCl). Only a small part of silver production comes from silver ores, it is mainly obtained as a co-product in copper or lead production. The main problem related to the production of silver from its ores is the transfer of non-active silver or its insoluble compounds into the solution. It can be achieved by blowing air through the suspension of silver ore in a diluted aqueous solution of sodium cyanide (NaCN). The reaction with native silver can be presented in the following way:

$$4Ag(s) + 8CN^- + 2H_2O + O_2(g) \longrightarrow 4Ag(CN)_2^- + 4OH^- \ [13\text{–}15]$$

If cyanide ions were not present, oxygen would not oxidize silver to a higher oxidation state. In the presence of cyanide ions Ag^+ ion produces strongly bound complex ion, which is stable. In order to reclaim silver from the stable complex it is necessary to use strongly reducing agent, such as metallic aluminum or zinc in alkaline solution. Probably the following reaction takes place:

$$Zn(s) + 2[Ag(CN)_2]^- + 4OH^- \longrightarrow 2Ag(s) + 4CN^- + [Zn(OH)_4]^{2-}$$

Solid silver appears to be nearly white metal because of its high glossiness. It is too soft to be used in pure form in jewelry or mintage, so it is used in alloys with copper.

By alloying silver with copper (10–20 %) an alloy of higher hardness is obtained, while the characteristic gloss of silver is conserved. Coins, jewelry and some other common use items are produced from this alloy.

Because of high price, some of the best properties of silver cannot be fully utilized, which are not exhibited to that extent by any other metal, such as very high thermal and electric conductivity. In the finely pulverized state silver appears to be black.

Silver compounds generally contain silver at +1 oxidation state. Ag^+ does not undergo significant hydrolysis in aqueous solutions, is a good oxidant and produces many complex ions, such as $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$, having linear structure. From the solutions of silver salts, under the action of bases, a brown oxide precipitates:

$$2Ag^+ + 2OH^- \longrightarrow Ag_2O(s) + H_2O$$

With the exception of AgF, silver halides are susceptible to light. That is why they are used to prepare photographic emulsions. The chemistry of photographic process is very complex. The basics of this process generally include: 1) exposure to light, 2) development and 3) fixing [13–15].

Silver as a metal resistant to oxidation is used to cover the surfaces of other, less noble metals. The production of silver coatings is an electrolytic process with the use of bath containing potassium silver dicyanide ($K[Ag(CN)_2]$). Silver plating of glass, employed at the production of mirrors is a chemical process. It occurs by mild heating of plated material in ammoniac solution of silver tartrate [5].

Silver compounds occurring in waters in low concentrations exhibit bactericidal action. In high concentration silver is highly toxic. The possibilities of silver occurrence in waters are low (the concentration of silver in surface waters can not exceed 0.01 mg/dm^3 Ag). The high price of silver causes that industrial plants using silver in their technological processes conduct the regeneration of silver from wastewaters and solid wastes. Silver can sometimes occur in mining waters and waste waters from factories producing photographic materials.

The determination of silver in water should be conducted as early as possible (less than 4 hours) after the collection of samples, because silver can become adsorbed on the walls of the container. If it is needed to store the samples they should be conserved by the addition of nitric acid.

For the determination of silver two methods are applied: rhodanine method and dithizone method [16].

Geochemical properties of silver are similar to those of copper but the frequency in geological structures is *ca* 1000 times lower than for copper. Silver is easily activated during erosion processes and subsequently precipitated in alkaline and sulphur rich environments. Despite its occurrence in mobile cations and anions, silver is bound in environments of $pH > 4$. Silver is partially accumulated biologically and its accumulation in some biolites is observed: 0.1–20 ppm in coals and 0.006–0.3 ppm in petroleum. Concentration of silver in ashes from some hard coals reaches the value even 200 times higher than in sedimentary rocks [11].

Silver in soils is easily sorbed by organic matter and on manganese concretions. Its average concentration in soils is between 0.03 and 0.1 ppm. In soils reach in organic substances the concentration of silver can reach even 2–5 ppm. Because of its low mobility silver is accumulated in surface layers of soils, particularly polluted ones. Highest levels of silver can be found in the areas near the mines of alkali metals. The excess of silver is less harmful for plants growing on organic soils compared with those growing on organic ones.

The source of silver contamination can be galvanizing plants and other factories using the salts of this metal. Also communal wastewaters can introduce increased amounts of silver into soils [11].

There is few data relating to the occurrence of silver in atmospheric air. In the rural areas in England it was found in air in concentrations of 0.2–0.5 ng/m^3 and the fall onto the ground of < 1 g/ha/year. Similar concentration of silver was (0.17 ng/m^3) was found in air near coal fired power plants in the USA, which was related to the emission of ashes.

The attempts to use silver iodide to stimulate the condensation of water vapour in the atmosphere were the cause of periodic increase of silver concentration in air.

Concentration of silver in plants varies from 0.03 to 2 ppm because it is absorbed proportionally to its concentration in soils. Similarly to other heavy metals, silver is accumulated in roots, where its concentration may reach 50 ppm. Highest concentrations of silver are found in mushrooms.

Physiological function of silver is not yet researched but its excess damages cell membranes, inhibiting the absorption of other ions. Silver in the concentration of 5 ppm in bean leaves inhibited its yields while the symptoms of toxicity were not observed. Silver bonds easily with vegetable proteins, particularly with their sulfhydryl groups.

The presence of silver was found in all tissues of sea and land organisms, in concentrations ranging from 0.005 to 0.6 ppm.

Physiological function of silver in animal organisms is not known. The excess of silver causes the necrosis of liver tissues, symptomatically similar to the lack of selenium and vitamin E. It is the effect of antagonism between these two elements. Similar interaction takes place in relation to copper and probably to zinc [11].

Experimental

Sodium water glasses produced in Rudnickie Chemical Plant in Rudniki, Poland were used in this study. Their properties are presented in Table 1.

Table 1

Composition of sodium silicates

Type of water glass	Concentration [% wt.]		Silicate modulus M_k	Density (20 °C) [g/cm^3]	Substances insoluble in water [% wt.]	Chemical formula
	Na_2O	SiO_2				
137	8.9	28.3	3.3	1.38	0.02	$Na_2O \cdot 3.3SiO_2$
149	11.8	33.1	2.9	1.51	0.02	$Na_2O \cdot 2.9SiO_2$
140	10.3	28.9	2.9	1.42	0.02	$Na_2O \cdot 2.9SiO_2$
145	12.4	28.8	2.4	1.47	0.02	$Na_2O \cdot 2.4SiO_2$
150	14.7	28.6	2.0	1.52	0.02	$Na_2O \cdot 2.0SiO_2$

$AgNO_3$ was used as silver salt. Concentration of Ag^+ ions in studied systems was 8 mmol/dm^3.

In this study turbidimetric and tensiometric methods were used.

Turbidimetry is a method used to measure the turbidity of a mixture by the measurement of absorption or dispersion of light on the dispersed particles [18, 19]. The method is based on the measurement of the changes of the intensity of light passed through optically inhomogeneous system.

The measurements were carried out for 20 minutes at the wavelength $\lambda = 610$ nm. The method and apparatus were presented in detail in earlier works [20–23].

Taking into account that the formation of optically inhomogeneous system and its stability depend also on the value of surface tension, this value was also measured. Surface tension is a work needed to unitarily increase the surface, related to intermolecular attraction forces, measured in a SI unit, N/m.

Measurements in this study were carried out with the use of Kruss K100 tensiometer, equipped with a platinum plate. In this method the liquid adhering to the plate is lifted until the moment preceding the breakage of contact between the liquid surface and the plate. At this time the weighing system records the highest value of force.

Results and discussion

Exemplary results of turbidimetric studies in the form of so called turbidity curves are presented in Fig. 1.

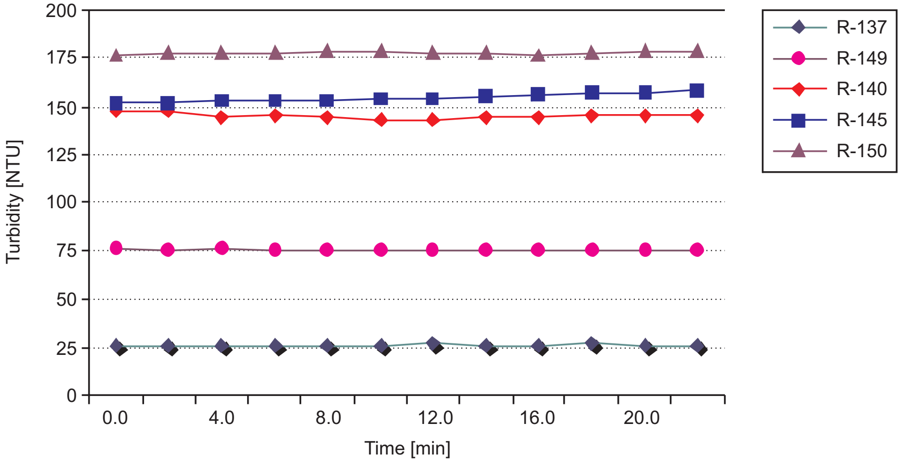

Fig. 1. The dependence between turbidity and time for the systems containing sodium water glasses and $AgNO_3$

From the course of turbidity curves it can be concluded that the silver silicate is formed immediately (t = 0) in the initial phase of measurement and no further increase of turbidity value in time is observed.

The results indicate that there is a correlation between *silicate modulus* M_k and *turbidity* (NTU). In the systems containing silicates of low moduli (150, 145) the turbidity values fall into the range of 150–180 NTU, while silicates of high moduli (137, 149) give the turbidity from 25 to 75 NTU.

These observations allow the conclusion that silicates of low modulus ($M_k < 2.4$) are more useful in this application area.

The results of surface tension measurements are presented in Table 2.

Table 2

The results of surface tension measurements for "sodium water glass – $AgNO_3$" systems

Type of water glass	Surface tension [mN/m]	Standard deviation [mN/m]
R-137 ($M_k = 3.3$)	46.846	0.017
R-149 ($M_k = 2.9$)	47.528	0.021
R-140 ($M_k = 2.9$)	47.959	0.020
R-145 ($M_k = 2.4$)	49.201	0.010
R-150 ($M_k = 2.0$)	50.622	0.040

Basing on the data presented in Table 2 it can be concluded that there is a regularity of changes of surface tension as a function of silicate modulus. The values of surface tension decrease with the increase of M_k.

Obtained results indicate a significant influence of M_k on the behavior of "sodium water glass – $AgNO_3$" systems.

Conclusions

1. Addition of silver salts to sodium water glasses causes the formation of colloidal silver silicates. They are formed in the initial phase of the measurement and no further increase of turbidity in time is observed.
2. The values of turbidity and surface tension of "sodium water glass – $AgNO_3$" systems depend on M_k.
3. For the removal of Ag^+ ions from aqueous media, low-modulus silicates 145 and 150 are more useful.

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OCENA MOŻLIWOŚCI WYKORZYSTANIA KRAJOWYCH SZKIEŁ WODNYCH SODOWYCH DO USUWANIA JONÓW Ag^+ Z MEDIÓW WODNYCH

Instytut Chemii, Wydziału Budownictwa, Mechaniki i Petrochemii w Płocku
Politechnika Warszawska

Abstrakt: Metodą turbidymetryczną polegającą na otrzymywaniu rozpuszczonego krzemianu srebra badano układy zawierające krajowe szkła wodne sodowe produkcji Zakładów Chemicznych w Rudnikach oraz azotan srebra. Z przebiegu krzywych zmętnienia wynika, że krzemiany srebra powstają natychmiast w początkowej fazie pomiaru i nie ma dalszego przyrostu zmętnienia w czasie. Wartość zmętnień i napięcia powierzchniowego badanych układów zależą od wartości M_k. Krzemiany niskomodulowe mozna uznac jako bardziej przydatne w usuwaniu jonów Ag^+ z mediów wodnych.

Slowa kluczowe: szkla wodne sodowe, azotan srebra, toksycznosc, turbidymetria, tensometria, koloidalne krzemiany srebra

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[1] Lowe DF, Oubre CL, Ward CH. Surfactants and cosolvents for NAPL remediation. A technology practices manual. Boca Raton: Lewis Publishers; 1999.

[2] Fasino CR, Carino M, Bombelli F. Oxidant profile of soy standardized extract. In: Rubin R, Stryger CS, editors. Joint Meeting 2001 – Book Abstracts '2001 Year of Natural Products Research'. New York: Harper and Row; 2001.

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