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CHANGES OF TOXICITY AND BIODEGRABILITY OF SULFONAMIDES SOLUTIONS DURING THEIR PHOTOCATALYTIC DEGRADATION

ZMIANY TOKSYCZNOŚCI I PODATNOŚCI NA BIODEGRADACJĘ ROZTWORÓW ZAWIERAJĄCYCH SULFONAMIDY PODCZAS ICH DEGRADACJI METODĄ FOTOKATALITYCZNĄ

Abstract: The aim of this study was to estimate the applicability of the photocatalytic process to: (1) sulfa-drugs degradation in aqueous solutions, (2) a decrease in their toxicity and (3) an increase in their biodegradability. Photocatalytic process initiated by UV-A radiation was carried out in open reactors containing a catalyst (TiO₂ suspension) and solutions of five sulfonamides. After a definite irradiation time, the change of sulfa-drugs concentration in solutions was estimated using HPLC method. Moreover, changes of total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD₅) as well as changes of sulfonamides toxicity relative to *Chlorella vulgaris* were examined. The biodegradability of investigated sulfonamides and their photocatalytic degradation products was determined based on BOD₅/COD ratio. It was found that under experimental conditions all investigated sulfonamides underwent the photocatalytic degradation and the decrease in TOC and COD of sulfa-drugs solutions was observed. Simultaneously, products of this process were less toxic and more biodegradable than initial sulfonamides.

Keywords: sulfonamides, photocatalytic process, TiO₂, biodegradation, ecotoxicity, *Chlorella vulgaris*

Sulfonamides have been commonly used for decades in medicine and veterinary as antibacterial agents. After excretion, they may be introduced into the environment as the unchanged products or as metabolites [1–3]. For these reasons their traces are present in almost all kinds of biotopes [3]. Taking into account their toxicity, the sulfa-drugs can induce changes in ecosystems exposed to their influence and, first of all, can cause generation of drug-resistant in microorganisms, including pathogenic ones.

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In the last decade, the problems concerning the occurrence of sulfa-drugs in the environment are subjects of high interest to researchers. This is evidenced by a very large number of scientific publications and conference communications published each year on this topic but available data often give discrepancies in information and results. These differences concern *i.a.* the estimation of susceptibility of sulfonamides to biodegradability. Published data showed that the values of degradation half-life for these compounds varied from about 2.5 days [4] to even one year [5]. Moreover, results of estimation of the environmental risk caused by these drugs are different [6–8]. These discrepancies form *i.a.* as result of differences in the estimation of sulfonamides ecotoxicity (the results depended on tests duration, type of tested organisms as well as sulfonamide type). For example in the case of sulfadimethoxime the values of $L(E)C_{50}$, determined in test with *Artemia solina* varied from $19,5_{96h}$ to 1866_{24h} mg dm^{-3} [2]. In turn, these values obtained in chronic test toxicity using *Lemna* test, were $10 \mu\text{g dm}^{-3}$ and $81 \mu\text{g dm}^{-3}$ for sulfadiazine [6] and sulfamethoxazole [8], respectively.

Particularly high concentration of sulfonamides (10 mg dm^{-3}) was identified in leachates from municipal landfills [9] and in sewage from stock-farming [2] while directly in liquid manure from animals' farm contained even hundreds mg kg^{-1} [4]. The effective treatment of these wastes may limit, in the considerable level, the propagation of sulfa-drugs in the environment and may eliminate disturbances in local ecosystems caused by their toxicity.

The opinions concerning the possibility of removal of sulfonamides from wastes during routine, biological treatment processes are also divergent [6, 11]. Moreover, the draining of toxic wastes into wastewater treatment plant using biological processes may disturb their effective functioning and it is unlawful. The physiochemical methods (ultramicrofiltration, reverse osmosis or adsorption [6]) used during wastewater treatment seem well founded and correct for sulfonamides. However, the discussed problem is dissolved only partly because the above-mentioned methods generate large amounts of wastes, still containing sulfa-drugs.

For this reason, the search of methods leading to total destruction of pollutants (mineralization) or their partial decomposition (transformation) to less toxic substances, which are easy biodegradable, seem to be proper and right. The authors of POSEIDON project [6] have proposed the fermentation of wastes and their ozonization as the most suitable methods for removal of sulfonamides. However, results of the latest studies have indicated that part of antibiotics still remains in effluents despite the biological treatment (including after fermentation) [12, 13]. In turn, high operating costs of wastewaters treatment using ozone are also barrier limiting their application. The photocatalytic process may be an alternative method leading to the degradation of organic substances. This process can be effective and cause the decomposition of almost all organic compounds occurring in wastes, irrespective from their toxicity and the resistance to biodegradation [14–16]. Under the influence of UV-A irradiation and in the presence of photocatalysts the organic pollutants can undergo total mineralization even to CO_2 , H_2O and inorganic ions [17]. Unfortunately, the total mineralization of pollutants using photocatalytic methods appeared to be too expensive. The overall cost of this process may be decreased by the shortening of its duration and obtaining only

part of the decomposition of sulfonamides to simpler organic compounds. However, this method may be connected with the risk that the obtained semi-products will be characterized by high toxicity and the resistance to biodegradation.

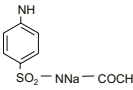
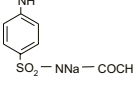
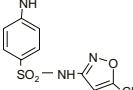
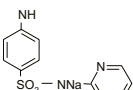
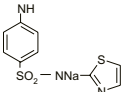
The aim of our work was: (1) the determination of possibility of photocatalytic process application to partial degradation of sulfa-drugs and (2) the estimation of toxicity and susceptibility to biodegradation of the products of this transformation.

Material and methods

All chemicals used throughout this study were analytical grade and their solutions were prepared in distilled water. A commercial TiO_2 from Riedel de Haën was used as catalyst (anatase 100 %, BET surface area of $9\text{--}11 \text{ m}^2 \text{ g}^{-1}$ and residues on filter $> 40 \mu\text{m}$ after dispersion in water $< 0.02 \%$). The photodegradation experiments were carried out using one of five selected sulfonamides (Table 1). TiO_2 powder (250 g dm^{-3}) was added to sulfonamide solutions (100 cm^3 , 0.1 mmol dm^{-3}) and the samples were homogenized for 30 min by means of magnetic stirrers. The applied amount of TiO_2 was established as optimal, based on preliminary experiments.

Table 1

Characteristics of investigated sulfonamides and their determination methods

Sulfonamide ^a	Abbr. in text	Structural formula	$\text{pK}_{\text{a}1}$	$\text{pK}_{\text{a}2}$	Manufacturer, purity	HPLC ^b mobile phase
Sulfanilamide	SN			10.43	POCH S.A. Gliwice, pure	Buffer: 20 mmol dm^{-3} K_2HPO_4 ; pH 8.9 Buffer: $\text{CH}_3\text{CN} - 92:8$
Sulfacetamide (natrium salt)	SA		1.78	5.38	Polfarma $\approx 98 \%$	Buffer: 20 mmol dm^{-3} K_2HPO_4 ; pH 8.9 Buffer: $\text{CH}_3\text{CN} - 92:8$
Sulfa-methoxazole	SM		1.60	5.81	Sigma $> 98.0 \%$	Buffer: 20 mmol dm^{-3} $\text{HCOONH}_4/\text{HCOOH}$; pH 4.0 Buffer: $\text{CH}_3\text{CN} - 1:1$
Sulfadiazine (natrium salt)	SD		2.00	6.48	Sigma $> 99.0 \%$	Buffer: 20 mmol dm^{-3} $\text{HCOONH}_4/\text{HCOOH}$; pH 4.0 Buffer: $\text{CH}_3\text{CN} - 1:1$
Sulfathiazole (natrium salt)	ST		2.36	7.23	Sigma $> 99.0 \%$	Buffer: 20 mmol dm^{-3} $\text{HCOONH}_4/\text{HCOOH}$; pH 4.0 Buffer: $\text{CH}_3\text{CN} - 1:1$

^a common name;

^b the choice of mobile phase was done based on kinetics studies of sulfonamides photodegradation, in the presence of TiO_2 .

The photocatalytic process was carried out in open glass reactors (the exposed surface of samples was 102 cm^2) and was initiated by UV-A light (a four lamps Philips TL-40W/05 with maximum emission at $\lambda = 366 \text{ nm}$; the intensity of UV radiation measured by Parker's actinometer was 2.9 mW cm^{-2}) or with use of the natural sunlight (the total intensity of the natural sunlight measured by luxometer Introl TES-1332 with natural gray filter ($\times 2$) was $\approx 60 \text{ mW cm}^{-2}$). During the whole experiment, the samples had free contact with atmospheric air and were constantly magnetically stirred. The pH value of the irradiated samples were not corrected and ranged from 5.63 (SM) to 7.35 (SA). The temperature of samples was $21 \pm 2 \text{ }^\circ\text{C}$ (during UV irradiation) and $25 \pm 3 \text{ }^\circ\text{C}$ (during natural sunlight irradiation). In order to separate the TiO_2 suspension, after the end of irradiation the samples were centrifuged for 30 min at 4000 RPM.

The concentration determination of sulfonamide remained in samples was performed using HPLC method (HPLC Merck Hitachi, detector UV $\lambda = 254 \text{ nm}$, column Separon SGX C-18, $5 \mu\text{m}$, $250 \times 4.6 \text{ mm}$). The conditions of experimental runs are described in details in Table 1. The degree of mineralization of irradiated samples was calculated based on the measurement of Total Organic Carbon (TOC), using a total carbon analyzer (TOC-5000A, Shimadzu). The values of Chemical Oxygen Demand (COD) of the samples were determined without centrifugation of TiO_2 , using chromate titration method according to HACH 8230 procedure. The values of 5-days Biochemical Oxygen Demand (BOD_5) were determined in Closed-Bottle test using mixed biological population of sewage treatment microbes (inoculum) in accordance with the test procedure described in OECD, method 301D [18a]. The measurement of dissolved oxygen concentration was done following the Winkler titration method. A theoretical oxygen demand (TOD) was estimated in accordance with method 301 D [18a].

The toxicity of sulfonamides and their photodegradation products were tested using a method for the determination of the toxic effects of chemical compounds on the growth on unicellular green alga *Chlorella vulgaris* (*C. vulgaris*) Beij., strain 264, Boehm and Borns 1972/1 (Culture Collection of Algal Laboratory – CCALA, Culture Collection of Autotrophic Organisms of the Institute of Botany, Czechoslovak Academy of Science, Trebon). After the end of irradiation, samples were centrifuged (30 min, 4000 RPM) in order to separate TiO_2 and natant was enriched with the liquid medium as a stock solution and an inoculum of alga was added. Besides cultures with photodegradation products (in solution after irradiation) and the cultures with the sulfonamides (individually added), the control cultures were conducted in parallel. The algal cells were cultivated in 250 cm^3 Erlenmeyer flasks with 50 cm^3 of modified Kuehl-Lorenzen [19] liquid medium (pH 6.5) at $24 \pm 2^\circ\text{C}$, under continuous illumination (3000–4000 lx) and at continuous stirring. Biological activity of cultures was determined by a measurement of absorbance at $\lambda = 680 \text{ nm}$. Growth inhibition and the $\text{EC}_{50(0-48)}$ (effective concentration 50 %) values were calculated according to OECD [18b] and ISO 8692 [20].

Results and discussion

The estimation of the susceptibility of each sulfonamide to photolysis and photocatalytic degradation processes was calculated based on the change in their concentration during

irradiation. Since the photocatalytic degradation processes belong to pseudo first-order reactions, the rate constants values (k) are experimentally determined as the slope of the linear function:

$$\ln(C/C_0) = kt + b \quad (1)$$

where t is reaction time.

The results, calculated from Eq. 1, are presented in Table 2.

Table 2

Reaction rate constants determined during photodegradation of sulfonamides

Sulfonamide	k [min ⁻¹]		
	UV-A without TiO ₂	UV-A with TiO ₂	sunlight with TiO ₂
SN	0.0016 ± 0.0016	0.031 ± 0.003	0.123 ± 0.008
SA	0.0005 ± 0.0022	0.013 ± 0.001	—
SM	0.0004 ± 0.0003	0.030 ± 0.004	—
SD	0.0005 ± 0.0008	0.013 ± 0.001	0.016 ± 0.009
ST	110 ⁻⁵ ± 0.0003	0.020 ± 0.002	—

It was found that the irradiation of solutions of each sulfonamides by UV-A light without TiO₂ did not induce any observable degradation. In this process, the reaction rate constants were basically nearly zero (Table 2). So it was concluded that under the studied conditions practically none of these sulfa-drugs did undergo photolysis. The phenomenon called photolysis was previously described for three from the investigated sulfonamides, namely for SM, ST [21] and SA [22] but this process was proceeded under conditions different than those used in our studies. In the case of ST and SM, it was carried out in the presence of atomic oxygen, free HO[•] radicals and Rose Bengales (a dye with photosensitizing properties), while the SA photolysis proceeded with the use of UV radiation of a greater energy.

During UV-A irradiation and in the presence of TiO₂ suspension all sulfonamides underwent fast degradation (Table 2). The degree of sulfonamide degradation was calculated using the equation:

$$DR = [1 - (C/C_0)] \cdot 100 \% \quad (2)$$

where: DR – degradation rate [%]; C_0 – the initial sulfonamide concentration; C – the determined sulfonamide concentration. The obtained DR values are presented in Fig. 1.

In the case of SN and SM this process proceeded more easily however using appropriately long irradiation time it was obtained high, almost 100 % degradation of all sulfonamides. The significant differences in photocatalytic degradation rate of each sulfa-drugs may be connected with the differences in their affinity to the surface of TiO₂ particles. Since the used TiO₂ had a point of zero charge at pH 3, so in our

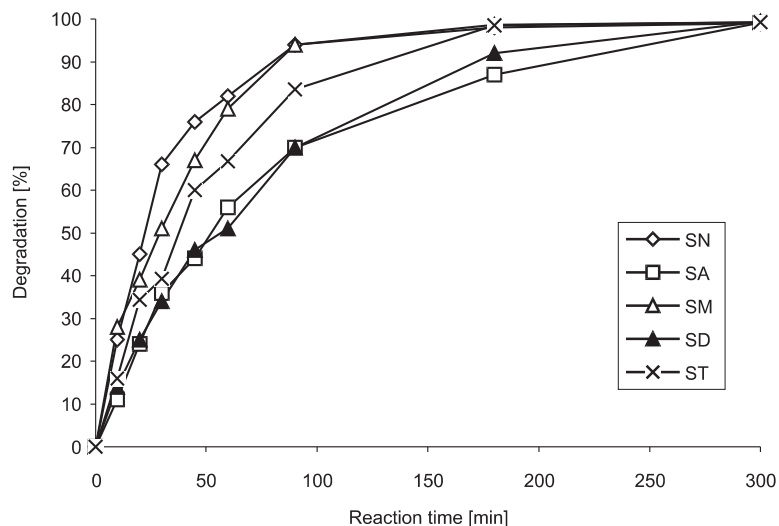


Fig. 1. Dynamics of degradation of sulfonamides during UV-A irradiation in the presence of TiO₂

experiments its surface had a negative charge. This fact can explain why slightly dissociated molecules of SN and SM (Table 1) undergo the photocatalytic degradation in the presence of TiO₂. On the other hand, others sulfonamides occurring in solutions as anions (coming from well-dissociated sodium salts) practically did not undergo any the degradation. In accordance with this hypothesis, the neutral molecules of SN and SM should be adsorbed onto TiO₂ surface in the highest level. However, before beginning irradiation but after addition of TiO₂ and after homogenization of samples for 30 min, the decrease in sulfonamide concentration (its adsorption) was observed in none of the investigated cases. The importance is that the photocatalytic sulfonamides degradation is also possible in solutions irradiated by solar light. This fact was confirmed by results of reactions with SN and SD (Table 2).

It is known that nearly total degradation of sulfonamides is not evidence of their simultaneous mineralization. On the basis of TOC determination it was found that after 300 min of irradiation the sulfonamides solutions contained from 30 to 75 % of initial concentration of organic carbon. There is the evidence that some of the intermediate organic products of sulfa-drugs degradation were remained in these solutions.

The COD value is an important parameter used as a measure of the oxygen needed for the complete oxidation of all organic compounds content in solution. The percentage decrease in COD values was estimated according to the equation:

$$Y = \left(1 - \frac{\text{COD}}{\text{COD}_0} \right) \cdot 100\% \quad (3)$$

where: Y – the decrease in COD value [%]; COD₀ – the value determined for the initial sulfonamide solution; COD – the value determined for solution after the end of irradiation.

In irradiated sulfonamide solutions containing TiO_2 the decrease in COD values proceeded considerably slower than the photocatalytic degradation. However, for the majority of the investigated sulfonamides after 300 min of irradiation the degree of COD removal was ranged from 82 to 98 % while for SD was about 40 % (Fig. 2).

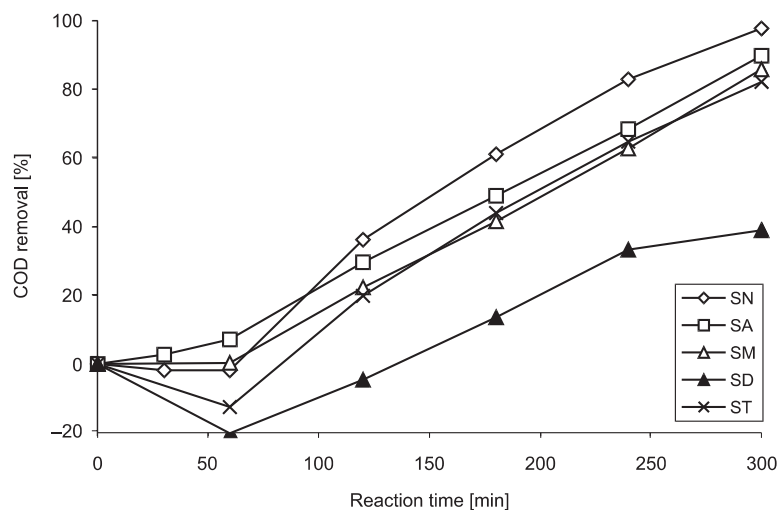


Fig. 2. Changes of COD of sulfonamides during UV-A irradiation in the presence of TiO_2

In our experiment some anomaly was observed. The COD values of SD and ST solutions increased after short-term irradiation (0–60 min). This phenomenon may explain that degradation products which form in the beginning stage of photocatalytic process are oxidized easier than the initial sulfonamides.

The BOD_5/COD ratio can be used to estimate the susceptibility to biodegradation (biodegradability) of organic compounds, including the investigated sulfa-drugs and products of their photocatalytic degradation. The percentage susceptibility to biodegradation of the investigated sulfonamides and products of photocatalytic reaction was calculated using the equation:

$$\text{BD} = \frac{\text{BOD}_5}{\text{COD}} \cdot 100\% \quad (4)$$

where: BD – biodegradability [%]; BOD_5 , COD – the values determined for the same solution after the end of irradiation.

The obtained results of biodegradability are presented in Fig. 3. Before irradiation, all investigated sulfonamides solutions had the BOD_5 nearly zero, (lower than 1.5 % of TOD) and very low BOD_5/COD ratio. This is the evidence that under experimental conditions these sulfa-drugs are completely biodegradation-resistant. However, even short-term irradiation (0–180 min) caused an increase of BOD_5/COD ratio. It may indicate that the organic products of degradation, forming under these conditions, are

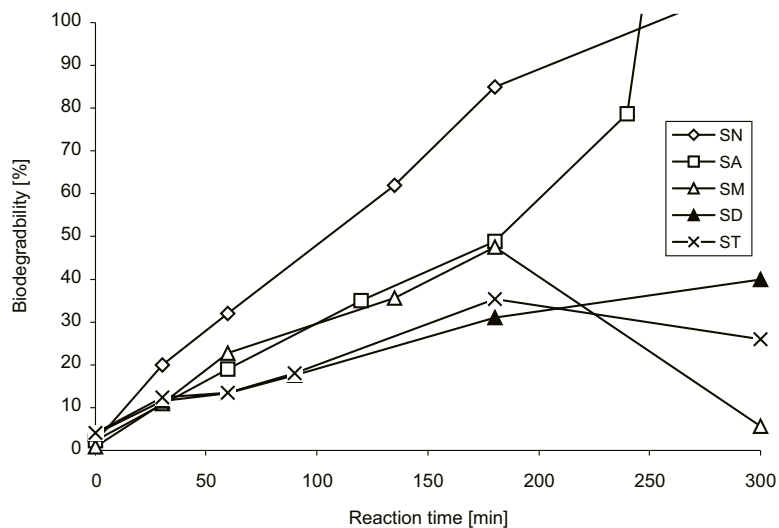


Fig. 3. Changes of biodegradability of sulfonamides solutions during UV-A irradiation in the presence of TiO_2

biodegradable, contrary to initial sulfonamides. The results obtained during long-term irradiation of samples (300 min) cause some problems with their interpretation. This fact may be caused by a high mineralization degree and a relatively low precision of COD determination that is obtainable at so low values of this parameter.

In order to estimate the ecotoxicity of sulfa-drugs and products their photocatalytic degradation, the test with *C. vulgaris* was carried out. The obtained $\text{EC}_{50(0-48)}$ values are presented in Fig. 4. In experiments, the toxicity of initial solutions containing one

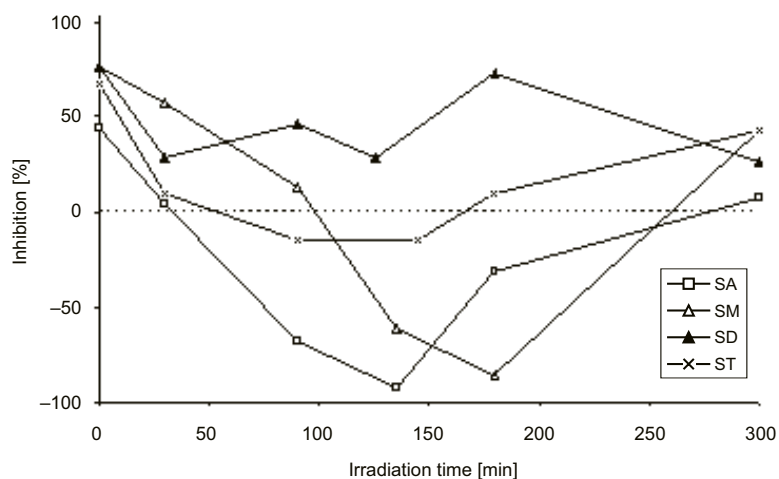


Fig. 4. Changes of toxicity of sulfonamides (changes of inhibition in relation to *C. vulgaris*) during UV-A irradiation in the presence of TiO_2

from four sulfonamides (SA, SM, SD or ST) and the toxicity of these solutions irradiated by UV-A light in the presence of TiO_2 were studied.

All sulfa-drugs were toxic relative to *C. vulgaris*. The determined values of $\text{EC}_{50(0-48)}$ for SA, SM, SD and ST were $6.2 \cdot 10^{-2}$, $6.2 \cdot 10^{-3}$, $4.9 \cdot 10^{-3}$ and $6.4 \cdot 10^{-2}$ mmol dm^{-3} , respectively. It means that two sulfonamides, namely SM and SD, having lower values of $\text{EC}_{50(0-48)}$ were more toxic to *C. vulgaris*. The influence of products obtained during photocatalytic degradation (0–300 min) of sulfonamides on the growth of cultures is shown in Fig. 4.

After short-term irradiation the inhibition of growth of algal culture caused by degradation products was, in each case, lower than the initial sulfonamides. The prolonged irradiation times (30–180 min) led to the formation of less-toxic products and were revealed as a stimulation of cultures growth (the inhibition values lower than zero were established as a stimulation of growth of culture). The long-term irradiation of sulfonamides (> 180 min) caused the inhibition of growth of alga cultures. For this reason the irradiation time (ranging from 135 to 180 min) is optimal to receive less-toxic products of photocatalytic degradation of sulfonamides.

Conclusions

The investigated sulfonamides do not undergo biodegradation. However, they undergo the photocatalytic degradation and the slow mineralization during irradiation by UV-A or sunlight, in the presence of TiO_2 . Contrary to investigated sulfonamides their degradation products, forming in these solutions, are biodegradable. Moreover, it was found that sulfonamides are toxic to *C. vulgaris*. The important is the fact that toxicity of products of photocatalytic degradation was significantly lower than the toxicity of initial sulfonamides. The above-mentioned facts indicate that the removal of sulfonamides from wastewaters using the photocatalytic method may be limited only to their partial degradation. Further steps of treatment leading to total mineralization of pollutants can continue using cheaper biodegradation methods.

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ZMIANY TOKSYCZNOŚCI I PODATNOŚCI NA BIODEGRADACJĘ ROZTWORÓW ZAWIERAJĄCYCH SULFONAMIDY PODCZAS ICH DEGRADACJI METODĄ FOTOKATALITYCZNĄ

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Abstrakt: Celem badań było określenie możliwości wykorzystania procesu fotokatalitycznego do degradacji leków sulfonamidowych w roztworach wodnych oraz do zmniejszenia ich toksyczności i zwiększenia podatności na biodegradację. Proces fotokatalityczny inicjowany za pomocą promieniowania UV-A oraz światła słonecznego prowadzono w otwartych reaktorach zawierających katalizator (zawiesinę TiO_2) oraz roztwory pięciu wybranych sulfonamidów. W roztworach uzyskanych po fotokatalitycznej degradacji oznaczano: stężenie sulfonamidów (metodą HPLC), stężenie ogólnego węgla organicznego (OWO) oraz zmiany chemicznego (ChZT) i 5-dobowego biochemicznego (BZT₅) zapotrzebowania na tlen. Ponadto, sulfonamidy i produkty ich fotokatalitycznej degradacji oceniano pod względem ich toksyczności wobec *Chlorella vulgaris* oraz podatności na biodegradację (BZT₅/ChZT). Stwierdzono, że w stosowanych warunkach wszystkie badane sulfonamidy ulegały fotokatalitycznej degradacji ze zmniejszeniem OWO i ChZT roztworów. Jednocześnie produkty tego procesu okazały się mniej toksyczne i bardziej podatne na biodegradację niż wyjściowe sulfonamidy.

Słowa kluczowe: sulfonamidy, proces fotokatalityczny, TiO_2 , biodegradacja, toksyczność, *Chlorella vulgaris*

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**STUDY OF THE POSSIBILITIES
OF UTILIZATION WASTES
FROM PHOSPHORUS INDUSTRY
IN MINERAL-ORGANIC FERTILIZERS**

**BADANIA NAD MOŻLIWOŚCIĄ WYKORZYSTANIA
W NAWOZACH MINERALNO-ORGANICZNYCH ODPADÓW
Z PRZEMYSŁU FOSFOROWEGO**

Abstract: The possibilities of agricultural utilization of wastes from the phosphorous industry were presented. Wastes from the industrial plant producing phosphorous salts were chemically analyzed in order to determine chemical composition, and in the next step the agricultural tests allowing to estimate the toxicity of waste were carried out. The relatively optimal dose, which can be applied in the prescription of mineral-organic fertilizer without causing damages in cultivations, was determined.

Keywords: phosphogypsum, sodium fluorosilicate, after-neutralization slimes, mineral-organic fertilizers

The degradation of the environment, one of the most considerable problems in the World, occurs as a consequence of negative phenomenon, caused by the irrational economy as well as the lack of sufficient natural environment protection. New technologies are still in progress of developing consuming more raw materials, including the large amounts of water, resulting in higher amounts of sewage and wastes. It is possible to conclude the amount and composition of industrial wastes on the basis of the branch of industry profile. Omitting waste management creates serious environmental problems. In Poland an about 140 millions kg of industrial wastes are produced annually. Raw material deficiencies connected mainly with the progress observed in the East economic (India, China) should be a stimulus of rational utilization of sewage and wastes that are produced in different

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branches of industry enabling maximum utilization of valuable contents contained in them [1, 2].

Nowadays the principles of the Sustainable Development, which aim is reconciliation of economic, social and environmental aspects, include prescriptions concerning calculating the life cycle of the product from *cradle to grave*. This idea is connected with maximum utilization of raw materials. It prefers waste-free and integrated technologies, determining not only the way of manufacturing products but also utilization of wastes produced. On the basis of signed by Poland Agenda 21, different ecological programs which were formalized in standards regarding to environmental management have been developed [3–5].

Wastes from the phosphorous compounds industry contain a certain amounts of the essential nutrients for the plants, mainly phosphorus. Application in the agriculture, in particular in degraded lands rehabilitation, all of wastes, fit for this destination, is the extremely important problem from the economical and environmental point of view. In many cases this wastes can be used as a components in mineral-organic fertilizers. However, many experiments, for estimation of composition and usefulness of wastes, and studies of fertilizer composition for specific cultivations should be done. The selection and the amount of fertilizer elements is dependent on the species and demand of plant [6].

Materials and methods

The aim of research was determination of chemical composition of wastes from the phosphorus salts factory, applied as components during production of household detergents in domestic chemistry. The main product, manufactured at the factory, is the extraction phosphoric acid and sodium tripolyphosphate. In these processes the following wastes are produced:

- phosphogypsum, in the process of obtaining H_3PO_4 with extraction method,
- sodium fluorosilicate, in the process of defluorinating phosphoric acid,
- wastes from the sedimentation pond, where the sodium fluorosilicate and after-neutralization slimes are being stored,
- technological after-neutralization slimes from Varney filters,
- after-neutralization slimes from the press.

Chemically-agricultural assessment of wastes

The range of research included physicochemical analysis of wastes from the phosphorous industry. The following were determined:

- dry remains (waste from sedimentation pond) – in Sartorius apparatus – according to PN-78/C-04541,
- P_2O_5 content – using colorimetric method – with using of yellow phosphorous-vanadium-molybdenum complex and measurement of absorbance at wavelength $\lambda = 420$ nm, according to PN-ISO 5310:1994,

- calcium content [wt.% of CaO] – with using complexometric method with ethylenediaminetetraacetic acid, according to PN-R-64803/97,
- sulphates content [wt.% of SO₃] – with using scale method with production of the barium sulphate precipitate, according to PN-90/C-84089,
- silica and insoluble in hydrochloric acid parts content [wt.% of SiO₂ + insoluble parts] – using scale method with emission of SiO₂, according to PN-90/C-84089,
- fluorine content – with using method with ion selective electrode with apparatus from the Orion company,
- iron and aluminium oxides content [wt.% of R₂O₃] – the estimation consists in precipitation of iron and aluminium with ammonia in the form of hydroxides, calcination of the precipitate to oxides and subsequently scale analysis, according to BN-86/6710-03/25.

The agricultural tests were carried out according to the standard PN-94/R-65950. These examinations have been consisted in estimation of the germination ability of the garden cress (*Lepidium sativum*) seed on medium from the soil with the addition of wastes. The aim of the biological test was the checking that the wastes were not limiting germination and growth of the cress, what means that the wastes were not toxic for the plants. The aim of introduced researches was also preliminary estimation of the optimal dose of waste which can be applied in the prescription of mineral-organic fertilizer. Tests were carried out in three series, on Petri dishes. The medium heavy soil free of germination limiting factors was the substrate. The substrate was thoroughly mixed with the wastes in the amount specified below and wetted with redistilled water. The seeds were distributed on the substrate so that they were not in contact with each other and did not stick to the edge of the dish. The germination capacity was evaluated after 10 days.

- Series 1: The waste and the soil at a mass ratio of
- | | |
|-------|---------------|
| 1 : 3 | – 25 of seeds |
| 1 : 4 | – 25 of seeds |
| 1 : 5 | – 25 of seeds |
- Series 2: The waste and the soil at a mass ratio of
- | | |
|--------|---------------|
| 1 : 10 | – 50 of seeds |
| 1 : 15 | – 50 of seeds |
| 1 : 20 | – 50 of seeds |
- Series 3: The waste and the soil at a mass ratio of
- | | |
|---------|---------------|
| 1 : 50 | – 50 of seeds |
| 1 : 100 | – 50 of seeds |
| 1 : 200 | – 50 of seeds |

Results and discussion

Results of physicochemical analyses of tested wastes are presented in Table 1. Examinations showed that wastes contain plant nutrients. In further research sodium fluosilicate has not been taken into consideration, due to its toxic activity.

Table 1

Chemical composition of wastes from phosphorus compounds production plants

Analysed compound	Phosphogypsum	Sodium fluosilicate	After-neutralization slimes from Varney filters	After-neutralization slimes from the press	Wastes from the sedimentation pond
	mass %				
P ₂ O ₅	2.26	7.46	19.98	23.03	11.87
CaO	25.01	1.47	4.84	9.12	8.53
SO ₃	42.95	0.72	0.86	0.79	0.22
SiO ₂ +insoluble parts	1.42	2.70	1.86	4.77	2.40
Fe ₂ O ₃ +Al ₂ O ₃	2.16	50.49	0.58	0.76	0.29
F	0.37	7.05	3.91	3.50	4.75

Agricultural tests for germination is shown in the Table 2.

Table 2

Results of *Lepidium sativum* germination test

Mass ratio of waste and soil	Germination capacity [%] of normally germinating seeds			
	phosphogypsum	after-neutralization slime from Varney filters	after-neutralization slime from press	waste from sedimentation ponds
Series I	1 : 3	100.0	—	—
	1 : 4	100.0	—	—
	1 : 5	100.0	—	4.0
Series II	1 : 10	93.5	2.2	28.3
	1 : 15	97.9	12.5	41.5
	1 : 20	97.9	25.0	70.8
Series III	1 : 50	98.2	74.5	93.6
	1 : 100	98.8	89.4	93.6
	1 : 200	100.0	98.4	97.9

In Table 2 the results of germination cress (*Lepidium sativum*) seeds test, on the different wastes, were presented. It was observed that overdose of waste caused total or partial development of plant impossible. In case of phosphogypsum the determination of optimal dose was very difficult, because large amount of insoluble calcium sulphate caused that this waste did not have influence on the inhibition of germination. In the case of the rest of the wastes it was observed that with the decreasing dose of waste, introduced into the soil, the amount and the quality of plant were increased. Dishes with the cress seeds on the soil without waste serve as a comparison sample.

Biological tests for estimating the toxicity of waste were carried out on phosphogypsum, sodium fluosilicate, slimes and waste from the sedimentation pond. It was observed that the ability of the seed germination of the cress was different on all objects. Comparison of different kind of doses of these wastes in order to determine the

optimal dose was one of purposes. During applying the proportion of waste to the soil, 1:3, 1:4 and 1:5 it was possible to observe germination only on the Petri dishes with phosphogypsum. Simultaneously with the decrease of waste doses better ability to germinate was observed in all objects. When weight ratio of the waste to soil was 1:200 the efficiency of germination reach satisfying level, near to the 100 %.

Nutrient requirements of chosen plants

Nutrient requirements of plants fulfill the amount of element, which should be taken by plant to yield optimum crop. This value is expressed in kg of compound per 1 hectare. For guarantee plant proper amount of nutrients, in whole growing season, it is necessary to conduct an efficient fertilization, which condition is knowledge of nutrient requirements of a particular species of plants [7–11].

Compositions of mineral-organic fertilizers for corn and winter rye were proposed on the basis of the experimental results and literature data. As an addition to mineral-organic fertilizers the lignite and the peat were used. The possibilities of utilization the lignite as a fertilization are great, because in Poland the deposits of lignite are not exploited for energetic purposes (for the reason of oversalinity). Using lignite and peat plays a crucial role in terms of introduction of large amount of organic matter into fertilization, which has a lot of benefits on physical, chemical and biological processes.

Table 3

The components content in mineral-organic fertilizer [kg/Mg of fertilizer] for corn, based on the wastes from sedimentation ponds and lignite (dose of fertilizer: 0.3 Mg/ha)

No.	Component	Pure compound content [kg] in 1 Mg of fertilizer	Amount of introduced components with waste from sedimentation pond [kg]	Amount of introduced components [kg/ha]	Amount of introduced components [kg]
1	N	24.8		70.8	244.9 NH ₄ NO ₃
2	P ₂ O ₅	8.0	8.0		
3	K ₂ O	39.2		72.49	250.7 K ₂ SO ₄
4	CaO	9.6	5.7	3.9	13.5 CaO
5	MgO	3.2		9.55	33.0 MgSO ₄
6	B	0.104		0.59	2.04 H ₃ BO ₃
7	Cu	0.104		0.41	1.42 CuSO ₄ · 5H ₂ O
8	Mn	0.64		2.60	8.99 MnSO ₄ · 4H ₂ O
9	Mo	0.012		0.03	0.10 Na ₂ MoO ₄ · H ₂ O
10	Zn	0.8		3.52	12.18 ZnSO ₄ · 7H ₂ O
11	Lignite			57.8	200.0
12	Waste			67	231.7
Altogether				252.1	~1000

In Table 3 the components content in mineral-organic fertilizer for corn, based on the wastes from sedimentation ponds and lignite, was presented. The amount of wastes, which are introduced with fertilizers per hectare of field, was 67 kg. This amount covers demand of corn for phosphorus and partially for calcium. In the last two columns an amount of introduced components in kg per hectare and in 1 Mg of fertilizers was presented.

In Table 4 the components content in mineral-organic fertilizer for winter rye, based on the wastes from after-neutralization slime from the press and peat, was presented. The amount of wastes, which are introduced with fertilizers per hectare of field, was 260 kg. This amount covers demand of winter rye for phosphorus and partial for calcium. In the last two columns an amount of introduced components in kg per hectare and in 1 Mg of fertilizers was presented.

Table 4

The components content in mineral-organic fertilizer [kg/Mg of fertilizer] for winter rye based on the wastes from after-neutralization slime from the press and peat (dose of fertilizer: 1.8 Mg/ha)

No.	Component	Pure compound content [kg] in 1 Mg of fertilizer	Amount of introduced components with waste from sedimentation pond [kg]	Amount of introduced components [kg/ha]	Amount of introduced components [kg]
1	N	156		445.7	247.1 NH ₄ NO ₃
2	P ₂ O ₅	60	60		
3	K ₂ O	153		282.9	156.8 K ₂ SO ₄
4	CaO	150	23.7	126.3	70.0 CaO
5	MgO	27		80.60	44.68 MgSO ₄
6	B	0.33		1.86	1.03 H ₃ BO ₃
7	Cu	0.142		0.56	0.31 CuSO ₄ · 5H ₂ O
8	Mn	0.998		4.04	2.24 MnSO ₄ · 4H ₂ O
9	Mo	0.021		0.052	0.029 Na ₂ MoO ₄ · H ₂ O
10	Zn	0.384		1.668	0.925 ZnSO ₄ · 7H ₂ O
11	Peat			600	332.6
12	Waste			260	144.1
Altogether				1803.7	~1000

In the Figure 1 the percentage composition of a mineral-organic fertilizer for winter rye, based on the after-neutralization slimes from Varney filters and lignite, is shown. The amount of wastes, which are introduced with fertilizers per hectare of field, was 500 kg. This amount covers demand of rye for phosphorus and partial for calcium. The proposed fertilization is up to 1.8 Mg/ha.

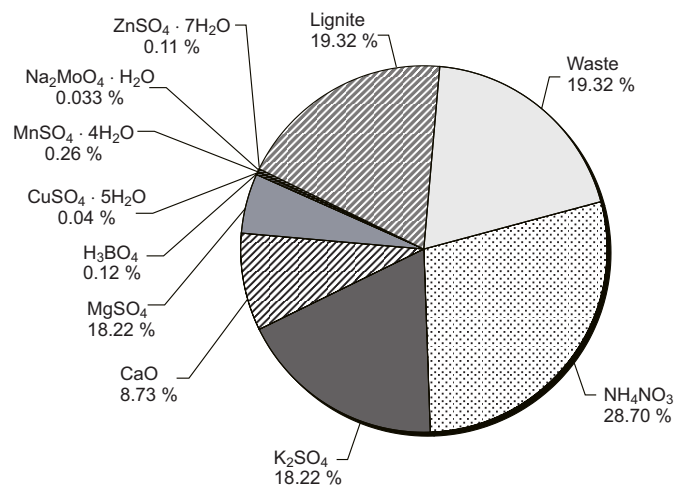


Fig. 1. Percentage composition of a mineral-organic fertilizer for winter rye, based on the after-neutralization slimes from Varney filters and lignite. The proposed fertilization: up to 1.8 Mg/ha

Conclusions

The aim of research was determination of chemical composition of wastes from the phosphorus salts factory. The phosphogypsum, sodium fluorosilicate, after-neutralization slimes from the filters and the press and wastes from sedimentation pond were analysed. Following the current trends and environmental protection regulations, recycling seems to be the best solution for wastes from phosphorus compounds production plants. The utilization of wastes in agriculture appear to be the most promising solution.

The satisfactory germination ability of cress (*Lepidium sativum*) seeds on all nine doses of phosphogypsum confirms the fact that a little amount of compounds from it penetrates into the soil. This amount has significant meaning for plant germination. Considering relatively large content of phosphorus in phosphogypsum satisfactory results were obtained.

The comparison of the results of the chemical analysis shows which waste can be used in fertilization and which doses should be use. The main nutrients, which are in wastes, are phosphorus and calcium.

In spite of phosphorus and calcium content in phosphogypsum, this waste is not suitable for utilization in fertilizers. It contain relatively large amount of heavy metals, huge amount of sulphates, which precipitate calcium in insoluble calcium sulphate, and for that reasons its fertilizers worth is small. However, phosphogypsum can be used to land rehabilitation and for improving soil acidity.

The sodium fluorosilicate is contaminated by phosphorus compounds and by calcium sulphate, which co-precipitate with phosphorus during production of sodium tripolyphosphate. This kind of waste is not suitable for agricultural utilization, because of huge fluorine content.

The after-neutralization slimes is a mixture of soluble sodium phosphates, insoluble phosphates of calcium, aluminium and iron. This kind of wastes can be used to the fertilization purposes.

The greatest abilities of utilization as a component of mineral-organic fertilizers slimes have after-neutralization slimes from Varney filters and from the press, as well as wastes from the sedimentation pond where after-neutralization slimes from the sodium tripolyphosphate production are being stored. In the composition of that wastes the significant amount of phosphates and calcium – that can be used as nutrients – was visible.

The mineral-organic preparations, which are proposed to use, can be independent substratum in chosen plant species (corn and winter rape). In this aim the suitable amounts of waste, inorganic components and lignite and peat (as an organic component) were used.

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BADANIA NAD MOŻLIWOŚCIĄ WYKORZYSTANIA W NAWOZACH MINERALNO-ORGANICZNYCH ODPADÓW Z PRZEMYSŁU FOSFOROWEGO

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Abstrakt: Przedstawiono możliwości rolniczego wykorzystania odpadów z przemysłu fosforowego. Odpady z zakładu produkującego sole fosforowe poddano analizie chemicznej w celu zbadania składu chemicznego, a następnie przeprowadzono testy rolnicze pozwalające ocenić toksyczność odpadów i ustalić optymalną dawkę, jaką można wykorzystać w recepturze nawozu mineralno-organicznego bez spowodowania szkód w uprawach.

Słowa kluczowe: fosfogips, fluorokrzemian sodowy, szlamy poneutralizacyjne, nawozy mineralno-organiczne

Anna CHRZAN¹ and Maria MARKO-WORŁOWSKA¹

INFLUENCE OF THE HEAVY METALS POLLUTING THE SOIL ON THE DENSITY AND DIVERSITY OF THE SOIL FAUNA

WPŁYW METALI CIĘŻKICH ZANIECZYSZCZAJĄCYCH GLEBĘ NA ZAGĘSZCZENIE I RÓŻNORODNOŚĆ FAUNY GLEBOWEJ

Abstract: Three, following areas were chosen to the research: the lawn near noisy street at the Vistula river, the lawn in the park situated 300 m from the noisy road and the lawn in the Mogilski Grove. The researches were conducted in 2007 and 2008 in the spring. The density and the diversity of the soil fauna as well as the content of metals in the soil and the humidity, temperature and pH reaction in the soil were analyzed. The relation between the content of Cd, Pb, Zn and Ni and the density and diversity of pedofauna was detected. In the area with the highest content of the metals cited above the density and the diversity of pedofauna were the lowest, whereas in the soil with the lowest concentration of these metals the parameters determined were the highest.

Keywords: heavy metals, soil fauna, diversity, density

The means of transport are the common sources of the environmental contamination. The diesel engines expel many toxic elements such as for example the heavy metals that are the parts of fumes and dusts [1, 2]. The lead compounds (toxic lead(IV) chloride) are the most important among them as well as Zn, Cd and Ni that get into the environment as a result of the consuming of the fuels, rubbing of the tyres and other vehicles parts [3]. Moreover among the roads the grease used in the vehicles can be the sources of the Cd contamination. The areas the most exposed to the transport contamination are urbanized ones as well as the areas situated near roads with heavy traffic. The risk generated by engine fumes is even higher when their toxic elements are expelled to the atmosphere on the densely populated areas, where the buildings make the natural air exchange difficult. As a result, the accumulation of these contaminations in the environment, especially in the soil appears. Because of the fact that the heavy metals migrate in the soil very slowly, they are its most durable pollutions [4]. It is

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particularly harmful, because the soil is the important part of the elements circulation and is the basic link of the trophic chain that reach also the man. Taking up the heavy metals from the soil by the organisms is conditioned by many factors such, as for example: pH of the soil, its humidity, the content of organic matter, the presence of other metals and the forms in which they appear in the soil.

Disregarding their origin, the heavy metals in excessive amount generate serious risk for plants, animals and man. Therefore there is a need for the current evaluation of their content in the areas exposed to the influence of the transport contaminations.

The aim of the research was the evaluation of the influence of the heavy metals – Cd, Pb, Zn and Ni on the density and diversity of the soil fauna.

Materials and methods

The researches were conducted in 2007 and 2008 in the spring, following three areas were chosen to the research:

- Locality I – the lawn near noisy street at the Vistula river,
- Locality II – the lawn in the park situated 300 m from the noisy road,
- Locality III – the lawn in the Mogilski Grove.

The density and the diversity of the soil fauna as well as the content of metals in the soil and the humidity, temperature and pH reaction in the soil were analyzed.

The way of taking up the samples, theirs number, methods of scampering away the pedofauna and the way of evaluation of the Cd, Pb, Zn and Ni content is described in the separated article [5].

Results and discussion

The anthropogenic soils analyzed were characterized by the slightly alkaline reaction in the interval of 7.13–7.2 pH. It is widely known that acidic pH of the soil considerably increase the assimilability of the heavy metals by the soil organisms. Due to the high pH, the reaction did not increase the mobility of the metals in the soil analyzed (Table 1).

Table 1

The features of the soil in the areas analyzed in Kraków (the means from 2007–2008)

Selected parameters	Locality I	Locality II	Locality III
Soil moisture [%]	16.32	15.93	14.80
Soil pH	7.13	7.16	7.20
Area temperature [°C]	16.20	10.05	13.80
Soil temperature [°C]	11.55	8.85	12.75

Locality I – the lawn near noisy street at the Vistula river; Locality II – the lawn in the park situated 300 m from the noisy road; Locality III – the lawn in the Mogilski Grove.

The important differences concerning the humidity and temperature of the soil were not detected (Table 1). However, the clear differences in the Cd, Pb, Zn and Ni content

were noted. The important differences concerned both the density and diversity of the mesofauna.

According to Kabata-Pendias et al [6] the highest admissible content of the metals in the soils that contain anthropogenic pollutions can be 1 mg Cd · kg, 70 mg Pb, 150 mg Zn. The Minister of Environment [7] order concerning the standards of the quality of the soil allows 15 mg Cd, 600 mg Pb, 1000 mg Zn in the top levels of the industrial and communication areas (group C).

The results of the research concerning Cd exceed the highest admissible content indicated by Kabata-Pendias. In the location I small exceeding of the limit was detected, in the location II the exceeding amounts more then two times and in the location III nearly seven times (Table 2).

Table 2

The density and diversity of the pedofauna in the areas analyzed (the mean from 2007–2008)

Selected parameters	Locality I	Locality II	Locality III
Density of pedofauna (sp.no. per m ²)	2296	1437	1277
Diversity (number of taxonomic group)	17	10	9

The highest contents of the others metals analyzed were detected in the location III as well, but only the content of the Pb (153.13 mg/kg) exceeded more than two times the highest possible content mentioned above (Table 3). The content of the metals analyzed in each particular location correlated closely with the number and diversity of the pedofauna. In the location that was characterised by the highest concentration of the Cd, Pb, Ni and Zn, almost two times higher density of the soil organisms analyzed and almost two times lower diversity in comparison with the location I (with the lowest concentration of the metals) were detected (Table 2, 3).

Table 3

The content of the heavy metals in the soils on the areas analyzed in mg/kg (mean from 2007–2008)

Metal	Locality I	Locality II	Locality III
Cd	1.770	2.489	6.97
Pb	46.788	64.480	153.13
Ni	10.710	15.857	20.80
Zn	10.390	17.080	39.37

Conclusions

1. The areas adjacent to the traffic, densely build-up and with the small number of trees and bushes are characterized by several times higher contamination of the soil by the heavy metals than the park and grove areas remote around 300 m from the street.

2. The high content of Cd, Pb, Ni and Zn have the influence on the reduction of the pedofauna density and diversity.

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WPLYW METALI CIĘŻKICH ZANIECZYSZCZAJĄCYCH GLEBĘ NA ZAGĘSZCZENIE I RÓŻNORODNOŚĆ FAUNY GLEBOWEJ

Instytut Biologii
Uniwersytet Pedagogiczny w Krakowie

Abstrakt: Do badań wybrano trzy stanowiska: 1) trawnik nad Wisłą w pobliżu ruchliwej ulicy, 2) trawnik w parku miejskim usytuowany w odległości ok. 300 m od ruchliwego traktu komunikacyjnego oraz 3) trawnik w Lasku Mogiłskim. Badania prowadzono w latach 2007–2008 w okresie wiosennym. Określono zagęszczenie i różnorodność fauny glebowej, zawartość metali w glebie, jej wilgotność, temperaturę i odczyn pH. Stwierdzono związek między zawartością Cd, Pb, Zn i Ni a zagęszczeniem i różnorodnością pedofauny. Na stanowisku o największej zawartości wyżej wymienionych metali zagęszczenie i różnorodność fauny glebowej było najmniejsze, natomiast w glebie o najmniejszej koncentracji tych metali badane parametry osiągnęły największą wartość.

Słowa kluczowe: metale ciężkie, fauna glebowa, zagęszczenie i różnorodność

Dorota KALEMBASA¹ and Elżbieta MALINOWSKA¹

**CONTENTS OF CADMIUM, LEAD AND NICKEL
AT DIFFERENT DEVELOPMENT STAGES
OF SELECTED *Miscanthus* GENOTYPES**

**ZAWARTOŚĆ KADMU, OŁOWIU I NIKLU
W RÓŻNYCH OKRESACH ROZWOJU
WYBRANYCH GENOTYPÓW TRAWY *Miscanthus***

Abstract: Bioaccumulation of three heavy metals (Cd, Pb, and Ni) at the second cultivation year of *Miscanthus sinensis* (2 diploid genotypes) and *Miscanthus sinensis* x *giganteus* (3 triploid genotypes) was examined on objects with no fertilization and with NPK nutrition in five dates. Higher mean contents of analyzed heavy metals in triploid than diploid genotypes biomass was found. Mineral nutrition significantly affected the cadmium level in diploid genotypes biomass as well as nickel in all studied genotypes. The highest cadmium concentration was recorded in *Miscanthus* biomass at the beginning of June, lead – at the beginning of September and October, whereas nickel – at the beginning of July.

Keywords: *Miscanthus*, diploid genotypes, triploid genotypes, cadmium, lead, nickel, mineral nutrition

Miscanthus grass is an interesting alternative plant species, the biomass of which may be utilized for many ways. Species that may be every time adjusted to specific cultivation and utilization conditions, are required as renewable plant-origin material [1]. Among 20 different species including *Miscanthus* genus, *Miscanthus sinensis* x *giganteus* finds its greatest interests in Europe due to its high efficiency [2, 3]. Mineral fertilization level does not directly influence on heavy metals accumulation within the plant, while indirectly through the soil acidity changes or precipitation of hardly soluble phosphates, mineral fertilizers can intensify or reduce the availability of these elements by plants [4].

Present research aimed at evaluating the dynamics of cadmium, lead, and nickel intake and accumulation under differentiated development stages, by five *Miscanthus* genotypes depending on mineral nutrition.

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Material and methods

The experiments were carried out in the field on the soil of loamy sand granulometric composition (according to PN-R-04033, $\text{pH}_{\text{KCl}} = 6.73$). Organic carbon content was $37.4 \text{ g} \cdot \text{kg}^{-1}$; total contents of selected heavy metals [$\text{mg} \cdot \text{kg}^{-1}$ soil] amounted to: Cd – 0.960; Pb – 63.99; Ni – 5.53, that were determined after combustion by means of ICP-EAS technique.

The experimental plots with *Miscanthus* grass cultivation were set in autumn 2000. Studies included five genotypes of the grass: two diploid ($2\times$) representing *Miscanthus sinensis* species, including one *Hybriden* (clone No. 1) and one German form named Goliath – MGo (clone No. 19), while other three genotypes belonged to triploid ($3\times$) *Miscanthus sinensis x giganteus* hybrid differing with their origin: clone No. 53 came from Germany, clone No. 63 from Denmark, and clone POL from Poland. Seedlings were achieved from the rhizome reproduction. Particular clones were set on plots of 1.5 m^2 area in three replications in completely randomized pattern. The biomass yields of studied genotypes were presented in earlier publication [3].

The plant samples (10 leaved stems) were collected at the beginning of June, July, August, September and October 2002. Mineral nutrition at the levels of: N – $60 \text{ kg} \cdot \text{ha}^{-1}$ (ammonium nitrate), P – $50 \text{ kg} \cdot \text{ha}^{-1}$ (triple superphosphate), K – $100 \text{ kg} \cdot \text{ha}^{-1}$ (potassium sulfate) was applied every year early spring before vegetation period. The experiment included control object (with no nutrition) and objects fertilized with NPK.

The plant samples were ground till 0.25 mm particle diameter and aliquots of 1 g were weighed into the crucibles. The organic matter was then combusted in muffle furnace at $450 \text{ }^\circ\text{C}$ for 15 hours. After that, 10 cm^3 of diluted HCl (1:1) was added to the crucible and evaporated on sand bath to decompose carbonates and separate silicates. The contents of the crucibles, after adding 5 cm^3 10 % HCl, were then transferred into 100 cm^3 capacity measure flask and adjusted volume using distilled water. Such prepared basic solution was subjected to determinations for cadmium, lead, and nickel concentrations by means of ICP-EAS technique on Optima 3200 RL device (Perkin Elmer). Differences between mean values for fertilization, genotypes, and sampling dates were evaluated by means of variance analysis; in the case of their significance, $\text{LSD}_{0.05}$ values were calculated applying Tukey's test. All calculations were made with a help of FR Analvar 3.2 software.

Results and discussion

Varied cadmium, lead, and nickel contents were found in the biomass of five *Miscanthus* genotypes depending on genotype, fertilization, and study date, in the second growing year. Less cadmium was recorded on control, and more cadmium on objects treated with NPK in the biomass of diploid than triploid genotypes (Table 1). More cadmium accumulation was found than in diploid, mineral fertilized genotypes than with no fertilization; diploid No. 1 was characterized by much higher cadmium content than No. 19. The element concentration (mean for fertilization) decreased along with the increase of biomass of cultivated grass (date): at the beginning of June, it

Table 1
Total content of cadmium [mg · kg⁻¹ d.m.] in the biomass of *Miscanthus* grass at different development stages

Genotypes	Month																
	June			July			August			September			October			Mean	
	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK
1	0.102	0.123	0.113	0.110	0.180	0.145	0.078	0.138	0.108	0.105	0.115	0.110	0.089	0.103	0.096	0.097	0.132
19	0.098	0.083	0.091	0.046	0.039	0.043	0.068	0.097	0.083	0.095	0.039	0.067	0.072	0.098	0.085	0.076	0.071
Mean for diploid genotypes	0.100	0.103	0.102	0.078	0.110	0.094	0.073	0.116	0.095	0.100	0.077	0.089	0.081	0.101	0.091	0.086	0.101
LSD _{0.05} for: A – fertilization B – genotypes C – month A/B; B/A; C/A; A/C; C/B; B/C – interaction	A = 0.007 B/A = 0.011 A/C = 0.011 B = 0.007 C/A = 0.015 C/B = 0.024 C = 0.017 A/B = 0.011 B/C = 0.017																
53	0.199	0.202	0.201	0.139	0.106	0.123	0.051	0.141	0.096	0.081	0.054	0.068	0.099	0.078	0.089	0.114	0.116
63	0.128	0.088	0.108	0.153	0.061	0.107	0.056	0.129	0.093	0.126	0.085	0.106	0.104	0.095	0.099	0.113	0.092
POL	0.116	0.098	0.107	0.098	0.063	0.081	0.092	0.111	0.102	0.122	0.046	0.084	0.094	0.086	0.090	0.104	0.081
Mean for triploid genotypes	0.148	0.129	0.139	0.130	0.077	0.104	0.083	0.127	0.105	0.109	0.062	0.086	0.099	0.086	0.093	0.114	0.096
Mean	0.124	0.116	0.120	0.104	0.094	0.099	0.078	0.122	0.100	0.105	0.069	0.087	0.090	0.094	0.092	0.100	0.099
LSD _{0.05} for: A – fertilization B – genotypes C – month A/B; B/A; C/A; A/C; C/B; B/C – interaction	A = n.s. B/A = n.s. A/C = 0.037 B = n.s. C/A = 0.053 C/B = n.s. C = 0.048 A/B = n.s. B/C = n.s.																

n.s. – not significant difference

amounted to $0.102 \text{ mg} \cdot \text{kg}^{-1}$, while at the beginning of October $0.091 \text{ mg} \cdot \text{kg}^{-1}$. Similar dependence was recorded for triploid genotypes, for which cadmium content were 0.139 and $0.093 \text{ mg} \cdot \text{kg}^{-1}$, respectively. The sampling date had significant influence on cadmium content in triploid clones, while genotype and mineral nutrition did not considerably differentiate the metal level.

Total cadmium contents [$\text{mg} \cdot \text{kg}^{-1}$] in biomass of studied *Miscanthus* genotypes can be lined up in the following sequences (mean values for study dates and nutrition):

- June: No. 53 (0.201) > No. 1 (0.113) > No. 63 (0.108) > POL (0.107) > No. 19 (0.091);
- July: No. 1 (0.145) > No. 53 (0.123) > No. 63 (0.107) > POL (0.081) > No. 19 (0.043);
- August: No. 1 (0.108) > POL (0.102) > No. 53 (0.096) > No. 63 (0.093) > No. 19 (0.083);
- September: No. 1 (0.110) > No. 63 (0.106) > POL (0.084) > No. 53 (0.068) > No. 19 (0.067);
- October: No. 63 (0.099) > No. 1 (0.096) > POL (0.090) > No. 53 (0.089) > No. 19 (0.085).

Studied experimental factors had not significant influence on lead content in *Miscanthus* grass, except from some interactions (Table 2). The metal bioaccumulation varied in diploid and triploid genotypes. Triploid genotypes contained more lead than diploid ones. Lead level decreased in subsequent study dates for triploid biomass. The lowest lead content was recorded in June for all studied genotypes, while the highest in September and October. A systematic increase of lead quantities in osier in following harvest dates was also observed by Kaniuczak et al [5].

Total lead contents [$\text{mg} \cdot \text{kg}^{-1}$] in *Miscanthus* biomass can be lined up in the following sequence (mean values for study dates and fertilization):

- June: No. 63 (1.05) > No. 19 (0.882) > POL (0.822) = No. 1 (0.822) > No. 53 (0.698);
- July: No. 63 (1.98) > No. 1 (1.74) > POL (1.68) > No. 19 (1.42) > No. 53 (1.41);
- August: No. 63 (2.16) > POL (1.90) > No. 53 (1.68) > No. 1 (1.49) > No. 19 (1.48);
- September: No. 53 (2.83) > POL (2.04) > No. 19 (1.99) > No. 1 (1.63) > No. 63 (1.63);
- October: No. 53 (2.70) > POL (2.27) > No. 63 (1.96) > No. 1 (1.39) > No. 19 (1.30).

Nickel content in tested grass biomass depended on the genotype, mineral nutrition, and study date (Table 3). Chemical analyses revealed less nickel in diploid than triploid genotypes. The highest bioaccumulation of that element was recorded in July, whereas the lowest in October (for diploid) and August (for triploid genotypes). The largest amounts of nickel on objects with no fertilization were found in the biomass of clone POL, while the lowest – clone No. 1; on objects treated with NPK – clone No. 53 and clone No. 19, respectively.

Table 2

Total content of lead [mg · kg⁻¹ d.m.] in the biomass of *Miscanthus* grass at different development stages

Genotypes	Month																	
	June			July			August			September			October			Mean		
	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	
1	0.826	0.817	0.822	2.39	1.090	1.74	0.932	2.05	1.49	1.63	1.51	1.63	1.42	1.36	1.39	1.46	1.37	
19	0.882	0.881	0.882	2.15	0.684	1.42	0.923	2.03	1.48	1.74	1.99	1.38	1.21	1.30	1.51	1.31	1.31	
Mean for diploid genotypes	0.854	0.849	0.852	2.27	0.887	1.58	0.928	2.04	1.48	1.63	1.81	1.40	1.33	1.37	1.49	1.34	1.34	
LSD _{0,05} for: A – fertilization B – genotypes C – month A/B; B/A; C/A; A/C; C/B; B/C – interaction	A = n.s. B = n.s. C = 0.567	B/A = n.s. C/A = 0.507 A/B = n.s.	A/C = 0.359 C/B = n.s. B/C = n.s.															
53	0.725	0.698	0.712	1.67	1.14	1.41	2.19	1.17	1.68	2.23	3.43	2.83	2.42	2.98	2.70	1.85	1.88	
63	0.985	1.120	1.050	2.42	1.54	1.98	2.17	2.15	2.16	1.41	1.67	1.54	2.05	1.86	1.96	1.81	1.67	
POL	0.836	0.808	0.822	2.25	1.11	1.68	2.07	1.72	1.90	2.30	1.77	2.04	2.38	2.16	2.27	1.97	1.51	
Mean for triploid genotypes	0.849	0.875	0.862	2.11	1.26	1.69	2.14	1.68	1.91	1.98	2.29	2.14	2.28	2.33	2.31	1.87	1.69	
Mean	0.852	0.862	0.857	2.19	1.07	1.63	1.53	1.86	1.70	1.99	1.96	1.98	1.84	1.83	1.84	1.68	1.52	
LSD _{0,05} for: A – fertilization B – genotypes C – month A/B; B/A; C/A; A/C; C/B; B/C – interaction	A = n.s. B = n.s. C = 0.466	B/A = n.s. C/A = 0.511 A/B = n.s.	A/C = 0.363 C/B = 0.808 B/C = 0.690															

n.s. – not significant difference

Table 3

Total content of nickel [mg · kg⁻¹ d.m.] in the biomass of *Miscanthus* grass at different development stages

Genotypes	Month																
	June			July			August			September			October			Mean	
	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK
1	2.56	2.79	2.68	12.00	7.06	9.53	3.25	3.02	3.14	0.650	5.80	3.23	0.945	1.25	1.10	3.83	3.98
19	2.86	2.82	2.84	12.21	7.53	9.87	1.93	2.75	2.34	3.73	5.20	4.47	1.94	2.99	2.47	4.53	4.26
Mean for diploid genotypes	2.71	2.81	2.76	12.11	7.30	9.71	2.59	2.89	2.74	2.19	5.50	3.85	1.44	2.12	1.78	4.21	4.12
LSD _{0.05} for: A – fertilization B – genotypes C – month A/B; B/A; C/A; A/C; C/B; B/C – interaction	A = 0.213 B/A = n.s. A/C = 0.301 B = n.s. C/A = 0.425 C/B = 0.672 C = 0.475 A/B = n.s. B/C = 0.476																
53	3.23	3.48	3.36	11.40	5.76	8.58	2.47	3.19	2.86	4.33	13.41	8.87	3.04	3.99	3.52	4.89	5.97
63	2.51	2.65	2.58	19.60	9.05	14.33	1.53	2.08	1.81	3.02	4.71	3.87	4.02	3.96	3.99	6.14	4.49
POL	3.45	3.67	3.56	23.01	13.03	18.02	2.96	1.66	2.31	5.91	7.12	6.52	3.98	3.87	3.93	7.86	5.87
Mean for triploid genotypes	3.06	3.26	3.16	17.82	9.28	13.55	2.34	2.31	2.33	4.42	8.41	6.42	3.68	3.45	3.57	6.30	5.44
Mean	2.89	3.04	2.97	14.97	8.29	11.63	2.47	2.60	2.54	3.31	6.96	5.14	2.56	3.94	3.25	5.26	4.78
LSD _{0.05} for: A – fertilization B – genotypes C – month A/B; B/A; C/A; A/C; C/B; B/C – interaction	A = 0.217 B/A = 0.453 A/C = 0.377 B = 0.320 C/A = 0.530 C/B = 0.837 C = 0.483 A/B = 0.377 B/C = 0.716																

n.s. – not significant difference

Total nickel concentration [$\text{mg} \cdot \text{kg}^{-1}$] in biomass of five *Miscanthus* genotypes during the second year of its cultivation can be lined up in the following sequence (means for study dates and fertilization):

- June: POL (3.56) > No. 53 (3.36) > No. 19 (2.84) > No. 1 (2.68) > No. 63 (2.58);
- July: POL (18.02) > No. 63 (14.33) > No. 19 (9.87) > No. 1 (9.53) > No. 53 (8.58);
- August: No. 1 (3.14) > No. 53 (2.86) > No. 19 (2.34) > POL (2.31) > No. 63 (1.81);
- September: No. 53 (8.87) > POL (6.52) > No. 19 (4.47) > No. 63 (3.87) > No. 1 (3.23);
- October: No. 63 (3.99) > POL (3.93) > No. 53 (3.52) > No. 19 (2.47) > No. 1 (1.10).

Contents of examined heavy metals in *Miscanthus* biomass were much lower than those recorded by Kaniuczak et al [5] and Niedźwiecki et al [6].

Conclusions

1. Biomass of triploid *Miscanthus* genotypes in the second year of the field experiment was characterized by higher cadmium, lead, and nickel bioaccumulation than that of diploid ones.
2. Total contents of all studied heavy metals in the biomass of five *Miscanthus* genotypes could be lined up in the following sequence [$\text{mg} \cdot \text{kg}^{-1}$]: Ni (0.650–23.01) > Pb (0.684–3.43) > Cd (0.039–0.141).
3. Chemical analyses revealed that cadmium, lead, and nickel amounts in the biomass of tested grass varied depending on the study date. The highest total cadmium level was recorded at the beginning of June, while lead at the beginning of September and October, and nickel at the beginning of July.
4. Mineral NPK nutrition significantly differentiated cadmium content in the biomass of diploid, whereas that of nickel – in diploid and triploid genotypes of *Miscanthus*.

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ZAWARTOŚĆ KADMU, OŁOWIU I NIKLU W RÓŻNYCH OKRESACH ROZWOJU WYBRANYCH GENOTYPÓW TRAWY *Miscanthus*

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Abstrakt: Badano bioakumulację trzech metali ciężkich (Cd, Pb i Ni) w drugim roku uprawy trawy *Miscanthus sinensis* (2 genotypy diploidalne) i *Miscanthus sinensis x giganteus* (3 genotypy triploidalne) na

objektach bez nawożenia i nawożonych mineralnie NPK, w pięciu terminach. Stwierdzono (średnio) większą zawartość analizowanych metali ciężkich w biomase genotypów triploidalnych niż diploidalnych. Nawożenie mineralne znacznie wpłynęło na zawartość kadmu w biomase genotypów diploidalnych oraz niklu we wszystkich badanych genotypach. Stwierdzono największą zawartość Cd w biomase miskanta w pierwszej dekadzie czerwca, Pb w pierwszej dekadzie września i października, a Ni w pierwszej dekadzie lipca.

Słowa kluczowe: trawa *Miscanthus*, genotypy di- i triploidalne, kadm, ołów, nikiel, nawożenie mineralne

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**INFLUENCE OF MUSHROOM SUBSTRATE
ON LITHIUM, BARIUM AND STRONTIUM CONTENTS
AT ITALIAN RYEGRASS**

**ODDZIAŁYWANIE PODŁOŻA POPIECZARKOWEGO
NA ZAWARTOŚĆ LITU, BARU I STRONTU
W BIOMASIE ŻYCICY WIELOKWIATOWEJ**

Abstract: The two-year pot experiment carried out in a green-house dealt with the influence of bed after mushroom production and complementary potassium, nitrogen, and potassium-nitrogen nutrition on lithium, barium, and strontium contents in a biomass of Italian ryegrass. Mean concentrations of studied elements in the tested grass biomass varied in particular experimental years and cuts forming the following sequence: Li > Ba > Sr.

Keywords: mushroom substrate, lithium, barium, strontium

The economic and live activities of a man along with a gradual industry development force societies in 21st century to solve problems with still growing waste amounts. Continuously increasing number of new mushroom-producing facilities in Poland, namely Siedlce region, a specific production cycle, and new substrate preparation technologies make that more and more mushroom substrate – ie spent mushroom substrate SMS – or mushroom compost after processing, is disposed into the natural environment every year.

The mushroom substrate is a waste organic product containing large amounts of organic matter and some level of nutrients important for plants. Thus, this post-production biological waste should be managed in such a way to return it – in non-toxic manner – to ecosystems. Properly prepared and performed mushroom substrate should not contain pests, disease-forming fungi and weed seeds, instead it should be of a good consistence and tolerated ground-recalling smell. It may be used as organic fertilizer in orchard, vegetable, and crop-producing farms localized mainly (due to economic reasons) near mushroom-producing facility. It can be used after con-

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taminated soils remediation. It has rich and diverse populations of microorganisms (bacteria) as well as mushroom mycelium remains [1].

The study aimed at evaluating the influence of mushroom substrate and complementary mineral nutrition on lithium, barium, and strontium contents at Italian ryegrass during the two-year pot experiment.

Materials and methods

The two-year pot experiment was carried out in a green-house in completely randomized design. The soil material was collected from the humus layer of light loamy sand soil (according to PTG). The percentage of particular fractions was as follows: sand (2–0.1 mm) 63 %, dust (0.1–0.02 mm) 20 %, fine particles (< 0.02 mm) 17 %, including clay (< 0.002 mm) 7 %; pH_{H_2O} of the soil 6.12, pH_{KCl} 6.04; contents of studied elements [$mg \cdot kg^{-1}$ soil] were: Li – 1.7; Ba – 82.18; Sr – 29.06.

A substrate after mushroom production as well as fermented bovine manure (as a standard) was applied as an organic material in the experiment. Contents of studied elements in the mushroom substrate were [$mg \cdot kg^{-1}$ d.m.]: Li – 10.4; Ba – 52.5; Sr – 97.6; while in the bovine manure: Li – 18.3; Ba – 49.8; Sr – 73.5.

Pots were filled with 12 kg of the soil and such weights of mushroom substrate and manure were added to introduce 4 g N \cdot pot⁻¹. Mineral nutrition (NPK) was applied in reference to N:P:K ratio as in the manure (1:0.8:1.2). Following experimental objects were created: a – soil – control; b – soil + fermented bovine manure; c – soil + mushroom substrate; d – soil + mushroom substrate + K₁; e – soil + mushroom substrate + K₂; f – soil + mushroom substrate + N₁; g – soil + mushroom substrate + N₂; h – soil + mushroom substrate + K₁N₁; i – soil + mushroom substrate + K₂N₂.

A complementary mineral nutrition with potassium in a form of K₂SO₄ and with nitrogen as NH₄NO₃ was applied in rates: K₁ – potassium at the level of 50 % of optimum rate; K₂ – potassium at optimum rate; N₁ – nitrogen at the level of 25 % of optimum rate; N₂ – nitrogen at the level of 50 % of optimum rate.

Italian ryegrass (*Lolium multiflorum* Lam) was tested plant species. The experiment was carried out in three replications. During the vegetation period, four cuts were harvested, which made up 8 for two experimental years. The plant samples were dried, ground, and total contents of Li, Ba, and Sr were determined. In order to determine selected elements concentrations, samples were combusted in a muffle furnace at 450 °C. Mineralized material were flooded in crucible (placed on a sand bath) with hydrochloric acid solution (HCl:H₂O = 1:1, v/v) to decompose carbonates and separate silicates. Achieved chlorides were transferred using 10 % HCl into the measure flask of 100 cm³ capacity separating the silicates on a filter paper. In such prepared solutions, contents of Li, Ba, and Sr were determined by means of emission atomic spectrometry with inductively-coupled plasma (ICP-EAS).

The difference significance related to studied elements contents was verified by applying variance analysis (Fisher-Snedecor's test), and LSD values were calculated using Tukey's test at the significance level of $p = 0.05$.

Results and discussion

The size of Italian ryegrass biomass yield [$\text{g} \cdot \text{pot}^{-1}$] grown in the two-year pot experiment with organic fertilization in a form of mushroom substrate and varied mineral nutrition application, was given earlier [4].

Mean contents of studied elements in Italian ryegrass biomass varied depending on years and cuts. They might be lined up in a following sequence [$\text{mg} \cdot \text{kg}^{-1}$ d.m.): Li (30.2–62.1) > Ba (12.4–39.1) > Sr (14.0–30.5).

Average lithium content at Italian ryegrass for all cuts of the 1st and 2nd cultivation year varied due to applied fertilization (Table 1), which was confirmed by LSD values. More that element was found at ryegrass biomass in the II (50.2 $\text{mg} \cdot \text{kg}^{-1}$), than I experimental year (43.1 $\text{mg} \cdot \text{kg}^{-1}$). For both years, the largest lithium amounts (64.0 $\text{mg} \cdot \text{kg}^{-1}$) were recorded in the biomass of grown grass harvested from the object fertilized with mushroom substrate with addition of mineral nitrogen at N_1 rate, while the smallest (36.7 $\text{mg} \cdot \text{kg}^{-1}$) at plants from object treated with mushroom substrate with potassium at K_2 rate. Lithium content in ryegrass biomass harvested from object fertilized with only mushroom substrate was lower (41.1 $\text{mg} \cdot \text{kg}^{-1}$) than that amended with bovine manure (49.2 $\text{mg} \cdot \text{kg}^{-1}$). The two-year experiments revealed that mineral nitrogen and potassium-nitrogen (N_1 , N_2 , K_1N_1 , K_2N_2) elevated the lithium concentration in tested grass biomass.

Barium concentration at Italian ryegrass biomass of the I, II, and IV cut of the second experimental year was significantly affected by varied organic-mineral fertilization, which was confirmed by LSD values (Table 2). Much higher average barium content in the biomass of tested species was found in the first year of study (23.1 $\text{mg} \cdot \text{kg}^{-1}$) than in the second (14.2 $\text{mg} \cdot \text{kg}^{-1}$). The largest amounts of that element (mean for two years) were recorded at the Italian ryegrass biomass on object fertilized with the mushroom substrate with addition of K_2N_2 (22.6 $\text{mg} \cdot \text{kg}^{-1}$), while the smallest – at plants from the object treated with mushroom substrate plus K_1 (14.7 $\text{mg} \cdot \text{kg}^{-1}$). Barium content at tested plant was lower on object fertilized with only mushroom substrate (17.6 $\text{mg} \cdot \text{kg}^{-1}$) than bovine manure (18.9 $\text{mg} \cdot \text{kg}^{-1}$). Complementary mineral nutrition at all tested rates (K_2 , N_1 , N_2 , K_1N_1) influenced on the increase of barium concentration in Italian ryegrass biomass as compared to only mushroom substrate.

Strontium contents in biomass of plants harvested from all cuts in the first and second experimental years indicated significant differentiation depending on the fertilization applied, which was proved by LSD values (Table 3). Mean strontium concentration in Italian ryegrass biomass harvested in the 2nd year was higher (23.3 $\text{mg} \cdot \text{kg}^{-1}$) than in the 1st year of study (16.0 $\text{mg} \cdot \text{kg}^{-1}$). The highest amounts of the element (average for two years) were recorded at plant harvested from the object treated with mushroom substrate and mineral nitrogen at N_2 rate (27.1 $\text{mg} \cdot \text{kg}^{-1}$), while the lowest from objects fertilized with mushroom substrate and potassium at K_1 and K_2 rates (15.8 and 15.3 $\text{mg} \cdot \text{kg}^{-1}$, respectively). Strontium contents in tested grass fertilized with the mushroom substrate only and bovine manure were similar (17.1 and 17.6 $\text{mg} \cdot \text{kg}^{-1}$, respectively). Complementary nitrogen and potassium-nitrogen fertilization

Table 1
The content of lithium [$\text{mg} \cdot \text{kg}^{-1}$ of d.m.] in the yield of *Lolium multiflorum* in I and II year of cultivation

Fertilizer objects	The content of lithium [$\text{mg} \cdot \text{kg}^{-1}$ of d.m.]														
	I year of cultivation (cuts)				II year of cultivation (cuts)				Mean from two years						
	I	II	III	IV	Mean	I	II	III	IV	Mean	I	II	III	IV	Mean
a	54.5	59.5	19.1	32.9	41.5	58.4	105	35.8	18.2	54.5	49.8				
b	46.5	66.0	28.4	64.1	50.5	48.4	86.6	41.5	12.8	44.5	47.5				
c	33.9	59.4	18.9	13.6	31.3	74.2	79.3	27.8	22.6	50.9	41.1				
d	73.3	58.5	24.0	19.3	41.3	59.7	54.8	18.3	30.9	38.4	39.6				
e	43.7	60.4	14.1	15.2	18.3	57.9	42.6	34.2	25.2	39.9	29.1				
f	50.7	58.6	35.2	27.5	43.0	55.1	99.6	96.3	88.6	85.1	64.0				
g	42.0	79.6	42.6	54.5	54.6	66.9	34.4	46.8	24.3	43.1	48.8				
h	35.5	52.2	30.7	22.6	35.2	69.4	46.2	41.8	33.8	47.8	41.5				
i	50.6	64.5	74.1	22.4	52.9	66.7	31.6	36.2	36.6	39.9	46.4				
Mean	47.6	62.1	31.9	30.2	43.1	61.8	64.4	42.1	32.5	49.4	46.5				
LSD _{0.05}	14.0	7.58	5.47	9.27		8.72	11.8	10.9	10.5						

Explanations: a – soil – control; b – soil + fermented bovine manure; c – soil + mushroom substrate; d – soil + mushroom substrate + K_1 ; e – soil + mushroom substrate + K_2 ; f – soil + mushroom substrate + N_1 ; g – soil + mushroom substrate + N_2 ; h – soil + mushroom substrate + K_1N_1 ; i – soil + mushroom substrate + K_2N_2 .

Table 2
The content of barium [$\text{mg} \cdot \text{kg}^{-1}$ of d.m.] in the yield of *Lolium multiflorum* in I and II year of cultivation

Fertilizer objects	The content of barium [$\text{mg} \cdot \text{kg}^{-1}$ of d.m.]												
	I year of cultivation (cuts)					II year of cultivation (cuts)					Mean from two years		
	I	II	III	IV	Mean	I	II	III	IV	Mean	Mean	Mean	Mean
a	12.3	20.6	7.90	33.8	15.6	19.5	11.4	10.2	8.34	12.3	13.9	12.3	13.9
b	9.72	34.2	8.42	40.7	23.2	19.5	17.7	10.8	10.7	14.6	18.9	14.6	18.9
c	11.3	37.3	7.96	40.0	42.0	15.4	10.6	10.6	7.94	11.1	21.5	11.1	21.5
d	10.7	15.9	7.87	40.5	18.7	17.0	11.3	7.65	6.78	10.7	14.6	10.7	14.6
e	10.9	30.5	8.29	42.0	23.0	18.2	20.4	7.65	7.88	14.8	18.9	14.8	18.9
f	13.1	17.6	8.24	41.0	20.1	18.1	13.8	12.4	15.7	16.2	18.1	16.2	18.1
g	16.6	44.4	10.5	39.4	23.9	20.9	15.8	17.4	14.9	18.3	21.1	18.3	21.1
h	13.7	40.4	8.29	28.3	22.6	20.3	12.6	21.2	13.9	15.7	19.1	15.7	19.1
i	13.6	48.4	10.2	45.7	29.5	19.8	10.9	16.3	16.4	16.2	17.5	16.2	17.5
Mean	12.4	32.1	8.63	39.1	23.1	18.7	13.8	12.7	11.4	14.2	18.6	14.2	18.6
LSD _{0.05}	4.86	5.88	n.i.	6.84		n.i.	4.25	2.73	3.84				

Table 3
The content of strontium [$\text{mg} \cdot \text{kg}^{-1}$ of d.m.] in the yield of *Lolium multiflorum* in I and II year of cultivation

Fertilizer objects	The content of strontium [$\text{mg} \cdot \text{kg}^{-1}$ of d.m.]												
	I year of cultivation (cuts)					II year of cultivation (cuts)					Mean from two years		
	I	II	III	IV	Mean	I	II	III	IV	Mean	Mean	Mean	
a	17.5	14.8	17.6	23.2	18.3	21.9	19.7	19.1	21.1	20.4	19.3	19.3	
b	12.7	13.6	11.2	16.4	13.5	25.2	19.7	21.1	20.8	21.7	17.6	17.6	
c	13.5	12.9	15.4	17.9	14.9	19.4	15.3	19.2	23.4	19.4	17.1	17.1	
d	12.9	11.2	16.4	16.1	14.1	19.2	17.3	14.5	19.4	17.6	15.8	15.8	
e	12.7	11.3	12.4	15.8	13.1	20.2	18.7	19.6	15.8	18.6	15.3	15.3	
f	14.4	15.6	14.7	15.4	15.0	23.3	21.1	27.3	49.6	30.3	22.6	22.6	
g	19.3	19.1	16.2	27.5	20.2	25.3	26.8	29.9	54.0	34.0	27.1	27.1	
h	13.5	12.3	15.8	24.6	16.5	23.3	19.3	18.9	35.5	24.2	20.3	20.3	
i	15.5	15.7	14.6	27.4	18.3	24.1	16.2	20.4	35.0	23.3	20.8	20.8	
Mean	14.7	14.0	14.9	20.5	16.0	22.4	19.3	21.1	30.5	23.3	19.7	19.7	
LSD _{0.05}	4.05	3.83	2.13	3.49		1.87	2.68	4.17	5.03				

(N₁, N₂, K₁N₁, K₂N₂) affected the increase of the element concentration in tested grass as compared with objects fertilized with only mushroom substrate.

Lithium and barium levels at Italian ryegrass were higher, while strontium lower, when compared with earlier studies [2, 3], in which the influence of various mushroom substrate rates on trace elements contents at Italian ryegrass was examined. Higher lithium and barium concentrations at the grass might result from a slight soil acidifying due to mineral fertilization used, which might invoke the elevated intake of these elements by tested grass.

Conclusions

1. Less lithium, slightly more barium, and similar amounts of strontium were recorded in the biomass of Italian ryegrass grown in the two-year pot experiment on objects fertilized with only mushroom substrate as compared with those treated with bovine manure.

2. Complementary nitrogen and potassium-nitrogen nutrition at N₁, N₂, K₁N₁ and K₂N₂ rates affected the increase, while potassium (K₁, K₂) the decrease of barium, lithium, and strontium contents in tested grass yields in reference to treating with only the mushroom substrate.

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ODDZIAŁYWANIE PODŁOŻA POPIECZARKOWEGO NA ZAWARTOŚĆ LITU, BARU I STRONTU W BIOMASIE ŻYCICY WIELOKWIATOWEJ

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Abstrakt: W dwuletnim doświadczeniu wazonowym, przeprowadzonym w warunkach szklarni, badano wpływ podłoża po produkcji pieczarek i uzupełniającego nawożenia potasowego, azotowego i potasowo-azotowego na zawartość Li, Ba i Sr w biomacie życicy wielokwiatowej. Średnia zawartość badanych pierwiastków w biomacie testowanej trawy była zróżnicowana w poszczególnych latach i pokosach, układając się w następującym szeregu malejących wartości: Li > Ba > Sr.

Słowa kluczowe: podłoże pieczarkowe, lit, bor, stront

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EFFECT OF DIVERSIFIED FERTILIZATION ON HEAVY METAL CONTENTS IN MEADOW SWARD IN THE MOUNTAIN AREA

WPLYW ZRÓŻNICOWNEGO NAWOŻENIA NA ZAWARTOŚĆ METALI CIĘŻKICH W RUNI ŁĄKOWEJ W REJONIE GÓRSKIM

Abstract: The research was conducted in 2005–2007 on a mountain meadow in Krynica. The experimental field was located at 640 m a.s.l. The experiment was set up on a brown soil with granulometric structure of loamy sand, pH_{KCl} 4.10 and comprised 6 treatments: the control, NPK, loose pen, loose pen + NP, tight pen and autumn loose pen. The mineral treatment was applied in the following doses: 120 N, 25 P and 50 K · ha⁻¹. Organic fertilization was applied as sheep penning. The penning was on two intensity levels: loose pen – 2 m² per sheep and tight pen – 1 m² per sheep. Each year the meadow was cut twice: in mid-June and at the beginning of September. The highest content of Ni, Cr and Pb was assessed on the treatment with autumn loose pen, Zn on NPK treatments and Cu on tight pen, whereas Cd on loose pen + NP. The second cut revealed higher contents of heavy metals than the first cut. The permissible limit of heavy metal contents for fodder plants was not exceeded in the meadow sward, whereas excessive amounts of cadmium were found only in plants on NPK treatment and loose fold supplemented with NP. The greatest deficiency of copper was found in the meadow sward. Irrespective of the experimental treatment, greater quantities of heavy metals were taken up with the first than the second cut yield, which was undoubtedly connected with greater plant biomass obtained on the first date of harvest.

Keywords: heavy metals, loose pen, tight pen, NPK, mountain meadow

In many countries grasslands play a crucial role in farm animal nutrition and cover a considerable part of their nutritional needs. Apart from organic component contents (proteins, carbohydrates) also minerals play an important role in the meadow sward quality assessment [1, 2]. According to many authors, food macroelement and trace element concentrations, including heavy metals determine the quality of fodder

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originating from these grasslands [3, 4]. The contents of heavy metals in feeds from grasslands depends on the individual species properties, habitat conditions, but also on fertilization [1, 4, 5]. Fertilization of meadows and pastures in mountain areas is conducted usually using sheep penning. Usually it proves the only way in which these grasslands can be fertilized, particularly if they are situated at higher altitude and have a considerable land slope. However, during the penning the sward may be partly damaged and its absorbability diminished. Therefore, if a great load of fertilizer components is left in a pen, its considerable amounts may remain unabsorbed by the vegetation and may be carried by seepage water leading to river water pollution. The investigations were conducted to assess the effect of diversified organic and mineral fertilization on heavy metal contents in a meadow sward.

Material and methods

The experiments were conducted in 2005–2007 on a mountain meadow in Krynica situated at the Experimental Unit of the Department of Grasslands, University of Agriculture in Krakow. The experimental field was located at the altitude of 640 m a.s.l. The experiment was set up on brown soil with granulometric structure of loamy sand, pH_{KCl} 4.10 and organic matter content $53 \text{ g} \cdot \text{kg}^{-1}$. Moreover, the soil revealed low content of available phosphorus ($12.3 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$) and potassium ($76.7 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$). The experiment comprised 6 treatments: the control, NPK, loose pen, loose pen + NP, tight pen and autumn loose pen. Mineral treatment was applied in the following doses: 120 N, 25 P and 50 K $\cdot \text{ha}^{-1}$. Organic fertilization was conducted using sheep penning. The penning was on two intensity levels: loose pen – 2 m^2 per sheep and tight pen – 1 m^2 per sheep. The sheep stayed in the pens for two nights per 8 hours. Plant vegetation period lasted from 1 May until 30 September. Each year the meadow was cut twice: in mid-June and at the beginning of September. Monitoring of the temperature and rainfall was conducted during the experiment (Table 1). After harvest the plant material was dried at $65 \text{ }^\circ\text{C}$ in a forced air dryer, then crushed in a laboratory mill and subjected to chemical analysis. The contents of zinc, copper, nickel, chromium, lead and cadmium in the plant material were assessed using ICP-EAS method (inductively coupled plasma-atomic emission spectrometry) after dry mineralization and dissolving the ashes in HNO_3 (1:3). The obtained results were verified statistically using one-way ANOVA and Tukey test at significance level $\alpha < 0.05$ by means of Statistica 7 programme.

Table 1

Monitoring of the weather factors in 2005–2007

Climatic factor	Temperature [$^\circ\text{C}$]			Rainfalls [mm]		
	2005	2006	2007	2005	2006	2007
Mean I–XII	5.6	6.1	7.4	1250	996.9	930.5
Mean IV–IX	12.4	13.0	13.4	732.6	610.3	504.6
Range	–6–16.7	–8.2–18.6	–2.4–17.1	24.6–199.5	19.9–164.3	25.8–212

Results and discussion

Among the determined heavy metals are elements which belong to microelements necessary for proper growth and development of plants (Zn, Cu and Ni) and animals (Cr), whose optimal contents in the sward should fulfill the nutritional requirements of these organisms. The other metals (Pb and Cd) are not necessary and even small amounts may have a toxic effect on living organisms [6]. In the presented research the assessment of heavy metal contents in meadow sward was based on its potential utilization for fodder according to limit values of heavy metals in plants as stated by various authors: Falkowski [7], Gorlach [8], Curyło et al [9], Kabata-Pendias et al [10] and the Regulation of the Minister of Agriculture and Rural Development of 23 January, 2007 on the admissible contents of undesired substances in fodders [11]. The permissible contents of heavy metals in fodder material have been determined as follows: < 100 mg Zn; < 10 mg Cu; < 10 mg Cr; < 10 mg Ni; < 0.5 mg Cd; < 10 mg Pb · kg⁻¹ d.m. The contents of the above-mentioned heavy metals in the analyzed plant material were diversified depending on the kind of applied fertilization and date of harvest, however the greatest changeability was demonstrated for Pb, then for Cd > Cr > Zn > Ni > Cu (Tables 2 and 3). In comparison with other metals the sward contained the greatest quantities of Zn, while levels of the other metals were as follows: Cu > Ni > Pb > Cr > Cd.

Table 2

Contents of zinc, copper and nickel in meadow sward (2005–2007)

Treatment	Zinc		Copper		Nickiel	
	I cut	II cut	I cut	II cut	I cut	II cut
	[mg · kg ⁻¹ d.m.]					
Control	39.13 ^a	60.68	5.85	6.74	1.60 ^{ab}	1.88
NPK	42.38 ^{ab}	67.37	5.36	6.81	1.49 ^{ab}	1.82
Loose pen	54.53 ^{bc}	57.53	6.23	6.38	1.65 ^b	1.68
Loose pen + NP	57.22 ^c	59.17	6.63	6.66	1.57 ^{ab}	1.75
Tight pen	42.80 ^{ab}	60.90	5.38	7.17	1.00 ^a	1.65
Autumn loose pen	38.18 ^a	55.88	4.87	6.38	2.19 ^b	2.09
LSD _{0.05}	18.32	n.s.	n.s.	n.s.	0.89	n.s.
Standard deviation	9.74		0.70		0.30	
V%	18.4		11.2		17.9	

Homogeneous groups according to the Tukey test, $\alpha < 0.05$; n.s. – not significant.

Mean content of Zn ranged from 38.18 to 67.90 mg · kg⁻¹ d.m. The highest zinc concentration was noted on the loose pen + NP (I cut) and on NPK (II cut), whereas irrespectively of the harvest date, the lowest amount was found on autumn loose pen, but no significant differences in this metal content were registered in II cut under the influence of diversified fertilization (Table 2). Analysis of the harvest date revealed 24 % higher content of zinc in the meadow sward harvested in the second cut. As found

by Falkowski et al [7] good quality feed should contain between 30 and 50 mg Zn · kg⁻¹ d.m., so 2 % of samples collected for the three year period of research revealed its deficit, 60 % had optimal content, whereas excessive quantities of zinc were assessed in 40 % of the samples. On the other hand, numerous authors reported frequent zinc deficits in meadow sward [12–14]. Zinc absorbability in plants is affected by soil pH, Ca:Zn and Fe:Zn ratios, the contents of phosphorus, magnesium, nitrogen and copper in soil and by fertilization [15].

Cu content in the analyzed meadow sward ranged from 4.87 to 7.7 mg · kg⁻¹ d.m. (Table 2). On all treatments II cut was characterized by on average a 14 % greater content of Cu in comparison with I cut (Table 2). the smallest amounts of this element, similarly as for zinc were detected in the meadow sward of loose autumn pen. On the other hand the sward in loose pen + NP (I cut) and in tight pen (II cut) revealed the highest copper contents. Optimal copper concentrations in feeds are between 7 and 10 mg · kg⁻¹ d.m. [7], therefore it may be said that a majority of the sward samples, ca 75 % revealed its deficiency. As has been found by various authors, copper deficiencies in feeds from grasslands are a common phenomenon in Poland [2, 13, 16]. Copper phytoavailability depends on the soil pH, contents of organic matter, phosphorus, manganese and iron in soil, and on plant biological properties [1, 15, 16].

The highest mean content of nickel in both cuts was found in the sward on autumn loose pen and the lowest on tight pen. Its contents ranged from 1.00 to 2.09 mg · kg⁻¹ d.m. (Table 2). As in the case of zinc and copper, on a majority of treatments II cut was characterized by on average 17 % bigger content of this metal than cut I. A reverse dependency was demonstrated only on autumn loose pen. Irrespective of the kind of fertilization and harvest date, nickel content in the harvested plants was low (below 10 mg · kg⁻¹ d.m.) allowing for the sward utilization for animal feed.

Depending on the kind of fertilization used and harvest date, chromium content ranged from 0.50 to 1.74 · kg⁻¹ d.m. (Table 3). Both in I and II cut the greatest amounts of chromium were registered on autumn loose pen, whereas the smallest in the control sward (Table 3). Therefore all kinds of applied fertilization caused a 12–53 % increase in this metal content in the meadow sward (I cut) in comparison with the treatment without fertilization and 19–67 % increase (II cut) in comparison with the control. On the other hand, the analysis of harvest date revealed on average 36 % greater content of zinc in the meadow sward harvested in II cut than in I cut. The exception was only the sward harvested from loose pen where I cut revealed 19 % higher chromium content than II cut. Like in the case of nickel, low chromium content allows to use the analyzed meadow sward for animal feed.

Lead and cadmium are counted to the heavy metals posing special hazards to feed quality. Lead content ranged from 0.43 to 1.92 mg · kg⁻¹ d.m. Irrespective of the harvest date, the greatest lead content was registered on autumn loose pen and the smallest on tight pen (I cut) and on the control (II cut) (Table 3). On all treatments II cut showed on average 49 % greater lead content in comparison with I cut. Assuming the standard lead content between 0.1 and 1.0 mg · kg⁻¹ d.m. stated by Gorlach [8] as safe for feeds, it was found that over the three year period of investigations 30 % of sward samples revealed excessive amounts of this metal. On the other hand, assessment of the sward

according to the criteria stated by the Minister of Agriculture and Rural Development of 23 January 2007 on admissible contents of undesired substances in feeds [11] revealed that it met the requirements concerning lead content for good quality feeds.

Table 3

Contents of chromium, lead and cadmium in meadow sward (2005–2007)

Treatment	Chromium		Lead		Cadmium	
	I cut	II cut	I cut	II cut	I cut	II cut
	[mg · kg ⁻¹ d.m.]					
Control	0.50	0.57 ^a	0.51	0.76 ^a	0.38 ^b	0.54
NPK	0.57	1.02 ^{abc}	0.50	1.27 ^{abc}	0.36 ^{ab}	0.75
Loose pen	0.87	0.70 ^{ab}	0.68	0.93 ^a	0.49 ^c	0.57
Loose pen + NP	0.56	0.82 ^{ab}	0.57	1.01 ^{ab}	0.41 ^{bc}	1.18
Tight pen	0.59	1.28 ^{bc}	0.43	1.57 ^{bc}	0.27 ^a	0.53
Autumn loose pen	1.06	1.74 ^c	0.84	1.92 ^a	0.36 ^{ab}	0.59
LSD _{0.05}	n.s.	0.92	n.s.	0.91	0.12	n.s.
Standard deviation	0.37		0.46		0.24	
V%	43.2		50.7		45.2	

Homogeneous groups according to the Tukey test, $\alpha < 0.05$; n.s. – not significant.

Cadmium content in the analyzed meadow sward fell within the 0.27–1.18 mg · kg⁻¹ d.m. range depending on treatment and harvest date (Table 3). The highest cadmium content in meadow sward was registered on loose pen (I cut) and on loose pen + NP (II cut), the lowest on tight pen, irrespective of the harvest date, but in I cut the differences in this metal content affected by diversified fertilization were statistically significant. On all treatments II cut was characterized by on average 42 % greater cadmium content in comparison with I cut (Table 3). According to the norms stated above, cadmium content below 0.5 mg · kg⁻¹ d.m. does not limit use of the analyzed plants for fodder. Therefore 70 % of the sward samples had optimal cadmium content, whereas its excess was found in 30 %.

Table 4

Values of correlation coefficients between heavy metal contents in meadow sward

Element	Zinc	Copper	Nickiel	Chromium	Lead
Copper	0.44***				
Nickiel	0.33**	-0.18			
Chromium	0.33**	-0.07	0.59***		
Lead	0.46***	0.15	0.50***	0.84***	
Cadmium	0.33**	0.12	0.25*	0.09	0.14

Significant: * $r \leq 0.05$, ** $r \leq 0.01$, *** $r \leq 0.001$

The interrelations of heavy metal contents in the sward fluctuated widely, which evidences changing quality of fodder obtained during the vegetation period (Table 4).

The research demonstrated significantly positive correlation between zinc content and the levels of copper and lead ($r \leq 0.001$) but also the levels of nickel, chromium and cadmium ($r \leq 0.01$). Nickel content was also apparently positively correlated with chromium and lead concentrations ($r \leq 0.001$). The same positive correlation was noted for chromium level and lead content ($r \leq 0.001$).

Heavy metal uptake per area unit is a resultant of the crop yield and their contents in the plant mass. Aggregate uptake of zinc by the meadow sward fluctuated during the three-year period of experiments from 214.52–369.05 g; uptake of copper 27.98–42.41 g; nickel 6.32–11.92 g; chromium 2.42–7.12; lead 2.78–6.49 g and cadmium 1.32 to 3.70 g · ha⁻¹ (Table 5).

Table 5

Heavy metal uptake by meadow sward (2005–2007)

Treatment	Zinc	Copper	Nickiel	Chromium	Lead	Cadmium
	[g · ha ⁻¹]					
Control	214.52	29.32	7.64	2.42	2.78	1.93
NPK	337.71	39.65	10.69	4.76	4.87	3.20
Loose pen	267.68	31.39	7.62	3.94	3.61	2.48
Loose pen + NP	369.05	42.41	9.78	3.81	4.27	3.70
Tight pen	263.04	34.67	6.32	4.25	4.25	1.92
Autumn loose pen	221.78	27.98	11.92	7.12	6.49	2.15
Standard deviation	62.24	5.79	2.14	1.55	1.26	0.73
V%	22	17	24	35	29	29

From among the analyzed heavy metals zinc was taken up with the sward yield in the greatest quantities, whereas cadmium in the smallest. Irrespective of the treatment higher uptake of the metals with I cut yield was noted than with II cut, which was undoubtedly connected with greater plant biomass obtained at the first harvest date. The increase was 42 % for zinc, 46 % for copper, 52 % for nickel, 39 % for chromium, 13 % for lead and 20 % for cadmium. Zinc uptake by meadow sward fertilized by loose penning supplemented by NP was the greatest. In comparison with the control treatment the increase was 42 %. The smallest quantity of zinc was taken up with control plant yield. Copper uptake by the sward was little diversified as evidenced by the lowest variation coefficient ($V \% = 17$). Like in the case of zinc, the highest copper uptake was revealed on loose pen + NP. In comparison with the control the increase was 31 %. The smallest quantities of copper were removed with the meadow sward yield on autumn loose pen (Table 5). The greatest nickel uptake was noted on autumn loose pen and the smallest on tight pen (Table 5). Chromium uptake by the meadow sward on the analyzed treatments was the most diversified ($V = 35 \%$). Like in the case of nickel, fertilization using autumn loose penning most influenced an increase in chromium uptake, which reached 66 % more than on the control. Non-fertilized plants absorbed the least quantities of chromium. The relationships were similar for lead uptake. The

greatest amounts of lead were removed with plants fertilized with autumn loose pen, where the increase in comparison with the control reached 57 %. The largest quantities of cadmium were taken up with the sward yield on NPK treatment, whereas the smallest on tight pen and on the control (Table 5).

Animal excrements are valuable organic fertilizer which plays an important role not only supplying necessary nutrients in plant and animal nutrition, but also in shaping soil fertility [17, 18]. According to Kasperczyk et al [19], organic fertilizers are a supplement of mineral fertilizers used on grasslands because they contain vital trace elements, which generally mineral fertilizers lack. A positive effect of applied organic fertilization was also revealed in the presented research since heavy metal contents in the meadow sward given in Tables 2 and 3 evidence that the permissible border for plants designed for animal feeds was not exceeded. Only in the case of cadmium plants on NPK treatments and loose pen supplemented with NP revealed its over the norm contents. Additionally it was found that a majority of the analyzed trace elements showed the optimal contents in the meadow sward, and only copper deficit was assessed in 75 % of samples.

Conclusions

1. Among the fertilizer treatments the highest contents of Ni, Cr and Pb were assessed on the treatment with autumn loose pen, Zn on NPK treatments, Cu on the treatment with tight pen, whereas Cd on treatments with loose pen + NP.
2. The second cut revealed on average: higher contents of heavy metals (24 % Zn; 14 % Cu; 17 % Ni; 36 % Cr; 49 % Pb and 42 % Cd) than the first cut.
3. The experiments revealed that the permissible limit of heavy metal contents in plants destined for animal feeds was not exceeded. Only in case of Cd the plants from NPK treatment and loose pen supplemented with NP revealed its over the norm content.
4. Among the analyzed metals the greatest deficiency in the meadow sward was registered for copper.
5. The greatest uptake of zinc and copper was found on the treatment with loose pen supplemented with NP, absorption of nickel, chromium and lead on the treatment with autumn loose pen and cadmium under the influence of NPK.
6. Irrespective of the experimental treatment, greater uptake of metals with I than II cut was found, which was undoubtedly connected with greater plant biomass obtained at the first harvest date.

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WPLYW ZRÓŻNICOWANEGO NAWOŻENIA NA ZAWARTOŚĆ METALI CIĘŻKICH W RUNI ŁĄKOWEJ W REJONIE GÓRSKIM

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Abstrakt: Badania prowadzono w latach 2005–2007 na łące górskiej w Krynicy. Pole doświadczalne znajdowało się na wysokości 640 m n.p.m. Doświadczenie założono na glebie brunatnej o składzie granulometrycznym piasku gliniastego, pH_{KCl} 4,10. Doświadczenie obejmowało 6 obiektów doświadczalnych: obiekt kontrolny, NPK, koszar luźny, koszar luźny + NP, koszar ciasny i koszar luźny jesienny. Na obiekcie z nawożeniem mineralnym zastosowano nawożenie w następującej dawce: 120 N, 25 P i 50 K $kg \cdot ha^{-1}$. Nawożenie organiczne przeprowadzono za pomocą koszarzenia, przy udziale owiec. Koszarzenie obejmowało dwa poziomy intensywności: koszar luźny – 2 m^2 na owcę, koszar ciasny – 1 m^2 na owcę. Łąkę corocznie koszono 2-krotnie w połowie czerwca i na początku września. Największą zawartość Ni, Cr i Pb stwierdzono w obiekcie z koszarem luźnym jesiennym, Zn w obiektach z NPK, Cu w obiekcie z koszarem ciasnym, natomiast Cd w obiektach z koszarem luźnym + NP. Pokos drugi charakteryzował się większą zawartością metali ciężkich niż pokos pierwszy. W runi łąkowej nie została przekroczona dopuszczalna granica zawartości metali ciężkich przewidziana dla roślin wykorzystywanych na paszę. Jedynie w przypadku kadmu rośliny w obiektach nawożonych NPK i koszarem luźnym uzupełnionym NP wykazywały ponadnormatywne jego zawartości. Największy niedobór w runi łąkowej wykazano w przypadku miedzi. Niezależnie od obiektu doświadczalnego większy wyciąg metali stwierdzono wraz plonem I pokosu niż II, co niewątpliwie było związane z większą biomasa roślin uzyskanych w pierwszym terminie zbioru.

Słowa kluczowe: metale ciężkie, koszar luźny, koszar ciasny, NPK, łąka górska

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INFLUENCE OF INDUSTRIAL POLLUTION ON THE WATER QUALITY OF THE LOWER RIVER DOBRA

WPLYW ZANIECZYSZCZEŃ PRZEMYSŁOWYCH NA JAKOŚĆ WÓD DOLNEGO ODCINKA RZEKI DOBREJ

Abstract: Between 2007 and 2008 water samples were collected from the River Dobra (right-side tributary of the River Widawa). The samples were gathered in four seasons from five sites of the Lower Dobra River. The following parameters were measured: temperature, water reaction, alkalinity, hardness, and oxygen, nitrites(III and V), ammonium, chlorides, calcium, phosphorus, sulfates and magnesium content.

The influence of contaminants from a plant on the quality of the Lower Dobra River was researched. Almost all examined parameters were on average higher on the site II in comparison with the other researched sites. The highest changes were observed in phosphorus (an increase of 192 %), chlorides (an increase of 155 %) and nitrates(V) (an increase of 153 %) concentration. No differences were determined in an average content of nitrates(III) but their concentration in sewage was different depending on the season. It was two-fold higher in summer and winter. There were no significant differences in water reaction between the River Dobra and sewage from the plant.

On the site II both higher significant increase in chlorides concentration and significant increase in phosphorus content as compared with other measurement sites were noted. These results cause higher significant increase of an electric conductivity of water. Despite the fact that many pollutants were introduced into the Lower Dobra River an average concentrations of magnesium (15 %) and nitrates(III) (7 %) were higher in water of the River Dobra near the Widawa (site V) than in water coming from the River Dobra above a sewage tributary (site I). Water conductivity was measured at higher level with the highest in autumn – 1345 $\mu\text{S} \cdot \text{cm}^{-1}$ and the lowest in winter – 706 $\mu\text{S} \cdot \text{cm}^{-1}$.

Keywords: water quality, Dobra River, sewage

Water contamination creates a considerable problem these days. However, natural environment plays a role of a limiting factor to an adverse antropogenic influence by the mobilization of purifying processes in water.

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Natural water environment as a very good dissolvent may contain different substances of both organic and inorganic origin as well as gases which enter into the water through hydrological cycle [1]. No natural water is chemically clean hence it should always be considered as a mixture of water and substances comprised of organic and inorganic contaminants and other substances [2]. Both substances that do not occur in ecosystems normally (eg pesticides, petroleum compounds) and compounds which flowing into the water causing their pollution are treated as contaminants. Such substances comprise of phosphorus, sulfates, nitrates etc. Too high amount of contaminants introduced to river course can contribute to the creation of open sewage channels. In spite of the fact that many sewage treatment plant have been established in the recent years there are still places supplying and discharging their effluents to the running and stagnant water [3]. Probably it is one of the most crucial factors influencing deterioration of water quality, although, rivers deal with this problem by mobilization of self-purifying processes. Self-purification is strongly related to biochemical transformation of the organic compounds into the simple, inorganic substances with the usage of microbial organisms operating on the oxygen taken directly from water and air [3]. Effective self-purification process can be observed if the ratio of the sewage to the surface water volume, where the effluents flow is not exceeding 1:50 ratio. The inflow of pollutants inhibits self-purification process by poisoning microorganisms causing a decay of organic compounds [4].

Big, pure rivers deal with contaminants a lot better than smaller ones. Due to the fact that sewage entering smaller rivers can lead to biological balance disturbance it was of the utmost importance to determine if water of the Lower Dobra River is capable of its self-purification. The aim of this research was to examine if self-purification processes allow contaminated water to return to the water of the previous cleanness condition before it flowed into the River Widawa.

Material and methods

The subject of the research was water obtained from the River Dobra which is also called the River Widawka and flows in the area of Lower Silesia being a right Widawa tributary. The source of the river is located at the height of 165 m above the sea level in the region of Bartków. The Widawa Basin is symmetrically built, fan-shaped with its lower part changing into parallel layout while the drainage area is getting asymmetric [5].

Analytic material was collected in four seasons between 2007 and 2008 on five different sites:

Site I – Pawłowice – above sewage inflow	59°09'42,95°N 17°06'56,32°E
Site II – Pawłowice – in the place of effluent inflow	51°09'42,07°N 17°06'55,71°E
Site III – Pawłowice – below sewage inflow	51°09'40,43°N 17°06'52,56°E
Site IV – Kłokoczycki bridge	51°09'17,70°N 17°06'17,25°E
Site V – Widawa Estuary – Kłokoczce	51°08'57,09°N 17°05'41,44°E

The following parameters were measured directly on the sites:

- temperature using using a Slandi TC 204 electronic thermometer;
- electrolytic conductivity [6];
- reaction using electrometric method [7];
- dissolved actual oxygen using Hanna Instruments 9143 oxygen probe [8].

The other parameters were measured under laboratory conditions:

- total hardness [9];
- calcium [10];
- magnesium as a difference between total hardness and calcium;
- nitrate(V) nitrogen [11];
- nitrate(III) nitrogen [12];
- ammonium nitrogen [13];
- phosphates [14];
- chlorides [15].

Obtained results were statistically analysed using Statistica 8.0 programme.

Results and discussion

Water temperature in the River Dobra was ranging between 4.5 °C and 21 °C which is a standard temperature for Polish waters. Temperature in surface water shows great variability depending on the season (in summer 20 °C and more while in winter 0 °C) [16].

Conductivity depends on the temperature and the kind of soluble ions contained in water. Conductivity in the River Dobra was ranging from 706 $\mu\text{S} \cdot \text{cm}^{-1}$ to 1345 $\mu\text{S} \cdot \text{cm}^{-1}$ (Table 1, Fig. 1). Exceeding standard values [4] the result is characteristic for water of the II class of water [17].

Table 1

Conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$] of the River Dobra water between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	908	1212	1028.2	128.02
Summer	748	1315	891.2	239.17
Autumn	834	1345	949.4	221.74
Winter	706	1043	785.6	145.48

Regardless of the season higher conductivity (up to 40 %) was measured in the place of sewage inflow introduction. The longer distance from the effluent inflow the lower conductivity. Above the place where sewage was introduced into the water of the River Widawa conductivity was achieving a level characteristic for water without effluent loading. Taking into account electric conductivity as the sole criteria for comparison it could be assumed that water of the River Dobra was considerably more polluted than

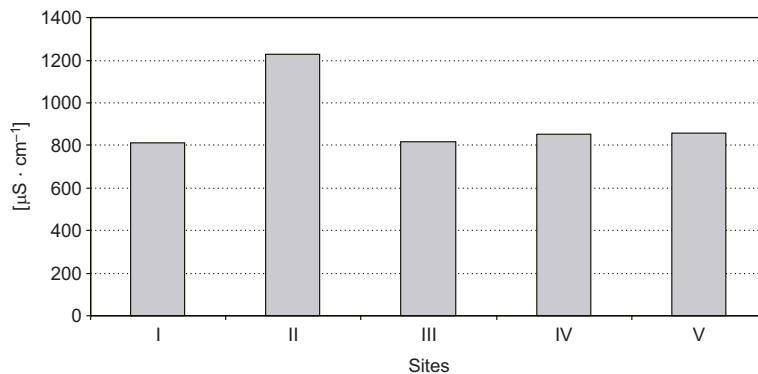


Fig. 1. Average water conductivity [$\mu\text{S} \cdot \text{cm}^{-1}$] on five sites of the River Dobra

mountain river [18]. However, its conductivity was similar to the conductivity of the Wisla flowing in lowland area near to Warsaw ($380\text{--}1360 \mu\text{S} \cdot \text{cm}^{-1}$) [19].

Water reaction of the River Dobra in the place where sewage was introduced ranged between 7.37 and 8.10 (Table 2). After sewage introduction reaction was increasing in all seasons except for winter (Fig. 2). Below the place of sewage inflow to the water no decrease in reaction was observed therefore it can be assumed that there were no salts of weak alkalis and strong acids in water on the II site with high probability of strong alkalis and weak acids occurrence. Water of the River Dobra are suitable for fish due to their favorable water reaction ranging from 6.5 to 8.5 [20] which is considered to be the most optimal for fish health and growth. Higher water reaction was noted in winter and autumn in comparison to other seasons. Similar phenomena was observed by Saleh et al [21]. When comparing the River Dobra waters in terms of their reaction it should be noted that they did not differ from other Polish waters [18, 22–24] and they could have been classified to the II class of water [17].

Table 2

Water reaction (pH) of the River Dobra water between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	7.43	8.97	8.16	0.56
Summer	8.00	8.38	8.174	0.15
Autumn	7.33	7.72	7.49	0.17
Winter	7.75	8.09	7.974	0.14

Dissolved oxygen presence in water is an undeniable proof for water ability to self-purification by oxidation of organic compounds (or their decomposition in the presence of oxygen bacteria) [25]. Oxygen in such form is often used for the determination of water quality. An average concentration of oxygen in clean rivers in temperate climate ranges from 5 to $7 \text{ mgO}_2 \cdot \text{dm}^{-3}$ and such levels of an oxygen were measured in the Dobra in autumn and winter. Lower concentrations may result from

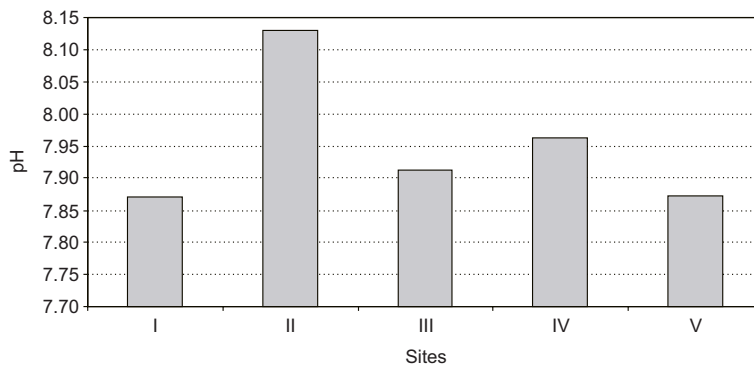


Fig. 2. Average water reaction (pH) on five sites of the River Dobra

higher water temperature or mineralization processes of organic compounds which use up oxygen [25]. In spring and summer it is undoubtedly for the increase in temperature why oxygen concentration is lower in the River Dobra. Dissolved oxygen was ranging from $0.00 \text{ mgO}_2 \cdot \text{dm}^{-3}$ to $13.90 \text{ mgO}_2 \cdot \text{dm}^{-3}$ (Table 3, Fig. 3).

Table 3

Dissolved oxygen [$\text{mgO}_2 \cdot \text{dm}^{-3}$] in the River Dobra water between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	0.00	4.73	3.03	1.80
Summer	1.29	5.01	3.03	1.49
Autumn	3.05	5.75	3.96	1.04
Winter	9.55	13.9	11.38	1.71

Based on the Regulation from 2004 [26] waters of the Dobra were classified to V class mainly due to the lack of oxygen in the place of sewage introduction in spring.

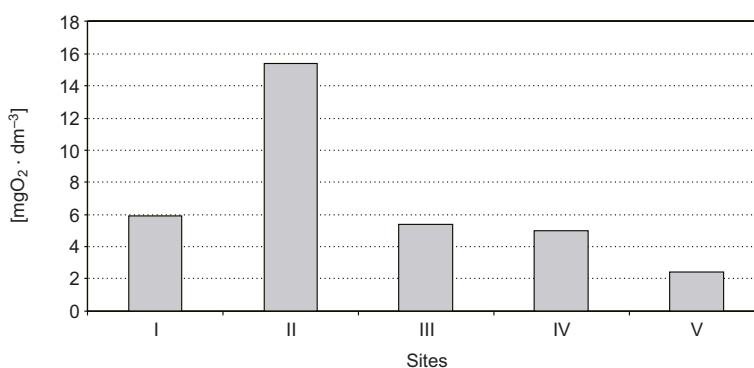


Fig. 3. Average dissolved oxygen [$\text{mgO}_2 \cdot \text{dm}^{-3}$] in water on five sites of the River Dobra

Current regulations do not allow for classification of the River Dobra waters to I nor II class. Temporary lack of oxygen in water is possible in other classes [17]. Low oxygen concentration may be influenced by the season as in spring due to higher activity of biota greater oxygen demand is noted. Oxygen concentration measured in the Dobra is low especially in spring and in water where sewage is introduced. The following rivers were compared in terms of oxygen concentration: the River Bystrzyca Dusznicka ($7.5\text{--}10.6 \text{ mgO}_2 \cdot \text{dm}^{-3}$) [18], the Stream Topór ($8.62\text{--}15.20 \text{ mgO}_2 \cdot \text{dm}^{-3}$) [22] and the River Nysa Szalona ($7.47\text{--}14.93 \text{ mgO}_2 \cdot \text{dm}^{-3}$) [24]. Oxygen concentration in the Dobra was lower than in other rivers from Lower Silesia. In the River Dobra maximum amount of oxygen was noted in winter because of higher oxygen solubility in cold water [27]. After the introduction of sewage waters of the Dobra better oxygen concentration on nearby site III was noted. At the estuary of the River Dobra to the Widawa oxygen concentration was the same as before sewage introduction. It was only in the place of effluent introduction in spring and summer where water was inappropriate even for *Cyprinidae* fish [20].

Table 4

BOD₅ [$\text{mgO}_2 \cdot \text{dm}^{-3}$] of the River Dobra water between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	1.05	3.57	1.96	1.03
Summer	0.98	4.67	2.41	1.53
Autumn	0.73	17.22	4.82	6.96
Winter	4.42	37.65	18.11	12.42

Biochemical Oxygen Demand (BOD₅) measured in the Dobra was very diverse depending mainly on a season (Table 4, Fig. 4). The parameter was ranging from 0.98 to $37.65 \text{ mgO}_2 \cdot \text{dm}^{-3}$. According to the Regulation of 2004 it allows for classification to V class [26]. In summer waters of the Dobra in terms of oxygen demand should have been classified to waters which were susceptible to contamination [28]. It could be

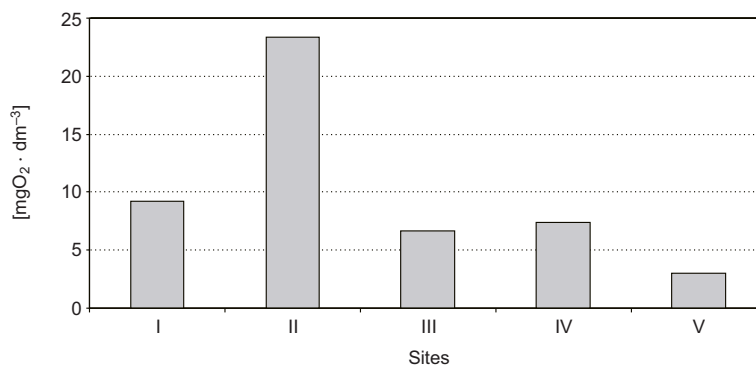


Fig. 4. Average BOD₅ [$\text{mgO}_2 \cdot \text{dm}^{-3}$] on five sites of the River Dobra

claimed that water on the site I in summer and autumn was not contaminated. Organic pollution occurred above the field of investigation in winter as even above the place of sewage introduction $BOD_5 > 5 \text{ mgO}_2 \cdot \text{dm}^{-3}$. Any effluent introduction into the water of the River Dobra resulted in an increase in oxygen demand. At the Widawa estuary water may be classified to insignificantly contaminated. BOD_5 results obtained in summer were similar to that of the Nysa Szalona ($0.48\text{--}8.14 \text{ mgO}_2 \cdot \text{dm}^{-3}$) [24], higher in the Bystrzyca Dusznicka ($0.1\text{--}1.7 \text{ mgO}_2 \cdot \text{dm}^{-3}$) [18] and lower in the Topór Stream ($5.26\text{--}7.00 \text{ mgO}_2 \cdot \text{dm}^{-3}$) [22]. However, in winter it was considerably higher in comparison with other rivers in the region.

Water hardness is a result of dissolved salts occurrence in water mainly calcium and magnesium, salts of iron, barium and manganese are less significant [29]. In 2007 in the Dobra hardness was ranging from $321.30 \text{ mgCaCO}_3 \cdot \text{dm}^{-3}$ to $1013.88 \text{ mgCaCO}_3 \cdot \text{dm}^{-3}$ (Table 5, Fig. 5). Hardness measured in the River Dobra at the estuary to the Widawa in 2006 was estimated to $298\text{--}490 \text{ mgCaCO}_3 \cdot \text{dm}^{-3}$ while in 2004 it was measured at $275\text{--}492 \text{ mgCaCO}_3 \cdot \text{dm}^{-3}$ [30]. Therefore, hardness of the Dobra was higher in 2007 in comparison with results from previous years especially in terms of maximum values. Except for the River Dobra high total hardness was also noted in the Topór Stream ($913.92\text{--}963.90 \text{ mgCaCO}_3 \cdot \text{dm}^{-3}$) [22].

Table 5

The water hardness [$\text{mgCaCO}_3 \cdot \text{dm}^{-3}$] of the River Dobra between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	321.3	414.12	367.71	43.87
Summer	571.2	1013.88	699.72	178.52
Autumn	703.29	963.90	774.69	111.62
Winter	714.0	874.65	753.27	69.59

According to Holden 1970 [19] water in the Dobra in terms of hardness was determined as very hard. The introduction of sewage into the water of the Dobra

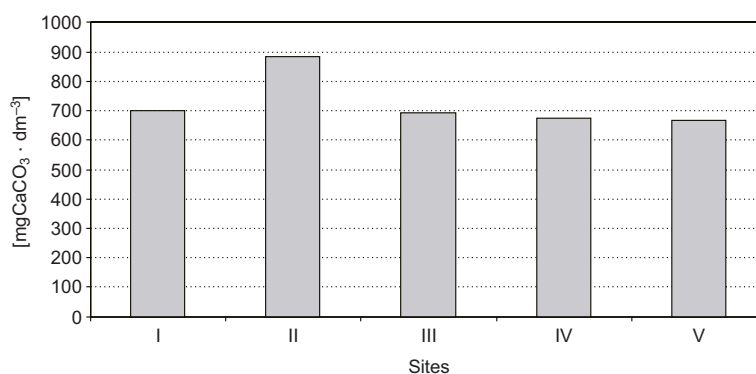


Fig. 5. Average water hardness [$\text{mgCaCO}_3 \cdot \text{dm}^{-3}$] on five sites of the River Dobra

changed the hardness of water so it can be suspected that effluent was rich in calcium, magnesium, iron and manganese salts introduced mainly as carbonates, sulfates and chlorides.

Calcium concentration in water of the River Dobra did not allow for classification to the I nor II class [17]. Higher calcium concentration was measured on the site II (Table 6, Fig. 6). However, on the site III a decrease in calcium content to preliminary values was apparent. An increase in Ca and Mg content in both the River Dobra and the Basin during autumn–winter period is justified when taking into account presence of fish farms above the field of research. After autumn fish catches are stored in storehouses which are limed and filled with water only late in autumn or winter. It explains elevated reaction of water in this season.

Table 6

Calcium concentration [$\text{mgCa} \cdot \text{dm}^{-3}$] in water of the River Dobra between 2007–2008 year

	Min	Max	Average	Standard deviation
Spring	112.97	155.87	124.97	17.53
Summer	168.74	211.64	182.75	17.41
Autumn	254.54	337.48	274.27	35.54
Winter	271.70	350.35	298.81	30.50

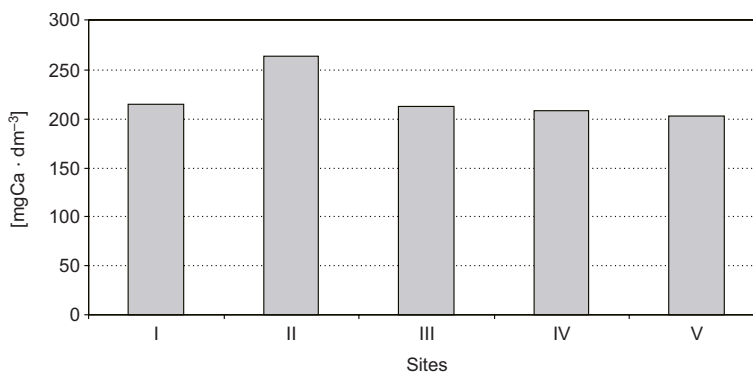


Fig. 6. Average calcium concentration [$\text{mgCa} \cdot \text{dm}^{-3}$] in water on five sites of the River Dobra

Magnesium concentration in water of the Dobra in 2007 was ranging from 6.07 to 175.33 $\text{mgMg} \cdot \text{dm}^{-3}$ (Table 7, Fig. 7) which prevented it from classification to the I nor II class. Previous legally binding norms would allow for water classification to the IV class. Higher amount of magnesium may have been caused by sewage drop and processes of washing from soil. Effluent introduction (especially in summer) influenced higher Mg concentration in waters of the Dobra although 50 m from the place of introduction considerable decrease in Mg content was observed. No increase in Mg concentration in sewage was noted in spring and autumn. High level of Mg in winter was probably caused by mentioned earlier liming in fish storehouses which with calcium introduces magnesium compounds.

Table 7

Magnesium concentration [$\text{mgMg} \cdot \text{dm}^{-3}$] in water of the River Dobra
between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	5.20	32.11	13.53	11.49
Summer	26.04	118.00	59.18	34.76
Autumn	15.62	31.24	21.87	7.82
Winter	143.22	175.33	151.03	13.91

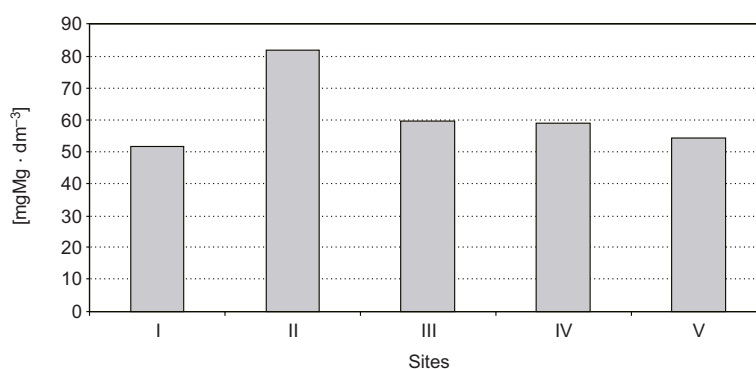


Fig. 7. Average magnesium concentration [$\text{mgMg} \cdot \text{dm}^{-3}$] in water of on five sites of the River Dobra

Occurrence of nitric compounds in water indicates permanent organic contamination of water. Nitrates are an indicator of long and constant pollution [25]. In surface waters nitrates are usually determined at low concentration. They belong to organic and inorganic compounds of the highest oxidation degree and are present in sewage treatment effluents after the process of biological purification. Sources of nitrates comprise of urban, industrial sewage and flow from fields fertilized with nitric fertilizers which penetrate to water [1]. The highest nitrates concentration in the Dobra was measured in the place of effluent introduction (Table 8, Fig. 8).

Table 8

Nitrates(V) concentration [$\text{mgNO}_3 \cdot \text{dm}^{-3}$] in water of the River Dobra
between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	0.04	0.07	0.046	0.01
Summer	0.04	0.06	0.048	0.01
Autumn	0.15	1.05	0.340	0.40
Winter	0.10	0.14	0.112	0.02

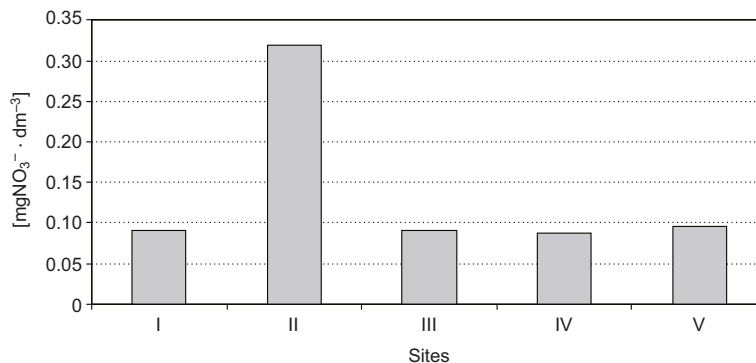


Fig. 8. Average nitrates concentration [mgNO₃ · dm⁻³] in water on five sites of the River Dobra

Presence of all these nitric compounds in water may indicate constant contamination of water with sewage also from surrounding fields and meadows. Nitrates levels were ranging from 0.10 to 1.05 mgNO₃ · dm⁻³ and despite an increase in their concentration on the site II they still were determined at low levels which allowed for classification of water to the I class according to both current and expired norms [17, 26]. Higher nitrates concentration was observed in spring, summer and autumn, however, it was not considerable.

Nitrates(V) concentration in the River Dobra in comparison with the mountain stream Brzęczek (8.63 mgNO₃ · dm⁻³) was considerably lower [31]. Waters of the Dobra at the estuary to the Widawa in 2006 indicated higher nitrates concentration up to 30 % (3.14–31.3 mgNO₃ · dm⁻³) while in 2004 up to 50 % (5.67–51.2 mgNO₃ · dm⁻³). High concentration of this parameter (6.38–17.3 mgNO₃ · dm⁻³) was noted in water of the researched River Dobra below Dobroszyce in 2007 [30]. Approximate levels of nitrates were measured also in other rivers such as the Postomia (0.01–0.74 mgNO₃ · dm⁻³) [32], the Topór Stream (0.14–0.17 mgNO₃ · dm⁻³) [22] and the Nysa Szalona (0.00–5.24 mgNO₃ · dm⁻³) [24].

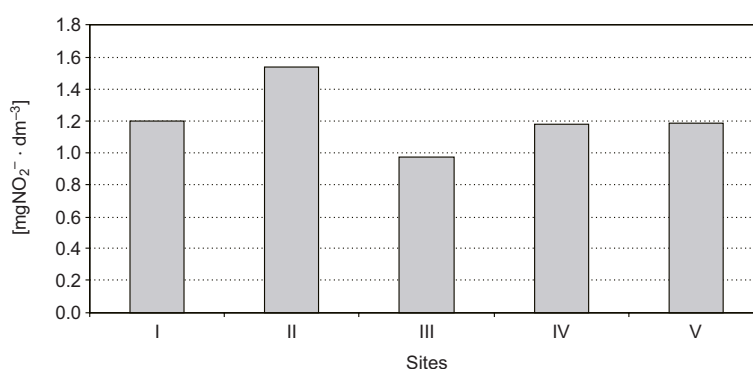
In terms of minimum nitrates(III) concentration of water Dobra River was similar to water of the Widawa (0.00–0.03 mgNO₂ · dm⁻³) [33], the Bystrzyca Dusznicka (0.00–0.25 mgNO₂ · dm⁻³) [18] and the Topór Stream (0.00 mgNO₂ · dm⁻³) [22]. A bit higher concentration was noted in water of the Dobra flowing into the Widawa in 2006 (0.006–1.41 mgNO₂ · dm⁻³) and in 2004 (0.115–1.06 mgNO₂ · dm⁻³) [30]. The River Brzęczek in Sudety showed similar nitrites concentration (0.23 mgNO₂ · dm⁻³) [23] to the Dobra in winter and spring although it was lower in other seasons. Diverse nitrites concentration in the River Dobra and the lack of their clear connection with the introduction of sewage may lead to assumption that there was an insignificant amount or complete lack of nitrites in the sewage.

Nitrates(III) concentration was ranging from 0.00 mgNO₂ · dm⁻³ to 5.87 mgNO₂ · dm⁻³ (Table 9, Fig. 9) what allowed for classification of the researched water to the V class (according to The Regulation from 2004) [26]. There are no current norms regulating the amount of nitrates(III) in Polish rivers.

Table 9

Nitrates(III) concentration [$\text{mgNO}_2 \cdot \text{dm}^{-3}$] in water of the River Dobra between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	0.002	0.210	0.09	0.10
Summer	2.950	5.870	3.98	1.18
Autumn	< 0.002	1.500	0.58	0.55
Winter	0.150	0.300	0.21	0.05

Fig. 9. Average nitrates(III) concentration [$\text{mgNO}_2 \cdot \text{dm}^{-3}$] in water on five sites of the River Dobra

During the year ammonium values were changing with the lowest concentration occurring in summer when ammonium in higher temperature was used by plants in nitrification processes. In winter higher concentration was observed due to the lower temperature and the inhibition of life in waters as there were no nitrification processes. The highest ammonium concentration in the Dobra was noted in spring [19]. Ammonium concentration was ranging from $0.00 \text{ mgNH}_4 \cdot \text{dm}^{-3}$ to $7.32 \text{ mgNH}_4 \cdot \text{dm}^{-3}$ (Table 10, Fig. 10).

Table 10

Ammonium concentration [$\text{mgNH}_3 \cdot \text{dm}^{-3}$] in water of the River Dobra between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	2.76	7.32	4.04	1.86
Summer	2.16	2.89	2.42	0.28
Autumn	0.60	3.00	1.26	0.98
Winter	< 0.04	3.00	1.80	1.44

According to the Regulation from 2008 waters with such parameters can not be classified to the I nor II class but to the III, IV or V class where no limiting

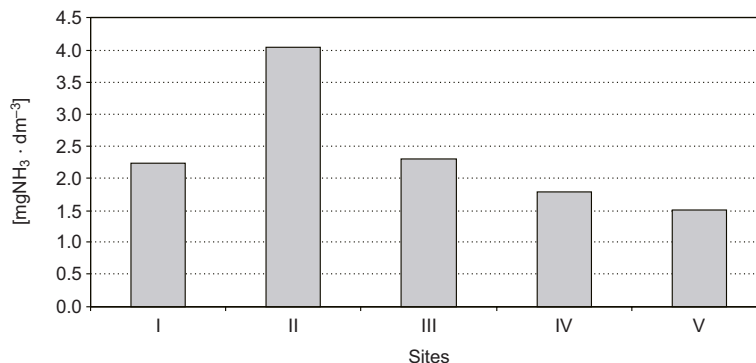


Fig. 10. Average ammonium concentration [mgNH₃ · dm⁻³] in water on five sites of the River Dobra

concentrations are defined [17]. The lowest concentration 0.00 mgNH₄ · dm⁻³ was measured at the estuary to the Widawa. Water on this site may be classified to I class [17]. Small amounts of ammonium may have been caused by nitrification processes and its consumption by water organisms. The highest values were always measured in the same place (sewage introduction) regardless of a season. Therefore, it can be assumed that effluent introduced to the water contained ammonium. Another source of ammonium are flows from the nearby fields. An increase in ammonium concentration was noted in the place of sewage introduction throughout the whole year. In spring an increase was up to 100 % while in autumn it was higher than 100 %. On the site II a considerable decrease in ammonia concentration was measured. Ammonium content in this place was lower from the values obtained on the site I. Lower ammonium amounts were measured up with the flow of the Widawa. In spite of the fact that ammonium concentration in the Dobra was low, in comparison with other rivers such as the Nysa Szalona (0.02–0.76 mgNH₄ · dm⁻³) [24], the Topór Stream (0.20–0.41 mgNH₄ · dm⁻³) [22] and the Bystrzyca Dusznicka (0.02–0.22 mgNH₄ · dm⁻³) [18] it was still higher.

Phosphates concentration in waters of the River Dobra was ranging from 0.10 to 5.70 mgPO₄ · dm⁻³ (Table 11, Fig. 11). Maximum values were noted on the site II (place of sewage introduction) regardless of a season. Obviously the sewage was responsible for their high content in water. An increase in phosphates concentration may be contributed to field runoffs. The River Dobra is surrounded by arable fields which may have been fertilized by fertilizers containing phosphorus. Higher phosphates amount was reported on the site II during the whole year. It was mainly an increase of 50 %. However, below the place of sewage introduction a considerable decrease of 50 % or a return to preliminary values in PO₄⁻³ content was measured. In the surface water phosphorus concentration was measured at 0.06 mg P in 1 dm³ [29] and its occurrence was periodical. In summer the lack of phosphorus in water was noted as it was assimilated by microorganisms, which used it for an optimal growth. On the contrary, in winter when microorganisms disappeared an increase in phosphorus concentration was noticed [3].

Table 11

Phosphates concentration [$\text{mgPO}_4^{-3} \cdot \text{dm}^{-3}$] in water of the River Dobra between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	1.13	2.2	1.41	0.44
Summer	3.20	5.7	3.82	1.07
Autumn	0.70	5.0	1.98	1.78
Winter	0.10	5.0	1.28	2.10

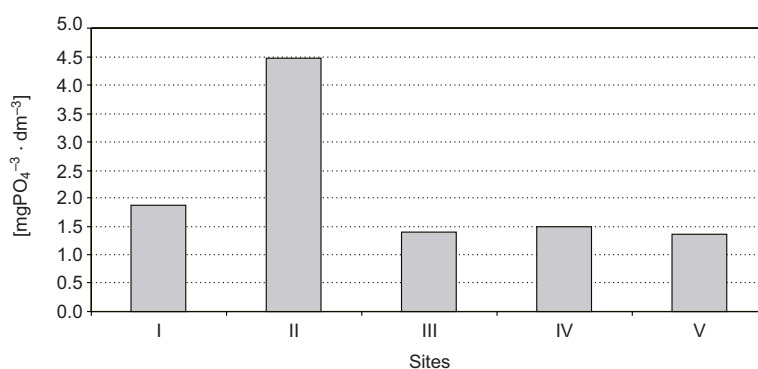


Fig. 11. Average phosphates concentration [$\text{mgPO}_4^{-3} \cdot \text{dm}^{-3}$] in water on five sites of the River Dobra

Water of the Dobra was defined as rich in phosphates with much higher phosphorus concentration in comparison with other rivers of the Lower Silesia [18, 24, 32]. However, similar phosphates concentration as in the Dobra was measured in summer in the Widawa ($0.18\text{--}1.52 \text{ mgPO}_4^{-3} \cdot \text{dm}^{-3}$) [33]. An analysis of the Dobra in 2006 at the estuary to the Widawa showed phosphates concentration ranging from $0.31\text{--}3.34 \text{ mgPO}_4^{-3} \cdot \text{dm}^{-3}$, the same amount as in 2007.

Chlorides in uncontaminated waters were measured at trace quantities or up to hundreds of $\text{mgCl}^- \cdot \text{dm}^{-3}$ [31]. According to the Regulation [17] water in terms of chlorides occurrence was classified to the class I. Waters were defined of good quality which means that sewage did not contain chlorides. Although maximum chlorides concentration occurred on the site II (place of effluent introduction) the values were statistically higher significant (Table 12, Fig. 12) independent of seasonality but they were introduced at low levels. Below the place of sewage introduction a constant decrease in chlorides concentration up to values obtained above the place of introduction was measured. However, an increase in chlorides content may have been observed on the site V. It is possible that this growth in chlorides concentration was a result of chlorides flows from the urbanization especially during winter. An analysis of the Dobra at the estuary of the Widawa in 2006 showed $47.7\text{--}98.1 \text{ mgCl}^- \cdot \text{dm}^{-3}$ while in 2004 $35.8\text{--}81 \text{ mgCl}^- \cdot \text{dm}^{-3}$. The result of 2004 was similar to that of 2007 [30].

Table 12

Chlorides concentration [$\text{mgCl}^- \cdot \text{dm}^{-3}$] in water of the River Dobra between 2007–2008 year

	Min.	Max	Average	Standard deviation
Spring	40	96	58.8	21.71
Summer	40	116	62.0	30.72
Autumn	44	140	65.2	41.94
Winter	46	98	67.2	25.56

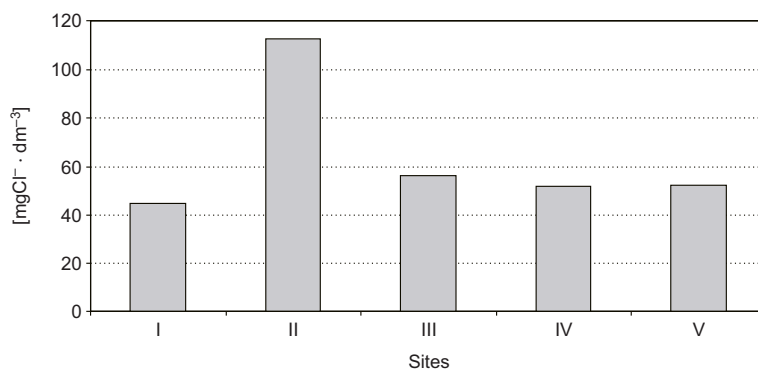


Fig. 12. Average chlorides concentration [$\text{mgCl}^- \cdot \text{dm}^{-3}$] in water on five sites of the River Dobra

Among the other researched physicochemical indicators an increase in ammonium, nitrates(V), sulfates, calcium and magnesium concentration were measured below the place of sewage introduction. However, the results were statistically insignificant. Elevated concentrations of the researched compounds in the place of effluent flow on the site II return to their previous values measured before sewage was introduced to the water.

Conclusion

Both statistically higher significant increase in chlorides and statistically significant increase of phosphates content was noted on the site II which resulted in statistically higher significant increase of electric conductivity. An increase in these compounds content was a consequence of detergents usage in the nearby industrial plant.

Contaminants flowing into the water of the River Dobra do not influence limitation of purification processes in the river. The amount of sewage is not too high and its composition is not toxic for water environment. Water of the Dobra at the estuary of the Widawa shows similar chemical composition to water above the place of effluent introduction.

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WPLYW ZANIECZYSZCZEŃ PRZEMYSŁOWYCH NA JAKOŚĆ WÓD DOLNEGO ODCINKA RZEKI DOBREJ

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Abstrakt: W latach 2007–2008 zebrano próbki wody z rzeki Dobrej (prawostronnego dopływu Widawy). Próbkę zebrano w 4 porach roku z 5 miejsc – dolnej rzeki Dobrej. Określono: temperaturę, odczyn, zasadowość, twardość, zawartość: tlenu, azotynów(III i V), amoniaku, chlorków, wapnia, fosforanów, siarczanów i magnezu.

Celem tej pracy było określenie wpływu zanieczyszczenia ściekami przemysłowymi dolnego odcinka rzeki Dobrej na jakość wody rzeki Widawy. Prawie wszystkie badane parametry były średnio większe na stanowisku II niż na pozostałych stanowiskach w rzece Dobrej. Największe średnie zmiany były w koncentracji fosforanów (wzrost o 192 %), koncentracji chlorków (wzrost o 155 %), koncentracji azotanów(V) (wzrost o 153 %). Nie było żadnych średnich różnic w zawartości azotanów(III), ale ich koncentracja w ściekach była zróżnicowana (latem i zimą dwukrotnie większa niż w rzece Dobrej). Nie było większych różnic pomiędzy odczynem pH rzeki Dobrej i ścieków z zakładu (3 % więcej).

Na stanowisku II zanotowano zarówno duży wzrost koncentracji chlorków, jak i wzrost zawartości fosforanów powodujący duży wzrost przewodności elektrolitycznej. Chociaż wiele związków było zawartych w ściekach wprowadzonych w dolnym odcinku rzeki Dobrej, jednakże tylko średnie koncentracje magnezu (15 %) i azotanów(III) (7 %) były większe w wodzie z rzeki Dobrej w pobliżu Widawy (stanowisko V) niż w wodzie pochodzącej z rzeki Dobrej powyżej dopływu ścieków (stanowisko I). Większa była także przewodność elektrolityczna, ale ten parametr był bardzo zróżnicowany. Największa przewodność była jesienią (max $1345 \mu\text{S} \cdot \text{cm}^{-1}$), a najmniejsza zimą (min. $706 \mu\text{S} \cdot \text{cm}^{-1}$).

Słowa kluczowe: jakość wody, rzeka Dobra, ścieki

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**HEAVY METALS BIOACCUMULATION AND
PHYSIOLOGICAL RESPONSES TO HEAVY METAL STRESS
IN POPULATIONS OF *Silene vulgaris* Moench (Garcke)
FROM HEAVY METAL CONTAMINATED SITES**

**BIOAKUMULACJA METALI CIĘŻKICH
I ODPOWIEDŹ FIZJOLOGICZNA ROŚLIN *Silene vulgaris* Moench (Garcke)
Z TERENÓW ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI**

Abstract: In this study we have evaluated the heavy metals accumulation in the leaves of *Silene vulgaris* and its influence on glutathione, free amino acids and anthocyanins concentrations.

Glutathione is a tripeptide (γ -Glu-Cys-Gly) which is involved in many metabolic processes of a plant cell. It is related to the sequestration of xenobiotics and heavy metals and it is also an essential component of the antioxidant system, which keeps reactive oxygen species under control.

The accumulation of anthocyanin pigments in the leaves can be induced by environmental and anthropogenic stressors, such as pollution, osmotic stress, and nutrients deficiency. The positive role of anthocyanins as well as amino acids and organic acids in metal sequestration is suggested.

Samples of *Silene vulgaris* leaves were collected in May and July 2003–2005 from the heavy metals contaminated sites – from the nearest vicinity of non-ferrous metal smelter Szopienice at the distance of 50, 250, 450 m, from zinc wastes heap in Katowice and from a former calamine site in Dąbrowa Górnicza (the South of Poland). In the previous study we noted that the nearest vicinity of non-ferrous metal smelter Szopienice was more polluted than the other areas. The highest Zn, Cd and Pb accumulation in the leaves of *Silene vulgaris* was noted in the plants collected in the nearest vicinity of the non-ferrous metal smelter Szopienice. The free amino acids concentrations have differed in the vegetative season. It was higher in the most polluted sites (50 and 250 m) in July. Higher content of the reduced form of glutathione was estimated in the plant leaves collected in the distance of 250 m from the emitter in July than at the beginning of the study. Also the highest anthocyanins accumulation in *Silene vulgaris* leaves was noticed in July and in plants from the most polluted area (250 m).

The estimations, especially glutathione content, seem to be promising in ecophysiological research connected with heavy metals stress in plants growing in the postindustrial areas.

Keywords: heavy metals, *Silene vulgaris*, glutathione, amino acids, anthocyanins

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The metallurgical processing of zinc, lead, copper and iron is responsible for considerable amounts of heavy metals introduced into environment (especially plant emissions, postindustrial dumps) [1–5]. Metallophyte – *Silene vulgaris* – is a specific plant to the calamine areas and it is a pioneer plant in the nearest vicinity of non-ferrous metal smelter [6–11]. Such plants are tolerant of high heavy metals concentration and have high heavy metals accumulation ability [7, 11–13]. Several plant species such as *Silene vulgaris*, *Cardaminopsis arenosa*, *Plantago lanceolata* have been shown to be good bioindicators of soil contamination with lead and zinc [3, 6]. Many investigations were undertaken to determine plants defense against heavy metals. The investigators looked for good stress and defense indicators. Glutathione is involved in the cellular defense against the toxic influence of xenobiotics as well as metal cations [14, 15] The positive role of anthocyanins next to amino acids and organic acids in metal sequestration is suggested [16, 17]. Anthocyanins are associated with the enhanced tolerance to effects of chilling and freezing, to heavy metal contamination, to desiccation and to wounding [18].

The aim of this work was to determine the heavy metal bioaccumulation in leaves of *Silene vulgaris* and to define the responses (glutathione, free amino acid and anthocyanin content) of *Silene vulgaris* to environmental metals exposure.

Material and methods

The investigation was carried out in May and July in 2003–2005. The leaves from *Silene vulgaris* (Moench) Garcke plants (from 20 individuals) were collected in the nearest vicinity of non-ferrous plant Szopienice at the distances of 50, 250, 450 m, on the zinc smelter spoil heap in Katowice Wełnowiec (H) and from the former calamine site in Dąbrowa Górnicza (C). In order to determine the heavy metal concentration, the plant material was washed in tap and in distilled water, dried at 105 °C to a constant weight and ground to fine powder, then mineralized and dissolved in 10 % HNO₃. After filtration Zn, Pb and Cd contents were measured using flame Atomic Absorption Spectrometry (AAS) [19]. The quality of the analytical procedure was controlled by using the samples of the reference material in each series of analysis. (Certified Reference material CTA-OTL-1 Oriental Tobacco Leaves). Anthocyanins was estimated according to method of Fuleki and Francis [20]; Giusti and Wrolstad [21] by extracting the pigment in methanol/HCl (99/1, v/v). Glutathione (reduced and oxidative forms) was extracted from plants by homogenizing plant material (0.5 g) at 4 °C in ice cold 5 % trichloroacetic acid with the addition of Na-phosphate buffer (pH 7.5) and then centrifuged at 11000 × g for 10 min and determined according to method of Anderson [22] and Nishimoto et al [23]. The supernatant was used for GSH and GSSG determinations by the DTNB-GSSG reductase recycling procedure. GSSG was determined after GSH had been removed by 2-vinylpyridine derivatizations. Changes in the absorbance of the reaction mixtures were measured at $\lambda = 412$ nm. Free amino acids were extracted from plants by homogenizing plant material (0.5 g) at 4 °C in 80 % acetone and determined with the usage of ninhydrin method of Keller [24]. All plant samples were carried out in six replications. The data was processed using the software

Statistica to compute significant statistical differences between samples ($p < 0.05$) according to Tukey's multiple range test and to compute Pearson's correlation coefficient.

Results and discussion

The highest bioaccumulation of the investigated metals was found in the nearest vicinity of non-ferrous plant "Szopienice". Cd (50, 250 m) and Zn (all investigated areas) were above the toxic level, Pb amounts accumulated in *Silene vulgaris* leaves were in the toxicity range [25] (Table 1). In the earlier study in these stands the declined plant biomass was noticed. However, the highest metal fitoextraction was found for plants in the distance of 450 m [13].

Anthocyanins can be formed as a reaction to lots of adverse environmental conditions. At nutrient shortage, such as N- and P-deficiency, a surplus of carbohydrates can be stored as anthocyanins [26]. The highest concentration of anthocyanins was found in the plant leaves collected in the distance of 250 m from the emitter in July (Fig. 1). Anthocyanins can be associated with enhanced resistance to the heavy metals contamination. The changes of plant colours (due to increased anthocyanins concentration) may be the first indication of insufficient detoxification of metals resulting in deregulation of a plant physiology. However these symptoms may be not necessarily related to a surplus but also to the shortage of metals [27]. Under strong light (in environmental condition in July in our study), however, the anthocyanins serve as a useful optical filter diverting excessive high energy quanta away from an already saturated photosynthetic electron transport chain. Chloroplasts irradiated with light that has first passed through a red filter have been shown to generate fewer superoxide radicals, thereby reducing the propensity for structural damage to the photosystems.

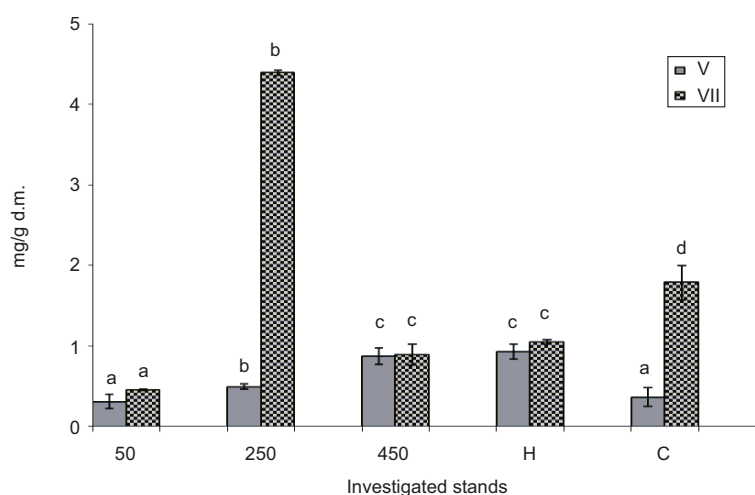


Fig. 1. Mean anthocyanins concentration in leaves of *Silene vulgaris*. Values with the same letter (for the month) are statistically the same for $p < 0.05$

Table 1
 Mean heavy metals concentration in *Silene vulgaris* leaves. Values with the same letter (in the columns) are statistically the same for $p < 0.05$

Site	Metal	Zn			Pb			Cd					
		May	SD	July	SD	July	SD	May	SD	July	SD		
50 m		3800.1a	145.5	4183a	125.6	241.5a	34.3	260.2a	28.3	38.5a	1.50	40.23a	3.5
250 m		3627.2a	241.7	3959.1a	119.5	112.5b	16.1	60.6b	6.6	31.51b	1.70	26.42b	1.5
450 m		1549.3b	180.5	2590b	130.1	25.2c	6.6	18.5c	2.5	4.1c	1.90	6.32c	1.4
H		2482.2c	102.7	2888.5c	148.2	29.9c	14.1	21.42c	4.9	4.3c	1.02	2.1d	0.8
C		846.1d	72.1	806.4d	34.8	35.23c	2.3	13.95d	2.5	7.5d	1.80	5.15e	0.4

Most likely elevated concentration of anthocyanins does not indicate a high surplus of heavy metals. Gould emphasized [28], that anthocyanins offer multifaceted, versatile and effective protection to a plant under stress.

Higher concentrations of free amino acids were found in May rather than in July, in plant leaves, where smaller metal bioaccumulation was noted. However the free amino acid content increased in the plant leaves collected in most polluted site in the distance of 50 m from the emitter during vegetative season – in July (Fig. 2). Amino acids and particularly phytochelatins and glutathione play an important role in metal binding [17]. Lesko and Sarcadi showed that cadmium treatment at higher concentration caused the highest accumulation of total amino acid content in the shoots and roots of wheat seedlings [29]. Positive correlation between metal concentration and free amino acid content was found in our study (Correlation coefficient were 0.8 for Zn, 0.9 for Cd and 0.7 for Pb). Heavy metals treatment modified free amino acid composition and concentration. It may be suggested that proline is involved in detoxification of heavy metals [14, 17]. Metal tolerant populations of *Deschampsia* and *Silene* have been shown to have higher constitutive content of proline as compared with nontolerant counterparts. *Allysum*, when exposed to nickel produce histidine, proportionally to an applied Ni dose [32]. The further research is needed to find out that free amino acid could be indicator of metal stress in laboratory and in the environmental conditions.

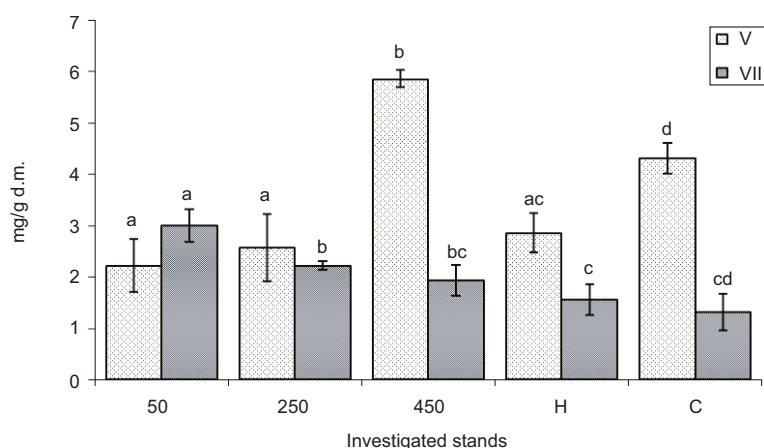


Fig. 2. Mean free amino acids content in *Silene vulgaris* leaves in May and July. Values with the same letter (for the month) are statistically the same for $p < 0.05$

The higher concentrations of the reduced form of glutathione were observed in the leaves of *Silene vulgaris* in July rather than in May. The increased concentration of glutathione in plant tissues in the distance of 250 m suggested a positive role of this tripeptide in plant metal defense (Figs. 3, 4). However, strong positive correlation was noted only with Zn (correlation coefficient was 0.84). The increased content of GSSG forms was observed in May. The increased GSSG level facilitates formation of mixed disulfides (protein glutathionation), which induces changes in redox status of thiols

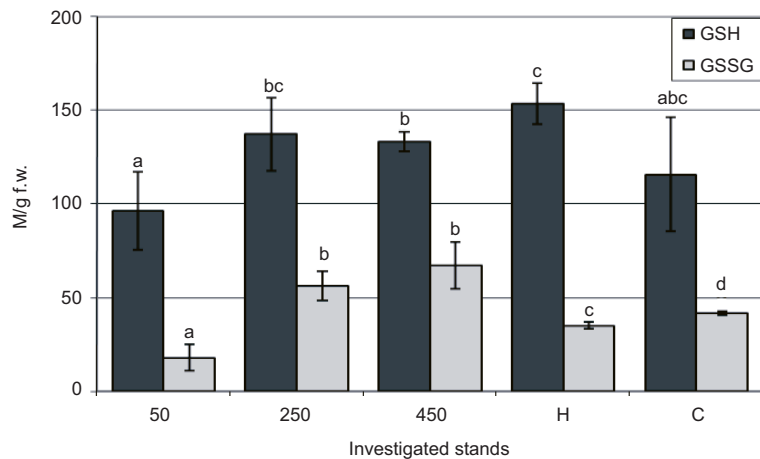


Fig. 3. Mean glutathione content in leaves of *Silene vulgaris* in May. Values with the same letter (for the glutathione form) are statistically the same for $p < 0.05$

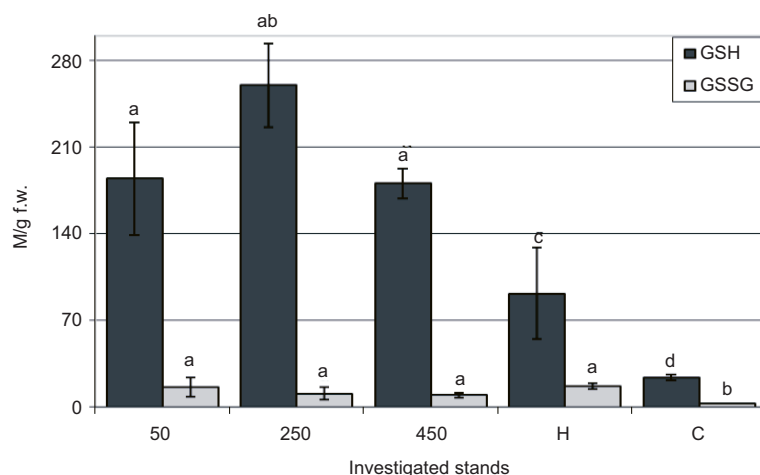


Fig. 4. Mean glutathione content in leaves of *Silene vulgaris* in July. Values with the same letter (for the glutathione form) are statistically the same for $p < 0.05$

[30]. Bruns et al pointed that the intracellular sequestration of heavy metals by GSH is favored in mosses treated with Cd [31]. Glutathione is related to the sequestration of xenobiotics and heavy metals and is also an essential component of the cellular antioxidative defense system, which keeps reactive oxygen species (ROS) under control [15]. Glutathione could be suitable candidate as a stress marker. Strong evidence has indicated that the elevated GSH concentration is connected with the plant ability to metal induced oxidative stress [32, 33].

Conclusions

Zinc was bioaccumulated in the highest amount in *Silene vulgaris* leaves on all investigated stands. The highest bioaccumulation of all investigated metals (Zn, Cd and Pb) was noticed for *Silene vulgaris* leaves collected in the distance of 50 and 250 m from the smelter.

Positive correlation between heavy metal concentrations and free amino acid contents in *Silene vulgaris* leaves was found. It is very likely that free amino acids were involved in plant heavy metals defense. The problem needs further investigations.

The anthocyanins content increase in July in the plant leaves from the most polluted area could be an effective protection to the plant under stress, however not only heavy metals.

The glutathione content was the highest in the plant leaves collected from the distance of 250 m from the smelter, where high levels of heavy metal concentrations in plant leaves was noted. It seems to be promising in further investigations.

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**BIOAKUMULACJA METALI CIĘŻKICH I ODPOWIEDŹ FIZJOLOGICZNA
ROŚLIN *Silene vulgaris* Moench (Garcke) Z TERENÓW
ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI**

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Abstrakt: Przeprowadzono badania nad akumulacją Zn, Pb i Cd w liściach *Silene vulgaris* i wpływie tych metali na zawartość glutationu, wolnych aminokwasów i antocyjanów. Glutation jest tripeptydem (γ -Glu-Cys-Gly), który jest zaangażowany w obronę przed ksenobiotykami i metalami ciężkimi i jest podstawowym komponentem komórkowej antyoksydacyjnej obrony, utrzymującym reaktywne formy tlenu (ROS) pod kontrolą. Akumulacja barwników antocyjanowych może być powodowana przez środowiskowe i antropo-

genne czynniki stresowe, takie jak zanieczyszczenie, stres osmotyczny, niedobór składników odżywczych. Sugeruje się pozytywną rolę antocyjan obok, wolnych aminokwasów i kwasów organicznych w oddzielaniu metali ciężkich.

Liście roślin *Silene vulgaris* zbierano w maju i lipcu 2003–2005 z terenów zanieczyszczonych metalami ciężkimi (z najbliższego sąsiedztwa Huty Metali Nieżelaznych „Szopienice” w odległości 50, 250, 450 m, z hałdy pocynkowej w Katowicach Wełnowcu oraz terenu po eksploatacji galmanu w Dąbrowie Górniczej). W poprzednich badaniach wykazano największe zanieczyszczenie metalami ciężkimi na terenie najbliższym położonym przy Hucie Metali Nieżelaznych „Szopienice”. Największą akumulację Zn, Cd, Pb stwierdzono w liściach roślin *Silene vulgaris* zbieranych w najbliższym sąsiedztwie emitora (50, 250 m). Stężenie wolnych aminokwasów różniło się podczas sezonu wegetacyjnego. Zawartości były większe na najbardziej zanieczyszczonym terenie w lipcu niż na początku badań. Większą zawartość zredukowanej formy glutationu oznaczono w liściach roślin zbieranych w odległości 250 m od emitora w lipcu niż na początku badań. Zanotowano także największą akumulację antocyjanów w liściach roślin w lipcu i u roślin z najbardziej zanieczyszczonego terenu (250 m). Szczególnie oznaczanie zawartości glutationu wydaje się być obiecujące w ekofizjologicznych badaniach nad stresem wywołanym przez metale ciężkie u roślin na terenach przemysłowych

Słowa kluczowe: metale ciężkie, *Silene vulgaris*, glutation, wolne aminokwasy, antocyjany

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and Vanio MITEV¹

**SPECTROPHOTOMETRIC DETERMINATION
OF SILVER WITH BRILLIANT GREEN
AND ITS APPLICATION
IN PHOTOGRAPHIC FIXING SOLUTIONS**

**SPEKTROFOTOMETRYCZNE OZNACZANIE SREBRA
ZA POMOCĄ ZIELENI MALACHITOWEJ
W UTRWALACZACH FOTOGRAFICZNYCH**

Abstract: A simple spectrophotometric determination of silver in aqueous solutions was developed based on the reaction between AgI_2^- and Brilliant Green. This reaction results in, under appropriate conditions, an ion-associated complex which absorbs at $\lambda = 680$ nm and no extraction of this complex is needed. Silver ions could be determined satisfactory in the linear range $y = 0.00025x + 0.0432$ with $r^2 = 0.9973$ of 10–800 $\mu\text{g Ag}^+/\text{L}$. The interfering in the determination ions was examined. The proposed method proved to be successful in determining silver in photographic fixing solutions, that are many times disposed off in the environment, and the relative error of this method was found to be 4 %.

Keywords: silver, Brilliant Green, spectrophotometric determination, photographic solution

Over the last years several researchers have reported spectrophotometric determinations of silver by reactions between organic reagents and silver, such as Pal and Maity [1] with silver-gelatin interaction, Tarin et al. [2] with 4-(*p*-nitrophenylazo)-2-amino-3-pyridinol, Pilipenco et al [3] with Michlers thioacetone in the presence of anionic surfactants, Oshita et al [4] with 4-(3,5-dibromo-2-pyridylazo)-*N,N*-diethylaniline in the presence of sodium dodecylsulfate, Zhou Nant et al [5] with 5-[*p*-(dimethyl-amino)benzylidene]rhodanine] and Sanchez et al [6] with dithizone.

The objectives of our work was to develop a spectrophotometric method for Ag^+ determination, based on the formation of an ion association complex with Ag^+ and

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Brilliant Green in the presence of potassium iodide and to propose this method for silver determination in photographic fixing solutions.

Experimental

Apparatus

A Perkin Elmer, model Lambda 2 spectrophotometer was used for absorbance measurements. A Metrohm, model 503 pH meter was used for pH measurements.

Reagents

A BDH stock solution of $1000 \text{ mg/dm}^3 \text{ Ag}^+$ was used for the preparation of the working standards by proper dilution. An one g/dm^3 of Brilliant Green (MERCK) was prepared by dissolving in distilled water. Potassium iodide was used for preparing a solution of 5000 mg/dm^3 iodide ions. Sulfuric acid (0.025 and 0.50 M) and sodium hydroxide (0.1 M) solutions were used for pH adjustments.

Calibration

Suitable aliquots of the 10 mg/dm^3 standard silver solution or of the samples are placed in 50 cm^3 volumetric flasks. Silver concentrations must lie in the range of $10\text{--}800 \text{ }\mu\text{g/dm}^3$. One cm^3 of potassium iodide solution (5 g/dm^3) is added followed by aliquots of dilute H_2SO_4 or NaOH solution to bring the pH of the final volume to 3.0. Then, 0.75 cm^3 of the Brilliant Green solution (1 g/dm^3) are added. The flasks are immediately swirled, brought to volume with distilled water stoppered and shaken well. No extraction is needed. Measurements are taken at 680 nm 60 min after mixing the reagents.

Results and discussion

A large excess of iodide ions in a silver solution, is known to lead to the formation of the anion complex AgI_2^- . This anion reacts with Brilliant Green cation, giving an ion association complex of the type RAgI_2 (where R: the Brilliant Green cation).

The complex was practically formed immediately after mixing the reagents but the maximum absorbance value, which was found by measurements taken every 10 min, was obtained and stabilized after 60 min, and remained stable for at least 24 hours. The variation of the maximum absorbance value from the initial one, obtained 5 min after the mixing of the reagents was found to be about 25 % (Fig. 1).

The optimum experimental variables for the complex formation (regarding pH value and concentrations of KI and Brilliant Green) were estimated in a previous work [7], which concerned silver fluorimetric determination by formation of the same complex.

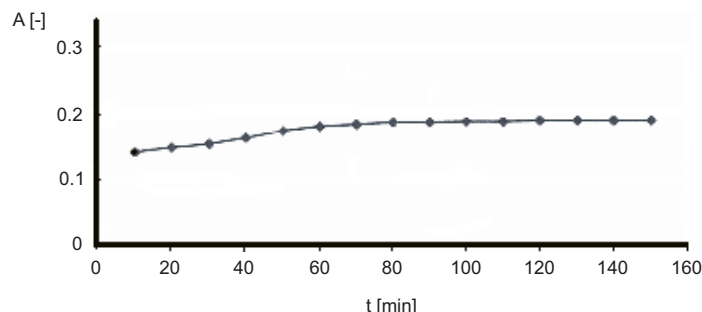


Fig. 1. Effect of time on the absorbance value

These are: pH = 3.0, concentration of KI = 100 mg/dm³ and concentration of Brilliant Green = 15 mg/dm³.

The measurements were taken at $\lambda = 680$ nm, because at this wavelength the repeatability of the measurements was better than the respective ones at $\lambda = 330$ and 460 nm (Fig. 2).

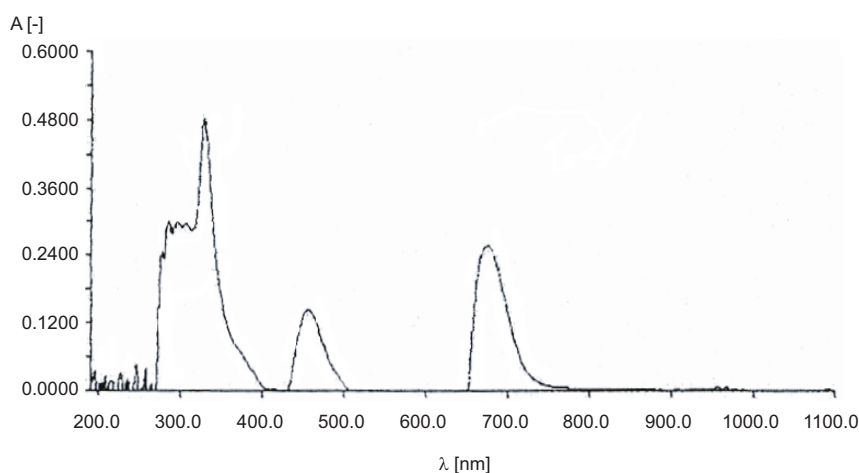


Fig. 2. Spectrophotometric spectra of the AgI_2^- – Brilliant Green complex

Calibration curve

The calibration curve was obtained using the above optimum experimental conditions and 10 calibration standards covering the range of 10 to 800 $\mu\text{g Ag}^+/\text{dm}^3$. Absorbance was a linear function of concentration over the range 10 to 800 $\mu\text{g Ag}^+/\text{dm}^3$, described by the equation $y = 0.00025x + 0.0432$ with $r^2 = 0.9973$. For better accuracy over the range 10 to 100 $\mu\text{g Ag}^+/\text{dm}^3$ the calibration curve covering this range is described by the equation $y = 0.0003x + 0.0391$ with $r^2 = 0.9758$.

Interferences

The interfering ions in the determination of Ag^+ were examined. Strong interference was exerted by the cations Hg^{2+} and Bi^{3+} with absorptions similar to that of Ag^+ . The cation Pt^{4+} did not interfere in concentrations up to 1 mg/dm^3 . The interference of the other cations is negligible. No interference was observed for cations such as Ba^{2+} , Sr^{2+} , Cu^{2+} and Sb^{3+} in concentrations up to 200 mg/dm^3 , Co^{2+} up to 500 mg/dm^3 , Ni^{2+} , Sn^{2+} , Zn^{2+} , Mn^{2+} , Ca^{2+} , Al^{3+} , As^{3+} , Fe^{3+} and Cr^{6+} up to 1000 mg/dm^3 , K^+ , Na^+ , Li^+ , NH_4^+ and Mg^{2+} up to $10\,000 \text{ mg/dm}^3$. From the anions, PO_4^{3-} up to 500 mg/dm^3 and NO_3^- , Cl^- , Br^- , F^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CO_3^{2-} and HCO_3^- up to 5000 mg/dm^3 did not interfere.

Application

The proposed method was applied to silver determination in a photographic fixing solution after processing a black white film. The sample was analyzed spectrophotometrically and by Atomic Absorption Spectrometry (AAS) which served as a reference value. The relative error of this method calculated as $\text{Er}\% = (\text{Ag}^+ \text{ found spectrophotometrically} - \text{Ag}^+ \text{ found by AAS}) \cdot 100 : (\text{Ag}^+ \text{ found by AAS})$ was found to be 4 %.

Conclusion

A new spectrophotometric determination of Ag^+ is proposed. The absorbance of the complex which is formed with an excess of I^- and Brilliant Green is observed at $\lambda = 680 \text{ nm}$. The linear range is from $10\text{--}800 \mu\text{gAg}^+/\text{dm}^3$. This proposed method is very simple, no extractions are needed, and it is of low cost. The method can be applied in photographic fixing baths and the results are reliable and comparable to those obtained by the AAS method.

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SPEKTROFOTOMETRYCZNE OZNACZANIE SREBRA ZA POMOCĄ ZIELENI MALACHITOWEJ W UTRWALACZACH FOTOGRAFICZNYCH

Abstrakt: Wykorzystując reakcję pomiędzy AgI_2^- a zielenią malachitową opracowano metodę prostego spektrofotometrycznego oznaczania srebra w roztworach wodnych. W odpowiednich warunkach w wyniku reakcji powstaje kompleks złożony absorbujący przy $\lambda = 680 \text{ nm}$. Stężenie jonów srebra można zadowalająco

oznaczyć w liniowym zakresie $y = 0,00025x + 0,0432$ z $r^2 = 0,9973$, od 10 do 800 $\mu\text{g Ag}^+/\text{L}$. Zbadano wpływ czynników przeszkadzających na wynik analizy. Proponowana metoda okazała się skuteczna w oznaczaniu srebra w utrwalaczach fotograficznych odprowadzanych do środowiska, a błąd względny tej metody wynosi 4 %.

Słowa kluczowe: srebro, zieleń malachitowa, oznaczenia spektrofotometryczne, roztwór fotograficzny

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and Magdalena BŁASZAK¹

**EFFECT OF MEDIUM SALINITY
WITH SODIUM CHLORIDE (NaCl),
SODIUM NITRATE (NaNO₃) AND THEIR COMPOUND
ON THE ENZYMATIC ACTIVITY
OF SELECTED SOIL FUNGI.
PART III. STARCH HYDROLYSIS**

**WPŁYW ZASOLENIA PODŁOŻA CHLORKIEM SODU (NaCl),
AZOTANEM SODU (NaNO₃) I ICH MIESZANINĄ
NA AKTYWNOŚĆ ENZYMATYCZNĄ
WYBRANYCH GRZYBÓW GLEBOWYCH.
CZĘŚĆ III. HYDROLIZA SKROBI**

Abstract: The results of research referring to the effect of medium salinity with sodium chloride (NaCl), sodium nitrate (NaNO₃) and their mixture on the starch activity of soil fungi were presented. All genera of isolated fungi hydrolysed the starch found in medium with high intensity, with the exception of *Alternaria* sp. This was manifested by the formation of hydrolysis zones, surpassing considerably the colony limits. Medium salinity affected the growth and the starch activity of analysed fungi, depending on a dose and type of salt, as well as on the given strain. The increase of salt concentration in medium reduced the growth of surface mycelium, affecting at the same time starch activity stimulation.

Keywords: fungi, salinity, starch activity

Metabolic processes in soil take place, among others, with contribution of fungi. Enzymes produced by these microorganisms decompose organic matter and play an important part in humification processes [1]. Both the number and the activity of fungi in soil depends on different factors, both natural and of anthropogenic origin, including environmental salinity [2–4]. The increase of soil salinity is first of all caused by using

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excessive amounts of mineral fertilisers, irrigation of soil with salt water, application of sodium and calcium chlorides for controlling snow slipperiness and wastes from soda plants [5–10]. Too high salt concentration significantly influences the living conditions of soil microorganisms. Salinity induces an increase in osmotic pressure, limits or even hinders water intake and may be also a reason of growth arrest or even of cell destruction [11–19].

The study aimed at determining the effect of salinity on the amylolytic activity of selected soil fungi.

Material and methods

In order to carry out this experimental work, the following genera of soil fungi were used: *Mucor*, *Aspergillus*, *Cladosporium*, *Alternaria*, *Penicillium*, *Fusarium*, *Trichoderma* and *Trichothecium*. The effect of sodium chloride (NaCl), sodium nitrate (NaNO₃) and their equimolar mixture was examined, in a dose of 1, 10, 100 and 1000 mmol · dm⁻³ of microbiological medium, ie starch agar according to Cooney and Emerson [20], on the fungi growth and their enzymatic activity. Sterile mediums were poured out into Petri dishes and inoculated point-wise with selected fungi after their setting. All experimental combinations were made in 3 repetitions. Incubation was carried out for 5 days at 25 °C. The index of amylolytic activity was calculated as a ratio of the hydrolysis zone of examined medium to the colony diameter. The obtained results were analysed statistically, calculating the analysis of variance and testing the factors with the Duncan's test.

Results and discussion

Soil salinity becomes an increasingly larger problem. Its source can be found in mining extractive industry and dust emissions containing sodium and potassium. The main reason of salt concentration increase in arable soils is intensive mineral fertilisation. Soil salinity affects negatively plant health, brings about inhibition of growth processes and reduction of photosynthesis performance and leads to physiological drought [5–8, 10]. Disturbances in soil ion balance and most frequently continuous fluctuations in its pH reaction resulting from an increase in salinity are also favourable for most soil microorganisms [11–19].

The largest colony growth on solid control media was shown by fungi of the genera *Mucor* sp., *Cladosporium* sp. and *Fusarium* sp. On the other hand, the largest amylum decomposition activity in this medium (activity index amounted to 1.6) was found in case of *Penicillium* sp. Fungus of the genus *Alternaria* sp. did not show any activity outside colony limits and did not form hydrolysis zones (Fig. 1).

Introduction of salts, eg NaCl and NaNO₃, and their mixture into microbiological medium had a significant effect on the growth of examined fungi and their activity (Table 1, Fig. 2). As a rule, application of the smallest salt concentration (1 mmol · dm⁻³) in the carried out experiment stimulated the growth of mycelium. Mean mycelium growth was larger by several to a dozen or so percent when compared with

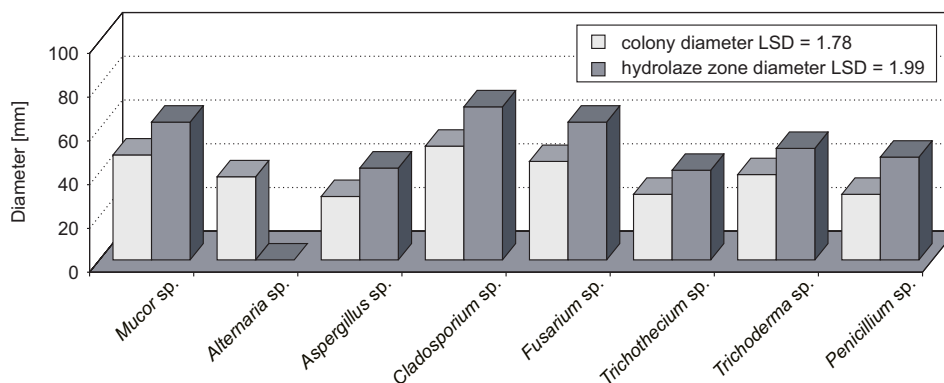


Fig. 1. Soil fungi growth on control starch medium

control. This effect was visible after NaCl application with the growth of all fungi and in most cases after NaNO₃ and their mixture application. The largest mycelium growth, over 20 % when compared with control, was observed in *Fusarium sp.* after application of 1 mmol · dm⁻³ NaCl and NaNO₃ mixture and in case of *Trichothecium sp.* after application of pure NaCl.

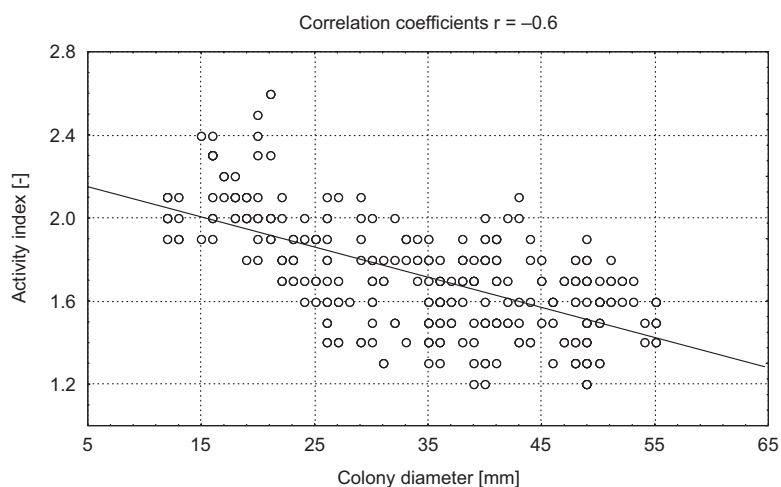


Fig. 2. Correlation between the growth of surface mycelium in soil fungi and their starch decomposition activity on a medium with increasing salinity

The increase of salt concentration induced reduction of the growth of fungi colonies irrespective of the type of introduced salt. The strongest inhibition under effect of salt concentration in medium [1000 mmol · dm⁻³] amounted even to 80 % when compared with control. Such changes were observed in case of the mycelium growth in *Fusarium sp.* and *Mucor sp.* when applying homogenous salts to mediums.

Table 1

Effect of salinity on the growth and developmet of soil fungi expressed by enyzmatic activity index

Salinity dose [mmol · dm ⁻³]	NaCl	NaNO ₃	NaCl × NaNO ₃	NaCl	NaNO ₃	NaCl × NaNO ₃
	Activity index					
	<i>Mucor</i> sp.			<i>Alternaria</i> sp.		
0	1.3	1.3	1.3	—	—	—
1	1.6	1.6	1.5	—	—	—
10	1.7	1.7	1.6	—	—	—
100	1.9	1.9	1.7	—	—	—
1000	1.9	2.1	1.9	—	—	—
LSD	0.1619					
	<i>Penicillium</i> sp.			<i>Aspergillus</i> sp.		
0	1.5	1.6	1.6	1.5	1.5	1.3
1	1.7	1.9	1.9	1.6	1.6	1.5
10	1.8	1.8	1.7	1.7	1.8	1.6
100	2.0	1.9	1.9	1.8	1.9	1.7
1000	2.4	2.3	2.6	2.4	2.4	2.0
LSD	0.1420			0.1739		
	<i>Trichothecium</i> sp.			<i>Cladosporium</i> sp.		
0	1.3	1.5	1.4	1.3	1.3	1.4
1	1.0	1.6	1.7	1.6	1.5	1.5
10	1.1	1.8	1.6	1.8	1.7	1.6
100	1.1	1.9	1.7	2.0	1.8	1.6
1000	2.2	2.3	2.1	2.6	2.0	2.1
LSD	0.1680			0.1680		
	<i>Fusarium</i> sp.			<i>Trichoderma</i> sp.		
0	1.3	1.3	1.6	1.3	1.3	1.4
1	1.6	1.6	1.5	1.4	1.4	1.5
10	1.6	1.7	1.6	1.8	1.6	1.5
100	1.9	1.9	1.7	1.9	1.8	1.7
1000	1.9	2.1	1.9	2.1	2.1	1.8
LSD	0.1680			0.1619		

The increase of salt concentration in medium significantly reduced the growth of surface mycelium but stimulated secretion of amyolytic enzymes, which is confirmed by significant coefficient of correlation ($r = -0.6$). Similar phenomenon of the reduction of mycelium growth and of the increase of different activities was found under effect of a large concentration of active substances contained in pesticides [21]. In the present study, largest enzymatic activity index, ie 2.6, was found in case of *Penicillium* sp. on a medium most salinated with salt mixture (NaCl and NaNO₃) and of *Cladosporium* sp. in

medium with NaCl. As a rule, higher intensity of enzyme secretion into medium was more frequently observed after introduction of single salts than their mixture.

Conclusions

1. All genera of the isolated soil fungi, except for *Alternaria* sp., hydrolysed the starch found in medium with high intensity, which was manifested by the formation of hydrolysis zones surpassing considerably the colony limits.

2. The increase of substrate salinity, both through NaCl, NaNO₃ and their mixture, affected the amylolytic activity in *Mucor* sp., *Aspergillus* sp., *Cladosporium* sp., *Fusarium* sp., *Penicillium* sp., *Trichothecium* sp. and *Trichoderma* sp. as well as the growth of surface mycelium in *Alternaria* sp. The direction and the intensity of changes depended on a dose and type of salt as well as on respective strains.

3. The increase of salt concentration in medium reduced the growth of surface mycelium, affecting at the same time amylolytic activity stimulation.

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**WPLYW ZASOLENIA PODŁOŻA CHLORKIEM SODU (NaCl), AZOTANEM SODU (NaNO₃)
I ICH MIESZANINĄ NA AKTYWNOŚĆ ENZYMATYCZNĄ
WYBRANYCH GRZYBÓW GLEBOWYCH. CZĘŚĆ III. HYDROLIZA SKROBI**

Katedra Mikrobiologii i Biotechnologii Środowiska
Akademia Rolnicza w Szczecinie

Abstrakt: W pracy przedstawiono wyniki badań dotyczące wpływu zasolenia podłoża chlorkiem sodu (NaCl), azotanem sodu (NaNO₃) i ich mieszaniną na aktywność amylolityczną grzybów glebowych. Wszystkie rodzaje wyizolowanych grzybów glebowych z wyjątkiem *Alternaria* sp. hydrolizowały skrobię obecną w podłożu z dużą intensywnością, co uwidaczniało się tworzeniem stref hydrolizy wykraczających znacznie poza obręb kolonii. Wzrost zasolenia podłoża zarówno przez NaCl, NaNO₃, jak i ich mieszaninę wpływał na aktywności amylolityczną u: *Mucor* sp., *Aspergillus* sp., *Cladosporium* sp., *Fusarium* sp., *Penicillium* sp., *Trichothecium* sp., *Trichoderma* sp. oraz wzrost grzybni powierzchniowej u: *Alternaria* sp. Kierunek i nasilenie zmian zależało od dawki i rodzaju soli, a także od poszczególnych szczepów. Wzrost stężenia soli w podłożu ograniczał wzrost grzybni powierzchniowej, wpływając jednocześnie na stymulację aktywności amylolitycznej.

Słowa kluczowe: grzyby, zasolenie, aktywność amylolityczna

Małgorzata RAFAŁOWSKA¹ and Andrzej SKWIERAWSKI¹

INFLUENCE OF AN AGRICULTURAL FARM ON THE EFFLUENT OF PHOSPHORUS BY A DRAINAGE NETWORK

WPLYW GOSPODARSTWA ROLNEGO NA ODPLYW FOSFORU SIECIĄ DRENARSKĄ

Abstract: The aim of the research was to determine the influence of intensive farming on seasonal changes in drainage waters flowing out of catchment areas classified as lands particularly exposed to water pollution from agricultural sources.

The research of the influence of farming on the outflow of phosphorus by a drainage network was conducted in 2005 and 2006 in the catchment area of Dobskie Lake. The research object is situated in the area of the Mazurian Lakeland, in the village of Doba. Agricultural areas surrounding the village are used by an agricultural farm named Dobrol, which specialises in pig husbandry.

During the 2-year research period, it was noted that the amount of phosphorus flowing by the drainage network depended most of all on atmospheric conditions, season and intensity of agricultural exploitation of the area.

Keywords: catchment area, drainage area, phosphorus

Waters flowing from agriculturally utilized areas are enriched with substances, whose type and amount depends on the geological structure of the subsoil, terrain relief, types of soils and their buffer and sorption capabilities. The quality of water also depends on the method of land management, intensity of agrotechnology, drainage systems and climate conditions influencing the availability of the water for plants [1–4]. Draining agriculturally utilised areas speeds up the outflow of water and intensifies the washing out of components from the soil, which is particularly visible on the example of light soil leaching [3, 4]. The main source of biogenic components in the agriculturally utilised catchment is mostly mineral and organic fertilization which, when misused, can contribute to a substantial overload of drainage waters. Mineral com-

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ponents, mostly nitrogen and phosphorus, not utilised in the process of agricultural production, lead to the pollution of ground and surface waters (eutrophication).

The aim of the research was to determine the influence of intensive farming on seasonal changes in phosphorus concentrations in drainage waters flowing from catchments classified as areas particularly exposed to water pollution from agricultural sources.

Research material and methods

The research on the influence of farming on the phosphorus effluence through a drainage network was conducted in 2005–2006 in the catchment of Dobskie lake. The research object is situated in the area of the Mazurian Lakeland, in the village of Doba. The agricultural lands surrounding the village are used by a farm which specialises in pig husbandry.

The research covered three drainage areas marked with numbers 520, 521, 523, situated in the vicinity of the Doba village in the catchment of Dobskie lake (Fig. 1). According to the guidelines of the Nitrate Directive [5], those catchments are part of an area particularly exposed to pollution, in which the nitrogen effluence from agricultural sources should be limited. The area was marked on the basis of the nitrate concentration in ground waters, which reaches $95 \text{ mg} \cdot \text{dm}^{-3}$ [6].

The catchment of the drainage area no. 520 is 9.7 ha. On the agricultural lands, in 2005 winter wheat was grown, and in 2006 – spring barley. In the research period,

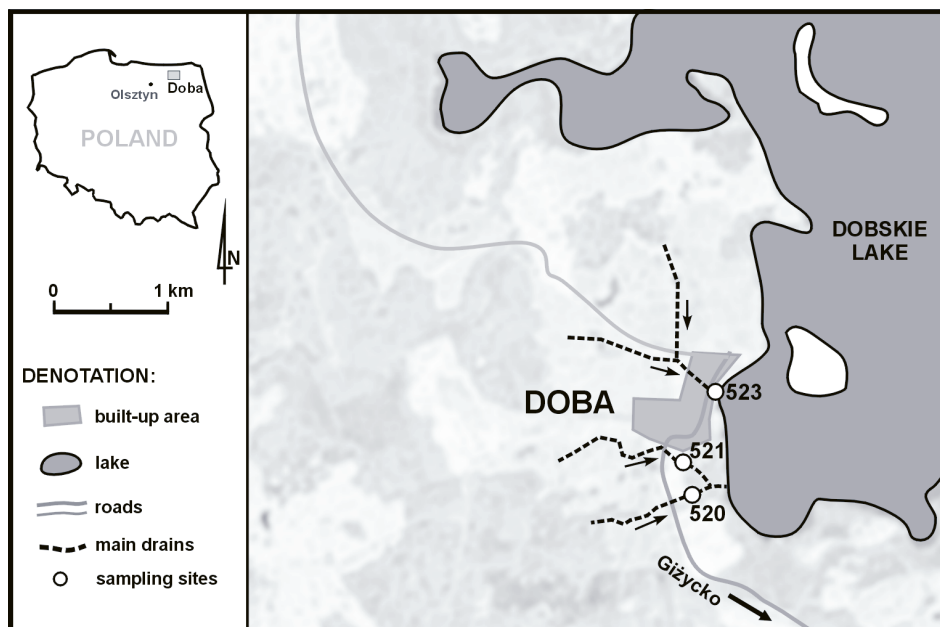


Fig. 1. Location of the research area and sampling sites

mineral fertilisation on similar levels was used – namely, in 2005 it was N-112 kg · ha⁻¹, P₂O₅-40 kg · ha⁻¹, K₂O-48 kg · ha⁻¹, and in 2006 N-98 kg · ha⁻¹, P₂O₅-46 kg · ha⁻¹, K₂O-60 kg · ha⁻¹.

The catchment of the drainage area no. 521 is 15.1 ha. In 2005, winter triticale was grown there. Mineral fertilisation was used in the amount of N-61 kg · ha⁻¹ and organic fertilisation in the form of liquid manure at 20 m³ · ha⁻¹. In 2006, spring barley was grown and the fertilization was the same as for the catchment of the area no. 520. In June 2006, liquid manure was poured out. There are some farm buildings in the area of the catchment. The arable lands of both catchments are located on moderately compact soils (strong clayey sands) classified as IVa and IIIb soil quality class.

The drain no. 523, located in the vicinity of the buildings of the village of Doba, drains water from fertilized agricultural lands (N-68 kg · ha⁻¹, P₂O₅-40 kg · ha⁻¹, K₂O-55 kg · ha⁻¹ in 2005 for barley cultivation, and in 2006 it was fertilized with N-88 kg · ha⁻¹, P₂O₅-41 kg · ha⁻¹, K₂O-54 kg · ha⁻¹ for rye cultivation) as well as from allotments and the village settlement. The soils are light, classified as quality class V. The catchment area is 41.7 ha. Considering particular drainage areas according to the intensity of utilisation measured by the amount of fertilizers and the level of anthropogenic impact (farms, housing buildings and gardens), they can be put in the following sequence: 521 > 520 > 523.

Water samples for physicochemical analyses were collected once a month from drainage outlets and determined for general phosphorus (after mineralisation) and P-PO₄ using colorimetry with ammonium molybdate and tin(II) chloride as a reductor. These tests were conducted according to generally accepted methods [7]. Seasonal variability of phosphorus concentrations was discussed on the basis of the following division of samples: winter (January–March), spring (April–June), summer (July–September), autumn (August–December).

Results and discussion

During the two-year research period, it was noted that the amount of phosphorus flowing by the drainage network depended mostly on atmospheric conditions, season and the intensity of farming in the area.

The highest average concentration (1.035 mg P · dm⁻³) of phosphorus was noted in waters flowing by the drain no. 521 in 2005 and it was 2.5 times higher than in 2006 (0.393 mg P · dm⁻³), which was caused by increased fertilization with liquid manure. The lowest average concentration of 0.243 mg P · dm⁻³ was noted in the waters of the drain no. 520 in 2006 (Table 1).

Average phosphatic phosphorus concentrations were distributed similarly to the general phosphorus concentrations. The highest concentration was noted in the waters of the drain no. 521, both in 2005 and in 2006 – respectively 0.336 and 0.208 mg P-PO₄ · dm⁻³, and the highest on the site no. 520 – 0.066 mg P-PO₄ · dm⁻³.

During the two research years, the greatest variability of general phosphorus concentrations was noted in the water of the drain no. 521, ranging from 0.210 to 3.729 mg P · dm⁻³ in 2005. The maximum concentration was noted in March, as a result of the

flow from the melting snow and because of the presence of farm buildings. In 2006, general phosphorus concentrations ranged from 0.151 to 1.144 mg P · dm⁻³. The maximum concentration was noted in June because of the liquid manure poured out in that time. The smallest variability of general phosphorus concentrations characterised the water from the drainage area no. 523 – from 0.198 to 0.468 mg P · dm⁻³ in 2005 (Table 1).

Table 1

Average values and ranges of general phosphorus (P) and phosphatic phosphorus (P-PO₄) in the drainage waters in the years 2005–2006 [mg · dm⁻³]

No. of drainage area	2005		2006	
	P	P-PO ₄	P	P-PO ₄
520	0.237* (0.045–0.507)**	0.098 (0.015–0.252)	0.243 (0.053–0.617)	0.066 (0.026–0.202)
521	1.035 (0.210–3.729)	0.336 (0.049–1.220)	0.393 (0.151–1.440)	0.208 (0.093–0.545)
523	0.304 (0.198–0.468)	0.171 (0.084–0.382)	0.279 (0.143–0.822)	0.145 (0.093–0.196)

* average concentration; ** range of concentrations

The variations in the concentration of phosphatic phosphorus were distributed similarly to the variations in the concentration of general phosphorus. Also in this case a much greater variation of concentrations was noted in the water of the drainage area no. 521, ranging from 0.049 to 1.220 mg P-PO₄ · dm⁻³, and the smallest in the drainage area no. 523, with values ranging from 0.093 to 0.196 mg P-PO₄ · dm⁻³.

As far as the seasonal distribution is concerned, the highest concentrations of general phosphorus and P-PO₄ in the drainage waters in 2005–2006 were noted in winter and spring. It is a result of the fact that very little of it was used by plants – in the conditions of excessive humidity and low temperatures leading to periodic oxygen deficits limiting the growth and development of plants. Phosphorus is a component which is easily released, particularly during oxygen deficits [8]. The maximum concentration was noted in the waters of the drain no. 521 – 1.62 mg P · dm⁻³ in 2005 and 0.80 mg P · dm⁻³ in 2006, which was influenced by the lack of vegetation and increased rainfall (Fig. 2). High concentrations of general phosphorus in 2005 in the water of the drainage area persisted practically for the whole year except for autumn, which confirms the role of the intensity of agricultural utilisation. As it was said before, this catchment area was fertilised with liquid manure. On the basis of the obtained results it can be stated that the largest amount of phosphorus can be found in the water coming from the area which was intensely fertilized with liquid organic fertilizers. The existence of such dependencies is also confirmed by high concentrations of phosphatic phosphorus, the highest in spring in the water of the drain no. 521 – 0.71 mg P-PO₄ · dm⁻³ in 2005, 0.35 mg P-PO₄ · dm⁻³ in 2006 (Fig. 3). The increased values of phosphorus concentrations should be attributed to the presence of areas with farm buildings. In 2006 (June) liquid manure was poured out near a drainage outlet, which increased the concentration of phosphorus forms, which additionally proves the negative influence of farming on the

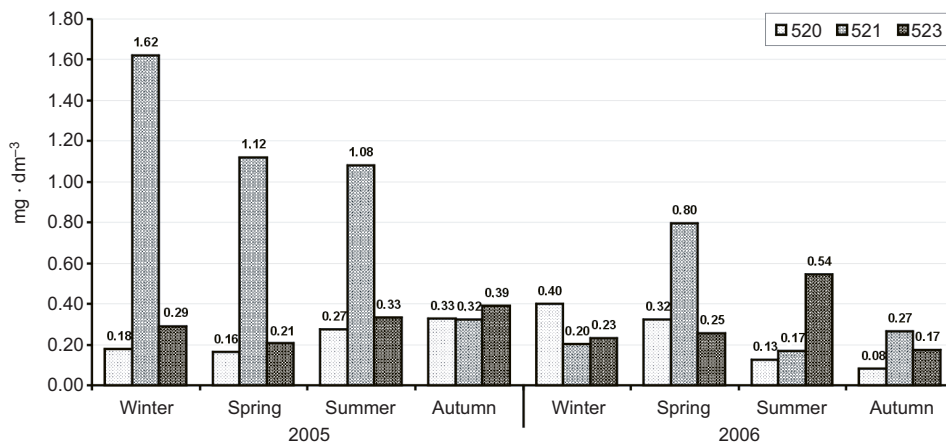


Fig. 2. Seasonal variability of general phosphorus concentrations in drainage waters flowing from the catchment of Doba in 2005–2006

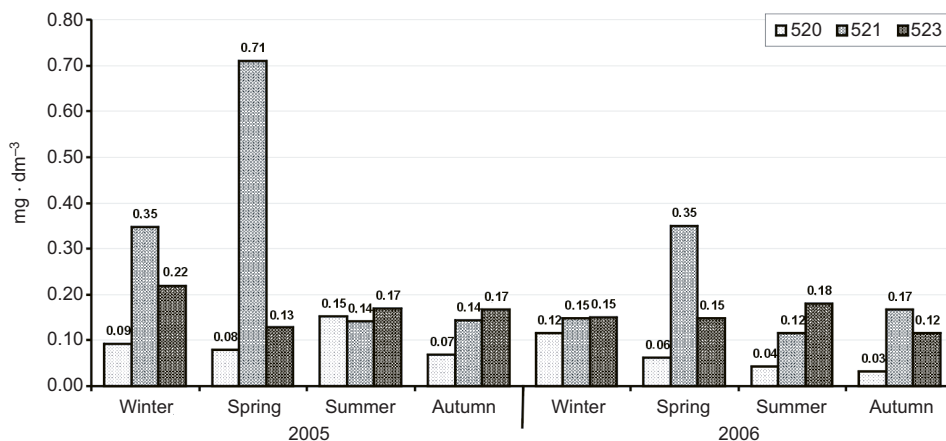


Fig. 3. Seasonal variability of phosphatic phosphorus (P-PO₄) concentrations in drainage waters flowing from the catchment of Doba in 2005–2006

quality of the catchment water. Of course, this action was not in accordance with the ‘good farming practice’ – actually, it was the contrary. The lowest concentration of general phosphorus and phosphatic phosphorus of all considered seasons was noted in the autumn.

The high concentration of general phosphorus contributed to the deterioration of the quality of the drainage waters to a larger extent than the concentration of phosphates. The average concentration of general phosphorus allows to classify the water from test sites no. 520 and 523 to the soil quality class II (good) and the water from the catchment of the liquid manure fertilized drainage area no. 521 to class V (poor). As far as the concentration of phosphates is concerned, the drainage waters represented mainly class II (good) [9].

Conclusions

1. During the 2-year test period it was noted that the amount of phosphorus flowing by a drainage network depended most of all on atmospheric conditions, season and intensity of agricultural utilisation of the area.

2. As far as seasonal distribution is concerned, the highest concentrations of general phosphorus and P-PO₄ for all drainage waters in 2005–2006 were noted in winter and spring. The maximum concentration was noted in drainage waters from the more intensely fertilized fields, where liquid manure was used – 1.62 mg P · dm⁻³ in 2005 and 0.80 mg P · dm⁻³ in 2006. These values were influenced by the lack of vegetation and increased rainfall.

3. The content of general phosphorus largely contributed to the lowering of the quality class of drainage waters. The average concentration of phosphorus allows to qualify the tested water from the areas of low fertilization to the II quality class (good), and the water from the catchment of the intensely fertilized drainage area close to rural buildings to the soil quality class V (poor).

4. The conducted research indicates that the area of the tested catchments, which was classified on the basis of phosphate content in the water as being at particular risk, also constitutes a potential threat due to its high phosphorus concentrations.

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WPLYW GOSPODARSTWA ROLNEGO NA ODPLYW FOSFORU SIECIĄ DRENARSKĄ

Katedra Melioracji i Kształtowania Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Celem badań było określenie wpływu intensywnej gospodarki rolnej na sezonowe zmiany stężeń w wodach drenarskich odpływających ze zlewni zakwalifikowanych do obszarów szczególnie narażonych na zanieczyszczenie wód ze źródeł rolniczych.

Badania nad wpływem gospodarstwa rolnego na odpływ fosforu siecią drenarską prowadzono w latach 2005–2006 w zlewni jeziora Dobskiego. Obiekt badań położony jest w obrębie Pojezierza Mazurskiego, w miejscowości Doba. Tereny rolnicze w otoczeniu wsi użytkowane są przez gospodarstwo rolne, które specjalizuje się w chowie trzody chlewnej.

W czasie 2-letniego okresu badań stwierdzono, iż ilość fosforu odprowadzanego siecią drenarską uzależniona była przede wszystkim od warunków atmosferycznych, pory roku oraz intensyfikacji rolniczego użytkowania terenu.

Słowa kluczowe: zlewnia, dział drenarski, fosfor

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Zenon PAWLAK² and Adekunle OLOYEDE³

LEAD LEACHABILITY FROM SHOOTING RANGE SOILS

BADANIA WYMYWALNOŚCI OŁOWIU Z GLEBY NA TERENIE STRZELNIC

Abstract: Lead contamination of soil in shooting ranges creates an environmental problem. Samples of soil were analyzed for total lead (T-[Pb]) and extracted lead (TCLP-[Pb]) using toxicity characteristic leaching procedure (TCLP). Total content of lead in soil samples varied from 640 to 4600 ppm. The TCLP test indicated that lead in most of soil samples exceeded the 5 ppm, a critical level of EPA regulation for solid and hazardous waste. The ratios of leaching lead (TCLP-[Pb]) to total lead (T-[Pb]) in soil samples ranged from 1.9 % to 5.2 %. The TCLP extracts from soil samples indicated lead concentration levels of 5 to 45 times over the US EPA regulatory level of 5 ppm and this was characterized as a toxic waste.

Keywords: soil, lead soil contamination, shooting range, total lead, extracted lead, TCLP

Heavy metals particularly damage groundwater and their movement through soil is of considerable concern. Soil contamination usually originates from industrial and human activities but can also be done due to a variety of natural phenomena. The eight toxic metals such as arsenic, cadmium, lead, selenium, barium, chromium, silver and mercury are considered relevant in terms of potential toxicity to biological life and human health. Lead is recognized in all countries as a potentially toxic metal for humans [1].

Firing range activities become a potentially significant source of soil contamination with lead because lead is used in ammunition production. New shotgun pellets contain 97 % lead, 2 % antimony, 0.5 % arsenic and 0.5 % nickel. The annual consumption of lead used for shotgun ammunition in some European countries (Denmark, Finland,

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Sweden, United Kingdom) is about 500–1000 Mg [2]. Shooting range soil contamination has been investigated in many countries [3–10].

Lead being an amphoteric metal is soluble over a wide range of pH, but is more soluble under acidic than alkaline conditions [11]. The oxidation and dissolution of metallic lead result in various compounds, predominantly: oxide, carbonate, sulfate, chloride, phosphate and sulfide.

Study on reuse of lead contaminating urban soils was done in the Netherlands [12]. The soil samples contained from 3 ppm to over 3000 ppm of lead. The leachability, based on test NVN 2508, was higher in sandy soils (4 % to 13 %) than in clay soils (1 % to 4 %). An increase of humic substances in soil up to 20 % reduced the leachability of lead to about 10 %. The lead mobility in soils was determined to be low. The study recommended the reuse of moderately lead-contaminated urban soils by overlaying the contaminated soil with a layer of clean soil.

Toxicity characteristics leaching procedure (TCLP) was carried out for determination of lead leachability. The determination of total lead content is not sufficient to assess the environmental impact on polluted soils. The TCLP simulates leaching of toxic lead in landfill environments, and the test could be important in evaluation of toxicity of wastes [6, 13]. Leaching tests are valuable as a supplementary tool to chemical analysis for the assessment of the mobility of inorganic compounds in soil. Depending on the kind of contaminated soil it may be satisfactory to leave the contamination as it is, as long as the mobility is low and predictable and does not present an unacceptable risk of harm to the environment or to the health [14].

Existing leaching procedures

A number of selected leaching procedures commonly used in various countries are summarized in Table 1 [14].

Table 1

The most common leaching procedures for granular waste and industrial sludges

Type of test	Test procedure (duration; leachant pH; liquid/solid ratio)	Country/region
Column leaching test	NEN 7343 column test (21 d; 4.0 with HNO ₃ ; 0.1 to 10)	The Netherlands
	Nordtest-column test (24 h; 4.0 with HNO ₃ ; 1 to 2)	Nordic Countries
	Combined column + batch leaching (24 h; 4.0 with HNO ₃ ; 24)	Denmark
Batch leaching test	DIN 38414 S4 (24 h; pH water; 10)	Germany, Austria
	AFNOR X31-210 (24 h; pH water; 10)	France
	JST-13 (6 h; pH water; 10)	Japan
	EN 12457 (6 h, 18 or 24 h; pH water; 2 to 10)	European Union
	Nordest (6 h, 18 h or 24 h; 4.0 with HNO ₃ ; 2 to 10)	Nordic Countries
	NEN 7349 serial (23 h; 4.0 with HNO ₃ ; 20)	The Netherlands
	ENA Skaktest (24 h; 4.0 with H ₂ SO ₄ ; 4)	Sweden
TVA Eluattest (24 h; pH water 5 to 6; 10)	Switzerland	

Table 1 contd.

Type of test	Test procedure (duration; leachant pH; liquid/solid ratio)	Country/region
	WRU Bach Extraction (2–80 h; 5.0 buffer NaOAc; 1)	United Kingdom
	EP Tox Method 1310 (24 h; 5.0 buffer NaOAc; 20)	USA
	TCLP Method 1311 (24 h; pH 2.9 HOAc, or pH 5.0 buffer HOAc/NaOAc; 20)	USA

To establish the parameters controlling leaching of element in the laboratory tests, two different types of leaching tests are used, those carried out in batches and those carried out in columns. In batch tests only solubility is considered as relevant in controlling the release process, whereas in column tests percolation and diffusion are considered to dominate. For batch experiments the most relevant controlling parameters are pH, temperature, time, ratio liquid/soil (L/S), shaking and type intensity, concentration and nature of the leachant, ionic strength, liquid/solid separation procedure, atmosphere (air or inert) and the volume of air in the shaking container. For column experiments the most relevant parameters are pH, elution rate, temperature, time filling procedure, particle separation, ionic strength, column material, column design and column dimensions [14].

The purpose of present study was to examine: 1) total lead concentration distributions in shooting range soils contaminated by lead pellets; and 2) using TCLP test for correlation between total lead and leaching characteristics of lead in these soils.

Experimental part

Samples of soil were collected from two rifle/pistol military shooting ranges. For each shooting range samples of surface soil (0–10 cm depth) were collected from the front, the middle and the end of the berm shooting range. Samples of soil were digested with nitric(V) acid and peroxide using the hot block digestion procedure and method 3050A [15] for determination of total metal concentrations. The toxicological characteristics leaching procedure (TCLP) method 1311 [16] is a test used to determine the heavy metal toxicity of contaminated soil. In this study, the soil samples were extracted with fluid solution no. 1 (pH = 4.93 ± 0.05), which was prepared by adding 11.4 cm^3 glacial acetic acid to 0.5 dm^3 D.I. water, and then adding 128.6 cm^3 1.0 M NaOH solution and diluting to a volume of 2.0 dm^3 .

The concentrations of total lead in soils and in TCLP extract were determined by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) using PerkinElmer Optima instrument. Calibration standards were prepared from multi-element standard. Three standards and blank were used for calibration. The standards were prepared in nitric(V) acid/hydrochloric acid matrix, as specified in method 6010 [17].

The performance of the instrument, during the analysis, was evaluated by determining the method detection limit (MDL) and several quality control (QC) parameters. The method reported level (MRL) value for lead is 0.3 ppm.

Several QC checks were performed to ensure that the ICP was operating properly. The calibration was initially checked using a standard at the midpoint of the calibration range. The standard was recovered within the $\pm 5\%$ guidelines specified in the standard procedure. The interference check sample was run to ensure that the wavelengths chosen are proper. The interference check sample contained high concentrations of Al, Na, Ca, and Mg, with low levels of the analytes of interest. A laboratory continuing check standard (CSTD) was run to verify the performance of instrument and method. The values of the CSTD were recorded within $\pm 10\%$ required limits. A duplicate sample was analyzed and the analyte recorded within $\pm 15\%$ of the original sample. The samples were spiked before digestion with (2 mgPb/dm^3). The spike recoveries for the samples were 94 % to 106 %. The laboratory spike blank (LSB) and laboratory spike duplicate blank (LSDB) were run with average recovery (or accuracy) 96 % to 107 %, the precision for data set was evaluated by calculating the difference between the results found for the LSB and LSDB, and then dividing the difference by the average of the two results. The relative percent difference (% D) or precision was 4 % to 8 %.

Quality assurance (QA)/quality control (QC)

Calibration standards were prepared from multi-element standard. Three standards and one blank were used for calibration. The standard samples were prepared in nitric(V) acid/hydrochloric acid matrix, as specified method 6010 [17]. To assure the accuracy and precision of a method, a series of QA/QC procedures were performed to validate the data from EPA methods (see summary Table 1 and 2) to ensure that the ICP was operating properly. The calibration was initially checked using a continuing check standard (CSTD) at the midpoint of calibration range. The CSTD was recovered within the range of acceptance ($\pm 5\%$) guidelines specified in the method, and during run the recovery was within the acceptance ($\pm 10\%$). An interference check sample was run to ensure that the wavelengths chosen for the method did not have any undetected spectra interference. The check sample contained high concentrations of Al, Na, Ca and Mg, with low levels of the analytes of interest. The samples were spiked before digestion (1 ppm for Ag, Ba, and 2 ppm for Cr, Cd, As, Pb, and Se). During the TCLP extraction, blank and duplicate samples, and standard reference materials (SRM) were processed along with the samples. Blank extraction samples were run used to detect contamination introduced in the sample processing and analysis procedure. Additionally, sample duplicates were also extracted to assure reproducibility of the method. The reported concentration could not deviate more than 20 % between the duplicates, and reference materials. An extraction blank was processed and analyzed with each extraction sample set (10 samples). In addition, laboratory spike blank (LSB) and laboratory spike blank duplicate (LSBD) were analyzed with each extraction set samples of (10 samples). The performance of instrument was evaluated by determining the method detection limit (MDL) for each analyte using EPA protocol (US EPA, 1984). Method reported limits (MRLs) are given in experimental part.

Results and discussion

Total lead concentration

Samples of soil were collected from two firing ranges. For each range samples were analyzed for total lead and extracted lead, the results are presented in Table 2. Range no. 1 had the highest pH (8.3 to 8.6) whereas range no. 2 (samples G to L) results were of the lowest pH (6.5 to 7.4) (Table 2).

Table 2

Lead leachability from soil contaminated with lead bullets pellets

Sample no. and range: (1) and (2); (sample: front, middle, berm)	pH in water	pH ^a (in water) and (HCl added)	Total [Pb] ^c [ppm]	TCLP [Pb] ^c [ppm]	Extraction ^b [%]
Range no. (1)					
A (1) front	8.3	1.1	1070	25.7	2.4
B (1) front	8.3	1.1	1240	32.2	2.6
C (1) middle	8.3	1.0	1680	36.9	2.2
D (1) middle	8.5	1.1	1740	33.1	1.9
E (1) berm	8.4	1.0	4400	206.8	4.7
F (1) berm	8.6	1.1	4600	225.4	4.9
Range no. (2)					
G (2) front	6.6	1.0	1080	45.4	4.2
H (2) front	6.5	1.1	1140	45.6	4.0
I (2) middle	6.9	1.0	640	20.5	3.2
J (2) middle	7.0	1.1	650	24.1	3.7
K (2) berm	7.3	1.1	2650	135.2	5.1
L (2) berm	7.4	0.9	2740	142.5	5.2

^a pH (5 g solids [not "dry solids"] + 96.5 cm³ D.I. water); if pH is < 5.0, use extraction fluid no. 1 and go to extraction. If pH is > 5.0, then 3.5 cm³ 1 M HCl was added to determine extraction fluid, if pH is < 5.0, use extraction fluid no. 1, if pH is > 5.0 use extraction fluid no. 2. Extraction fluid no.1 (11.4 cm³ HOAc + 128.6 cm³ 1.0 M NaOH for 2.0 dm³) pH = 4.93 ± 0.05. Extraction fluid no. 2 (11.4 cm³ HOAc for 2.0 dm³) pH = 2.88 ± 0.05.

^b Ratio of TCLP [Pb] to total [Pb] × 100 %.

^c Quality control (QC) parameters: Reference standard material, SRM (94–105 % recovery), Continuing check standard, CSTD (95–104 %), Lab spike blank, LSB (96–107 %), Lab spike blank duplicate, LSBD (95–104 %), Lab spike matrix, LSM (94–106 %), Lab spike matrix duplicate, LSMD (96–104 %).

Accuracy and precision of metals analysis: Accuracy was determined as a ratio of LSB and LSBD (96 to 103 %), or a LSM and a LSMD (96 to 105 %); the precision was determined by calculating the difference between the results found for the LSB and LSBD, and then dividing the difference by the average of the two results (4 to 8 %).

Lead concentrations in five samples (A to F, range no. 1) were exceptionally high (1070 ppm to 4600 ppm), and the other six samples (G to L, range no. 2) exhibited high concentration of Pb (from 640 ppm to 2740 ppm), exceeding US EPA critical levels of 400 ppm. The higher concentrations measured were probably obtained due to the

the presence of large lead particles in those soil samples. The solids appear fine enough to pass through a 9.5 mm sieve. This indicates that substantial accumulation of lead was primarily due to large lead particles. Lead distribution in surface soils was related to the number of lead bullets (ie, the more bullets, the greater lead concentration in the soil). Total lead concentration in surface soils in the area in front of the berm ranged from 1070 to 1240 ppm (range 1) with the highest concentration in middle 1740 ppm (range 1) and the lowest in middle 640 ppm (range 2) from the shooting stands (Table 2). The highest lead concentration (4600 ppm, range 1; and 2740 ppm, range 2) was in the backstop berm which includes lead associated with metallic bullet fragments. Most soils are considered contaminated with lead if they contain more than 200 ppm, the upper limit for a common soil [18].

Elemental lead can be readily dissolved in acid solutions. The lead pellets in the presence of oxygen, water and carbon dioxide could form: PbO , PbCO_3 , $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. Formation of these compounds produces an increase in soil pH and reduces the migration of lead [3].

Toxicity characteristic leaching procedure (TCLP)

The leaching procedure uses a buffered acetic aqueous solution at a liquid to solid ratio (L/S) of 20:1 [16]. In this study, TCLP of lead in the shooting range soils was performed with solution no. 1 (pH 4.93 ± 0.05). The extraction procedure requires the preliminary evaluation of the soil pH to determine the proper extraction solution necessary for the experiment. All samples in the study were calcareous. When concentrations of lead in soil samples exceed 400 ppm, the TCLP test is recommended [17]. The leachates from twelve soil samples indicated higher lead concentration which was of 5–45 times over the US EPA regulatory critical level of (5 ppm) and would be characterized as hazardous waste [19]. The ratios of TCLP lead values to total lead values from soil samples from range no. 1 varied from 2.2 % to 4.9 % and for range no. 2 from 3.2 % to 5.2 %. The variation in these data suggests that lead retention was site dependent.

Prediction of extractable components based on the total contents is very uncertain and a laboratory extraction can not reflect the chemistry of a waste placed in the environment. There are many variables that affect leaching behavior including redox properties, reduction by metal not being hazardous eg, iron, additives present, sorption processes, precipitation of hydroxides and acid-base changes. In some cases when iron metal, hydrous ferric oxide, zinc metal, phosphate and lime are present in waste, such a mixture passes the TCLP test. It is difficult to predict result of a sample that can be very specific for a waste sample. Even with a large number of tests done for waste samples it is hard to assess if they meet regulations based on total-metal (T-Me) concentrations but only on leached amounts in the TCLP test. Even if the content of total metals is very high, a leached fraction can pass the TCLP test.

To understand what really happens in the field and TCLP test, the process of oxidation and reduction should be considered [20]. The standard potentials of the reduction of divalent ions to metals are as follows: copper, 0.34 V; lead, -0.13 V; iron,

−0.45 V, and zinc, −0.76 V. This means that iron can reduce Pb(II) as follows: $\text{Fe} + \text{Pb}^{+2} \rightarrow \text{Fe}^{+2} + \text{Pb}$. Lead(II) cations in solution will be reduced by iron, so that the lead concentration will remain very low if metallic iron is present and accessible in solution.

Conclusions

Soil of firing range has been characterized for total and leached lead content. Concentration levels of lead were found in the range of 640 to 4600 ppm (twelve samples). TCLP was carried out on size-fractionated homogeneous soil. The TCLP tests indicated a high leaching possibility of lead in firing ranges that exceeded critical level (5 ppm). The leachates from all soil samples indicated high lead concentration which were of 5 to 45 times over the US EPA regulatory critical level (5 ppm) and would be considered as hazardous waste [19].

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BADANIA WYMYWALNOŚCI OŁOWIU Z GLEBY NA TERENIE STRZELNIC

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Abstrakt: Problem środowiskowy stanowi zanieczyszczenie na terenie strzelnic gleby ołowiem. Analizowano próbki gleby na zawartość ołowiu ogółem i ekstrahowanego, wykorzystując metodę ługowania TCLP. Ogólna zawartość ołowiu w próbkach glebowych wahała się od 640 do 4600 ppm. Test TCLP wskazał, że ołów w większości próbek glebowych przewyższył 5 ppm, co dla stałych/trwałych niebezpiecznych odpadów oznacza poziom krytyczny według regulacji EPA. W próbkach gleby stosunek ługowanego ołowiu do ołowiu ogółem waha się od 1,9 % do 5,2 %. Ekstrakty TCLP z próbek glebowych wykazały poziom stężenia ołowiu od 5 do 45 razy przewyższający poziom 5 ppm, określony przez amerykańską regulację EPA i gleby z terenu strzelnic oceniono jako toksyczne.

Słowa kluczowe: gleba, zanieczyszczenie gleby ołowiem, teren strzelnic, ołów ogółem, ekstrahowany ołów, TCLP

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**INFLUENCE OF THE COMBINATED BIOACCUMULATION
OF FLUORIDE AND SULFUR
ON CHLOROPHYLL CONTENT IN NEEDLES
OF SELECTED TREES FROM THE AREAS
OF SOUTHERN POLAND**

**WPLYW ŁĄCZONEJ BIOAKUMULACJI FLUORU I SIARKI
NA ZAWARTOŚĆ CHLOROFILU W IGLACH WYBRANYCH DRZEW
ROSNĄCYCH NA TERENACH POLSKI POŁUDNIOWEJ**

Abstract: It was the fluorine (F), sulfur (S) and chlorophyll (Chl) content that was determined in the needles of conifer species: European spruce (*Picea abies*), Colorado spruce (*Picea pungens*), Scots pine (*Pinus silvestris* L.) and Common silver (*Abies alba*). The materials were collected in the regions located in the vicinity of steel and power engineering industry impact and in a place situated in a non-industrial area. The obtained results were analyzed from the viewpoint of the relationships between the S, F and chlorophyll content. From the findings, it appears that, accumulation of F and S in needles only in case of Scots pine has been accompanied by more evident decrease in the Chl content. In the case of remaining conifer species increased accumulation of F and S in older needles did not influence the Chl content therein.

Keywords: industrial pollution, fluorine, sulfur, chlorophyll, needles of conifer

Sulfur (S) as SO₂ and fluorine (F) usually in the form of HF or SiF₄ are one of the most important air pollutants damaging the plants. The main emission source of the industrial gases and dusts, which introduce toxic compounds of S and F to environment are cement and aluminum works, phosphate fertilizers plants, iron- and steel works and power industry [1]. Increasing concentration of S and F in the soil of agricultural regions results from application of fertilizers and plant protection substances [2].

The high concentration of S and F in the atmosphere and long duration of exposure, induce chlorosis, necrosis and growth distortion in the plants, whereas the first symptom of concentration of S and F that does not cause visible damage are photosynthesis

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processes disturbances [3, 4]. Thus, one of the manners in which it is possible to evaluate the conditions of the trees growing in a polluted environment is to analyze the changes in the chlorophyll content in the tree leaves and needles [5–7].

These studies have been aimed at determination of the relationship between chlorophyll and fluorine and sulfur concentration in needles of selected conifers exposed to fluorine and sulfur bearing gaseous emissions.

Materials and method

The needles of four conifer species growing in Poland: European spruce (*Picea abies*), Colorado spruce (*Picea pungens*), Scots pine (*Pinus sylvestris*) and Common silver (*Abies alba*) were examined. The current-year and one-year-old needles were collected between November and February in the physiological rest period, during the same season in the years 2001–2003. The samples come from Polish southern towns of Strzemieszyce, Ustroń Polana and Zebrzydowice located in areas of iron, steel and heat-power generating plants and also from Brzezna near Nowy Sącz situated in a non-industrial area. Strzemieszyce is located within a distance of 6 km from Huta Katowice (presently ArcelorMittal Steel branch of Dąbrowa Górnicza). In Ustroń Polana (situated in Beskid Śląski) the needles were torn off the tree growing on the slopes of the Czantoria Mount. The needles of the Colorado spruce come from allotment gardens and the needles of Common silver were collected only on the Czantoria Mount. The needles without visible symptoms of chlorosis and necrosis were collected at an altitude of 2.5–3 m above ground.

The uniform samples were prepared for analysis. Fluoride ion (F^-) concentration was determined potentiometrically [8], using fluoride selective electrode (Orion, USA) and sulfur (S) concentration was determined nephelometrically with $BaCl_2$ as sulfate (SO_4^{2-}), after dry ashing the needles in nickel crucible. Fresh needles were extracted with acetone for spectrophotometric determination of chlorophyll (Chl) [9].

Results and discussion

In order to evaluate the impact of F and S accumulation in the needles of the conifer species on the Chl content therein, the materials were collected in the places that were under influence of differential emission of these compounds. The average F and S content in the needle samples from all the collection sites are shown in Table 1. A significant concentration diversification was observed, both in the case of F and S, which indicates their accumulation from atmospheric air (Table 1). The highest and the lowest F contents were found in needle samples of the coniferous trees grown in Strzemieszyce (near the steel works) and in Brzezna (situated in a non-industrial area), respectively. Considerably, unexpectedly high S content in the needles coming from Brzezna may have been associated with the household combustion of high-sulfur-content coal in this area [10]. On the other hand, Innes [11] argued, that the good

nutritional status of trees may be a possible reason for the unexpectedly high sulfur content.

Table 1

Average of fluorine (F) and sulfur (S) content in the needle samples depending on the collection site

Element	Collection site			
	Strzemieszyce	Ustroń Polana	Zebrzydowice	Brzezna
F [$\mu\text{g g}^{-1}$ d.m.]	15.52 ± 10.20	14.86 ± 6.51	8.99 ± 2.97	6.86 ± 1.98
S [$\mu\text{g g}^{-1}$ d.m.]	1706 ± 363	1432 ± 245	1562 ± 295	1794 ± 299

In Figs. 1A, B it is shown that accumulation level of F and S depends on the needle age. The S content showed no significant decrease between current- and one-year-old needles, while the F content was increasing with the ageing of needles. The results of average F, S and Chl content in the needle samples from particular species are presented in Table 2. In all examined needles the content of F varied from $4.44 \mu\text{g g}^{-1}$ d.m. to $41.87 \mu\text{g g}^{-1}$ d.m. and the content of S was between $842 \mu\text{g g}^{-1}$ d.m. and $2552 \mu\text{g g}^{-1}$ d.m. The obtained results are similar to the results reported by other authors. The content of S obtained by Ciepał [12] was between $1400 \mu\text{g g}^{-1}$ d.m. and $1750 \mu\text{g g}^{-1}$ d.m. and by Mańkowska [13] was from $2251 \mu\text{g g}^{-1}$ d.m. to $2590 \mu\text{g g}^{-1}$ d.m. for needles of the European spruce. The lowest concentration of all the elements analyzed was found in the Scots pine needles. However, these values were higher than the values assumed as non-toxic, this is, $1300 \mu\text{g g}^{-1}$ d.m. [14, 15] and $6 \mu\text{g g}^{-1}$ d.m. [16] for S and F, respectively.

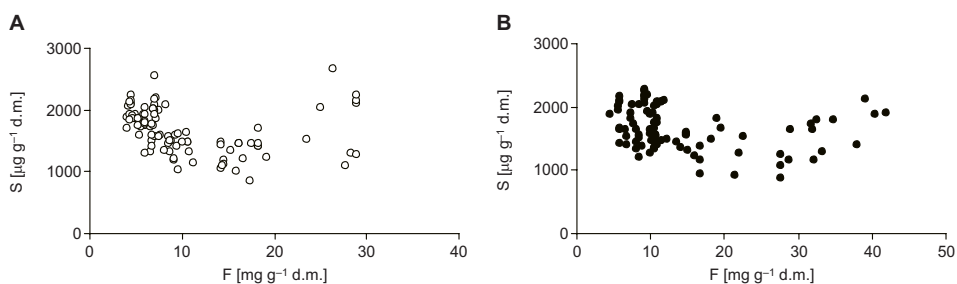


Fig. 1. Relationships between fluorine and sulfur content in (A) current-year needles and (B) one-year-old needles of the investigated conifer species from all of the collection sites. Explanation: F – fluoride; S – sulfur

The interdependency between the F, S and Chl content is depicted in Figs. 2A–C and Figs. 3A–C. From the results, it appears that accumulation of both elements in needles only in the case of Scots pine has been accompanied by more evident decrease in the Chl content. In the case of remaining conifer species increased accumulation of F and S in older needles did not cause decrease of Chl content therein.

Table 2
 Fluorine (F), sulfur (S) and chlorophyll (Chl) content in needles of conifer species from all of the collection sites

Element	Age of needles	Conifer species			
		<i>Scots pine</i>	<i>European Spruce</i>	<i>Colorado Spruce</i>	<i>Common silver</i>
		Mean (min.–max.)			
F [$\mu\text{g g}^{-1}$ d.m.]	current-year	11.66	11.02	10.62	15.92
	one-year-old	14.25 (4.32–32.14)	12.48 (4.44–34.83)	14.70 (4.59–41.87)	16.53 (13.55–19.14)
S [$\mu\text{g g}^{-1}$ d.m.]	current-year	1538	1744	1694	1675
	one-year-old	1543 (1171–2081)	1740 (952–2552)	1556 (842–2246)	1626 (1127–2311)
Chl [$\mu\text{g g}^{-1}$ d.m.]	current-year	1.44	1.74	1.54	1.82
	one-year-old	1.59 (1.07–2.07)	2.25 (1.26–2.71)	2.02 (1.29–2.68)	2.56 (1.31–2.78)

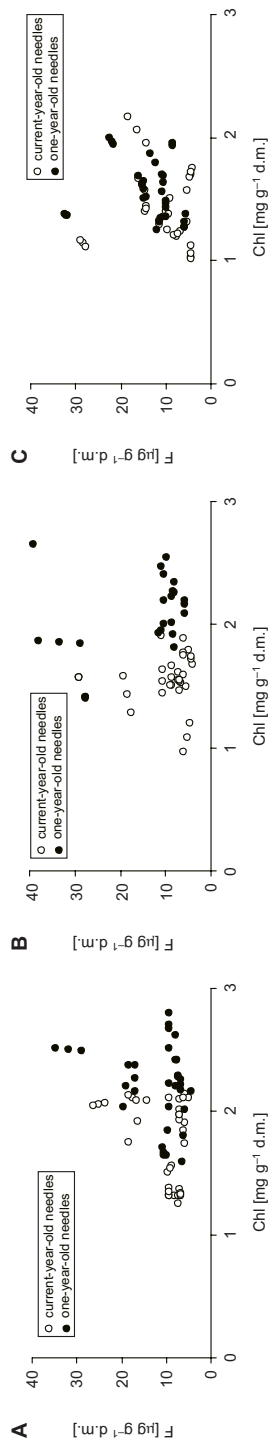


Fig. 2. Relationships between chlorophyll and fluoride contents in current- and one-year-old needles of (A) European spruce, (B) Colorado spruce and (C) Scots pine from all of the collection sites. Explanation: F – fluoride; Chl – chlorophyll

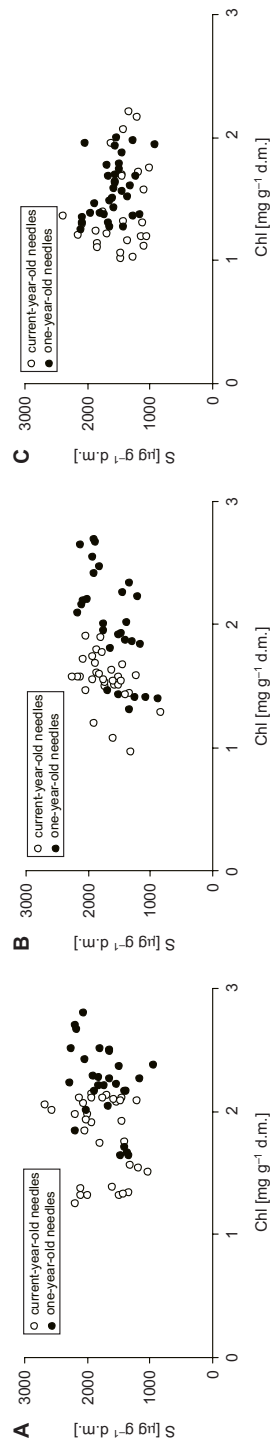


Fig. 3. Relationships between chlorophyll and sulfur contents in current- and one-year-old needles of (A) European spruce, (B) Colorado spruce and (C) Scots pine from all of the collection sites. Explanation: S – sulfur; Chl – chlorophyll

In the light of the results achieved, one may conclude that the investigated needles of coniferous trees growing in the same area are characterized by differential sensibility on the same pollution impact. These results may show that needles of Scots pine are more sensitive to F and S from atmospheric air.

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WPŁYW ŁĄCZONEJ BIOAKUMULACJI FLUORU I SIARKI NA ZAWARTOŚĆ CHLOROFILU W IGŁACH WYBRANYCH DRZEW ROSNĄCYCH NA TERENACH POLSKI POŁUDNIOWEJ

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Abstrakt: Zawartość siarki (S) i fluoru (F) oraz chlorofilu (Chl) oznaczano w igłach świerka pospolitego (*Picea abies*), świerka kłującego (*Picea pungens*), sosny pospolitej (*Pinus sylvestris*) i jodły pospolitej (*Abies alba*). Materiał do badań pobierano w miejscowości Strzemieszyce, Ustroń Polana (Beskid Śląski) i Zebrzydowice (powiat cieszyński) znajdujących się w strefach oddziaływania zanieczyszczeń z ośrodków przemysłowych Polski i zanieczyszczeń transgranicznych oraz w miejscowości Brzezna położonej koło Nowego Sącza. Uzyskane wyniki analizowano z punktu widzenia zależności pomiędzy zawartością S i F i zawartością chlorofilu w igłach. Spośród badanych gatunków drzew iglastych jedynie w przypadku igieł sosny pospolitej stwierdzono zmniejszenie zawartości chlorofilu związane z akumulacją F i S.

Słowa kluczowe: zanieczyszczenia przemysłowe, fluor, siarka, chlorofil w igłach drzew

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**INFLUENCE OF A FARM INFRASTRUCTURE
ON CALCIUM, MAGNESIUM, ZINC,
AND IRON IONS CONCENTRATIONS IN WELL WATER**

**WPLYW INFRASTRUKTURY ZAGRODY WIEJSKIEJ
NA STĘŻENIE JONÓW WAPNIA, MAGNEZU, CYNKU I ŻELAZA
W WODACH STUDZIENNYCH**

Abstract: Study was carried out in 16 villages localized in Podlasie province. One dug well in agricultural farm was selected in each village. Calcium, magnesium, zinc, and iron ions concentrations were determined in well water samples. Moderate influence of some elements of a farm on calcium and magnesium contents in well water was observed. Study revealed the effect of well distance from inventory buildings on zinc concentrations in analyzed water.

Keywords: dug wells, zinc, farm

There are many sources of underground water contamination, and most often, their negative influence superimpose [1].

Well localization and its sanitary status within the farm as well as proper management of animal wastes determine the water quality in wells [2].

Supplying the underground water with calcium and magnesium is due to elution from geological environment as well as these elements migration from organic fertilizers stored in farms [3]. According to Wolak [4], wrong stored wastes in dumps are considerable source of zinc in underground water. High zinc concentrations are also associated with that metal ore zones and anthropogenic pollution; its significant contents are present in municipal and industrial sewage [5].

Wells of several to dozen meters depth can be most frequently met in farms. Well water is exposed to contamination due to improperly stored animal wastes and runoff from the farm area. Uncontrolled sewage disposal from households is another source of that pollution [6].

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The paper aimed at evaluating the influence of farm elements on calcium, magnesium, zinc and iron ions concentrations in water of selected farm wells within upper Narew river catchment.

Material and methods

Study was carried out in 16 villages localized in Podlasie province. One dug well in agricultural farm was selected in each village. All studied wells are supplied by water from the first water-carrying layer. Water samples from every farm were collected in spring, summer, autumn, and winter 2005. Calcium, magnesium, zinc, and iron concentrations were determined in water samples by means of AAS technique after filtering through microporous filters ($d = 0.45 \mu\text{m}$). Only soluble forms of the elements were determined. The correctness of applied method referring to Ca, Mg, Zn, and Fe ions contents was verified on a base of reference material (SRM 1643e, Trace Elements in Water) analysis. Also distances of the well from inventory buildings, household, and cultivated fields were measured.

Values of arithmetic mean and Pearson correlation coefficients were calculated using the experimental data. Statistical data was applied clustering analysis for analysis of the study results; it is based on a notion of object or variable distance within multi-dimensional space. That technique makes possible to present grouped objects or their features in a form of bundle diagram. Calculation of Euclidean distance is a direct way to calculate distances between objects. This measure determines a real geometric distance between objects in space and is calculated on a base of raw data. The method presents the similarity between objects or their features, which is a function of a distance. Objects are grouped in arrangements (clusters) with curly bracket combining particular variables. Those variables are more similar to each other when the distance between them is smaller.

Analyses results were the background to the evaluation of water quality taking into account the Decrees from 2000, 2002, and 2004 [7–9].

Results and discussion

According to the Decree (2002), the distance of wells providing with drinking water for people and farm purposes should be at least 15 meters from inventory buildings. The real distances were different in particular studied villages (Table 1). Wells were the worst localized in Fasty, Złotoria, Tykocin, Michałowo, Bokiny, Uhowo and Doktorce. Well in Nowodworce was characterized by the smallest distance from household (1 m), that in Rzędziany was the farthest (30 m). Distances of studied wells from cultivated fields were within the range from 5 m (Tykocin) up to 600 m (Doktorce). Study revealed the lowest calcium content ($56.23 \text{ mg} \cdot \text{dm}^{-3}$, II class) according to limit values given in the Decree (2004) in water from well localized in Narew, the highest ($108.42 \text{ mg} \cdot \text{dm}^{-3}$, III class) from well in Rzędziany (Table 1). Calculations revealed a slight dependence of calcium concentration in studied well water on their distance from inventory buildings (Pearson coefficient $r = -0.26$ at $p = 0.0001$). The lowest

Table 1
Localization of studied wells and general statistical parameters of well water

Well localization	Statistical parameter	Ca	Mg	Fe	Zn	Well distance from:		
						inventory buildings	household	cultivated field
[m]								
Narew	Mean	56.23	20.91	0.031	0.016	19	2	400
	SD	20.21	4.3	0.015	0.009			
Rzędziany	Mean	108.42	28.03	0.024	0.042	14	30	25
	SD	52.1	14.2	0.011	0.021			
Nowodworce	Mean	79.16	20.49	0.023	0.067	13	1	250
	SD	38.31	12.21	0.012	0.031			
Doktorce	Mean	93.55	26.13	0.015	0.287	12	7	600
	SD	41.32	12.56	0.007	0.136			
Zarzezany	Mean	87.83	26.41	0.014	0.038	16	9	200
	SD	42.12	13.21	0.007	0.016			
Supraśl	Mean	96.11	29.38	0.017	0.023	17	15	150
	SD	46.21	15.12	0.008	0.012			
Siekierki	Mean	78.96	27.61	0.019	0.077	14	11	100
	SD	36.21	13.21	0.011	0.031			
Bokiny	Mean	90.84	29.38	0.015	0.011	11	8	500
	SD	43.12	16.78	0.007	0.006			
Fasty	Mean	106.44	29.45	0.018	0.168	7	6	10
	SD	54.12	15.23	0.009	0.083			

Table 1 contd.

Well localization	Statistical parameter	Ca	Mg	Fe	Zn	Well distance from:					
						inventory buildings	household	cultivated field			
		[mg · dm ⁻³]							[m]		
Uhowo	Mean	86.32	26.57	0.018	0.063	11	10	200			
	SD	43.23	14.21	0.010	0.031						
Tykocin	Mean	85.67	28.91	0.019	0.093	8	8	5			
	SD	42.12	14.27	0.011	0.042						
Mościska	Mean	104.05	23.48	0.022	0.057	15	10	95			
	SD	51.21	11.21	0.010	0.021						
Michałowo	Mean	63.91	19.78	0.021	0.116	9	2	9			
	SD	31.21	10.24	0.012	0.061						
Płoski	Mean	79.33	25.19	0.019	0.049	16	5	20			
	SD	39.62	12.45	0.012	0.024						
Bondary	Mean	83.61	19.95	0.024	0.068	15	15	150			
	SD	41.23	10.23	0.011	0.033						
Złotoria	Mean	94.31	27.92	0.019	0.077	7	20	65			
	SD	46.32	13.54	0.010	0.032						

magnesium content ($19.78 \text{ mg} \cdot \text{dm}^{-3}$) was recorded in water from well in Michałowo, the highest ($29.45 \text{ mg} \cdot \text{dm}^{-3}$) in Fasty. Those values were within the I class of water quality according to the Decree (2004). Decree from 2000 stated that magnesium concentration in studied water was lowest than its permissible level, which was announced in Attachment No. 2. Moderate dependence of magnesium concentration in well water on their distance from inventory buildings was recorded (Pearson coefficient $r = -0.32$ at $p = 0.001$). According to Pokojaska and Dopierała [10], manure that can be found in cow-houses and storage dumps within the farm contains 0.36 % of calcium and 0.12 % of magnesium. Previously presented interdependencies confirm these reports. The lowest iron level ($0.014 \text{ mg} \cdot \text{dm}^{-3}$) was found in water from well in Zarzecznany, the highest ($0.031 \text{ mg} \cdot \text{dm}^{-3}$) in Narew. These values are within the I class for underground water quality and are lower than $0.2 \text{ mg} \cdot \text{dm}^{-3}$ – permissible limit for drinking water. Studies and analyses revealed the lowest zinc content ($0.011 \text{ mg} \cdot \text{dm}^{-3}$) in water from well in Bokiny, and the highest ($0.287 \text{ mg} \cdot \text{dm}^{-3}$) in Doktorce. Those values are within the I class of underground water purity as well as below permissible limit for drinking water (up to $3 \text{ mg} \cdot \text{dm}^{-3}$). Poor dependence of zinc concentration in analyzed water on well distance from inventory buildings occurred at Pearson coefficient $r = -0.46$ and at $p = 0.001$ (Fig. 1). The data clustering analysis (Fig. 2) revealed small Euclidean distance of following variables: well distance from cow-house and zinc concentration in well water. That probably resulted from the influence of pollution containing zinc ions on well water. The analysis is the confirmation of above discussed Pearson's correlations. In Poland, manure and liquid manure cattle main-

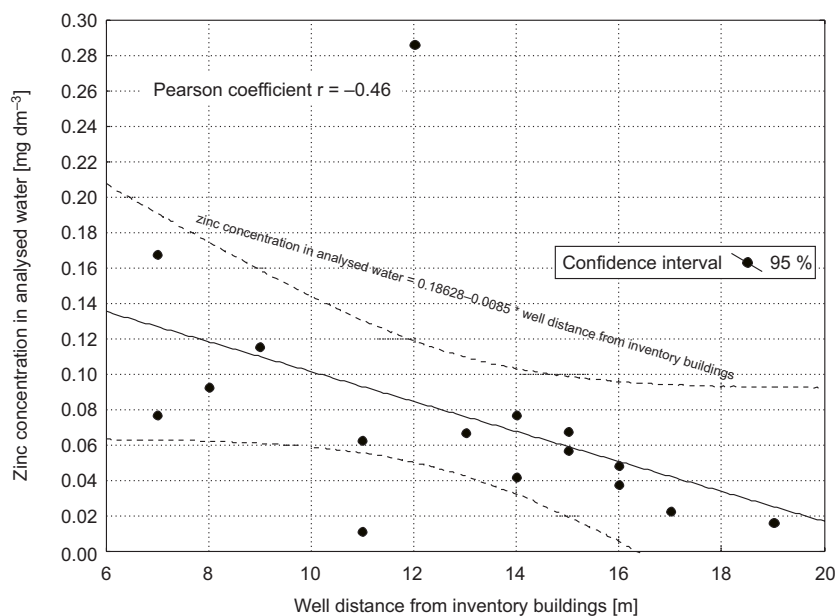


Fig. 1. Dependence of well distance from inventory buildings on zinc concentration in analyzed water

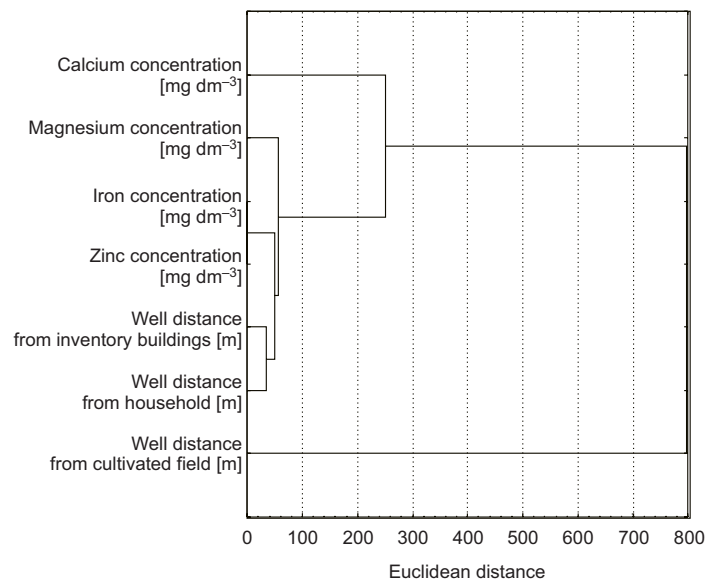


Fig. 2. Euclidean distances between studied parameters

tenance system dominates and the ways of these fertilizers storage favor the water contamination [11]. Durkowski [12] confirmed the influence of manure storage within the farm on well water quality.

Conclusions

1. Moderate influence of some farm elements on calcium and magnesium concentrations in well water was observed.
2. Studies revealed the influence of well distance from the inventory buildings on zinc ions concentrations in analyzed water.
3. In order to make water quality better in studied wells, the improvement of their sanitary status as well as rational water and sewage management within farms is necessary.

Acknowledgements

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WPLYW INFRASTRUKTURY ZAGRODY WIEJSKIEJ NA STĘŻENIE JONÓW WAPNIA, MAGNEZU, CYNKU I ŻELAZA W WODACH STUDZIENNYCH

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Abstrakt: Badania prowadzono w 16 wsiach położonych w województwie podlaskim. W każdej wsi do badań wybrano po jednej studni kopanej z gospodarstw prowadzących działalność rolniczą. W próbkach wody oznaczono jony wapnia, magnezu, cynku i żelaza. Na podstawie badań stwierdzono umiarkowany wpływ niektórych elementów zagrody wiejskiej na stężenia wapnia i magnezu w wodach studziennych. Badania wykazały wpływ odległości studni od budynku inwentarskiego na stężenie jonów cynku w analizowanych wodach

Słowa kluczowe: studnie kopane, cynk, zagroda wiejska

Tomasz STASZEWSKI¹, Piotr KUBIESA¹ and Anna BŁOCKA¹

FATE OF AIR POLLUTANTS FROM KONIN INDUSTRIAL COMPLEX IN PINE FOREST ECOSYSTEMS

MIGRACJA ZANIECZYSZCZEŃ POWIETRZA EMITOWANYCH Z KOMPLEKSU PRZEMYSŁOWEGO KONINA W DRZEWOSTANACH SOSNOWYCH

Abstract: In agricultural area of Konin where previously no industrial activity was performed the complex of power stations combusting brown coal was built in the end of the fifties followed by the aluminium smelter which was put into operation in 1965.

Both these industrial works emit considerable amounts of phytotoxic gases (F₂, SO₂, NO₂). Aluminium smelter emits vast amount of fluorine as aluminum is produced by thermo-electrolysis of aluminum oxide in electrolyte consisting of cryolite and aluminum fluoride as well as it is a major emitter of PAHs due to carbon electrode "combustion".

Because these plants did not meet technology parameters and production was poorly controlled in first period of activity harmful effects of their emission in the natural environment were observed.

Beginning from the nineties intensive proecological efforts were made and intensive modernization of the plants was performed. All these activities resulted in a significant reduction of air pollutants emission.

The paper presents the results of investigation carried out in the monitoring net established in Konin area. The fate of air pollutants currently emitted and deposited to the soil within a long period of the plants activity was determined. The vacuum ceramic cup lysimeters were used to assess the concentration and hazard of inorganic and organic chemicals for water – soil environment. On the basis of differences in concentration of cations and anions the rate of nitrification and acidification processes in the soil was also analysed.

Keywords: aluminium smelter, power plant, fluorine, benzo[a]pirene, acid deposition, pine forest, pine forests integrated monitoring

In the period of 1960–1990 Poland – due to intensive development of heavy industry at simultaneous lack of emission control – was one of the main emitters of air pollutants into the air. Big industrial plants apart from their long range effect caused a vast environmental damage in a local scale.

Since the middle sixties the activity of the aluminium smelter in Konin together with PAK (Pałnów, Adamów, Konin) power complex have adversely affected the surrounding

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agricultural and forest area. It resulted in excluding a big area from the agricultural activity and displacement of local people from the areas threatened by industrial emissions.

Implementation of the principles of the State Environmental Policy established in 1991 (eg reduction of pollutants at source and “polluter pays” principles extorted modernization of production technology.

Aluminium smelter emits vast amounts of fluorine as aluminium is produced by thermoelectrolysis of aluminium oxide in electrolyte consisting of cryolite and aluminium fluoride. Fluorine is regarded to be the most hazardous gas which may injure plants at much lower concentrations than other pollutants [1].

After 1993 modernization of the electrolysis process has started. “Wet” anode mass was replaced with “dry” one consisting of a less amount of aromatic hydrocarbons. The use of dry anode mass leads to stabilization of production process which results in the decrease in dust and fluorine compounds emission into the environment (Fig. 1).

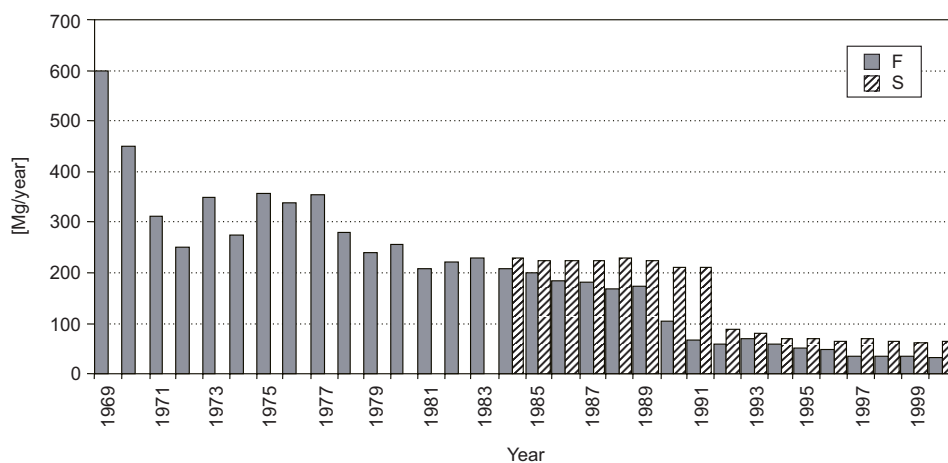


Fig. 1. Fluorine and sulphur emissions from “Konin” Aluminium Smelter

In power stations new boilers fitted with low-emission burners and new electrofilters were mounted as well as installation of wet desulfurization was put into operation. This contributed to the reduction of concentrations of eg phytotoxic gases around the threatened region (Table 1).

Table 1

Emission of pollutants from the PAK power complex in the period of 1980–2005 (Mg/year)
(<http://www.zepak.com.pl/pl/ekologia>)

Pollutant	Year				
	1980	1990	1995	2000	2005
SO ₂	198 000	125 000	135 000	110 000	115 000
NO _x	n.a.	n.a.	30 000	21 500	20 000
Dust	160 000	55 000	25 000	5 000	4 000

In the paper the present burden of pine stand ecosystems with compounds characteristic for aluminium smelting industry (fluorides, benzo[a]pirene) and other plants of Konin industrial complex (sulphur and nitrogen compounds) was analyzed.

Materials and methods

Site description

Three sites represent Scots pine forests located in the vicinity of the Konin Aluminium Smelter (Fig. 2). Site 1 (Sulanki) is situated 0.4 km from the smelter and represents 35 year-old Scots pine trees planted in the abandoned agricultural area after emission controls had been incorporated. Sites 2 and 3 (Anielew and Rudzica, respectively) are composed of mature Scots pine trees (80 year-old) located 2.5–3.0 km from the smelter.

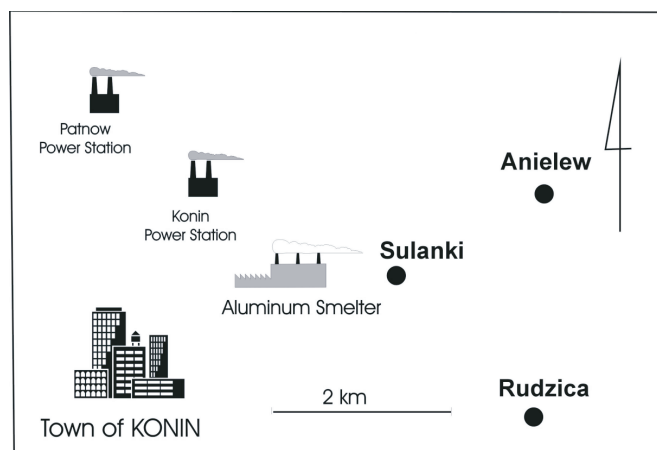


Fig. 2. Location sites

The soils are: dystric cambisols at Sulanki, eutric cambisols at Anielew and haplic podzols at Rudzica [2, 3].

In 2005 each plot was equipped with 15 randomly distributed throughfall collectors and six vacuum ceramic cup lysimeters for soil solution sampling [4]. Lysimeters were distributed regularly at 25 cm depth. Bulk deposition was sampled in an open area, close to the permanent plots. Polyethylene (PE) collectors were used for bulk deposition and throughfall sampling. Six nets 1 m in diameter were mounted to collect litterfall.

The water samples were collected monthly. The concentrations of cations were determined by the AAS method (SpectraAA 300 Varian). Ion chromatographic method was used for determination of Cl^{-1} , SO_4^{2-} and NO_3^{-1} concentrations (Dionex DX100, column AS4A). Concentration of NH_4^{+} in water samples was determined using the Nessler method; pH of water samples was measured using a glass electrode.

Organic compounds were extracted from water and plant material using dichloromethane. Benzo[a]pyrene was separated on florosil and analysed by HPLC (BECKMAN liquid chromatograph) using a UV detector. Identification of the separated compound was carried out by comparison of its retention times with the values obtained from a mixture of the Supelco PAH – Mixture 610-M [5].

Results and discussion

Mean annual pH of precipitation in the investigated area was about 5.0 which testifies to its acidic character (Fig. 3); pH value of throughfalls in all pine stands was higher when compared with bulk deposition and ranged from 4.22 to 4.44. The increase in pH of soil solutions when compared with throughfall pH was observed in all three sites; it was most pronounced for Sulanki where soil solution shows alkaline character (Fig. 3).

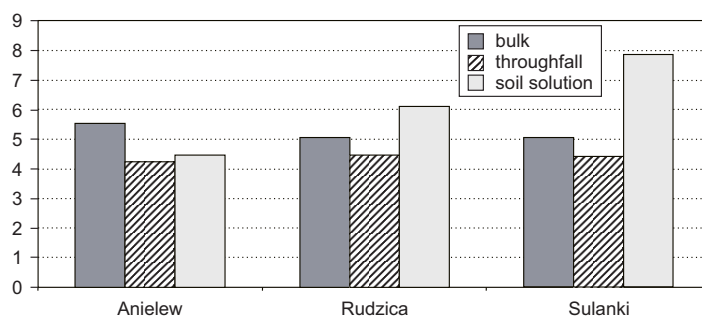


Fig. 3. pH of water

Concentrations of fluorine and sulfur increased in the following order: bulk, throughfall, soil solution (Fig. 4, 5). Increase in the concentrations of ions after passing the crowns points out that dynamic processes occur in the course of the water passing through canopy. Concentrations of individual ions and their quantity ratios differed significantly in both forms of precipitation.

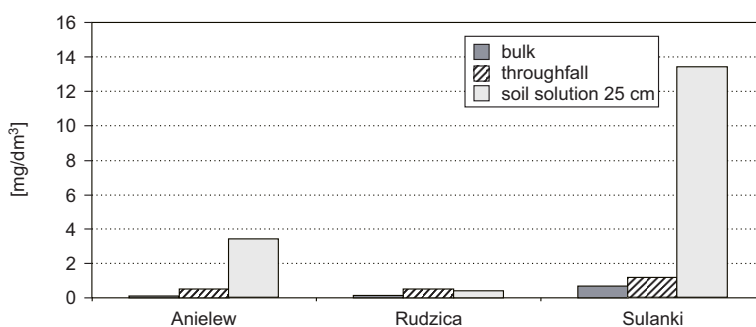


Fig. 4. Concentration of fluorine in compartments of pine ecosystem

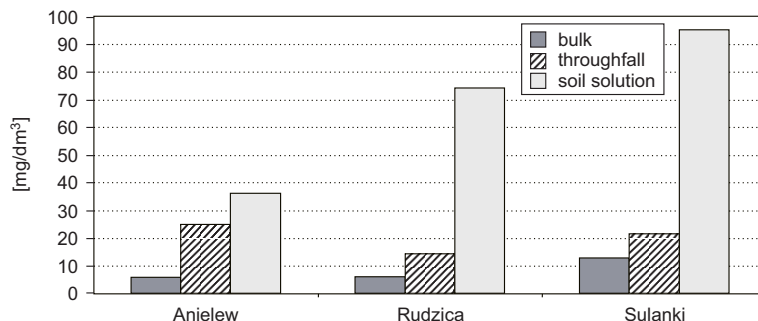


Fig. 5. Concentration of sulfate ions in compartments of pine ecosystem

This trend was the most intensive for Sulanki – site located close to the smelter. Permissible level of fluorides in surface water amounting to 1.5 mg/dm^3 was exceeded in soil solution in Anielew and Sulanki [6] (Fig. 4).

The analysis of loads reaching the forest ecosystem shows that in regard to acidifying substances the annual load of sulfur exceeded the load of total nitrogen (1.5–3 times) (Fig. 6). It is a consequence of the power plants activity. In all throughfalls ammonium form prevailed over nitrate form in the total pool of nitrogen (Fig. 7). The fluorine load

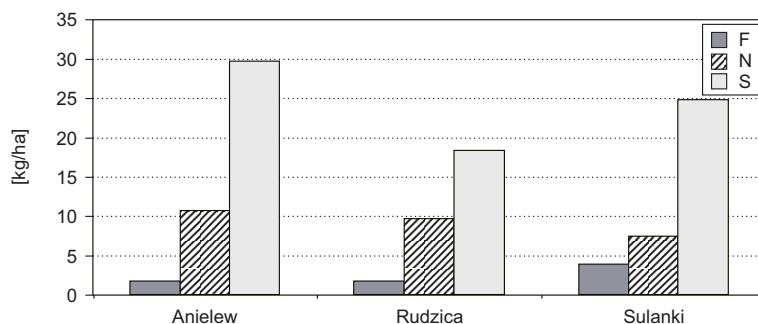


Fig. 6. Annual loads of fluorine, nitrogen and sulfur reaching the forest soil

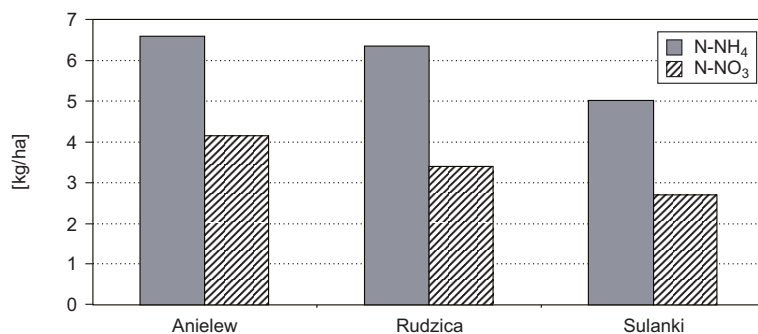


Fig. 7. Annual loads of nitrogen forms reaching the forest soil

Table 2
Annual loads of elements reaching the pine stands in 3 sites [kg/ha]

Site	Type of water	F	NH ₄	NO ₃	SO ₄	N-NH ₄	N-NO ₃	N _{tot}	S	Al	Na	Mg	K	Ca
Anielew	Bulk	0.47	4.98	18.02	25.03	3.87	4.07	7.94	8.34	0.25	8.29	2.33	2.61	16.94
	Throughfall	1.75	8.47	18.35	89.30	6.59	4.14	10.73	29.77	1.08	12.86	4.98	17.97	25.65
Rudzica	Bulk	0.62	7.04	17.62	30.13	5.48	3.98	9.46	10.04	0.33	9.75	2.14	3.09	13.24
	Throughfall	1.71	8.42	14.70	57.17	6.34	3.28	9.62	18.40	0.74	12.55	3.47	7.01	18.37
Sulanki	Bulk	2.99	6.43	10.50	57.38	5.00	2.37	7.37	19.13	0.47	11.53	1.28	1.82	8.16
	Throughfall	3.94	7.22	8.05	74.54	5.61	1.82	7.43	24.85	1.48	21.69	2.36	5.31	13.16

was found to be the highest in Sulanki, close to the smelter – the main emitter of this element in the region (Fig. 6). It should be noted that in 1994 in Sulanki site the loads of fluorine, nitrogen and sulfur amounted to 6.9, 21.4 and 34.1 kg/ha, respectively [7].

The increase in load of ammonium was observed in both throughfalls when compared with bulk deposition, but it was not such pronounced as for alkalic ions (Table 2). One of the reasons may be the exchange of alkalic cations with ammonium ions in leaves. Laboratory studies showed that at low concentrations of $(\text{NH}_4)_2\text{SO}_4$ solution the leaching of magnesium and calcium from Austrian pine (*Pinus nigra var. maritima*) needles was over ten times higher than from needles treated with distilled water [8].

In Table 3 the ratio of ammonium to alkalic cation concentrations in successive environment compartments is presented. The level of exchange is differentiated. The highest level of exchange was observed for potassium – cation not firmly bound with structure of leaf cells so easy washable. The level of ammonium ion exchange to calcium was the lowest.

Table 3

The ratios of NH_4^+ /alkalic ions and NO_3^- , and the Al/Ca ratio in different parts of ecosystem [meq/meq]

Site	Type of water	NH_4/K	NH_4/Mg	NH_4/Ca	NH_4/NO_3	Al/Ca
Anielew	Bulk	4.14	1.42	0.65	0.95	0.02
	Throughfall	1.04	1.18	0.78	1.66	0.06
	Soil solution	3.28	0.46	0.22	0.15	0.51
Rudzica	Bulk	4.95	2.17	1.18	0.69	0.04
	Throughfall	3.18	1.94	1.19	2.50	0.06
	Soil solution	1.74	0.34	0.18	0.27	0.33
Sulanki	Bulk	7.67	3.31	1.75	2.11	0.09
	Throughfall	3.42	2.25	1.35	3.22	0.17
	Soil solution	0.27	0.01	0.08	0.55	0.14

After passing the canopy the concentration of ammonium form exceeded the nitrogen concentration in the nitrate form. (Table 3). In all soil solutions this proportion is reverse (Table 3). On this basis you can conclude about occurrence of nitrification processes in the upper layer of soil.

In soils with no or relatively low nitrification rates the enhanced ammonium fluxes may lead to accumulation of ammonium in the top layer of the mineral soil and the loss of potassium, magnesium and calcium in the deeper soil layers. This results in the increased ammonium/cation ratios [8].

The NH_4/Mg and NH_4/K ratios in soil solutions of three sites were definitely lower than values regarded as a critical for coniferous trees growth and vitality, amounting to 5 and 10, respectively [8].

The high Al/Ca ratio resulting from the dissolution of aluminum by mineral acids and from leaching of calcium is harmful to the root system. The value of Al/Ca ratio > 5 in soil solution was mentioned as very critical for root system [9], and the Al/Ca ratio = 1

was regarded as inhibiting calcium uptake [10]. Values of this ratio observed on the investigated plots were lower and ranged from 0.14 to 0.51 (Table 3).

Fate of benzo[a]pyrene – carcinogenic compounds emitted mainly from the aluminium smelter through 35 m stacks was also investigated. Short range of B[a]P emission was found. Table 3 shows that the main portion of this compound is accumulated close to the emitter. At the distance of about 3 km from the smelter (Anielew, Rudzica) the amount of B[a]P reaching the forest stands makes only about 25 % deposition of this compound found in Sulanki. A part of B[a]P is kept in tree crowns (difference between bulk and throughfall) which after time reaches also forest soil with litterfall (Table 4).

Table 4

Loads and concentration of B[a]P in pine stands compartments

Site	Bulk	Throughfall	Litterfall	Concentration in soil solution
	g/ha			ng/dm ³
Sulanki	2.25	1.58	0.12	180
Anielew	0.50	0.40	0.03	25
Rudzica	0.35	0.27	0.02	15

A similar distance-dependent pattern of B[a]P concentration changes was observed in soil solutions. Only in Sulanki the amount of B[a]P was found to be at a high level – 180 ng/dm³, which is close to the permissible value for surface water – 200 ng/dm³ [6].

Conclusions

The investigation has shown that the consequent activities in metallurgical and energetic sectors, consisting in modernization and proecological activities, result in the decrease of acidic deposition to forest ecosystems. It leads also to improvement of soil water quality. Slight hazard to forest posed by water taken up by the roots can be observed only in the close distance (0.5 km) from the aluminium smelter.

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MIGRACJA ZANIECZYSZCZEŃ POWIETRZA EMITOWANYCH Z KOMPLEKSU PRZEMYSŁOWEGO KONINA W DRZEWOSTANACH SOSNOWYCH

Instytut Ekologii Terenów Uprzemysłowionych

Abstrakt: W otoczeniu Konina na obszarze typowo rolniczym, gdzie uprzednio nie prowadzono działalności przemysłowej, na początku lat pięćdziesiątych, wykorzystując węgiel brunatny z kopalni odkrywkowych uruchomiono kompleks elektrowni PAK (Pańków, Adamów, Konin), a w roku 1966 oddano do eksploatacji Huta Aluminium "Konin". Zakłady te emitowały znaczne ilości gazów fitotoksycznych (F_2 , SO_2 , NO_2). Huta aluminium emituje duże ilości fluoru, ponieważ aluminium produkowane jest w procesie termoelektrolizy tlenku glinu w elektrolicie zawierającym kriolit i fluorek glinu, jak również jest znaczącym emitorem WWA (PAHs) powstających w wyniku „spalania” elektrod węglowych.

Ze względu na to, że zakłady przemysłowe w początku swej działalności nie spełniały wymaganych parametrów technologicznych, a emisje do atmosfery gazów odlotowych były niewystarczająco kontrolowane w środowisku przyrodniczym występowały wyraźnie szkodliwe efekty. W latach dziewięćdziesiątych podjęto intensywne działania proekologiczne i modernizacyjne zakładów, które doprowadziły do znacznej redukcji emisji zanieczyszczeń powietrza.

W pracy przedstawiono wyniki badań przeprowadzonych w lasach sosnowych znajdujących się w sieci monitoringowej ustanowionej na obszarze Konina. Przedstawiono poziom depozycji zanieczyszczeń do ekosystemów leśnych oraz migrację aktualnie emitowanych zanieczyszczeń i zdeponowanych w glebie w okresie długoletniej działalności zakładów. Do oceny stężeń i zagrożenia środowiska wodno-glebowego związkami organicznymi i nieorganicznymi zastosowane ceramiczne lizymetry próżniowe. Na podstawie różnic w stężeniach kationów i anionów w różnych przedziałach ekosystemu leśnego określono także natężenie procesów nityfikacyjnych w glebie.

Słowa kluczowe: huta aluminium, elektrownie, fluor, benzo[a]piren, depozycja kwaśna, lasy sosnowe, monitoring zintegrowany

Anca-Iulia STOICA¹ and George-Emil BAIULESCU¹

CADMIUM IN ECOSYSTEMS

KADM W EKOSYSTEMACH

Abstract: Cadmium and its derivatives are considered the most toxic compounds between heavy metals. Beside cadmium have very few independent minerals it is associated in many cases with zinc. Cadmium interacts with zinc in organisms and is a big dependence on the rate of these elements in various humans, animals and plants. It was demonstrated that cadmium compounds can influences to fall ill with cancer. A lot of scientists studied the damage of DNA due to exposure at cadmium compounds in various conditions. It is very interesting to mention the role of trace elements including cadmium in agrosystems. A real source of cadmium is the use of fertilizers. One important studied on cadmium toxicity is the induced oxidative stress.

The paper presents some data obtained by the authors concerning the presence of cadmium in waters, foods as well as in various types of clinical and pharmaceutical compounds.

Keywords: cadmium, toxicity, ecosystem

Cadmium was discovered by Friedrich Stromeyer in 1917. It can be considered one of the most dangerous inorganic pollutants, due to the fact that it has effects on kidney, liver and in general on metabolic system. There are only few cadmium ores such as: Grenokite – CdS with 77 % cadmium, Otawite – cadmium basic carbonate and Monteponite CdO. In general, in ores cadmium is associated with zinc, copper and lead. It is ejected in the atmosphere by volcanic activity and cadmium is used as anticorrosive agent, stabilizer in PVC products, color pigment, neutron-absorber in nuclear power plants, nickel-cadmium batteries. It is very interesting that cadmium can be found also in phosphate fertilizers.

Total global emission of cadmium amounts is around 7000 Mg/year and in lithosphere, the quantity of cadmium is $5 \cdot 10^{-5}$ %. In general, the maximum permissible value of cadmium for workers is $15 \mu\text{g}/\text{dm}^3$. Cadmium resorption is possible by gastrointestinal, pulmonary and dermal ways.

Cadmium is listed by the US Environmental Protection Agency as one of 126 priority pollutants, the half-life in humans is estimated to be between 15 and 20 years

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[1] and it can produce osteoporosis, non-hypertrophic emphysema, irreversible renal tubular injury, anaemia, eosinophilia, anosmia and chronic rhinitis.

Cadmium it is very similar with zinc, and these two metals frequently are present in some ores together. The effects of acute cadmium poisoning in humans are very serious – high blood pressure, kidney damage, damage of red blood cells. Some physiological action of cadmium are due to its chemical similarity to zinc and may replace zinc in some enzymes, producing a disturbance of enzyme stereostructure and impairing its catalytic activity. The zinc status of the body is important in relation to cadmium toxicity development. The increased zinc supply may reduce cadmium absorption and accumulation and prevent or reduce the adverse action of cadmium, whereas zinc deficiency can intensify cadmium accumulation and toxicity. In biological systems cadmium and zinc are linked to macromolecules, primarily through sulphur, oxygen and nitrogen. They bind preferentially to some proteins-albumin in the blood stream and metallothionein (MT) and other proteins in tissues. In this way, one of the metals can influence the uptake and action of the other, depending of the level. The role of the cell wall, the plasma membrane in the mycorrhizas, as the main barrier's against cadmium entrance to the cell, as well as some aspects related to phytochelatin-based sequestration and compartmentalization process are studied. The most studied topics of cadmium toxicity are considered cadmium-induced oxidative stress.

In general, plant accumulation of a given metal is a function of uptake capacity and intracellular binding sites. At every level, concentration and affinities of chelating molecules, as well as the presence and selectivity of transport activities affect total accumulation rates. Trace elements mean elements present at low concentration ($\text{mg} \cdot \text{kg}^{-1}$ or less) in agrosystems. Trace elements such as Cd, Pb, Cr, Ni, Hg and As have toxic effects on living organism and are often considered as contaminants. In Fig. 1 handling of cadmium in human body are presented [2].

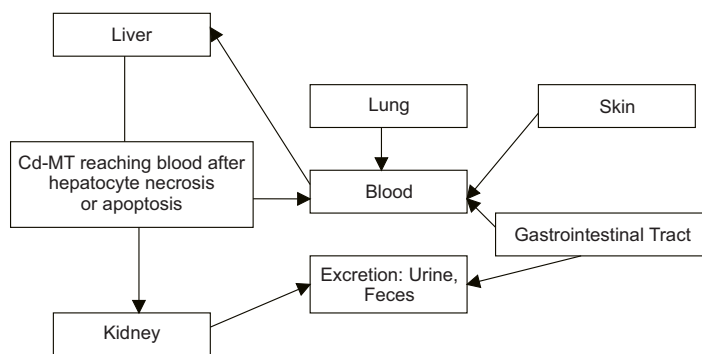


Fig. 1. Handling of cadmium in human body [2]

And in Fig. 2 the effects of cadmium on several organ systems are presented [3].

Cadmium affects both gene transcription and translation. The major mechanism of gene induction by cadmium known so far are modulation of cellular signal transduction pathways by enhancement of protein phosphorylation and activation of transcription

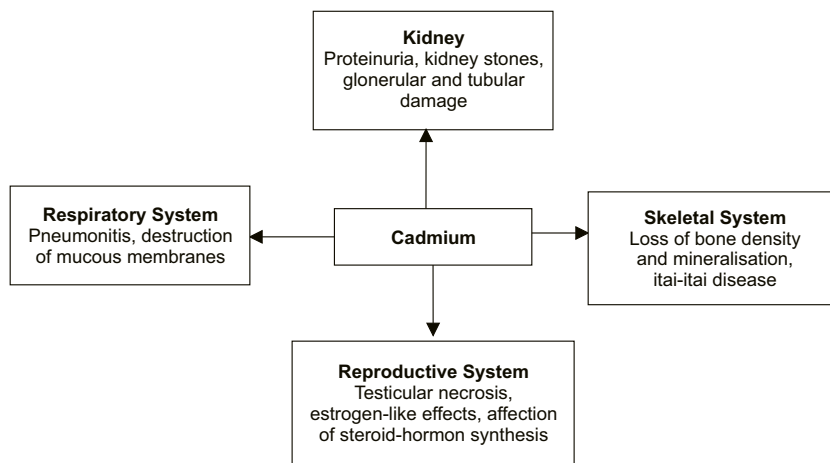


Fig. 2. Cadmium effects on several organ systems [3]

and translation factors. Cadmium interferes with antioxidant defence mechanisms and stimulates the production of reactive oxygen species, which may act as signalling molecules in the induction of gene expression and apoptosis. The inhibition of DNA repair process by cadmium represents a mechanism by which cadmium enhances the genotoxicity of other agents and may contribute to the tumour initiation by this metal.

Cadmium is a potent human carcinogen and occupational exposure to it has been associated with cancers of the lung, the prostate, the pancreas, and the kidney. Because of its characteristics as a lung carcinogen, cadmium has been classified as a category 1 carcinogen (human carcinogen) by the International Agency for Research on Cancer and the National Toxicology Program of the USA [4]. Another source of cadmium is the cigarettes that contain about 20 μg of cadmium per pack, or about 1 μg per cigarette. About 30 % of that goes into the lungs and is absorbed, and the remaining 70 % goes into the atmosphere to be inhaled by others or to contaminate the environment, thus cadmium is dangerous for active, but also for passive smokers [5].

In our previous studies [6, 7], cadmium was determined from different samples, such as waters, foods as well as in various types of clinical and pharmaceutical compounds.

In Table 1 the comparative studies on cadmium and zinc concentration by ICP-AES and ASV methods are presented [6]. Twelve water samples were collected from Arges River and filtered before heavy metals analysis. Heavy metals from water samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The instrument used, a SPECTROFLAME-P (SPECTROanalytical Instruments, Germany), has the following characteristics: argon was of spectral purity (99.998 %), cooling flow rate $12 \text{ dm}^3 \cdot \text{min}^{-1}$, auxiliary flow rate $0.8 \text{ dm}^3 \cdot \text{min}^{-1}$, nebulizer flow rate $1 \text{ dm}^3 \cdot \text{min}^{-1}$, and consumption rate of the liquid sample was about $2 \text{ cm}^3 \cdot \text{min}^{-1}$. The instrument has 30 fixed spectral channels that can simultaneously be monitored by the three polychromators and allows for background correction, application of internal standard method and other facilities. For ASV determinations, an electrochemical

system polarographic and voltammetric ensemble, Trace Master 5, and POL 150 Polarographic Analyzer (Radiometer, Copenhagen), were used. The electrochemical cell contained a working electrode: hanging mercury drop electrode (HMDE), a reference electrode: Ag/AgCl and as auxiliary electrode, platinum wire.

Table 1

Comparative studies on cadmium and zinc concentration by ICP-AES and ASV methods [6]

Sample	Cadmium [$\mu\text{g}/\text{dm}^3$]				Zinc [$\mu\text{g}/\text{dm}^3$]			
	April 1999		May 1999		April 1999		May 1999	
	ICP-AES	ASV	ICP-AES	ASV	ICP-AES	ASV	ICP-AES	ASV
1	0.40	0.30	3.60	4.33	0.50	0.21	0.50	0.23
2	6.70	5.50	3.60	4.40	0.50	0.15	0.50	0.41
3	—	—	7.30	7.08	0.50	0.19	0.50	0.39
4	—	—	9.40	7.60	0.50	0.18	0.50	0.35
5	—	—	1.30	0.72	0.50	0.27	15.70	14.60
6	4.90	3.01	3.00	1.93	0.50	0.22	46.00	57.23
7	—	—	1.70	1.60	6.00	4.60	66.10	58.77
8	—	—	6.00	4.82	3.70	7.92	95.20	90.50
9	1.30	0.80	6.80	5.50	0.50	0.35	126.10	120.80
10	8.90	7.22	3.40	2.80	18.70	15.00	164.80	139.00
11	7.10	5.40	4.30	3.72	43.90	40.10	207.30	201.20
12	0.40	0.50	3.80	3.45	28.70	28.40	240.70	236.00

Another study concerned with heavy metals determination from Rosia Montana District, a gold mining area in Romania. Twelve samples were collected, four from Corna River, five from Rosia Montana River (the mining processing waters flow in this river) and three samples from Abrud river. Increased concentrations of metal ions are observed especially for samples collected from Rosia Montana River, and for sample collected from Abrud town, the concentration can be explained by domestic wastewaters that are discharged into Abrud River and other waste materials deposited on the river bed. Presently, the mining activity was reduced, but the solid rock (waste) deposited by the river side remained the main pollution source. The highest concentrations were found for cadmium in September 2004: $0.17 \text{ mg}/\text{dm}^3$. Comparing the results obtained with the maximum concentration accepted by Romanian Standard the limit-concentration has exceeded by over 1,000 times [7]. To re-establish equilibrium in this ecosystem, mining activities must stop or pollution controls must be established. While these water courses are not used for industrial purposes or for human consumption, they do flow into the Mures River, an important water supply for industry.

Table 2

Cadmium concentration in water samples collected from Rosia Montana District

Sample	Cd [mg/dm ³]		
	April 2004	July 2004	September 2004
1	0.009	0.020	0.010
2	0.060	0.010	0.009
3	0.020	0.020	0.009
4	0.009	0.009	0.009
5	0.090	0.009	0.009
6	0.020	0.009	0.009
7	0.009	0.009	0.030
8	0.090	0.030	0.150
9	0.070	0.140	0.009
10	0.060	0.100	0.170
11	0.020	0.080	0.090
12	0.009	0.009	0.010

By observing these data it is possible to have an idea about the pollution degree at a local level. It can be observed that in some location sites the concentration of cadmium were very high (Table 2). The samples in which the concentrations are very high were collected from Roşia River, where the area was intensely affected by mining activity. Heavy metals present in the waste from mining and metallurgical activities are often dispersed in the environment by wind and water. The extent and degree of heavy metals contamination in the vicinity of mines may vary depending of geochemical characteristics, the mineralization of tailings, physical-chemical conditions and the process used to extract metals. Pollutant cadmium in water may arise from industrial discharges and mining wastes.

Conclusions

One can conclude that cadmium is present in water, soil, plants and human body in various quantities, but due to the toxicity of this element, the establishment of real concentration is very important. Water contamination by cadmium can influence the agrosystems as well as the body system, because cadmium affect especially lung, liver and kidney.

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KADM W EKOSYSTEMACH

Abstrakt: Kadm i jego związki są uważane za najbardziej toksyczne wśród metali ciężkich. Kadm występuje w bardzo niewielu minerałach, często wraz z cynkiem. Ze względu na interakcje pomiędzy kadmem a cynkiem ich zawartość w organizmach ludzkich, zwierzęcych i roślinnych jest zróżnicowana. Wykazano, że związki kadmu wpływają na zwiększenie zachorowań na raka. Badano wpływ związków kadmu na występowanie uszkodzeń w DNA w różnych warunkach. Interesująca jest rola mikropierwiastków, w tym kadmu, w agrosystemach. Dużym źródłem kadmu są stosowane nawozy. Jednym z ważnych kierunków badań jest wpływ toksyczności kadmu na wywołanie stresu oksydacyjnego. Przedstawiono dane uzyskane przez autorów dotyczące obecności kadmu w wodach, żywności, jak i w różnego rodzaju substancjach klinicznych oraz farmaceutycznych.

Słowa kluczowe: kadm, toksyczność, ekosystem

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**COMPARISON OF REFLECTOMETRIC
AND GRAVIMETRIC METHODS FOR EXAMINATION
OF SEWAGE SLUDGE ADDITIONS INFLUENCE
ON WATER PROPERTIES OF RECLAMATED SOILS**

**PORÓWNANIE METOD REFLEKTOMETRYCZNYCH
I GRAWIMETRYCZNYCH PRZY BADANIU
WPŁYWU DODATKU OSADU ŚCIEKOWEGO
NA WŁAŚCIWOŚCI WILGOTNOŚCIOWE UZDATNIANYCH GLEB**

Abstract: This paper is concerned with a comparison of two methods used for water properties measurement in porous materials – the gravimetric and the reflectometric (TDR) ones. The TDR method, opposite to the common gravimetric one, enables continuous and almost non-invasive monitoring of water states of examined medium. It was used in our experiment to prove the advantage of introduction of sewage sludge additions on reclaimed areas.

Keywords: soil reclamation, sewage sludge, TDR, reflectometric measurement, gravimetric measurement, moisture profile

During rehabilitation of areas degraded by industrial activities a very important role plays sand as a basic reclamation material. It is especially caused by its low price and general accessibility. Because of its poor water properties it is not an ideal material. Soils reclaimed with sand do not keep water in upper layers which is necessary for plants to grow. These poor water parameters can be improved with sewage sludge additions, which increase water retention and improve water conditions for plants.

The TDR methodology

Both, pure sand and sand enriched with sewage sludge are the porous media, with air pores between the medium grains. Like any porous medium it consists of three phases –

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solid, liquid and gaseous. It is essential for the TDR measurement technique, that any of above-mentioned phases is characterized by different electrical parameters, with the biggest difference for water.

The most important electrical parameter is dielectric constant (relative permittivity) which for low pressure gases values, a bit greater than 1, for solid materials dielectric constant is about 10 (Table 1).

Table 1

Values of dielectric permittivity depending on medium [1]

Medium	Apparent permittivity (20 °C)
Air	1
Water	80
Basalt	12
Granite	7–9
Sandstone	9–11

As it is presented in the table above – dielectric constant for water equals to 80. This property is used in water content measurement in porous media with TDR methodology.

Resultant dielectric constant of the dry medium (containing mainly the air and mineral phase) is low and its value comes from dielectric constant of phases building this material. Increase of medium moisture is directly connected with replacement of the air by water, which increases the resultant dielectric constant value, and in the extreme situations (saturation) – total replacement of the air by water. In such situation resultant dielectric constant takes maximal values and its value is dominated by influence of the water dielectric constant. Resultant dielectric constant value of the porous medium can be expressed by formula:

$$\varepsilon = \varepsilon_s^{\theta_s} \cdot \varepsilon_g^{\theta_g} \cdot \varepsilon_l^{\theta_l} \quad (1)$$

where: ε – dielectric constant of three-phases material,

$\varepsilon_s, \varepsilon_g, \varepsilon_l$ – dielectric constants of solid, gaseous and liquid phase,

$\theta_s, \theta_g, \theta_l$ – volumetric water content of each considered phase.

Typical TDR set contains three basic elements (Fig. 1) – measuring device, probes and the PC computer functioning as a control station and the data storage.

TDR measurement runs in the following way – TDR device [2] generates electromagnetic signal and measures time between outgoing signal and returning reflection. The result of such measurement can be shown on the screen in the form of TDR reflectograms or, using some special algorithms as a time of pulse propagation in analyzed medium.

Measurement is optionally repeated many times with frequency needed by the user. Computer lets the measurement generate pulse in specified sequence for each probe.

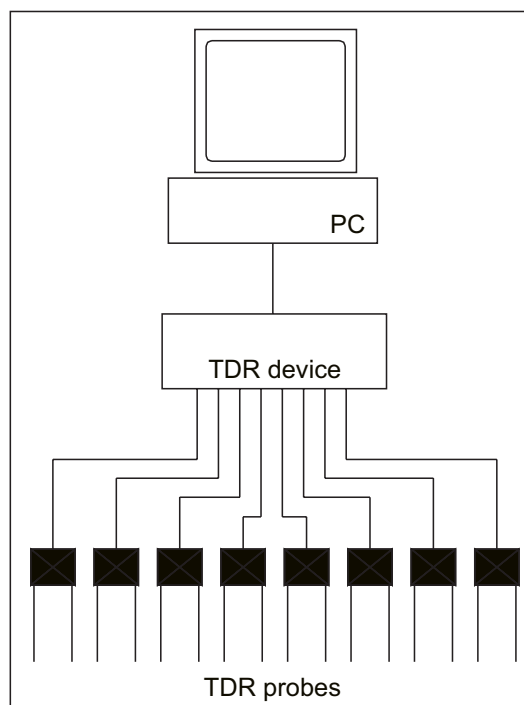


Fig. 1. Typical TDR set

Pulse generator in the measuring device sends electromagnetic signal, which propagates along concentric cable to the examined medium with probes installed in it.

TDR probes are the terminations of the concentric cable, differing from it not only in shape, but also in dielectric material between the conduits. For concentric cable the dielectric material is polyethylene and for probes – examined material. Dielectric constant of the polyethylene is well known and generally constant along the cable and does not influence the results achieved. Dielectric constant of the examined material depends on its structure and, which is the most important – on water content. Each impedance change in the system cable-probe generates partial or full signal reflection. That is why first reflection occurs in the interface cable-probe (dielectric properties of the medium rapidly change). Another reflection appears in the end of the probe, where the signal runs towards the free space and the wave is reflected.

Signal reflection caused by the impedance changes in the cable-probe system can be shown in the form of reflectograms. Typical reflectogram shows reflection spots, where the discontinuities of the cable are noticed.

Fig. 2 shows TDR reflectograms for three sets differing with dielectric constant. Two first peaks in each reflectogram are control ones and are not important from our point of view. They are the result of the intentional cable discontinuities and are independent from conditions during measurement.

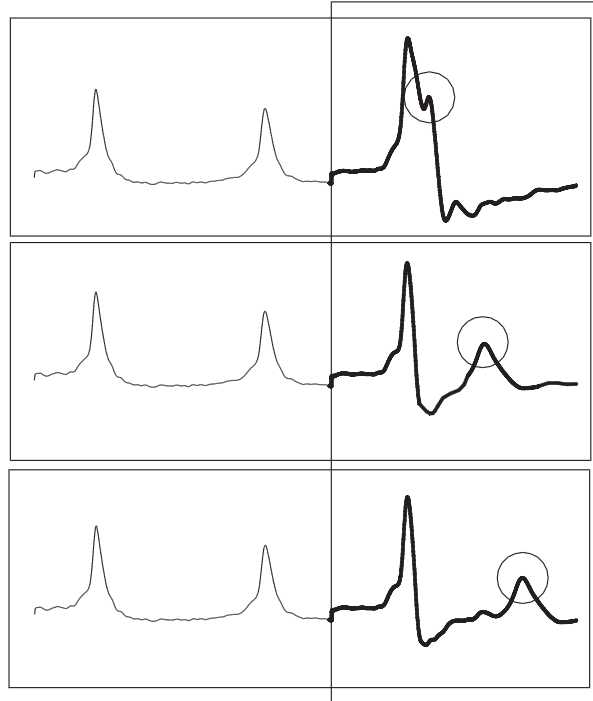


Fig. 2. TDR reflectograms depending on water content. Bold line represents pulse propagation in the TDR probe. Upper reflectogram indicates dry material, middle – intermediate, unsaturated states and finally bottom reflectogram is typical for water (circle indicates reflection of the wave returning from examined material)

With the pulse propagation velocity or time it is possible to determine the dielectric constant value of the porous medium using formula below (no. 2 in the denominator means that signal runs in two directions – as a pulse and then as a response):

$$\varepsilon = \left(\frac{c \cdot t_p}{2L} \right)^2 \quad (2)$$

where: ε – relative dielectric constant of the porous medium,
 c – light velocity in vacuum ($3 \cdot 10^8 \text{ m} \cdot \text{s}^{-1}$),
 t_p – velocity of signal propagation along the rods of the probe,
 L – length of the rods of the probe installed in porous medium.

Having the relative dielectric constant of the medium there is a possibility to estimate the value of water content in such a system. Among the most popular empirical methods there are Topp [3] and Malicki [4] formulas which relate dielectric constant of the medium with water content.

In realized experiments for material moisture determination we used semi-empirical Malicki's formula which besides the dielectric constant takes into account the bulk density of the material, which gives more precise values of the measurement results.

$$\theta = \frac{(\varepsilon^{0.5} - 0.819 - 0.168\rho - 0.159\rho^2)}{7.17 + 1.18\rho} \quad (3)$$

where ρ is a bulk density of the medium [$\text{g} \cdot \text{cm}^{-3}$].

Gravimetric method

For the experiment four PCV columns were constructed with the diameter of 150 mm and the height 0.5 m. Soil sampling ports (10 mm diameter) were drilled with 5 cm intervals down the columns, and plugged with rubber stoppers. Two columns were filled with loose, dry, medium grained (0.5–0.2 mm) sand with about 15 % additives of dust. Another two columns were filled with the same sandy material, but their surface layer (20 cm) was amended by 6 % (wt./wt.) of the sewage sludge stabilized in mesophilic conditions (37 °C). The amount of additives equals the biggest acceptable dose for reclamation – 200 $\text{Mg} \cdot \text{ha}^{-1}$ (20 $\text{kg} \cdot \text{m}^{-2}$).

Two of the columns we prepared for gravimetric measurement and another two for reflectometric measurement with TDR technology. This way we obtained four combinations of columns (Fig. 3):

- sand for gravimetric measurement,
- sand for TDR measurement,
- sand with sewage sludge for gravimetric measurement,
- sand with sewage sludge for TDR measurement.

Holes in the columns prepared for gravimetric measurement were temporarily clogged with rubber and the holes in columns for TDR were used to install the TDR probes and sealed with silicon.

All prepared columns were filled with water in the amount of 1 dm^3 . During this experiment we collected data by gravimetrical method and by TDR. Gravimetrical

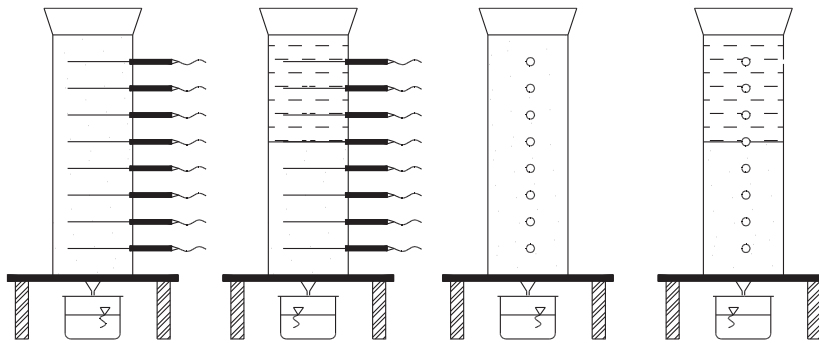


Fig. 3. Set of 4 columns used in the experiment

measurement was released in two series for pure sand and three series for sand enriched with sewage sludge additives – only single measurement was possible for one series, which is a disadvantage of this method comparing to the reflectometric one. Soil samples taken from different levels of the column were dried at the temperature of 105 °C during 24 h. Differences in mass before and after drying represented water content in examined material.

Discussion of the results

Basing on the experimental results we obtained moisture profiles in the form of the diagrams. Both gravimetric and reflectometric methods show the positive influence of sewage sludge addition on water properties of the reclaimed soils.

Pure sand does not keep water in its profile – which is a disadvantage for reclamation, because water runs deeper and becomes unavailable for plants introduced into rehabilitated area. This vertical water flow is caused by gravity force and indicates bad water storage properties of the sand.

Gravimetric measurement was done 24 hours after watering of each column. And it indicated constant water loss along all profile – upper layers water content exceeded the value of 5 % and in bottom layers it reached about 10 percent (final bottom sample falsifies the results because of the membrane influence which stopped the water).

Sewage sludge additions increase water retention parameters which is a big advantage during reclamation. Gravimetric measurements – realized in three series 24 hours after watering indicate the increase of water content in upper layers of the reclaimed soil. At the depth of 15 centimetres water content reaches about 36 % which is very attractive for plants introduced into reclaimed ground. In the bottom we observe rapid loss of water content but it is less important for plants.

Similar results were observed for TDR measurements. Soil reclaimed with pure sand presents very poor water retention parameters. Shortly after watering moisture reached about 20 % but then it rapidly decreased – within one hour for about 7–8 %. After 24 hours (comparably to gravitational method) we observed water content about 10 % high, which was continuously going down. Differences between gravitational and reflectometric readings in this situation are mainly caused by problems with gravitational sampling – the amount of soil taken for measurement was small (about 2 g of raw material) which raised the error margin of gravimetric measurement.

Addition of sewage sludge increased retention parameters and shortly after watering we read water content in upper layers of the profile – 35 %. It was successively going down but the rate of the decrease was smaller than before (without additions). Within 24 hours moisture decreased, but, comparably to gravimetric measurement it kept the level of 20 % or more and this state was stable for longer periods of time. Lower levels of the profile, made of sand did not show water retention parameters and we observed high loss of water content within profile, which is of course less important for plants. The lowest water content was observed at the depth of 25 centimetres (first probe beneath the sewage sludge additives) which is interpreted as place under highest influence of sewage sludge suction force.

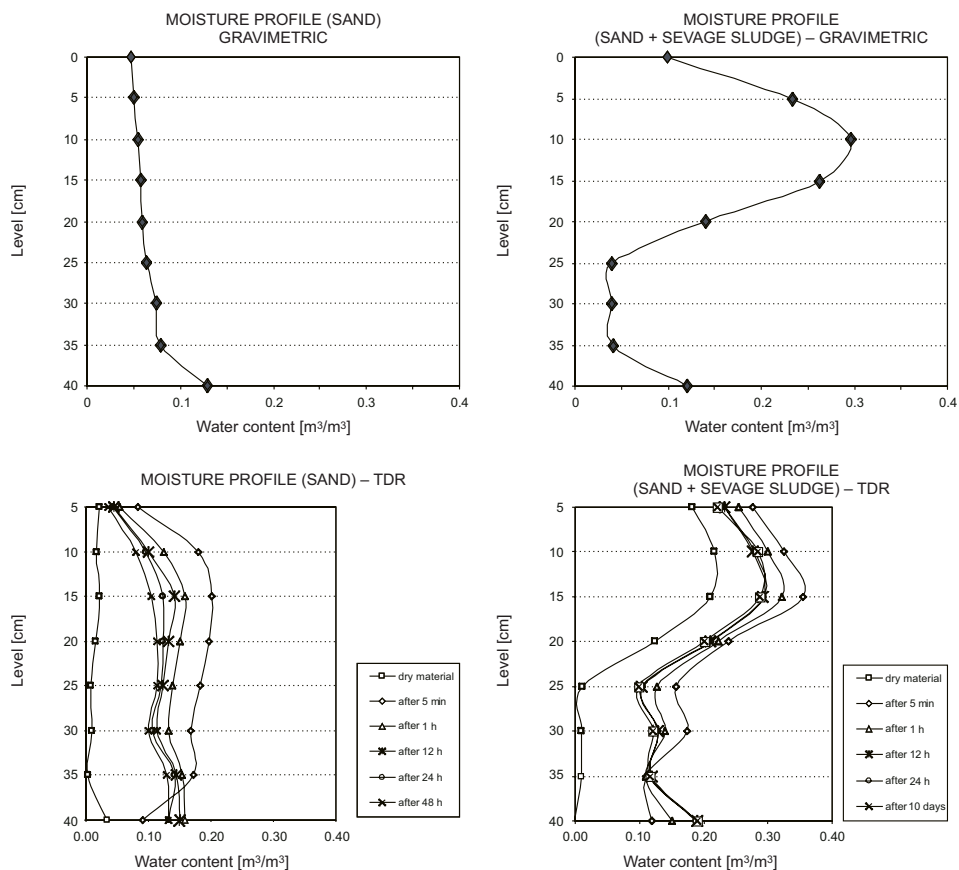


Fig. 4. Moisture profiles measured in model columns for sand and sand with sewage sludge additions determined using gravimetric and reflectometric techniques

Measurements realized within this research indicate the positive influence of sewage sludge additives on water retention parameters of reclaimed soils but also underline advantages of TDR method over classical methods. Gravimetric results give a lot of information about water profiles in reclaimed ground – but they are invasive, change the structure of the soil and do not indicate the dynamics of water flow processes. TDR method is a very good opportunity to obtain all necessary information without disturbing the structure and observe changes of the profile in time.

Conclusions

Soil replacement by sand in reclaimed areas is not a good option which is confirmed by results of our measurement. They indicate bad water retention parameters which is inconvenient for plants used for the area rehabilitation. Using of sewage sludge

additions may provide them more water necessary to grow. This column experiments clearly [5] indicate that sewage sludge additions increase water content in upper layers of reclaimed soils and which makes them useful during rehabilitation.

This paper is also a confirmation of the high potential of TDR technique for water state determination. We used TDR technology to prove the advantage of application of sewage sludge additions on reclaimed soils. All reflectometric data were confirmed by gravimetric measurement and the results obtained were comparable. This indicates good perspectives for application of TDR method for measurement of the dynamics of water states in different points of moisture profile without gravimetric examinations.

Gravimetric determination of soil profiles is an invasive method – it destroys and changes the structure of the soil and after one sampling it is practically impossible to repeat the measurement in the same place. That is why it is very difficult to apply in field conditions.

TDR does not require sampling and as a practically non-invasive method enables constant monitoring of water states both in laboratory and also field conditions [6].

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PORÓWNANIE METODY REFLEKTOMETRYCZNEJ I GRAWIMETRYCZNEJ PRZY BADANIU WPŁYWU DODATKU OSADU ŚCIEKOWEGO NA WŁAŚCIWOŚCI WILGOTNOŚCIOWE UZDATNIANYCH GLEB

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Abstrakt: Przedstawiono i porównano dwie metody pomiarowe stosowane w badaniach właściwości wodnych gruntów – metodę grawimetryczną i metodę reflektometryczną (TDR). Metoda TDR w przeciwieństwie do metody wagowej pozwala na ciągły i niemal bezinwazyjny monitoring stanów wilgotnościowych w badanym układzie.

Słowa kluczowe: rekultywacja gruntów, osady ściekowe, TDR, pomiary reflektometryczne, pomiary grawimetryczne, profile wilgotnościowe

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and Anna TRAWCZYŃSKA

INFLUENCE OF SALINITY ON THE SORPTIVE FEATURES IN SOILS OF LODZ CITY CENTRE

WPLYW ZASOLENIA NA WŁAŚCIWOŚCI SORPCYJNE GLEB CENTRUM ŁODZI

Abstract: Paper presents the results of salinity measurements in Lodz city centre. Salinity research regarding to chosen physico-chemical properties was characterized. Spatial variability of salinity in city centre was described. Analysis of soils salinity in proportion to the growth of distance from the roads was shown. Authors presented the statistical analysis of correlation between soils salinity and measured features.

Keywords: soil salinity, Lodz city centre, sorptive properties, correlation

The problem of soils salinity in urban areas, despite of its common appearance, is not well recognized. So far, not many compilations about this issue were published. The salinity was mostly studied according to its intensity of occurrence [1–4], relations with microbiology and its influence on soil germs [5, 6].

The snowfalls recorded during the winter 2005/2006 contributed to increased usage of melting substances – mainly: sodium chloride – NaCl, calcium chloride – CaCl₂ and sodium carbonate – Na₂CO₃. High concentration of these compounds in soils is harmful for plants [7–11], especially for trees and shrubs [12–17].

Furthermore, salinity is one of the more important factors in soil degradation [5, 17–19]. The increase of soils salinity is observed especially in urban areas and first of all in the city centers, where the permeability of transport system (especially during winter period) in relation with prevention of snow covering on streets and sidewalks is a yearly priority. The increase of salty substances influences negatively on soil quality and ecological condition of green areas in the city centre. This effect is strictly connected with snow and salts accumulation on the lawns between roads and sidewalks. This is a result of snow clearing and lack of free spaces within dense building where the snow can be accumulated. This fact was affirmed by the field observations.

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Many of plant species grow normally, when the salts concentration is lower than $5 \text{ g} \cdot \text{dm}^{-3}$ of soil solution. The sucking strength of soil solution, which can be higher than roots sucking strength, increases with the growth of salts content in the soil. Consequently, the sucking strength of soil solution can stop plants ability to water uptake. The extended physiological drought, which was caused by the big salt concentration in soil solution, can lead up to withering and death of plants [9, 14, 17].

The aim of present study was to describe degrees of urban soils salinity in the centre of Lodz city. Salinity was measured in the surface layer of soil. Moreover, other physico-chemical features connected with soil salinity were studied. The analysis of correlation between the measured soil parameters was also prepared.



Fig. 1. The localization of soil sample points in the Lodz city centre

Methods and study area

The study was started after the snow thawed in March 2006. The research covered 32 locations situated in the city centre. The described area was determined by the streets: from the north – Pojezierska, Julianowska and Inflancka; from the west – Aleja Włókniarzy (al. Jana Pawła II); from the south – I.J. Paderewskiego and W. Broniewskiego; from the east – E. Śmigłego-Rydza, S. Kopcińskiego and Strykowska. Localization of sampling sites are shown in Fig. 1.

Each of the locations was assembled from 3 control points (A, B, C), which have made a 10 m transect starting from the road. Each of the points fulfilled following conditions: A – located in the lawn between the roadway and the sidewalk; B – situated in the distance of 0.5m from the sidewalk; C – located in the distance of about 10 m from the sidewalk.

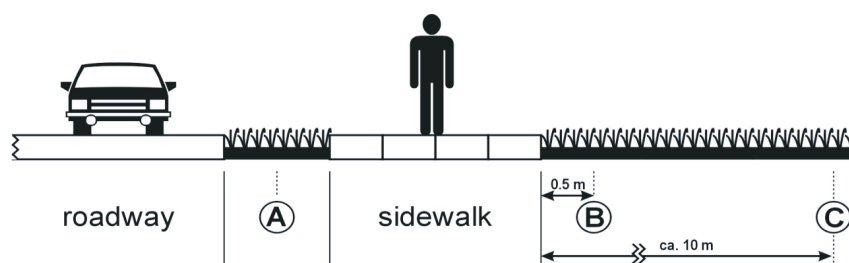


Fig. 2. Scheme of transects in studied points

In total 96 soil samples were collected from the depth between 0 to 20 cm. Following properties were signified in the soil material: sum of salts by digital salt meter CC-216, soil reaction in water and potassium chloride by pH-meter, hydrolytic acidity and sum of exchangeable alkaline cations with Kappen methods. The strength of dependence between measured soil parameters was estimated by Spearman rank correlation ratio with confidence level $\alpha \leq 0.05$ [20].

Results and discussion

The obtainable data showed that the highest values of soils salinity occurred in strict city centre. The highest concentrations of salts were noted in locations 26–32, where they took average value of $2.21 \text{ g} \cdot \text{dm}^{-3}$. Average concentration of salty substances in whole studied area was $0.69 \text{ g} \cdot \text{dm}^{-3}$. In places with lower salinity (sampling sites 1–25) it was $0.39 \text{ g} \cdot \text{dm}^{-3}$ and that applied to outskirts places of the area and mostly north part of it. The salinity values of Lodz city centre, considering the scale of occurrence, are low and correspond to FAO standards as non-salted. Only soils with highest salinity (up to $2 \text{ g} \cdot \text{dm}^{-3}$) can be accepted as lightly salted [4]. Based on our observations it was ascertained that studied area is in rather good ecological condition. These places are also cultivated during the year.

Table 1

Salinity and other physico-chemical features of soils in the Lodz city centre

Sample number	Location	Soils salinity [g · dm ⁻³]	Reaction pH		Hydrolytic acidity [cmol(+) · kg ⁻¹]	Sum of alkaline cations [cmol(+) · kg ⁻¹]
			in KCl	in H ₂ O		
1	A	0,32	7.0	8.3	0.9	18.5
	B	0.24	7.1	7.5	0.7	19.7
	C	0.23	7.4	7.9	0.4	24.2
2	A	0.42	7.3	8.4	0.6	20.6
	B	0.13	6.4	7.1	1.7	6.8
	C	0.07	5.0	6.0	2.6	2.4
3	A	0.62	7.6	8.7	0.4	9.8
	B	0.24	7.2	7.8	0.6	16.4
	C	0.22	7.0	7.6	0.5	20.5
4	A	0.48	7.5	8.4	0.5	22.7
	B	0.86	7.1	7.6	0.5	14.2
	C	0.29	6.8	7.3	0.8	8.1
5	A	0.47	7.1	8.1	0.6	15.2
	B	0.50	5.0	5.4	3.8	4.0
	C	0.29	6.3	6.9	1.6	6.4
6	A	0.25	7.3	8.3	0.5	10.1
	B	0.50	6.7	6.9	1.1	10.3
	C	0.26	7.0	7.6	0.6	12.7
7	A	0.64	7.1	8.1	0.7	22.1
	B	0.28	7.0	7.4	0.8	18.1
	C	0.24	6.7	7.3	0.8	12.7
8	A	0.26	6.9	7.5	0.8	13.4
	B	0.42	6.9	7.2	1.0	10.3
	C	0.18	6.7	7.2	1.0	8.9
9	A	0.26	7.1	7.9	0.8	17.0
	B	0.29	7.1	7.7	0.8	15.3
	C	0.22	7.4	7.8	0.4	14.9
10	A	0.44	7.3	8.6	0.6	16.1
	B	0.28	7.0	7.7	0.7	12.0
	C	0.25	6.5	6.9	1.1	10.1
11	A	0.32	7.0	7.9	0.7	14.0
	B	0.28	6.7	7.2	0.7	9.0
	C	0.29	7.0	7.6	0.6	9.3
12	A	0.37	6.3	7.5	1.7	5.1
	B	0.17	6.2	6.8	1.7	6.2
	C	0.20	7.1	7.6	0.8	9.7

Table 1 contd.

Sample number	Location	Soils salinity [g · dm ⁻³]	Reaction pH		Hydrolytic acidity [cmol(+) · kg ⁻¹]	Sum of alkaline cations [cmol(+) · kg ⁻¹]
			in KCl	in H ₂ O	Hh	S
13	A	0.18	6.9	7.4	0.6	16.2
	B	0.25	6.8	6.8	1.0	9.3
	C	0.17	6.7	7.2	1.1	13.8
14	A	0.47	7.2	7.8	0.7	24.2
	B	0.26	7.3	7.8	0.6	12.5
	C	0.23	6.9	7.4	0.7	13.5
15	A	0.31	7.1	8.1	0.5	19.9
	B	0.18	6.3	6.8	1.3	6.0
	C	0.18	6.4	6.9	1.7	5.9
16	A	0.36	7.0	7.8	0.7	13.4
	B	0.23	7.0	7.3	0.8	13.7
	C	0.22	7.0	7.0	0.7	15.9
17	A	0.41	6.8	7.4	0.9	17.9
	B	0.22	6.5	7.1	1.1	7.6
	C	0.19	6.8	7.1	1.0	7.7
18	A	0.35	7.6	8.6	0.3	21.4
	B	0.31	6.9	7.3	0.7	20.4
	C	0.23	6.8	7.6	1.3	23.6
19	A	0.58	7.9	8.7	0.8	7.8
	B	0.24	6.3	6.8	1.7	5.7
	C	0.25	6.2	6.8	1.5	6.1
20	A	0.30	7.0	7.7	0.5	8.9
	B	0.17	6.6	7.0	0.8	4.2
	C	0.23	6.7	7.4	0.8	5.0
21	A	0.37	7.1	7.6	0.6	11.0
	B	0.30	6.7	7.1	1.0	13.9
	C	0.47	5.8	6.3	1.9	5.5
22	A	0.29	6.8	7.3	0.7	7.3
	B	0.20	5.6	6.5	1.1	3.1
	C	0.22	6.8	7.1	0.8	9.1
23	A	0.36	7.5	8.4	0.4	15.3
	B	0.29	7.2	7.6	0.6	10.4
	C	0.22	6.6	7.2	0.8	14.6
24	A	0.49	7.6	8.5	0.4	23.8
	B	0.47	7.5	8.4	0.3	21.6
	C	0.24	7.1	7.4	0.5	23.6

Table 1 contd.

Sample number	Location	Soils salinity [g · dm ⁻³]	Reaction pH		Hydrolytic acidity [cmol(+) · kg ⁻¹]	Sum of alkaline cations [cmol(+) · kg ⁻¹]
			in KCl	in H ₂ O	Hh	S
25	A	0.40	6.6	7.4	1.0	13.8
	B	0.38	7.1	8.0	0.5	17.3
	C	1.06	6.7	7.3	0.9	14.2
26	A	2.35	6.6	7.6	1.2	7.1
	B	2.11	6.1	6.5	1.5	6.3
	C	2.18	6.7	6.8	1.0	17.8
27	A	2.39	7.5	8.5	0.4	22.9
	B	2.26	6.7	7.2	0.7	9.2
	C	2.40	6.5	6.8	0.9	19.6
28	A	2.09	7.9	8.1	0.3	22.9
	B	1.92	6.5	7.1	1.3	10.2
	C	2.10	6.7	7.1	0.9	10.5
29	A	2.12	6.8	7.6	0.5	16.5
	B	2.11	6.7	7.2	1.0	11.9
	C	2.03	5.4	6.1	2.7	6.4
30	A	2.14	6.8	7.4	1.0	15.0
	B	2.10	5.8	6.4	1.9	9.4
	C	2.04	7.2	7.8	0.5	23.0
31	A	2.22	7.3	8.1	0.6	19.1
	B	2.21	7.0	7.3	0.8	16.4
	C	0.42	6.5	7.1	1.2	18.2
32	A	2.20	6.9	8.2	0.9	15.1
	B	1.98	6.2	6.7	1.5	7.4
	C	0.49	7.0	7.5	0.7	10.1

Spatial variability of salinity shows Fig. 3.

The variability of salinity in studied transects proves, that the most salted samples are those located close to the roads, whereas the least salted samples collected in the distance of several meters from the roadway. This relationship is visualized by Fig. 4. For better presentation they were presented from highest to lowest value variation without their location number.

Within the whole area the soils reaction showed small variability and fluctuated in range 5.0–7.9 of pH units measured in 1 M KCl solution and 5.4–8.7 in H₂O. Similarly small variability was noted in case of hydrolytic acidity, which average value for entire area was 0.9 cmol(+) · kg⁻¹, within the range 0.3–2.7 cmol(+) · kg⁻¹. A little bit higher variability was recorded for the alkaline cations, which average sum was 13.2 cmol(+) · kg⁻¹, in within the range 2.4–24.2 cmol(+) · kg⁻¹. In linear system of every

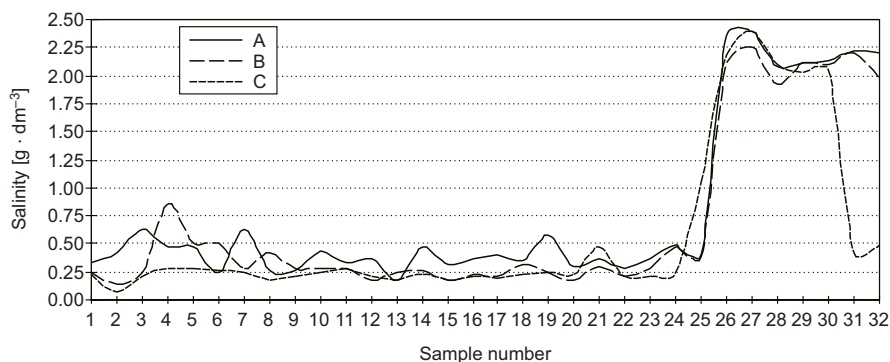


Fig. 3. Variability of salinity in soil surface levels in Lodz city centre

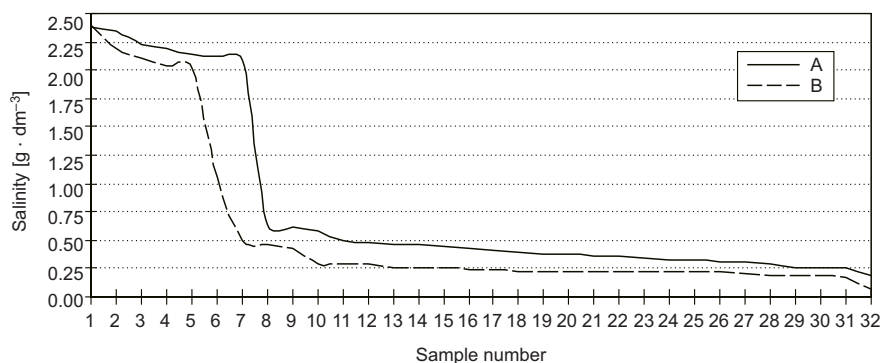


Fig. 4. Change of soil salinity value according to distance from the road

measuring point it was noted that the highest values of salinity appeared in roadside samples (A) and it was moderately $0.79 \text{ g} \cdot \text{dm}^{-3}$. Besides these samples showed the highest values of cations sum – $15.75 \text{ cmol}(+) \cdot \text{kg}^{-1}$ and reaction – 7.9 pH units in KCl and 8.7 in H_2O , whereas lowest values of hydrolytic acidity – $0.68 \text{ cmol}(+) \cdot \text{kg}^{-1}$. Lower values of salinity were recorded in samples located behind the sidewalk (B) – $0.70 \text{ g} \cdot \text{dm}^{-3}$ and farthest from the road (C) – $0.57 \text{ g} \cdot \text{dm}^{-3}$. Hydrolytic acidity showed small changes in both groups. For B samples their value was $1.07 \text{ cmol}(+) \cdot \text{kg}^{-1}$ and for C samples $1.03 \text{ cmol}(+) \cdot \text{kg}^{-1}$. Group C characterized by not too much higher values of alkaline cations sum – $12.62 \text{ cmol}(+) \cdot \text{kg}^{-1}$ in comparison with group B – $11.21 \text{ cmol}(+) \cdot \text{kg}^{-1}$. The values of reaction measured in water and potassium chloride in both described groups were similar.

Correlation values counted between soils salinity of Lodz city centre and other properties showed weak dependence on level 0.21 with reaction measured in water and with sum of alkaline cations on level 0.27 . Second of these values is a confirmation of cations increase in soils relatively to salinity increase. Owing to distinctive growth of salinity values in locations $26\text{--}32$, it was determined to split all data into two groups with higher and lower salinity and count the correlation for both of them separately.

Table 2

Correlation ρ values between salinity and chosen soil features

Soil property	Salinity	
	all samples	samples with lower salinity (locations 1–25)
pH in KCl	—	0.41
pH in H ₂ O	0.21	0.50
Hydrolytic acidity	—	-0.27
Sum of alkaline cations	0.27	0.34

Additionally to avoid the statistical errors the outliers, that were found by Grubbs test analysis, were eliminated from data series. Interesting is that only samples with lower salinity (locations 1–25) showed positive correlation between measured parameters, eg: between salinity and reaction in 1M KCl the value of ratio was 0.41; between salinity and reaction in H₂O it was 0.5; with hydrolytic acidity $\rho = -0.27$ and with sum of alkaline cations $\rho = 0.34$. Therefore, they were weak and medium. The correlation between soil properties in second group of samples with higher salinity was not noted. Probably it was a result of the too early period of study, although in view of intensity and long-lasting snowfalls the melting substances should affect on soil earlier. The soaking character of soil substance, which was built in most places from sand fraction, had also restricted the soil sorption. This applies particularly to the surface soil layer. As a result of this process the compounds of salts can appear on big depth of soil profile and migrate to the underground water. The removal of collected snow also have influenced on the reduction of salinity occurrence scale in the city centre. Thawing of snow cover from their surface caused the seizure of considerable salt load through the storm sewage system and also limited the scale of salinity in the study area. Both mentioned mechanisms can decide about the soil cleaning process not only from salts but also from other pollutions.

Conclusions

The results obtained from measurements and calculations let for following conclusions:

The affirmed low salt content in soils does not confirm its harmful influence in green areas flora in Lodz city centre. It is connected with availability of salty compounds into the soil in pre-vegetation period. Moreover, high quantity and long snow thawing period had influence on significant dilution of salt concentration. Additionally small sorption complex limited the influence of salt on chemical composition of researched soils.

Despite of common opinions it was not noted that the soil salinity in thawing period influenced on deterioration of soil quality and flora. It happens because the huge water mass with salts infiltrates gravitationally into big depths beyond the plants roots zone.

From the presumption big amount of thawing water must be also intercepted by the sewage system what diminishes the general quantity of salts which get into the soil.

Places located near the roads are mostly liable on salinity increase and therefore on degradation.

Soils salinity showed correlation with physico-chemical featured and influenced weakly on sum of alkaline cations and soil reaction.

Soils with lower salinity values showed its medium influence on reaction and small influence on sum of alkaline cations and hydrolytic acidity. The mutual dependence of salinity and sum of alkaline cations answers to the increase of second feature, according to cations supply from melting substances.

The maximum values of salinity in city centre (locations 26–32), which amounted to $2.4 \text{ g} \cdot \text{dm}^{-3}$ are low in comparison with the quantity of melting substances used in winter. The removal of snow from city centre and the seizure of salty thawing waters through sewage system affected the salinity values.

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WPLYW ZASOLENIA NA WLAŚCIWOŚCI SORPCYJNE GLEB CENTRUM ŁODZI

Zakład Gleboznawstwa i Geoekologii, Uniwersytet Łódzki

Abstrakt: Zaprezentowano wyniki badania zasolenia gleb śródmieścia Łodzi poprzez pomiary wybranych wielkości fizykochemicznych. Scharakteryzowano przestrzenną zmienność zasolenia w centrum miasta. Przedstawiono analizę statystyczną korelacji pomiędzy zasoleniem i zmierzonymi parametrami. Stwierdzono występowanie zależności pomiędzy zasoleniem i odczynem gleb oraz właściwościami sorpcyjnymi.

Słowa kluczowe: zasolenie gleb, centrum Łodzi, właściwości sorpcyjne, związki korelacyjne

Varia

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On the first day the debates of sections SI and SII will take place. The second day will be started with an ecological excursion. Afterwards the plenary Session with lectures on **environmental education** as well as **grants within the EU Programmes** and presentation of **EU Centres of Excellence** will be held. Then the **Forum of Young Scientists** – the presentation (lectures and posters) of young scientists work will take place.

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Surname and First Name

Scientific Title/Position

Affiliation

Address

Tel./fax email

Title of presentation

.

KIND OF PRESENTATION

	YES	NO
Oral		
Poster		
Taking part in discussion		

ACCOMMODATION

14/15 X		15/16 X		16/17 X	
YES	NO	YES	NO	YES	NO

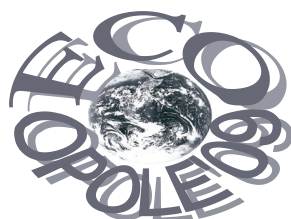
MEALS

Date	Breakfast	Lunch	Dinner
14 X	—	—	
15 X			
16 X			
17 X			—



ZAPRASZAMY
DO UDZIAŁU W ŚRODKOWEUEUROPEJSKIEJ KONFERENCJI
ECOpole '09
w dniach 14–17 X 2009

SUBSTANCJE CHEMICZNE
W ŚRODOWISKU PRZYRODNICZYM



Będzie to osiemnasta z rzędu konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w ośrodku „Uroczysko” na Wzgórzu Wilhelma w Piechowicach. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole '09 będą zgrupowane w czterech Sekcjach SI–SIV:

Obrady konferencji ECOpole '08 będą zgrupowane w czterech Sekcjach SI–SIV:

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

Materiały konferencyjne będą opublikowane w postaci:

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

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 15 lipca 2009 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2009 r. na stronie internetowej konferencji

ecopole.uni.opole.pl

Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami

stawianymi artykułom drukowanym w czasopiśmie *Ecological Chemistry and Engineering*, które jest dostępne w wielu bibliotekach naukowych w Polsce i zagranicą. Są one takie same dla prac drukowanych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*. Zalecenia te są również umieszczone na stronie internetowej konferencji.

Koszt uczestnictwa w całej konferencji wynosi 1000 zł i pokrywa opłatę za udział, koszt noclegów i wyżywienia oraz rocznej prenumeraty *Ecol. Chem. Eng.* (razem blisko 2000 ss.) łącznie z materiałami Konferencji. Jest możliwość udziału tylko w jednym wybranym przez siebie dniu, wówczas opłata wyniesie 650 zł i będzie upoważniała do uzyskania wszystkich materiałów konferencyjnych, jednego noclegu i trzech posiłków (śniadanie, obiad, kolacja), natomiast osoby zainteresowane udziałem w dwóch dniach, tj. w pierwszym i drugim lub drugim i trzecim, winny wnieść opłatę w wysokości 800 zł. Opłata dla magistrantów i doktorantów oraz młodych doktorów biorących aktywny udział w Forum Młodych może być zmniejszona do 600 zł, przy zachowaniu takich samych świadczeń. Osoby te winny dodatkowo dostarczyć: rozszerzone streszczenia (4–6 stron) swoich wystąpień (**do 15.08.2009 r.**). Jest także wymagana opinia opiekuna naukowego. Sprawy te będą rozpatrywane indywidualnie przez Radę Naukową oraz Komitet Organizacyjny Konferencji. Członkowie Towarzystwa Chemii i Inżynierii Ekologicznej i Polskiego Towarzystwa Chemicznego (z opłaconymi na bieżąco składkami) mają prawo do obniżonej opłaty konferencyjnej o 25 zł. Opłaty wnoszone po dniu 15 września 2009 r. są większe o 10% od kwot podanych powyżej. Wszystkie wpłaty winne być dokonane na konto w Banku Śląskim:

BSK O/Opole Nr 65 1050 1504 1000 0005 0044 3825

i mieć dopisek ECOpole '09 oraz nazwisko uczestnika konferencji.

Po konferencji zostaną wydane 4–6-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2009 r.** Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej. Wszystkie streszczenia oraz program Konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także umieszczony na stronie internetowej konferencji.

Za Komitet Organizacyjny

dr hab. inż. Maria Waclawek, prof. UO

Wszelkie uwagi i zapytania można kierować na adres:

Maria.Waclawek@uni.opole.pl

lub mrajfur@o2.pl

tel. 077 401 60 42

tel. 077 455 91 49

fax 077 401 60 51

Kalendarium

1. 1992 Monitoring '92 Opole
2. 1993 Monitoring '93 Turawa
3. 1994 Monitoring '94 Pokrzywna
4. 1995 EKO-Opole '95 Turawa
5. 1996 EKO-Opole '96 Kędzierzyn Koźle
6. 1997 EKO-Opole '97 Duszniki Zdrój
7. 1998 ŚEK EOpole '98 Kędzierzyn Koźle
8. 1999 ŚEK EOpole '99 Duszniki Zdrój
9. 2000 ŚEK EOpole 2000 Duszniki Zdrój
10. 2001 ŚEK EOpole '01 Duszniki Zdrój
11. 2002 ŚEK EOpole '02 Duszniki Zdrój
12. 2003 ŚEK EOpole '03 Duszniki Zdrój
13. 2004 ŚEK EOpole '04 Duszniki Zdrój
14. 2005 ŚEK EOpole '05 Duszniki Zdrój
15. 2006 ŚEK EOpole '06 Duszniki Zdrój
16. 2007 ŚEK EOpole '07 Duszniki Zdrój
17. 2008 ŚEK EOpole '08 Piechowice

ZGŁASZAM UCZESTNICTWO W KONFERENCJI ECOpole '09

(Prosimy o wypełnienie zgłoszenia drukowanymi literami)

Nazwisko i imię

Tytuł (stopień) naukowy/stanowisko

Miejsce pracy

Adres

Tel./faks e-mail

Dane instytucji (nazwa, adres, NIP), dla której ma być wystawiona faktura:

.

.

.

RODZAJ PRZEWIDYWANEGO WYSTĄPIENIA:

TAK

NIE

	TAK	NIE
Referat		
Poster		
Głos w dyskusji		

TYTUŁ WYSTĄPIENIA

.

ZAMAWIAM NOCLEG

14/15 X		15/16 X		16/17 X	
TAK	NIE	TAK	NIE	TAK	NIE

ZAMAWIAM POSILKI

Data	Śniadanie	Obiad	Kolacja
14 X	—	—	
15 X			
16 X			
17 X			—



- - - - -



15th ICHMET



**15th International Conference on Heavy Metals
in the Environment
September 19–23, 2010
Gdańsk, Poland**

**Organized by
Chemical Faculty, Gdańsk University of Technology (GUT)
together with
Committee on Analytical Chemistry of the Polish Academy Sciences (PAS)**

15th ICHMET – is a continuation of a series of highly successful conferences that have been held in major cities of the world since 1975. These conferences typically draw 500–1000 participants from countries in many parts of the world. Well over 5000 scientists have taken part in this series of conferences including most leaders in the field. Apart from the city's natural beauty, Gdansk is logical choice for the 15th Conference to highlight the outstanding work that is being done on heavy metals in central Europe. The venue for the meeting will be the Gdansk University of Technology (GUT) which features many tourist attractions.

The Conference will include a number of invited lectures treating frontier topics prepared by specialist with international reputation, oral presentation and poster sessions. ICHMET welcomes contributions on all aspects of any heavy metal in the environment. All presentation will be connected with such topics as:

- Risk assessment and risk management pertaining to toxic metals in the environment
- Susceptibility and protection of children from toxic metals in their environment
- Measurement and exposure assessment
- Biomarkers of exposure and effects of heavy metals
- Gene-environment-metal interactions
- Trend tracking/analysis of heavy metal data – spatial and temporal
- Risk communication pertaining to heavy metals
- Life cycle analysis for metalliferous consumer products
- Soil quality criteria
- Remediation technologies
- Control strategies for heavy metal emissions and deposition
- Metal mixtures – mechanistic and epidemiological studies
- Nutrient-metal interactions
- Advancements in analytical tools (procedures and measurement devices)

- Toxicology of heavy metals, from cellular and genomic to ecosystem levels
- Heavy metals in foods
- Impact of global change on heavy metal cycle

For further information on the conference, please contact:

Professor Jacek Namieśnik (Conference Chairman)
Gdansk University of Technology,
Chemical Faculty, Department of Analytical Chemistry
G. Narutowicza 11/12, 80–233 Gdansk, (Poland),
e-mail: chemanal@pg.gda.pl
homepage: <http://www.pg.gda.pl/chem/ichmet/>

GUIDE FOR AUTHORS ON SUBMISSION OF MANUSCRIPTS

A digital version of the Manuscript addressed –

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Editorial Office of monthly *Ecological Chemistry and Engineering*
(Ecol. Chem. Eng.)
Uniwersytet Opolski
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Tel. +48 77 452 71 34, fax +48 77 455 91 49,
Email – waclawek@uni.opole.pl

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Papers submitted are supposed to be written in English language and should include a summary and keywords, if possible also in Polish language. If not then the Polish summary and keywords will be provided by the Editorial Office. All authors are requested to inform of their current addresses, phone and fax numbers and their email addresses.

It is urged to follow the units recommended by the *Système Internationale d'Unites* (SI). Graph axis labels and table captions must include the quantity units. The use of the following commonly applied expressions is recommended: mass – m/kg, time – t/s or t/min, current intensity – I/A; thermodynamic temperature – T/K, Celsius scale temperature – t/°C or θ /°C (if both time and Celsius scale units need to be used, the symbol θ /°C for temperature is to be taken) etc.

Symbols recommended by the International Union of Pure and Applied Chemistry (Pure and Appl. Chem., 1979, **51**, 1–41) are to be followed.

Graphics (drawings, plots) should also be supplied in the form of digital vector – type files, e.g. Corel-Draw, Grapher for Windows or at least in a bitmap format (TIF, PCK, BMP). In the case of any query please feel free to contact with the Editorial Office.

Footnotes, tables and graphs should be prepared as separate files.

References cited chronologically should follow the examples given below:

[1] Kowalski J. and Malinowski A.: Polish J. Chem. 1990, **40**(3), 2080–2085.

[2] Nowak S: Chemia nieorganiczna, WNT, Warszawa 1990.

Journal titles should preferably follow the Chem. Abst. Service recommended abbreviations.

Receipt of a paper submitted for publication will be acknowledged by email. If no acknowledgement has been received, please check it with the Editorial Office by email, fax, letter or phone.

ZALECENIA DOTYCZĄCE PRZYGOTOWANIA MANUSKRYPTÓW

Praca przeznaczona do druku w miesięczniku *Ecological Chemistry and Engineering A/Chemia i Inżynieria Ekologiczna A* powinna być przesłana na adres Redakcji:

Profesor Witold Waclawek
Redakcja Ecological Chemistry and Engineering
Uniwersytet Opolski
ul. Oleska 48, 45–951 Opole
tel. 077 401 60 42, fax 077 455 91 49
email: waclawek@uni.opole.pl

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Przypisy i tabele podobnie jak rysunki zapisujemy jako osobne pliki.

Literaturę prosimy zamieszczać wg poniższych przykładów:

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[2] Nowak S.: Chemia nieorganiczna, WNT, Warszawa 1990.

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