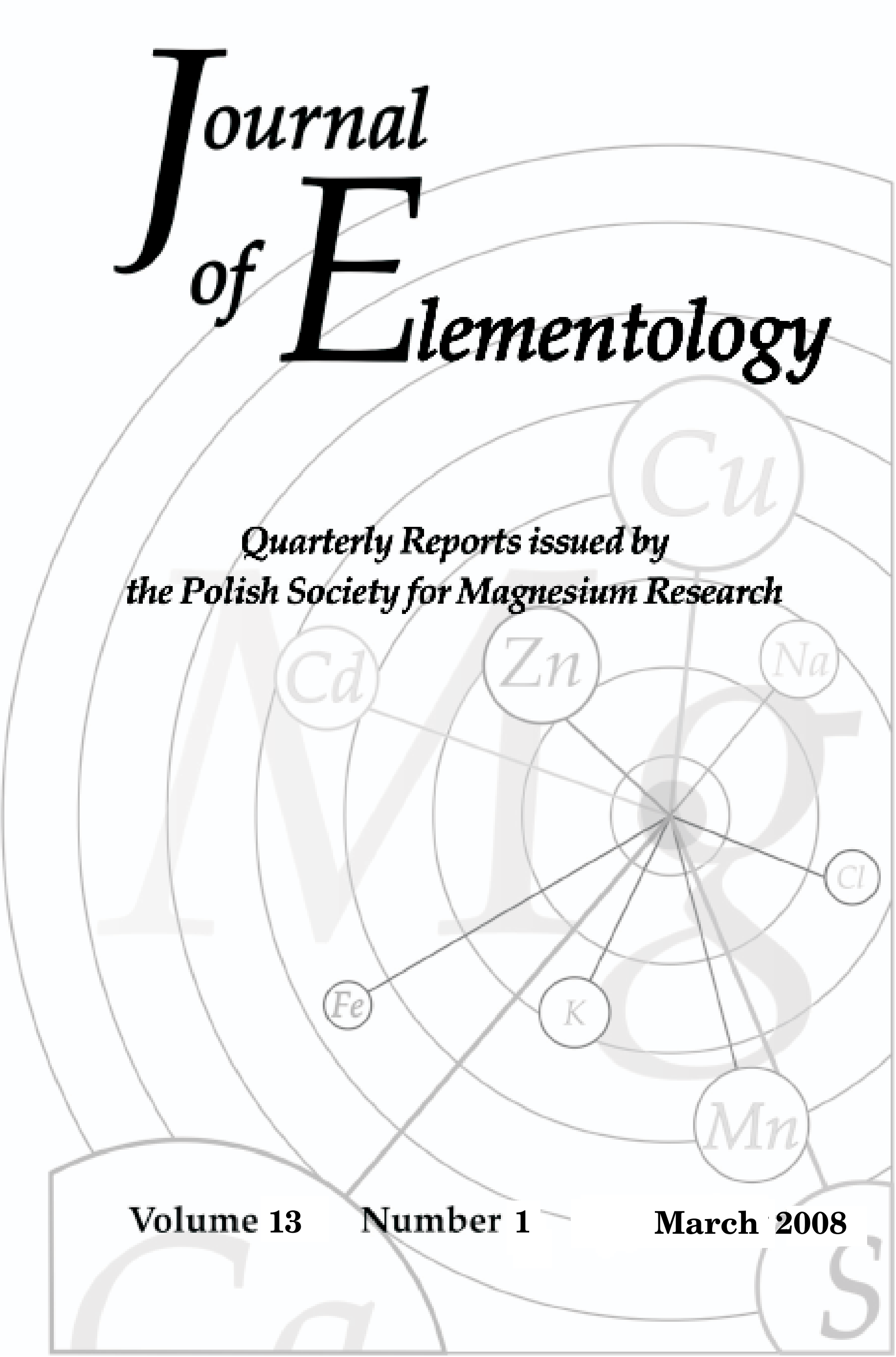


Journal of Elementology

Quarterly Reports issued by
the Polish Society for Magnesium Research

Volume 13 Number 1 March 2008

Editorial Office
University of Warmia and Mazury
Michała Oczapowskiego 8, 10-719 Olsztyn, Poland, phone: +48 089 5233231
http:// www.uwm.edu.pl/jelementol

Autor strony internetowej: Sławomir Krzebietke

Publishing company is funded by Ministry of Science and Higher Education
and supported by University of Warmia and Mazury in Olsztyn

Ark. wyd. 12,0; ark druk. 10,25; pap. offset. kl. III 80 g B-1
Druk: MIRDRUK, 10-080 Olsztyn, ul. Profesorska 9, tel. 857-90-34

Contents

Spis treści

J. Elementol. 2008, 13(1): 5–16

ASSESSMENT OF HEAVY METAL CONTAMINATION OF SOILS IMPACTED BY A ZINC SMELTER ACTIVITY

Diatta J. B.[1], Chudzinska E.[2], Wirth S.[3]

[1]Department of Biogeochemistry of Ecosystems,
Agricultural University, Poznan
[2]Adam Mickiewicz University, Department of Genetics, ul. Umultowska 89,
61-614, Poznan, Poland
[3]ZALF, Leibniz Centre for Agricultural Landscape and Landuse Research
Institute of Primary Production and Microbial Ecology,
Eberswalder Str. 84, D-15517 Müncheberg, Germany

Abstract

Four metals (Cu, Zn, Pb and Cd) were assayed in soils within the impact zone of the Miasteczko Slaskie Zinc Smelter (southern Poland). The investigated area is afforested and has been subjected for a long time to intensive deposition of metal-bearing dusts. Soil pH_{KCl} varied broadly from very acidic (pH_{KCl} = 3.4) to slightly alkaline (pH_{KCl} = 7.2). Organic carbon (C_{org}) content fluctuated within a large range, i.e., 5.5 – 66.4 g kg^{-1}, whereas the cation exchange capacity (CEC) was in most cases markedly low (from 1.4 to 5.9 $cmol_{(+)}kg^{-1}$), with exception for two sites (C and D) exhibiting values of 26.8 and 15.1 cmol(+)kg^{-1}, respectively. Total Zn, Pb and Cd contents exceeded manifold their respective levels in the Earth crust (reference value – RV)) as well as those suggested as background levels for Poland (BLP). The assessment of the contamination of soils by these metals was undertaken on the basis of geoaccumulation indices (I_{geo}), contamination factors C^i_f and degrees of contamination (C_{deg}). The overall metal contamination represented practically two classes: low contamination for Cu; considerable to extreme contamination (in ascending order) for Zn, Cd, and Pb. The contribution (BLP-based assessment) of each metal to the degree of contamination index varied from 2.14 % (for Cu), via 26.33% (for Zn) to quite equally for Cd and Pb, both representing 35.22% and 36.32, respectively. It is worth pointing out that copper was the sole metal to threaten the least (Figure 1) the soils of the investigated ecosystem.

Key words: metallurgy, heavy metal contamination, index of geoaccumulation, ontamination factor, degree of contamination.

---

dr hab. Jean Diatta, Department of Biogeochemistry of Ecosystems, Agricultural University of Poznan, ul. Wojska Polskiego 71F, 60-625, Poznan, Poland, e-mail: Jeandiatta@yahoo.com

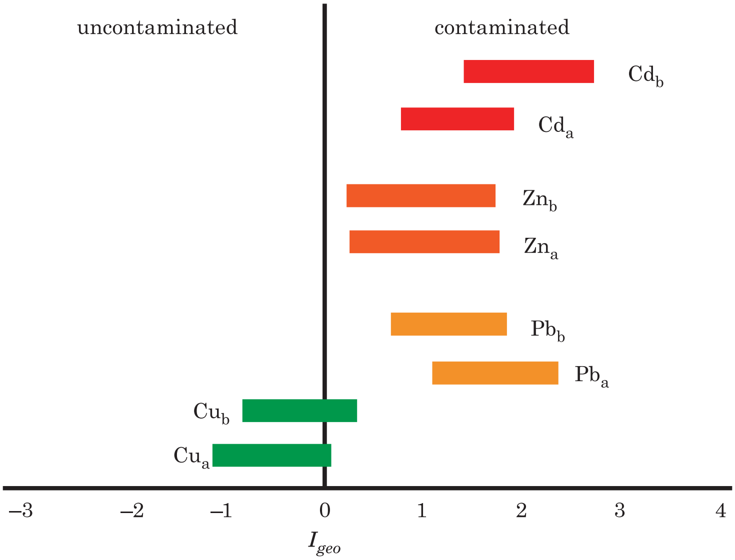


Fig. 1. Indices of geoaccumulation (I_{geo}) for metals within the impact zone of the Miasteczko Slaskie Zinc Smelter (footnotes a and b, see Table 2 and Table 3)

INTRODUCTION

The content of heavy metals in soils is a joint action of both natural processes and human activity, with a prevalence of anthropogenic sources (NRIAGU, PACYNA 1988, BAIZE, STERCKEMAN 2001). In many areas of Europe, soil is being irreversibly lost and degraded as a result of increasing and often conflicting demands from nearly all economic sectors. The combined action of these activities affects quality and limits many soil functions including the capacity to remove contaminant from the environment by filtration and adsorption. This capacity and the resilience of soil mean that damage is not perceived until it is far advanced. Significant increases in soil heavy metal content are generally found in lands under high industrial activity, where accumulation may be several times higher as compared to average content of unconcontaminated lands (VAN LYNDEN 2000). Among the many heavy metals released from various products and processes, cadmium, lead and mercury are of great concern to human health because of their toxicity and potential to induce harmful effects at low concentrations and to bio(geo)accumulate. When assessing the persistence of soil contamination with heavy metals one should take into consideration that the half-life of cadmium ranges from 15 to 1,100 years as compared to lead, whose half-life may vary from 740 to 5,900 years depending on several biogeochemical factors. Therefore, due to such a slow process of soil self-purification and the tendency of heavy metals to accumulate any assessment dealing with threats to the soil environment should consider the whole duration of their detrimental impact (FAGIEWICZ et al. 2006).

Several approaches have been used for evaluating the degree of heavy metals contamination in different ecosystems. They are commonly based on the amounts of metals extracted by applying specified soil tests or on the elaboration of phytotests, which are expected to confirm or not metal concentrations extracted by soil tests (KABATA-PENDIAS et al. 1993, GRZEBISZ et al. 1997, REIMANN et al. 2000).

Indices-based assessment of soils contamination by heavy metals seem to be a useful geochemical method, since it "shifts" from commonly reported concentrations of particular heavy metals into unitless parameters (DIATTA et al. 2003). Therefore the current work is intented to focus on indices, such as the index of geoaccumulation (Igeo), contamination factor (Cf) and degree of contamination (Cdeg.) for evaluating the potential contamination of soils impacted by the Miasteczko Slaskie Zinc Smelter activity.

Index of geoaccumulation (I_{geo})

This index enables the assessment of heavy metal contamination by comparing current and preindustrial metal contents. It was originally used for bottom sediments (MÜLLER 1969), but may be applied for assessing soil contamination on the basis of the following equation:

$$I_{geo} = \log_{10} \frac{C_n}{1.5 B_n} \tag{1}$$

where C_n is the measure concentration of the element n in the pelitic sediment fraction (< 2 μm) and B_n is the geochemical background value in the fossil argillaceous sediment (i.e., average shale). The constant 1.5 allows for involving natural fluctuations in the concentration of a given substance in the environment and very small anthropogenic influences. Six classes were suggested by MÜLLER (1981) as reported below:

Class	Value	Soil quality
0	$I_{geo} \leq 0$	practically uncontaminated
1	$0 < I_{geo} < 1$	uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	moderately contaminated
3	$2 < I_{geo} < 3$	moderately to heavily contaminated
4	$3 < I_{geo} < 4$	heavily contaminated
5	$4 < I_{geo} < 5$	heavily to extremely contaminated

A modified method was applied in the current paper for the computations of the I_{geo} values and deals with the following details: C_n expresses the total concentration of a given metal in the surface layer of the tested soils, while B_n, the concentration of the same metal in the Earth's crust (i.e., Cu – 39; Zn – 67; Pb – 17 and Cd – 0.10 mg kg^{-1}) as reported by TAYLOR and MCLENNAN (1995).

Contamination factor (C_f^i) and degree of contamination (C_{deg})

Soil contamination was also evaluated by using indices such as the contamination factor (C_f^i) and the degree of contamination (C_{deg}), (HAKANSON 1980), which were computed on the basis of the equation reported below:

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \tag{2}$$

where, C_{0-1}^i is the mean concentration of metals from at least five sampling sites and C_n^i is the preindustrial concentration of individual metals. A modification was done and consisted of using the concentration of metals in the Earth's crust as reference values (TAYLOR, MCLENNAN 1995).

Four categories have been suggested by HAKANSON (1980) and represented the following ranges:

Contamination factor	**Description**
$C_f^i < 1$	low contamination factor
$1 \le C_f^i < 3$	moderate contamination factor
$3 \le C_f^i < 6$	considerable contamination factor
$6 \le C_f^i$	very high contamination factor

Moreover it should be mentioned that C_f^i is a single-element index. The sum of C_f^i for all studied metals yields the so-called the contamination degree (C_{deg}) of the ecosystem and is represented by four classes as follows:

Contamination degree	**Description**
$C_{deg} < 8$	low degree of contamination
$8 \leq \; < C_{deg}$ 16	moderate degree of contamination
$16 \leq \; < C_{deg}32$	considerable degree of contamination
$32 \leq C_{deg}$	very high degree of contamination

MATERIALS AND METHODS

Location of the research area

The research area lays within the impact zone of the Miasteczko Slaskie Zinc Smelter, (N 51°41’03” and E 15°57’12”, Poland) whose activity started since 1966. This zone is surrounded in the north, west and east by a large Lubliniec Forest complex, and in the south-east by the localities of Zyglin and Zygliniec, quarters of the Miasteczko Slaskie. A population of pine as part of artificial restoration, mainly of mixed forest, sporadically mixed wood grows in the impact zone. In the Miasteczko Slaskie region, the prevailing winds are from the south-westerly (21.4%) and westerly (18.7%) quarters, hence the pollution emitted by the Zinc Smelter creates the greatest threat to areas north-east and east of the Zinc Smelter.

Sample collection and analytical procedures

Five samples ordered like the five on a dice, with 15 m distance from the central point were collected (20 cm depth) at 8 selected sites (Table 1) on June 08, 2006. They were air-dried and sieved through a 1 mm polyethylene sieve before physical and chemical analysis. Prior to basic analyses soil samples were air-dried and crushed to pass through a 1 mm sieve. Granulometric composition was determined by the areometric method (Gee, Bauder 1986) and organic carbon by the Walkly-Black method as reported by Nelson and Sommers (1996). Soil pH at soil/solution (water or 1 mol KCl dm^{-3}) ratio of 1:2.5 was determined potentiometrically using a pH-meter. The cation exchange capacity (CEC) was obtained by summation of 1 mol KCl dm^{-3} extractable acidity and exchangeable alkaline cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) extracted by 1 mol CH$_3$COONH$_4$ dm^{-3} (pH 7.0) as described by Thomas (1982). The total content of heavy metals was determined by using the *aqua regia* procedure (International Standard, 1995). All analyses were performed in duplication; computations and statistical evaluations were made by using the Excel® sheet.

Table 1

Selected physical and chemical properties of soils in the impact zone of the Miasteczko Slaskie Zinc Smelter (mean, $n = 5$)

Site*	Particles (g kg^{-1})		C_{org} (g kg^{-1})	EC** (µS cm^{-1})	pH		Ca	CEC***
	Silt	Clay			H_2O	1 mol KCl dm^{-3}	cmol (+) kg^{-1}	
A	90	90	5.5	34.7	6.7	5.7	1.0	1.4
B	150	90	9.1	41.6	6.2	4.9	1.4	1.8
C	490	260	15.5	189.0	7.6	7.2	24.1	26.8
D	240	260	20.0	128.5	7.5	7.0	13.3	15.1
E	270	130	11.2	68.3	6.3	5.6	4.3	5.4
F	290	80	7.5	72.3	6.8	6.0	4.9	5.9
G	410	90	31.1	65.7	6.0	4.6	2.2	2.9
H	180	60	66.4	134.6	4.7	3.4	1.8	2.5

* **A**, **B** – experimental area 500 and 1100 m ESE, respectively; **C** – Cynkowa Street, 100 m SE from the Zinc Smelter (Miasteczko Śląskie); **D** – Dworcowa Street, 500 m W from the Zinc Smelter (Miasteczko Śląskie); **E** – Brynicka Street, 500 m E from the Zinc Smelter (Zyglin); **F** – Sw. Marka Street, 1500 m SE from the Zinc Smelter (Zyglin); **G** – Zyglinska Street, 4500 m E from the Zinc Smelter (Brynica); **H** – Staromiejska Street, 6000 m E from the Zinc Smelter (Bibiela);

** Electrical Conductivity; *** Cation Eexchange Capacity

RESULTS AND DISCUSSION

Soils within the impact zone of the Miasteczko Slaskie Zinc Smelter are characterized by significantly different physical and chemical properties summarized in Table 1. Soil reaction (pH) varied broadly from very acidic ($pH_{KCl} = 3.4$) at the site H to slightly alkaline ($pH = 7.2$) for soils of the site C. Organic carbon (C_{org}) content fluctuated within a large range, i.e., 5.5–66.4 g kg^{-1}, whereas the cation exchange capacity (CEC) was in most cases markedly low (from 1.4 to 5.9 cmol$_{(+)}$kg^{-1}), except for sites C and D with CEC values of 26.8 and 15.1 cmol$_{(+)}$kg^{-1}, respectively. The amount of silt and clay fractions reveals that investigated soils are preponderatingly sandy, *ca* 75% of soils exhibited silt + clay < 500 g kg^{-1}). Such soil texture may create a serious threat due to strengthened pollutants migration downward. The mean heavy metals content as reported in Table 2 showed significant variations related most specifically with both sites and type of metal. In the case of Zn, Pb and Cd, their levels exceeded *ca* 3 to 72 times; 13 to 176 times and 44 to 520 times, respectively, the reference values (RV) – Table 2, in opposite to Cu with 75% of its content

Table 2

Total (aqua regia) metal contents within the impact zone of the Miasteczko Slaskie Zinc Smelter, (mean ±SD*, n = 5)

Site**	Cu	Zn	Pb	Cd
	mg kg^{-1}			
A	5.15 ± 0.45	614.50 ± 30.43	404.15 ± 46.96	5.75 ± 1.16
B	5.40 ± 1.29	368.50 ± 39.47	542.15 ± 61.44	5.05 ± 1.08
C	69.60 ± 12.40	4832.0 ± 517.48	2986.0 ± 147.88	52.00 ± 5.82
D	56.55 ± 9.69	1351.8 ± 247.69	1009.65 ± 95.60	16.35 ± 2.45
E	6.60 ± 0.80	246.0 ± 31.10	352.15 ± 14.65	5.52 ± 0.38
F	6.20 ± 1.36	649.0 ± 88.56	226.95 ± 12.34	5.05 ± 0.84
G	5.00 ± 0.40	202.0 ± 7.62	288.10 ± 24.04	4.50 ± 0.47
H	5.95 ± 0.86	240.0 ± 31.42	446.15 ± 30.35	4.35 ± 0.78
Mean	20.06 ± 3.40	1062.98 ± 124.22	781.91 ± 54.16	12.32 ± 1.62
RV*	39.0	67.0	17.0	0.10
BLP***	17.5	75.0	40.0	0.65

*Standard deviation; **see Table 1; ***Reference value (Taylor, McLennan 1995); ****Background Level for Poland (Kabata-Pendias 1995)

not exceeding the RV. These orders of magnitude clearly show that cadmium is the most threatening heavy metal in the impact zone, followed by lead and zinc, respectively.

Copper

The mean Cu content in the study area amounted to 20.06 mg kg^{-1} and was significantly lower than the reference value (RV = 39.0 mg kg^{-1}) reported by Taylor and McLennan, (1995) and slightly higher as compared to the background level (BLP), (mean value, *ca* 17.5 mg kg^{-1}) of the natural heavy metal content in the top layers of various soils in Poland (Kabata-Pendias 1995). On the other hand, the mean Cu content in soils in Poland is 6.7 mg kg^{-1} (Kabata-Pendias, Pendias 2001), i.e., *ca* 3-times lower than the mean value obtained for the studied area.

Copper geoaccumulation indices (Cu-I_{geo}) calculated on the basis of the RV and BLP varied within ranges from -1.07 to 0.07 and from -0.72 to 0.42, indicating unambiguously a lack of contamination (Figure 1). This is in agreement with data reported by Fagiewicz et al. (2006), who pointed out significantly low Cu concentrations in dusts emitted by the Zinc Smelter. Both RV and BLP values used for assessing the Cu-I_{geo} exhibited a quite similar contamination trend, which differed in range only. This is important in cases of delineating areas subjected to metal contamination or pollution. The low contamination may be also related to Cu uptake by plants, a process leading to Cu depletion in the tested soils. However, copper depletion in soils could be induced by the elevated content of toxic bivalent metals (i.e., Zn, Pb and Cd) specifically "competing" with Cu for binding to soil particles as well as to organic matter (KABALA, SINGH 2001). This process may tend to increase Cu solubility and consequently its uptake by plants or leaching.

Zinc

Investigated soils exhibited a significantly high Zn level (mean content for the whole area is 1062.98 mg kg^{-1}, Table 2), which is higher than those reported for Norway, 62.0 mg kg^{-1} (STEINNES et al. 1997); the Baltic Countries, 53.8 mg kg^{-1} (REIMANN et al. 2000); for rural soils of Vietnam, 65.5 mg kg^{-1} (THUJ et al. 2000) and for forest soils of Switzerland, 60.0 mg kg^{-1} (BLASER et al. 2000). Zinc is an essential element, which is involved in plant metabolism. But at extremely high levels, it may impair – *via* toxicity - any biological growth (microorganisms and plants), hence the depletion process may not occur under conditions similar to those considered in the current study.

The calculated zinc geoaccumulation indices (Zn-I_{geo}) varied from 0.30 to 1.68 (for RV) and 0.25 to 1.63 (for BLP) as illustrated by the Figure 1. The reported ranges indicate that the relevant contamination state may be described as uncontaminated to moderately contaminated (MÜLLER 1981). Such "fair" Zn-I_{geo}-based contamination state is partly related to both slightly high RV and BLP values as compared to Cu, whose values are lower. The fact that most soils exhibited markedly weak buffer mechanisms (CEC, Table 1), strengthens the assumption that a real contamination threat still exists, in spite of relatively low Zn-I_{geo} indices.

Lead

Lead, in opposite to zinc, is by essence harmful for the biota. Natural attenuation processes – sorption, precipitation, retention creating suitable soil "sink" conditions for Pb, due to its high metal retention capacities (BORUVKA et al. 1997, KABALA, SINGH 2001), mostly control its transformation in soils. Therefore the persistence and (im)mobility of Pb should be dictated by the extent to which Pb is incorporated to soils. The mean Pb content of the studied area amounted for 781.91 mg kg^{-1} (Table 2) and is *ca* 46 and 20 times higher than the RV and BLP values, respectively and 57 times higher as compared to the mean heavy metal content (i.e., 13.8 mg kg^{-1}) in Polish soils (KABATA-PENDIAS 2001).

Lead geoaccumulation indices indicated a contamination state, whose magnitude depended on the RV and BLP values exhibiting Pb-I_{geo} indices in the ranges from 0.95 to 2.07 and 0.58 to 1.70, respectively as shown in the

Figure 1. These ranges fit the contamination class extending mostly from 0 to 2 and may be designated as uncontaminated to moderately contaminated (Müller 1981). A similar contamination class was established for Zn, but with the specificity that Zn-I_{geo} indices tended to shift more to the uncontaminated than contaminated class. The assessment of soils contamination on the basis of Pb-I_{geo} indices does not reveal a serious concern and threat, even. Amounts reported in Table 2 represented significant contamination level, which implied that care should be taken to these areas, due to the harmful and detrimental effect of lead.

Cadmium

The mean cadmium content in the impact zone amounted to 12.32 mg kg^{-1} and was significantly higher than mean contents in soils of Poland (i.e., < 0.05 mg kg^{-1}, Lis, Pasieczna 1995 and 0.22 mg kg^{-1}, Kabata-Pendias 2001). The same applies for the RV and BLP values (Table 2), being exceeded *ca* 123 and 19 times, respectively. Such cadmium content is a matter of great concern since cadmium may exhibit toxicity properties at soils concentration above 3.0 mg kg^{-1} (Buczkowski et al. 2002). This supports the fact that the frequently suggested toxicity threshold values are relatively low, as shown just above.

Indices of Cd geoaccumulation (Cd-I_{geo}) indicated ranges extending from 1.46 to 2.54 and 0.64 to 1.72, accordingly to the BLP and RV values (Figure 1, Table 2). Contamination assessment based on these indices may create some discrepancies related to the establishment of a proper Cd-I_{geo} class. Therefore it could be reasonable to group both classes into one with a range varying from 0.64 to 2.54, i.e., uncontaminated to moderately-heavily contaminated (Müller 1981). Cadmium contamination of this area confirms data reported by Fagiewicz et al. (2006), that Cd, Zn and Pb displayed the highest levels relative to the background values. The high Cd-I_{geo}, is consistent with the findings of Lis and Pasieczna (1995), who stated that soils in Upper Silesia are characterized by much higher cadmium content as compared to the whole area of Poland.

Copper, Zn, Pb and Cd contribution to soils contamination within the impact zone

The estimation of the overall contamination of investigated soils was carried out on the basis of the degree of contamination (C_{deg}) – Table 3. A detailed assessment was made throughout contamination factors (), whose mean values allowed to classify soils accordingly to the RV and BLP values. Two classes (Hakanson 1980) were operationally established, relatively to both values: low contamination for Cu, and considerable to extreme contamination for Zn, Pb and Cd, gradually. The BLP-based contamination assessment should be suggested in this case, due to the fact that this value has been

Table 3

Contamination factors and degrees for particular heavy metals within the impact zone of the Miasteczko Slaskie Zinc Smelter for RV and BLP values*

Metal	Contamination factor (range)		Mean	Share (%) of C_f^i to C_{deg}
$^{x}Cu_a$	C_f^i	0.13 – 1.78	0.51	0.27
$^{y}Cu_b$		0.29 – 3.98	1.15	2.14
Zn_a		3.01 – 72.12	15.87	8.57
Zn_b		2.69 – 64.43	14.17	26.33
Pb_a		13.35 – 175.65	45.99	24.83
Pb_b		5.67 – 74.65	19.55	36.32
Cd_a		43.50 – 520.0	123.22	66.54
Cd_b		6.92 – 80.0	18.96	35.22
Degree of contamination (a) [$C_{dg} = \sum(C_f^{Cu,Zn,Pb,Cd})$]		26.94 – 537.65	185.59	-
Degree of contamination (b)		6.90 – 119.08	53.83	

* details in Table 2; x and y: footnotes a and b refer to RV and BLP, respectively

intrinsically elaborated for Polish conditions. The re-evaluation of the degree of contamination on the basis of the BLP value gave similar contamination classes as those reported above. This rank confirmed the I_{geo}-based indices contamination assessment. Furthermore, the C_{deg} for mean heavy metal concentrations in the impact zone amounted to 53.83, which implied (HAKANSON 1980), that these soils were on the whole, considerably contaminated.

Cadmium and lead contributed the most to the degree of contamination index of the soils, with a share of 35.22 and 36.32%, respectively, followed by Zn, representing 26.33%. Copper, as reported throughout the current paper, was the sole metal to threaten the least (2.14%) the soils of the investigated ecosystem.

CONCLUSIONS AND STATEMENTS

The assessment of soils contamination throughout the application of the geoaccumulation index, contamination factor and degree has revealed that soils were differently contaminated by Cu, Zn, Pb and Cd. Metal contamination represented mostly two classes: low contamination for Cu and extremely high contamination for Zn, Cd, and Pb, in ascending order. It is worth pointing out that copper, was the sole metal to threaten the least (2.14%) the soils of the investigated ecosystem. The impact zone is predominantly afforested; hence, the transfer of Pb, Cd, and Zn to the food chain is reduced enough. The great concern deals with the so-called forest fruits (bilberries, mushrooms), seasonally collected for sale or direct consumption (household). This topic is out of the scope of the paper.

REFERENCES

BAIZE D., TERCKEMAN T. 2001. *Of the necessity of knowledge of the natural pedogeochemical background content in the evaluation of the contamination of soils by trace elements*. Sci. Total Environ., 264,127-139.

BLASER P., ZIMMERMANN S., LUSTER J., SHOTYK W. 2000. *Critical examination of trace element enrichments and depletions in soils. As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils*. Sci. Total Environ., 249,257-280.

BUCZKOWSKI R., KONDZIELSKI I., SZYMANSKI T. 2002. *Methods for the reme-diation of soils contaminated by heavy metals*. Mikolaj Kopernik University Editions, Torun. First Edition, 110 p.

BORUVKA L.S., KRISTOUFKOVA L., KOZAK J., HUAN WEI C. 1997. *Speciation of cadmium, lead and zinc in heavily polluted soils*. Rostliná Vyroba, 43: 187-192.

DIATTA J.B., GRZEBISZ W., APOLINARSKA K. 2003. *A study of soil pollution by heavy metals in the city of Poznan (Poland) using Dandelion (Taraxacum officinale) as a bioindicator*. EJPAU, 6(2): 9 (http:/www.ejpau.media.pl).

FAGIEWICZ K., KOZACKI L., PRUS-GŁOWACKI W., CHUDZINSKA E., WOJNICKA-PÓŁTORAK A. 2006. *Genetic-environmental controls of the tolerance of forest Trees to industrial pollution. Archiv. Environ. Protect.,* 32(1): 73-88.

GEE G.W., BAUDER J.W. 1986. *Particle size analysis*. In *Methods of Soil Analysis*. Part 1. *Physical and Mineralogical Methods*. KLUTE A. (ed) 2nd ed. Agron. Monogr. 9, ASA and SSSA, Madison, WI. p. 383-411.

GRZEBISZ W., KOCIALKOWSKI W. Z., CHUDZIŃSKI B. 1997. *Copper geochemistry and availability in soils contaminated by a copper smelter.* J Geochem. Exploration, 58:301-307.

HAKANSON L. 1980. *An ecological risk index for aquatic pollution control. A sedimentological approach*. Wat. Res., 14: 975-1001.

International Standard. 1995. *Soil Quality – Extraction of trace elements soluble in aqua regia*. ISO 11466, Geneva.

KABALA C., SINGH B.R. 2001. *Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter*. J. Environ. Qual., 30: 485-492.

KABATA-PENDIAS A. 1995. *Heavy metals in soils – issues in Central and Eastern Europe*. Int. Conf., Hamburg, 1: 20-27.

KABATA-PENDIAS A. 2001. *Trace elements in soils and plants*, (3-rd ed). CRC Press, 432 p.

KABATA-PENDIAS A., MOTOWICKA-TERELAK, PIOTROWSKA M., TERELAK H., WITEK T. 1993. *Assessment of the level of contamination of soils and plants by heavy metals and sulphur*. IUNG, P-53, Pulawy, p. 5-14 (in Polish).

LIS J., PASIECZNA A. 1995. *Geochemical Atlas of Upper Silesia*. Warsaw, PIG. (in Polish).

MONTANERELLA L., OLAZABAL C., SELVARADJOU S.-K. 2004. *Reports of the Technical Working Groups Established under the Thematic Strategy for Soil Protection.* EUR 21319 EN/4., p. 493-654. Office for Official Publications of the European Communities, Luxemburg.

MÜLLER G. 1969. *Index of geoaccumulation in sediments of the Rine River*. Geojournal 2: 108-118.

MÜLLER G. 1981. *Die Schwermetallbelastung der Sedimenten des Neckars und Seiner Nebenflusse*. Chemiker-Zeitung, 6: 157-164.

NELSON D.W., SOMMERS L.E. 1996. *Total carbon, organic carbon and organic matter*. In: *Methods of soil analysis*. Part 3. *Chemical methods.* SPARKS D.L. (ed.) SSA Book Ser. 5. SSSA, Madison, WI. p. 961-1010.

NRIAGU J.O., PACYNA J.M. 1988. *Quantitative assessment of worldwide contami-nation of air, water and soils by trace elements*. Nature, 333: 134-139.

REIMANN C., SIEWERS U., TARVAINEN T., BITYUKOVA L. ERIKSSON J., GILUCIS A. 2000. *Baltic soil survey: Total concentrations of major and selected elements in arable soils from 10 countries around the Baltic Sea*. Sci. Total Environ., 257: 155-170.

STEINNES E., ALLEN R.O., PETERSEN H.M., RAMBAEK J.P., VARSKOG P. 1997. *Evidence of large-scale contamination of natural surface soils in Norway from long-range atmospheric transport.* Sci. Total Environ., 205: 255-266.

TAYLOR S.R., MCLENNAN S.M. 1995. *The geochemical evolution of the continental crust.* Rev. Geophys., 33: 241-265.

THUJ H.T.T., TOBSCHALL H.J., AN P.V. 2000. *Distribution of heavy metals in urban soils – a case study of Danang-Hoian Area (Vietnam)*. Environ. Geol., 39: 603-610.

THOMAS G.W. 1982. *Exchangeable cations*. In: *Methods of soil analysis*. PAGE A.L. et. al. (ed.) 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI p. 159-164.

VAN-CAMP L., BUJARRABAL B., GENTILE AR., JONES R.J.A., VAN LYNDEN G. W.J. 2000. *Soil degradation in Central and Eastern Europe. The assessment of human-induced degradation*. FAO Report 2000/05 and ISRC.

J. Elementol. 2008, 13(1): 17–28

EFFECT OF ZINC FOLIAR APPLICATION AT AN EARLY STAGE OF MAIZE GROWTH ON PATTERNS OF NUTRIENTS AND DRY MATTER ACCUMULATION BY THE CANOPY

Part I. Zinc uptake patterns and its redistribution among maize organs

Witold Grzebisz[1], Małgorzata Wrońska[2], Jean B. Diatta[1], Piotr Dullin[3]

[1]Department of Agricultural Chemistry, University of Agricultural Sciences, Poznań, Poland
[2]Agencja Rezerw Materiałowych, 00-400 Warszawa, ul. Nowy Świat 6/12
[3]Department of Biochemistry and Biotechnology, University of Agricultural Sciences, Poznań Poland

Abstract

As reported in the paper by Grzebisz et al. (this issue), maize crop treated foliarly with fertilizer zinc at early stages of growth produced significantly high yields. Growth analysis procedures were applied to explain various effects of fertilizer zinc on grain yield increase and zinc accumulation and redistribution among maize organs in the course of the growing season. Therefore, based on the obtained zinc uptake characteristics, two major and one minor, but time-separated *hot spots* of zinc accumulation by maize plants have been distinguished. The first one, as described by RUR-Zn data, extended from the BBCH7 to BBCH9 stages. The second one, as expressed by CUR-Zn data, appeared during the milk stage of kernels growth and could be decisive for kernels sink capacity for accumulating carbohydrates. A minor *hot spot*, which occurred at tasselling may be responsible for pollen production and activity. The first zinc *hot spot* has also revealed the diagnostic problem of soil and plant tests for zinc. Current tests tend to overestimate plant zinc nutritional status, and therefore need to be urgently revised. Vegetative organs such as leaves and stems were only the minor sources of

---

prof. dr hab. Witold Grzebisz, Department of Agricultural Chemistry, University of Agricultural Sciences, street Wojska Polskiego 71F, 60-625 Poznań, Poland, e-mail: witegr@au.poznan.pl

zinc for developing maize kernels. During grain filling period, most zinc absorbed by maize plants originated from soil resources.

Keywords: relative uptake rate (RUR), crop uptake rate (CUR), zinc, maize.

Wpływ dolistnego stosowania cynku we wczesnej fazie wzrostu kukurydzy na wzorce akumulacji składników pokarmowych i suchej masy przez łan

Cz. I. Wzorce akumulacji cynku i rozmieszczenie składnika między organami rośliny

Abstrakt

Z pracy wynika, że kukurydza traktowana dolistnie nawozem cynkowym we wczesnej fazie rozwoju wydała większe plony ziarna. Celem wyjaśnienia mechanizmu działania nawozu cynkowego na plony ziarna i na akumulację cynku przez rośliny w okresie wegetacji zastosowano procedury analizy wzrostu. Na podstawie parametrów pobrania cynku, wyznaczono dwie główne i jedną drugorzędną fazę krytyczną akumulacji tego pierwiastka przez kukurydzę. Pierwsza faza, opisana przez RUR-Zn, pojawiła się w okresie od 7. (BBCH 17) do 9. liścia (BBCH 19) i była prawdopodobnie związana z inicjacją zawiązków kwiatowych. Druga, reprezentowana przez CUR-Zn, zaznaczyła się w fazie dojrzałości mlecznej ziarniaków i mogła wpływać na zdolność ziarniaków do akumulacji węglowodanów. Trzecia faza krytyczna, pojawiająca się w fazie wiechowania, wiąże się prawdopodobnie z produkcją i żywotnością pyłku. Pierwsza faza krytyczna ujawniła także problem wiarygodności obecnych testów glebowych i roślinnych dla cynku, które przeszacowują stan odżywienia kukurydzy cynkiem i wymagają pilnej rewizji. Organy wegetatywne, takie jak liście i źdźbła, nie były głównymi źródłami cynku dla rosnących ziarniaków kukurydzy. W fazie nalewania ziarna kukurydza pobierała większość cynku z zasobów glebowych.

Słowa kluczowe: względna szybkość pobierania (RUR), szybkość pobierania przez łan (CUR), cynk, kukurydza.

INTRODUCTION

Zinc is one of the most important micronutrients in the production of many crop plants such as rice, maize and wheat, or soybean, which all are worldwide cultivated. It has been well recognized by scientists that zinc affects many processes governing plant life cycles. Some metabolic processes such as enzymatic activity, auxin synthesis, carbohydrate metabolism, protein synthesis are of crucial importance for plant growth and in turn for efficient control of nitrogen metabolism. There are also many physiological processes such as pathogen pressure, drought or heat, effectively controlled by zinc activity and in turn resulting in higher resistance of cultivating plants to abiotic and biotic stresses (GRUSAK et al. 1999, MARSCHNER 1986). Soils poor in available zinc are a serious quantitative and qualitative stress factor for crop plants. These soils cover almost 50% of world arable lands, mostly in dry and acid areas of the world (Sillanpaa 1990).

The yield potential of maize is extremely high, but its realization is possible provided that supply of nutrients and efficiency of applied nitrogen are high (Murrel, Childs 2000). There are few scientific papers reporting quantitative aspects of zinc fertilizers in maize grain production (Fecenko, Ložek 1998; Grzebisz et al. (this issue). All these papers stress the importance of zinc applied at early stages of maize growth on its yields, which in turn is related to higher efficiency of fertilizer nitrogen. The found yield increases are directly related to the components of yield structure, mainly the number of kernels per cob in response to zinc application.

A plant growth analysis procedure (Hunt et al. 2002) was applied in order to explain the experimentally corroborated effect of zinc on maize yielding. In this specific case, it was necessary to determine the most crucial stages of zinc accumulation in order to exhibit plant behavior in the course of the growing season.

The main objectives of this study were to describe the patterns of zinc uptake by maize plants in order to point out its effect on grain yield.

MATERIALS AND METHODS

One-factor experiments with four rates of zinc application, i.e., 0.0, 0.5, 1.0 and 1.5 kg Zn ha^{-1} as zinc oxy-sulphate were conducted in 2002 and 2003 growing seasons. The general design and experimental details of this study are presented by Grzebisz et al., (this issue). For purposes of this particular study, 8 plants were sampled (equal to 1 m^2) in 10 consecutive stages of maize growth according to the BBCH code: 14 (37 days after sowing – DAS), 17 (48 DAS), 19 (58 DAS), 39 (69 DAS), 59 (79 DAS), 67 (89 DAS), 75 (104 DAS), 83 (118 DAS), 87 (132 DAS), 89 (140 DAS). At each stage of maize growth, the harvested plant sample was partitioned, according to its stage of development, into sub-samples of leaves, stems, cobs, shanks, husks, kernels, and then dried (65°C). The results are expressed on a dry matter (DM) basis.

The growth analysis procedure was applied to determine the Crop Growth Rate (CGR) parameter, which for the purpose of this study is termed Crop Uptake Rate of Zinc (CUR$_{Zn}$), as reported below (Hunt et al. 2002):

$$CUR = \frac{W_2 - W_1}{T_2 - T_1} .$$

The second growth parameter used in the study was the Relative Growth Rate (RGR), termed as Relative Uptake Rate of zinc ($\mathrm{RUR}_{\mathrm{Zn}}$). It was calculated for any individual plant using the formula:

$$RUR = \frac{\ln W_2 - \ln W_1}{T_2 - T_1} ,$$

where:

CUR_{Zn} – crop zinc uptake rate, mg m^{-2} d^{-1};

RUR_{Zn} – plant zinc uptake rate, µg mg^{-1} d^{-1} per maize plant;

W_2, W_1 – yield of dry matter; or nitrogen uptake; or zinc uptake in two consecutive samplings; g, or mg, or µg per m^2, respectively;

T_2, T_1 – consecutive sampling, days after sowing (DAS).

The experimentally obtained data were subjected to conventional analysis of variance with least significant difference (LSD) values calculated at $P = 0.05$, and analysis of simple regressions.

RESULTS

Zinc accumulation patterns

Significant effect of zinc applied at early stages of maize growth on its own accumulation by plants was found in 8 out of 10 sampling dates (Figure 1). The general pattern of zinc accumulation, based on a quantitative factor, can be divided into two distinct time-phases. The first one extended from the stage of 7th leaf (BBCH 17) up to full flowering (BBCH 67), when Zn uptake by maize first exceeded 100 g Zn ha^{-1}. The second one extended from full flowering up to final maturity (BBCH 89). The first significant effect of fertilizer zinc was noted at the stage of 7th leaf. However, at this particular stage, the most important reason of enhanced zinc uptake was not the plant's biomass increase but a huge rise of Zn plant concentration (Table 1). Plants grown on the control plots contained about 35 mg Zn kg^{-1} DM, as compared to 87 mg Zn kg^{-1} DM for those fertilized with 1.0 kg Zn ha^{-1}. In the case of maize grown in the two other zinc treatments (i.e., 0.5 and 1.5 kg Zn ha^{-1}), Zn concentration was close to 80 mg kg^{-1} DM.

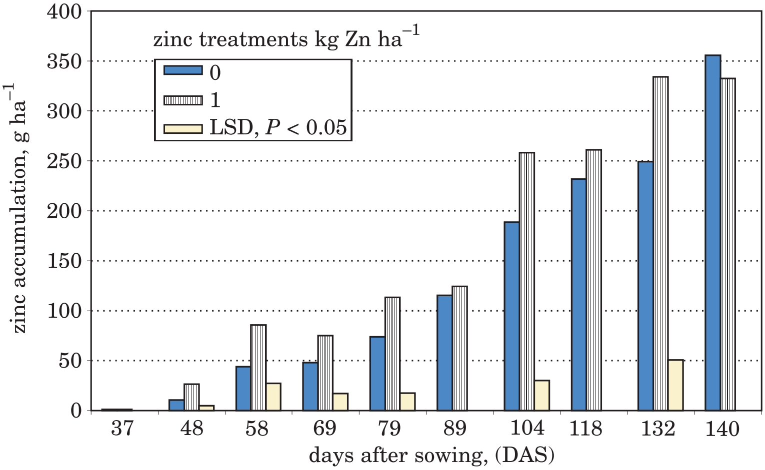


Fig. 1. Effect of zinc application on its total accumulation in the course of the vegetative season

Table 1

Effect of zinc rates on zinc concentration in maize leaves during vegetation, mean for 2002-2003 (mg kg^{-1} DM)

Growth stages (BBCH code)	Zinc treatments, kg ha^{-1}				LSD $P \leq 0.05$
	0.0	0.5	1.0	1.5	
17	34.9	79.9	86.9	76.7	10.78
19	29.4	45.9	67.1	43.4	13.02
39	20.6	25.1	24.9	29.0	3.26
59	21.5	23.5	33.0	35.3	5.29
67	19.1	15.8	19.9	20.8	2.65
75	19.4	21.8	20.3	21.3	–
83	11.0	13.4	15.2	20.2	3.12
87	12.3	16.3	15.1	16.0	–
89	15.6	11.7	10.6	10.4	3.52

In the second time-phase, extending from full flowering (BBCH 67) up to full milk grain maturity (BBCH 75), plants fertilized only with nitrogen increased zinc uptake by 163%. At the same time, plants fertilized with zinc at the rate 1.0 kg Zn ha^{-1}, almost doubled zinc accumulation, i.e., increased its uptake by 207%. Further increase was much lower and stage to stage variable among the treatments. However, the final uptake of zinc by plants grown in these two distinct zinc treatments was almost the same and did not show any significant differences. The general Zn uptake (U_{Zn}) trend over the whole reproductive phase of maize growth, in spite of stage to stage variability, can be described using the linear regression model:

1. Control: $U_{Zn} = 4.05DAS - 244.0$ for $R^2 = 0.91$; $n = 5, P \leq 0.01$
2. Zinc plots: $U_{Zn} = 3.87DAS - 189.1$ for $R^2 = 0.88$; $n = 5, P \leq 0.01$

where: DAS represents days from sowing

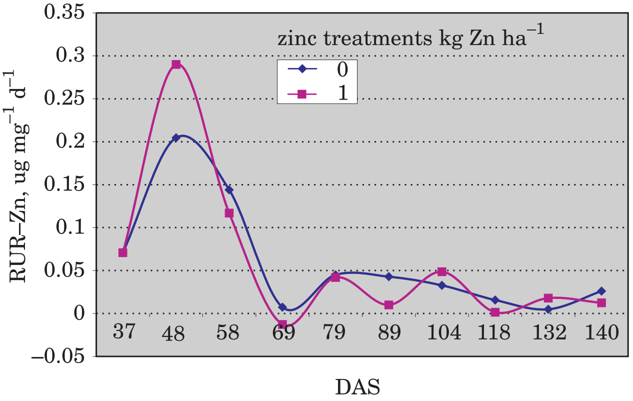


Fig. 2. Relative uptake rate of zinc by maize plants in the course of the vegetative season

The significant effect of zinc application on its own uptake was confirmed by the analysis of kinetics of its accumulation. As shown in Figure 2, for both treatments, the highest values of the Relative Uptake Rate of zinc (RUR_{Zn}) were found for the period extending from the stage of 7th to 9th leaf (BBCH17 to BBCH 19). At BBCH 17, the RUR_{Zn} for Zn-treated plants was 30% higher in comparison to the control ones. From this particular stage onwards, the studied parameter showed a declining trend, even reaching negative values for the Zn-fertilized plants. At tasselling, both groups of plants increased their RUR_{Zn} values, implying a signal of high requirements for zinc of newly growing organs or tissues. During the whole reproductive phase of maize growth, values of RUR_{Zn} were low and showed constant declining tendency, as was found for the control plot. However, plants treated with zinc showed smooth variability, raising the RUR_{Zn} at full milk stage of kernels growth (BBCH 75). The importance of this stage for maize general growth was confirmed by the analysis of Crop Uptake Rate of zinc (CUR_{Zn}). The calculated indices generally showed extremely high variability over the course of the growing season. However, at this particular stage, plants fertilized with zinc accumulated Zn at a rate of 900 mg $m^{-2}d^{-1}$, but those from the control treatments reached only 500 mg Zn m^{-2} d^{-1} (Figure 3).

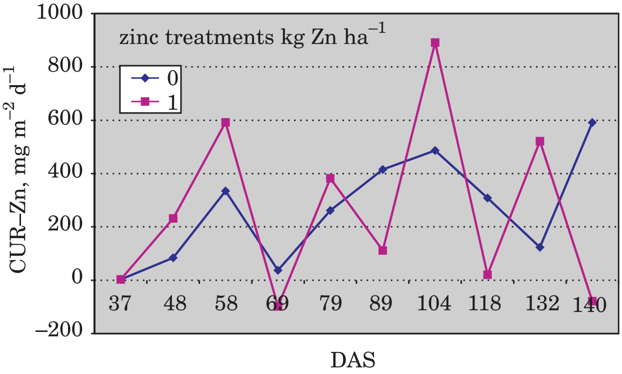


Fig. 3. Absolute uptake rate of zinc by maize crop in the course of the vegetative season

Structure of zinc accumulation

Four parts of maize plants were considered in order to evaluate the time course of zinc uptake and its partitioning. General structure of zinc partitioning among leaves, stems, cobs and kernels are shown in Figures 4a and 4b, for control and zinc treated plants, respectively. These two treatments were chosen as presenting completely distinct patterns of yield structure elements (Grzebisz et al., this issue).

Leaves require special attention due to their production and diagnostic functions. For 7 out of 9 samplings, in the course of the growing season, higher Zn concentrations were always noted for Zn-treated plants (Table 1). The highest Zn concentrations were found at vegetative stages of maize growth, i.e., from the stage of 7th leaf up to the stage of 9th leaf. From the stage of 9th leaf onwards, the concentrations of zinc in leaves showed a declining trend, best described by means of a quadratic function. Zinc concentration in plants fertilized with 1.0 and 1.5 kg Zn ha^{-1} reached the lowest values at the end of the vegetation. For plants grown on the control plot and fertilized only with 0.5 kg Zn ha^{-1}, the lowest concentrations were noted at the beginning of the dough stage of kernels growth. However, this specific behavior of leaves should not be treated as a classical exemplification of the *law of dilution*, because the total zinc content in leaves progressed up to full milk of kernels maturity (BBCH 75) – Figure 4a. It was observed from this particular stage onwards that the amount of zinc in leaves slightly declined while its quantity in grains increased remarkably. This quasi *leaf zinc dilution effect* reflects mainly the permanent process of maize leaf extension in the course of the growing season and could be termed as *internal zinc remobilization*. Therefore, leaves could not be treated as an important source of zinc for developing kernels. However, in the period from the stage of 9th leaf (BBCH 39) up to tasselling (BBCH 59) a high decrease in zinc content in leaves

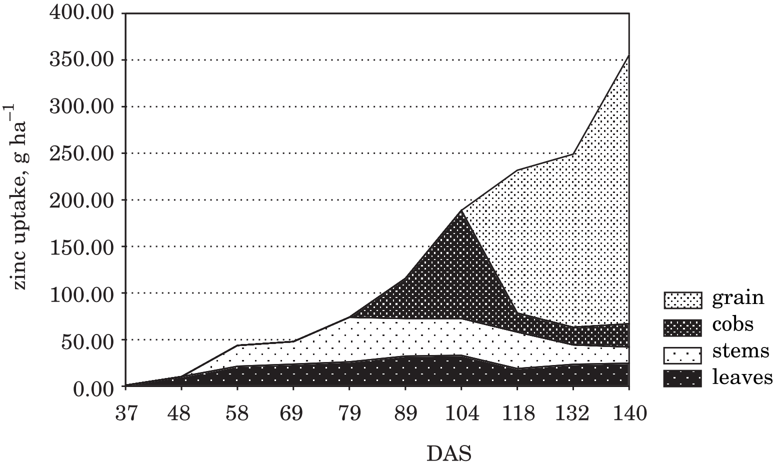


Fig. 4a. Redistribution of zinc among organs of maize in the course of the growing season – the zinc control (N)

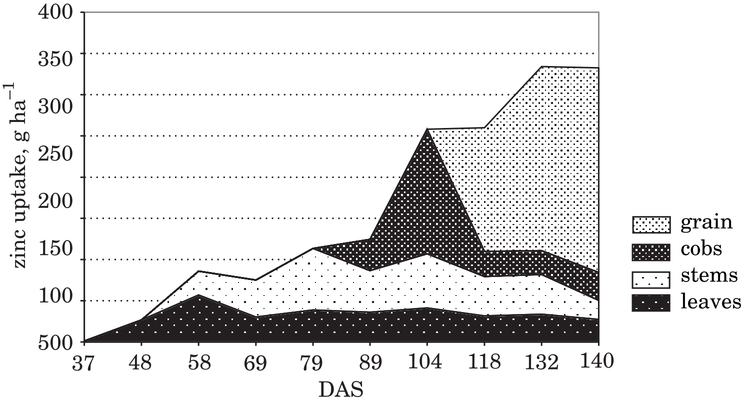


Fig. 4b. Redistribution of zinc among organs of maize in the course of the vegetative season – the zinc treatment (N+Zn)

and simultaneously sharp rise in stems occurred. This is the clearest indicator of zinc remobilization from leaves. It could be related to pollen production by tassels (Westgate et al. 2003).

Stems were a much more important source of zinc for developing reproductive organs, which reached the maximal Zn accumulation at tasselling (Figure 5b). From this particular stage of maize growth up to full maturity, the amount of zinc in these organs decreased by 50% in the case of plants grown in the zinc control treatment, and down to 40% for plants fertilized with zinc (1.0 kg ha^{-1}). It is necessary to point out that extended remobilization of this nutrient from vegetative organs occurred

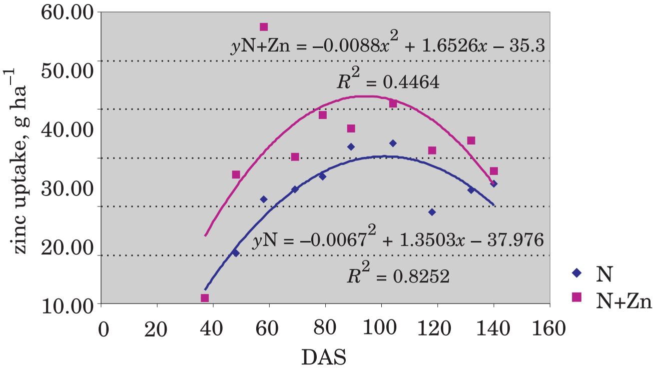


Fig. 5a. Dynamics of zinc accumulation by maize organs in the course of the vegetative season – leaves

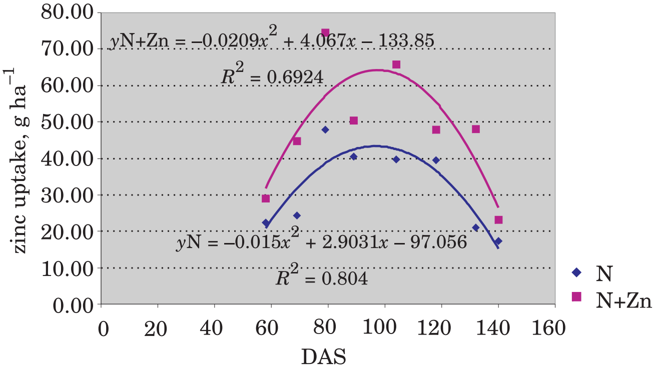


Fig. 5b. Dynamics of zinc accumulation by maize organs in the course of the vegetative season – stems

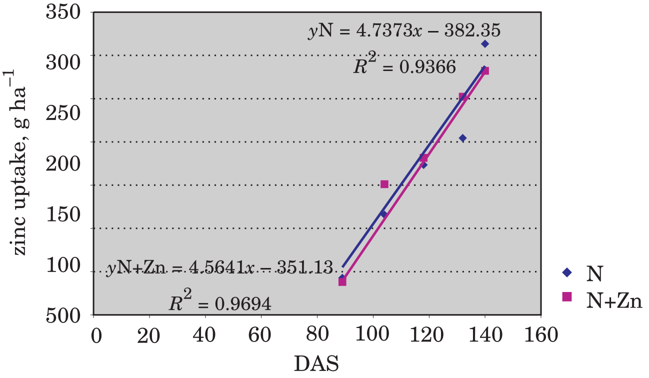


Fig. 5c. Dynamics of zinc accumulation by maize organs in the course of the vegetative season – cobs

at the beginning of the dough stage of kernels maturity. At this stage, zinc treated plants increased Zn uptake by 90 g ha^{-1}, whereas those grown on the control plot by *ca* 20 g Zn ha^{1}. However, plants from the latter treatment showed the same trend albeit one stage later, but without any effect on yield.

In general, both vegetative organs were only a minor source of zinc to growing kernels. During the reproductive phase of maize growth, soil was the main zinc source for plants. Therefore, at the grain filling period, irrespective of the studied treatment, maize plants showed extremely high requirements for zinc, as presented by the linear trend of accumulation in growing cobs (Figure 5c). Therefore, the patterns of zinc uptake by maize plants at the reproductive phase were generally very similar. Amounts of zinc taken up from soil resources by maize plants during this phase contributed to 76% and 66% of the total uptake by plants fertilized with N and N + Zn, respectively.

DISCUSSION

The main question of this study is when and how zinc fertilizer applied to maize foliage affects its yield. In order to obtain a reliable answer to these questions, the study focused mainly on patterns from two quite distinct treatments, i.e., zinc control, which relates to standard farmer's practice and the 1.0 kg Zn ha^{-1} treatment as a new optimum standard (GRZEBISZ et al. this issue). As recorded by WROŃSKA et al. (2007), the optimal timing for zinc application to maize foliage extends from BBCH 0 to BBCH 17. Maize plants well supplied with zinc at this particular stage have significantly increased the number of kernels per ear and in turn grain yield.

The second question refers to the practical importance of zinc application to maize plants cultivated on soils rich in available zinc (an assessment based on DTPA extract, LINDSAY 1978). The current study revealed that in spite of high zinc availability maize plants responded to fertilizer zinc and yielded 10-20% higher that those cultivated without zinc (GRZEBISZ et al. this issue, FECENKO, LOZEK 1998, WROŃSKA et al. 2007 and POTARZYCKI, personal communication). The maize crop response to fertilizer zinc determined in our study implicates a problem of soil and plant tests reliability. According to SCHULTE and KELLING (2000), the optimum Zn concentration range in maize leaves at the stage of 7th leaf (BBCH 17) is 20–
–60 mg kg^{-1}. The data obtained in the current experiment indicate that only plants grown without zinc fertilizer dressing were within this range. However, the highest grain yield was related to Zn leaf concentration above 80 mg kg^{-1} and referred to the Zn rate of 1.0 kg Zn ha^{-1}. Therefore, the present indices of soil and maize plant nutritional zinc status need to

be revised urgently. Maize crop requirements for zinc are much higher and at the time much more sophisticated than those currently recommended to farmers.

These specific patterns of zinc accumulation by maize plants, as described by the two uptake kinetic parameters such as RUR and CUR, clearly stress the importance for this crop *hot yield responsive phases*, which are time interrelated. The first one, which could be termed *primary*, stresses two facts (i) the highest requirement for zinc at early stages of maize development (ii) and its extra extension due to external supply of zinc. The relative uptake rate of zinc (RUR) by any individual maize plant treated with fertilizer zinc increased by 30%, and was the best indicator for zinc requirement of newly growing maize organs. This can be related to the stage of ovules initiation in developing cobs. The outlined hypothesis is supported by the current physiological data (ELMORE, ABENDROTH 2006). According to the authors, these stages of maize growth are very important and even decisive for building up potential numbers of ovules per row and per cob. Hence, the physiological role of zinc can be related to the potential increase of the number of ovules per cob, which is a prerequisite of kernel sink size during grain filling. The second *hot phase*, which could be termed *secondary*, but a major one, occurred at full milk grain maturity and is considered to reflect the size capacity of kernels for carbohydrates. The third one, minor, took place at tasselling, as indicated by a sharp rise of zinc concentration in the stem and was probably responsive to pollens production (WESTGATE et al. 2003).

Leaf longevity is of great importance for maize kernel weight as a factor responsible for production of carbohydrates (RAJCAN, TOLLENAAR 1999, POMMEL et al. 2006). The effects of fertilizer zinc on kernels sink capacity for carbohydrates were confirmed by generally higher thousands kernels weight (TKW). According to GULIEV et al. (1992), maize plants well supplied with zinc expresses higher activity of carbonate anhydrase, which is turn is responsible for the photosynthetic activity of leaves.

CONCLUSIONS

1. Maize plants showed the highest sensitivity to zinc at three different stages of growth, (i) from 7 to 9th leaf stage (ii) at tasselling (iii) during milk stage of kernels growth.

2. These three critical phases of kernels yield formation are a key to increasing the yielding potential of maize.

3. Vegetative organs of maize were only minor sources of zinc for growing kernels; the majority of zinc in kernels was taken up by maize plants during grain filling, directly from the soil.

4. Both soil and plant tests generally overestimate the actual zinc nutritional status of maize. Therefore, revision of such tests is urgently needed.

REFERENCES

ELMORE R., ABENDROTH L. 2006. *To be determinated: ear row numbers and kernels per row in corn.* Integrated Crop Management, IC-496, 151-152.

FECENKO J. LOŽEK O. 1998. *Tvorba úrody zrna kukurice v závislosti od aplikovaných dávok zinku a jeho obsahu v pôde.* Rostlinná Výroba, 44 (1) 15-18.

GRUSAK M.A., PEARSON J.N., MARENTES E. 1999. *The physiology of micronutrient homoestasis in field crops.* Field Crops Res., 60: 41-56.

GRZEBISZ W., WROŃSKA M., DIATTA B., 2008. *Effect of zinc foliar application on maize grain yield and its yielding components.* J. Elementol., 13 (1): 17-28.

GULIEV N., BAIRAMOV S., ALIEV D. 1992. *Functional organization of carbonic anhydrase in higher plants.* Sov. Plant Physiol., 39: 537-544.

HUNT R., CAUSTON D.R, SHIPLEY B., ASKEW A.P. 2002. *A modern tool for classical plant growth analysis.* Ann. Bot., 90: 485-488.

MARSCHNER H. 1986. *Mineral Nutrition in Higher Plants.* Academic Pres, pp. 300-312.

MURREL T.S. CHILDS F.R. 2000. *Redefining corn yield potential*. Better Crops, 80 (1): 33-37.

POMMEL B., GALLAI A., COQUE M., QUILLERE I., HIREL B., PRIOUL J.L., ANDRIEU B., FLORIOT M. 2006. *Carbon and nitrogen allocation and grain filling in three maize hybrids differing in senescence*. Europ. J. Agronomy 24: 200-211.

RAJCAN I., TOLLENAAR M. 1999. *Source: sink ratio and leaf senescence in maize:* I. *Dry matter accumulation and partitioning during grain filling.* Field Crops Res., 60: 245-253.

SCHULTE E.E., KELLING K.A. 2000. *Plant analysis*: *A diagnostic tool.* UW-M, www.ces.purdue.edu/extmedia/NCH/NCH-46.html.

SILLANPAA M. www.iza.com/zwo_org/Publications/ZincProtects/ZP1108/110808.htm

WESTGATE, M.E., LIZASO J., BATCHELOR W. 2003. *Quantitative relationships between pollen shed density and grain yield in maize.* Crop Sci., 43: 934-942.

WROŃSKA M., GRZEBISZ W., POTARZYCKI J., GAJ R. 2007. *Reakcja kukurydzy na nawożenie azotem i cynkiem.* Cz. I. *Plon i struktura plonu.* Fragm. Agronom., 2 2(94): 390-399.

J. Elementol. 2008, 13(1): 29–39

EFFECT OF ZINC FOLIAR APPLICATION AT AN EARLY STAGE OF MAIZE GROWTH ON PATTERNS OF NUTRIENTS AND DRY MATTER ACCUMULATION BY THE CANOPY

Part II. Nitrogen uptake and dry matter accumulation patterns

Witold Grzebisz[1], Małgorzata Wrońska[2], Jean B. Diatta[1], Witold Szczepaniak[1]

[1]Department of Agricultural Chemistry, University of Agricultural Sciences, Poznań, Poland
[2]Agencja Rezerw Materiałowych, 00-400 Warszawa, ul. Nowy Świat 6/12, Poland

Abstract

A two-year field trial was carried out in order to outline reasons of maize grain yield increase due to foliar application of zinc, and to evaluate its effects on the dynamics of nitrogen and dry matter accumulation in the course of the growing season. Growth analysis methods were applied to describe the trends exhibited by the canopy and plant's growth. Maize plants fertilized with zinc were able to increase the rate of nitrogen uptake, as indicated by the values of absolute crop uptake rate for N (CUR-N), at two distinct time-separated phases of growth, i.e., (i) from 7th to 9th leaf and (ii) from milk to physiological maturity of kernels growth. Physiological processes occurring in these two time-separated phases resulted in an increase of maize yielding capacity. The effect of zinc as recorded in the first phase resulted in extension rate of new organs or tissues ingrowth, as confirmed by the RGR analysis. At the reproductive phase of maize growth, plants well supplied with zinc accumulated more nitrogen, which was a prerequisite for significantly higher rate of dry matter accumulation, as confirmed both by CGR and RGR analyses. The amount of extra nitrogen taken up by Zn treated plants was sufficiently high to increase grain yield by 1.5 t ha^{-1}, which was achieved in the conducted experiment.

---

prof. dr hab. Witold Grzebisz, Department of Agricultural Chemistry, University of Agricultural Sciences, ul. Wojska Polskiego 71F, 60-625 Poznań, Poland, e-mail: witegr@au.poznan.pll

Key words: growth analysis, absolute crop growth rate (CGR), relative plant growth rate (RGR), maize, nitrogen, dry matter.

Wpływ dolistnego stosowania cynku we wczesnej fazie wzrostu kukurydzy na wzorce akumulacji składników pokarmowych i suchej masy przez łan

Cz. II. Wzorce pobierania azotu i akumulacji suchej masy

Abstrakt

Dwuletnie doświadczenie polowe przeprowadzono w celu wyjaśnienia przyczyn wzrostu plonu ziarna kukurydzy dolistnie traktowanej nawozem cynkowym i oceny jego wpływu na dynamikę procesów akumulacji azotu i suchej masy w okresie wegetacji. Do opisu uzyskanych trendów zastosowano metody analizy wzrostu łanu i rośliny. Kukurydza nawożona cynkiem była w stanie, jak wykazały wartości wskaźnika absolutnej szybkości pobierania azotu przez łan (CUR-N), zwiększyć pobieranie azotu w dwóch czasowo różnych fazach rozwoju, to znaczy (i) od fazy 7. do 9. liścia oraz (ii) od fazy dojrzałości mlecznej do fizjologicznej ziarniaków. Procesy fizjologiczne ujawniające się w tych dwóch czasowo odległych fazach rozwoju kukurydzy determinowały wzrost potencjału produkcyjnego kukurydzy. Działanie cynku w pierwszej fazie przejawiło się wzrostem szybkości akumulacji azotu, który spowodował wydłużenie fazy intensywnego przyrostu nowych tkanek lub/i organów, jak potwierdziła analiza RGR. W fazie reproduktywnej rozwoju kukurydzy rośliny dobrze odżywione cynkiem akumulowały azot z większą szybkością, co było podstawowym warunkiem zwiększonej akumulacji suchej masy, potwierdzonej analizami CGR i RGR. Ilość azotu pobranego ekstra przez rośliny nawożone cynkiem była dostatecznie duża do wzrostu plonu ziarna o 1,5 t ha^{-1}, co uzyskano w przeprowadzonym eksperymencie.

Słowa kluczowe: analiza wzrostu, absolutna szybkość wzrostu łanu, względna szybkość wzrostu łanu, kukurydza, sucha masa, azot.

INTRODUCTION

Agricultural production is under permanent pressure of abiotic and biotic stresses, negatively affecting plant crops growth and yields (MITTLER 2006). On the other hand, the inefficient use of nitrogen fertilizers is of great concern to the environment and human health (CAKMAK 2002, TOWNSEND et al. 2003). Maize requirements for nutrients, in spite of its high yielding potential, are comparable to other cereals (STURM et al. 1994). The decisive effect of nitrogen on plant growth and yielding of cereal crops is well known. However, nitrogen recovery efficiency of maize in farm production is generally low, in the range from 20 to 40% (ROBERTS 2006). This finding is supported by scientifically developed *production functions for nitrogen*, which stresses a moderate scale of maize response to the applied fertilizer N. This syndrome of maize response to nitrogen is termed as *the smooth reaction* (FOTYMA 1994).

In the light of great challenges and simultaneous low utilization of fertilizer nitrogen, the main target to maize growers is to search for factors which may increase both the uptake and utilization-efficiency of the applied fertilizer N. The actual yield increase of crop plants, including maize, can be therefore achieved by ameliorating the factors decisive for nitrogen use efficiency (SINCLAIR et al. 2004, ROBERTS 2006). Among micronutrients, zinc plays a great metabolic effect on plant economy and nitrogen efficiency, as has been recognized by plant biochemists and physiologists (MARSCHNER 1986, CAKMAK 2002).

The harvested yield of a given crop plant, including maize, and its yield components reflect, but only *ex post*, conditions of dry matter accumulation over the growing season (RAJCAN, TOLLENAAR 1999). Therefore, the plant growth analysis seems to be a reliable scientific tool for discriminating the most sensitive stages of maize plants growth to external factors, including supply of nutrients, for example zinc. Unfortunately, the quantitative effects of Zn on maize yielding physiology are poorly recognized.

The objective of the present studies was to determine the effects of foliarly applied zinc on nitrogen and dry matter accumulation dynamics over the course of maize crop growth.

MATERIAL AND METHODS

The general design and experimental details of this study are reported by GRZEBISZ et al., (Part I, this issue). Plants growth analysis was applied as an analytical tool in order to explain the quantitative effect of zinc on dry matter accumulation by maize. Two kinetic parameters of crop growth were calculated, i.e., absolute Crop Growth Rate (CGR) and Relative Growth Rate (RGR). In the same way, kinetic parameters of nitrogen uptake were calculated for nitrogen: absolute crop uptake rate – CUR_N and relative uptake rate – RUR_N. Both parameters express growth rate on a daily basis, but the former one - per unit area whereas the latter one outlines growth as an aspect of new dry matter increase per plant (HUNT et al. 2002). For details see GRZEBISZ et al. (2008).

RESULTS

Nitrogen accumulation patterns

It has been assumed that dry matter yield and the rate of its accumulation depends directly on nitrogen supply. Therefore, patterns of nitrogen accumulation were investigated in detail over the course of maize growth in the growing season. In all consecutive stages of growth, beginning at the stage of 9th leaf, higher amounts of nitrogen were recorded in plants grown in the Zn-fertilized treatments. However, in only 2 out of 10 stages of maize growth we analyzed, i.e., at the beginning of dough maturity and at the final maturity, the effect of zinc application was significant (Figure 1). At these two particular stages, the application of 1.0 kg Zn ha^{-1} increased N uptake by 39.0 kg ha^{-1} and 46.4 kg N ha^{-1}, respectively, versus the control. In addition, during these two consecutive reproductive stages, plants progressed nitrogen uptake, irrespective of the experimental treatments. Nitrogen uptake by maize plants grown on the control plots increased from 150.0 to 202.5 kg ha^{-1} and on the plots fertilized with 1.0 kg Zn ha^{-1}, from 188.3 to 248.9 kg ha^{-1}. Hence, it can be concluded that maize crop accumulated nitrogen progressively to the end of its growth. Nitrogen accumulation trends over the course of the growing season followed the linear regression model:

1. Zn control $U_N = 2.05DAS - 89.13$ $R^2 = 0.96$; $n = 10$, and $P \leq 0.001$
2. Zn treatment $U_N = 2.54DAS - 114.55$ $R^2 = 0.97$; $n = 10$, and $P \leq 0.001$

where:

U_N – nitrogen uptake, kg N ha^{-1};
DAS – days after sowing.

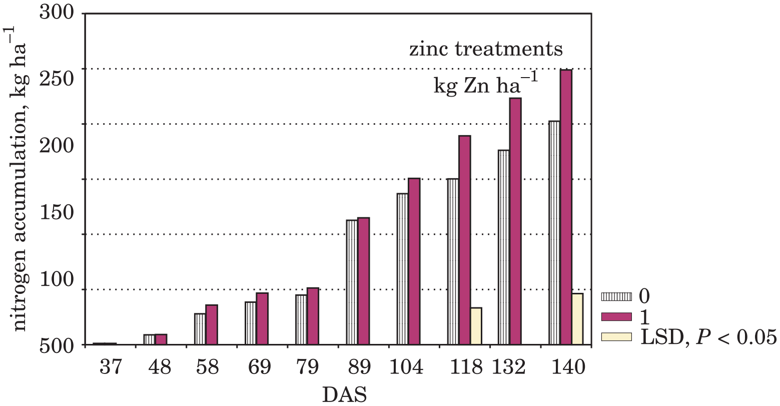


Fig. 1. Effect of zinc application on nitrogen accumulation by maize in the course of the growing season

Plants fertilized with zinc showed a much higher rate of nitrogen accumulation, as indicated by the direction coefficients of the equation developed for Zn treatment.

Plants treated with zinc at the early stage of maize growth have significantly accelerated their rate of nitrogen accumulation. A very distinct shape of curves describing parameters of crop uptake rate for nitrogen (CUR_N) was determined. As shown in Figure 2, the most critical time-point of maize plant nitrogen economy was the onset of flowering. Within a period of 10 days, from tasselling till full flowering, amounts of nitrogen accumulated by maize plants have almost doubled (Figure 1). This high increase was attributed to a manifold increase of CUR_N, from *ca* 50 to 650 g m^{-2} d^{-1}, irrespective of the experimental treatments. However, effects of zinc were found in two significant stages of maize growth. The first one, minor, appeared at the stage of 9th leaf, whereas the second one, considered major, started at the beginning of full milk maturity and extended up to the physiological maturity of maize. The rate of nitrogen accumulation by Zn-treated plants, estimated on the basis of CUR_N, was higher than on the control plot, by 48% at full milking stage, 88% at the beginning of the dough maturity and 31% at physiological maturity. However, the relative uptake rate values for N (RUR_N) did not show any differences in the rate of nitrogen accumulation by maize plant due to the experimental treatments (Figure 3). Nevertheless, two main *hot points* of nitrogen uptake patterns were discriminated on the basis of RUR_N parameters. The first one, major, appeared from the stage of 7th to 9th leaf and the second one, minor, occurred from tasselling (BBCH 59) to full flowering (BBCH 67).

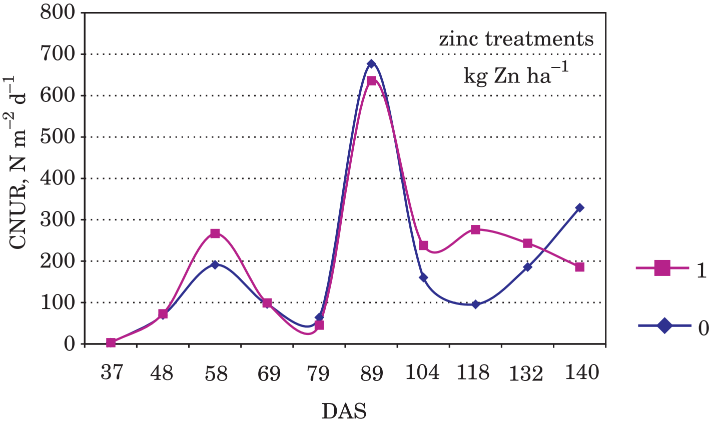


Fig. 2. Effect of zinc application on absolute nitrogen uptake rate by maize crop in the course of the growing season

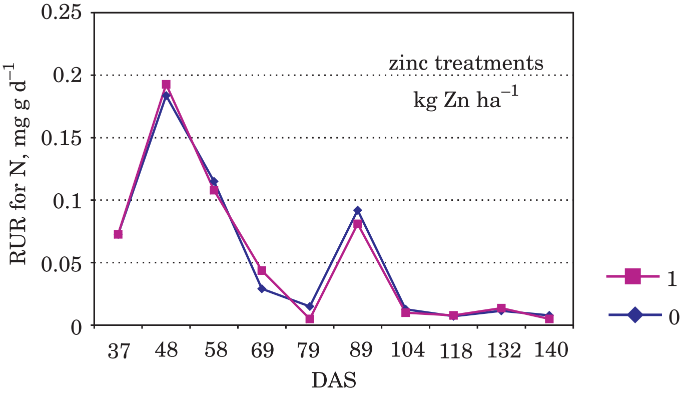


Fig. 3. Effect of zinc application on relative nitrogen uptake rate by maize crop in the course of the growing season

Dry matter accumulation patterns

The yields of dry matter of maize crop increased progressively over the growing season, reaching maximum at full maturity (BBCH 89) for both studied treatments (Figure 4). Zinc stimulated the accumulation of dry matter since the stage of 9th leaf (BBCH 19), although a significant effect was noticed first at the stage of full milking growth of kernels (BBCH 75). Dry matter accumulation by plants increased progressively in all the consecutive stages of growth, but an especially high rise was observed from flowering (BBCH 67) to the beginning of dough kernels maturity (BBCH 83).

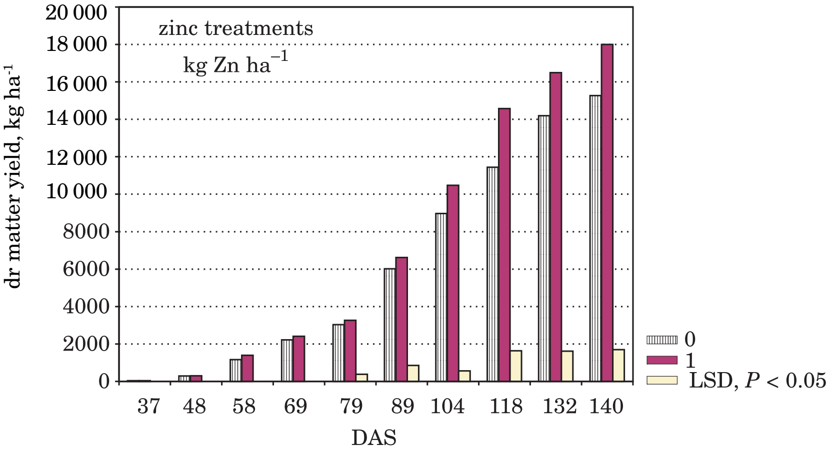


Fig. 4. Effect of zinc application on dry matter accumulation by maize in the course of the growing season

The rate of dry matter accumulation by maize, as expressed by crop growth rate parameters (CGR), achieved its maximum at full flowering (BBCH 67) – Figure 5. During a period of 10 days, i.e., from tasselling to full flowering, plants increased almost 4-fold their rate of growth, irrespective of the studied treatments. This increase is time-related to the rise of RUR_N, reflecting a huge rate of new tissue ingrowth. In the period of 4 weeks following tasselling, plants fertilized with zinc accumulated dry matter yield at a much higher rate than those grown on the control plot, i.e., without external zinc supply. The CGRs values of Zn-treated plants were higher at full flowering by 25%, at milk maturity by 31%, and at the beginning of dough maturity by 65%, as compared to the control plants. These data clearly stress higher *sink* potential of zinc fertilized plants to accumulate carbohydrates by developing kernels.

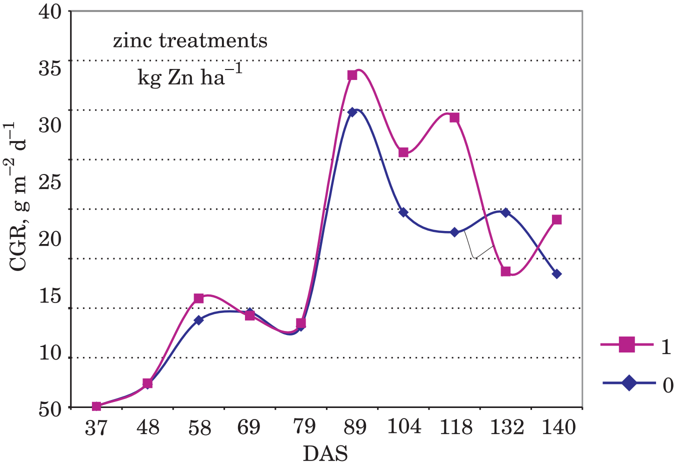


Fig. 5. Effect of zinc application on absolute crop dry matter growth by maize crop in the course of the growing season

The analysis of maize growth by means of relative growth rate (RGR) parameters revealed that zinc application stimulated dry matter accumulation in two distinct growth periods (Figure 6). Generally, an individual plant expressed its own highest rate of growth at the stage of 7th leaf, followed by a gradual decline, reaching the lowest values at maturity. However, plants fertilized with 1.0 kg Zn ha^{-1}, were able to keep the highest rate of growth during the next 10 days following the stage of 7th leaf. At the stage of 9th leaf, Zn-treated plants accumulated dry matter 3-fold faster than those grown on the control plot. An identical trend, albeit less pronounced, was found during the full milk stage of maize growth.

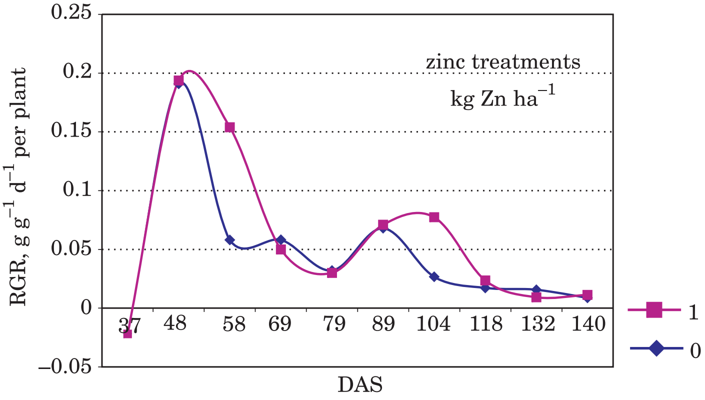


Fig. 6. Effect of zinc application on relative growth rate of maize plant in the course of the growing season

DISCUSSION

The main concept regarding the actual yield of maize crop is considered by plant physiologists as a ratio between *sink size*, i.e., an ability of a developing cob to accumulate assimilates, and *source size*, supply of nitrogen and assimilates as well (Uhart, Andrade 1995, Cazetta et al. 1999). Jones et al. (1996) reported that two plant characteristics, i.e., kernel number (per) plant (KNP) and plant growth rates, in the period of 4 weeks, beginning one week before silking, are decisive for establishing the final grain yield of maize. This statement is in close agreement with the results obtained in our study and reflects the processes responsible for cob sink capacity build up during preanthesis and postanthesis cob growth.

The main difference between the maize treatments studied occurred first in the vegetative phase of maize growth, around the stage of 7th leaf. At this particular stage, plants well supplied with zinc (i.e., 1.0 kg Zn ha^{-1}) increased zinc concentration in leaves 2.5-fold in comparison to the control ones, i.e. fertilized only with nitrogen (Grzebisz at al. 2008). Consequently, maize plants fertilized with zinc accelerated (i) the uptake rate of nitrogen (ii) and new biomass ingrowth. But both processes were not conducted by plants simultaneously. The increased plant uptake rate of zinc and nitrogen took place at the same stage of maize growth, i.e., at the 7th leaf. At this particular stage, plants fertilized with zinc increased uptake rate of nitrogen in comparison to the control plants by 40%. Consequently, these plants were in position to continue their very high growth rate (RGR), i.e. ingrowth of new biomass up to the stage of 9th leaf. The high dependency of the relative uptake rate for nitrogen – RUR_N (y) on the relative supply of zinc – RUR_{Zn} (x) was confirmed by the linear type relationships:

1. Zn control $y = 0.85x + 0.005$ $R^2 = 0.86$ $n = 10$; $P \leq 0.01$
2. Zn treatment $y = 0.59x + 0.019$ $R^2 = 0.76$ $n = 10$; $P \leq 0.05$

The specific plant responses to zinc we discovered had a significant effect on plant growth in consecutive growth stages, appearing again during the reproductive phase, from flowering up to full milking stage of kernels. Hence, the physiological role of zinc can be related to the potential increase of the number of ovules per cob, as related to current nitrogen supply, indicated by the CUR data for nitrogen. This particular stage for a growing maize plant is decisive for the ovules in row formation (ELMORE, ABENDROTH 2006). This hypothesis is supported by SUBEDI, MA (2005), who found that nitrogen deficiency before BBCH 18 (stage of 8th leaf) resulted in decreasing cob length and number of kernels per cob.

In addition, there was a tremendous increase in the uptake rate of zinc followed the highest values of CUR for N, which occurred at full anthesis. Therefore, plants well supplied with zinc in the vegetative growth period were able to accumulate more nitrogen in the most critical stage of kernels development, i.e., 2 weeks after pollination. At that time, the availability of nitrogen is decisive for division of endosperm cells and initiation of starch granules (JONES at al. 1992). At these particular stages, maize plants well supplied with nitrogen significantly increased the absolute rate of nitrogen uptake from soil resources. At the final maturity, these plants accumulated *ca* 46 kg N ha^{-1} more than those grown on the control plot, i.e., fertilized only with N. Based on the specific uptake of nitrogen as 20 or 30 kg N per 1 tone of kernels with appropriate amounts of straw (WICHMANN 1996/2006), one may calculate the yield increase, which in this particular case was up to 2.32 and 1.55 t ha^{-1}, respectively, due to higher zinc availability.

The plant behavior we observed should not be related to the current Zn uptake but to increased kernels sink capacity, established at preanthesis stages of maize plants growth. These processes progressed efficiently under non-limited availability of nitrogen. Another aspect of our experiments refers to leaf longevity, a factor of great importance for maize kernel rate of growth and final weight (RAJCAN, TOLLENAAR 1999, POMMEL et al. 2006). Higher uptake of nitrogen by Zn-treated plants was probably a prerequisite of higher longevity of maize leaves, which in turn were capable to increase their rate of photosynthesis (GULIEV et al. 1992.

CONCLUSIONS

1. Zinc fertilizer application at an early stage of maize growth accelerated the plant rate of zinc accumulation at the stage of 7th leaf, and,

in turn, increased the rate of crop nitrogen uptake, a factor decisive to the formation of ovules, i.e., potential kernels number per row.

2. At the reproductive phase of maize growth, plants well supplied with zinc accumulated more nitrogen at the most critical stages of kernels development, just 2 weeks after pollination, which is crucial for both the vitality (number) and the size of an individual kernel.

3. The main reason of higher uptake of nitrogen by plants well supplied with zinc was probably extended longevity of leaves, producing in turn enough carbohydrates to supply developing kernels.

4. Modern maize cultivars of high yielding potential, even cultivated on soils rich in available zinc, may respond significantly to fertilizer zinc, increasing grain yield even up to 20%.

REFERENCES

CAKMAK I. 2002. *Plant nutrition research: Priorities to meet human needs for food in sustainable ways.* Plant Soil, 247: 3-24.

CAZETTA J.O. SEEBAUER J.R., BELOW F.E. 1999. *Sucrose and nitrogen supplies regulate growth of maize kernels.* Ann. Bot., 84: 747-754.

ELMORE R., ABENDROTH L. 2006. *To be determinated: ear row numbers and kernels per row in corn.* Integrated Crop Management, IC-496, 151-152.

FOTYMA E. 1994. *Crop plants response to nitrogen fertilization.* Part III. *Maize.* Fragm. Agronom., 4 (44): 21-34, (in Polish).

GRZEBISZ W., WROŃSKA M., DIATTA B., DULLIN P. 2008. *Effect of zinc foliar application at the early stage of maize growth on the patterns of nutrients and dry matter accumulation by the canopy.* Part I. *Zinc uptake patterns and its redistribution among maize organs.* J. Elementol., 13(1): 17-28.

GULIEV N., BAIRAMOV S., AD ALIEV D. 1992. *Functional organization of carbonic anhydrase in higher plants.* Sov. Plant Physiol., 39: 537-544.

HUNT R., CAUSTON D.R., SHIPLEY B., ASKEW A.P. 2002. *A modern tool for classical plant growth analysis.* Ann. Bot., 90: 485-488.

JONES R.J., SCHREIBER B.M.N., ROESSLER J.A. 1996. *Kernel sink capacity in maize: Genotypic and maternal regulation.* Crop Sc., 36: 301-306.

MARSCHNER H. 1986. *Mineral nutrition in higher plants.* Acad. Pres, pp. 300-312.

MITTLER R. 2006. *Abiotic stress, the field environment and stress combination.* Trends Plant Sci., 11: 15-19.

POMMEL B., GALLAI A., COQUE M., QUILLERE I., HIREL B., PRIOUL J.L., ANDRIEU B., FLORIOT M. 2006. *Carbon and nitrogen allocation and grain filling in three maize hybrids differing in senescence.* Europ. J. Agronomy, 24: 200-211.

RAJCAN I., TOLLENAAR M. 1999. *Source: sink ratio and leaf senescence in maize:* I. *Dry matter accumulation and partitioning during grain filling.* Field Crops Res., 60: 245-253.

ROBERTS T. 2006. *Improving nutrient use efficiency*. In: Proc. of the IFA Agriculture Conference: *Optimizing resource use efficiency for sustainable intensification of agriculture.* 27 February–2 March, 2006. Kunming, China, pp 8.

SINCLAIR T.R., PURCELL L.C., SNELLER C.H. 2004. *Crop transformation and the challenge to increase yield potential.* Trends Plant Sci., 9 (2) 70-75.

STURM H., BUCHNER A., ZERULLA W. 1994. *Gezielter Duengen.* DLG Verlag, pp. 319-326.

SUBEDI K.D., MA B.L. 2005. *Nitrogen uptake and partitioning in stay-green leafy maize hybrids.* Crop Sci., 45: 740-747.

TOWNSEND A. et al. 2003. *Human health effects of a changing global nitrogen cycle*. Front Ecol. Environ., 1(5): 240-246.

UHART S.A., ANDRADE F.H. 1995. *Nitrogen and carbon accumulation and remobilization during grain filling in maize under different source/sink ratio.* Crop Sci., 35: 183-190.

WICHMANN W. 1996/2006. World Fertilizer Use Manual IFA, Paris, France.

J. Elementol. 2008, 13(1): 41–56

EFFECT OF LONG-TERM VARIOUS MINERAL FERTILIZATION AND LIMING ON THE CONTENT OF MANGANESE, NICKEL AND IRON IN SOIL AND MEADOW SWARD

Krzysztof Gondek, Michał Kopeć

Department Agricultural Chemistry
Agricultural University in Cracow

Abstract

Research on grasslands is conducted to assess the yielding potential and determine changes of sward quality depending on applied fertilization. Therefore, the present study was undertaken to assess the contents of manganese, nickel and iron in soil and meadow sward shaped under the influence of diversified mineral fertilization and liming. The experiment is established in the village Czarny Potok near Krynica, about 720 m above sea level., at the foot of Mount Jaworzyna Krynicka. The experiment was set up in 1968 on a natural mountain meadow of mat-grass (*Nardus stricta* L.) and red fescue (*Festuca rubra* L.) type with a large share of dicotyledonous plants. Total content of manganese, nickel and iron was determined in the plant and soil material after sample mineralization in a muffle furnace. The studied were extracted with 0.025 mol·dm^{-3} NH_4EDTA solution and the content of Mn, Ni and Fe in the solutions was assessed with the ICP-AES method. The content of total forms of manganese was higher in the soil of the limed series. The soil reaction significantly affected amounts of this element extracted with NH_4EDTA solution. Soil liming limited manganese bioavailability and improved the forage value of the analyzed biomass. Small quantities of nickel bound to the soil organic substance were found in the analyzed soil, which suggested considerable mobility of this elements and its translocation into deeper levels of the soil profile, beyond the reach of the plant root system. Liming increased the content of iron forms in combinations with the soil organic substance. Iron deficiency in the meadow sward may have a physiological basis such as difficult iron transport from the root system to aerial plant parts, but it was not caused by limited iron uptake from soil.

Key words: manganese, nickel, iron, soil, meadow sward, long term experiment.

Krzysztof Gondek, PhD, Michał Kopeć, PhD, DSc., al. Mickiewicza 21, 31-120 Crakow, Poland

WPŁYW DŁUGOTRWAŁEGO ZRÓŻNICOWANEGO NAWOŻENIA MINERALNEGO I WAPNOWANIA NA ZAWARTOŚĆ MANGANU, NIKLU I ŻELAZA W GLEBIE I RUNI ŁĄKOWEJ

Abstrakt

Badania na użytkach zielonych są prowadzone m.in. w celu wyznaczenia potencjału plonowania oraz określenia zmian jakości runi w zależności od zastosowanego nawożenia. Dlatego celem podjętych badań było określenie zawartości manganu, niklu i żelaza w glebie oraz runi łąkowej ukształtowanej pod wpływem zróżnicowanego nawożenia mineralnego i wapnowania. Doświadczenie jest zlokalizowane w Czarnym Potoku k. Krynicy, na wysokości ok. 720 m n.p.m., u podnóża Jaworzyny Krynickiej. Doświadczenie założono w 1968 r. na naturalnej łące górskiej typu bliźniczki – psiej trawki (*Nardus stricta* L.) i kostrzewy czerwonej (*Festuca rubra* L.) ze znacznym udziałem roślin dwuliściennych. Zawartość ogólną manganu, niklu i żelaza w materiale roślinnym i glebowym oznaczono po mineralizacji próbek w piecu muflowym, ponadto wykonano ekstrakcję badanych pierwiastków roztworem NH_4EDTA o stężeniu 0,025 $mol \cdot dm^{-3}$. W uzyskanych roztworach zawartość Mn, Ni i Fe wykonano metodą ICP-AES. Zawartość ogólnych form manganu była większa w glebie wapnowanej, a istotny wpływ na ilość tego pierwiastka wyekstrahowanego roztworem NH_4EDTA oraz jego zawartość w runi miał odczyn gleby. Wapnowanie gleby ograniczając dostępność manganu dla roślin poprawiło wartość paszową analizowanej biomasy. W badanej glebie oznaczono niewiele niklu związanego z substancją organiczną gleby. Świadczy to pośrednio o dużej mobilności tego pierwiastka i jego przemieszczaniu do głębszych poziomów profilu glebowego, poza zasięg systemu korzeniowego roślin. Wapnowanie zwiększyło zawartość form żelaza w połączeniach z substancją organiczną gleby. Niedoborowa zawartość żelaza w runi łąkowej może mieć podłoże fizjologiczne związane z trudnościami w transporcie żelaza z systemu korzeniowego do organów nadziemnych roślin, a nie wynikać z możliwości jego pobierania z gleby.

Słowa kluczowe: mangan, nikiel, żelazo, gleba, ruń łąkowa, doświadczenie długotrwałe.

INTRODUCTION

Progressing industrialization and urbanization as well as changes in fertilization systems can be responsible for potential excess of trace elements in soil and plants. Fertilization is an important factor which modifies soil abundance in trace elements. With fertilizers we introduce some trace elements to the soil and modify their availability through changes of soil properties, mainly soil reaction, as well as changes in the content and composition of soil humus.

Trace elements can be beneficial to living organisms, including plants, but they may also be a cause of disturbances in physiological processes and metabolism in plants (RUSZKOWSKA, WOJCIESZKA-WYSKUPAJTYS 1996). As a result of the unfavourable influence of trace elements on plants, disorder in the uptake, transport and assimilation of some macroelements may occur (BURZYŃSKI 1987, BURZYŃSKI, BUCZEK 1989).

The evidence presented in literature (ANDRZEJEWSKI 1993) shows that soil humus, next to soil reaction, determines availability of some trace elements. Maintaining an adequate level of soil humus requires fertilization with materials abundant in organic matter, liming and supply of appropriate amounts of basic nutrients, such as nitrogen, phosphorus or potassium, which are taken up with plant yields. Among many positive features of soil humus which affect soil fertility there is sorption capacity. Sorption capacity makes soil humus vital for plant nutrition and ecologically important. Soil humus is a kind of nutrient store for plants which also acts as a neutralizer of trace elements, whose concentration is often too high in the soil solution.

Formation and durability of humus compounds in soil, including organic-mineral combinations with trace elements, depends on many factors. The important ones comprise are the amount and structure of humic compounds, soil reaction as well as the kind and concentration of a given element in soil (DZIADOWIEC 1993, MERCIK, KUBIK 1995).

This study has been conducted on grasslands to assess potential crop yield and determine changes of the sward quality depending on the fertilization used. Therefore, analyses were made to asses the content of manganese, nickel and iron in the soil and meadow sward grown under diversified mineral fertilization and liming.

MATERIAL AND METHODS

The experiment is set up in the village Czarny Potok near Krynica (20°54"E; 49°24"N), on the altitude of about 720 m above sea level, at the foot of Mount Jaworzyna Krynicka, in the south-eastern Beskid Sądecki massif on a 7° inclination slope and NNE aspect. The experiment was established in 1968 on a natural mountain meadow of mat-grass (*Nardus stricta* L.) and red fescue (*Festuca rubra* L.) type with a large share of dicotyledonous plants. The soil was classified as acid brown soil developed from the Magura sandstone with a texture of light silt loam (% of fractions: 1 – 0.1 mm: 40; 0.1 – 0.02 mm: 37; > 0.02 mm: 23) and three characteristic genetic horizons: turf – AhA (0 – 20 cm), browning – ABbr (21 – 46 cm) and parent rock BbrC (47 – 75 cm). Detailed data about the experiment were presented in the earlier publications (MAZUR, MAZUR 1972, KOPEĆ 2000).

The experiment has been receiving the same level of fertilization since the autumn 1985, but it is conducted in two series: without liming (0 Ca) and limed (+Ca). Liming was repeated in 1995. The first liming was conducted with a dose calculated on the basis of 0.5 Hh value while the second one was based on the total hydrolytic acidity.

Mineral fertilization was discontinued in the years 1974–1975 and in 1993–1994 when the experiment was restricted to assessment of the sward yield and its chemical composition.

The experiment comprises 8 treatments in five replications (Table 1) receiving unilateral nitrogen or phosphorus fertilization (90 kg N or 39.24 kg P·ha^{-1}) and (39.24 kg P·ha^{-1} and 124.5 kg K_2O·ha^{-1}) against PK background; nitrogen is applied in two forms (ammonium nitrate and urea) and two doses (90 and 180 N·ha^{-1}). In 1968-1980, phosphorous and potassium fertilizers were applied in autumn but since 1981 the fertilization treatments have been performed in spring, although potassium (1/2 of the dose) is supplemented in summer after the first cut. In 1968-1973 thermophosphate was applied; afterwards triple superphosphate has been used. Over the whole period of the experiment nitrogen fertilizers have been applied on two dates: 2/3 of the annual dose in the spring at the start of vegetation and 1/3 of the dose – several days after the first cut harvest. A single regenerative treatment with copper (10 kg·kg^{-1}) and magnesium (8 kg·ha^{-1}) was applied in 1994. Foliar nutrition (2 dm^3·ha^{-1} applied twice) with microelement Mikrovit -1 fertilizer has been used since 2000. The microelement fertilizer contains (per 1 dm^3): 23.3 g Mg; 2.3 g Fe; 2.5 g Cu; 2.7 g Mn; 1.8 g Zn; 0.15 g B and 0.1 g Mo.

Table 1
Tabela 1

Design of fertilization in the static experiment in Czarny Potok
Schemat nawożenia w statycznym doświadczeniu w Czarnym Potoku

Fertilizer objects Obiekty nawozowe		Annual nutrient rate in Roczna dawka składnika w serii 0 Ca and + Ca (kg · ha^{-1})			Nitrogen form Forma azotu
A	PK	P	K	N	
A	PK	39.24	124.5	-	
B	90 kg N (a) + PK	39.24	124.5	90	ammonium nitrate saletra amonowa
C	180 kg N (a) + PK	39.24	124.5	180	ammonium nitrate saletra amonowa
D	90 kg N (u)+ PK	39.24	124.5	90	urea – mocznik
E	180 kg N (u) + PK	39.24	124.5	180	urea – mocznik
F	90 kg N (a)	-	-	90	ammonium nitrate saletra amonowa
G	90 kg P	39.24	-	-	
H	no fertilization bez nawożenia	-	-	-	

(a) ammonium nitrate – saletra amonowa; (u) urea – mocznik;
0 Ca unlimed series – seria bez wapnowania; + Ca limed series – seria wapnowana

In the investigated area, the growing season lasts from April till September (150 – 190 days). The local weather conditions are characterized by a considerable variability of precipitation (Table 2).

Table 2
Tabela 2

Statistical parameters of the distribution of precipitation and temperatures in 1968–2001
Parametry statystyczne rozkładu opadów i temperatur dla okresu 1968–2001

Parameter Parametr	Precipitation Opady (mm)		Temperature Temperatura (°C)	
	Jan.-Dec.	April-Sept.	Jan.-Dec.	April-Sept.
Arithmetical mean Średnia arytmetyczna	856.5	567.9	5.78	11.96
Standard deviation Odchylenie standardowe	184.1	132.5	0.90	0.86
Range 25-75% of cases Przedział 25-75% przypadków	728.5-909.0	466.1-649.7	5.30-6.30	11.3-12.5

The results of the research presented in this paper were obtained in the 36th year of the experiment. In 2003 two cuts were harvested: on 26 June and 10 September. Manganese, nickel and iron content in the plant material were assessed using the ICP-AES method after drying and dry mineralization (at 450°C for 5 hrs.). A soil sample was collected for analyses from the 0 – 10 cm level of each treatment after II cut harvest. The following assessments were made in the soils: pH in 1 $\text{mol}\cdot\text{dm}^{-3}$ KCl and in water solution with a potentiometer, organic carbon content after mineralization in potassium(VI) dichromate using Tiurin method, total content of manganese, nickel and iron after organic substance incineration in a muffle furnace (at 500° C for 8 hrs) and the sample mineralization in concentrated HNO_3 and $HClO_4$ acids (2:1) (v/v) (OSTROWSKA et al. 1991). Manganese, nickel and iron were extracted from the soil using 0.025 $\text{mol}\cdot\text{dm}^{-3}$ NH_4EDTA solution with ZEIEN, BRÜMMER method (1989). The results underwent statistical analysis. Two factor analysis of variance was conducted and the significance of differences between the arithmetic means was estimated with Fisher test at the significance level $p < 0.05$. Standard deviation and coefficient of variation were computed for the values obtained within series.

RESULTS AND DISCUSSION

Long-term, systematic mineral fertilization established a stabile level of meadow sward yields (Kopeć 2000) on individual treatments (Figure 1). The computed values of a yield variability coefficient within the series were relatively small for both cuts: $V\%_{0Ca} = 32$ and $V\%_{+Ca} = 39$. As the results show, crop yields have been so stable that, despite the cultivation techniques carried out on the whole field, including microelement fertilization, no significant differences were revealed between the ammonium nitrate and urea treatments for both nitrogen doses against the PK background in either series. It is so because of the botanical composition of the sward and the degradation of grassland caused by PK + 180 kg $N \cdot ha^{-1}$, which was discussed in our earlier publication (Kopeć, Szewczyk 2006). On the basis of the experiments, the first cut yield was larger by an average 122% for the non-limed series and 165% for the limed series. Severe soil

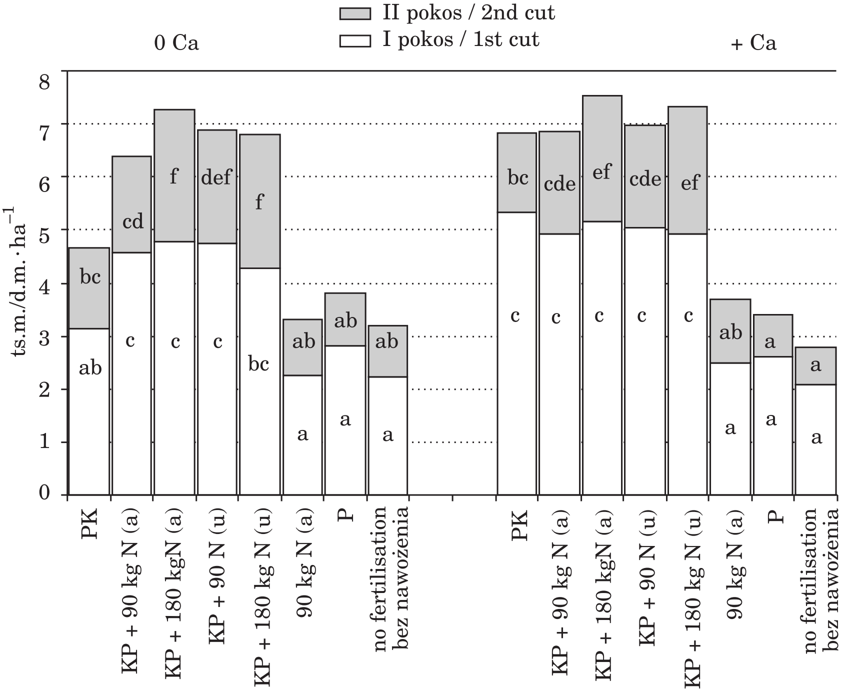


Fig. 1. Yields of meadow sward in 2003: (a) – ammonium nitrate, (u) – urea
Means designated the same letters did not differ significantly at $p < 0.05$ according to the Fisher test

Rys. 1. Plony runi łąkowej w 2003 r.: (a) saletra amonowa, (u) mocznik
Średnie oznaczone tymi samymi literami nie różnią się istotnie dla $p < 0,05$ wg testu Fishera

exhaustion caused by the unilateral nitrogen or phosphorus fertilization led to significantly lower yields of meadow sward biomass in comparison with the PK treatment, particularly in the limed series. Crop yields, including meadow sward, are strictly related to the habitat and agronomic factors. There is no direct dependence between the dose of a fertilizer component and the amount of crop yield. Plant response to fertilization is a resultant of many factors (MALHI et al. 1992). Relatively considerable yield stabilization in individual treatments results mainly from the botanical composition of the plant community, stabilized during the period of over thirty years, which was discussed in detail in an earlier publication (KOPEĆ, SZEWCZYK 2006). The lack of notable differences in biomass yields between 90 kg and 180 kg N treatments (irrespective of the nitrogen form) may have been caused by some disturbance in the ratio between the biomasses of grassland aerial parts versus the roots and runners. Water and nutrients accumulated in the rhizosphere enables plants to survive unfavourable conditions. Intensive fertilization, particularly with nitrogen, means that the soil layer penetrated by roots seeking nutrients and water becomes shallower. This effect may be strengthened by certain physical processes stimulated by increased fertilization (SIEGEL-ISSEM et al. 2005). Obtaining comparable biomass yields on fields fertilized with a single and double dose of nitrogen points indirectly to a positive balance of this component in soil, which, if unused, may migrate into the soil profile and cause groundwater pollution.

The values of soil reaction measured in water suspension, as shown in Table 3, ranged between 5.20 and 5.96 for the non-limed series and between 5.80 and 6.09 for the limed series. Soil pH values measured in the suspension and 1 $mol \cdot dm^{-3}$ KCl fell within the range of 3.36 to 4.21 for the non-limed series and 4.39 to 4.72 for the limed series. The lowest values of soil reaction (in water suspension) were found in the soil (the non-limed series) fertilized with nitrogen used as ammonium nitrate + PK in the dose 180 kg $N \cdot ha^{-1}$. In the limed series, the lowest reaction was measured in the non-fertilized treatment soil. In the soil suspension and KCl, the lowest pH value was determined in the soil treated with urea supplied as 180 kg N + $PK \cdot ha^{-1}$ (the non-limed series) and in the soil unilaterally fertilized with ammonium nitrate dosed 90 kg $N \cdot ha^{-1}$ (the limed series). The investigations conducted by MAZUR and MAZUR (1972) demonstrated similar soil reaction relationships found during the initial years of the experiment, whereas the changes in the soil reaction observed over time suggest increasing soil acidification (MAZUR, KOPEĆ 1993, KOPEĆ, NOWOROLNIK 1999).

Humus concentrations, expressed as a percentage of organic carbon content, observed in soils of individual treatments were lower than determined in non-fertilized soils, irrespective of a series (Table 3). Greater diversification in the content of this component was found in the non-

Table 3
Tabela 3

Soil reaction and organic carbon content in soil
Odczyn i zawartość węgla organicznego w glebie

Fertilizer objects* Obiekty nawozowe*		0 Ca			+ Ca		
		pH		org. C C org. $g \cdot kg^{-1}$	pH		org. C C org. $g \cdot kg^{-1}$
		H_2O	KCl		H_2O	KCl	
A	PK	5.55	3.85	13.34	5.95	4.53	9.40
B	90 kg N (a) + PK	5.61	4.17	10.40	5.99	4.45	8.42
C	180 kg N (a) + PK	5.21	3.73	10.16	6.07	4.44	9.14
D	90 kg N (b) + PK	5.52	4.02	10.28	6.04	4.63	9.44
E	180 kg N (b) + PK	5.20	3.36	13.12	6.07	4.48	8.32
F	90 kg N (a)	5.58	3.83	10.28	5.93	4.39	9.70
G	90 kg P	5.71	4.12	13.02	6.09	4.51	9.28
H	no fertilization bez nawożenia	5.96	4.21	19.30	5.80	4.72	12.00
SD**		-	-	3.10	-	-	1.14
V%***		-	-	24.8	-	-	12.0

* see Table 1 – jak w tabeli 1
** standard deviation – odchylenie standardowe
*** coefficient of variation – współczynnik zmienności

limed series. Less organic carbon occurred in the soil of the limed series (between 5.6% and 37.8% in comparison with the non-limed series). Particularly big differences in the humus content were found in the soil fertilized unilaterally with P, PK,180 kg $N \cdot kg^{-1}$ + PK (as urea) and in unfertilized soil. Niemyska-Łukaszuk et al. (1999) found similar dependencies concerning humus concentrations in the soil of the same experiment assayed in the 30th year, although the differences between the series were not so pronounced, i.e. between 0.5% and 14.8%. An increase in the humus content in soil was registered between the 18th and 30th year of the experiment, irrespective of the treatment (Niemyska-Łukaszuk et al. 1999). However, after 36 years of the experiment, humus concentrations in the analyzed soil samples were found to have declined (Table 3). According to Dechnik (1987) and Myśkow and Stąsiek (1976), long-term application of mineral fertilizers, especially the ones which acidify the environment, leads to a decline in the soil fertility, its biological activity as well as quantitative and qualitative degradation of humus. Changes in the humus content in soil after 36 years of the experiment may have resulted from the increased mineralization of organic matter, which might have been stimulated by the cultivation techniques and weather conditions. A study conducted by Wołoszyk and Nowak (1993), which dealt with changes in the organic carbon content in light soil as a result of mineral fertilization of grasses under field cultivation, revealed that organic carbon concentrations in soil decreased after three years of the treatments, increasing again after the fifth year. The periodic character of changes in soil humus concentrations was also reported by KRAJCOVIC et al. (1993).

The mean total content of manganese in soil (for treatments) of the non-limed series was almost 10% smaller than for the limed series (Table 4). Such a higher content of total manganese forms in the soils of the limed series was most probably due to the poorer bioavailability of this element determined by the soil reaction. Manganese extracted with NH_4EDTA solution ranged between 22.8 – 33.5 $mg \cdot kg^{-1}$ (the non-limed series) and 19.0 and 25.1 $mg \cdot kg^{-1}$of soil dry mass (the limed series) – Table 4. This fraction, irrespective of the series or treatment, constituted between 6.1% and 11.5% of the total content, although a greater proportion of this manganese form was noticed in the soil of the non-limed series, with small albeit noticeable differences between the treatments. Concentrations of manganese in the sward ranged between 93 and 322 $mg \cdot kg^{-1}$ d.m. for the non-limed series and 48 and 123 $mg \cdot kg^{-1}$ for the limed series (Table 4). Irrespective of the applied fertilization and liming, the sward from the second cut contained more manganese. Statistical analysis of the results also points to a greater variability between the treatments in terms of manganese concentrations in the second cut sward, but higher manganese concentrations were conditioned by significantly smaller biomass yields in comparison with the first cut. Solubility of manganese compounds is a resultant of many factors (Figure 1). Transformations of this element in soil, apart from oxidation-reduction conditions and the soil reaction, depend on the soil concentrations of iron and aluminum hydroxides, clay minerals, carbonates and the content of organic substance (KABATA-PENDIAS, PENDIAS 1999, HALASOVA et al. 2000). However, unlike other metals, manganese is relatively weakly bound by organic matter, as the present study has confirmedwas. Nonetheless, it should be emphasized that the soil reaction significantly influenced the amount of manganese extracted with NH_4EDTA, as demonstrated by the results obtained by VALLMANNOVA et al. (2001). Also, higher levels of the total forms of this element were found in the limed series except for the unfertilized soil. This can be attributed to the poorer manganese bioavailability and formation of hardly soluble combinations with solid soil particles (CZEKAŁA et al. 1996). Despite its higher total content, limited mobility of manganese in the + Ca series soil became reflected in its concentrations in the meadow sward. Similar results, although for a different plant, were cited by BEDNAREK and LIPIŃSKI (1996). Considering the forage value, it was favourably affected by liming, which limited manganese bioavailability (GORLACH 1991).

The total content of nickel in the soil of the non-limed series fell within the range of 7.42 – 10.10 $mg \cdot kg^{-1}$ and 8.42 – 10.55 $mg \cdot kg^{-1}$ of soil

Table 4
Tabela 4

Content of manganese (mg·kg^{-1} d.m.) in soil and meadow sward
Zawartość manganu (mg·kg^{-1} s.m.) w glebie i runi łąkowej

Fertilizer objects* Obiekty nawozowe*	0 Ca				+ Ca			
	soil – gleba		cut – pokos		soil – gleba		cut – pokos	
	total ogólny Mn	Mn-NH$_4$EDTA	I	II	total ogólny Mn	Mn-NH$_4$EDTA	I	II
A	275	28.9 fgh	146 e	215 bcd	303	22.9 a-e	63 a-d	96 a
B	239	27.6 d-g	141 e	268 de	281	24.0 a-f	69 a-d	116 ab
C	268	27.8 efg	135 e	272 de	278	23.2 a-e	50 ab	82 a
D	278	29.1 gh	101 a-e	238 de	293	25.1 c-g	50 ab	92 a
E	270	25.6 c-g	113 de	322 e	284	20.7 abc	57 abc	90 a
F	285	22.8 a-d	109 cde	221 cde	304	19.9 ab	48 a	123 abc
G	275	24.3 b-g	104 b-e	181 a-d	298	24.0 a-f	62 a-d	93 a
H	368	33.5 h	93 a-e	146 a-d	310	19.0 a	55 a-d	71 a
SD**	37.2	3.3	20.1	55.3	11.8	2.2	7.4	16.9
CV****	13	12	17	24	4	10	13	18

* see Table 1 – jak w tabeli 1,
** standard deviation – odchylenie standardowe,
*** coefficient of variation – współczynnik zmienności;
Means designated the same letters in columns did not differ significantly at $p < 0.05$ according to the Fisher test.
Średnie oznaczone tymi samymi literami w kolumnach nie różnią się istotnie dla $p < 0.05$ wg testu Fishera.

dry mass in the limed series (Table 5). Among the applied fertilization patterns, it was only liming which diversified the total content of this element. This may have resulted from a certain load of nickel supplied with the calcium fertilizers used for liming and the reduced uptake of this element under higher soil pH values. The content of nickel extracted from the soil with NH_4EDTA solution was not varied among the experimental series (0 Ca and + Ca) except for the soil from the treatments where PK and 180 kg $N \cdot ha^{-1}$ + PK (ammonium nitrate) were used. In the soil samples from these treatments of the 0 Ca series, the content of Ni-NH_4EDTA form was almost twice as high as in the soil from the + Ca series treatments (Table 5). An opposite relationship was noticed in the soil of unfertilized treatments. The nickel content in the soil organic fraction, which was influenced by the long-term mineral fertilization caused a considerable diversification within the series ($V\%_{0Ca} = 43$; $V\%_{+Ca} = 40$). The factors which diversified nickel concentrations in sward more than mineral fertilization were liming and harvest (cut) date. Irrespective of the fertilization applied, more nickel was detected in the sward of the non-limed series. Generally, higher nickel concentrations were characteristic for the sward of the second cut (Table 5). Mobility of nickel, like that of other trace metals, is mainly determined by soil reaction. According to Kabata-Pendias, Pendias (1999), nickel readily forms combinations with soil organic substance, mostly mobile chelates, as the above authors emphasized. In the present experiments, nickel forms bound to soil humus made up only a slight proportion in comparison with the total content of this element in soil, irrespective of the experimental series. According to Karczewska et al. (1997) and Bran et al. (1997), considerable mobility of nickel inhibits accumulation of its bioavailable forms in the surface horizons of soils, which is of crucial importance for plants with shallow roots systems such as grasses. In the mountains, where there is more precipitation than on lowlands, rainfall water seeping through the soil profile may transport this element into deeper layers, beyond the reach of plant root systems (Gondek, Kopeć 2002). This may partially account for the smaller concentration of nickel in the second cut sward despite the lower biomass yield. As there is no evidence to confirm participation of nickel in metabolic processes in plants, this element is not considered to be essential to plants. Therefore, excessively high nickel concentrations in forage are undesirable. The content of nickel in the analyzed biomass, as set against the values suggested by Gorlach (1991), did not restrict the use of the grass for forage, irrespective of the cut.

Soil concentrations of the total iron forms within each series varied only slightly ($V\%_{0Ca} = 9\%$; $V\%_{+Ca} = 4\%$) – Table 6. On average, the content of the total forms of iron in soils was 8314 $mg \cdot kg^{-1}$ dry soil mass in the non-limed series (0 Ca) and 9009 $mg \cdot kg^{-1}$ in the limed series. The determined amount of iron extracted with NH_4EDTA solution was higher in

Table 5
Tabela 5

Content of nickel (mg·kg^{-1} d.m.) in soil and meadow sward
Zawartość niklu (mg·kg^{-1} s.m.) w glebie i runi łąkowej

Fertilizer objects* Obiekty nawozowe*	0 Ca				+ Ca			
	soil – gleba		cut – pokos		soil – gleba		cut – pokos	
	total ogólny Ni	Ni-NH$_4$EDTA	I	II	total ogólny Ni	Ni-NH$_4$EDTA	I	II
A	8.58	0.53 ab	1.81 b	1.60 e	8.90	0.27 a	1.67 b	0.55 a
B	7.42	0.36 a	1.71 b	1.12 cd	9.13	0.36 a	0.98 a	0.50 a
C	8.18	1.01 c	1.91 b	1.08 bcd	8.42	0.52 ab	0.89 a	0.36 a
D	9.05	0.36 a	1.66 b	1.11 cd	8.86	0.38 a	0.90 a	0.32 a
E	8.36	0.34 a	1.41 ab	1.51 de	10.55	0.34 a	0.85 a	0.35 a
F	8.92	0.41 a	1.35 ab	1.72 e	9.10	0.45 a	0.88 a	0.62 ab
G	8.74	0.52 ab	1.32 ab	1.31 de	8.99	0.55 ab	0.88 a	0.39 a
H	10.1	0.49 a	1.42 ab	1.27 cde	9.73	0.86 bc	1.20 ab	0.60 abc
SD**	0.8	0.2	0.2	0.2	0.7	0.2	0.3	0.1
CV****	9	43	14	18	7	40	27	26

* see Table 1 – jak w tabeli 1,
** standard deviation – odchylenie standardowe,
*** coefficient of variation – współczynnik zmienności;
Means designated the same letters in columns did not differ significantly at $p < 0.05$ according to the Fisher test.
Średnie oznaczone tymi samymi literami w kolumnach nie różnią się istotnie dla $p < 0.05$ wg testu Fishera.

Table 6
Tabela 6

Content of iron (mg·kg^{-1} d.m.) in soil and meadow sward
Zawartość żelaza (mg·kg^{-1} s.m.) w glebie i runi łąkowej

Fertilizer objects* Obiekty nawozowe*	0 Ca				+ Ca			
	soil – gleba		cut – pokos		soil – gleba		cut – pokos	
	total ogólny Fe	Fe-NH$_4$EDTA	I	II	total ogólny Fe	Fe-NH$_4$EDTA	I	II
A	8625	192 a	101 a-d	108 a	9215	286 de	114 cd	137 a
B	6855	193 a	73 a-d	112 a	9070	283 de	67 abc	96 a
C	7585	196 a	76 a-d	112 a	9055	346 f	74 a-d	75 a
D	8925	211 a	61 abc	107 a	9155	276 cd	57 ab	89 a
E	8470	204 a	63 abc	201 a	9240	311 e	99 a-d	96 a
F	8335	215 ab	98 a-d	224 b	9435	254 cd	48 a	77 a
G	8345	245 bc	64 abc	131 a	8580	312 e	57 ab	206 a
H	9375	267 cd	127 bcd	121 a	8325	247 bc	141 d	208 ab
SD**	782.1	27.0	23.5	46.1	369.6	32.7	32.7	55.2
CV****	9	13	28	33	4	11	40	45

* see Table 1 – jak w tabeli 1,
** standard deviation – odchylenie standardowe,
*** coefficient of variation – współczynnik zmienności;
Means designated the same letters in columns did not differ significantly at $p < 0.05$ according to the Fisher test.
Średnie oznaczone tymi samymi literami w kolumnach nie różnią się istotnie dla $p < 0.05$ wg testu Fishera.

the soil of the limed series (between 27% and 77%) than in the non-limed treatments except for unfertilized soil, where the absolute content of Fe-NH_4EDTA was lower (Table 6). The amount of iron extracted with the above reagent constituted between 2.2% and 2.9% of the total content of iron in the soil of the non-limed treatments and between 2.7% and 3.8% in the limed treatments. Although the soil reaction was favourable, iron concentrations in the meadow sward were on a similar level, irrespective of the series and applied fertilization (Table 6). The factor which significantly diversified concentrations of this element in sward was the date of harvest (cut). The content of iron bound to organic substance made up a small percentage of the total iron content, which was high. Unlike manganese and nickel, whose soil concentrations extracted with NH_4EDTA were lower in limed soils, iron responded differently to liming. Relatively little iron was determined in forms bound to organic substance, which may suggest a much greater affinity of this element to form stable combinations with other soil constituents (KABATA-PENDIAS, PENDIAS 1999). Iron often seems to be in short supply for plants, but this is most probably due to the fact that plants cannot take it up readily because of some very dynamic changes of its bioavailability rather than because of its low soil concentrations. Relatively small concentrations of iron in the sward may be attributed to the physiological characteristics of plants, which make it difficult to transport this element from the root system to the aerial organs (GONDEK AND FILIPEK-MAZUR 2005). According to MACIEJEWSKA, KOTOWSKA (2001), iron content in hay may also be affected by the harvest date. Analysis of plant material in view of animal nutritional requirements for iron (GORLACH 1991) generally revealed iron deficiency.

CONCLUSIONS

1. The content of total manganese forms was higher in the soil of the limed series and the soil reaction significantly affected amounts of this metal extracted with NH_4EDTA solution and its content in the sward. Soil liming, while limiting manganese bioavailability, improved forage value of the analyzed biomass.

2. The small amount of nickel bound to the soil organic substance indirectly proves considerable mobility of this element and its translocation into deeper levels of the soil profile, beyond the reach of the plant root system.

3. Liming increased the content of iron forms in combinations with the soil organic substance. Iron deficiency in the meadow sward may have a physiological basis such as difficulties in iron transport from the root system to aerial organs, but it does not result from limited possibilities of its uptake from soil.

REFERENCES

ANDRZEJEWSKI M. 1993. *Znaczenie próchnicy dla żyzności gleby*. Zesz. Post. Nauk Rol., 411: 11-22.

BARAN S., FLIS-BUJAK M., ŻUKOWSKA G., KWIECIEŃ J., PIETRASIK W., SZCZEPANOWSKA I., ZALESKI P. 1997. *Formy niklu w glebie lekkiej użyźnionej osadem ściekowym*. Zesz. Probl. Post. Nauk Rol., 448 a: 21-27.

BEDNAREK W., LIPIŃSKI W. 1996. *Zaopatrzenie jęczmienia jarego w mangan i cynk w warunkach zróżnicowanego nawożenia fosforem, magnezem i wapnowania*. Zesz. Probl. Post. Nauk Roln., 434: 30-35.

BURZYŃSKI M. 1987. *The influence of lead and cadmium on the absorption and distribution of potassium, calcium, magnesium and iron in cucumber seedlings*. Acta Physiol. Plant., 9: 229-238.

BURZYŃSKI M., BUCZEK J. 1989. *Interaction between cadmium and molybdenum affecting the chlorophyll content and accumulation of some heavy metals in the second leaf of Cucumis sativus* L. Acta Physiol. Plant., 11: 137-146.

CZEKAŁA J., JAKUBUS M., GŁADYSIAK S. 1996. *Zawartość form rozpuszczalnych mikroelementów w zależności od odczynu gleby i roztworu ekstrakcyjnego*. Zesz. Probl. Post. Nauk Rol., 434: 371-376.

DECHNIK I. 1987. *Wpływ nawożenia na właściwości gleby*. Zesz. Probl. Post. Nauk Rol., 324: 81-106.

DZIADOWIEC H. 1993. *Ekologiczna rola próchnicy glebowej*. Zesz. Probl. Post. Nauk Rol., 411: 269-282.

GONDEK K., FILIPEK-MAZUR B. 2005. *Zawartość i pobranie mikroelementów przez owies w warunkach nawożenia kompostami rożnego pochodzenia w aspekcie wartości paszowej i wpływu na środowisko.* Woda Środ. Obszary Wiejskie, 5(13): 81-93.

GONDEK K., KOPEĆ M. 2002. *Degree of permanent meadow soil profile contamination with heavy metals*. Chem. Inż. Ekol., 9 (11): 1357-1363.

GORLACH E. 1991. *Zawartość pierwiastków śladowych w roślinach pastewnych jako miernik ich wartości*. Zesz. Nauk. AR w Krakowie, 34 (1): 13-22.

HALÁSOVÁ M., VOLLMANNOVÁ A., TOMÁŠ J. 2001. *Influence of physicochemical properties of soil on Mn bioavailability*. Biul. Magnezol., 6(3): 276-280.

KABATA-PENDIAS A., PENDIAS H. 1999. *Biogeochemia pierwiastków śladowych.* Wyd. Nauk. PWN, Warszawa, ss. 1-397.

KARCZEWSKA A., SZERSZEŃ L., KHDRI J. 1997. *Frakcje niklu w glebach wytworzonych z różnych skał macierzystych Polski i Syrii*. Zesz. Probl. Post. Nauk Rol., 448b: 117-123.

KOPEĆ M. 2000. *Dynamika plonowania i jakości runi górskiej w okresie trzydziestu lat trwania doświadczenia nawozowego*. Zesz. Nauk. AR w Krakowie, ser. Rozpr., 267: 1-84.

KOPEĆ M. SZEWCZYK W. 2006. *Wpływ wprowadzenia dolistnego nawożenia mikroelementami runi długotrwałego doświadczenia w Czarnym Potoku na zawartość wapnia*. Ann. UMCS, ser. E, Agricult., 61: 175-188.

KOPEĆ M., NOWOROLNIK A. 1999. *Wybrane właściwości fizykochemiczne gleby w 30-letnim doświadczeniu nawozowym na górskim użytku zielonym (Czarny Potok)*. Zesz. Probl. Post. Nauk Rol., 465: 559-567.

KRAJCOVIC V., FIALA., ONDRASEK L. 1993. *Long-term trias on semi-natural grasslands*. In: Proc. Int. Symp. "Long-term ststic fertiliser experiments", Warszawa – Kraków, 15-18 June 1993, Part I, pp. 187-211.

MACIEJEWSKA M., KOTOWSKA J. 2001. *Zawartość mikroelementów w sianie w warunkach zróżnicowanego nawożenia NPK.* Biul. Magnezol., 6(3): 295-303.

MALHI S. S., HARAPIAK J. T., NYBORG M., FLORE N. A. 1992. *Dry matter yield and N recovery from bromegrass in south-central Alberta as affected by time of application of urea and ammonium nitrate*. Commun. Soil Sci. Plant Anal., 23 (9/10): 953-964.

MAZUR K., KOPEĆ M. 1993. *Dynamika odczynu, kwasowości potencjalnej i glinu aktywnego w glebie górskiej w okresie 6 lat od wapnowania*. Mat. Konf. Nauk. „Problemy wapnowania użytków zielonych", Falenty, 11-13.05.1993, IMUZ, Falenty, ss. 51-56.

MAZUR K., MAZUR T. 1972. *Wpływ nawożenia mineralnego na plon, skład botaniczny i chemiczny masy roślinnej z łąki górskiej*. Acta Agr. et Silv., ser. Agr., 12 (1): 85-115.

MERCIK S., KUBIK I. 1995. *Chelatowanie metali ciężkich przez kwasy humusowe oraz wpływ torfu na pobieranie Zn, Pb i Cd przez rośliny*. Zesz. Probl. Post. Nauk Rol., 422: 19-30.

MYŚKOW W., STĄSIEK S. 1976. *Wpływ wieloletniego nawożenia na aktywność biologiczną i substancje organiczne gleby*. Symp. Nauk. „Skutki wieloletniego stosowania nawozów", Puławy, cz. II, ss. 49-56.

NIEMYSKA-ŁUKASZUK J., FILIPEK-MAZUR B., NICIA P. 1999. *Zawartość i skład frakcyjny próchnicy w glebie łąki górskiej w 30-tym roku statycznego doświadczenia nawozowego*. Zesz. Probl. Post. Nauk Rol., 465: 569-578.

OSTROWSKA A., GAWLIŃSKI A., SZCZUBIAŁKA Z. 1991. *Metody analizy i oceny gleby i roślin*. Wyd. IOŚ, Warszawa, ss. 325.

RUSZKOWSKA M., WOJCIESZKA-WYSKUPAJTYS U. 1996. *Mikroelementy – fizjologiczne i ekologiczne aspekty ich niedoborów i nadmiarów*. Zesz. Probl. Post. Nauk Rol., 434: 1-11.

SIEGEL-ISSEM C. M., BURGER J. A., POWERS R. F., PONDER F., PATTERSON S. C. 2005. *Seedling root growth as a function of soil density and water content*. Soil Sci. Soc. Am. J., 69: 215-226.

VOLLMANNOVÁ A., TOMÁŠ J., HALÁSOVÁ M., LAZOR P. 2001. *Suppression of possible phytotoxic Mn effects in a soil-plant system*. Biul. Magnezol., 6(4): 664-670.

WOŁOSZYK CZ., NOWAK W. 1993. *Zmiany zawartości węgla organicznego oraz azotu ogółem w glebie lekkiej pod wpływem nawożenia mineralnego traw w uprawie polowej*. Zesz. Probl. Post. Nauk Rol., 411: 85-90.

ZEIEN H., BRÜMMER G. W. 1989. *Chemische extractionen zur bestimmung von schwermetallbindungsformen in böden*. Mitteilgn. Dtsch. Bodenkundl. Gesellsch., 59/1: 505-510.

J. Elementol. 2008, 13(1): 57–68

PRELIMINARY CHARACTERIZATION OF THE TROPHIC STATE OF MAŁY KOPIK LAKE NEAR OLSZTYN AND ITS DRAINAGE BASIN AS A SUPPLIER OF BIOGENIC SUBSTANCES

Jolanta Grochowska, Renata Tandyrak

Chair of Environmental Protection Engineering
University of Warmia and Mazury in Olsztyn

Abstract

The study was carried out on a small (7.8 ha) and shallow (9.0 m) lake Mały Kopik, situated 9 km on south western from Olsztyn, drainage basin of Giłwa and Pasłęka rivers. The catchment area of the lake is 194.7 ha. Forests cover the most of the drainage basin area (64.2%), agriculture land comprises 28.7% (21% grass land and 7.7% arable land) and urban land – 7.1%. Lake Mały Kopik is not susceptible to degradation (III category), and drainage basin having a great potential for supplying matter to the reservoir, was included in basin category 4. The lake with its drainage basin belong to the 4th type of lake-drainage basin ecosystems. In such a system the natural eutrophication of the lake is expected to proceed at a fast rate.

As evidenced in the study, lake Mały Kopik is highly eutrophic reservoir. The lake waters were characterized by a high content of nutrients, up to 0.673 mg $P \cdot dm^{-3}$ and 10.61 mg $N \cdot dm^{-3}$. The high fertility of the lake was exhibited also by the values of BOD_5 reaching 7.5 mg $O_2 \cdot dm^{-3}$, chlorophyll *a* content – 50 $\mu g \cdot m^{-3}$, and low water transparency – 2 m.

Key words: lake, drainage basin, nutrients, external loading, eutrophication, susceptibility to degradation.

Jolanta Grochowska, PhD, Eng., Junior Professor, Chair of Environmental Protection Engineering, University of Warmia and Mazury, Prawocheńskiego 1, 10-957 Olsztyn, Poland, e-mail: jgroch@uwm.edu.pl

WSTĘPNA CHARAKTERYSTYKA TROFICZNA JEZIORA MAŁY KOPIK K. OLSZTYNA ORAZ JEGO ZLEWNI JAKO DOSTAWCY ZWIĄZKÓW BIOGENICZNYCH

Abstrakt

Badaniami objęto małe (7,8 ha) i niezbyt głębokie (9 m) jezioro Mały Kopik, położone ok. 9 km na południowy zachód od Olsztyna, w dorzeczu Giłwy-Pasłęki. Zlewnia jeziora to obszar o powierzchni 194,7 ha. Największy udział (64,2%) mają w niej lasy, 28,7% zajmują tereny użytkowane rolniczo, w tym 21% stanowią użytki zielone, 7,7% grunty orne, pozostała część tego terenu (7,1%) to nieskanalizowane gospodarstwa rolne.

Jezioro Mały Kopik jest zbiornikiem nieodpornym na wpływy zewnętrzne, należy do III kategorii podatności na degradację. Jego zlewnia charakteryzuje się dużą możliwością uruchamiania obszarowego ładunku związków biogenicznych, należy do 4. typu zlewni. Kombinacja grupy podatności zlewni i odporności jeziora na degradację pozwala zaliczyć jezioro Mały Kopik i jego zlewnię do czwartego typu układów ekologicznych w systemie BAJKIEWICZ-GRABOWSKIEJ (2002), w którym następuje szybka eutrofizacja wód jeziornych. Przypuszczenie to potwierdziły badania chemiczne wód, które wykazały, iż jezioro Mały Kopik jest zbiornikiem silnie zeutrofizowanym. W wodach zbiornika stwierdzono bardzo wysoką zawartość związków biogenicznych, tj. 0,673 mg P dm^{-3} i 10,61 mg N dm^{-3}. O dużej żyzności jeziora świadczyły także wartości BZT_5, dochodzące do 7,5 mg O_2 dm^{-3}, ilość chlorofilu *a* (ok. 50 µg m^{-3}) i niska przezroczystość wody – 2 m.

Słowa kluczowe: jezioro, zlewnia, związki biogeniczne, obciążenie zewnętrzne, eutrofizacji, podatność na degradację.

INTRODUCTION

Lakes are the least permanent element of the hydrosphere as they readily collect energy and matter from the watershed, which gradually changes their limnological properties (LANGE 1986). Many authors (HILLBRICHT-ILKOWSKA 1999, BAJKIEWICZ-GRABOWSKA 2002, GROCHOWSKA, TEODOROWICZ 2006) share the opinion that the course of evolutionary changes in lakes is comparable but the rate and character of such changes differ, depending on the morphometry of the bowl of a lake as well as the hydrology and influence of its watershed, which vary according to the geological structure and land use. The physical and geographic features of a watershed may stimulate or limit surface run-off, although the natural features of a lake may sustain its waters in a certain trophic condition (BAJKIEWICZ-GRABOWSKA 1999).

Increased productivity of lake waters has many adverse effects (deoxygenation of near-bottom waters and occurrence of hydrogen sulphide, internal loading with nutrients stored in bottom sediments, phytoplankton blooms, shortage of species on all trophic levels), indicating the need to seek methods to reverse, remove or at least slow down the process (KUBIAK, TÓRZ 2005).

Regarding multiple functions of lakes and the ensuing necessity to protect them, the aim of the study was defined as determination of the trophic condition of Mały Kopik Lake, previously not studied, and its natural vulnerability to degradation. Another objective was to evaluate the watershed as a supplier of matter to the reservoir. Such analysis should allow us to determine the eutrophication rate of the lake.

MATERIAL AND METHODS

Mały Kopik Lake (20°24’4”E and 53°41’3”N) lies approximately 9 km south-west of Olsztyn, at 119.3 m above sea level, in a drainage basin of the Giłwa-Pasłęka Rivers (Topographical Map of Poland 1999) – Figure 1. Its surface area is 7.8 ha, maximal depth 9.0 m, mean depth 3.2 m and the volume 248.1 thousand m^3 (IRŚ 1964). The shoreline is poorly developed

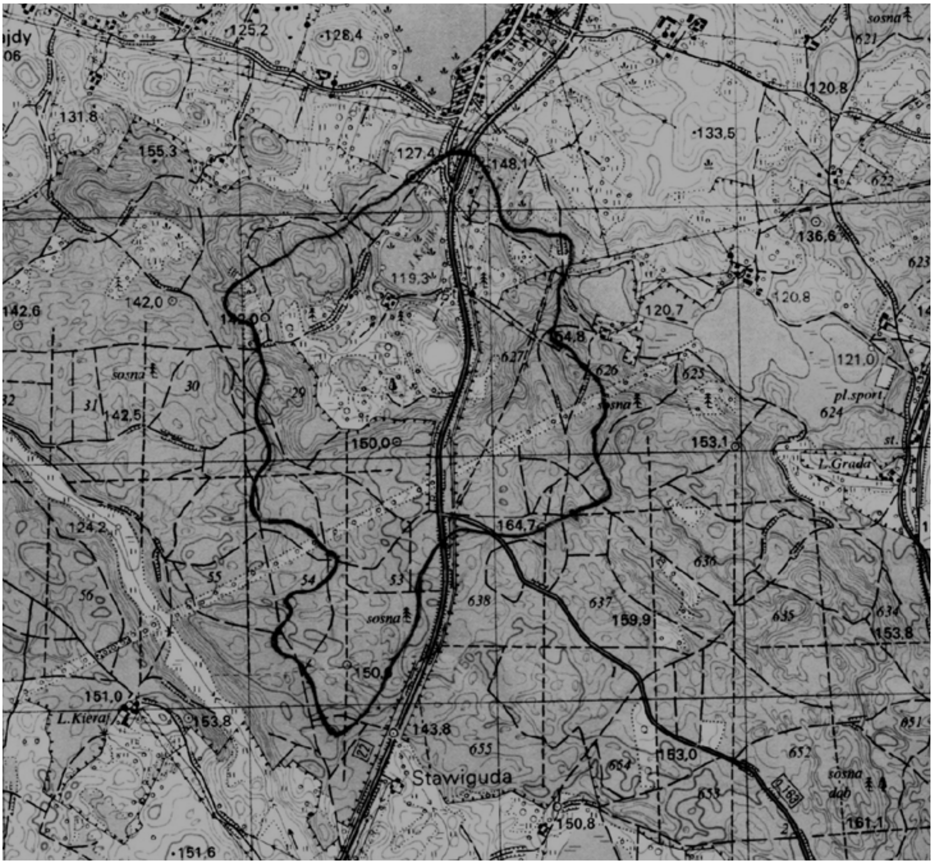


Fig. 1. Catchment's area of Mały Kopik Lake
Rys. 1. Zlewnia jeziora Mały Kopik

(K-1.26) but the depth indicator of 0.36 and the relative depth of 0.032 indicate a relatively big depression (Table 1). Kopik Mały Lake has no outflows.

The lake is not resistant to the impact of external factors. In accordance with the guidelines given by KUDELSKA et al. (1994), it can be classified as representing degradation vulnerability class III (Table 2).

The lake drains an area of 194.7 ha. Most of the watershed is forested (64.2%) and the remaining area is used by agriculture (28.7%, including 21% grassland and 7.7% cultivated land) or occupied by non-sewered farmsteads (7.1%) – Figure 1. An average watershed slope is 25‰. The substratum is built mainly of clay and glacial-fluvial sand (PANFIL 1978).

Table 1
Tabela 1

Detailed morphometric data and lake parameters (after the Institute of Inland Fisheries, Olsztyn, 1964)
Szczegółowe dane morfometryczne i współczynniki charakteryzujące jezioro Mały Kopik (wg IRŚ w Olsztynie, 1964)

Parameter Parametr	Values Wartości
Water table surface area Powierzchnia zwierciadła wody (ha)	7.8
Maximum depth Głębokość maksymalna (m)	9.0
Mean depth Głębokość średnia (m)	3.2
Relative depth Głębokość względna	0.032
Depth index Wskaźnik głębokościowy	0.36
Volume (thousand m^3) Objętość (tys. m^3)	248.1
Maximum length Długość maksymalna (km)	0.420
Maximum width Szerokość maksymalna (km)	0.300
Elongation Wydłużenie	1.4
Shoreline length of the lake bowl Linia brzegowa misy jeziora (km)	1.240
Shoreline development Rozwój linii brzegowej	1.26

Table 2
Tabela 2

Degradation vulnerability of Mały Kopik Lake
Podatność na degradację jeziora Mały Kopik

Index Wskaźnik	Value Wartość	Score Punkty
Mean depth Głębokość średnia (m)	3.2	3
Volume (thousand m^3) / Shoreline length (m) Objętość jeziora (tys. m^3) / Długość linii brzegowej (m)	0.20	4
Stratification (%) % stratyfikacji	0.00	4
Active bottom area (m^2) / Epilimnion volume (m^3) P dna czynnego(m^2) / V epilimnionu (m^3)	0.27	3
% of water exchange % wymiany wody w roku	0.00	1
Schindler's factor Współczynnik Schindlera	8.16	2
Direct drainage area management Zagospodarowanie zlewni bezpośredniej (%)	> 60% forest – lasów	1
Average score Wartość średnia punktacji	2.57	
Susceptibility category Kategoria podatności	III	

The watershed belongs to group 4 in the classification designed by BAJKIEWICZ-GRABOWSKA (2002) – Table 3, which means that it supplies large quantities of matter to the lake.

The lake was surveyed 3 times: in the spring (11 May), summer (11 September) and autumn (24 November) of 2006. Samples of water were taken for complete chemical examinations from the sub-surface (1 m) and near-bottom (8 m) water layers at the deepest site of the lake determined with the help of a bathymetric chart and the global positioning system. Water temperature and dissolved oxygen readings were taken from surface to bottom at 1-m intervals, each time the water was sampled for analyses. The samples were taken using 3.5-l Ruttner apparatus with an in-built mercury thermometer (0.2°C accuracy). Chemical analyses of the water were done in accordance with the methods of HERMANOWICZ et al. (1999).

The vulnerability to degradation of Lake Mały Kopik was assessed using the criteria given by KUDELSKA et al. (1994). The role of the watershed in supplying matter to the lake and the rate of its eutrophication

Table 3
Tabela 3

Assessment of Mały Kopik Lake drainage basin as nutrient supplier
Ocena zlewni jeziora Mały Kopik jako dostawcy materii do zbiornika

Indicator Wskaźnik	Value Wartość	Score Punkty
Ohle's coefficient Współczynnik Ohlego	24.96	1
Water budget type of the lake Typ bilansowy	no run-off bezodpływowe	2
Density of the river network Gęstość sieci rzecznej (km · km^{-2})	0.1	0
Mean sloping of the drainage basin Średni spadek zlewni (‰)	25	3
No run-off areas Obszary bezodpływowe (%)	< 20	3
Geological construction of the drainage basin Budowa geologiczna zlewni	clay and sand gliniasto-piaszczysta	2
Soil use in the drainage basin Użytkowanie ziemi	forests, agriculture and residential leśno-rolnicza z zabudową	3
Mean score Wartość średnia punktacji	2.0	
Susceptibility category of the drainage basin Kategoria podatności zlewni	group 4 4 grupa	

were determined in accordance with the guidelines given by BAJKIEWICZ-GRABOWSKA (2002).

The size of the watershed and land use types in the watershed were determined by *in situ* surveys and demarcation of the watershed borderlines as well as by analysing the planimetry of its surface on a topographic map 1:10,000.

The surface run-off of nutrients was calculated using the coefficients given by GIERCUSZKIEWICZ-BAJTLIK (1990). In order to calculate the allowable and dangerous loadings of phosphorus and nitrogen we used the statistical model of VOLLENWEIDER (1968).

The analyses of the trophic state of the lake were conducted on the grounds of the classifications given by the following authors: PATALAS (1960b), ZDANOWSKI (1983), HILLBRICHT-ILKOWSKA and WIŚNIEWSKI (1993), and FARAŚ-OSTROWSKA and LANGE (1998).

Table 4
Tabela 4

Annual loadings of N and P to Mały Kopik Lake
Całkowite roczne obciążenie jeziora Mały Kopik ładunkiem N i P

Sources Źródła	Loadings Ładunki	
	phosphorus (kg P·year^{-1}) fosfor (kg P·rok^{-1})	nitrogen (kg N·year^{-1}) azot (kg N·rok^{-1})
1. Spatial sources – Źródła przestrzenne	80.8	1886.8
a) forests – lasy	37.5	1125.0
b) build up land – teren zabudowany	12.4	82.8
c) grass land – użytki zielone	20.4	409.0
d) arable land – grunty orne	10.5	270.0
2. Scattered sources – Źródła rozproszone	17.5	43.8
3. Atmospheric sources – Źródła atmosferyczne	4.5	93.6
3. Total – Razem	102.8	2024.2

RESULTS AND DISCUSSION

Lakes are dynamic ecosystems, changing over time and aiming to enrich and intensify the biological productivity. It is well known (Patalas 1960a, Grochowska, Tandyrak 2006, Grochowska et al. 2006) that in lakes with lower water dynamics eutrophication runs more slowly and that such lakes are less vulnerable to man-made pressure.

Mały Kopik Lake is a small reservoir situated in a land hollow, whose southern and western shores are strongly elevated and covered by a mixed forest. Wind access to the lake is considerably limited, which is reflected by poor water dynamics. The theoretical depth of mixing (2.64) calculated after Patalas (1960a) indicates degree IV of the lake stability. This assumption was confirmed by the results of the study conducted in 2006: as early as in the first days of May, the difference in temperatures across the water column was considerable and lasted throughout the summer. At the peak of the summer stagnation (early September) the epilimnion was 4 m thick (the temperature oscillated around 18°C) with a thermocline beneath with the max. gradient of 4.8°C·m^{-1}.

Other parameters, such as morphometric characteristics (especially the low mean depth 3.2 m), the ratio between volume and shoreline length, incomplete thermal stratification in the summer (no hypolimnia) and a high volume of the epilimnion compared to the active bottom area, indicated that the lake belonged to category III of vulnerability to degradation.

(KUDELSKA et al. 1994). Category III can be attributed to lakes which are not vulnerable to degradation. The values of the above parameters reflect intensive exchange of nutrients from the lake sediments to the trophogenic layer, which may augment the primary production.

The watershed of Mały Kopik Lake is classified as a group 4 watershed according to the classification of BAJKIEWICZ-GRABOWSKA (2002), i.e. it has a large ability to mobilize loadings from non-point sources. The unfavourable features of the lake's immediate surroundings are a low share of non-draining areas, steep sloping (25 ‰) and land use pattern. The evidence that the watershed enriches the lake with large loads of nutrients consists of the estimated annual loads of nitrogen (N) and phosphorus (P) as calculated with the coefficients of watershed use types and unit run-off given by GIERCUSZKIEWICZ-BAJTLIK (1990). It was determined that the total load of N was 2,024.2 kg and that of P – 102.8 kg (Table 4). The corresponding values calculated per unit surface area were 25.95 g $N \cdot m^{-2} \cdot year^{-1}$ and 1.32 g $P \cdot m^{-2} \cdot year^{-1}$.

The allowable and critical loadings in this lake, calculated using the statistical model by VOLLENWEIDER (1968), are 0.804 g $N \cdot m^{-2} \cdot year^{-1}$ and 1.608 g $N \cdot m^{-2} \cdot year^{-1}$, and 0.050 g $P \cdot m^{-2} \cdot year^{-1}$ and 0.100 g $P \cdot m^{-2} \cdot year^{-1}$, respectively.

Compared to the actual loadings of N and P to the lake, the values calculated after VOLLENWEIDER (1968) indicate that the actual loading exceeds more than ten-fold the critical values, being the reason for the lake's accelerated eutrophication.

The combination of the watershed vulnerability and the lake's resistance to degradation meant that Mały Kopik Lake and its watershed belonged to type IV of ecological systems (BAJKIEWICZ-GRABOWSKA 2002). In such a combination, the natural features of the watershed support surface run-off and the lake is largely vulnerable to external impacts, which was also confirmed by a comparison between the actual loading and the theoretical „Vollenweider" loadings (1968). As a result, eutrophication of the lake waters should proceed rapidly.

The influence of the watershed is reflected by the quality of the lake waters.

Oxygen profiles in Mały Kopik Lake are poor. In the surface water layers oxygen saturation oscillated around 90%, reaching 116% in May, which proved intensive primary production. Other concurrent parameters were: 8.42 pH, lack of free carbon dioxide and BOD_5–1.9 mg $O_2 \cdot dm^{-3}$. In the deeper layers, particularly near the bottom, oxygen depleted rapidly until total oxygen deficiency occurred. Such conditions, observed in May through September, were definitely caused by decay of the matter produced in the lake and deposited in the sediment. The oxygen curve in the lake was a clinograde (ABERG, RHODE 1942), typical for eutrophied lakes.

Eutrophication of a lake is demonstrated by concentrations of nutrients, particularly N and P (Stauffer 1987, Van der Molen et al. 1998). Both elements occurred in large quantities in Mały Kopik Lake: up to 0.673 mg P·dm^{-3} and 10.61 mg N·dm^{-3} (Figures 2, 3).

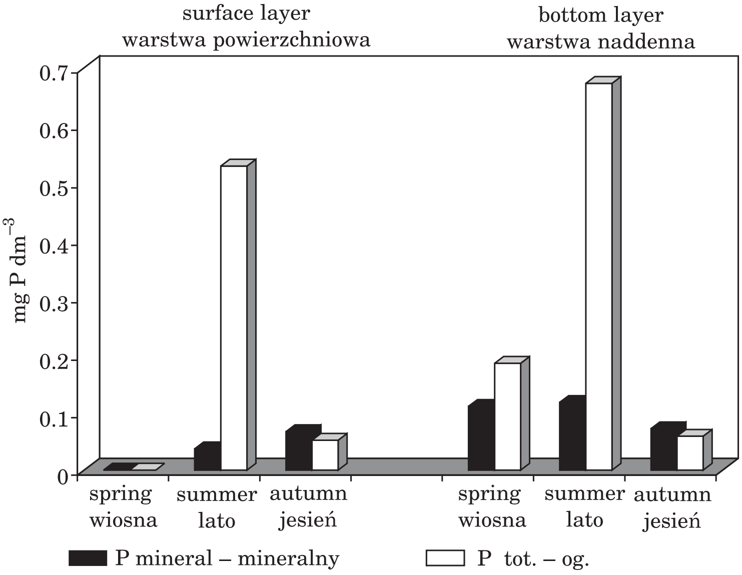


Fig. 2. Mineral and total phosphorus content in the waters of Mały Kopik Lake
Rys. 2. Zawartość fosforu mineralnego i ogólnego w wodach jeziora Mały Kopik

Total P was dominated by the organic form, except for the summer stagnation peak, when the dominant form in the near-bottom water was phosphate-0.529 mg P·dm^{-3} (Figure 2). The latter was caused by the release of mineral P from the bottom sediments during a severe oxygen deficit. Taking into account the division of lakes by Zdanowski (1983) and based on the spring concentration of total P in the water, Mały Kopik Lake can be described as polytrophic (degree IV of the productivity). The classification of Hillbricht-Ilkowska and Wiśniewski (1993), based on the water transparency, total P content and chlorophyll a (up to 50 mg·m^{-3}) – Figure 4, indicates that Mały Kopik Lake is a heavily eutrophied reservoir.

The overall amount of nitrogen compounds in the lake was dominated by the organic form. Mineral N occurred in the lake waters constantly and in high concentrations (Figure 3). Mineral forms of N were dominated by ammonium and nitrate. On the one hand, the mineral forms of N measurable in the water throughout the whole vegetative period suggest the abundance of nitrogen. On the other hand, they imply intensive mineralization and nitrification in the water. With regard to the richness in mineral N (Patalas 1960c), Kopik Mały can be classified as 'poly'.

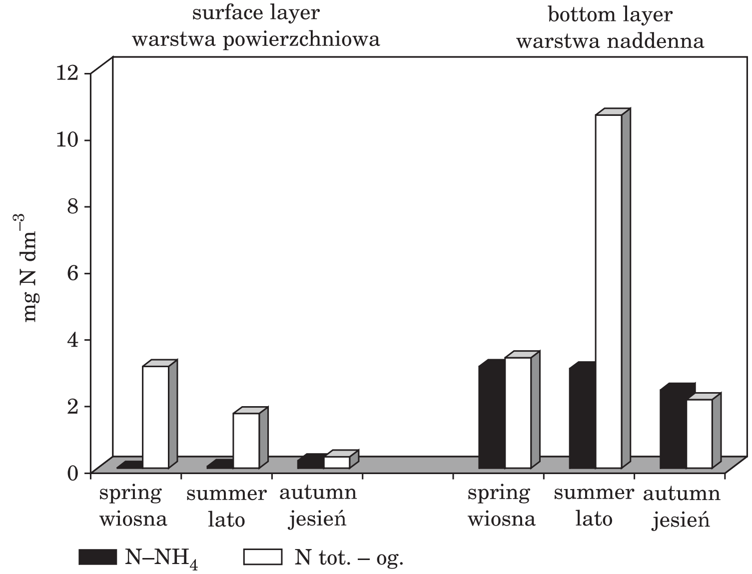
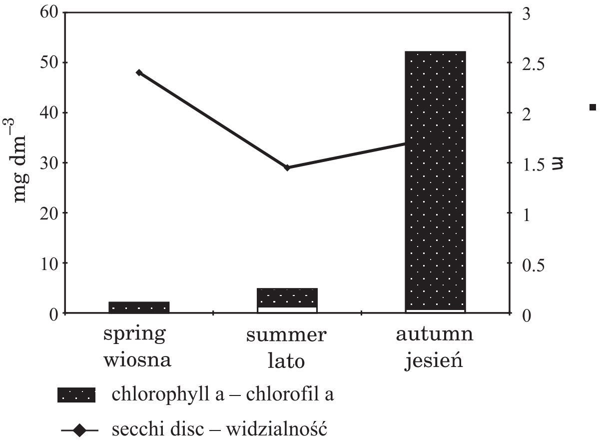


Fig. 3. Ammonium and total nitrogen content in the waters of Mały Kopik Lake

Rys. 3. Zawartość azotu amonowego i ogólnego w wodach jeziora Mały Kopik



Rys. 4. Widzialność wód oraz ilość chlorofilu *a* w wodach jeziora Mały Kopik

Fig. 4. Visibility and chlorophyll *a* content in the waters of Mały Kopik Llake

The fairly advanced eutrophication and the resultant high productivity of Mały Kopik Lake can be further evidenced by the high BOD$_5$–up to 7.2 mg $O_2 \cdot dm^{-3}$ and permanganate value–up to 72 mg $O_2 \cdot dm^{-3}$ (Figure 5). Throughout the study, the ratio between permanganate value and BOD$_5$ was much higher than 1, which indicates widespread presence of allochthonous (coming from the watershed) organic matter in the lake waters.

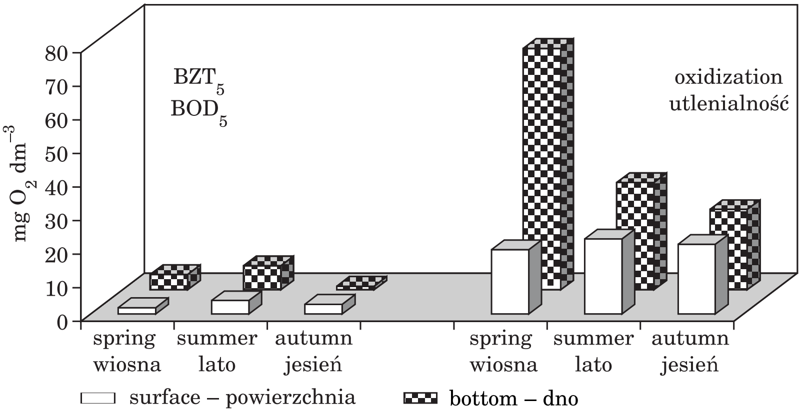


Fig. 5. Organic matter content in the waters of Mały Kopik Lake
Rys. 5. Zawartość materii organicznej w wodach jeziora Mały Kopik

Water transparency in the surveyed lake oscillated around 2 m. According to Faraś-Ostrowska and Lange (1998), the value meets the criteria of a eutrophic lake.

At present, Mały Kopik Lake has low water quality, thus action in the watershed is critically needed to protect the lake and reduce the external loadings entering the lake. Further development in the watershed comprising expansion of residential areas or arable land may lead to total degradation of this reservoir.

CONCLUSIONS

1. Mały Kopik Lake is vulnerable to external impacts. It can be classified to category III of degradation vulnerability.

2. The lake's watershed has a high potential ability to mobilize non-point nutrient loadings.

3. The lake is subjected to high rate eutrophication.

4. According to Zdanowski's criteria (1983), Mały Kopik Lake can be described as polytrophic – trophic condition degree IV.

5. According to the classification by Hillbricht-Ilkowska and Wiśniewski (1993), the lake can be classified as heavily eutrophied.

6. With regard to the richness in mineral N the lake is a 'poly' type (Patalas 1960b).

7. Following the division of Faraś-Ostrowska and Lange (1998), Mały Kopik can be qualified as eutrophic.

8. Prompt action should be undertaken in the lake's watershed in order to reduce the nutrient loadings running off to the lake. Further development in the watershed aimed such as expansion of built-up area or agricultural growth can result in total degradation of the reservoir.

REFERENCES

ABERG B., RHODE W. 1942. *Über die Milieufaktoren in Einigen Südschwedischen Seen.* Symp. Bot. Upsal., 5(3): 256.

BAJKIEWICZ-GRABOWSKA E., 1999. *Struktura fizyczno-geograficzna układu krajobrazowego zlewnia-jezioro i jej wpływ na tempo naturalnej eutrofizacji jezior*. Wyd. IRŚ w Olsztynie, 77-84.

BAJKIEWICZ-GRABOWSKA E. 2002. *Obieg materii w systemach rzeczno – jeziornych*. Wyd. UW, Wydz. Geografii i Studiów Regionalnych, 274.

FARAŚ-OSTROWSKA B., LANGE W. 1998. *Przezroczystość wody jako miara nasilenia eutrofizacji jezior. Zagrożenia degradacyjne a ochrona jezior*. Zakł. Limnologii UG, Bad. Limnol., 1: 181-191.

GIERCUSZKIEWICZ-BAJTLIK M. 1990. *Prognozowanie zmian jakości wód stojących*. Inst. Ochr. Środ., Warszawa.

GROCHOWSKA J., TANDYRAK R. 2006. *Temperature and dissolved oxygen profiles in Lake Plusze.* Limnol. Rev., 6(2006): 117-122.

GROCHOWSKA J., TEODOROWICZ M. 2006. *Ocena możliwości oddziaływania zlewni na jeziora górnej Pasłęki oraz podatności jezior na degradację.* Acta Scient. Polonorum ser. Formatio Circumiectus, 5: 99-111.

GROCHOWSKA J., TEODOROWICZ M., TANDYRAK R. 2006. *Temperature and dissolved oxygen characteristics of the lakes in the upper Pasłęka river catchment.* Pol. J Natur. Sci. 20(1): 291-305.

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

HILLBRICHT-ILKOWSKA A., WIŚNIEWSKI R. J. 1993. *Trophic differentiation of lakes the Suwałki Landscape Park (North-Eastern Poland) and its Buffer Zone – Present State, Changes Over Years. Position in trophic classification of lakes*. Ekol. Pol., 41(1-2): 195-219.

HILLBRICHT-ILKOWSKA A. 1999. *Jezioro a krajobraz: Związki ekologiczne, wnioski dla ochrony.* Wyd. IRŚ w Olsztynie, 19-40.

IRŚ, 1964. *Mapa batymetryczna i opracowanie danych morfometrycznych jeziora Mały Kopik.*

KUBIAK J., TÓRZ A., 2005. *Zmienność poziomu trofii bradymiktycznego jeziora Morzycko w latach 1974–2002.* Zesz. Probl. Post. Nauk Rol., 505: 199-209.

LANGE W. 1986. *Fizyczno-limnologiczne uwarunkowania tolerancji systemów jeziornych Pomorza.* Zesz. Nauk. UG, Rozpr. Monogr., 79.

Mapa Topograficzna Polski (skala 1:10 000), 1999. *Olsztyn, cz. Bartąg.* Główny Geodeta Kraju.

PANFIL J. 1978. *Pojezierze Mazurskie.* WP, Warszawa.

PATALAS K. 1960a. *Mieszanie wody jako czynnik określający intensywność krążenia materii w różnych morfologicznie jeziorach okolic Węgorzowa.* Rocz. Nauk Rol., 77(B-1): 223-242.

PATALAS K. 1960b. *Charakterystyka składu chemicznego wody 48 jezior okolic Węgorzowa.* Rocz. Nauk Rol., 77(B-1): 243-297.

STAUFFER R. E. 1987. *Vertical nutrient transport and its effects on epilimnetic phosphorus in four calcareous lakes*. Hydrobiologia, 154: 87-112.

VAN DER MOLEN D., PORTIELJE R., BOERS P. C. M., LIJKLEMA L 1998. *Changes in sediment phosphorus as a result of eutrophication in lake Veluwe, the Netherlands*. Wat. Res., 32(11): 3281-3288.

VOLLENWEIDER R. A. 1968. *Scientific fundamentals of the eutrophication of lakes and flowing water, with particular reference to nitrogen and phosphorus as factor in eutrophication.* Tech. report Organisation for Economic Cooperation and Development, Paris.

ZDANOWSKI B. 1983. *Variability of nitrogen and phosphorus contents and lake eutrophication*. Pol. Arch. Hydrob., 29(3-4): 541-597.

J. Elementol. 2008, 13(1): 69–79

THE INFLUENCE OF SYNBIOTICS ON MAGNESIUM BIOAVAILABILITY FROM DIETS IN RATS

Jan Kłobukowski[1], Monika Modzelewska-Kapituła[2], Danuta Wiśniewska-Pantak[1], Kazimierz Kornacki[3]

[1]Chair of Human Nutrition
[2]Chair of Meat Technology and Chemistry
[3]Chair of Industrial and Food Microbiology
University of Warmia and Mazury in Olsztyn

Abstract

Products containing pro- and prebiotics are known as synbiotics. The benefits of pro- and prebiotics on the host include: normalization of the microbial balance in the gastrointestinal tract, increase of mineral bioavailability, reduction of cholesterol level in blood and prevention of gastrointestinal disorders. The aim of the work was to compare the apparent absorption and retention indexes in rats fed diets containing probiotic or synbiotic soft cheeses. As a probiotic, the strain *Lactobacillus plantarum* 14 was used, whereas as prebiotics inulin HPX and maltodextrin were used. For 10 days, the animals were fed diets consisting of 61-81% of soft cheese with probiotic (A diet), probiotic and 2,5% of inulin HPX (B diet) and probiotic and 2.5% of maltodextrin (C diet). On the basis of the magnesium concentration in the diets and the urine and faeces excreted during the last 5 days of the experiment, the apparent absorption (A) and retention (R) indexes (%, mg 5 days^{-1}) were calculated. The apparent absorption indexes obtained did not differ statistically among the groups, although the highest value of apparent absorption (A%) was obtained in group B. The apparent retention indexes in group A were significantly higher ($p < 0.05$) compared to groups B and C. On the other hand, in B and C groups increased faecal mass was detected, but the inulin influence was stronger than that of maltodextrin. Although the short-term supplementation of rat diets with inulin HPX and maltodextrin did not increase magnesium absorption and retention, their use in probiotic products is reasonable because of the beneficial physiological effects.

Key words: probiotics, prebiotics, magnesium, absorption, retention, rats, soft cheese.

---

dr hab. inż. Jan Kłobukowski, Chair of Human Nutrition, University of Warmia and Mazury, Sloneczna 44A, 10-718 Olsztyn, Poland, phone +48 89 523 41 12, e-mail: jan.klobukowski@uwm.edu.pl

WPŁYW SYNBIOTYKÓW NA BIODOSTĘPNOŚĆ MAGNEZU Z DIETY U SZCZURÓW

Abstrakt

Jako produkty synbiotyczne są określane wyroby zawierające jednocześnie probiotyki i prebiotyki. Korzystny wpływ pro- i prebiotyków na organizm obejmuje m.in. normalizację składu mikroflory przewodu pokarmowego, zwiększanie biodostępności składników mineralnych, obniżanie poziomu cholesterolu we krwi oraz zapobieganie występowaniu zaburzeń jelitowych. Celem pracy było porównanie wpływu diety zawierającej probiotyczny i synbiotyczne serki twarogowe na absorpcję i retencję magnezu u szczurów. Zastosowanym szczepem probiotycznym był *Lactobacillus plantarum* 14, a prebiotykami inulina HPX oraz maltodekstryna średniosckukrzona. Zwierzętom przez 10 dni podawano diety, w skład których wchodził serek twarogowy, w ilości 61-81%, zawierający: probiotyk (dieta A), probiotyk i 2,5% inuliny HPX (dieta B) lub probiotyk i 2,5% maltodekstryny (dieta C). Na podstawie zawartości magnezu w diecie, kale i moczu wydalonego w czasie ostatnich 5 dni eksperymentu, wyznaczono współczynniki absorpcji (A) i retencji (R) pozornej (%, mg 5 dni^{-1}). Uzyskane współczynniki absorpcji nie różniły się znacząco między grupami zwierząt, chociaż najwyższy (A%) odnotowano w grupie B, natomiast wartości współczynników retencji pozornej w grupie A były istotnie wyższe (p < 0,05) w porównaniu z grupami B i C. W grupach przyjmujących dietę synbiotyczną obserwowano zwiększenie masy kału w porównaniu z grupą kontrolną A, przy czym działanie inuliny HPX było silniejsze niż maltodekstryny. Chociaż krótkotrwała suplementacja diety szczurów inuliną HPX i maltodekstryną średnioscukrzoną nie przyczyniła się do wzrostu absorpcji i retencji magnezu, to stosowanie tych prebiotyków łącznie ze szczepem probiotycznym jest uzasadnione ze względu na korzystne efekty fizjologiczne.

Słowa kluczowe: probiotyki, prebiotyki, magnez, absorpcja, retencja, szczury, ser twarogowy.

INTRODUCTION

Studies into the acquisition of new probiotic cultures and their application in the food production process have been underway for years. Probiotics, live cultures of bacteria and fungi (Sanders, Klaenhammer 2001, Holzapfel, Schillinger 2002), are applied both in food of animal origin, including fermented dairy drinks, ripening cheeses, white fresh cheeses, fermented sausages, as well as in food of plant origin. Such products are sought by consumers aware of the positive effect of probiotic bacteria on the human body. These effects include: normalization of intestinal microflora, prevention or attenuation of disorders and diseases of the alimentary tract, and strengthening the immune system. Probiotic bacteria synthesize B group vitamins, folic and nicotinic acids, increase the availability of proteins as well as the absorption of the minerals Ca, Cu, Fe, Mn, P and Zn, and are likely to contribute to a reduction in the blood level of cholesterol (Defecińska, Libudzisz 2000, Kaur et al. 2002). Similar effects in terms of normalizing the composition of alimentary tract microflora, increasing bioavailability of minerals, preventing intestinal disorders and reducing cholesterol level in blood are produced by prebiotics (BLAUT 2002, LOSADA, OLLEROS 2002). They are the dietary components which escape digestion in the small intestine, are transferred intact to the colon, where they are utilized by probiotic microflora. Prebiotics are substrates that selectively stimulate the development of a given species or strain of probiotic bacteria, thus exerting a beneficial effect on the health status of the host (ŚLIŻEWSKA, LIBUDZISZ 2002, ZDUŃCZYK 2002, CUMMINGS et al. 2004). Carbohydrates that display characteristics of prebiotic substances include inulins and maltodextrin, widely applied in the food industry due to their functional properties, i.e. gel-forming ability, stabilization and concentration of emulsions and providing foodstuffs with attractive sensory attributes (VORAGEN 1998, FORTUNA, SOBOLEWSKA 2000, JAKUBCZYK, KOSIKOWSKA 2000, POLAK 2001, KŁĘBUKOWSKA et al. 2002, KRZYŻANIAK et al. 2003, SKOWRONEK, FIEDUREK 2003).

Other food products that also contain prebiotics are referred to as synbiotics. Since the concept of synbiotics is relatively new, there are few reports of interactions between pro- and prebiotics. Bearing in mind their properties, prebiotics should positively affect the growth and survivability of probiotics. By adapting its metabolism to a specified substrate (prebiotic), a probiotic strain has a greater chance for colonizing the gastrointestinal tract owing to increased ability to compete with the existing microflora (FOOKS et al. 1999, SAARELA et al. 2000, PUPPONEN-PIMIA et al. 2003). A combined application of probiotics and prebiotics should, therefore, increase the efficacy of their action onto the host's body.

The research was aimed at comparing the absorption and retention of magnesium in rats administered a prebiotic diet containing soft cheese produced with addition of *Lactobacillus plantarum* strain as well as a probiotic-containing diet additionally supplemented with prebiotics, inulin HPX and medium-saccharified maltodextrin.

MATERIAL AND METHODS

Experiments were carried out on 18 standardized white experimental rats of Wistar strain, obtained from the Department of Biological Analysis of Food, Institute of Animal Reproduction and Research of the Polish Academy of Sciences in Olsztyn. Initial body weight of the animals ranged from *ca* 91 to 98 g. They were divided into 3 experimental groups, 6 rats each, and kept in single metabolic cages, which enabled separate collection of urine and faeces.

Experimental diets were prepared based on soft cheeses, produced in a dairy plant, containing inulin HPX (Orafti, Belgium), medium-saccharified maltodextrin (Pepes Sp. z o.o., Poland) and a potentially probiotic strain *Lactobacillus plantarum* 14. The basic composition of the diets was as follows: protein – 10% (N x 6.38), vitamins – 1% (AOAC 1975), mineral salts – 3% (NRC 1976), potato starch – 5%, and maize starch – supplementing diet composition to 100 g of dry matter of diet. Fat content of the soft cheese was taken into account while balancing the diets. Three diets were prepared in the study: A – probiotic diet (control): with soft cheese containing *L. plantarum* as well as synbiotic diets containing, apart from the probiotic culture, a prebiotic: inulin HPX (diet B) or medium-saccharified maltodextrin (diet C). The addition of prebiotics to the soft cheeses reached 2.5%. In order to obtain a similar dry matter content in all products, 2.5% of skimmed milk powder was added to the probiotic soft cheese. The contribution of particular components in the experimental diets is presented in Table 1, whereas the physicochemical characteristics of soft cheeses used in the study can be found in Table 2. The count of *L. plantarum* 14 strain in the products was 10^7cfu g^{-1}.

Table 1
Tabela 1

Compositions of diet used in the feeding trial (g 100 g^{-1} of d.m.)
Udział poszczególnych komponentów w dietach sporządzonych do doświadczenia żywieniowego (g 100 g^{-1} s.s.)

Specification Wyszczególnienie	Diets Diety		
	A	B	C
Cheese Ser	60.8	81.1	69.6
Vitamins Witaminy	1.0	1.0	1.0
Mineral salts Sole mineralne	3.0	3.0	3.0
Potato starch Skrobia ziemniaczana	5.0	5.0	5.0
Corn starch Skrobia kukurydziana	30.3	9.9	21.4

Diets containing soft cheese with: A – probiotic strain *L. plantarum*, B – probiotic strain *L. plantarum* and 2.5% of inulin HPX, C – probiotic strain *L. plantarum* and 2.5% of maltodextrin.
Diety zawierające serek z: A – probiotycznym szczepem *L. plantarum*, B – probiotycznym szczepem *L. plantarum* i 2,5% inuliny HPX, C – probiotycznym szczepem *L. plantarum* i 2,5% maltodekstryny średnioscukrzonej.

A balanced experiment was conducted, including a 5-day preliminary period and a 5-day experimental period. Diet intake was monitored each day by collection of leftovers and samples of faeces and urine were collected for analyses.

Table 2
Tabela 2

Physicochemical composition of white cheeses
Charakterystyka fizykochemiczna serków twarogowych

Specification Wyszczególnienie	Cheese Ser		
	A	B	C
Dry weight Sucha masa (%)	35.2	35.4	36.0
Protein Białko ogółem (%)	5.8	4.4	5.2
Fat Tłuszcz (%)	24.5	25.0	26.0
Ash Popiół ogółem (%)	0.7	0.5	0.5
Magnesium Magnez (mg g^{-1})	96.4	69.4	70.5

Soft cheese with: A – probiotic strain *L. plantarum*, B – probiotic strain *L. plantarum* and 2.5% of inulin HPX, C – probiotic strain *L. plantarum* and 2.5% of maltodextrin
Serek z: A – probiotycznym szczepem *L. plantarum*, B – probiotycznym szczepem *L. plantarum* i 2,5% inuliny HPX, C – probiotycznym szczepem *L. plantarum* i 2,5% maltodekstryny średnioscukrzonej

A quantitative analysis of magnesium in the diet, faeces and urine of rats was carried out by means of flame atomic absorption spectrophotometry (Unicam 393, Solar). Measurements were performed at a wavelength of 285.2 nm.

Bioavailability of magnesium was expressed by means of coefficients of apparent absorption (A) and apparent retention (R). The first was calculated from the difference between the quantity of the mineral absorbed with diet and its quantity excreted with faeces, whereas the latter was computed as the difference between the quantity of the mineral absorbed with the diet and that excreted with faeces and urine. The values obtained were expressed in mg 5 $days^{-1}$ and in percentage units. The results were presented as mean values ± standard deviation.

Statistical analysis of the results was carried out with Duncan's test (Statistica 6.0, StatSoft. Inc.) at a significance level of $p < 0.05$.

RESULTS AND DISCUSSION

Soft cheeses produced with addition of potentially probiotic bacteria and prebiotics were observed to differ in magnesium content (Table 2).

The highest content of this mineral was determined in probiotic cheeses (96.4 mg g^{-1}), whereas the lowest one was in synbiotic products (69.4 mg g^{-1} and 70.5 mg g^{-1}). The intake of magnesium was at a similar level in all groups (Table 3), though its lowest level was observed in group B. Coefficients of apparent absorption (mg 5 $days^{-1}$, %) did not differ significantly between the groups of animals, yet the lowest value of A (%) was recorded in the group of rats administered a diet with synbiotic soft cheese containing inulin HPX (Table 3). In turn, values of apparent retention coefficients (mg 5 $days^{-1}$ and %) determined in the control group, fed a diet with the probiotic soft cheese, were significantly higher ($p < 0.05$) as compared to the groups administered synbiotic soft cheeses.

Table 3
Tabela 3

Mean values of Mg intake, apparent absorption and retention in rats fed probiotic or synbiotic cheeses
Średnie wartości spożycia, absorpcji i retencji magnezu u szczurów karmionych probiotycznym lub synbiotycznymi serkami twarogowymi

Specification Wyszczególnienie		Diet Dieta		
		A *n*=5	B *n*=6	C *n*=4
Mg intake Spożycie Mg	(mg 5 $days^{-1}$) (mg 5 dni^{-1})	22.8 ± 1.5 ^{A}	20.5 ± 1.1 ^{B}	22.8 ± 0.8 ^{A}
Apparent absorption Absorpcja pozorna	(mg 5 $days^{-1}$) (mg 5 dni^{-1})	19.1 ± 1.7 ^{A}	17.6 ± 1.2 ^{A}	18.6 ± 1.2 ^{A}
Apparent absorption Absorpcja pozorna	(%)	83.6 ± 3.6 ^{A}	85.8 ± 3.8 ^{A}	81.7 ± 5.0 ^{A}
Apparent retention Retencja pozorna	(mg 5 $days^{-1}$) (mg 5 dni^{-1})	6.0 ± 1.2 ^{A}	4.0 ± 0.5 ^{B}	4.7 ± 0.5 ^{B}
Apparent retention Retencja pozorna	(%)	26.1 ± 4.2 ^{A}	19.6 ± 2.9 ^{B}	20.6 ± 2.0 ^{B}

Diets containing soft cheese with: A – probiotic strain *L. plantarum*, B – probiotic strain *L. plantarum* and 2.5% of inulin HPX, C – probiotic strain *L. plantarum* and 2.5% of maltodextrin; ^{AB}row mean values without the same superscripts differ statistically ($p < 0.05$).
Diety zawierające serek z: A – probiotycznym szczepem *L. plantarum*, B – probiotycznym szczepem *L. plantarum* i 2,5% inuliny HPX, C – probiotycznym szczepem *L. plantarum* i 2,5% maltodekstryny średnioscukrzonej; ^{AB}średnie w rzędach bez wspólnych indeksów różnią się statystycznie ($p < 0,05$)

Among the physiological effects of administering a prebiotic-enriched diet to the rats increased mass of faeces was observed. In the groups fed diets with synbiotic soft cheese, the mass of faeces (group B – 2.86 g, group C – 2.24 g) was higher than in control group A (1.81 g), although the effect of inulin HPX was stronger than that of maltodextrin. Simultaneously, no increased excretion of magnesium along with the increased mass of faeces was observed in the group of animals fed a diet with inulin-containing soft cheese (Figure 1).

Issues referring to a possible increase in bioavailability of elements, i.e. calcium, phosphorus or magnesium, achieved through diet supplementation with prebiotics have already been addressed to and described. Studies on this subject enabled researchers to clarify the mechanism of prebiotic action. It has been demonstrated that microbiological fermentation of prebiotics in the colon decreases pH of intestinal digesta, which in turn causes an increase in the solubility of mineral compounds, thus enhancing their bioavailability (Baba et al. 1996, Scholz-Ahrens et al. 2001). Stimulation of magnesium absorption upon diet enrichment with prebiotic has already been observed in both long- and short-term studies (Lopez et al. 2000, Coudray et al. 2005) carried out on young, growing animals and on mature individuals (Rashka, Daniel 2005), which received diets that either met demands for this mineral or were magnesium-deficient (Ohta et al. 1994), and various prebiotics (Coudray et al. 2003a) at doses of 1–10%. The results obtained by Lobo et al. (2006) indicate that a 5% contribution of fructooligosaccharides (FOS) in a diet of animals lead to a decrease in the quantity of magnesium excreted with faeces as well as an increase of intestinal absorption of this element as compared to the control group. Similar observations were made in the reported study – the group of rats fed a diet with soft cheese containing *L. plantarum* strain and 2.5% of inulin HPX (B) was characterized by the lowest quantity of magnesium excreted with faeces and the highest apparent absorption (A%). Nevertheless, caution should be paid to the fact that in this group absorption

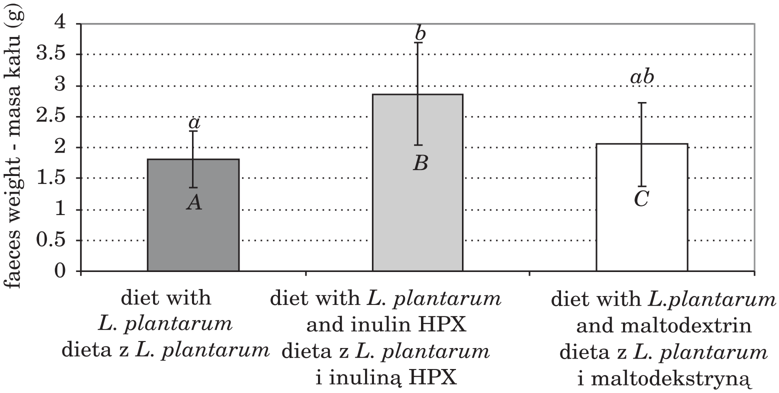


Fig. 1. The influence of the diet on faeces weight
^{ab}mean values in the figure without the same superscripts differ statistically ($p < 0.05$)

Rys. 1. Wpływ diety na masę kału
^{ab}średnie wartości na wykresie bez wspólnych indeksów różnią się statystycznie ($p < 0,05$)

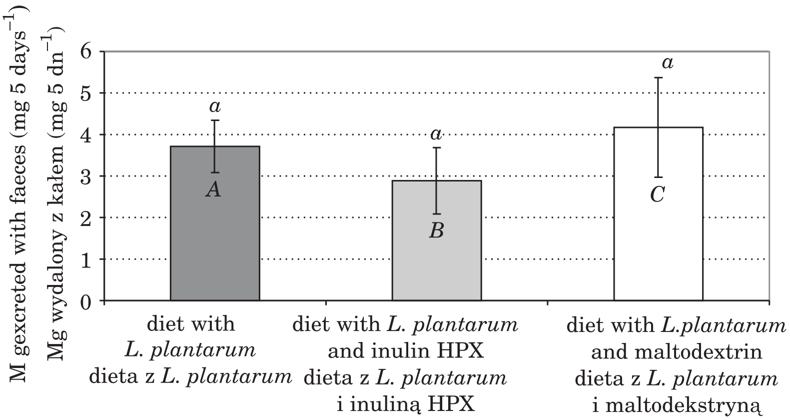


Fig. 2. The influence of the diet on amount of magnesium excreted with faeces
^{ab}mean values in the figure without the same superscripts differ statistically ($p < 0.05$)

Rys. 2. Wpływ diety na ilość magnezu wydalonego z kałem
^{ab}średnie wartości na wykresie bez wspólnych indeksów różnią się statystycznie ($p < 0{,}05$).

expressed in mg 5 days^{-1} was lower, and differences in the absorption coefficients (A%, A mg 5 days^{-1}) and quantity of magnesium excreted with faeces were not statistically significant between the groups examined.

Ohta et al. (1998) as well as Wolf et al. (1998) demonstrated the possibility of increasing magnesium absorption through diet supplementation with fructooligosaccharides (FOS) applied at concentrations of 1–10%. A dependency was reported between the content of prebiotics in a diet and their effect on magnesium absorption – increased absorption was observed along with an increasing concentration of prebiotic and, what is more, that effect occurred already at 1% FOS addition to diet (Wolf et al. 1998). Simultaneously, Wolf et al. (1998) did not found any increase in the apparent retention of magnesium in any of the experimental groups administered with 1–5% FOS, which was also confirmed in the current experiment.

In the studies by Lopez et al. (2000), Coudray et al. (2003a), Rashka, Daniel (2003), coefficients of apparent absorption of magnesium ranged from 27% (in groups fed diets without prebiotics) to 84%. In the reported study, all groups of animals were characterized by high coefficients of apparent absorption (82-86%). It was due to the administration of a diet whose major component (61-81%) were soft cheeses containing lactose. The presence of such monosaccharides as lactose or lactullose in a diet was likely to contribute to the increased permeability of cellular membranes of the intestinal epithelium, thus facilitating magnesium absorption. Furthermore, lactose – which is utilized by bacteria colonizing the colon – contributes to a decreasing pH of intestinal digesta, which additionally makes magnesium absorption easier (Coudray et al. 2003b). A correlation between apparent absorption of magnesium and lactose content of diet was also observed by DELISLE et al. (1995), who reported on the higher bioavailability of this element in a diet containing milk and milk powders, as compared to a diet with the addition of cheese – containing less lactose than milk and milk powder. The effect of lactose partly digested in the upper sections of the alimentary tract on the absorption of magnesium is, however, weaker than that of carbohydrate prebiotics undergoing fermentation already in the colon (COUDRAY et al. 2003b).

CONCLUSIONS

1. Unlike food products of plant origin, dairy products do not constitute a rich source of magnesium, yet the lactose they contain improves the bioavailability of this element.

2. The application of inulin HPX and medium-saccharified maltodextrin together with a prebiotic strain in diets for rats contributed to increased absorption and retention of magnesium, in contrast to a group fed a diet with probiotic soft cheese.

3. Supplementation of probiotic food products with prebiotics is advisable due to their beneficial physiological effects, including increasing mass of faeces observed in groups of animals fed diets containing inulin HPX and maltodextrin.

The study was financed from funds of the State Committee for Scientific Research for the years 2004-2006 and from means of the WAMADAIREC Warmia and Mazury Dairy Excellence Centre (Qlk1-CT-2002-30401).

REFERENCES

AOAC, 1975. *Official Methods of Anal*ysis. Association of Official Analytical Chemists. Washington D.C.

BABA S., OHTA A., OHTSUKI M., TAKIZAWA T., ADACHI T., HARA H. 1996. *Fruktooligosaccharides stimulate the absorption of magnesium from the hindgut in rats*. Nutr. Res., 16 (4): 657-666.

BLAUT M. 2002. *Relationship of prebiotics and food to intestinal microflora*. Eur. J. Nutr., 41, Suppl. 1: 11-16.

COUDRAY C., TRESSOL J.C., GUEUX E., RAYSSIGUIER Y. 2003a. *Effects of inulin-type fructans of different chain length and type of branching on intestinal absorption and balance of calcium and magnesium in rats*. Eur. J. Nutr., 42: 91-98.

COUDRAY C., DEMIGNÉ C., RAYSSIGUIER Y. 2003b. *Effects of dietary fibers on magnesium absorption in animals and humans*. J. Nutr., 133: 1-4.

COUDRAY C., FEILLET-CAUDRAY C., TRESSOL J.C., GUEX E., THIEN S., JAFFRELO L., MAZUR A., RAYSSIGUIER Y. 2005. *Stimulatory effect of inulin on intestinal absorption of calcium and magnesium in rats is modulated by dietary calcium intakes.* Eur. J. Nutr., 44: 293-302.

Cummings J.H., Edmond L.M., Magee E.A. 2004. *Dietary carbohydrates and health: do we still need the fibre concept?* Clin. Nutr. Suppl., 1: 5-17.

Defecińska A., Libudzisz Z. 2000. *Bakterie fermentacji mlekowej – wpływ na funkcje życiowe człowieka.* Prz. Mlecz., 8: 247-251.

Delisle J., Amiot J., Doré F. 1995. *Biological bioavailability of calcium and magnesium from dairy products*. Int. Dairy J., 5: 87-96.

Fooks L. J., Fuller R., Gibson G.R. 1999. *Prebiotics, probiotics and human gut microbiology*. Int. Dairy J., 9: 53-61.

Fortuna T., Sobolewska I. 2000. *Maltodekstryny i ich wykorzystanie w przemyśle spożywczym*. Żywność, 2 (23): 100-108.

Holzapfel W.H, Schillinger U. 2002. *Introduction to pre- and probiotics*. Food Res. Int., 35: 109-116.

Jakubczyk E., Kosikowska M., Jaworski S. 2004. *Ocena zgodności wybranych asortymentów jogurtu z Polską Normą i projektem Normy FAO/WHO*. Mat. IX Międz. Sesji Nauk. „Postęp w technologii, technice i organizacji mleczarstwa", Olsztyn, 39-42.

Kaur I.P., Chopra K., Saini A. 2002. *Probiotics: potential pharmaceutical applications*. Eur. J. Pharmaceut. Sci., 15: 1-9.

Kłębukowska L., Dajnowiec F., Zander L., Kornacki K. 2002. *Characteristics of the natural yogurt containing inulin*. Pol. J. Natur. Sci., 11 (2): 123-132.

Krzyżaniak W., Olesienkiewicz A., Białas W., Słomińska L., Jankowski T., Grajek W. 2003. *Charakterystyka chemiczna maltodekstryn o małym równoważniku glukozowym otrzymywanych przez hydrolizę skrobi ziemniaczanej za pomocą alfa-amylaz*. Tech. Aliment., 2: 5-15.

Lobo A.R., Colli C., Filisett T. 2006. *Fructooligosaccharides improve bone mass and biochemical properties in rats*. Nutr. Res., 26: 413-420.

Lopez H.W., Courday C., Levrat-Verny M.A., Feillet-Courday C., Demigné C., Rémésy C. 2000. *Fructooligosaccharides enhance mineral apparent absorption and counteract the deleterious effects of phytic acid on mineral homeostasis in rats*. J. Nutr. Biochem., 11: 500-508.

Losada M.A., Olleros T. 2002. *Towards a healthier diet for the colon: the influence of fructooligosaccharides and lactobacilli on intestinal health*. Nutr. Res., 22: 71-84.

National Research Council NRC, 1978. *Nutrient Requirement of Domestic Animals. Nutrient Requirements of Laboratory Animals*. National Academy of Science, Washington D.C.

Ohta A., Baba S., Takizawa T., Adachi T., 1994. *Effects of fructooligosaccharides on the absorption of magnesium in the magnesium-deficient rat model*. J. Nutr. Sci. Vitaminiol., 40: 171-180.

Ohta A., Ohtsuki M., Baba S., Hirayama M., Adachi T. 1996. *Comparison of the nutritional effects of fructo-oligosaccharides of different sugar chain length in rats*. Nutr. Res., 18 (1): 109-120.

Polak E. 2001. *Zastosowanie pro- i prebiotyków w lodach*. Przem. Spoż., 3: 22-23.

Puupponen-Pimia R., Aura A.-M., Oksman-Caldentey K.-M., Myllärinen P., Saarela M., Mattila-Sandholm T., Poutanen K. 2002. *Development of functional ingredients for gut health.* Trends Food Sci. Tech., 13: 3-11.

Raschka L., Daniel H. 2005. *Diet composition and age determine the effects of inulin-type fructans on intestinal calcium absorption in rat.* Eur. J. Nutr., 44: 360-364.

Saarela M., Mogemsen G., Fondén R., Mättö J., Mattila-Sandholm T. 2000. *Probiotic bacteria: safety, functional and technological properties.* J. Biotech., 84: 197-215.

Sanders M.E., Klaenhammer T.R. 2001. *Invited review: The scientific basis of Lactobacillus acidophilus NCFM functionality as a probiotic.* J. Dairy Sci., 84: 319-331.

Scholz-Ahrens K.E., Schaafsma G., van den Heuvel E., Schrezenmeir J. 2001. *Effects of prebiotics on mineral metabolism*. Am. J. Clin. Nutr., 73: 459-464S.

SKOWRONEK M., FIEDUREK J. 2003. *Inulina i inulinazy – właściwości, zastosowania, perspektywy*. Przem. Spoż., 3: 18-20.

ŚLIŻEWSKA K., LIBUDZISZ Z. 2002. *Wykorzystanie oligosacharydów jako prebiotyków*. Przem. Spoż., 4: 10-12, 16.

ZDUŃCZYK Z. 2002. *Probiotyki i prebiotyki, oddziaływania lokalne i systemowe*. Przem. Spoż., 4: 6-8.

WOLF B.W., FIRKINS J.L., ZHANG X. 1998. *Varying dietary concentrations of fructooligosaccharides affect apparent absorption and balance of minerals in growing rats*. Nutr. Res., 18 (10): 1791-1806.

VORAGEN A.G.J. 1998. *Technological aspects of functional food-related carbohydrates.* Trends Food Sci. Tech., 9: 328-335.

J. Elementol. 2008, 13(1): 81–90

ISOTOPES: CESIUM-137 AND POTASSIUM-40 IN SOILS OF THE *POWIAT* OF GARWOLIN (PROVINCE OF MAZOWSZE)

Elżbieta Królak, Barbara Krupa, Katarzyna Sarnowska, Jadwiga Karwowska

Departament of Ecology and Environment Protection
University of Podlasie

Abstract

In 2005, in the administrative district *(powiat)* of Garwolin (the Province of Mazowsze), the samples of forest, cropland and fallow land soils were collected from three depths: 0-3 cm, 3-7 cm, 7-12 cm. The litter from the sampling sites located in forests was also collected for studies. In the samples, the contents of isotopes ^{137}Cs and ^{40}K were measured. The highest amount of ^{137}Cs was measured in litter and the upper layer of forest soils; the content of the isotope decreased in deeper layers of the soil. Forest soils were the richest in ^{137}Cs; fallow and cropland soils contained less of this isotope. The content of ^{40}K in forest and fallow land soils did not depend on the depth from which the samples were collected. The highest amount of ^{40}K isotope was found in arable soil, the lowest – in forest soils. The content of ^{137}C in the soils decreased as the soil reaction increased but rose at higher organic carbon content. The content of ^{40}K isotope correlated negatively with the soil reaction and with the content of sand fraction but it correlated positively with the content of clay fraction.

Key words: radioactivity isotopes, cesium-137, potassium-40, forest soil, fallow land, field, Garwolin powiat.

Elżbieta Królak, University of Podlasie, ul. Prusa 12, 08-110 Siedlce, Poland, e-mail: ekologia@ap.siedlce.pl

IZOTOPY CEZU-137 I POTASU-40 W GLEBACH POWIATU GARWOLIN (WOJEWÓDZTWO MAZOWIECKIE)

Abstrakt

W 2005 r., w glebach powiatu Garwolin (woj. mazowieckie) z trzech poziomów: 0–3 cm, 3–7 cm i 7–12 cm pobierano do badań próbki gleb leśnych oraz nieużytkowanych i użytkowanych rolniczo jako pola uprawne. Dodatkowo w punktach poboru gleb leśnych pobrano do badań ściółkę leśną. W próbkach oznaczono zawartość izotopów ^{137}Cs i ^{40}K. Największą zawartość ^{137}Cs zmierzono w ściółce i powierzchniowej warstwie gleb leśnych, w głąb gleby zawartość izotopu się zmniejszała. Najbardziej wzbogacone w ^{137}Cs były gleby leśne, gleby nieużytkowane rolniczo i pola uprawne zawierały mniejsze ilości tego izotopu. W wierzchnich warstwach gleb leśnych i nieużytków zawartość ^{40}K nie zależała od głębokości poboru prób, natomiast była zależna od sposobu użytkowania gleby. Największe ilości izotopu ^{40}K zmierzono w badanej warstwie gleb ornych, najmniejsze w glebach leśnych. Zawartość ^{137}Cs w badanych glebach zmniejszała się wraz z ze wzrostem odczynu gleby i wzrastała wraz z zawartością węgla organicznego. Zawartość potasu-40 była skorelowana ujemnie z odczynem gleby i zawartością frakcji piasku oraz dodatnio z zawartością frakcji iłu.

Słowa kluczowe: radioaktywne izotopy, cez-137, potas-40, gleba leśna, nieużytek rolny, pole uprawne, powiat Garwolin.

INTRODUCTION

^{137}Cs and ^{40}K isotopes are forms of the elements that differ only very slightly in their chemical properties but are of different origins. Cesium has one stable isotope (^{133}Cs) and 20 artificial radioactive isotopes (AVERY 1996). The latter group includes ^{137}Cs isotope, which escaped to the environment as a result of the 1986 Chernobyl disaster in the amounts estimated at 85 PBq. Due to its long half-time ($T_{1/2}$ = 30.1 years), the isotope persists in the environment. The content of ^{137}Cs isotope in soil depends on the level of radioactive contamination and the type of soil. In Poland, the Central Anti-Radiation Protection Laboratory reported the average concentration of ^{137}Cs in soil at 18.8 Bq kg^{-1} in 2004 (BIERNACKA, ISAJENKO 2006). Substantial amounts of ^{137}Cs are detected in the surface layers of soil (e.g. DOŁHAŃCZUK-ŚRÓDKA et al. 2002, KUBICA 2002, ZHIYANSKI et al. 2005, PACHOCKI et al. 2006), but particularly high concentrations of ^{137}Cs are present in forest soils, where the isotope is very well absorbed by organic matter (e.g. VAN BERGEIJK et al. 1992, ZGŁOBICKI 2002, DOŁCHAŃCZUK-ŚRÓDKA et al. 2005). Cesium is taken up by the root system of a plant, and its highest concentrations are observed in plants with roots in the upper layers of the soil, e.g. mosses and fungi (FALANDYSZ and CABOŃ 1992, AVERY 1996, WACŁAWEK et al. 2000).

Under natural conditions, potassium appears in three isotopic forms: ^{39}K (93.08%), ^{40}K (0.0119%) and ^{41}K (6.91%), with only ^{40}K being radioactive ($T_{1/2}$ = $1.32 \cdot 10^9$ years) (Polański 1961). Potassium in soil mainly binds with inorganic particles (Raczuk 1990, Brogowski, Chojnicki 2005).

The nuclei of ^{137}Cs and ^{40}K isotopes are subject to β-transformation, which is accompanied by the emission of γ-quanta with energies of 0.661 MeV and 1.46 MeV respectively.

The activity of ^{40}K isotope is directly proportional to the total content of potassium in soil – 1 g of potassium contains 31.7 Bq of ^{40}K (Kubica 2002). The content of ^{40}K isotope depends on the type of soil (Niesiobędzka 1999, Kubica 2002) as well as on human activity, e.g. spraying fields with potassium fertilizers. The mean activity of ^{40}K in soil is 400 Bq kg^{-1} (Eisenbud, Gesell 1997).

Following the breakdown of the Chernobyl power reactor in 1986, different regions of Poland became contaminated to a varied degree (Biernacka, Isajenko 2006). In 2004, particularly high activity of soil was observed in the following provinces: Opole, Silesia, Lower Silesia and Małopolska. The average concentration of ^{137}Cs in the soils of Masovia was slightly below the mean values marked for Poland (Biernacka, Isajenko 2006).

As ^{137}Cs and ^{40}K isotopes have similar chemical properties, it was interesting to determine their contents in the soils in the powiat of Garwolin, the Province of Mazowsze (Masovia) and establish the connection between their concentrations and soil use as well as soil physical and chemical parameters.

The scope of the research covered:

- determination of the activities of ^{137}Cs and ^{40}K isotopes in soils under forest, fields and fallow lands,
- assessment of the migration of the isotopes into the soil profile,
- correlation between the activities of ^{137}Cs and ^{40}K in soils and selected soil parameters (reaction, Corg content, granulometric composition)

The area of the research

The research was carried out in the *powiat* of Garwolin, situated in the Central-Masovian Lowlands (Kondracki 1988). In the area podzol soils are predominant. The *powiat* of Garwolin is an agricultural area (Polkowski, Janiszewska 2004). The samples were taken in four villages: Borowie, Samogoszcz, Skurcza and Wróble.

MATERIAL AND METHODS

The samples were picked up in October 2005. In each of the villages, samples of forest, fallow land and cropland soils were picked up. Additionally, forest litter was sampled to be analyzed. The samples came from the surface layers of soil to a depth of 12 centimeters. The forest and fallow land soils were collected so that the soil core 12 cm high could be obtained. The cores were then cut into three parts, the uppermost of which was taken from a maximum depth of 3 cm, the middle one – from a depth of 3 – 7 cm, and the bottom one – from a depth of 7 – 12 cm. Each subsample weighed *ca* 1 kg. Altogether, 12 samples of forest soil, 4 samples of litter, 12 samples of fallow land soil and 4 samples of arable land soil were picked up.

The samples were initially air-dried. Then they were dried at 60°C and finally sifted through a sieve with holes 2 mm in diameter. In the soil samples the following parameters were determined: reaction in 1 M KCL, Corg content with the use of Tiurin method, granulometric composition with the use of Bouyous aerometric method modified by Casagrande and Pruszyński (OSTROWSKA et al. 2001). The soils were classified into granulometric groups according to the Polish Standard PN–R –04033 (1998).

The activities of ^{137}Cs and ^{40}K isotopes were marked in the soil and litter samples with the use of ă-spectrometry method and a semi-conductor spectrometer with a coaxial germanium detector made by Canberra Company. The spectrum analysis was carried out with Genie 2000 Application Software. The measurement of each sample took 80.000 seconds.

The results of the analysis of the concentrations of ^{137}Cs and ^{40}K isotopes in the soils and of the chosen physical and chemical parameters of the soils were put to a statistical analysis. Pearson’s linear correlation coefficients were calculated using a Statistica 5.0 software package.

RESULTS

The soils were sandy soils, mainly represented by weakly loamy sand and loamy sand. The soils were acid in reaction, with pH values ranging from 3.07 to 5.94. In forest soils, the surface layers (up to a depth of 3 cm) had the lowest pH values (3.33), the deeper into the soil (7–12 cm), the higher the reaction (up to pH = 4.00). No such regularities were observed in fallow land soils. Cropland soils had the weakest acid reaction.

In most soils, the content of organic carbon did not exceed 2%. The surface layers of forest soils contained most organic carbon (1.150% on average). Deeper into the soil, this percentage decreased to 0.418%. Fallow land soils did not reveal such a tendency. The average Corg content in the analyzed layer of ploughed soils was comparable with that in forest soils (Table 1).

The highest activity of ^{137}Cs was detected in litter – 62.84 Bq kg^{-1} on average. Its surface layer contained the largest amount of the isotope (mean activity – 37.72 Bq kg $^{-1}$). Deeper in the soil the value drastically decreased to 4.509 Bq kg^{-1} (the layer 7 – 12 cm deep) (Figure 1a). The mean concen-

Table 1
Tabela 1

Physical and chemical properties of the soils of the powiat of Garwolin
Właściwości fizyczno-chemiczne gleb powiatu Garwolin

Fractions of soil	(mm)		Soils			Range
			forests	fallow land	field	
Sand	2v0.05	%	84.8	82.3	76.0	69–93
Silt	0.05v0.002		12.6	14.5	19.7	7–28
Clay	<0.002		2.6	3.2	4.3	2-–6
Reaction		pH	3.33	4.43	5.14	3.07–5.94
Corg		%	0.662	0.393	0.677	0.055–2.271

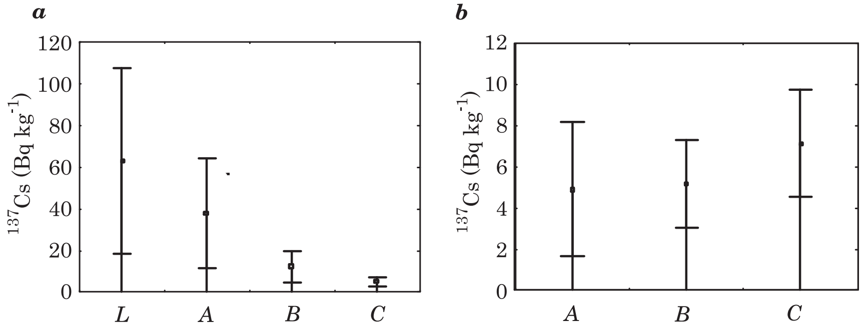


Fig. 1. The mean content of 137Cs (±SD) in the layers of forest (a) and wasteland soils (b) of the Garwolin county
L – litter, layers of soils: A – 0–3 cm, B – 3–7 cm, C – 7–12 cm
Rys. 1. Średnia zawartość 137Cs (±SD) w warstwach gleb leśnych (a) i nieużytków (b) powiatu Garwolin
L – ściółka, warstwy gleby: A – 0–3 cm, B – 3–7 cm, C – 7–12 cm

tration of ^{137}Cs isotope in forest soils at a maximum depth of 12 cm was 15.53 Bq kg $^{-1}$. The mean activity of ^{137}Cs in fallow land soils at a maximum depth of 12 cm was 5.915 Bq kg $^{-1}$. Unlike forest soils, fallow land soils contained slightly higher concentrations of ^{137}Cs – 7.124 Bq kg $^{-1}$ in their bottom layers (7-12 cm deep). In the uppermost (0-3 cm deep) and middle (3-7 cm deep) layers the activities of ^{137}Cs were 4.917 and 5.152 Bq kg $^{-1}$, respectively (Figure 1b). In cropland soils the mean concentration of ^{137}Cs isotope was 9.657 Bq kg^{-1} (Figure 2).

The activities of ^{40}K in the soil samples ranged between 97.15 and 215.0 Bq kg $^{-1}$. The samples of arable soil had the highest content of ^{40}K (173.7 Bq kg $^{-1}$ on average) – Figure 2) and the samples of forest soils – the lowest content (126.4 Bq kg^{-1} on average). The concentrations of po-

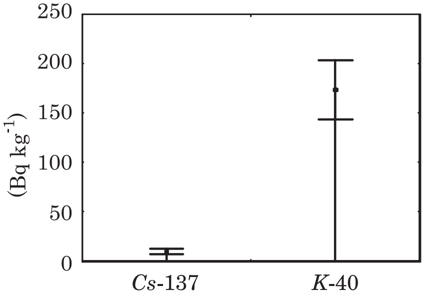


Fig. 2. The mean contents of 137Cs and 40K (±SD) in ploughland soils of the Garwolin county

Rys. 2. Średnia zawartość 137Cs i 40K (±SD) w glebach ornych powiatu Garwolin

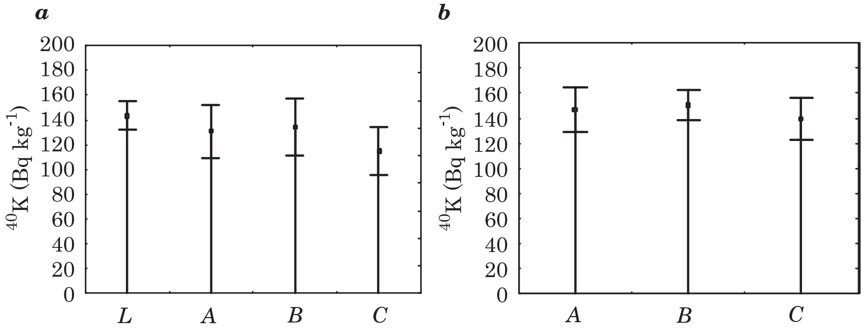


Fig. 3. The mean content of 40K (±SD) in the layers of forest (a) and wasteland soils (b) of the Garwolin county
L – litter, layers of soils: A – 0–3 cm, B – 3–7 cm, C – 7–12 cm

Rys. 3. Średnia zawartość 40K (±SD) w warstwach gleb leśnych (Rys. 2a) i nieużytków (b) powiatu Garwolin
L – ściółka, warstwy gleby: A – 0–3 cm, B – 3–7 cm, C – 7–12 cm

tassium in the individual layers of forest (Figure 3a) and fallow land soils (Figure 3b) did not differ considerably.

The concentrations of ^{137}Cs in the analyzed soils were significantly correlated: positively with Corg content and negatively with the soil reaction. The concentrations of ^{40}K were positively correlated with the soil reaction and the content of a clay fraction, but negatively correlated with a sand fraction (Table 2).

Table 2
Tabela 2

Pearson's correlation factors for ^{137}Cs and ^{40}K activity concentrations and some physical and chemical properties of soils (*p* - level of significance)
Współczynniki korelacji liniowej Persona między zawartością Cs-137 i K-40 w glebach a wybranymi właściwościami fizyczno-chemicznymi gleb

Isotopes	pH	% Corg	Fractions of soils		
			sand	silt	clay
Cs-137	-0.4923 p=0.008	0.5002 p=0.007	ns	ns	ns
K-40	0.6968 p<0.001	ns	-0.3800 p=0.046	ns	0.5609 p=0.002

DISCUSSION OF THE RESULTS

The mean activities of ^{137}Cs marked in the soil samples taken near Garwolin are reported (Biernacka, Isajenko 2006) to have been lower than the mean activities of the isotope elsewhere in Poland in 2004.

Out of the three types of soil it is the forest soil that contains the highest concentration of radioactive cesium, particularly in its surface layer. This fact is also pointed out by other authors, e.g. Dołchańczuk-Śródka i in. (2005, 2006), Kubica (2002), Zgłobicki (1992). The high activity of ^{137}Cs in a surface layer of the soil in forest areas results from the accumulation of the isotope in litter (Zgłobicki 1992), which is confirmed by the author's study. Cesium is definitely better absorbed by plants from sandy soils than from clayey soils. Sand-rich soils are characterized by low retention of the element (Chibowski et al. 1994). The analyzed soils were represented by sands and they had a relatively low content of silt and clay fractions.

The concentration of cesium in arable soils was definitely smaller than in forest soils. Harvest of crops contributes to a decrease in the content of cesium in cropland soils (Grabowski et al.1993). Moreover, cropland soils were less acidic than forest soils. The statistical analysis showed that the reaction of soils was reversely proportional to the concentration of ^{137}Cs, which is indicated by the Pearson's linear correlation coefficient between the activity of ^{137}Cs and the reaction of soil. The research also demonstrated positive correlation between the concentration of ^{137}Cs and organic carbon. The reports (e.g. Dołchańczuk-Śródka et al. 2005, 2006, Van Bergeijk et al. 1992, Zgłobicki 2002) point out that the highest concentrations of radioactive cesium are found in the genetic layers of the soil, where humus is formed. Organic matter is a filter, in which various elements, including radioactive cesium, accumulate.

Potassium, represented by ^{40}K isotope, has chemical properties resembling those of cesium. Potassium mainly binds with inorganic parts of the soil (RACZUK 1990, BROGOWSKI and CHOJNICKI 2005), and the activity of ^{40}K isotope is directly proportional to the total content of potassium in soil, which depends on the type of soil and the soil use (NIESIOBĘDZKA 1999, KUBICA 2002). The author's research showed that more potassium was in cropland than in forest soils. This result was entirely predictable. Fields are sprayed, inter alia, with potassium fertilizer. The analyzed soils were mainly sandy soils. More potassium is washed away from sandy soils than from loess or clayey soils as the former type of soil has a low content of clay fraction and, consequently, demonstrates poor ability to soak up ions (TERELAK, SADURSKI 1981). CHIBOWSKI et al. (1994) point out the relationship between the potassium concentration and the content of a clay fraction in the soils. The present study confirmed such observations by establishing statistically significant positive correlation between the clay content and the activity of ^{40}K isotope in the soils.

The results of determination of the ^{137}Cs content in the soils are diverse in comparison with the ^{40}K content, which is due to the uneven contamination of the area after the breakdown of the power reactor in Chernobyl. The ^{40}K content in the soils depends on the composition of primary minerals. The results of determination of the ^{40}K content in the soils near Garwolin indicate that the soils, including the surface layers of field soils, are relatively poor in potassium. The potassium content in the soils in the *powiat* of Garwolin, derived from from the activity of ^{40}K isotope and corresponding to 0.55% of the potassium content in the soil, is below the mean values reported by PONDEL et al. (1979) for an arable layer of soils in Poland. A statistically significant positive correlation between the ^{40}K content in the soils and the content of a clay fraction confirms other reports (MERCIK 1982, ŁABĘTOWICZ and RUTKOWSKA 2001), indicating that the potassium content in soil is affected by the content of mineral fractions, including clay fractions, rather than by organic fractions of the soil.

^{137}Cs and ^{40}K isotopes in the soils in the *powiat* og Garwolin behave differently although they are forms of elements that have similar chemical properties.

CONCLUSIONS

1. The contamination of the soils in the powiat of Garwolin nearly 20 years after the breakdown of the power reactor in Chernobyl is below the average for Poland. The highest activities of ^{137}Cs were observed in forest soils. The isotope was less active in cropland and fallow land soils.

The largest amounts of ^{137}Cs isotope accumulate in the surface layers of forest soils (to a depth of 3 cm).

2. The soils in the *powiat* of Garwolin powiat contain relatively little potassium. Cropland soils are the richest and forest soils – the poorest in potassium. The surface layers of the soils contain similar amounts of potassium, independently from the depth from which samples are picked up.

3. The concentration of ^{137}Cs isotope is positively correlated with the Corg content and negatively correlated with the soil reaction.

4. The content of ^{40}K isotope is positively correlated with the soil reaction and the content of a clay fraction, but negatively correlated with the content of a sand fraction.

REFERENCES

Avery S.V. 1996. *Fate of caesium in the environment: distibution between the abiotic and biotic components of aquatic and terrestrial cosystem.* J.Environ. Radioactiv., 30(2): 139-171.

Biernacka M., Isajenko K. 2006. *Radiologiczna mapa Polski w latach 1988-2005. In: Czarnobyl 20 lat później: skażenia środowiska i żywności, skutki zdrowotne. Energetyka jądrowa w Polsce: za i przeciw.* Mat. Konf. XXI Szkoła Jesienna Polskiego Towarzystwa Badań Radiacyjnych im. Marii Skłodowskiej-Curie, Zakopane, 95-111.

Brogowski Z., Chojnicki J. 2005. *Rozmieszczenie potasu ogólnego w wydzielonych frakcjach granulometrycznyh gleb brunatnych.* Rocz. Glebozn., LVI (1-2): 27-39.

Chibowski S., Solecki J., Szczypa J., Suprynowicz R. 1994. *Study of radioactive contamination of Eastern Poland.* Sci. Total Environ., 158: 71-77.

Dołchańczuk- Śródka A., Kiczma B., Wacławaek M. 2002. *Ocena skażenia gleb ^{137}Cs.* Chem. Dydakt. Ekol. Metro., 7(1/2): 69-71.

Dołchańczuk-Śródka A., Ząbkowska-Wacławek M., Kusza G. 2005. *Radiocez w środowisku leśnym. Obieg pierwiastków w przyrodzie.* Inst. Ochr. Środ., Monografia, 3: 27-30.

Dołchańczuk-Śródka A., Ziembik Z., Majcherczyk T., Smuda M., Wacławek M., Wacławek W. 2006. *Czynniki wpływające na poziomy i pionowy transfer radiocezu w środowisku leśnym. W: Czarnobyl 20 lat później: skażenia środowiska i żywności, skutki zdrowotne. Energetyka jądrowa w Polsce*: za i przeciw. Mat. Konf. XXI Szkoła Jesienna Polskiego Towarzystwa Badań Radiacyjnych im. Marii Skłodowskiej-Curie, Zakopane, 427-435.

Eisenbud M., Gesell T.F. 1997. *Environmental radioactivity from natural, industrial and military sources.* Acad. Press, 655 pp.

Falandysz J., Caboń J. 1992. *Wyniki oznaczeń radiocezu w grzybach na terenie województwa gdańskiego.* Przem. Spoż., 46: 146-147.

Grabowski D., Muszyński W., Petrykowska M., Rubel B., Smagała G., Wilgos J. 1993. *Skażenie promieniotwórcze środowiska i żywności w Polsce w 1992 roku.* Bibl. Monitoringu Środowiska, Warszawa, 45 pp.

Kondracki J. 1988. *Geografia fizyczna Polski.* PWN, Warszawa, 463 pp.

Kubica B. 2002. *Pilotażowe badania zawartości ^{137}Cs, $^{239+240}$Pu, ^{40}K w próbkach gleby z Tatrzańskiego Parku Narodowego.* Kosmos, 51(4): 408-413.

Łabędowicz J., Rutkowska B. 2001. *Czynniki kształtujące stężenie potasu w roztworze glebowym gleb użytkowanych rolniczo w Polsce.* Zesz. Probl. Post. Nauk Rol., 480: 95-102.

Mercik S. 1982. *Działanie potasu i magnezu w zależności od niektórych właściwości fizykochemicznych gleb.* Rocz. Glebozn., 34 (1-2): 15-30.

OSTROWSKA A., GAWLIŃSKI S., SZCZUBIAŁKA Z. 1991. *Metody analizy i oceny właściwości gleb i roślin*. Katalog Inst. Ochr. Środ., Warszawa, 334 pp.

NIESIOBĘDZKA K. 1999. *Transport naturalnych radionuklidów promieniotwórczych w ekosystemie gleba-szata roślinna*. Chem. Inż. Ekol., 6(1): 77-87.

PACHOCKI K., BEKAS M., RÓŻYCKI Z. 2006. *Analiza skażeń cezem powierzchniowych warstw gleby w Polsce po awarii w Czarnobylu*. W: *Czarnobyl 20 lat później: skażenia środowiska i żywności, skutki zdrowotne. Energetyka jądrowa w Polsce: za i przeciw*. Mat. Konf. XXI Szkoła Jesienna Polskiego Towarzystwa Badań Radiacyjnych im. Marii Skłodowskiej-Curie, Zakopane, 441.

POLAŃSKI A. 1961. *Geochemia izotopów*, Wyd. Geologiczne, Warszawa, 392 pp.

POLKOWSKI J., JANISZEWSKA M. 2004. *Program ochrony środowiska dla powiatu garwolińskiego na lata 2004-2007 z uwzględnieniem perspektywy na lata 2008-2011*. Zarząd powiatu garwolińskiego, Warszawa.

PONDEL H., TERELAK H., TERELAK T., WILKOS S. 1979. *Właściwości chemiczne gleb Polski*. Pam. Puł., 71 Supl.: 25-35.

RACZUK J. 1990. *Chemical properties of the granulometric fractions of sand soils from the Siedlce Upland and the Łuków Plain*. Part I. *Phosphorus, potassium, calcium and magnesium*. Pol. J. Soil Sci., 23 (2): 133-141.

TERELAK H., SADURSKI W. 1981. *Badania modelowe nad kształtowaniem się niektórych wskaźników zawartości potasu w glebach w zależności od dawek tego składnika i wapnowania*. Rocz. Glebozn., 32 (2): 87-102.

VAN BERGEIJK K.E., NOORDIJK H., LEMBRECHTS J., FIRSSEL M.J. 1992. *Influence of pH, soil type and soil organic matter content on soil-to-plant transfer of radiocesium and –strontium as analyzed by a nonparametric method*. J. Environ. Radioactiv., 15(3): 265-276.

WACŁAWEK W., MAJCHERCZYK T., DOŁCHAŃCZUK A. 2000. *Pomiar radioaktywności cezu w grzybach z lasów Opolszczyzny*. Chem. Inż. Ekol., 7: 405-415.

ZGŁOBICKI W. 2002. *Pokrycie terenu a przestrzenne zróżnicowanie skażenia 137Cs gleb na Wyżynie Lubelskiej (na przykładzie okolic Rogalowa)*. Czas. Geogr., 73(1-2): 101-111.

ZHIYANSKI M., SOKOLOWSKA M., LUCOT E., BADOT P.M. 2005. *Cs-137 contamination in forest ecosystems in southwest Rila Mountain, Bulgaria*. Environ. Chem. Letters, 3: 49-52.

J. Elementol. 2008, 13(1): 91–99

EFFECT OF PHOSPHORUS DEFICIENCY ON GAS EXCHANGE PARAMETERS, LEAF GREENNESS (SPAD) AND YIELD OF PERENNIAL RYEGRASS (*LOLIUM PERENNE* L.) AND ORCHARD GRASS (*DACTYLIS GLOMERATA* L.)

Marzenna Olszewska[1] , Stefan Grzegorczyk[1],
Jacek Olszewski[2], Anna Bałuch-Małecka[1]

[1]Department of Grassland Management
[2] Department of Plant Diagnostics and Patophysiology
University of Warmia and Mazury in Olsztyn

Abstract

Phosphorus is essential for the growth and development of plants. It also determines the quantity and quality of plant yields. Phosphorus actively participates in many vital processes and forms part of numerous substances indispensable for a normal course of certain biochemical changes. Unfortunately, phosphorus deficiency is quite common in grasslands. As a result, the content of phosphorus in soil is insufficient to meet nutritional requirements of forage crops and, consequently, the concentration of this element in green forage is insufficient to meet nutritional requirements of ruminants. The aim of the present study was to determine the effect of phosphorus deficiency in soil on the rate of photosynthesis and transpiration, water use efficiency, leaf greenness and the yield of some cultivars of perennial ryegrass (*Lolium perenne* L.) and orchard grass (*Dactylis glomerata* L.). A greenhouse experiment was conducted to assess the rate of photosynthesis and transpiration, water use efficiency (WUE), leaf greenness (SPAD – Soil-Plant Analysis Development) and the yield of perennial ryegrass (*Lolium perenne* L.) and orchard grass (*Dactylis glomerata* L.) grown under conditions of phosphorus deficiency in soil. The rate of photosynthesis and transpiration was measured using a Li-Cor 6400 gas analyzer (Portable Photosynthesis System), and leaf greenness was estimated with a Minolta SPAD-502 chlorophyll meter. Dry matter yield was determined by drying green matter to constant weight at 105°C. The results of the study indicate that phosphorus deficiency significantly decreased the rate of photosynthesis, water use efficiency and the yield of

---

dr Marzenna Olszewska, Department of Grassland Management, University of Warmia and Mazury in Olsztyn, Poland, pl. Łódzki 1/8 Olsztyn. phone +48 89 523 35 01, e-mail: marzenna.olszewska@uwm.edu.pl

perennial ryegrass and orchard grass. At the same time, it increased the rate of transpiration and leaf greenness values. Among the tested cultivars, orchard grass cv. Areda was found to be the most resistant to phosphorus deficiency in soil, which was confirmed by the slightest reduction in the examined parameters.

Key words: photosynthesis, leaf greenness (SPAD), orchard grass, phosphorus deficiency, transpiration, yield, water use efficiency (WUE), perennial ryegrass.

WPŁYW NIEDOBORU FOSFORU NA WSKAŹNIKI WYMIANY GAZOWEJ, INDEKS ZIELONOŚCI LIŚCI (SPAD) ORAZ PLONOWANIE ŻYCICY TRWAŁEJ (*LOLIUM PERENNE* L.) I KUPKÓWKI POSPOLITEJ (*DACTYLIS GLOMERATA* L.)

Abstrakt

Fosfor jest pierwiastkiem niezbędnym do prawidłowego funkcjonowania każdej rośliny i decyduje o ilości oraz jakości uzyskanego plonu. Bierze on udział w przebiegu podstawowych procesów życiowych, wchodzi w skład wielu substancji, ważnych z punktu widzenia przemian biochemicznych. W paszach uzyskiwanych na użytkach zielonych może występować niewystarczająca zawartość fosforu w kryteriach prawidłowego żywienia roślin i żywienia przeżuwaczy. Celem pracy jest ocena wpływu niedoboru fosforu w glebie na intensywność fotosyntezy i transpiracji, współczynnik wykorzystania wody, indeks zieloności liści oraz plonowanie wybranych odmian życicy trwałej (*Lolium perenne* L.) i kupkówki pospolitej (*Dactylis glomerata* L.). W doświadczeniu szklarniowym badano intensywność fotosyntezy, transpiracji, współczynnik wykorzystania wody (WUE– Water Use Efficiency), indeks zieloności liści SPAD (Soil Plant Analysis Development) oraz plonowanie życicy trwałej (*Lolium perenne* L.) i kupkówki pospolitej (*Dactylis glomerata* L.) uprawianych w warunkach niedoboru fosforu w podłożu. Intensywność fotosyntezy i transpiracji mierzono przenośnym analizatorem gazowym LI-COR 6400, a indeks zieloności liści optycznym chlorofilometrem Minolta SPAD-502. Plon suchej masy określono przez wysuszenie zielonej masy w temp. 105°C, do stałej wagi. Wykazano, że niedobór fosforu istotnie ograniczał intensywność fotosyntezy, współczynnik wykorzystania wody oraz plonowanie badanych odmian, natomiast zwiększał intensywność transpiracji i indeks zieloności liści. Spośród badanych odmian najbardziej odporną na niedobór fosforu w glebie okazała się odmiana Areda kupkówki pospolitej, która w najmniejszym stopniu ograniczała badane cechy.

Słowa kluczowe: fotosynteza, indeks SPAD, kupkówka pospolita, niedobór fosforu, transpiracja, plonowanie, WUE, życica trwała.

INTRODUCTION

Phosphorus is essential for the growth and development of plants. It also determines the quantity and quality of yield. Phosphorus actively participates in many vital processes and forms part of numerous substances indispensable for a normal course of certain biochemical changes. It can be found in compounds responsible for energy storage and flow in plant cells (ATP, NADPH). Phosphorus is also present in nucleic acids (DNA and RNA) so it takes part in the processes of genetic information transfer. It plays an important role in enzyme activation, thus participating in photosynthesis and synthesis of proteins and fats (GAJ, GRZEBISZ

2003). Phosphorus deficiency is quite common in grasslands. As a result, the phosphorus content of soil is insufficient to meet nutritional requirements of forage crops. Consequently, the concentration of this element in green forage is too low to meet nutritional requirements of ruminants (CZUBA 1998, GRZEGORCZYK et al. 2001, TRĄBA and WOLAŃSKI 2001). According to FALKOWSKI et al. (1990), the optimum phosphorus content of dry matter in grassland vegetation should be 0.3%. However, this level is often difficult to reach. Long-term investigations carried out by NICZYPORUK, JANKOWSKA-HUFLEJT (2001) indicate that adequate concentrations of phosphorus in green fodder may be maintained provided that equal doses of this element are supplied to soil over longer periods of time. Phosphorus contributes to changes in the botanical composition of sward, promoting dicotyledonous plants, which usually contain more phosphorus than grasses. Another way to increase the concentration of mineral components, including phosphorus, is growing legume-grass mixtures (KRYSZAK 2001) and legume-grass mixtures with herbs (BENEDYCKI et al. 2001).

The aim of the present study was to determine the effect of phosphorus deficiency in soil on the rate of photosynthesis and transpiration, water use efficiency, leaf greenness and the yield of some cultivars of perennial ryegrass and orchard grass.

MATERIALS AND METHODS

The experiment was conducted in a greenhouse of the University of Warmia and Mazury in Olsztyn. Kick-Brauckmann pots were filled with 10 kg of soil formed from loose sand, characterized by a low content of phosphorus (31 $mg \cdot kg^{-1}$), potassium (42 $mg\ kg^{-1}$) and magnesium (13 $mg\ kg^{-1}$). The soil reaction was slightly acidic – pH_{KCl} 5.8. The experiment involved two cultivars of perennial ryegrass (*Lolium perenne* L.): tetraploid Maja and diploid Argona, and two cultivars of orchard grass (*Dactylis glomerata* L.): tetraploid Dala and diploid Areda. Control pots were fertilized with a nutrient solution containing 1.00 g N as $CO(NH_2)_2$, 0.25 g P as KH_2PO_4, 1.00 g K as K_2SO_4 and 0.50 g Mg as $MgSO_4 \cdot 7H_2O$. A micronutrient solution (30 mg/pot), composed of 2.65 mg Fe in EDTA, 0.09 mg $MnCl_2 \cdot 4H_2O$, 0.1 mg $ZnCl_2$, 0.03 mg $CuCl_2 \cdot 2H_2O$, 0.12 mg H_3BO_3 and 0.01 mg $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ per kg of soil, was also applied. The remaining pots were not fertilized. During the growing season leaf greenness was estimated with a Minolta SPAD-502 chlorophyll meter, while the rate of photosynthesis and transpiration was measured using a Li-Cor 6400 gas analyzer (Portable Photosynthesis System), at air temperature of around 25°C, a constant CO_2 concentration of 400 ppm and illumination of 1000 $\mu mol\ m^{-2}\ s^{-1}$. Four measurements were performed for each cut. Means for the cuts are presented in the paper. Water use efficiency (WUE) was calculated based on instantaneous values of photosynthesis and transpiration. The aerial parts of plants were cut three times over the growing season. Dry matter yield was determined by drying green matter to constant weight at 105°C. The results were processed statistically with the use of STATISTICA software.

RESULTS AND DISCUSSION

The average rate of photosynthesis was comparable in all grass leaves, ranging from 6.45 to 7.00 µmol CO_2 $m^{-2}s^{-1}$ (Table 1). Cultivar Maja was characterized by the highest rate of photosynthesis. This process was widely differentiated in particular cuts. The lowest rate of photosynthesis was observed in the first cut, while the highest – in the second cut. Phosphorus deficiency in the soil significantly limited photosynthesis intensity in leaves of all the cultivars. Compared to the control, the rate of photosynthesis decreased by 24%. The strongest response to phosphorus deficit was recorded in the first cut, whereas in the successive cuts the differences in CO_2 assimilation between the control and experimental (phosphorus-deficient) treatments were smaller. This was most probably caused

Table 1

Intensity of photosynthesis (µmol CO_2 m^{-2} s^{-1})

Cultivars	Fertilization	1st cut	2nd cut	3rd cut	Mean
Areda	control object phosphorus deficiency	6.63 *b 4.58 a	8.15 cd 7.05 ab	6.65 c 5.68 ab	7.14 b 5.77 a
Dala	control object phosphorus deficiency	6.78 b 4.40 a	8.68 cd 6.80 a	6.45 bc 5.25 a	7.30 bc 5.48 a
Argona	control object phosphorus deficiency	7.48 b 4.55 a	9.25 d 7.00 a	6.75 c 5.40 a	7.83 bc 5.65 a
Maja	control object phosphorus deficiency	6.43 b 3.98 a	10.45 e 7.70 ab	7.10 c 6.38 bc	7.99 c 6.02 a
Mean for cultivars					
Areda Dala Argona Maja		5.60 ab 5.59 ab 6.01 b 5.20 a	7.60 a 7.74 a 8.13 a 9.08 b	6.16 a 5.85 a 6.08 a 6.74 b	6.45 a 6.39 a 6.74 ab 7.00 b
Mean for fertilization					
Control object Phosphorus deficiency		6.82 b 4.38 a	9.13 b 7.14 a	6.74 b 5.68 a	7.56 b 5.73 a

* homogeneous statistical groups

by changes in phosphorus content which occurred over the growing season, namely by a decrease in the concentration of this element observed during the growth and development of plants (Falkowski et al. 1990). Among the tested cultivars, cv. Areda orchard grass was found to be the most resistant to phosphorus deficiency. The rate of photosynthesis decreased to the slightest degree in this cultivar, i.e. by 19% on average, compared to a 25–28% decline in the other cultivars. According to literature data, the effect of phosphorus on photosynthesis depends on plant species. Olszewski (2004) demonstrated that a reduction in phosphorus doses resulted in a significant photosynthesis intensity decrease in pea, and a slight increase in the rate of this process in faba bean. Pszczółkowska et al. (2002) reported a decrease in the rate of photosynthesis in leaves of pea and yellow lupine under phosphorus deficit conditions. In a study conducted by Fredeen et al. (1989), the rate of photosynthesis decreased by 55% due to phosphorus deficiency stress in soybean. Dietz and Foyer (1986) postulated that the negative impact of phosphorus deficiency on photosynthesis in leaves may be reversible. In an experiment performed by these authors, CO_2 assimilation inhibited due to phosphorus deficit was restored to the normal rate following phosphorus supply to plants.

In the present study, phosphorus deficiency increased transpiration intensity by 52% on average (Table 2). The tested cultivars differed in their responses to phosphorus deficit. The weakest response was recorded in cv. Areda, while the strongest in cv. Dala – the rate of transpiration

Table 2

Intensity of transpiration (m mol H_2O m^{-2} s^{-1})

Cultivars	Fertilization	1st cut	2nd cut	3rd cut	Mean
Areda	control object phosphorus deficiency	1.10 a 1.48 a	0.98 a 1.37 bc	0.60 a 0.85 bc	0.89 a 1.23 b
Dala	control object phosphorus deficiency	1.40 a 2.43 c	1.05 ab 1.96 d	0.73 ab 1.07c	1.06 ab 1.82 d
Argona	control object phosphorus deficiency	1.30 a 2.00 bc	1.05 ab 1.65 cd	0.58 a 0.95 bc	0.98 a 1.53 c
Maja	control object phosphorus deficiency	1.58 ab 2.38 c	1.40 c 1.98 d	0.85 bc 1.08 c	1.27 b 1.81 d
Mean for cultivars					
Areda Dala Argona Maja		1.29 a 1.91 bc 1.65 b 1.98 c	1.18 a 1.51 bc 1.35 ab 1.69 c	0.73 a 0.90 ab 0.77 a 0.96 b	1.06 a 1.44 c 1.26 b 1.54 c
Mean for fertilization					
Control object Phosphorus deficiency		1.34 a 2.07 b	1.12 a 1.74 b	0.69 a 0.99 b	1.05 a 1.60 b

increased in these cultivars by 38% and 72% respectively. The tetraploid cultivars evaporated more water than the diploid ones. Particular cuts differed with respect to the rate of transpiration, which was the fastest in the first cut and the slowest in the third cut. An increase in transpiration intensity caused by insufficient phosphorus supply was also reported by PSZCZÓŁKOWSKA et al. (2002).

The values of photosynthesis and transpiration provide information about plant water relations, reflected in water use efficiency (WUE). In the current experiment, water use efficiency was higher in the diploid rather than in the tetraploid cultivars (Table 3). Phosphorus deficit considerably affected water use efficiency in the analyzed grass cultivars. In comparison with the control treatments, WUE decreased by 48% on average. The cultivars differed in their responses to phosphorus deficiency. The weakest response was recorded in cv. Areda, and the strongest in cv. Dala – water use efficiency decreased in these cultivars by approximately 42% and 55% respectively. Water use efficiency was at the lowest level in the first cut, then improving gradually.

Table 3

Water use efficiency (μmol CO_2 $m^{-2}s^{-1}$ · m mol H_2O m^{-2} s^{-1})

Cultivars	Fertilization	1st cut	2nd cut	3rd cut	Mean
Areda	control object phosphorus deficiency	6.07 e 3.10 b	8.42 b 5.15 a	11.21 de 6.78 bc	8.57 de 5.01 b
Dala	control object phosphorus deficiency	4.90 de 1.81 ab	8.39 b 3.47 a	9.09 de 4.91 a	7.46 cd 3.39 a
Argona	control object phosphorus deficiency	5.79 e 2.30 ab	8.88 b 4.27 a	11.86 e 5.77 ab	8.84 e 4.11 ab
Maja	control object phosphorus deficiency	4.16 cd 1.70 a	7.48 b 3.90 a	8.47 cd 5.95 bc	6.70 c 3.85 ab
Mean for cultivars					
Areda Dala Argona Maja		4.59 c 3.36 ab 4.04 bc 2.93 a	6.79 a 5.93 a 6.57 a 5.69 a	9.00 a 7.00 a 8.81 a 7.21 a	6.79 b 5.43 a 6.48 b 5.28 a
Mean for fertilization					
Control object Phosphorus deficiency		5.23 b 2.23 a	8.29 b 4.20 a	10.16 b 5.85 a	7.89 b 4.09 a

Phosphorus deficiency in the soil had a non-significant effect on leaf greenness values, which increased by 3.5% on average. The response of the tetraploid cultivars was stronger than that of the dipolid ones (Table 4). Perennial ryegrass cultivars contained significantly more chlorophyll in leaves than orchard grass cultivars. The highest chlorophyll concentration

Table 4

Leaf greenness index (SPAD)

Cultivars	Fertilization	1st cut	2nd cut	3rd cut	Mean
Areda	control object phosphorus deficiency	35.83 a 37.10 ab	36.83 a 38.53 b	39.60 a 40.53 ab	37.42 a 38.72 b
Dala	control object phosphorus deficiency	37.68 c 38.80 c	38.98 b 41.33 cd	40.48 ab 41.58 c	39.04 b 40.57 cd
Argona	control object phosphorus deficiency	38.75 c 40.35 d	41.10 c 42.15 cd	40.00 ab 41.10 bc	39.95 c 41.20 de
Maja	control object phosphorus deficiency	40.98 d 43.08 e	42.43 d 43.83 e	40.65 ab 41.68 c	41.35 d 42.86 e
Mean for cultivars					
Areda Dala Argona Maja		36.46 a 38.24 b 39.55 c 42.03 d	37.68 a 40.15 b 41.63 c 43.13 d	40.06 a 41.03 b 40.55 ab 41.16 b	38.07 a 39.80 b 40.58 c 42.10 d
Mean for fertilization					
Control object Phosphorus deficiency		38.31 a 39.83 b	39.83 a 41.46 b	40.18 a 41.22 b	39.44 a 40.84 b

was noted in cv. Maja (SPAD 42.1 on average). The highest chlorophyll content of leaves was recorded in the second cut of perennial ryegrass and in the third cut of orchard grass. An increase in leaf greenness values under phosphorus deficiency conditions is most probably part of a physiological reaction. Phosphorus-deficient plants produce dark-green leaves due to inhibited cell growth and a higher number of cells per unit area (Gaj, Grzebisz 2003). The present results are consistent with the findings of Peng et al. (1999), who demonstrated that at the early development stages of rice, SPAD readings were by 1 to 2 units higher in phosphorus-poor soils compared to phosphorus-fertilized fields; those differences were no longer noticeable at the beginning of panicle emergence.

Under optimum fertilization conditions, the yield of cv. Maja was significantly higher than the yields of the other investigated cultivars, which remained at a comparable level, showing no statistically significant differences (Table 5). Deficit in soil P caused a highly significant yield decline. Dry matter yield decreased in all cultivars, by 36.5% on average. Orchard grass cv. Areda exhibited the weakest response to phosphorus deficit – the dry matter yield of this cultivar decreased by 21%. In all the cultivars the strongest response to phosphorus deficiency was noticed in the first cut. In the successive cuts the differences between the control and non-fertilized treatments with regard to yielding were substantially smaller.

Table 5

Dry matter yield ($g \cdot pot^{-1}$)

Cultivars	Fertilization	1st cut	2nd cut	3rd cut	Mean
Areda	control object	9.38 d	8.08 cd	5.48 bc	22.93 d
	phosphorus deficiency	6.08 b	6.93 c	5.08 ab	18.08 c
Dala	control object	9.43 d	7.03 cd	5.43 bc	21.88 d
	phosphorus deficiency	4.15 a	3.70 a	4.68 a	12.53 a
Argona	control object	8.38 c	7.43 cd	6.30 d	22.10 d
	phosphorus deficiency	3.60 a	4.05 a	5.20 bc	12.85 a
Maja	control object	9.35 d	8.13 d	7.13 e	24.60 e
	phosphorus deficiency	3.48 a	5.28 b	5.98 cd	14.73 b
Mean for cultivars					
Areda		7.73 c	7.50 c	5.28 a	20.50 b
Dala		6.79 b	5.36 a	5.05 a	17.20 a
Argona		5.99 a	5.74 a	5.75 b	17.48 a
Maja		6.41 ab	6.70 b	6.55 c	19.66 b
Mean for fertilization					
Control object		9.13 b	7.66 b	6.08 b	22.88 b
Phosphorus deficiency		4.33 a	4.99 a	5.23 a	14.54 a

CONCLUSIONS

1. Phosphorus deficiency significantly decreased the rate of photosynthesis, water use efficiency and the yield of perennial ryegrass and orchard grass, while increasing the rate of transpiration and leaf greenness values.

2. Among the tested cultivars, orchard grass cv. Areda was found to be the most resistant to phosphorus deficiency in soil, which was confirmed by the slightest reduction in the examined parameters.

REFERENCES

Benedycki S., Grzegorczyk, Grabowski K., Puczyński J. 2001. *Zawartość składników pokarmowych w runi mieszanek pastwiskowych.* Zesz. Probl. Post. Nauk Rol., 479: 31- 36.

Czuba R. 1998. *Ocena poziomu zawartości fosforu w krajowych ziemiopłodach w kryteriach konsumpcyjnych i paszowych*. Pr. Nauk. AE we Wrocławiu, 792: 195-202.

Dietz J.K., Foyer C. 1986. *The relationship between phosphate status and photosynthesis in leaves. Reversibility of the effects of phosphate deficiency on photosynthesis*. Planta, 167: 376-381.

Falkowski M., Kukułka I., Kozłowski S. 1990. *Właściwości chemiczne roślin łąkowych*. Wyd. AR Poznań, ss. 111.

Fredeen A.L., Rao J., Terry N. 1989. *Influence of phosphorus nutrations on growth end carbon partitioning in Glycine max*. Plant Physiol., 89:225-230.

GAJ R., GRZEBISZ W. 2003. *Fosfor w roślinie*. W: *Pierwiastki w środowisku. Fosfor*. J. Elementol., 8(3) suppl.: 5-18.

GRZEGORCZYK S., ALBERSKI J., BENEDYCKI S., BERNATOWICZ T. 2001. *Zioła jako źródło składników pokarmowych w paszy z użytków zielonych*. Zesz. Probl. Post. Nauk Rol., 479: 89- 94.

KRYSZAK J. 2001. *Plonowanie i jakość mieszanki Festulolium braunii (K. Richter) A. Camus z koniczyną łąkową i lucerną siewną na gruntach ornych*. Zesz. Probl. Post. Nauk Rol., 479: 173- 178.

NICZYPORUK A., JANKOWSKA-HUFLEJT H. 2001. *Zawartość fosforu w runi łąkowej w warunkach zróżnicowanego nawożenia*. Zesz. Probl. Post. Nauk Rol., 479: 217-221.

OLSZEWSKI J. 2004. *Wpływ wybranych stresów abiotycznych i biotycznych na intensywność fotosyntezy i transpiracji, plonowanie oraz zdrowotność bobiku i grochu siewnego*. Rozp. i Monogr. UWM Olsztyn, ss. 109.

PENG S., SANICO A.L., GARCIA F.V., LAZA R.C., VISPERAS R.M., DESCALSOTA J.P., CASSMANN K.G. 1999. *Effect of leaf phosphorus and potassium concentration on Chlorophyll meter reading in Rice*. Plant. Prod. Sci., 2(4): 227-231.

PSZCZÓŁKOWSKA A., OLSZEWSKI J., PŁODZIEŃ K., ŁAPIŃSKI M., FORDOŃSKI G., ŻUK-GOŁASZEWSKA K. 2002. *Effect of mineral stress on productivity of selected genotypes of pea (Pisum sativum L.) and yellow lupin (Lupinus luteus L.)*. Electron. J. Pol. Agric. Univ., v.5 ser. Agronomy. www.ejpau.media.pl/series/volume5/issue2/agronomy/art.-07.html

TRĄBA CZ., WOLAŃSKI P. 2001. *Współzależność pomiędzy składem chemicznym gleby a zawartością składników w runi zespołu Arrhenatheretum elatioris*. Zesz. Probl. Post. Nauk Rol., 479: 261- 266.

J. Elementol. 2008, 13(1): 101–108

ORGANIC CARBON CONTENTS IN BOTTOM SEDIMENTS FROM THE UPPER RIVER NAREW AND ITS TRIBUTARIES*

Elżbieta Skorbiłowicz, Mirosław Skorbiłowicz

Department of Technology in Engineering and Environmental Protection
Technical University in Bialystok

Abstract

The study dealt with the bottom sediments from the Narew River in the section Bondary-Tykocin 1 8 tributaries in he catchment of the upper Narew. Samples were collected in summer (August) and autumn (October) 2005 from the surface layer of bottom sediments in the shore zone. Determinations of organic carbon were performed on a TOC 1200 analyzer (Thermo Euroglas). The bottom sediments collected from the upper Narew contained less organic carbon, which resulted from intensive mineralization. Sediments from the small rivers were most abundant in organic carbon. These rivers are characterized by a low flow rate and, in most cases, they are overgrown by water plants. The organic carbon contents were highly varied between the sampling points. Positive linear correlation was found between combustion loss and organic carbon content.

Keywords: organic carbon, bottom sediments, rivers.

KSZTAŁTOWANIE SIĘ ZAWARTOŚCI WĘGLA ORGANICZNEGO W OSADACH DENNYCH GÓRNEJ NARWI I JEJ DOPŁYWACH

Abstrakt

Badaniami objęto osady denne z rzeki Narew na odcinku Bondary-Tykocin oraz 18 jej dopływów w obrębie zlewni górnej Narwi. Próbki pobrano latem (sierpień) i jesienią (październik) 2005 r. z powierzchniowej warstwy osadu dennego w strefie brzegowej. Węgiel organiczny oznaczano na analizatorze TOC 1200 firmy Thermo Euroglas. Osady denne pobrane z rzeki Narew zawierały mniej węgla organicznego – jest to wynik intensywnej mineralizacji. Naj-

---

*The work was financed by the Ministry for Education and Science as part of the Scientific Project No 3 TO9D 112 28, (2005-2007).

zasobniejsze w węgiel organiczny były osady denne małych rzek. Rzeki te mają małe prędkości przepływu, w większości przypadków są porośnięte roślinnością wodną. Zawartość węgla organicznego wykazała dużą zmienność w zależności od lokalizacji punktów poboru próbek. Stwierdzono dodatnią korelację liniową między zawartością straty prażenia a węglem organicznym.

Słowa kluczowe: węgiel organiczny, osady denne, rzeki.

INTRODUCTION

Water has considerable chemical influence on bottom sediments in rivers and lakes. Sediments accumulated at the bottom of rivers and water reservoirs are a very useful geochemical medium to control the surface water quality in terms of contamination by heavy metals and hazardous organic compounds (Chen et al. 2000, Wardas 2001, Bojakowska, Gliwicz, 2003, Kania et al. 2005, Skorbiłowicz 2005). Organic carbon content in water and bottom sediments is of interest, too (Helland et al. 2003, Warnken Santschi 2004, Ouyang et al. 2006, Wiśniowska-Kielian 2007). Carbon, one of the most widespread elements, is also a general constituent of organic matter. Organic compounds in surface waters are produced from minerals by autotrophic organisms during photosynthesis (algae, blue-green algae, macrophytes) and chemosynthesis (bacteria) (Azan et al. 1983). A significant portion of organic compounds in water consists of decaying aqueous plant and animal-origin organisms (decomposed by parasites) or active metabolite excretion (urea, feces, enzymes, pheromones, etc.) (Górniak, Zieliński 1999). All those substances directly produced in water are called *autochthonic organic matter* (Wetzel 1990). Humus substances are the main group of natural organic compounds in waters and bottom sediments (De Haan 1992, Górniak 1996). Jambers (1999) suggests that organic matter may play an important role in forming and aggregating minerals. Large amounts of organic matter are present in particles abundant in heavy metals, which suggests the occurrence of organic complexes and a high probability of metal sorption on fine organic fraction (Eisma 1992).

The present study was aimed at evaluating the organic carbon contents in bottom sediments of the upper Narew River and its tributaries.

MATERIAL AND METHODS

The study dealt with the bottom sediments from the Narew in the section Bondary-Tykocin and 18 tributary rivers in its upper catchment basin (Figure 1). Depending on the catchment area, river length and flow

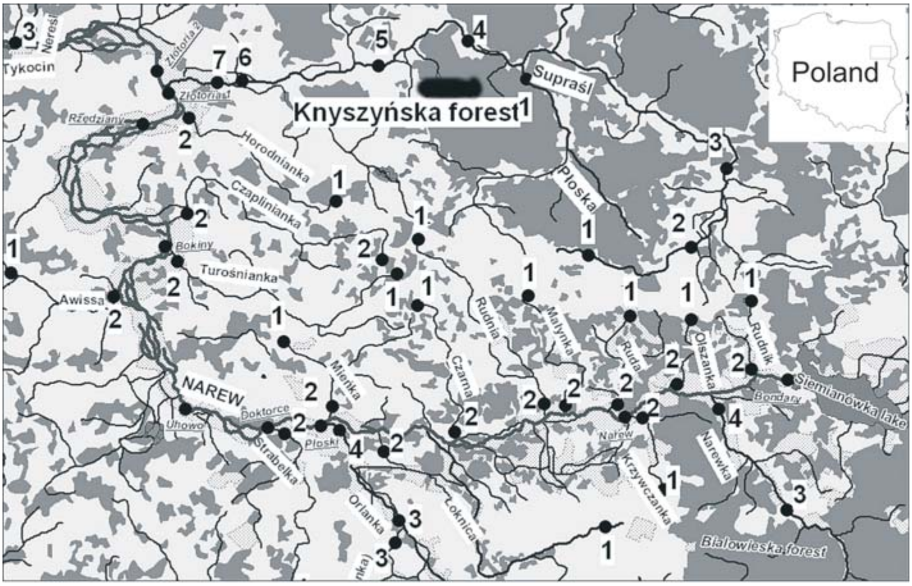


Fig.1. Sediment sampling points

speed, the rivers were divided into larger (the Orlanka, Narewka, Nereśl) and smaller ones (the Awissa, Ruda, Małynka, Rudnia, Czarna, Mieńka, Czaplinianka, Horodnianka, Jaskranka, Krzywczanka, Łoknica, Strabelka, the Biała, a tributary of the Orlanka, and the Płoska, a tributary of the Supraśl). The Narew and Supraśl were analyzed separately. In the case of the smaller rivers, sampling points were set at their mouths to the main rivers. The number of sampling points along with their location on the Narew, Supraśl, and other larger rivers was established according to the contamination sources. Samples were collected in summer (August) and autumn (October) of 2005 at 44 sampling points from the surface layer of bottom sediments in the shore zones. Acidity of the sediments was measured by potentiometry; combustion loss was determined by combusting sediments for 2 hrs in a muffle oven at 550°C. Samples were weighed on analytical scales at ± 0.0001 g precision. Sample weight loss defined as the combustion loss was expressed in per cents to the initial weight. Organic carbon contents were determined using a TOC 1200 analyzer (Thermo Euroglas).

RESULTS AND DISCUSSION

The results of the analyses of the contents of organic carbon in the bottom sediments from the Narew and tributary rivers are presented in Tables 1 and 2. Acidity of the sediments was neutral and weakly acidic, which proves good buffering properties of aqueous environment. The lowest pH values were measured in the Narew River (at the village Narew) – 5.80, while the highest pH occurred in the Orlanka (the village Chraboły)

Table 1

Results of analyses of bottom sediments from the Narew and Supraśl

River	Sampling point	Combustion loss (%)		Organic carbon (%)		Acidity in H_2O	
		August	October	August	October	August	October
Narew	Bondary	3.99	5.5	2.27	2.84	7.77	6.66
	Narew	3.66	6.9	1.98	3.61	7.45	5.8
	Ploski	3.21	0.55	1.99	0.33	7.33	6.64
	Doktorce	3.54	1.98	1.98	1.23	7.22	7.25
	Uhowo	4.99	4.86	2.71	2.5	7.23	6.99
	Bokiny	4.3	6.39	2.79	4.8	7.03	6.36
	Rzędziany	4.12	2.33	2.29	1.98	6.76	6.83
	Złotoria	6.7	1.32	3.74	0.49	7.11	7.14
	Weir Złotoria	4.94	4.97	2.97	2.6	7.42	7.23
	Tykocin	3.56	2.8	2.19	1.73	7.43	7.01
Minimum		3.21	0.55	1.98	0.33	6.76	5.8
Maximum		6.7	6.39	3.74	4.8	7.77	7.25
Arithmetic mean		4.3	3.76	2.49	2.21	-	-
Supraśl	Topolany	5.78	6.84	4.89	3.77	7.32	6.45
	Mościska	5.12	5.32	4.66	4.26	7.36	6.99
	Michałowo	15.21	12.54	10.07	9.12	7.1	7.12
	Gródek	3.98	3.68	2.36	2.22	7.15	7.06
	Supraśl	4.92	0.98	3.58	0.4	7.31	7.2
	Nowodworce	5.32	2.9	3.32	1.49	7.45	7.2
	Fasty	3.82	3.9	2.34	2.95	7.35	7.21
Minimum		3.82	0.98	2.34	0.4	7.1	6.45
Maximum		15.21	12.54	10.07	9.12	7.45	7.21
Arithmetic mean		6.31	5.17	4.46	3.46	-	-

Table 2

Results of analyses of bottom sediments from some tributaries of the Narew

River	Sampling point	Combustion loss (%)		Organic carbon (%)		Acidity in H_2O	
		August	October	August	October	August	October
Narewka	Eliaszuki	3.61	1.87	2.49	1.54	6.73	6.56
	Lewkowo	2.52	2.65	1.53	1.95	6.94	6.83
	Białowieża	6.43	4.18	5.74	2.28	6.88	6.77
Nareśl	Piaski	4.98	4.8	3.18	2.83	6.69	7.16
	Czechowizna	7.4	11.5	5.71	6.49	7.39	7.34
	Kalinówka (Dutki)	16.34	8.43	12.83	5.04	6.84	7.02
Orlanka	Chraboły	3.97	3.4	2.1	2.15	7.12	7.39
	Kotły	3.94	11.6	2.27	6.15	6.92	6.66
	Krzywa	4.9	1.51	3.03	0.91	7.08	7.13
	Orla	2.87	1.4	2.07	0.8	7.12	6.99
Minimum		2,52	1.4	1.53	0.8	6.69	6.56
Maximum		16,34	11.6	12.83	6.49	7.39	7.39
Arithmetic mean		5,7	5.13	4.1	3.01	-	-
Awista	Płonka Kościelna	4.92	4.09	3.38	2.7	7.5	6.69
Czaplinianka	Zawady	4.67	3.32	3.54	2.9	7.01	7.23
Czarna	Pawły	4.21	1.98	2.26	1.2	7.36	7.16
Horodnianka	Choroszcz	4.93	6.18	2.67	4.35	7.38	7.06
Jaskranka	Knyszyn	3.65	10.74	1.95	5.6	7.31	6.76
	Zofiówka	10.23	10.33	5.61	5.3	6.54	7.17
Krzywczanka	Hajdukowszczyzna	4.91	2.33	2.51	1.8	7.12	6.69
Łoknica	Kożyno	2.95	5.84	1.77	2.95	7.45	6.65
Małynka	Trześcianka	13.2	10.6	9.56	5.69	7.3	6.06
Mieńka	Czerewki	3.78	0.93	2	0.5	6.84	7.02
Ruda	Narew	4.67	2.31	3.81	1.65	7.53	6.72
Rudnia	Trześcianka	8.34	2.5	5.01	1.19	7.3	6.65
Strabelka	Strabla	3.19	1.81	2.56	1.17	6.82	6.71
Płoska	Rudnica	15.32	12.34	8.78	7.56	7.21	7.15
Biała	Kuriany	4.89	4.99	2.73	2.58	7.26	7.2
	Bielsk Podlaski	3.96	15.6	2.25	6.13	7.25	7.05
	Lewki	26.32	25.21	20.11	18.6	7.27	7.23
Minimum		2.95	0.93	1.77	0.5	6.54	6.06
Maximum		26.32	25.21	20.11	18.6	7.53	7.23
Arithmetic mean		7.3	7.12	4.74	4.23	-	-

– 7.39. Organic carbon was present at varied concentrations: from 0.40 to 18.6%. The highest value of an arithmetic mean for organic carbon (4.74% in summer and 4.23% in autumn) occurred in group of small rivers, whereas the lowest levels were recorded in the Narew River (2.49% in summer and 2.21% in autumn). Such a low content of organic carbon in the bottom sediments of the upper Narew River, as compared to the Supraśl River and the other rivers, probably resulted from slight sedimentation of particles suspended in the water as well as intensified mineralization of organic matter, which was affected by several factors including aerobic conditions in the river. The rate at which oxygen penetrates from the atmosphere into water depends on the water surface area in contact with air, the flow rate (SQ 5.44 $m^3 \cdot s^{-1}$) and waves. Similar levels of organic carbon were found in the bottom sediments in the Danube (from 0.14% to 4.26% with an arithmetic mean about 2%) (WIŚNIOWSKA-KIELIAN 2007). Some screening studies performed in Norway revealed carbon content in bottom sediments from large rivers ranging from 0.35% to 4.38% (HELLAND et al. 2003).

The bottom sediments from the small rivers were most abundant in organic carbon. These rivers are characterized by a low flow rate and they are mostly overgrown by aqueous plants. Plant communities create conditions favorable for matter accumulation and, at the same time, they are a considerable source of organic matter. The study revealed similar concentrations of organic carbon in the Supraśl and other larger rivers, with an arithmetic mean above 4% in summer and above 3% in autumn. In autumn, a decrease in the organic carbon content became apparent. It is possible that organic matter formed from decaying macrophytes mainly precipitated from the solution and the dissolution process was weaker as the temperatures dropped in autumn (ŁAWACZ 1971). Higher organic carbon concentrations recorded in summer (August) probably resulted from life separation of organic matter by aqueous organisms, as well as decomposition of phytoplankton, which developed abundantly in that season. However, no significant differences in the organic carbon levels between the seasons were observed. WIŚNIOWSKA-KIELIAN (2007) claims that organic carbon concentration in sediments from flows is a resultant of properties of the soil in the catchment, land use, surface runoffs and contamination sources, a conclusion which was confirmed by the present study. The content of organic carbon varied greatly and depended on the location of the sampling points. The highest levels of organic matter and carbon were recorded in the Biała River in the village Lewki. Higher values of these parameters were due to the surface runoffs from fields and the influx of municipal and industrial sewage from Bielsk Podlaski. ALLAN (1998) found that rivers flowing through an urban area carry large amounts of suspensions. DOJLIDO (1995) reported that organic carbon penetrates into water along with municipal and industrial sewage. The excess of unused organic fertilizer components contributes to increase of organic matter in aqueous environment. In the Supraśl (Michałowo) and Płoska Rivers the elevated level of organic matter and carbon may have been generated by the post-bog soils, which are found in that area (Mirowski et al. 1990).

The statistical analysis of the data did not reveal statistically significant correlation between the acidity of the bottom sediments and their organic carbon content. As expected, there was significant dependence between combustion loss and organic carbon content in the Narew and Supraśl Rivers as well as in the groups of smaller and larger rivers, where correlation coefficients were R = 0.9403, R = 0.9769, R = 0.9606, and R = 0.9667, respectively.

CONCLUSIONS

1. Bottom sediments collected from the Narew River contained the lowest amounts of organic carbon, which was a consequence of intensive mineralization.
2. Bottom sediments from the smaller rivers were most abundant in organic matter, which was due to the low flow rates and aqueous plant communities growing on the banks of these rivers.
3. The content of organic matter was highly varied between the sampling points.
4. Positive correlation between the combustion loss and organic carbon content was recorded.

REFERENCES

Allan J. 1998. *Ekologia wód płynących.* Wyd. Nauk. PAN, ss. 451.

Azam F., Fenchel T., Field J., Gray J., Meyer-Reil L., Thingstad F. 1983. *The ecological role of water –column microbes in the sea*. Mar. Ecol. Prog. Ser. 10: 257-263.

Bojakowska I., Gliwicz T. 2003. *Wyniki geochemicznych badań osadów wodnych Polski w latach 2000-2002. Bibl. Monitoringu Środowiska,* Warszawa ss. 120.

Chen J.S. Wang F.Y., Li X. D., Song J.J. 2000. *Geographical variations of trace elements in sediments of the major rivers in eastern China.* Environ. Geol., Springer-Verlag, 39 (12), 1334-1340.

De Haan H. 1992. *Impacts of environmental changer on the biogeochemistry of aquatic humic substances* .Hydrobiologia, 229,59-71.

Dojlido J. 1995. *Chemia wód powierzchniowych.* Wyd. Ekonomia i Środowisko, ss. 342.

Eisma D. 1992. *Suspend matter in the Aquatic Environment*. Springer, Berlin, pp. 315.

Górniak A. 1996. *Substancje humusowe i ich rola w funkcjonowaniu ekosystemów słodkowodnych*. Dissertiones Universitatis Vrsovuensis 448, Białystok, 151ss

Górniak A. Zieliński P. 1999. *Rozpuszczalne związki węgla organicznego w jeziorze Wigry*. Mat. ogólnopolskiej konf. „Funkcjonowanie i ochrona ekosystemów wodnych na obszarach chronionych", 141-152.

HELLAND A, HOLTAN G, JORGENSEN P. 2003. *Riverine inputs of organic karbon and nitrogen to Norwegia coastal areas.* Ambio., 32(6): 412.-421.

KANIA K., MALINA G., GROTENHUIS J. T. C. 2005 *Osady denne rzeki Stoły: wtórne ognisko zanieczyszczeń czy bariera ochronna dla wód powierzchniowych*. Monog. Kom. Inż. Środ., PAN, 33, 1001-1009.

ŁAWACZ W. 1971. *Substancje organiczne rozpuszczone w wodzie, ich pochodzenie i udział krążenia w materii.* Wiad. Ekol., 17 (2): 147-156.

MIROWSKI Z., NIKLEWSKA A., WÓJCIAK H. 1990. *Wpływ sposobu użytkowania na profilowe rozmieszczenie azotu we frakcjach humusowych zmeliorowanych gleb torfowo-murszowych*. Wiad. Ekol., 17 (3): 147-156.

OUYANG Y., ZHANG J. E., OU L. T. 2006. *Temporal and spatial distributions of sediment total organic carbon in an estuary river.* J. Environ Qual., 35: 93 – 102.

SKORBIŁOWICZ E. 2005: *Heavy metal content in bottom sediments of rivers in Podlasie province near selected communication tracts*. Chem. Inż. Ekol., 12 (1-2): 109-120.

WARDAS M. 2001 *Badania metali ciężkich w osadach rzecznych w rejonie Polski południowej.* Symp. Nauk. Kom. Chemii Analitycznej PAN, Komisja Analizy Wody, Mat. pokonferencyjne pod red. J. SIEPAKA, 63-74.

WARNKEN K., SANTSCHI P., H. 2004. *Biogeochemical behavior of organic karbon in the Trinity River downstream of a lage reservoir lake in Teras, USA.* Sci. Total Environ., 329 (1-3): 131-139.

WETZEL R. G., MANNY B. A. 1977. *Seasonal changes in particulate and dissolved organic carbon and nitrogen in hardwater stean*. Arch. Hydrobiol,. 80 (10): 20-39.

WIŚNIOWSKA-KIELIAN B. 2007. *Dynamics of organic carbon content in bottom sediments of the Dunajec river in the vegetation season,* Pol. J Environ. Stud., 6 (2A): 372-377.

J. Elementol. 2008, 13(1): 109–116

MACROELEMENTS: ZINC AND IRON IN WELL WATER IN THE UPPER NAREW RIVER CATCHMENT*

Mirosław Skorbiłowicz, Elżbieta Skorbiłowicz

Department of Technology in Engineering and Environmental Protection
Technical University in Bialystok

Abstract

The aim of the present study was to evaluate the spatial distribution of concentrations of some elements in shallow ground waters as well as to find the main sources of their origin. The investigations were carried out in 8 villages in Podlasie region. The water sampling sites were in the villages Sobótka, Narew, Ciełuszki, Kaniuki, Zawyki, Uhowo, Topilec, and Złotoria, all on or near the Narew River. Water samples were collected in spring, summer, and autumn of 2006. The samples underwent determinations of calcium, magnesium, sodium, potassium, zinc, and iron concentrations by means of AAS and EAS techniques after previous filtering through micro-pore filters (d=0.45 μm). None of the tested water samples met the standards for potable water specified in the Decree of the Ministry for Health of 2007 as they exceeded permissible concentrations of iron ions. Regarding potassium ions, the well waters were classified to underground waters quality class V. The waters with the highest values of the tested parameters were found in wells in Kaniuki, Złotoria and Zawyki.

Keywords: well, macroelements, potassium.

MAKROELEMENTY, CYNK I ŻELAZO W WODACH STUDZIENNYCH DOLINY GÓRNEJ NARWI

Abstrakt

Celem pracy było określenie rozkładu przestrzennego stężenia wybranych składników płytkich wód podziemnych oraz określenie głównych czynników ich pochodzenia. Badania przeprowadzono w 8 wsiach położonych w województwie podlaskim. Miejsca poboru próbek wody wyznaczono w miejscowościach: Sobótka, Narew, Ciełuszki, Kaniuki, Zawyki, Uhowo, Topilec,

---

*The research was financed by the Ministry for Education and Science as part of the Scientific Project No 3 TO9D 112 28, (2005-2007)

Złotoria, zlokalizowanych wzdłuż rzeki Narew w jej bezpośrednim sąsiedztwie. Próbki wody pobierano w terminach: wiosna, lato, jesień 2006 r. W próbkach oznaczono stężenie jonów wapnia, magnezu, sodu, potasu, cynku i żelaza metodą AAS i ESA po ich przefiltrowaniu przez filtry mikroporowate o średnicy porów 0,45 µm. Badane wody nie odpowiadały standardom wody przeznaczonej do spożycia określonym w Rozporządzeniu Ministra Zdrowia z 2007 r., z powodu przekroczenia wartości dopuszczalnych stężenia jonów żelaza. Ze względu na stężenie jonów potasu wody badanych studni zakwalifikowano do V klasy jakości wód podziemnych. Wody o najwyższych wartościach stężenia badanych parametrów stwierdzono w studniach zlokalizowanych we wsiach Kaniuki, Złotoria i Zawyki.

Słowa kluczowe: studnia, makroelementy, potas.

INTRODUCTION

The monitoring of shallow ground waters in Poland is not performed regularly and lacks uniform water quality criteria. It is accepted that chemical composition of shallow ground waters is very similar to that of water disposed through drainage system (Igras 2000).

Unsatisfactory water quality in wells in rural households has been indicated by several authors (Sapek, Sapek, Rzepiński 1993, Misztal, Sapek 1997, Sikorski 1997, Ostrowska et al. 1999, Pietrzak 1997, Sapek 2002, Sapek 2002).

Depending on their type, technical status and capacity, sites where natural fertilizers are stored (manure plates, reservoirs for liquid and solid manure) are the gravest hazard to soil and ground water, including the nearest water flows and small water reservoirs, as they can be a source of such elements as phosphorus, nitrogen, potassium, heavy metals and other ingredients contained in farm animal fodder (Chadwick, Chen 2002, Ritter, Bergstrom 2001, De Vries et al. 2002).

The aim of the present study was to evaluate the spatial distribution of concentrations of some elements in shallow ground waters and to identify the main sources of their origin.

MATERIAL AND METHODS

The investigations were carried out in 8 villages situated in Podlasie, a region in the east of Poland. One dug well in each village was selected among farmsteads which are involved in agricultural production. All the wells were filled with water from the first water-bearing layer. The study embraced well water within the river Narew section from Sobótka to Złotoria villages. The sites where the water was collected were set up in the villages Sobótka, Narew, Ciełuszki, Kaniuki, Zawyki, Uhowo, Topilec, and Złotoria, all on or very near the Narew River (Figure 1).

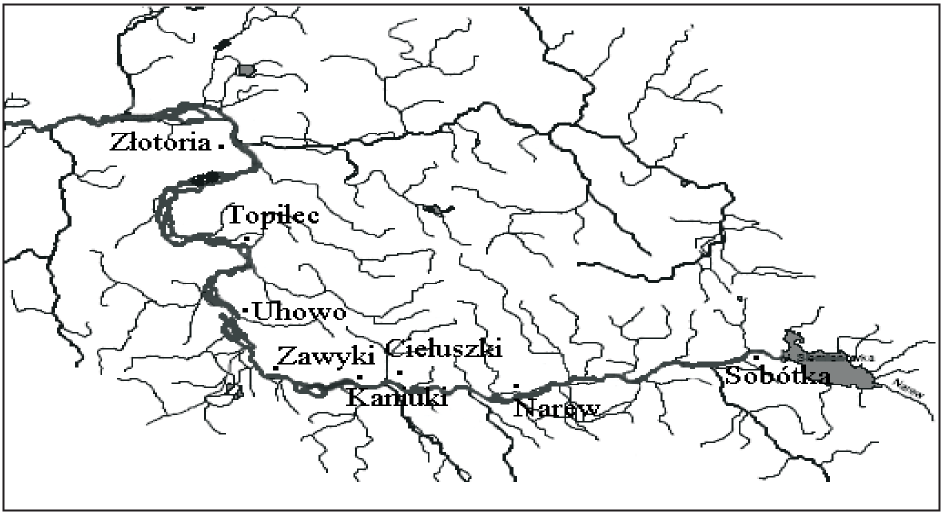


Fig. 1. Location of the well water sampling points

The water samples were collected in spring, summer, and autumn of 2006. The samples underwent determinations of calcium, magnesium, sodium, potassium, zinc, and iron concentrations by means of AAS and EAS after previous filtering through micro-pore filters (d=0.45 µm). In the AAS and EAS techniques, oxidizing flame air-acetylene was applied as an atomization source.

The precision and accuracy was estimated by testing the recovery of analytes from 5 model samples with various concentrations of the analyzed metals. Specific conductivity measurements were made *in situ* during the sample collection. Soluble forms of the above components were studied. Correctness of the determinations of soluble Ca, Mg, Na, Zn, and Fe forms was verified using the reference material SRM 1643e (Trace Elements in Water, NIST). Parameters of the analytical methods were adjusted to recommendations set in the Decree of the Ministry for Environment (2004). The data thus obtained enabled us to calculate arithmetic means for concentrations of the metals in the samples collected from 3 wells in each village on three sampling dates. Factorial analysis (FA), which is a multi-dimensional analysis applied to describe and explore a large sets of data, was used for statistical computations. The present study supplied 576 measurement results, which were subsequently analyzed. In order to isolate factors, the main components method, which uses a primary correlation matrix for calculations, was applied. This method is used in hydrochemistry to investigate processes occurring in underground waters and to identify the supplying and origin sources which shape the chemical composition of waters (SIMEONOVA et al. 2003, Simeonov et al. 2004). In order to interpret the factorial analysis results, it was assumed that associations of primary variable with a factor are strong when absolute values of its charges are greater than 0.70 (Evans et al. 1996, Pucket, Bricker 1992).

RESULTS AND DISCUSSION

The concentrations of the elements analyzed were found to be variable. The highest concentration of calcium ions was determined in well water from Złotoria (178.97 mg·dm^{-3} – II quality class for underground waters), while the lowest one – in Ciełuszki (104.65 mg·dm^{-3} – II quality class for underground waters) – Figures 2, 3, 4. Similarly, the highest

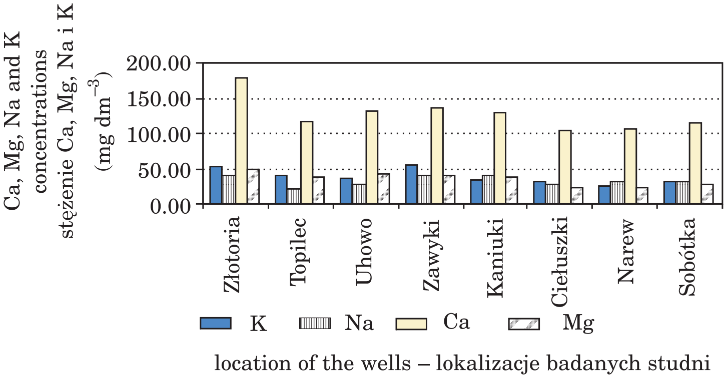


Fig .2. Arithmetic mean values of concentrations of macroelements in wel waters
Rys. 2. Wartości średniej artmetycznej ze stężenia makroelementów studziennych

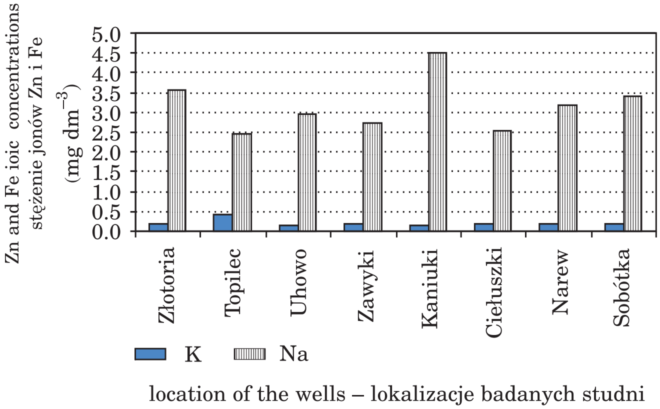


Fig .3. Arithmetic mean values of zinc and iron ionic concentrations in well waters
Rys. 3. Wartości średniej artmetycznej ze stężenia jonów cynku i żelaza
w wodach studziennych

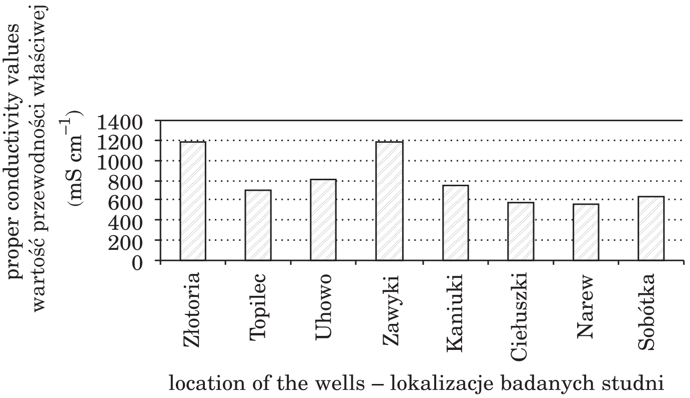


Fig .4. Arithmetic mean values of vell water proper conductivity
Rys. 4. Wartości średniej artmetycznej przewodności właściwej w wodach studziennych

content of magnesium ions (48.19 mg·dm^{-3} – II quality class for underground waters) was observed in well water from Złotoria, whereas the lowest one – in Narew (23.60 mg·dm^{-3} – I quality class for underground waters). In these villages, the distribution of potassium ions was similar: Złotoria – 52.27 mg·dm^{-3}, Narew – 26.43 mg·dm^{-3} (higher than V quality class for underground waters).

According to Jaszczyński et al. (2006), elevated levels of potassium ions was caused by agricultural activity, because potassium content in crops or plants growing under natural conditions is over 100-fold higher than that of sodium (also in plants from natural potassium-deficient soils).

Chadwick and Chen (2002) as well as Foy and O'Connor (2002) identify point sources next to area contamination from which potassium and organic matter are transferred from natural fertilizers to water systems. These authors claim that silage liquids which penetrate into the ground water and soil, together with fertilizers components, cause soil acidification, which accelerates their migration in a soil profile and, consequently, their washing out.

The concentration of sodium ions followed a similar pattern to that of calcium – the highest value of sodium was recorded in well water from Złotoria – 39.77 mg·dm^{-3}, while the lowest occurred in Ciełuszki – 26.85 mg·dm^{-3} (I quality class for underground waters). The highest specific conductivity values were measured in well water from Złotoria (1184 mS·cm^{-1}), while the lowest ones – in Narew (558 mS·cm^{-1} – II quality class for underground waters). The highest iron concentration was found in water from Kaniuki (4.50 mg·dm^{-3}), the lowest – in Topilec (2.44 mg·dm^{-3} – III quality class of underground waters). The highest zinc content was recorded in water collected in Topilec (0.43 mg·dm^{-3}), the lowest – in Uhowo (0.17 mg·dm^{-3}); both values are within the range corresponding to I quality class for underground waters.

The so-called pre-mixes, that is mineral fodder concentrates used in animal feeding, except plant ones, are a source of microelements and heavy metals such as zinc in natural fertilizers. Their excess which has not been absorbed by farm animals is found in their excreta and, consequently, in natural fertilizers (Klocek, Osek 2001, De Vries et al. 2002).

None of the tested water samples met the norms of the Ministry for Health (2007) due to high concentrations of iron ions.

The results of the statistical multi-factorial analysis implied the main factor responsible for supplying of the well waters with such ions as Ca, Mg, and K as well as increasing the specific conductivity value (Figure 5). The factor seems to be associated with the fact that, according to Skorbiłowicz et al. (2001), well water receives macroelements through the elution of geological environment and migration of elements from organic fertilizers stored on a farm. The analysis revealed another source of iron and sodium in well waters. The low quality of the well waters we studied caused by high concentrations of iron was probably caused by the influx of water characterized by a much inferior quality from the central fragments of the upper Narew River valley.

All the wells lie near the Narew River (from 50 m to only 200 m). High levels of iron ions in water samples from most of the wells can also be attributed to a constant contact of well waters with the so-called long distance underground waters, which are rich in iron. The analysis of the changes in the values of the factors (Figure 6) revealed that the intensification of factor I was the strongest in Złotoria and Zawyki, whereas that of factor II – in Kaniuki.

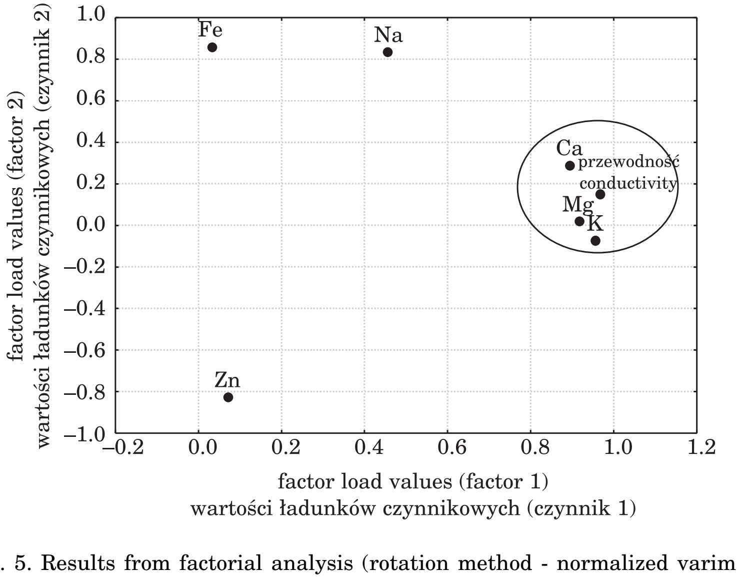


Fig. 5. Results from factorial analysis (rotation method - normalized varimax); determined loads are > 0.7

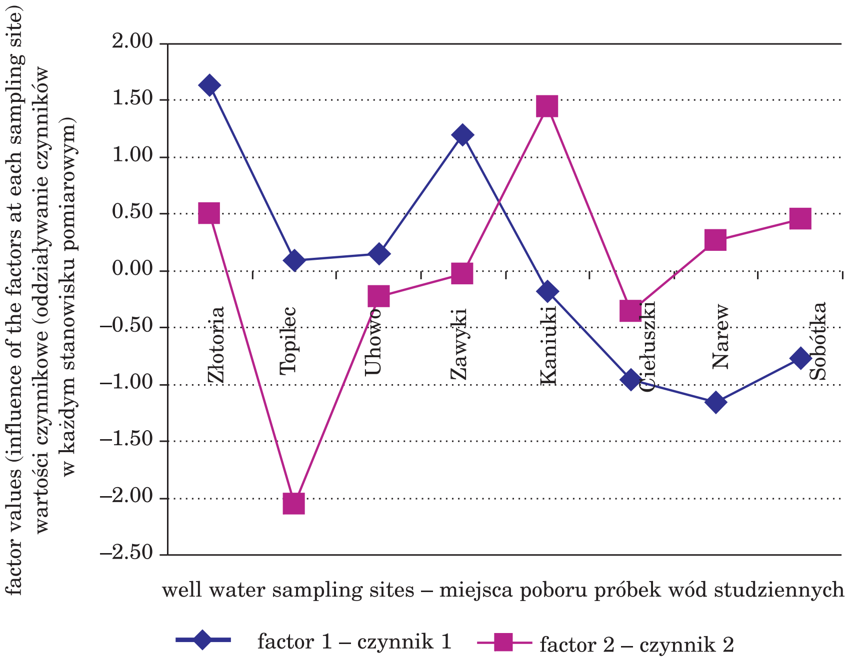


Fig. 6. Changes in the dynamics of the factors at sampling points
Rys. 6. Zmiany dynamiki czynników w punkach poboru próbek

CONCLUSIONS

1. The water samples we analyzed failed to meet the potable water standards specified in the Decree of the Ministry for Health of 2007 as they exceeded permissible concentrations of iron ions.

2. Regarding potassium ions, the water from the wells was classified to underground waters quality class V.

3. Water samples yielding the highest values of the parameters we examined were collected from the wells in Kaniuki, Złotoria and Zawyki.

REFERENCES

Chadwick D.R., Chen S. 2002. Manures. In: *Agriculture, hydrology and water quality*. Ed. P.M. Haygarth, S.C. Jarvis. Wallingford: CABI Publ. CAB Intern., 57–82 pp.

De Vries W., Römkens P.F.A.M., Van Leeuven T., Bronswijk J.J.B. 2002. *Heavy metals. In: Agriculture, hydrology and water quality*. Wallingford: CABI Publ. CAB Intern., 107–132 pp.

Evans C.D., Davies T.D., Wigington JRP.J., Tranter M., Kretschier W.A. 1996. *Use od factor analysis to investigate processes controlling the chemical composition of four streams in Adirindack Mountaions*. New York. J. Hydrol., 185: 297-316.

FOY R.H., O'CONNOR W.C.K. 2002. *Managing the effect of agriculture and water quality in Northern Ireland.* In: *Agriculture, hydrology and water quality.* Ed. P.M. HAYGARTH, S.C. JARVIS. Wallingford: CABI Publ. CAB Intern., 417-440 pp.

IGRAS J. 2000. *Skład chemiczny wód glebowo-gruntowych w Polsce*. Nawozy i Nawożenie, 3a: 38-49.

JASZCZYŃSKI J., SAPEK A., CHRZANOWSKI S. 2006. *Wskaźniki chemiczne wody do picia z ujęć własnych w gospodarstwach wiejskich w otulinie Biebrzańskiego Parku Narodowego.* Woda Środ. Obsz. Wiej., 6 (2-18): 129-142.

KLOCEK B., OSEK M. 2001. *Mieszanki mineralne, preparaty witaminowe i witaminowo-mineralne.* W: *Żywienie zwierząt i paszoznawstwo.* Red. D. JAMROZ, W. PODKÓWKA, J. CHACHUŁOWA. PWN, Warszawa, ss. 359-371.

MISZTAL A., SAPEK A. 1997. *Jakość wody w studniach zagrodowych i charakterystyka rolniczo-socjologiczna gospodarstw w wybranych zlewniach Zbiornika Dobczyckiego*. Wydaw. IMUZ, Falenty, Zesz. Eduk., 7: 83-99.

OSTROWSKA B., PŁODZIK M., SAPEK A., WESOŁOWSKI P., SMOROŃ S. 1999. *Jakość wody pitnej z ujęć własnych w gospodarstwach rolnych.* Wiad. IMUZ, 20 (1): 7-18.

PIETRZAK S. 1997. *Postępowanie z nawozami organicznymi pochodzenia zwierzęcego w aspekcie ochrony jakości wody.* Wydaw. IMUZ, Falenty, Zesz. Eduk., 2: 31-44.

PUCKETT L.J., BRICKER O.P. 1992. *Factors controlling the major ion chemistry of streams in the Blue Ridge Valley and physiographic provinces of Virginia and Maryland*. Hydrol. Proces., 6: 79-98.

RITTER W., BERGSTROM L. 2001. *Nitrogen and water quality*. In: Agricultural nonpoint sources pollution. Eds. W.F. RITTER, A. SHIRMOHAMMADI. Boca Raton: Lewis Publ., 59–90 pp.

Rozporządzenie Ministra Środowiska z dnia 11 lutego 2004 r. w sprawie klasyfikacji dla prezentowania stanu wód powierzchniowych i podziemnych, sposobu prowadzenia monitoringu oraz sposobu interpretacji wyników i prezentacji stanu tych wód. (Dz. U. Nr 32, poz. 284).

Rozporzadzenie Ministra Zdrowia z dnia 29 marca 2007 r. w sprawie jakosci wody przeznaczonej do spozycia przez ludzi (DzU z 2006 r. Nr 123, poz. 858).

SAPEK A. 2002. *Rozpraszanie fosforu do środowiska – mechanizmy i skutki*. Wydaw. IMUZ, Falenty, Zesz. Eduk., 7: 9-24.

SAPEK A., SAPEK B., RZEPIŃSKI W. 1993. *Wstępne rozpoznanie zanieczyszczenia wody do picia z ujęć własnych w gospodarstwach rolnych na terenie województwa ostrołęckiego.* W: *Ochrona zasobów wodnych przed zanieczyszczeniem.* Mat. na sympozjum IAWQ. Kraków, Polski Kom. Międz. Stow. Jakości Wody IAWQ.

SAPEK B. 2002. *Jakość gleby i wody w gospodarstwach demonstracyjnych*. Wydaw. IMUZ Falenty, Zesz. Eduk., 7: 57–71.

SIKORSKI M. 1997. *Sanitacja zagrody wiejskiej.* Wydaw. IMUZ, Falenty, Zesz. Eduk., 3: 51-81.

SIMEONOV V., SIMEONOVA P., TSITOURIDOU R. 2004. *Chemometric quality assessment of surface waters: two case studies.* Chem. Engin., Ecol., 11 (6): 449-469.

SIMEONOVA P., SIMEONOV V., ANDREEV G. 2003. *Environmetric analysis of the Struma River water quality*. Central Europ. J. Chem., 2: 121-126.

SKORBIŁOWICZ M., WIATER J., SKORBIŁOWICZ E. 2001. *Zastosowanie analizy wieloczynnikowej do oceny jakości płytkich wód podziemnych na obszarach wiejskich*. Inż. Ekol. 5: 125-130.

J. Elementol. 2008, 13(1): 117–125

DIRECT AND RESIDUAL EFFECT OF MUNICIPAL SOLID WASTE COMPOST ON THE LEAD CONTENT OF SOIL AND PLANTS

Wiera Sądej, Anna Namiotko

Chair of Environmental Chemistry
University of Warmia and Mazury in Olsztyn

Abstract

The objective of this study was to determine the possibility of using composts obtained from heterogeneous municipal wastes for agricultural purposes. The study involved an analysis of the lead content of plants grown in soil enriched with municipal solid waste compost heap-stored for different periods of time, compost obtained from municipal green waste, and manure. Municipal waste compost was applied at the rates of 10, 20 and 30 $g \cdot kg^{-1}$ soil, while the compost obtained from green waste was administered at a rate of 10 $g \cdot kg^{-1}$ soil. Maize and sunflowers were grown in the first year of the experiment, spring barley and white mustard – in the second year, and *Phacelia tanacetifolia* – in the third year.

It was found that compost produced from municipal green waste had a substantially higher lead content compared to municipal solid waste compost, although both types of composts could be used for agricultural purposes in accordance with the relevant trade standards. The application of bio-waste composts increased the lead content of the green tops of all investigated crops. The accumulation of this element was dependent on plant species, as well as on the type and rate of compost. The highest lead concentrations were recorded in mustard, slightly lower in maize and phacelia, lower in sunflowers and the lowest – in barley. In the case of barley, mustard and phacelia, the highest lead content was reported in pots amended with municipal waste compost heap-stored for 3 months. With respect to maize, such an effect was observed after the application of compost stored for 1 month, whereas in sunflowers – after soil enrichment with compost obtained from urban green waste. At the completion of the experiment, the largest amounts of lead were found in soil amended with municipal solid waste compost heap-stored for 6 months. Soil enriched with compost produced from urban green waste contained on average 14% lead more than soil amended with identical rates of municipal waste compost stored for 6 months.

Key word: lead, municipal compost, plant, soil.

Wiera Sądej, Department of Environmental Chemistry, University of Warmia and Mazury, pl. Łódzki 4, 10-718 Olsztyn, Poland, phone: 089 523 39 64, e-mail: wersad@uwm.edu.pl

BEZPOŚREDNI I NASTĘPCZY WPŁYW KOMPOSTÓW Z ODPADÓW KOMUNALNYCH NA ZAWARTOŚĆ OŁOWIU W GLEBIE I ROŚLINACH

Abstract

Oceniano przydatność kompostów z nieselekcjonowanych odpadów komunalnych w rolnictwie. Oceny tej dokonano na podstawie zawartości ołowiu w roślinach nawożonych kompostami z odpadów miejskich o różnym stopniu dojrzałości, kompostem z zieleni miejskiej oraz obornikiem. Komposty z odpadów komunalnych stosowano w dawkach: 10, 20 i 30 g·kg^{-1} gleby, kompost z zieleni miejskiej w dawce 10 g·kg^{-1} gleby. W pierwszym roku doświadczenia uprawiano kukurydzę i słonecznik, w drugim roku jęczmień i gorczycę, w trzecim roku – facelię.

Wykazano, że kompost z zieleni miejskiej zawierał znacznie więcej ołowiu, w porównaniu z kompostami z odpadów miejskich, aczkolwiek oba rodzaje kompostów zgodnie z Normą Branżową kwalifikowały się do rolniczego wykorzystania. Nawożenie kompostami z bioodpadów spowodowało podwyższenie zawartości ołowiu w zielonej masie wszystkich uprawianych roślin. Kumulacja tego pierwiastka zależała od gatunku rośliny, rodzaju kompostu oraz dawki. Najwięcej ołowiu zawierała gorczyca, zbliżone zawartości tego metalu stwierdzono w kukurydzy i facelii, mniej ołowiu zawierał słonecznik, najmniej zaś jęczmień. W jęczmieniu, gorczycy i facelii najwyższą koncentrację ołowiu stwierdzono w obiektach nawożonych 3-miesięcznym kompostem z odpadów komunalnych. W kukurydzy taki efekt zaobserwowano po zastosowaniu kompostu 1-miesięcznego, a w przypadku słonecznika po zastosowaniu kompostu z zieleni miejskiej. Po zakończonym cyklu badawczym najwięcej ołowiu pozostało w glebie użyźnianej 6-miesięcznym kompostem z odpadów komunalnych. Gleba użyźniona kompostem z zieleni miejskiej zawierała średnio o 14% więcej ołowiu, w porównaniu z glebą, do której wprowadzono identyczne dawki półrocznego kompostu z odpadów komunalnych.

Słowa kluczowe: ołów, komposty z odpadów komunalnych, roślina, gleba.

INTRODUCTION

Municipal waste contains large amounts of organic matter, which, from the point of view of economy as well as ecology, should be used for environmental purposes (Lekan, Kacperek 1990, Drozd et al. 1999). Composts produced from municipal soil waste to be used in agriculture should meet the criteria determined by the standard norm (BN 89/9103-09) which specifies their reaction, content of nutrients and permissible concentrations of heavy metals. Lead is one of the elements which are frequently determined in composts produced from municipal waste. This is a metal which demonstrates extreme toxicity in natural environment (Fergsson 1990). Excessive amounts of lead in soil not only cause changes in the biological properties of soil but also modify the uptake of macro- and microelements by plants, which affects their growth and development. Lead is relatively less toxic to emerging plants, but in heavily polluted areas such an adverse effect on new plants can be observed (Woźny 1995). Lead is often reported to be highly mobile in acidic soils (Brümmer 1986, Basta, Tabatabai 1992).

The objective of the study has been to determine the concentration of lead in aerial parts of crop plants growing in soil fertilised with composts produced from municipal solid and green waste.

MATERIAL AND METHODS

The study consisted of a 3-year pot experiment, in which soil was fertilised with Dano, a compost produced from heterogeneous municipal waste using the MUT biothermal method, or with a compost produced from municipal green waste. The experiment was carried out in a greenhouse at the University of Warmia and Mazury in Olsztyn. For the trials, Kick-Brauckman pots were filled with 10 kg of soil each. A more detailed description of the soil can be found in the previous paper (SĄDEJ et al. 2004). Composts produced from municipal solid waste matured in heaps for 1, 3 and 6 months. They were applied in three rates: 10, 20 and 30 $g \cdot kg^{-1}$, which corresponded to 30, 60 and 90 $t \cdot ha^{-1}$. The compost based on green waste, which matured in a heap for half a year, was administered at 10 $g \cdot kg^{-1}$ of soil (30 $t \cdot ha^{-1}$). The effect of the composts was compared to that generated by a natural fertiliser, FYM, which was applied at the rates balanced in terms of organic carbon with the lowest rates of the composts. All the composts were used in the first year of the trials, when maize and sunflower were grown. These crops were followed by spring barley and white mustard in the second year, and *Phacelia tanacetifolia* in the third year. Maize was harvested at the heading phase, sunflower – at the onset of flowering, spring barley – at the shooting phase, and white mustard and *Phacelia tanacetifolia* were collected at the full flowering phase. The content of lead in the plant material, composts, FYM and soil samples was determined by the atomic emission spectrophotometry with induction activated plasma, using an ICP-AES apparatus (Leeman Labs), in a mixture of HNO_3 and $HClO_4$ acids at a 5 : 4 ratio, in a heating block manufactured by VEL.

RESULTS AND DISCUSSION

It has been found out that the process of composting increased the content of lead by nearly 60% in a six-month old compost compared to the youngest compost (Table 1). It has also been demonstrated that the compost produced from municipal green waste contained nearly twice as much lead as the composts based on solid waste. The content of lead in the soil was within the range accepted as the natural concentration, that is ‘the background’ contamination.

Table 1

Content of lead in composts, FYM and soil used in pot experiment (mg·kg^{-1}d.m.)

Municipal solid waste compost heap-stored for			Green waste compost	FYM	Soil
1 month	3 months	6 months			
121.8	145.2	191.9	281.7	8.40	4.37

Lisk et al. (1992) arrived at contrary results, as they showed that municipal solid waste composts contained more lead than composts produced from green waste. Low concentrations of lead in green waste composts were also implied by Filipek-Mazur and Mazur (2003). The composts produced from municipal solid waste which we analysed contained far less lead that it has been reported by other authors (Rutkowska et al. 2003). Drozd et al. (1996) concluded that the composting process could lead to a four-fold increase in the concentration of this element in a 1-month-old compost compared to fresh compost, but further composting might be accompanied by a gradual decline in the lead concentration.

Studies completed by other researchers (Pinamonti et al. 1997, Kolota et al. 1998, Drozd et al., 1999) suggest that fertilisation of soil with municipal waste composts can produce a varied effect on accumulation of lead in plants. The actual concentration of lead in plants is more strongly correlated with the species of crops rather than the rates of fertilisers.

In our own investigations, fertilisation of soil with municipal waste and green waste composts resulted in raised levels of lead in crops grown immediately after fertilisation treatments as well as those cultivated in the subsequent years. The concentration of lead in plant green matter was to a greater extent modified by the species of a crop rather than the type of compost applied (Figures 1-5).

Maize, which was grown directly after adding the composts to soil, contained the highest levels of lead in the combinations fertilised with the freshest compost. Increasing rates of composts, irrespective of their maturity, raised the content of lead in plants. When green waste compost was used, the concentration of lead was over 9% higher versus the combination with the same rate of six-month old municipal solid waste compost (Figure 1).

Sunflower, which was grown as an aftercrop, contained the highest level of lead in the object fertilised with green waste compost (Figure 2). By increasing the rates of 1- and 6-month-old solid waste composts, a large increment in the lead concentration in sunflower plants was obtained. Higher rates of 3-month-old solid waste compost did not produce such an unambiguous effect. More lead was determined in sunflower grown in soil amended with 10 g of compost per 1 kg^{-1} of soil than in that treated with 20 g·kg^{-1}. Three-month-old compost caused the highest increase in lead in aerial parts of sunflower plants.

Table 2

Total content of lead in the experiment

Object	Rate of compost/FYM ($g \cdot kg^{-1}$ soil)	Application of lead into soil ($mg \cdot pot^{-1}$)	Total uptake of lead by plants ($mg \cdot pot^{-1}$)	Residual amount of lead in soil ($mg \cdot pot^{-1}$)
Control	0	43.70	0.27	43.43
One-month-old municipal solid waste compost				
Compost	10	55.88	0.39	55.49
Compost	20	68.06	0.51	67.55
Compost	30	80.24	0.56	79.68
FYM	15	44.96	0.30	44.66
Three-month-old municipal solid waste compost				
Compost	10	58.22	0.53	57.69
Compost	20	72.74	0.57	72.17
Compost	30	87.26	0.67	86.59
FYM	14	44.88	0.28	44.60
Six-month-old municipal solid waste compost				
Compost	10	62.89	0.38	62.51
Compost	20	82.08	0.35	81.73
Compost	30	101.27	0.41	100.86
FYM	13	44.79	0.29	44.50
Green waste compost	10	71.87	0.37	71.50

Regarding barley, increased rates of 1- and 3-month-old composts caused increased lead levels in plants, with the highest rate of 3-month-old compost raising the concentration of lead over three-fold (Figure 3). The concentration of lead in barley plants fertilised with green waste compost was lower than the control, albeit higher than the levels detected in barley treated with 6-month-old Dano compost applied at 10 $g \cdot kg^{-1}$ soil. Barley plants from the latter object were determined to have only trace amounts of lead. In FYM fertilised barley, the content of lead was similar to that in the control.

White mustard contained the highest concentrations of lead among all the analysed crops. There was one exception, however. White mustard from the control object had only trace amounts of this metal (Figure 4). All the types of composts caused increased levels of lead in white mustard. The sharpest rise in the lead concentration in this plant occurred after fertilisation with the compost heap-stored for 3 months. Increasing

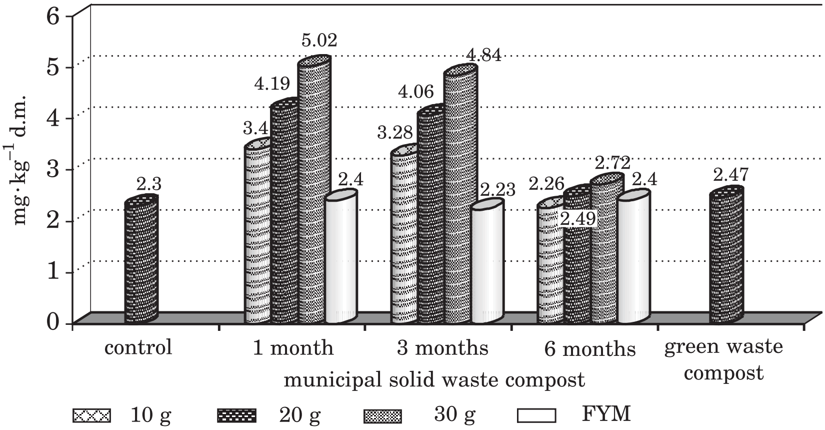


Fig. 1. Content of lead in maize (*Zea mays*)

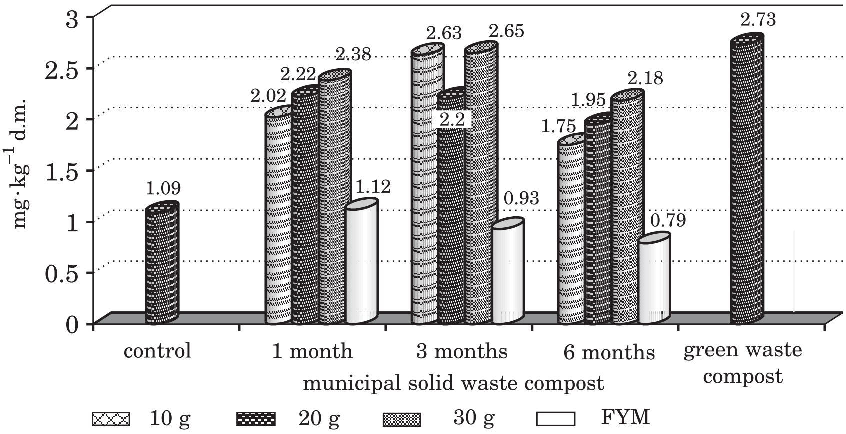


Fig. 2. Content of lead in sunflower (*Helianthus annuus*)

rates of the composts, independent of their maturity, were followed by depressed concentrations of lead in white mustard dry matter. In the plants fertilised with green waste compost, the content of lead was 0.7 mg·kg^{-1} d.m. lower compared to the plants fertilised with 6-month-old compost produced from solid waste.

The concentration of lead in *Phacelia tanacetifolia* ranged between 1.12 and 4.25 mg·kg^{-1}d.m. Analogously to white mustard, fertilization with higher rates of composts resulted in lower lead concentrations in plant tissues. The most severe lead contamination of phacelia was observed after the fertilization treatment involving 3-month-old compost. The content of lead in phacelia fertilized with FYM was only slightly different from the control.

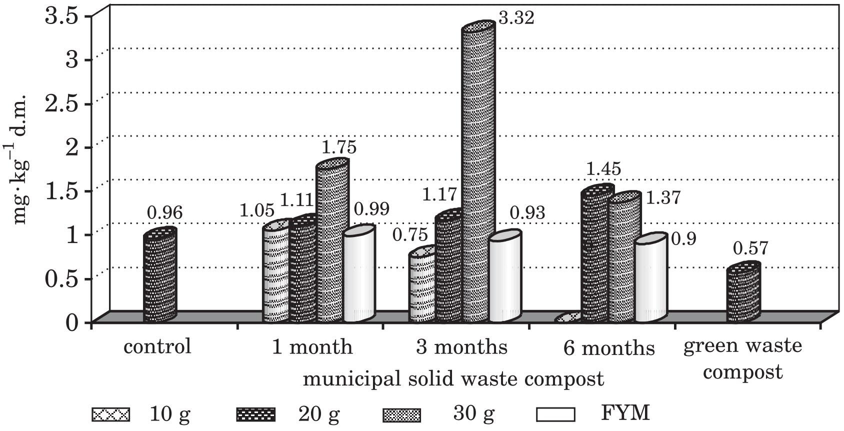


Fig. 3. Content of lead in spring barley (*Hordeum sativum*)

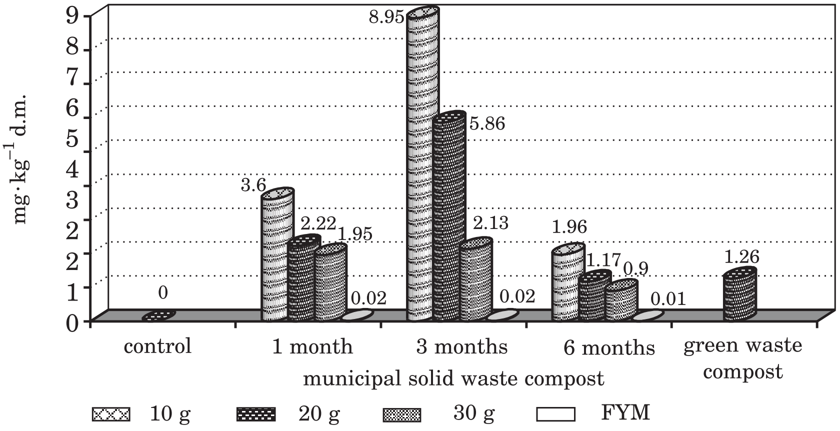


Fig. 4. Content of lead in white mustard (*Sinapis alba*)

Jamroz et al. (2004) emphasize that when applying municipal waste composts in agriculture special attention should be paid to edible plants due to a possible risk of heavy metal pollution. Their studies proved that, regardless fertilization rates, municipal waste composts increased lead concentrations in green lettuce to such a level that the crop became unsuitable for consumption. Other crops, such as cabbage and celery, were observed to contain elevated levels of lead following fertilization with composts, but in that case the differences were not statistically significant. Our own research clearly shows that it is necessary to take into consideration levels of heavy metals contained in municipal waste composts when designing fertilization rates. A simplified balance of lead we prepared

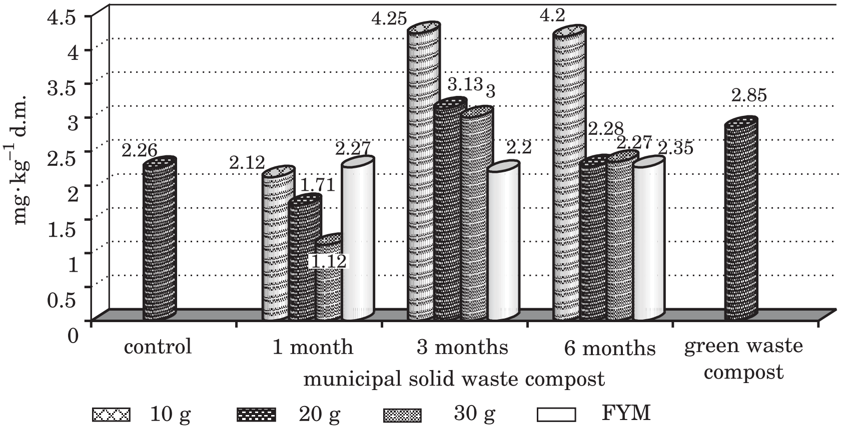


Fig. 5. Content of lead in phacelia (*Phacelia tanacetifolia*)

makes it evident. It shows that increased fertilization rates of composts resulted in increased content of lead in fertilized soil, which persisted for a few years after the fertilization treatments (Figure 2). The highest residual amounts of lead were found in soil fertilized with the oldest compost, which was a consequence of its initial composition (Table 1). The lead balance elaborated for the object treated with municipal green waste compost was similar.

CONCLUSIONS

1. The content of lead in the composts did not exceed permissible concentrations set in the standard norm. The green waste compost contained nearly twice as much lead as the municipal solid waste composts.

2. Fertilization of soils with the composts caused increased levels of lead in the dry matter of crops. The actual accumulation of this element by plants depended on their species, type of compost and fertilization rates.

3. The concentrations of lead were the highest in white mustard, lower in maize, *Phacelia tanacetifolia* or sunflower and the lowest – in barley. Maize grown immediately after fertilization contained the highest levels of lead in the objects treated with 1-month-old compost. In the aftercrops, such results were observed after the application of 3-month-old compost.

4. When the trials had been terminated, the highest concentration of lead in soil was discovered in the soil treated with 6-month-old compost made from municipal solid waste. The soil fertilized with municipal green

waste compost contained on average 14% less lead than the soil which received identical rates of 6-month-old solid waste compost.

REFERENCES

Basta N.T., Tabatabai M.A. 1992. *Effect of cropping systems on adsorption of metals by soils. Effects of pH.* Soil Sci., 153: 195-204.

Brümmer G. W. 1986. *Heavy metals species, mobility and availability in soil.* In: *The importance of chemical „speciation" in environmental processes*. Eds. M. Bernhard, F.E. Brinckman and P.J. Sadler. Dahlen Konferenzen. Springer – Verlag Berlin, Heidelberg, 169-192.

Drozd J., Licznar M., Patorczyk-Pytlik B., Rabikowska B. 1996. *Zmiany w składzie chemicznym kompostów z odpadków miejskich w czasie ich kompostowania.* Zesz. Prob. Post. Nauk Rol., 437: 131-137.

Drozd J., Jamroz E., Licznar M., Licznar S.E., Weber J. 1999. *Wpływ stosowania kompostów z odpadów miejskich na kształtowanie poziomu metali ciężkich w glebie i ich pobieranie przez rośliny.* W: *Kompostowanie i użytkowanie kompostu.* I Konf. Nauk.-Tech., Puławy – Warszawa, ss. 247-256.

Fergusson J. E. 1990. *The heavy elements.* Pergamon Press, Oxford, 461-577 pp.

Filipek-Mazur K., Mazur K. 2003. *Komposty z odpadów zielonych i ich wpływ na właściwości gleby*. Monog. Kom. Inż.i Środ. PAN, 17: 67-75.

Fritz D., Venter F. 1988. *Heavy metals in some vegetable crops as influences by municipal waste compost.* Acta Horticult., 222: 51-62.

Jamroz E., Drozd J., Licznar M., Weber J. 2004. *Wpływ nawożenia gleb kompostami z odpadów komunalnych (KOM) na wysokość i jakość plonu.* W: *Komposty z odpadów komunalnych, produkcja, wykorzystanie i wpływ na środowisko*. Red. J. Drozd, PTSH, ss. 235-254.

Kołota E., Biesiada A., Osińska M. 1998. *Możliwości wykorzystania kompostów ze śmieci miejskich w uprawie warzyw.* Zesz. Nauk. AR w Krakowie, 57: 169-172.

Lekan S., Kacperek K. 1990. *Ocena wartości nawozowej kompostu z odpadków miejskich („Dano") w doświadczeniu wazonowym.* Pam. Puł., 97: 187-200.

Lisk D.J., Gutenmann W. H., Rutzke M., Kuntz H.T., Hu G. 1992. *Survey of toxicants and nutrients in composted waste materials*. Arch. Environ. Contam. Toxicol, 22: 190-194.

Pinamonti F., Stringari G., Gasperi F., Zorzi G. 1997. *Heavy metals levels in apple orchards after the application of two composts.* Commun. Soil Sci. Plant Anal., 28 (15-16): 1403-1419.

Rutkowska B., Ożarowski G., Łabętowicz J., Szulc W. 2003. *Ocena zagrożeń dla środowiska glebowego wynikających z wnoszenia metali ciężkich w kompoście ze śmieci miejskich „Dano".* Zesz. Prob. Post. Nauk Rol., 493: 839-845.

Sądej W., Namiotko A., Bowszys T. 2004. *Przemieszczanie się metali ciężkich do roślin w warunkach użyźniania gleb kompostami z odpadów komunalnych.* W. *Komposty z odpadów komunalnych, produkcja, wykorzystanie i wpływ na środowisko*. Red. J. Drozd. Pol. Tow. Substancji Humusowych, ss. 255-271.

Woźny A. 1995. *Ołów w komórkach roślinnych. Pobieranie – reakcje – odporność.* Uniw. im. A. Mickiewicza w Poznaniu, wyd. Sorus, s. 37.

J. Elementol. 2008, 13(1): 127–137

MICROBIOLOGICAL AND BIOCHEMICAL PROPERTIES OF SOIL DEPENDING ON ADENINE AND AZOTOBACTERIN APPLIED

Jadwiga Wyszkowska, Mirosław Kucharski,
Jan Kucharski

Chair of Microbiology
University of Warmia and Mazury in Olsztyn

Abstract

The aim of the study was to determine how adenine affected biological proprieties of soil. The performance of this precursor cytokinine was tested in a pot trial. The question posed was whether it was possible to improve efficacy of adenine by enlarging populations of bacteria from *Azotobacter* species in soil. The experiment was carried out on proper brown soil, formed from dust clay sand with pH_{KCl} 6,9. Pots were filled with 3.2 kg of soil. The investigations were performed in two series: with and without addition Azotobacterin to soil. Tow rates of nitrogen fertilisation: 0 and 50 mg $N \cdot kg^{-1}$ of soil were applied in test. Adenine was applied in the following quantities: 0; 5; 10 and 15 $mg \cdot kg^{-1}$ of soil. Radish, 6 plants per pot, was the test plant.

It was confirmed that the adenine had a significant effect on growth and development of radish. It positively affected microbiological and the biochemical proprieties of soil. The counts of total oligotrophic bacteria, oligotrophic sporulation bacteria, total copiotrophic bacteria, copiotrophic sporulation bacteria, ammonifying bacteria, immobilizing bacteria, celulolytic bacteria, *Azotobacter* sp., *Artrobacter* sp. and *Pseudomonas* sp. were increased, and the number of fungi diminished. Adenine also stimulated activities of dehydrogenase, urease and alkaline phosphatase, although it depressed the activity of acid phosphatase. The inoculation with bacteria from *Azotobacter* species applied to soil failed to improve efficacy of adenine. Nevertheless, it increased counts of these bacteria, which had a beneficial influence on the development of oligotrophic bacteria, immobilizing bacteria, celulolytic bacteria and actinomyces, while negatively affecting fungi, ammonifying bacteria and *Arthrobacter*.

Key words: adenine, enzymes activity, microorganisms numbers.

---

prof. dr hab. Jan Kucharski, Chair of Microbiology, Univwersity of Warmia and Mazury, ul. pl. Łódzki, 10 -727 Olsztyn, Poland, phone: 089-49-38, e-mail: jan.kucharski@uwm.edu.pl.

MIKROBIOLOGICZNE I BIOCHEMICZNE WŁAŚCIWOŚCI GLEBY KSZTAŁTOWANE PRZEZ ADENINĘ I AZOTOBAKTERYNĘ

Abstrakt

Celem badań było określenie wpływu adeniny na biologiczne właściwości gleby. Działanie tego prekursora cytokinin testowano w doświadczeniu wazonowym. Sprawdzano możliwość wzmocnienia efektywności adeniny przez zwiększenie w glebie puli bakterii z rodzaju *Azotobacter*. Badania wykonano w próbkach gleby brunatnej właściwej, wytworzonej z piasku gliniastego pylastego o pH_{KCl} 6,9. W wazonach umieszczono po 3,2 kg gleby. Badania obejmowały dwie serie: bez i z dodatkiem do gleby szczepionki Azotobakteryny. W doświadczeniu zastosowano zróżnicowane nawożenie azotem: 0 i 50 mg N $\cdot$ kg^{-1} gleby. Adeninę stosowano w następującej ilości: 0; 5; 10 i 15 mg$\cdot$kg^{-1} gleby. Rośliną doświadczalną była rzodkiewka – 6 roślin w wazonie.

Stwierdzono, że adenina istotnie wpływała na wzrost i rozwój rzodkiewki. Korzystnie oddziaływała na mikrobiologiczne i biochemiczne właściwości gleby. Zwiększała liczebność bakterii: oligotroficznych ogółem, oligotroficznych przetrwalnikujących, kopiotroficznych ogółem, kopiotroficznych przetrwalnikujących, amonifikacyjnych, immobilizujących azot, celulolitycznych, *Azotobacter* sp., *Arthrobacter* sp., *Pseudomonas* sp. oraz promieniowców, a zmniejszała liczbę grzybów. Stymulowała także aktywność dehydrogenaz, ureazy i fosfatazy alkalicznej, natomiast hamowała aktywność fosfatazy kwaśnej. Zastosowana szczepionka złożona z bakterii z rodzaju *Azotobacter* nie poprawiała efektywności adeniny. Zwiększała jednak liczbę tych bakterii w glebie, co wpłynęło korzystnie na rozwój bakterii oligotroficznych, immobilizujących azot, celulolitycznych oraz promieniowców, natomiast negatywnie – na grzyby oraz bakterie amonifikacyjne i bakterie z rodzaju *Arthrobacter*.

Słowa kluczowe: adenina, aktywność enzymów, liczebność drobnoustrojów, rzodkiewka.

INTRODUCTION

Phytohormones are synthesised by plants, lichens, mosses and by microorganisms (ERGÜN et al. 2002, KHALID et al. 2004). According to JAMESON (2000), 80% of microorganisms isolated from the rhizosphere are capable of synthesising phytohormones. For this reason, plants can be supplied with growth regulators by introducing their precursors into the soil and by relying on the ability of soil microbes to synthesise phytohormones (JAMESON 2000, KARADENIZ et al. 2006, KUCHARSKI et al. 1999, WYSZKOWSKA, KUCHARSKI 2001). Phytohormone biosynthesis is most intense in the rhizosphere due to higher availability of substrates in this environment as well as the quantitative and qualitative diversity of microorganisms. The rate of biosynthesis is determined by soil fertility and the availability of the appropriate precursors. Their synthesis can be enhanced by providing soil-dwelling microbes with optimal conditions for growth and development (NIETO, FRANKENBERGER 1990, TAYLOR et al. 2006).

Cytokinins are an important group of growth regulators. They are produced by, among others, bacteria of the genera *Arthrobacter, Azospirillum, Azotobacter* and *Rhizobium.* They are also synthesised in large quantities by selected phytopathogens, such as *Corynobacterium fascians,* *Agrobacterium tumefaciens, Pseudomonas savastanoi*), and fungi of the genera *Amanita, Boletus, Dictyostelium, Exobasidium, Glomus, Monilia, Nectria, Plasmodiophora, Rhizopagon, Suillus* and *Taphrina* (JAMESON 2000, KARADENIZ et al. 2006, NIETO, FRANKENBERGER 1990, TAYLOR et al. 2006). Cytokinin biosynthesis can also be enhanced through the application of adenine to soil (JAMESON 2000, KARADENIZ et al. 2006, KUCHARSKI et al. 1999, WIERZBOWSKA 2006, WYSZKOWSKA, KUCHARSKI 2001).

The above findings encouraged us to conduct a study investigating the effect of adenine (cytokinin precursor), interacting with nitrogen-fixing bacteria (*Azotobacter*), on the biological properties of soil.

MATERIALS AND METHODS

The study was carried out in 4 replications in a greenhouse at the University of Warmia and Mazury in Olsztyn. The experiment involved samples of typical brown soil developed from very fine, light loamy sand with pH_{KCl} of 6.9, hydrolytic acidity of 5.7 $mmol(H^+)\cdot kg^{-1}$, total exchangeable bases of 68.5 $mmol(+)\cdot kg^{-1}$ and organic carbon content of 6.6 $g\cdot kg^{-1}$. Prior to pot filling, soil was fertilised with the following macroelements in $mg\cdot kg^{-1}$ of soil (expressed as pure substance): P – 50 [K_2HPO_4]; K – 90 [KH_2PO_4+ KCl]; Mg – 20 [$MgSO_4\cdot 7H_2O$]. Different rates of nitrogen fertiliser were applied at 0 and 50 $mg\cdot kg^{-1}$. Mineral fertilisers were introduced into the soil in a single application before plant sowing, and they were thoroughly mixed with the entire soil material intended for 1 pot (3.2 kg of soil). The study covered two series of experiments: with and without Azotobacterin inoculation. Azotobacterin was applied in the form of a water suspension (one package was dissolved in 1 dm^3 of water and 20 cm^3 of the suspension was added per pot). Prior to the experiment, soil was mixed with mineral fertilisers and, in respective plots, it was combined with adenine which was administered in the following quantities: 0; 5; 10 and 15 $mg\cdot kg^{-1}$ soil.

Soil was placed in pots and kept at a moisture level of 60% of capillary water capacity throughout the entire experiment (42 days). The experimental plant was radish cv. Saxa (6 plants per pot). The plants were harvested on day 42 of the experiment. Soil samples were collected repeatedly at the same time, and they were subjected to microbiological and biochemical analyses.

Microbiological analyses involved the determination of the counts of: oligotrophic bacteria (Olig), spore-forming oligotrophic bacteria ($Olig_p$), copiotrophic bacteria (Cop) and spore-forming copiotrophic bacteria (Cop_p) – on ONT and HATTORI medium (1983); *Azotobacter* spp. (Az) – as described by FENGLEROWA (1965); *Arthrobacter* (Art), *Pseudomonas* (Ps), nitrogen-immobilising bacteria (Im), ammonification bacteria (Am) and cellulose-decomposing bacteria (Cel) – on a medium described by Wyszkowska et al. (2007); actionomyces (Act) – on Kuster and Williams medium with the addition of nystatin and actidione (Parkinson et al. 1971); fungi (Fun) – on Martin medium (1950). Microorganisms were cultured on Petri dishes at a temperature of 28°C for 2 (*Azotobacter*) to 21 (oligotrophic bacteria) days. The counts of spore-forming oligotrophic and copiotrophic bacteria were determined in material pasteurised for 15 minutes at 85°C. The number of colony-forming units (cfu) was estimated with the use of a colony meter.

Biochemical analyses involved the determination of the activity of: dehydrogenases with TTC substrate (Öhlinger 1996), urease – by the method proposed by Alef and Nannpieri (1998), acid phosphatase and alkaline phosphatase – as described by Alef et al. (1998). The activity of dehydrogenases was indicated in cm^3 H_2 required to reduce TTC to TFP, of urease – in mg $N\text{-}NH_4$ produced from hydrolysed urea, of phosphatases – in mmol p-nitrophenol (PNP) produced from sodium 4-nitrophenyl phosphate.

The results were verified statistically by Duncan's multiple range test with the use of a three-factorial analysis of variance (StatSoft, Inc....2005). This study presents only selected results obtained in respect of the investigated factors, but it does not illustrate the interactions observed between those factors because the reported interactions had no significant effect on the quality and reliability of the presented results.

RESULTS AND DISCUSSION

Adenine applied at a dose of 5 to 15 $mg \cdot kg^{-1}$ d.m. of soil significantly increased the abundance of oligotrophic, copiotrophic, ammonification, nitrogen-immobilising bacteria, *Azotobacter*, *Arthrobacter*, cellulose-decomposing bacteria, *Pseudomonas* and actionomyces (Table 1). Adenine had a strong inhibitory effect on fungi. The stimulating effect on the above microorganisms and the inhibitory effect on fungi increased at higher adenine doses. The highest increase was observed in respect of ammonification bacteria, and the lowest – in *Azotobacter* populations. The population size of ammonification bacteria increased 2.5-fold following the application of an adenine dose of 15 $mg \cdot kg^{-1}$ d.m. of soil.

Adenine also had a stimulating effect on the activity of dehydrogenases, urease and alkaline phosphatase in the soil, and it inhibited the activity of acid phosphatase (Table 2). Changes in enzymatic activity were intensified with an increase in adenine doses.

Table 1
Tabela 1

The effect of adenine on numbers of soil microorganisms (cfu kg^{-1} of d.m. soil)
Wpływ adeniny na liczebność drobnoustrojów glebowych (jtk·kg^{-1} s.m. gleby)

Microorganisms Drobnoustroje	Adenine dose (mg kg^{-1} of d.m. soil) Dawka adeniny mg·kg^{-1} s.m. gleby				r	LSD$_{0.01}$ NIR$_{0,01}$
	0	5	10	15		
Olig·10^8	16.13	20.16	20.70	29.66	0.930	3.89
Oligp·10^7	10.57	14.52	16.94	20.88	0.995	1.54
Cop·10^8	47.94	54.12	58.16	66.67	0.990	4.11
Copp·10^7	14.13	16.52	16.70	17.68	0.927	1.11
Am·10^8	48.93	65.77	95.07	124.19	0.993	6.18
Im·10^8	45.07	44.81	50.45	56.27	0.936	5.06
Cel·10^7	47.40	51.26	56.72	60.93	0.998	4.63
Az·10^4	16.16	17.62	18.53	20.11	0.995	1.96
Art·10^7	20.43	23.03	27.06	29.12	0.993	3.47
Ps·10^7	41.40	41.49	47.76	52.33	0.951	4.52
Act·10^8	50.90	65.95	74.55	79.57	0.973	5.56
Fun·10^6	54.75	46.33	41.31	37.37	-0.984	4.78

r – correlation coefficient – współczynnik korelacji; Olig – oligotrophic bacteria – bakterie oligotroficzne, Olig$_p$ – oligotrophic sporulation bacteria – bakterie oligotroficzne przetrwalnikujące, Cop – copiotrophic bacteria (bakterie kopiotroficzne), Cop$_p$ – copiotrophic sporulation bacteria – bakterie kopiotroficzne przetrwalnikujące) Am – ammonifying bacteria – bakterie amonifikacyjne, Im – immobilizing nitrogen bacteria – bakterie immobilizujące azot, Cel – cellulolytic bacteria – bakterie celulolityczne, Az –*Azotobacter* sp., Art – *Artrobacter* sp., Ps – *Pseudomonas* sp., Act – actinomyces – promieniowce, Fun – fungi – grzyby

Adenine had a positive effect on the microbiological and biochemical properties of soil and it stimulated the growth and development of the analysed radish cultivar (Figure 1). Adenine increased the yield of both radish shoots and roots as higher doses of the substance were administered.

Azotobacterin had a much less pronounced effect on the biological properties of soil than adenine. The inoculum did not increase the abundance of all analysed microorganisms (Table 3). Azotobacterin stimulated the growth of oligotrophic bacteria, spore-forming copiotrophic bacteria, nitrogen-immobilising bacteria, cellulose-decomposing bacteria and actionomyces, while it reduced the total counts of copiotrophic bacteria, ammonification bacteria, *Arthrobacter* and fungi. The inoculum had no impact on bacteria of the genus *Pseudomonas*. For obvious reasons, Azotobacterin enriched the soil with *Azotobacter* bacteria whose population increased 89-fold.

Table 2
Tabela 2

The effect of adenine on soil enzymes activity (per kg^{-1} of d.m. soil)
Wpływ adeniny na aktywność enzymów w 1 kg s.m. gleby

Enzymes Enzymy	Adenine dose (mg kg^{-1} of d.m. soil) Dawka adeniny mg·kg^{-1} s.m. gleby				*r*	LSD$_{0.01}$ NIR$_{0,01}$
	0	5	10	15		
Dehydrogenases Dehydrogenazy (cm^3 H$_2$·d^{-1})	2.73	3.21	3.26	3.48	0.938	0.12
Urease Ureaza (mg N-NH$_4$·h^{-1})	6.90	7.20	7.56	8.16	0.986	0.18
Alkaline phosphatase Fosfataza alkaliczna (mmol PNP·h^{-1})	1.15	1.23	1.27	1.31	0.984	0.05
Acid phosphatase Fosfataza kwaśna (mmol PNP·h^{-1})	1.15	1.17	1.08	1.08	-0.793	0.05

r – correlation coefficient – współczynnik korelacji

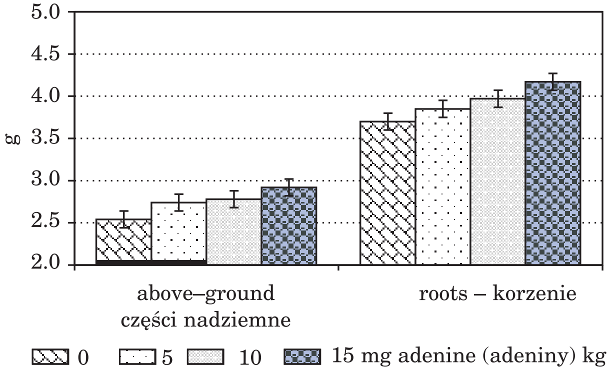


Fig. 1. Effect of adenine on radish yield (in g d.m. per pot)
Rys. 1. Wpływ adeniny na plon rzodkiewki (g s.m.·wazon^{-1})

Azotobacterin had a completely different effect on the activity of soil enzymes than adenine (Table 4). It inhibited dehydrogenase and urease activity. Azotobacterin had a stimulating effect on acid phosphatase, but no interactions with alkaline phosphatase were observed. Azotobacterin did not affect the growth and development of radish (Figure 2).

The third investigated factor – nitrogen fertilisation – also influenced the biological properties of soil. Nitrogen had a varied impact, which was less explicit than that of adenine, but it was more pronounced than the influence of Azotobacterin. Nitrogen fertilisation enriched the soil with

Table 3
Tabela 3

The effect of Azotobacterin on numbers of soil microorganisms (cfu kg^{-1} of d.m. soil)
Wpływ Azotobakteryny na aktywność drobnoustrojów glebowych (jtk · kg^{-1} s.m. gleby)

Microorganisms* Drobnoustroje*	Without Azotobacterin Bez Azotobakteryny	With Azotobacterin Z Azotobakteryną	$LSD_{0.01}$ $NIR_{0,01}$
Olig · 10^8	20.07	23.26	2.76
Oligp · 10^7	14.38	17.07	1.09
Cop · 10^8	61.29	52.15	2.91
Copp · 10^7	15.81	16.70	0.78
Am · 10^8	87.86	79.12	4.37
Im · 10^8	43.64	54.66	3.58
Cel · 10^7	50.05	58.11	3.28
Az · 10^3	4.08	357.98	13.82
Art · 10^7	26.84	22.98	2.45
Ps · 10^7	46.42	45.07	n.s.
Act · 10^8	59.81	75.67	3.93
Fun · 10^6	51.66	38.22	3.38

* Explanations under Table 1 – Objaśnienia podano pod tabelą 1

Table 4
Tabela 4

The effect of Azotobacterin on soil enzymes activity (per kg^{-1} of d.m. soil)
Wpływ Azotobakteryny na aktywność enzymów w 1 kg s.m. gleby

Enzymes Enzymy	Without Azotobacter inoculum Bez Azotobakteryny	With Azotobacter inoculum Z Azotobakteryną	$LSD_{0.01}$ $NIR_{0,01}$
Dehydrogenases Dehydrogenazy (cm^3 H_2 · d^{-1})	3.32	3.02	0.08
Urease Ureaza (mg N-NH_4 · h^{-1})	7.92	6.99	0.13
Alkaline phosphatase Fosfataza alkaliczna (mmol PNP · h^{-1})	1.25	1.23	n.s.
Acid phosphatase Fosfataza kwaśna (mmol PNP · h^{-1})	1.06	1.18	0.04

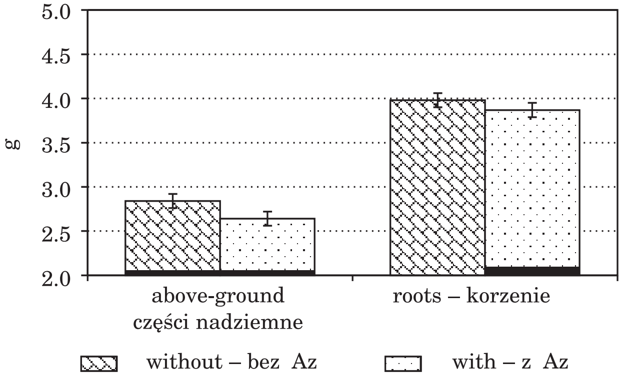


Fig. 2. Effect of Azotobacterin (Az) on radish yield (in g d.m. per pot)
Rys. 2. Wpływ Azotobakteryny (Az) na plon rzodkiewki (g s.m.·wazon^{-1})

spore-forming oligotrophic bacteria, copiotrophic bacteria, ammonification bacteria and *Arthrobacter*, and reduced the counts of nitrogen-immobilising bacteria, *Azotobacter*, *Pseudomonas*, actionomyces and fungi (Table 5). Nitrogen enhanced the activity of urease and phosphatases, but it inhibited dehydrogenase activity (Table 6). It created a favourable environment for radish growth and development (Figure 3). Nitrogen had a particularly beneficial impact on the growth of radish aboveground parts.

Various research studies (ARKIPOVA et al. 2007, KANO, FUKUOKA 1996, MUHAMMAD et al. 2007, NIETO, FRANKENBERGER 1990, WIERZBOWSKA 2006) suggest that phytohormone precursors are capable of increasing plant biomass. Phytohormone precursors are converted by microorganisms into growth-regulators, and they have a beneficial effect on the microbiological properties of soil (KUCHARSKI et al. 1999, TAYLOR et al. 2006, WYSZKOWSKA, KUCHARSKI 2001). These interactions most probably occurred in the discussed experiment. Adenine increased the total counts of soil microbes and stimulated the activity of most enzymes, thus creating favourable conditions for the growth and development of radish and, consequently, increasing radish yield.

Contrary to our expectations, the Azotobacterin inoculum and nitrogen fertilisation did not enhance adenine's positive effect on the microbiological and biochemical properties of soil. Although its stimulating impact on the effectiveness of adenine was not determined, Azotobacterin had a beneficial influence on the majority of the investigated bacteria and actionomyces.

Table 5
Tabela 5

The effect of urea fertility on numbers of soil microorganisms (cfu kg^{-1} of d.m. soil)
Wpływ nawożenia mocznikiem na liczebność drobnoustrojów glebowych (jtk $\cdot$ kg^{-1} s.m. gleby

Microorganisms* Drobnoustroje*	Without urea Bez mocznika	With urea Z mocznikiem	$LSD_{0.01}$ $NIR_{0,01}$
Olig $\cdot 10^8$	21.15	22.18	n.s.
Oligp $\cdot 10^7$	13.71	17.75	1.09
Cop $\cdot 10^8$	53.05	60.40	2.91
Copp $\cdot 10^7$	16.21	16.30	n.s.
Am $\cdot 10^8$	67.83	99.15	4.37
Im $\cdot 10^8$	55.29	43.01	3.58
Cel $\cdot 10^7$	54.31	53.85	n.s.
Az $\cdot 10^3$	209.28	152.78	13.82
Art $\cdot 10^7$	23.07	26.75	2.45
Ps $\cdot 10^7$	49.37	42.12	3.19
Act $\cdot 10^8$	70.92	64.56	3.93
Fun $\cdot 10^6$	51.66	38.22	3.38

* Explanations under Table 1 – Objaśnienia podano pod tabelą 1

Table 6
Tabela 6

The effect of urea fertility on soil enzymes activity (per kg^{-1} of d.m. soil)
Wpływ nawożenia mocznikiem na aktywność enzymów w 1 kg s.m. gleby

Enzymes Enzymy	Without urea Bez mocznika	With urea Z mocznikiem	$LSD_{0.01}$ $NIR_{0,01}$
Dehydrogenases Dehydrogenazy (cm^3 $H_2 \cdot d^{-1}$)	3.24	3.10	0.08
Urease Ureaza (mg $N\text{-}NH_4 \cdot h^{-1}$)	7.08	7.83	0.13
Alkaline phosphatase Fosfataza alkaliczna (mmol PNP $\cdot h^{-1}$)	1.15	1.33	0.04
Acid phosphatase Fosfataza kwaśna (mmol PNP $\cdot h^{-1}$)	1.06	1.18	0.04

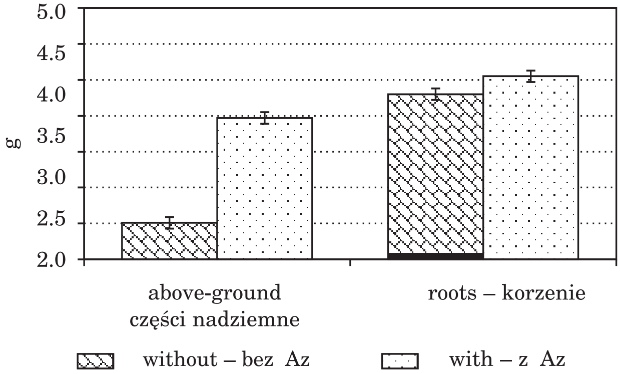


Fig. 3. Effect of urea fertility (N) on radish yield (in g d.m. per pot)

Rys. 3. Wpływ nawożenia mocznikiem (N) na plon rzodkiewki (g s.m.·wazon^{-1})

CONCLUSIONS

1. Adenine had a positive influence on soil bacteria, as it enhanced the activity of dehydrogenases, urease and alkaline phosphatase, and had an inhibitory effect on fungi and acid phosphatase.

2. The investigated inoculum improved the microbiological and biochemical properties of soil and positively affected radish growth and development.

3. Azotobacterin and urea fertilisation did not enhance the beneficial effect of adenine on the biological properties of soil.

REFERENCES

ALEF K., NANNIPIERI P. 1998. *Urease activity*. In: *Methods in applied soil microbiology and biochemistry*. ALEF K., NANNIPIERI P. (eds), Acad. Press. Harcourt Brace & Company, Publishers, London, 316-320 pp.

ALEF K., NANNIPIERI P., TRAZAR-CEPEDA C. 1998. *Phosphatase activity*. In: *Methods in applied soil microbiology and biochemistry*. ALEF K., NANNIPIERI P. (eds), Academic Press. Harcourt Brace & Company, Publishers, London, 335-344 pp.

ARHIPOVA T.N., PRINSEN E., VESELOV S.U., MARTINIENKO E.V., MELENTIEV A.J., KUDOYAROVA G.R. 2007. *Cytokinin producing bacteria enhance plant growth in drying soil*. Plant Soil, 292: 305-315.

ERGÜN N., TOPCUODLUS., F., YILDIZ A. 2002. *Auxin (indole-3-acetic acid), gibberellic acid (GA$_3$), abscisic acid (ABBA) and cytokinin (zeatin) production by some species of mosses and lichens.* J. Bot., 26: 13-18.

FENGLEROWA W. 1965. *Simple method for counting Azotobacter in soil samples.* Acta Microb. Polon., 14(2): 203-206.

JAMESON P. 2000. *Cytokinins and auxins in plant-pathogen interactions – an overview.* Plant Growth Regulat., 32: 369-380.

KANO Y., FUKUOKA N. 1996. *Role of endogenous cytokinin in the development on hollowing in the root of Japanese radish (Raphanus sativus L.).* Scientia Hort., 65: 105-115.

KARADENIZ A., TOPCUOGLU S.F., INAN S. 2006. *Auxin, gibberellin, cytokinin and abscisic acid production in some bacteria.* Word J. Microb. Biotech., 22: 1061-1064.

KHALID A., ARSHAD M., ZAHIR Z.A. 2004. *Screening plant growth-promoting rhizobacteria for improving growth and yield of wheat.* J. Appl. Microbiol., 96: 473-480.

KUCHARSKI J., WYSZKOWSKA J., NOWAK G. 1999. *Response of field bean plants and soil microorganisms to cytokinine precursors and N-benzyladenine.* Pol. J. Soil Sci., 32(2): 89-95.

MARTIN J. 1950. *Use of acid rose bengal and streptomycin in the plate method for estimating soil fungi.* Soil Sci., 69: 215–233.

MUHAMMAD A., RASHID H., HUSSAIN I., SAQLAN NAQVI S.M. 2007. *Proliferation-rate of BAP and kinetin on Bababa (Musa spp. AAA Group).* Hort Sci., 27(5): 1253-1255.

NIETO K.F., FRANKENBERGER W.T. 1990. *Microbial production of cytokinins.* Soil Biochem., 6: 191-246.

ÖHLINGER R. 1996. *Dehydrogenase Activity with the Substrate TTC* In: Methods in Soil Biology. SCHINNER F., ÖHLINGER R., KANDELER E., MARGESIN R. (eds), Springer Verlag Berlin Heidelberg, 241-243.

ONTA H., HATTORI T. 1983. *Oligotrophic bacteria on organic debris and plant roots in paddy field.* Siol Biol. Biochem., 1: 1-8.

PARKINSON D., GRAYF.R.G., WILLIAMS S.T. 1971. *Methods for studying the ecology of soil microorganisms.* Blackweel Scientific Publications Oxford and Einburg, IBP Handbook, 19: 116.

StatSoft, Inc. 2005. STATISTICA (data analysis software system), version 7.1. www.statsoft.com.

TAYLOR J. L., ZAHARARIA L.I., CHEN H., ANDERSON E., ABRAMS S.R. 2006. *Biotransformation of adenine and cytokinins by the rhizobacterium Serratia proteamaculans.* Pytochemistry, 67: 1887-1894.

WIERZBOWSKA J. 2006. *Wpływ regulatorów wzrostu stosowanych w powłokach nasiennych bobiku na wzrost i strukturę plonu oraz gospodarkę azotem.* UWM Olsztyn, Rozpr. i Monogr., 117: 5-128.

WYSZKOWSKA J., BOROS E., KUCHARSKI J. 2007. *Effect of interactions beteewn nickel and other heavy metals on the soil microbiological properties.* Plant Soil Environ., 53(12): 544-552.

WYSZKOWSKA J., KUCHARSKI J. 2001. *Role of Azotobacter sp. and adenine in yield formation of letucce and bacteria abundance in soil.* Scientific works of the Lithuanian Institute of Horticulare and Lithuanina University of Agriculture, 20(3): 279-285.

J. Elementol. 2008, 13(1): 139–151

ENZYMATIC ACTIVITY OF NICKEL-CONTAMINATED SOIL

Jadwiga Wyszkowska, Edyta Boros, Jan Kucharski

Chair of Microbiology
University of Warmia and Mazury in Olsztyn

Abstract

A pot experiment was performed to determine the effect of soil contamination with nickel, applied at a dose of 100, 200, 300 and 400 mg kg^{-1}, on the activity of dehydrogenases, urease, acid phosphatase and alkaline phosphatase. The impact of nickel on the enzymatic activity of soil was studied on samples of heavy loamy sand and light silty loam. The experiment was conducted in two series: in the first one soil was cropped to yellow lupine, and in the second one it was left uncropped. Soil samples were analyzed on day 14, 28, 42 and 56.

It was found that soil contamination with nickel reduced the activity of all the enzymes. This negative influence was most noticeable in the case of dehydrogenase. The activity of urease and alkaline phosphatase was higher in light silty loam, while the activity of dehydrogenases and acid phosphatase was higher in heavy loamy sand. The activity of dehydrogenases and urease was higher in soil cropped to yellow lupine, whereas the activity of acid phosphatase and alkaline phosphatase was higher in uncropped soil. Yellow lupine was sensitive to excessive amounts of nickel in the soil, and partly alleviated the adverse impact of this heavy metal on urease activity, but did not reduce its inhibitory effect on the other enzymes.

Key words: nickel, enzymatic activity, soil, yellow lupine.

AKTYWNOŚĆ ENZYMATYCZNA GLEBY ZANIECZYSZCZONEJ NIKLEM

Abstrakt

W doświadczeniu wazonowym określono wpływ zanieczyszczenia gleby niklem w dawkach 100, 200, 300 i 400 mg kg^{-1} na aktywność dehydrogenaz, ureazy, fosfatazy kwaśnej oraz fosfatazy alkalicznej. Wpływ niklu na aktywność enzymatyczną badano w dwóch gatunkach gleb: piasku gliniastym mocnym oraz glinie lekkiej pylastej. Badania przeprowadzono w dwóch se-

---

prof. dr hab. Jan Kucharski, Department of Microbiology, Univwersity of Warmia and Mazury in Olsztyn, ul. pl. Łódzki, 10 -727 Olsztyn, Poland, phone: 089-49-38, e-mail: jan.kucharski@uwm.edu.pl

riach, tj. na glebie obsianej łubinem żółtym i nie obsianej. Próbki glebowe analizowano: w 14., 28., 42. i 56. dniu.

Stwierdzono, że zanieczyszczenie gleby niklem spowodowało zmniejszenie aktywności wszystkich badanych enzymów. Najbardziej niekorzystnie nikiel wpływał na aktywność dehydrogenaz. Wyższą aktywność ureazy i fosfatazy alkalicznej stwierdzono w glinie lekkiej pylastej niż w piasku gliniastym mocnym, natomiast dehydrogenaz i fosfatazy kwaśnej – w piasku gliniastym mocnym. Wyższą aktywność dehydrogenaz i ureazy odnotowano w glebie obsianej łubinem żółtym, natomiast fosfatazy kwaśnej i fosfatazy alkalicznej – w glebie nie obsianej. Łubin żółty okazał się wrażliwy na nadmiar niklu w glebie. Jego uprawa częściowo łagodziła niekorzystny wpływ niklu na ureazę, lecz nie zmniejszała hamującego oddziaływania tego pierwiastka na pozostałe enzymy.

Słowa kluczowe: nikiel, aktywność enzymatyczna, gleba, łubin żółty.

INTRODUCTION

Enzymatic activity, similarly to total microbial count, is an important indicator of soil quality since it provides information about the specific metabolic activity and functions of soil microbial communities (Kizilkaya et al. 2004, Bielińska, Tomaszewicz 2006). In general, enzymes may be divided into biotic and abiotic ones. The first group includes enzymes synthesized by plants during metabolic processes and soil organisms, while the other comprises enzymes forming complexes with minerals or organic colloids as well as those found in dead plant cells or microbial cells (Guibaud et al. 2005). The enzymes produced as a result of microbial metabolism may differ with respect to some specific properties, e.g. preferences for a given type of substrate, pH, susceptibility to inhibitors and resistance to proteolysis (Criquet et al. 2002).

Studies on soil microbial activity involve enzymes which are known to respond to stress factors. Their activity is dependent on total microbial count (Nowak et al. 2000, Antil et al. 2001). Enzymatic activity may be stimulated if the concentration of heavy metals in the soil is low, and irreversibly inhibited if their content in the soil increases several times (Klose, Tabatabai 1999). This depends, to the greatest extent, on the physicochemical properties of the soil, in particular on its pH (VepsÄlÄinen 2001).

The nickel content of soil has increased in recent years (Barałkiewicz, Siepak 1999). The origin of nickel is allochthonous and its presence is correlated with the degree of industrialization and motorization as well as with the use of means of agricultural production containing nickel, such as some mineral fertilizers, wastewater and crop protection chemicals (Oliveira, Pampulha 2006). According to Terelak et al. (2000), 95% of all soils used for agricultural purposes in Poland have a natural nickel content (0°) and in 4.23% of soils the concentration of this heavy metal is increased (I°). In 0.34% of soils nickel contamination is slight (II°), in

0.06% – medium (III°) and in 0.01% – severe (IV°). No arable land in Poland is characterized by very severe (V°) nickel contamination.

The aim of the present study was to determine the effect of soil contamination with nickel on the activity of such enzymes as dehydrogenases, urease, acid phosphatase and alkaline phosphatase.

MATERIAL AND METHODS

The experiment was conducted in a greenhouse. Plastic pots were filled with 3 kg of typical brown soil developed from heavy loamy sand and 3 kg of typical brown soil developed from light silty loam. The soil material was taken from the organic layer. The detailed characteristics of soils are given in Table 1.

Table 1
Tabela 1

Some physicochemical properties of soils used in the experiment
Niektóre właściwości fizykochemiczne gleb użytych w doświadczeniu

Soil species Gatunek gleby	Granulometric composition Skład granulometryczny (mm)			pH_{KCl}	Hh	S	Corg (g kg^{-1})
	1 – 0.1	0.1 – 0.02	< 0.02		(mmol(+) kg^{-1} soil – gleby)		
hls – pgm	66	17	17	6.90	11.25	89.30	7.50
lsl – glp	42	32	26	7.00	8.77	159.00	11.15

hls – heavy loamy sand – pgm – piasek gliniasty mocny; lsl – light silty loam – glp – glina lekka pylasta; Hh – hydrolytic acidity – kwasowość hydrolityczna; S – sum of exchangeable basic cations – suma wymiennych kationów zasadowych; Corg – organic carbon content – zawartość węgla organicznego

Variable experimental factors were as follows:

1) dose of nickel in the form of $NiSO_4 \cdot 7H_2O$ (mg Ni^{2+} kg^{-1} soil): 0, 100, 200, 300 and 400;
2) soil species: heavy loamy sand, light silty loam;
3) method of soil management: soil cropped to yellow lupine and uncropped soil;
4) time of biochemical analysis (days): 14, 28, 42, 56.

The tested crop, yellow lupine cv. Markiz (5 plants per pot), was collected at the flowering stage and dry matter yield was determined. All treatments were regularly fertilized with macro- and micronutrients, as follows (pure component per mg kg^{-1} soil): P – 66 [KH_2PO_4], K – 125 [KH_2PO_4 + KCl], Mg – 20 [$MgSO_4 \cdot 7H_2O$], Cu – 5 [$CuSO_4 \cdot 5H_2O$], Zn – 5

[$ZnCl_2$], Mn – 5 [$MnCl_2 \cdot 4H_2O$], Mo – 5 [$Na_2MoO_4 \cdot 2H_2O$], B – 0,33 [H_3BO_4]. Over the entire experimental period soil moisture content was 60% of the capillary water capacity of the soil. The experiment was carried out in six replications for soil cropped with yellow lupine, and in three replications for uncropped soil.

On day 14, 28, 42 and 56 (factor 4) soil samples were assayed for the activity of dehydrogenases (Deh) – by the Lenhard method modified by ÖHLINGER (1996), urease (Ure) – by the method developed by ALEF and NANNIPIERI (1998), acid phosphatase (Pac) and alkaline phosphatase (Pal) – as described by ALEF et al. (1998).

The results were processed statistically by Duncan's multiple range test and a four-factorial analysis of variance. Statistical analysis was performed with the use of Statistica (Statsoft, INC. 2003).

RESULTS AND DISCUSSION

The activity of dehydrogenases (Table 2) depended on the nickel dose, soil species, method of soil management and time of analysis. It was found to be substantially higher in heavy loamy sand than in light silty loam. Until day 28 of the experiment it remained at a higher level in bare soil than in soil cropped with yellow lupine. This trend was no longer observed on day 42, and on day 56 – during yellow lupine harvest – higher activity of dehydrogenases was recorded in samples of cropped soil. Soil contamination with nickel significantly reduced the activity of dehydrogenases, which was negatively correlated with the degree of nickel contamination in both types of soil. The activity of urease (Table 3), similarly to the activity of dehydrogenases, was negatively correlated with the degree of soil contamination with nickel. Regardless of the date of analysis, the activity of this enzyme was higher in soil cropped with yellow lupine compared to bare soil, and in light silty loam compared to heavy loamy sand. Yellow lupine partly alleviated the adverse impact of nickel on urease activity, but there was no such relationship in the case of dehydrogenases, acid phosphatase (Table 4) or alkaline phosphatase (Table 5). Both acid and alkaline phosphatase were most active in soils not contaminated with nickel, and the least active – in soils containing the largest amounts of this element (400 mg kg^{-1}). The coefficients of correlation between the degree of soil contamination with nickel and enzymatic activity were -0.84 to -0.99 for acid phosphatase, and -0.89 to -0.99 for alkaline phosphatase. The activity of acid phosphatase was higher in heavy loamy sand, and the activity of alkaline phosphatase was higher in light silty loam.

Soil contamination with nickel had an adverse effect not only on enzymatic activity, but also on the yield of yellow lupine (Table 6). The val-

Table 2
Tabela 2

Effect of soil contamination with nickel on the activity of dehydrogenases in 1 kg d.m. of soil (cm^3 H_2 kg^{-1} d.m. d^{-1})
Wpływ zanieczyszczenia gleby niklem na aktywność dehydrogenaz w 1 kg s.m. gleby (cm^3 H_2 kg^{-1}s.m. d^{-1})

Ni dose (mg kg^{-1} of soil) Dawka Ni (mg kg^{-1} gleby)	Time of analysis (days) Termin analizy (dni)								$\bar{x}$	
	14		28		42		56			
	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl
Heavy loamy sand – Piasek gliniasty mocny										
0	5.35	4.65	5.92	3.65	5.52	5.91	3.04	4.31	4.96	4.63
100	4.43	3.52	5.21	3.30	4.31	4.70	2.68	4.28	4.16	3.95
200	4.16	3.29	4.74	2.99	3.63	3.40	1.86	3.31	3.60	3.25
300	3.71	2.92	4.76	2.48	3.20	3.12	1.64	2.64	3.33	2.79
400	3.03	2.43	3.90	2.11	2.69	2.73	1.38	1.58	2.75	2.21
r	-0.98	-0.96	-0.96	-0.99	-0.98	-0.96	-0.97	-0.97	-0.99	-0.99
$\bar{x}$	4.14	3.36	4.91	2.91	3.87	3.97	2.12	3.22	3.76	3.37
Light silty loam – Glina lekka pylasta										
0	4.25	4.09	5.66	3.86	4.95	4.71	2.04	4.52	4.23	4.30
100	4.00	3.40	4.68	2.88	4.14	4.00	1.87	3.64	3.67	3.48
200	3.64	2.88	4.05	2.42	3.58	3.49	1.60	3.11	3.22	2.98
300	3.13	2.59	3.84	2.01	3.21	3.13	1.47	2.38	2.91	2.53
400	3.04	2.24	3.47	1.80	2.36	2.53	1.33	1.94	2.55	2.13
r	-0.98	-0.98	-0.96	-0.96	-0.99	-0.99	-0.99	-0.99	-0.99	-0.99
$\bar{x}$	3.61	3.04	4.34	2.59	3.65	3.57	1.66	3.12	3.32	3.08
$LSD_{0.05}$ $NIR_{0.05}$	a – 0.07; b – 0.05; c – 0.05; d – 0.07; a x b – 0.11; a x c – 0.11; a x d – 0.15; b x c – 0.07; b x d – 0.09; c x d – 0.09; a x b x c – n.s.; a x b x d – 0.21; a x c x d – 0.21; b x c x d – 0.13; a x b x c x d – 0.30									

Yl – uncropped soil – gleba nieobsiana, +Yl – soil cropped to yellow lupine – gleba obsiana łubinem żółtym; LSD for - NIR dla: a - soil species – gatunek gleby, b – nickel dose – dawki niklu, c – time of analysis – terminu analizy, d - method of soil management - obsiania gleby; n.s – non-significant – nieistotne statystycznie; *n* = 15

Table 3
Tabela 3

Effect of soil contamination with nickel on the activity of urease in 1 kg d.m. of soil (mg N-NH_4 kg^{-1} d.m.)
Wpływ zanieczyszczenia niklem na aktywność ureazy w 1 kg s.m. gleby (mg N-NH_4 kg^{-1} s.m.)

Ni dose (mg kg^{-1} of soil) Dawka Ni (mg kg^{-1} gleby)	Time of analysis (days) – Termin analizy (dni)								$\overline{x}$	
	14		28		42		56			
	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl
Heavy loamy sand – Piasek gliniasty mocny										
0	23.65	23.90	14.48	16.88	14.51	27.00	18.15	15.56	17.70	20.84
100	20.33	26.44	10.14	15.52	11.10	25.71	9.53	12.14	12.78	19.95
200	16.04	15.51	9.28	14.19	8.09	14.62	7.55	10.11	10.24	13.61
300	12.06	11.94	8.41	10.23	7.27	13.24	6.65	7.13	8.60	10.64
400	11.69	10.85	7.59	9.79	6.84	10.32	5.15	7.10	7.82	9.52
r	-0.98	-0.91	-0.91	-0.97	-0.94	-0.95	-0.89	-0.97	-0.95	-0.97
$\overline{x}$	16.75	17.73	9.98	13.32	9.56	18.18	9.41	10.41	11.43	14.91
Light silty loam – Glina lekka pylasta										
0	27.96	85.49	22.82	65.43	31.27	79.54	53.79	71.14	33.96	75.40
100	24.69	73.82	19.40	64.97	25.37	58.20	52.83	67.88	30.57	66.22
200	23.42	71.57	14.66	57.96	21.36	55.95	49.79	57.80	27.31	60.82
300	22.32	64.74	12.92	54.16	20.62	51.82	27.78	54.75	20.91	56.37
400	21.44	55.80	10.55	48.37	16.63	46.99	18.40	35.44	16.76	46.65
r	-0.96	-0.98	-0.99	-0.98	-0.97	-0.90	-0.93	-0.95	-0.99	-0.99
$\overline{x}$	23.97	70.28	16.07	58.18	23.05	58.50	40.52	57.40	25.90	61.09
$LSD_{0.05}$ $NIR_{0,05}$	a – 0.67; b – 0.43; cm – 0.43; d – 0.60; a x b – 0.95; a x c – 0.95; a x d – 1.35; b x c – 0.60; b x d – 0.85; c x d – 0.85; a x b x c – 1.35; a x b x d – 1.91; a x c x d – 1.91; b x c x d – 1.21; a x b x c x d – 2.70									

* explanations under Table 2 * objaśnienia podano pod tabelą 2

ues of all components of yield structure (mass of aerial parts, roots and nodules and the number of nodules per root) were lower in nickel-contaminated soils than in soils with a natural nickel content. The dry matter yield of yellow lupine grown on heavy loamy sand and light silty loam decreased 3.8-fold and 2-fold, respectively, following the application of the highest dose of nickel. Excessive quantities of nickel in the soil negatively affected the root growth and contributed to almost complete disappearance of root nodules. This trend was particularly noticeable when nickel was introduced into the lighter soil at a dose of 200 mg Ni^{2+} kg^{-1} and into the heavier soil at a dose of 300 mg Ni^{2+} kg^{-1}. The current results indicate that the activity of dehydrogenases, urease, acid phosphatase and alkaline phosphatase was significantly positively correlated with yellow lupine yield (Figure 1).

Literature data (WELP 1999, KUCHARSKI, WYSZKOWSKA 2000, GIRIDHARA, SIDDARAMAPPA 2002) show that the harmful effect of heavy metals, including nickel, on the biological properties of soil is dependent on their concentration in the environment. When present in low amounts, those elements may stimulate enzymatic activity of soil. However, if their threshold limit values are exceeded, they become typical inhibitors of the activity of enzymes and soil microorganisms.

In the present study all the doses of nickel, even the lowest one (100 mg Ni^{2+} kg^{-1}), reduced the enzymatic activity of both types of soil, but this activity was inhibited to a greater extent in heavy loamy sand (considered poorer) than in light silty loam. This is related primarily to a higher content of colloids in more compact soils, confirmed by their higher adsorbing capacity which plays an important role in permanent binding of metals (including nickel), thus reducing their impact on enzymes. This hypothesis is supported by the results of previous investigations (WELP 1999, KUCHARSKI, WYSZKOWSKA 2000, WYSZKOWSKA et al. 2005), which demonstrated that the abundance of mineral and organic colloids in the soil could partly neutralize the negative influence of heavy metals on enzymes. A strong correlation between urease activity and the organic matter content of soil was also reported by STĘPNIEWSKA and SAMBORSKA (1999). This could also explain the role of yellow lupine in alleviating the adverse effects of nickel on urease activity, observed in the present experiment. The organic compounds secreted by roots into the soil positively affect microbial communities, thus increasing the pool of enzymes. In addition, those substances may form complexes with heavy metals, including nickel (KANDELER et. al. 1999). However, this hypothesis was not confirmed in the case of dehydrogenases, acid phosphatase and alkaline phosphatase, whose activity was not significantly affected by yellow lupine grown in nickel-contaminated soil.

Environmental pollution with heavy metals has a harmful impact not only on the biological activity of soil, but also on the quality and yield of

Table 4
Tabela 4

Effect of soil contamination with nickel on the activity of acid phosphatase in 1 kg d.m. of soil (mmol PNP h^{-1})
Wpływ zanieczyszczenia gleby niklem na aktywność fosfatazy kwaśnej w 1 kg s.m. gleby (mmol PNP h^{-1})

Ni dose (mg kg^{-1} of soil) Dawka Ni (mg kg^{-1} gleby)	Time of analysis (days) – Termin analizy (dni)								$\overline{x}$	
	14		28		42		56			
	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl
Heavy loamy sand – Piasek gliniasty mocny										
0	1.96	2.20	2.20	1.71	3.07	1.99	2.48	2.15	2.43	2.01
100	1.84	1.66	2.11	1.68	2.55	1.88	2.34	1.98	2.21	1.80
200	1.65	1.61	1.79	1.53	2.44	1.66	2.06	1.78	1.99	1.65
300	1.59	1.48	1.70	1.49	2.41	1.55	1.78	1.66	1.87	1.55
400	1.50	1.31	1.68	1.33	2.26	1.37	1.83	1.56	1.82	1.39
r	-0.98	-0.93	-0.95	-0.98	-0.90	-0.99	-0.96	-0.99	-0.97	-0.99
$\overline{x}$	1.71	1.65	1.90	1.55	2.55	1.69	2.10	1.83	2.06	1.68
Light silty loam – Glina lekka pylasta										
0	1.95	2.05	1.79	1.83	2.55	1.86	2.15	2.05	2.11	1.95
100	1.78	2.01	1.67	1.79	2.38	1.76	2.10	1.97	1.98	1.88
200	1.73	1.88	1.72	1.61	2.28	1.67	1.98	1.70	1.93	1.72
300	1.66	1.79	1.67	1.60	2.12	1.52	1.84	1.60	1.82	1.63
400	1.51	1.71	1.62	1.32	1.95	1.34	1.73	1.49	1.70	1.47
r	-0.98	-0.99	-0.84	-0.95	-0.99	-0.99	-0.99	-0.98	-0.99	-0.99
$\overline{x}$	1.73	1.89	1.69	1.63	2.26	1.63	1.96	1.76	1.91	1.73
$LSD_{0.05}$ $NIR_{0,05}$	a – 0.04; b – 0.02; c – 0.02; d – 0.03; a x b – 0.05; a x c – n.s.; a x d – 0.07; b x c – 0.03; b x d – 0.05; c x d – 0.05; a x b x c – n.s.; a x b x d – n.s.; a x c x d – 0.10; b x c x d – 0.07; a x b x c x d – 0.15									

* explanations under Table 2 * objaśnienia podano pod tabelą 2

Table 5
Tabela 5

Effect of soil contamination with nickel on the activity of alkaline phosphatase in 1 kg d.m. of soil (mmol PNP h^{-1})
Wpływ zanieczyszczenia gleby niklem na aktywność fosfatazy alkalicznej w 1 kg s.m. gleby (mmol PNP h^{-1})

Ni dose (mg kg^{-1} of soil) Dawka Ni (mg kg^{-1} gleby)	Time of analysis (days) – Termin analizy (dni)								$\overline{x}$	
	14		28		42		56			
	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl	-Yl	+Yl
Heavy loamy sand – Piasek gliniasty mocny										
0	2.06	1.68	2.25	1.75	2.07	1.64	2.08	2.49	2.12	1.89
100	1.96	1.29	2.04	1.38	1.63	1.44	1.57	2.44	1.80	1.64
200	1.77	1.22	1.86	1.18	1.45	1.18	1.41	1.92	1.62	1.38
300	1.67	1.15	1.82	1.16	1.40	1.08	1.27	1.67	1.54	1.27
400	1.59	1.09	1.74	1.02	1.37	1.05	1.28	1.55	1.50	1.18
r	-0.99	-0.90	-0.96	-0.94	-0.89	-0.96	-0.90	-0.97	-0.94	-0.97
$\overline{x}$	1.81	1.29	1.94	1.30	1.58	1.28	1.52	2.01	1.71	1.47
Light silty loam – Glina lekka pylasta										
0	10.65	3.07	4.54	3.37	3.96	2.82	4.57	4.55	5.93	3.45
100	10.40	2.62	3.97	2.55	3.20	2.78	4.38	4.49	5.49	3.11
200	10.31	2.43	3.78	2.36	3.15	2.45	4.14	3.64	5.35	2.72
300	10.16	2.31	3.50	2.25	2.93	2.50	3.55	3.37	5.04	2.61
400	10.15	2.27	3.43	2.02	2.56	1.98	3.39	3.02	4.88	2.32
r	-0.95	-0.93	-0.95	-0.92	-0.95	-0.92	-0.98	-0.97	-0.98	-0.99
$\overline{x}$	10.33	2.54	3.84	2.51	3.16	2.51	4.01	3.81	5.34	2.84
$LSD_{0.05}$ $NIR_{0.05}$	a – 0.05; b – 0.03; c – 0.03; d – 0.05; a x b – 0.07; a x c – 0.07; a x d – 0.10; b x c – 0.05; b x d – 0.07; c x d – 0.07; a x b x c – n.s.; a x b x d – 0.14; a x c x d – 0.14; b x c x d – 0.09; a x b x c x d – 0.20									

* explanations under Table 2 * objaśnienia podano pod tabelą 2

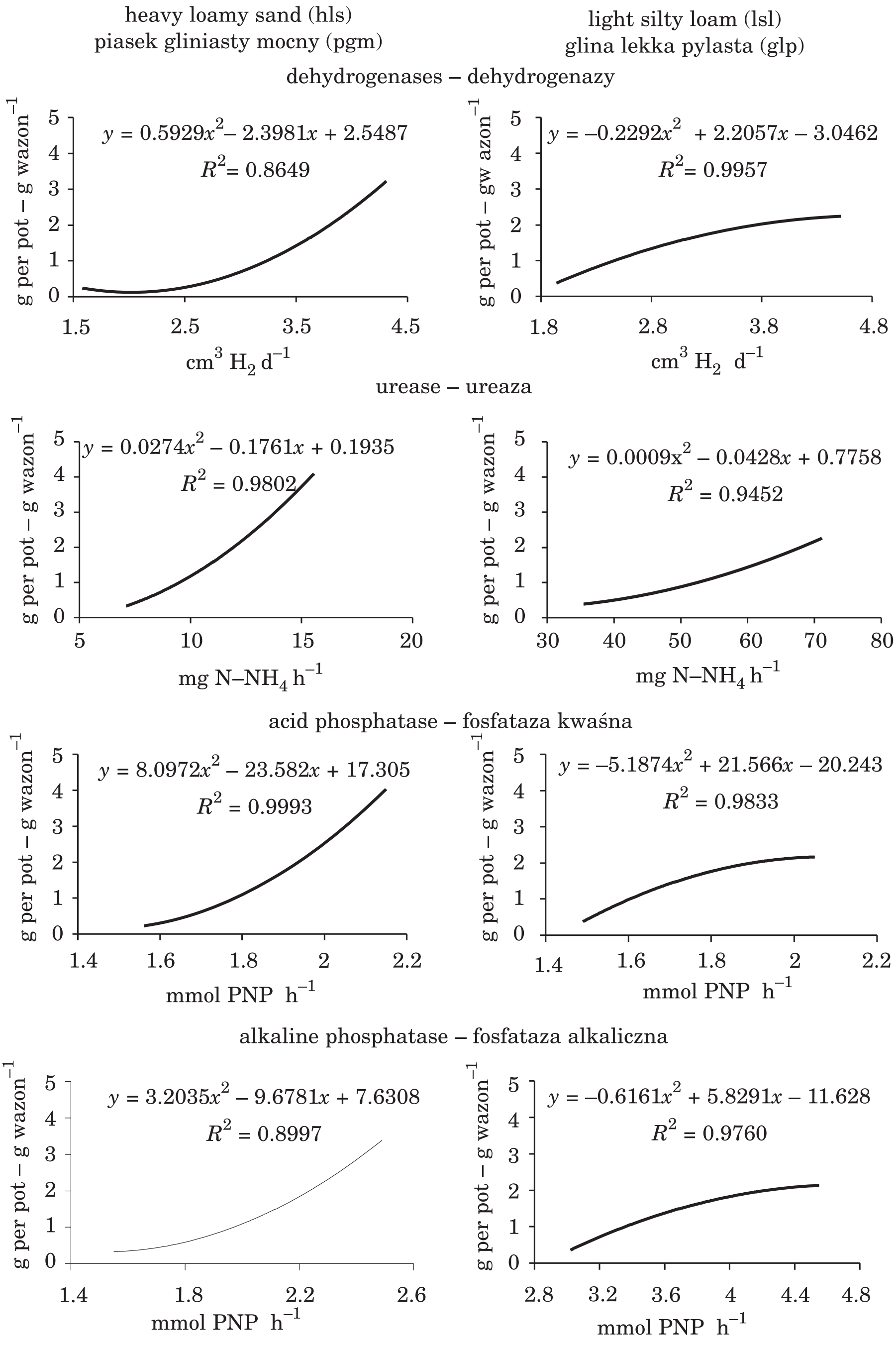


Fig. 1. Correlation between yellow lupine yield and enzymatic activity in 1 kg d.m. of soil
Rys. 1. Zależność między plonem łubinu żółtego a aktywnością enzymów w 1 kg s.m. gleby

crops, and – in consequence – on the health of humans and animals (Oleszek et al. 2003). According to Pandey and Sharma (2002), excessive quantities of nickel in the soil inhibit the growth and development of plants because this metal exerts a deleterious effect on the metabolic processes taking place in the plant. The negative influence of nickel on plants was also observed by other authors (Koszelnik-Leszek 2002, Wyszkowski, Wyszkowska 2004, Wyszkowska et al. 2005). Tibazarwa et al. (2001) demonstrated that this metal may adversely affect crops even when present at substantially lower concentrations than those applied in the current experiment with yellow lupine.

Table 6
Tabela 6

Effect of soil contamination with nickel on yellow lupine yield, g d.m. pot^{-1}
Wpływ zanieczyszczenia gleby niklem na plon łubinu żółtego, g s.m. $\cdot$wazon^{-1}

Ni dose (mg kg^{-1} of soil) Dawka Ni (mg kg^{-1} gleby)	Yield (g d.m. pot^{-1}) Plon (g s.m. wazon^{-1})		Root nodule yield (g d.m. root^{-1}) Plon brodawek (g s.m. korzeń$^{-1}$)	Number of nodules per root Liczba brodawek na 1 korzeniu
	above-ground parts naziemny	of roots korzeni		
Heavy loamy sand – Piasek gliniasty mocny				
0	4.04	1.19	0.18	21.33
100	2.35	0.58	0.07	6.00
200	0.95	0.26	0.00	0.00
300	0.54	0.09	0.00	0.00
400	0.19	0.04	0.00	0.00
r	-0.95	0.89	0.98	0.97
Light silty loam – Glina lekka pylasta				
0	2.22	0.56	0.16	16.00
100	2.02	0.46	0.10	10.33
200	1.55	0.48	0.03	7.00
300	0.87	0.28	0.00	0.00
400	0.40	0.05	0.00	0.00
r	-0.99	0.96	0.90	0.87
LSD$_{0.05}$ NIR$_{0.05}$	a -0.23; b -0.15; a x b -0.33	a -0.19; b -n.s.; a x b -0.27	a -0.03; b -n.s.; a x b -n.s.	a -4.42; b -n.s.; a x b -n.s.

LSD for – NIR dla: a - soil species – gatunek gleby, b – nickel dose – dawki niklu;
n.s – non-significant – nieistotne statystycznie; *r* – coefficient of correlation significant at – współczynnik korelacji istotny dla $p = 0.05$;
$n = 15$

CONCLUSIONS

1. Soil contamination with nickel, applied at a dose of 100 to 400 mg Ni^{2+} kg^{-1}, disturbed its biological balance measured by enzymatic activity. The activity of dehydrogenases, urease, acid phosphatase and alkaline phosphatase was reduced along with an increase in the nickel dose.
2. The activity of urease and alkaline phosphatase was higher in light silty loam, while the activity of dehydrogenases and acid phosphatase was higher in heavy loamy sand.
3. The activity of dehydrogenases and urease was higher in soil cropped to yellow lupine, whereas the activity of acid phosphatase and alkaline phosphatase was higher in uncropped soil.
4. The negative effect of nickel on the activity of the tested soil enzymes was observed over the entire experimental period (56 days).
5. Yellow lupine partly alleviated the adverse impact of nickel on urease activity, but did not reduce the inhibitory effect of this heavy metal on the other enzymes.
6. Yellow lupine grown in more compact (light silty loam) and less compact (heavy loamy sand) soil was found to be sensitive to nickel contamination.

REFERENCES

ALEF K., NANNIPIERI P. 1998. *Urease activity.* In: *Methods in applied soil microbiology and biochemistry*. ALEF K., NANNIPIERI P. (eds), Acad. Press. Harcourt Brace & Company, Publishers, London, 316-320 pp.

ALEF K., NANNIPIERI P., TRACAR-CEPEDA C. 1998. *Phosphatase activity.* In: *Methods in applied soil microbiology and biochemistry*. ALEF K., NANNIPIERI P. (eds), Acad. Press. Harcourt Brace & Company, Publishers, London, 335-344 pp.

ANTIL R.S., GUPTA A.P., NARWAL R.P. 2001. *Nitrogen transformation and biomass content in soil contaminated with nickel and cadmium from industrial wastewater irrigation*. Urban Water., 3: 299-302.

BARAŁKIEWICZ D., SIEPAK J. 1999. *Chromium, nickel and kobalt in environmental samples and existing legal norms*. Pol. J. Environ. Stud., 8(4): 201-208.

BIELIŃSKA E.J., TOMASZEWICZ T. 2006. Wpływ czynników antropogenicznych na aktywność enzymatyczną poboczy dróg. Rocz. Glebozn., 57(1/2): 50-58.

CRIQUET S., TAGGER G., VOGT G., PETIT J. LE. 2002. *Endoglucanase and b-glycosidase activities in an evergreen oak litter: annual variation and regulating factors*. Soil Biol. Biochem., 34: 1111-1120.

GIRIDHARA M., SIDDARAMAPPA R. 2002. *Effect of heavy metals on urease activity in soil.* Cur. Res. Uni. Argi. Sc. Ban., 31(1-2): 4-5.

GUIBAUD G., COMTE S., BORDAS F., DUPUY S., BAUDU M. 2005. *Comparison of the complexation potential of extracellular polymeric substances (EPS), extracted from activated sludges and produced by pure bacteria strains, for cadmium, lead and nickel*. Chemosphere, 59: 629-638.

KANDELER E., LUXHŘI J., TSCHERKO D., MAGID J. 1999. *Xylanase, invertase and protease at the soil-litter interface of a loamy sand.* Soil. Biol. Biochem., 31: 1171-1179.

Kizilkaya R., Askin T., Bayrakli B., Sadlam M. 2004. *Microbiological characteristics of soils contaminated with heavy metals*. Eur. J. Soil Biol., 40: 95 – 102.

Klose S., Tabatabai M.A. 1999. *Urease activity of microbial biomass in soils*. Soil. Biol. Biochem., 31: 205-211.

Koszelnik-Leszek A. 2002. *Dynamika pobierania niklu przez dwie odmiany jęczmienia jarego.* Rocz. Glebozn., 53(1/2): 41-49.

Kucharski J., Wyszkowska J. 2000. *Microbiological properties of soil contaminated with chromium*. Natur. Sc., 7: 7-16.

Nowak J., Tyrakowska–Bielec U., Szymczak J. 2000. *Wpływ chlorku rtęci i niklu na zmiany aktywności fosfataz w czarnych ziemiach.* Rocz. Glebozn., 51(1/2): 5-6.

Oleszek W., Terelak H., Maliszewska-Kordybach B., Kukuła S. 2003. *Soil, food and agroproduct contamination monitoring in Poland*. Pol. J. Environ. Stud., 12(3): 261-268.

Oliveira A., Pampulha M.E. 2006. *Effects of long-term heavy metal contamination on soil microbial characteristics.* J. Biosci. Bioeng., 102(3): 157-161.

Öhlinger R. 1996. *Dehydrogenase activity with the substrate TTC* In: *Methods in soil biology*. Schinner F., Öhlinger R., Kandeler E., Margesin R. (eds), Springer Verlag Berlin Heidelberg, 241-243 pp.

Pandey N., Sharma C.P. 2002. *Effect of heavy metals* Co^{2+}, Ni^{2+} *and* Cd^{2+} *on growth and metabolism of cabbage.* Plant Sc., 163: 753-758.

STATSOFT, INC. 2003. STATISTICA *(data analysis software system), version 6.0.* www.statsoft.com.

Stępniewska Z., Samborska A. 1999. *Aktywność ureazy w wybranych glebach Polski*. Acta Agrophys., 22: 219-228.

Terelak H., Motowicka-Terelak T, Stuczyński T, Pietruch Cz. 2000. *Pierwiastki śladowe (Cd, Cu, Ni, Pb, Zn) w glebach użytków rolnych Polski.* IOŚ, ss. 27-31.

Tibazarwa C., Corbisier P., Mench M., Bossus A., Solda P., Mergeay M., Wyns L., van der Lelie D. 2001. *A microbial biosensor to predict bioavailable nickel in soil and its transfer to plants*. Environ. Pollut., 113: 19-26.

VepsÄlÄinen M. 2001. *Poor enzyme recovery by extraction from soils*. Soil Biol. Biochem., 33: 1131-1135.

Welp G. 1999. *Inhibitory effects of the total and water-soluble concentrations of nine different matals on the dehydrogenase activity of a loess soil.* Biol. Fertil. Soils, 30: 132-139.

Wyszkowska J., Kucharski J., Boros E. 2005. *Właściwości biochemiczne gleby zanieczyszczonej niklem i innymi metalami ciężkimi*. J. Elementol., 10(3): 585-596.

Wyszkowski M., Wyszkowska J. 2004. *Wpływ zanieczyszczenia gleby cynkiem, niklem, miedzią i ołowiem na plonowanie i gospodarkę makroelementami w owsie.* J. Elementol., 9(1): 61-70.

BOOK REVIEW

Arsenic in Soil and Groundwater Environment. Biochemical Interactions, Health Effects and Remediation, edited by Bhattacharya P., Mukherjee A. B., Bundschuh J., Zevenhoven R., and Loeppert R.H.; Volume 9: TRACE METALS IN THE ENVIRONMENT. Series edited by J. Nriagu, Elsevier, Amsterdam, ISBN 978-444-51820-0, 653 pp. Price: GBP 68.99/ USD 120/ EUR 99.95

The book opens with these words: "Contamination of the environment with arsenic from both anthropogenic and natural sources has occurred in many parts of the world and is recognized as a global problem". This statement clearly suggests that increased contents of arsenic in soils and its transfer to the alimentary chain is of crucial importance to human health.

This monograph contains IX sections, with 24 subchapters by different authors. The main topics included in these chapters are: arsenic (As) in: (i) groundwater, (ii) soil, (iii) plants and corps, and (iv) contaminated sites. Other chapters discuss the biocheochemistry of arsenic in soil and aquatic environment and the remediation technologies. One chapter discusses association of As with a bladder cancer.

Studies on As in groundwater have developed rapidly since the mid-1980s, when its increased levels in groundwater from aquifers in several countries, mainly in Asia, were noticed and became to be of health risks to human. Soon, several research projects focused on increased levels of As in soils due to effects of parent material or of mine and industrial wastes.

The section on As in groundwaters presents data reporting its concentration in drinking water from shallow and deep tubewells in Bangladesh and a conceptual model for the prediction of increased As concentration with time and with other (deeper) aquifers. The data are presented for As levels in geothermally influenced groundwater originating in Precambrian rocks in Central Arizona, the USA. The shallow groundwater and alkaline lake water of the Pantanal wetland in Brazil contain elevated amounts of As (up to 3.68 mg/l), which are dangerous to the cattle grazing in this area. The As concentrations in surface- and groundwater in Serbia (Balkan Peninsula in Europe) are elevated due to impacts of both ore deposits and industrial activities (metal mines and smelters).

In the section on As in soil, environmental processes of As adsorption on Fe and Al oxides in soils are broadly discussed, as well as interactions with other anions and cations. Simulation models for these reactions are presented. Occurrence and speciation of As in soils is presented for Balkan Peninsula and Nigeria. Anthropogenic sources of As in urban topsoil, and especially in sandboxes at playgrounds in Oslo (Norway), are emphasized.

The section on As in plants and crops contains three chapters. These chapters deal with: (i) the spatial distribution and speciation of As in hyperaccumulating fern, (ii) using As hyperaccumulator plant for phytoremediation of As-contaminated soils, and ((iii) impact of As-contaminated irrigation water on the growth and yield of rice.

Arsenic in contaminated sites is discussed in six chapters, in which concentrations and speciation of As in soils and groundwater are presented mainly for various historic and present mining areas. Very high As levels (50-1000 mg /kg) are reported in soils of residential areas in Brazil which around 250 years ago were occupied by gold mines and industries. Extremely high As concentration (up to 40 600 mg/kg) is reported for soils from mine spoilt areas in Poland, which for centuries were the main As source in Europe. Mine wastes from a Cu-As mine in UK contain up to 80 000 mg As/kg and special waste management practices for mine sites need to be developed. Increased As concentration (up to 5.9 mg/l) is reported in groundwater from a historic mining area in Mexico, where As originates from both As-mineral zones of potable water wells and springs and from mining wastes. Elevated concentration of As in shallow and groundwaters of Tulare Basin in California (USA) is a result of both natural processes and anthropogenic activities. This creates a problem of obtaining clean drinking water and agricultural water (irrigation and drainage).

Studies on the behavior of As in thermo-mineral spring water in the French Massif Central have indicated that Fe oxyhydroxides precipitate As in relatively stable forms, whereas carbonates do not trap As and increase its desorption due to increased pH of the system.

A synoptic review is presented for As flows in the environment of the European Union. Increased use of As in various industries is noticeable and causes high As emission to the atmosphere (also from coal-fired power plants and coal-fired residential heating) as well as its leaching from landfills. Thus, As flows and fate in the environment need more attention.

There is strong evidence linking a bladder cancer and increased As level (exceeding 300-500 µg/l) in drinking water. In addition to As in water, some food plants and tobacco grown in soil with elevated content of As are its significant sources in human diet. However, there is a need for further epidemiological studies to assess human exposure to arsenic.

Removal of arsenic from waters, mainly household water, is discussed in three chapters. Natural red earth composed of Fe-coated quartz and Fe minerals (ilmenite and magnetite) has a high capacity to adsorb As compounds from water. Addition of water-soluble chelating agents and changes in the Fe(II) to Fe(III) ratio after exposure to sunlight may be very effective in the precipitation of As compounds from water and is recommended as a "friendly" technique for the removal of As from ground water. The oxidation of As compounds [As(III) to As(V)] by ferrate [Fe(VI)] is possible under different pH conditions and is suggested as an alternative technique for the As removal from aqueous solution.

All the chapters discuss and emphasize the global health problem associated with As in drinking water. Increased level of As in crops in certain regions of the world is also presented. Further studies are necessary to understand the behavior of As in soil-groundwater systems and to develop effective remediation techniques.

Although the book was written by many authors, the style and presentation of the current problems and knowledge of major biogeochemical processes involved in As cycle in the environment are easy to follow. All the chapters provide an overview of topics in As geo- and hydrochemistry and the health risk associated with elevated As in drinking water sources. For those interested in As in potable water and related heath problems, this is an excellent book and will remain an important source of information.

All the authors are well known experts in the field of As environmental and health problems. Their contribution to the updated review of these topics should be highly recognized.

prof. dr Hab. Alina Kabata-Pendias
IUNG-PIB
24-100 Pulawy, POLAND

Recenzenci

Journal of Elementology nr 13(1) 2008

Jolanta Zielińska, Izabela Bojakowska, Jolanta Ejsmont-Karabin, Barbara Filipek-Mazur, Stefan Grzegorczyk, Stefania Jezierska-Tys, Jan Kryszak, Józef Koc, Magdalena Maj-Żurawska, Regina Olędzka, Barbara Wiśniowska-Kielian

Regulamin ogłaszania prac w „Journal of Elementology”

1. Journal of Elementology (kwartalnik) zamieszcza na swych łamach prace oryginalne, doświadczalne, kliniczne i przeglądowe z zakresu przemian biopierwiastków i dziedzin pokrewnych.
2. W JE mogą być zamieszczone artykuły sponsorowane, przygotowane zgodnie z wymaganiami stawianymi pracom naukowym.
3. W JE zamieszczamy materiały reklamowe.
4. Materiały do wydawnictwa należy przesłać w 2 egzemplarzach. Objętość pracy oryginalnej nie po-winna przekraczać 10 stron znormalizowanego maszynopisu (18 000 znaków), a przeglądowej 15 stron (27 000 znaków).
5. Układ pracy: ***imię i nazwisko autora (-ów),*** **TYTUŁ PRACY**, **nazwa jednostki, z której pochodzi praca, WSTĘP, MATERIAŁ I METODY, WYNIKI I ICH OMÓWIENIE, WNIOSKI, PIŚ-MIENNICTWO,** streszczenie w języku polskim i angielskim – minimum 250 słów. Streszczenie powinno zawierać: wstęp (krótko), cel badań, omówienie wyników, wnioski. Przed streszczeniem w języku polskim: ***imię i nazwisko Autora (-ów),*** **TYTUŁ PRACY,** Słowa kluczowe (maks 10 słów), Abstrakt, **TYTUŁ ANGIELSKI,** Key words, Abstract. U dołu pierwszej strony należy podać tytuł naukowy lub zawodowy, imię i nazwisko autora oraz dokładny adres przeznaczony do korespondencji w języku polskim i angielskim.
6. Praca powinna być przygotowana wg zasad pisowni polskiej. Jednostki miar należy podawać wg układu SI np.: $\mathrm{mmol(+)\ kg^{-1}}$; $\mathrm{kg \cdot ha^{-1}}$; $\mathrm{mol \cdot dm^{-3}}$; $\mathrm{g \cdot kg^{-1}}$; $\mathrm{mg \cdot kg^{-1}}$ (obowiązują formy pierwiastkowe).
7. W przypadku stosowania skrótu po raz pierwszy, należy podać go w nawiasie po pełnej nazwie.
8. Tabele i rysunki należy załączyć w oddzielnych plikach. U góry, po prawej stronie tabeli, należy napisać Tabela i numer cyfrą arabską, również w języku angielskim, następnie tytuł tabeli w języku polskim i angielskim wyrównany do środka akapitu. Ewentualne objaśnienia pod tabelą oraz opisy tabel winny być podane w języku polskim i angielskim. Wartości liczbowe powinny być podane jako zapis złożony z 5 znaków pisarskich (np. 346,5; 46,53; 6,534; 0,653).
9. U dołu rysunku, po lewej stronie, należy napisać Rys. i numer cyfrą arabską oraz umieścić podpisy i ewentualne objaśnienia w języku polskim i angielskim.
10. Piśmiennictwo należy uszeregować alfabetycznie, bez numerowania, w układzie: Nazwisko Inicjał Imienia (kapitaliki) rok wydania. Tytuł pracy (kursywa). Obowiązujący skrót czasopisma, tom (zeszyt): strony od-do. np. Kowalska A., Kowalski J. 2002. *Zwartość magnezu w ziemniakach*. Przem. Spoż., 7(3): 23-27.
11. W JE można także cytować prace zamieszczone w czasopismach elektronicznych, wg schematu: Nazwisko Inicjał Imienia (kapitaliki), rok wydania. Tytuł pracy (kursywa). Obowiązujący skrót czasopisma internetowego oraz pełny adres strony internetowej. np. Antonkiewicz J., Jasiewicz C. 2002. *The use of plants accumulating heavy metals for detoxication of chemically polluted soils*. Electr. J. Pol. Agric. Univ., 5(1): 1-13. hyperlink „http://www” http://www.ejpau.media.pl/series/volume5/issue1/environment/art-01.html
12. Cytując piśmiennictwo w tekście, podajemy w nawiasie nazwisko autora i rok wydania pracy (Kowalski 1992). W przypadku cytowania dwóch autorów, piszemy ich nazwiska rozdzielone przecinkiem i rok (Kowalski, Kowalska 1993). Jeżeli występuje większa liczba nazwisk, podajemy pierwszego autora z dodatkiem i in., np.: (Kowalski i in. 1994). Cytując jednocześnie kilka pozycji, należy je uszeregować od najstarszej do najnowszej, np.: (Nowak 1978, Nowak i in. 1990, Nowak, Kowalska 2001).
13. Do artykułu należy dołączyć pismo przewodnie kierownika Zakładu z jego zgodą na druk oraz oświadczenie Autora (-ów), że praca nie została i nie zostanie opublikowana w innym czasopiśmie bez zgody Redakcji JE.
14. Dwie kopie wydruku komputerowego pracy (Times New Roman 12 pkt, z odstępem akapitu 1,5, bez dyskietki) należy przesłać na adres Sekretarzy Redakcji:

dr hab. Jadwiga Wierzbowska
Uniwersytet Warmińsko-Mazurski w Olsztynie
ul. Michała Oczapowskiego 8, 10-719 Olsztyn
jawierz@uwm.edu.pl
dr Katarzyna Glińska-Lewczuk
Uniwersytet Warmińsko-Mazurski w Olsztynie
pl. Łódzki 2, 10-759 Olsztyn
kaga@uwm.edu.pl

15. Redakcja zastrzega sobie prawo dokonywania poprawek i skrótów. Wszelkie zasadnicze zmiany tekstu będą uzgadniane z Autorami.
16. Po recenzji Autor zobowiązany jest przesłać w 2 egzemplarzach poprawiony artykuł wraz z dyskietką, przygotowany w dowolnym edytorze tekstu pracującym w środowisku Windows.

Redakcja Journal of Elementology uprzejmie informuje, iż w 2006 r. wprowadziła opłatę za druk prac.

Koszt wydrukowania maszynopisu (wraz z rysunkami, fotografiami i tabelami) o objętości nie przekraczającej 6 stron formatu A4, sporządzonego wg następujących zasad:

- czcionka: Times New Roman, 12 pkt, odstęp 1,5;
- 34 wiersze na 1 stronie;
- ok. 2400 znaków (bez spacji) na 1 stronie;
- rysunki i fotografie czarno-białe

wynosi 250 PLN + VAT.

Koszt druku każdej dodatkowej strony (wraz z rysunkami, fotografiami i tabelami) wynosi 35 PLN + VAT

Koszt druku 1 rysunku lub fotografii w kolorze wynosi 150 PLN + VAT

Uwaga:

Z opłaty za druk pracy są zwolnieni lekarze nie zatrudnieni w instytutach naukowych, wyższych uczelniach i innych placówkach badawczych.

Komitet Redakcyjny

Guidelines for Authors „Journal of Elementology”

1. Journal of Elementology (a quarterly) publishes original scientific or clinical research as well as reviews concerning bioelements and related issues.
2. Journal of Elementology can publish sponsored articles, compliant with the criteria binding scientific papers.
3. Journal of Elementology publishes advertisements.
4. Each article should be submitted in duplicate. An original paper should not exceed 10 standard pages (18 000 signs). A review paper should not exceed 15 pages (27 000 signs).
5. The paper should be laid out as follows: ***name and surname of the author(s)***, **TITLE OF THE ARTICLE**, **the name of the scientific entity, from which the paper originates**, **INTRODUCTION**, **MAETRIAL AND METHODS**, **RESULTS AND DISCUSSION**, **CONCLUSIONS**, **REFERENCES**, abstract in the English and Polish languages, min. 250 words. Summary should contain: introduction (shortly), aim, results and conclusions. Prior to the abstract in the English language the following should be given: ***name and surname of the author(s)***, **TITLE,** Key words (max 10 words), Abstract, **TITLE**, Key words and Abstract in Polish. At the bottom of page one the following should be given: scientific or professional title of the author, name and surname of the author, detailed address for correspondence in the English and Polish languages.
6. The paper should be prepared according to the linguistic norms of the Polish and English language. Units of measurements should be given in the SI units, for example mmol(+) kg^{-1}; $kg \cdot ha^{-1}$; $mol \cdot dm^{-3}$; $g \cdot kg^{-1}$; $mg \cdot kg^{-1}$ (elemental forms should be used).
7. In the event of using an abbreviation, it should first be given in brackets after the full name.
8. Tables and figures should be attached as separate files. At the top, to the right of a table the following should be written: Table and table number in Arabic figures (in English and Polish), in the next lines the title of the table in English and Polish adjusted to the centre of the paragraph. Any possible explanation of the designations placed under the table as well as a description of the table should be given in English and Polish. Numerical values should consist of five signs (e.g. 346.5, 46.53, 6.534, 0.653).
9. Under a figure, on the left-hand side, the following should be written: Fig. and number in Arabic figures, description and possible explanation in Polish and English.
10. References should be ordered alphabetically but not numbered. They should be formatted as follows: Surname First Name Initial (capital letter), year of publication, Title of the paper (italics). The official abbreviated title of the journal, volume (issue): pages from - to. e.g. KOWALSKA A., KOWALSKI J. 2002. *Zawartość magnezu w ziemniakach.* Przem. Spoż., 7(3): 23-27.
11. It is allowed to cite papers published in electronic journals formatted as follows: Surname First Name Initial (capital letters), year of publication. Title of the paper (italics). The official abbreviated title of the electronic journal and full address of the website. e.g. ANTONKIEWICZ J., JASIEWICZ C. 2002. *The use of plants accumulating heavy metals for detoxication of chemically polluted soils*. Electr. J. Pol. Agric. Univ., 5(1): 1-13. hyperlink „http://www.ejpau.pl/series/volume5/issue1/environment/art-01.html” http://www.ejpau.pl/series/volume5/issue1/environment/art-01.html
12. In the text of the paper a reference should be quoted as follows: the author's name and year of publication in brackets, e.g. (KOWALSKI 1992). When citing two authors, their surnames should be separated with a comma, e.g. (KOWALSKI, KOWALSKA 1993). If there are more than two authors, the first author's name should be given followed by et al., e.g. (KOWALSKI et al. 1994). When citing several papers, these should be ordered chronologically from the oldest to the most recent one, e.g. (NOWAK 1978, NOWAK et al. 1990, NOWAK, KOWALSKA 2001).

13. A paper submitted for publication should be accompanied by a cover letter from the head of the respective institute who agrees for the publication of the paper and a statement by the author(s) confirming that the paper has not been and will not be published elsewhere without consent of the Editors of the Journal of Elementology.
14. Two computer printed copies of the manuscript (Times New Roman 12 fonts, 1.5-spaced, without a diskette) should be submitted to the Editor's Secretary:

dr hab. Jadwiga Wierzbowska
University of Warmia and Mazury in Olsztyn
ul. Michała Oczapowskiego 8, 10-719 Olsztyn
jawierz@uwm.edu.pl

dr Katarzyna Glińska-Lewczuk
University of Warmia and Mazury in Olsztyn
Pl. Łódzki 2, 10-759 Olsztyn, Poland
kaga@uwm.edu.pl

15. The Editors reserve the right to correct and shorten the paper. Any major changes in the text will be discussed with the Author(s).
16. After the paper has been reviewed and accepted for publication, the Author is obliged to sent the corrected version of the article together with the diskette. The electronic version can be prepared in any word editor which is compatible with Windows software.